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SUMMARY OF THE CAMPAIGN DURING JULY 1968 TO PROCESS FOURTEEN IRRADIATED HFIR TARGETS IN THE TRANSURANIUM PROCESSING PLANT

L. J. King and E. D. Collins

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ABSTRACT

Fourteen irradiated HFIR targets were processed in the Transuranium Processing Plant (TRU) to recover the transuranium elements. Each target originally contained 8 g of plutonium (95.85% ^{242}Pu), in the form of PuO_2, dispersed in aluminum powder in 35 aluminum-jacketed pellets. Thirteen of the targets had been irradiated since the HFIR first attained full power and had received total exposures of from 37,000 to 41,000 Mwd. Examination of the targets prior to processing disclosed no cladding failures. Purified products contained about 15 g of ^{242}Pu, 5 g of ^{243}Am, 40 g of ^{244}Cm, 1 mg of ^{249}Bk, 6 mg of ^{252}Cf, 30 μg of ^{253}Es and 7×10^7 atoms of ^{257}Fm. The amount of einsteinium product was nearly ten times the quantity that was previously available. The fermium product was the first usable amount of fermium recovered in TRU. Processing steps were: dissolution of the aluminum using caustic-nitrate solution, dissolution of the actinide oxides using concentrated hydrochloric acid, recovery and purification of unburned plutonium using a batch solvent extraction process (Pubex), decontamination of the transplutonium elements using the Tramex solvent extraction process, and separation of americium and curium from the transcurium elements using a LiCl-based anion exchange process. The transcurium elements were separated and purified using laboratory-scale equipment installed in one of the processing cells. The entire processing campaign was completed in only three weeks. Equipment performance was satisfactory: no major problems were encountered.

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1. INTRODUCTION

The Transuranium Processing Plant (TRU) and the High Flux Isotope Reactor (HFIR) have been built at Oak Ridge National Laboratory to produce large quantities of the heavy actinide elements as part of the USAEC Heavy Element Production Program. Transuranium elements are formed in the HFIR

by successive transmutation, beginning with ^{242}Pu which is incorporated in aluminum-clad targets. The irradiated targets are processed in TRU to recover the heavier transuranium elements for distribution to research workers, and to recover americium, curium, and unburned plutonium and fabricate them into targets for recycle to the HFIR.

This report deals with the processing in the Transuranium Processing Plant of 14 irradiated HFIR targets, each of which originally contained 8 g of plutonium (95.85% ^{242}Pu) in the form of calcined oxide. Thirteen of the targets had been irradiated since the HFIR first went to full power and had received total exposures of from 37,000 to 41,000 Mwd. Examination disclosed no cladding failures. The other target was dissolved and the plutonium was recovered, using batch extraction, to test a new system for iodine retention.

The processing steps used for the 13 targets included (1) dissolution and removal of the aluminum jackets and aluminum matrix material, using a solution of NaOH and $NaNO_3$; (2) dissolution of the actinide-oxide residue using HCl; (3) separation, purification and recovery of plutonium using batch extraction and ion exchange; (4) purification of the transplutonium elements using the Tramex solvent extraction process; and (5) separation of the transcurium elements from americium and curium using a LiCl-based anion exchange process. The transcurium elements were separated and purified using laboratory-scale equipment installed in one of the processing cells.

This report contains a summary of the results of the processing campaign, a description of the targets and their irradiation history, and a description and analysis of the processes and equipment used for chemical processing. A major purpose of this report is to serve as a repository for data.

2. SUMMARY OF RESULTS

Purified products of this processing campaign contained about 15 g of ^{242}Pu, 5 g of ^{243}Am, 40 g of ^{244}Cm, 1 mg of ^{249}Bk, 6 mg of ^{252}Cf, 30 μg of ^{253}Es and 7×10^7 atoms of ^{257}Fm. The campaign was completed in only

3 weeks. No major problems were encountered. The amount of ^{253}Es product was nearly ten times the quantity that was previously available. The fermium product was the first usable amount of fermium recovered in TRU.

The campaign was planned to maximize the recovery of 20-day-half-life ^{253}Es. We compromised between processing the 13 targets after a very short cooling period, which would have resulted in a better yield of einsteinium and a large amount of radioiodine, and waiting for a long cooling period, which would have eliminated concern over iodine and given a poor yield of einsteinium. A caustic scrubber and a charcoal trap were installed in the off-gas line from the condensate collection system, which serves all of the evaporators and the dissolver, and the piping was modified so that all off-gas from these vessels would pass through the scrubber and charcoal trap. The targets contained 460 Ci of ^{131}I when they were dissolved after a 22-day cooling period. About 1.1 Ci of ^{131}I was released during the three-week processing period and 0.6 Ci was released during the following two weeks when we were transferring waste solutions, consolidating rework material and concentrating products. Although the release of this quantity of ^{131}I during a processing campaign is acceptable, we feel that our operations are confined excessively by concern over radioiodine. Therefore, we intend to continue to try to improve our capability for iodine retention.

The Tramex process equipment that was used in this campaign was new equipment that was designed to be operated with the organic phase continuous. The old equipment was replaced since it had been difficult to operate because of corrosion, wear, and damage. Organic-continuous operation is not significant to the Tramex process but is required for another process, Hepex, which will be operated in the same equipment. The new equipment operated satisfactorily for Tramex.

3. TARGET DESCRIPTION

The configuration of the HFIR target element is shown in Fig. 3.1. Details of the fabrication have been published.[1] The 20-in.-long active column contained 8 g of plutonium (95.85% ^{242}Pu) in the form of PuO_2,

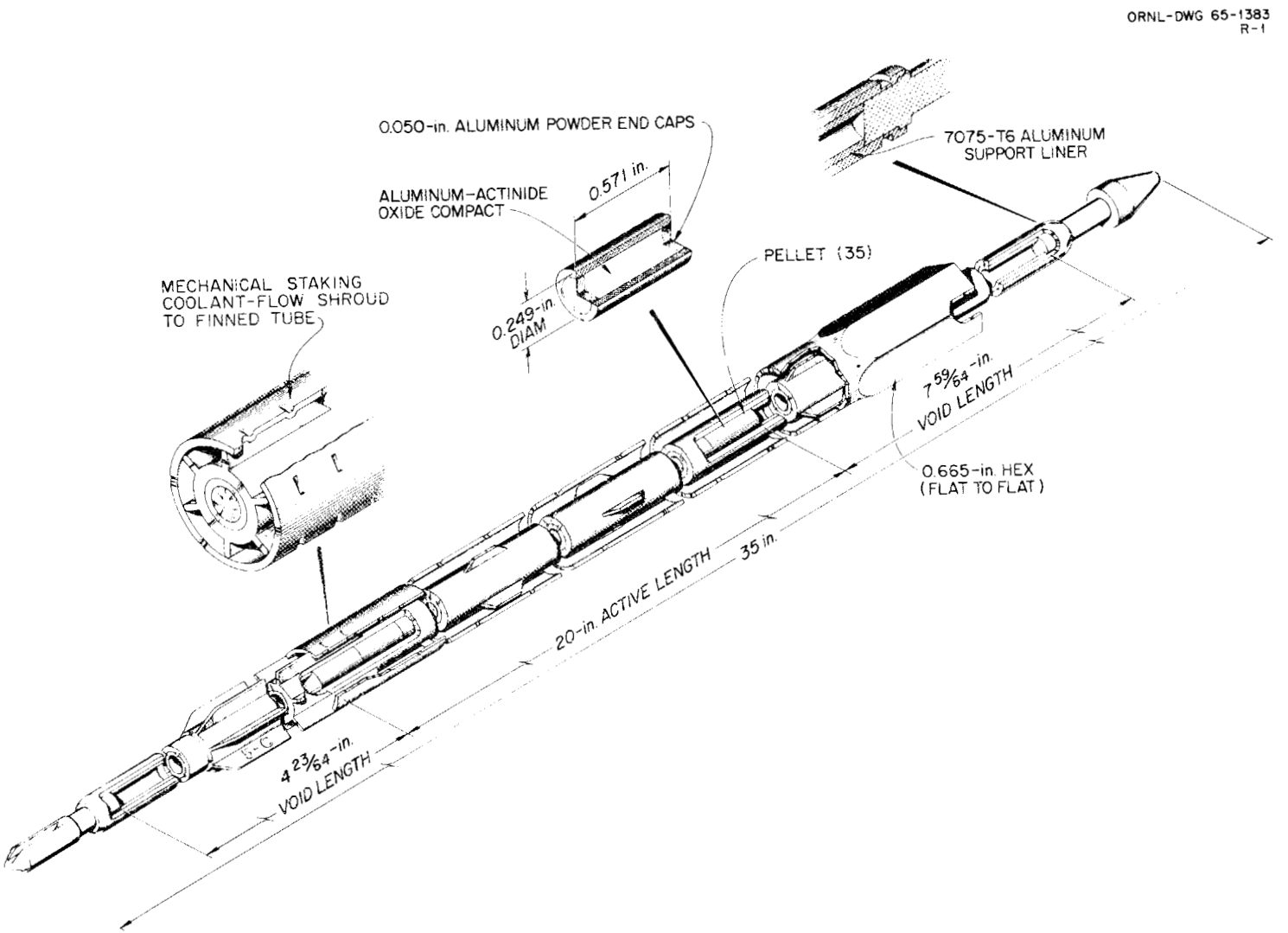

Fig. 3.1. HFIR Target Rod.

dispersed in aluminum powder (Alcoa grade 101, type 1100) in 35 aluminum-jacketed pellets. The pellet jackets were fully annealed type 1100 aluminum tubes (0.025 in. wall) with an 0.050-in.-thick pressed aluminum powder (type 1100) cap on each end. The pellet cores, which contained the plutonium oxide particles in an aluminum matrix, were pressed to 90% of theoretical density.

The 0.249-in.-diam by 0.571-in.-long pellets were pressed separately and then loaded into the finned, aluminum target tube which was sealed by welding and was collapsed onto the pellets by the application of hydraulic pressure of 10 tsi. The plenums, designed to accomodate any fission product gases released during irradiation, were lined with 7075-T6 aluminum sleeves to support the target tube during the hydrostatic-collapse step in fabrication. The coolant-flow shroud tube (X-8001 aluminum) was attached to the target tube by a mechanical-staking procedure.

3.1 Plutonium Oxide

A solution of 0.5 M $Pu(NO_3)_4$ in 4 M HNO_3 was rapidly mixed with an equal volume of 8 M NH_4OH to precipitate $Pu(OH)_4$. The precipitate was washed with 2 M NH_4OH, dried at 150°C, and calcined at 1200°C, which produced glassy solid particles from 1 to 3 mm in diam with a density close to theoretical. This was ground and screened to obtain the desired range of particle sizes. The nominal particle size distribution is given in Table 3.1 and the mass analysis of the plutonium is given in Table 3.2.

Table 3.1. Particle Size Distribution of PuO_2

Screen Size (U. S. Standard Mesh)	Particle Size (μ)	PuO_2 (wt %)
-70 + 100	210 - 149	48.0
-100 + 200	149 - 74	23.6
-200 + 325	74 - 44	11.0
-325	<44	17.4

Table 3.2. Initial Composition of the Targets

Isotope	g/Target	Atom %
^{238}Pu	0.037	0.46
^{239}Pu	0.069	0.86
^{240}Pu	0.149	1.86
^{241}Pu	0.078	0.97
^{242}Pu	7.667	95.85
Total plutonium	8.0	

3.2 Irradiation

The targets were irradiated 17 reactor fuel cycles (8 cycles for target D52) in the flux trap of the High Flux Isotope Reactor. Irradiation histories are given in Table 3.3.

The flux trap will hold a "bundle" of 31 targets arranged in a holder as shown in Fig. 3.2. The faces of the hexagonal portions of the target rods are placed against each other as shown to form five "rings" of targets. At the start of reactor cycle No. 8, the HFIR hydraulic rabbit tube was inserted into ring "0", thereby reducing to 30 the number of targets that can be irradiated simultaneously. All of the positions in each ring are equivalent except for local flux depressions: there is no way to fix or determine the angular orientation of the target holder in the reactor. The location of each target during each reactor cycle is listed in Table 3.4.

The volume-averaged, integral thermal flux has been calculated to be 2.14×10^{15} neutrons$\cdot$cm$^{-2}\cdot$sec^{-1}. The thermal flux factors (the ratio of average thermal flux in the ring to the volume averaged thermal flux) for target rings 0 through 4 are 1.083, 1.058, 1.022, 1.007, and 0.9566, respectively. The volume averaged epithermal (0.414 to 101 ev) flux per unit lethargy is 8.54×10^{13} neutrons$\cdot$cm$^{-2}\cdot$sec^{-1} and the epithermal flux factors (the ratio of the average epithermal flux for the ring to the volume averaged epithermal flux) for rings 0 through 4 are 0.958, 0.976, 0.986,

Table 3.3. Irradiation Histories of the Targets and Predicted Concentrations of Some Transuranium Isotopes

	Target D52	Targets D10, D18, D23, D24, D28, D33, D39, D51, D58, D59, D61, D65, E33
Reactor	HFIR	HFIR
No. of reactor cycles	8	17
Average thermal neutron exposure, n/cm^2	3.0×10^{20}	6.6×10^{20}
Reactor discharge date	5-24-68	6-16-68
Cooling time, days	36	22
Dissolution date	6-29-68	7-8-68
Dissolution run no.	10-DS-1	11-DS-1
Predicted Target Composition		
^{242}Pu, g/target	3.7	1.1
^{243}Am, g/target	1.0	0.43
^{244}Cm, g/target	2.1	3.2
^{249}Bk, μg/target	10.0	48
^{252}Cf, mg/target	0.019	0.46
^{253}Es, μg/target		2.3

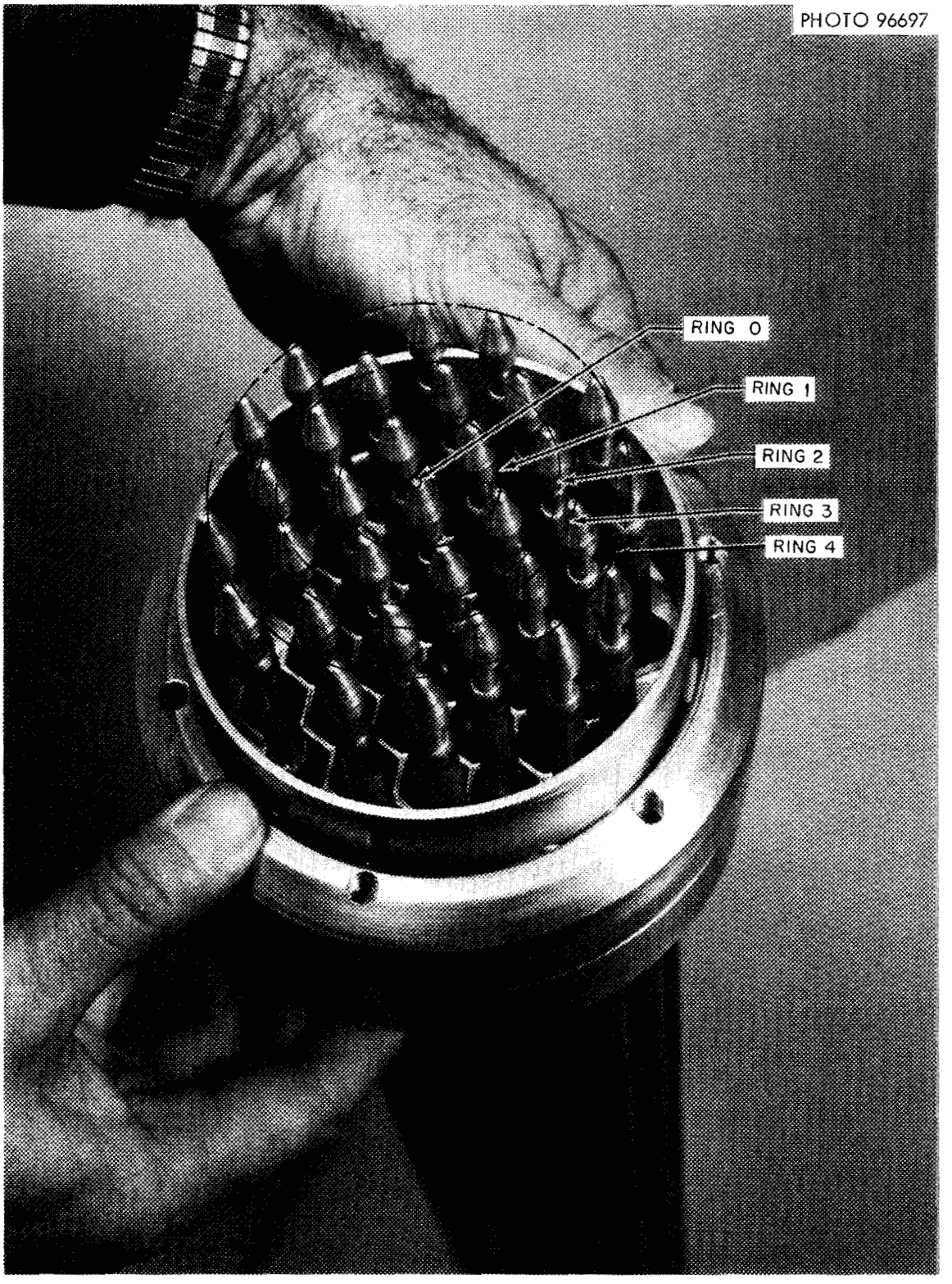

Fig. 3.2. HFIR Target Bundle.

Table 3.4. Locations of the Targets in the HFIR Target Island During Irradiation

HFIR Cycle Number	Total Power MwD	Target D52 Ring No.	Target D10 Ring No.	Target D18 Ring No.	Targets D23, D24 D51, E33 Ring No.	Target D28 Ring No.	Targets D33, D59, D65 Ring No.	Targets D39, D61 Ring No.	Target D58 Ring No.
5	2266.627		3	1	2	2	1	1	0
6	2313.141		3	1	2	2	1	1	0
7	2360.660		3	1	2	2	1	1	0
8	2360.146		3	1	2	2	1	1	2
9	2361.895		3	1	2	2	1	1	2
10A, 10B	1346.419		3	1	2	2	1	1	2
11A	575.048		2	1	4	2	1	1	2
12	2306.068		2	1	4	2	1	1	2
13	2025.820		2	1	4	2	1	1	2
14	2294.575	3	2	1	4	2	1	1	2
15	2124.409	3	2	1	4	2	1	2	2
16	2308.556	3	2	1	4	2	1	2	2
17	2316.784	4	3	4	4	3	1	3	3
18	2345.856	4	3	4	4	3	1	3	3
11B	1747.000	4	3	1	4	3	1	3	3
19	2360.290	4	3	1	4	3	1	3	3
20	2342.986	4	3	1	4	3	1	3	3
21	2316.754		3	1	4	3	1	3	3

0.995, and 1.021, respectively. The fast neutron flux on the reactor centerline at the midplane is 7.5×10^{14} neutrons·cm^{-2}·sec^{-1}. Fast flux is not considered in calculations of transuranium element production.

3.3 Compositions of Irradiated Targets

Tables 3.5 and 3.6 contain estimates of the compositions of the targets at the time of discharge from the reactor. The values given represent our best estimates, based on analysis of all of the data that were collected during the processing campaign. The data are presented in this form to simplify calculations that will be made to deduce effective cross sections and other nuclear parameters.

4. PROCESSING

About 10 days before starting the main campaign to process 13 targets (campaign 11) we tested a newly installed iodine retention system by dissolving another target (D52) and recovering the plutonium using the Pubex batch extraction process. The procedures used were identical to those used for these steps in processing the 13 targets. The plutonium products from the one target and from the 13 targets were combined for additional purification. The fractions containing all the actinides heavier than plutonium were combined prior to Tramex processing.

The aluminum in the targets was dissolved using 6 M NaOH--3 M $NaNO_3$ solution which was decanted from the residue of undissolved actinide oxides. The oxides were slurried in water and transferred to another tank in which they were dissolved in concentrated HCl. The plutonium was recovered using the Pubex batch extraction process and was purified further using Pubex and anion exchange. The solutions of the transplutonium actinides were combined and decontaminated using the Tramex solvent extraction process. Americium and curium were separated from the transcurium elements using an LiCl-based anion exchange process and the transcurium elements were separated from each other, and purified using laboratory-scale equipment. The entire campaign to recover the transcurium elements from the 13 targets was completed in only 3 weeks, about half the time that was required in the preceding comparable campaign.

Table 3.5. Probable Compositions of the Targets When They Were Discharged from the High Flux Isotope Reactor

Listed Values were deduced from data collected during chemical processing.

Isotope	Target D52			Targets D10, D18, D23, D24, D28, D33, D39, D51, D58, D59, D61, D65, E33		
	g/target[a]	g/10 g of[a] Initial Pu	Atom % of each element	g/target[a]	g/10 g of[a] Initial Pu	Atom % of each element
^{238}Pu	2.75×10^{-4}	3.43×10^{-4}	0.009	1.12×10^{-5}	1.40×10^{-5}	0.001
^{239}Pu	1.83×10^{-4}	2.29×10^{-4}	0.006	1.12×10^{-5}	1.40×10^{-5}	0.001
^{240}Pu	2.92×10^{-2}	3.65×10^{-2}	0.957	1.08×10^{-2}	1.35×10^{-2}	0.962
^{241}Pu	1.16×10^{-3}	1.45×10^{-3}	0.038	1.45×10^{-3}	1.81×10^{-3}	0.129
^{242}Pu	3.00	3.75	98.35	1.08	1.35	97.12
^{244}Pu	1.95×10^{-2}	2.44×10^{-2}	0.640	2.01×10^{-2}	2.51×10^{-2}	1.79
^{243}Am[b]	8.10×10^{-1}	1.01		4.20×10^{-1}	5.2×10^{-1}	
^{244}Cm	1.74	2.18	94.20	2.99	3.74	88.74
^{245}Cm	1.55×10^{-2}	1.94×10^{-2}	0.839	2.38×10^{-2}	2.97×10^{-2}	0.705
^{246}Cm	8.77×10^{-2}	0.11	4.75	3.32×10^{-1}	4.15×10^{-1}	9.865
^{247}Cm	2.24×10^{-3}	2.79×10^{-3}	0.121	9.33×10^{-3}	1.17×10^{-2}	0.277
^{248}Cm	1.53×10^{-3}	1.92×10^{-3}	0.083	1.39×10^{-2}	1.74×10^{-2}	0.413
^{249}Bk	9.9×10^{-6}	1.2×10^{-5}		1.10×10^{-4}	1.38×10^{-4}	
^{249}Cf	5.54×10^{-7}	7.2×10^{-7}	1.37[c]	8.2×10^{-7}	1.02×10^{-6}	0.11[c]
^{250}Cf	7.72×10^{-6}	1.0×10^{-5}	19.08	9.92×10^{-5}	1.24×10^{-4}	12.17
^{251}Cf	2.17×10^{-6}	2.82×10^{-6}	5.37	2.67×10^{-5}	3.33×10^{-5}	3.26
^{252}Cf	3.0×10^{-5}	3.9×10^{-5}	74.19	5.41×10^{-4}	6.76×10^{-4}	82.90
^{253}Cf				1.23×10^{-5}	1.54×10^{-5}	1.51
^{254}Cf				3.8×10^{-7}	4.7×10^{-7}	0.05
^{253}Es	2.0×10^{-7}	2.5×10^{-7}		2.6×10^{-6}	3.25×10^{-6}	
Fission products (calculated from ^{137}Cs)		0.84			3.11	

[a] Atomic weights of ^{242}Pu, ^{244}Cm, and ^{252}Cf were used to calculate g/target and g/10 g of initial Pu.
[b] Americium analyses were not available. Values given were calculated.
[c] Calculated from mass analysis by subtracting ^{249}Cf grown in after discharge from the reactor.

Table 3.6. Probable Amounts of Fission Products and Activation Products in the Targets When They Were Discharged from the Reactor

Radionuclide	Target D52		Targets D10, D18, D23, D24, D28, D33, D39, D51, D58, D59, D61, D65, E33	
	Ci/target	Ci/10 g of Initial Pu	Ci/target	Ci/10 g of Initial Pu
^{65}Zn			3.67	4.59
$^{95}ZrNb$	63-71	78-89	203	254
^{103}Ru	149	186	242	303
^{110m}Ag			$\leq$9.5	$\leq$11.9
^{131}I	95.2	119	146	183
^{134}Cs	1.61	2.01	9.29	11.6
^{136}Cs	15.0	18.8	203	254
^{137}Cs	2.60	3.25	9.64	12.1
$^{140}BaLa$	193	241	246	308
^{141}Ce			211	264
^{144}Ce	319	399	97.3	122

Figure 4.1 is a block diagram showing the processing steps that comprised this campaign, and descriptions of the individual runs are listed in Table 4.1.

4.1 Target Dissolution

The procedure used for dissolving the 13 targets (run 11-DS-1) is described below. Essentially the same procedure was used for dissolving target D52 (run 10-DS-1).

The aluminum coolant-flow shroud tube was mechanically removed from each of the targets. The remaining aluminum (jacket and matrix material) was dissolved from the 13 targets in three groups: two groups of 4 targets and one group of 5 targets. For each group a solution of approximately 6 M NaOH--3 M $NaNO_3$ (16 liters for 4 targets and 20 liters for 5 targets) was added to the Zircaloy-2 dissolver (T-70), one target was put into the dissolver and the solution was heated to initiate the dissolving, which proceeded exothermally. The reaction began at about 85°C. The dissolver was cooled to 50°C, a second target was added and the dissolver was again heated to initiate the dissolution. This was repeated until the aluminum had been dissolved from the entire group of 4 or 5 targets. After the last target in each group was dejacketed, the solution was held 30 min at 100°C to assure complete dissolution of the aluminum, and the solution was cooled and pumped through a fritted metal filter (10 microns) to a waste storage tank. The residue of actinide oxides was left in the dissolver and the next group of targets was dejacketed in the same way as the first group, using a fresh batch of caustic-nitrate solution. The procedure was then repeated for the last group of targets and the dissolver was flushed once with 3 liters of 2 M NaOH and twice with 3 liters of 0.05 M NaOH to reduce the sodium content. About 0.03% of the curium was lost to the dejacketing waste.

Exact run conditions for the dissolvings are given in Table 4.2 and the concentrations of various components in the dejacketing and dissolving solutions are listed in Table 4.3. The aluminum-bearing solutions were difficult to pump. The transfer rate was only 0.7 liter/hr. This

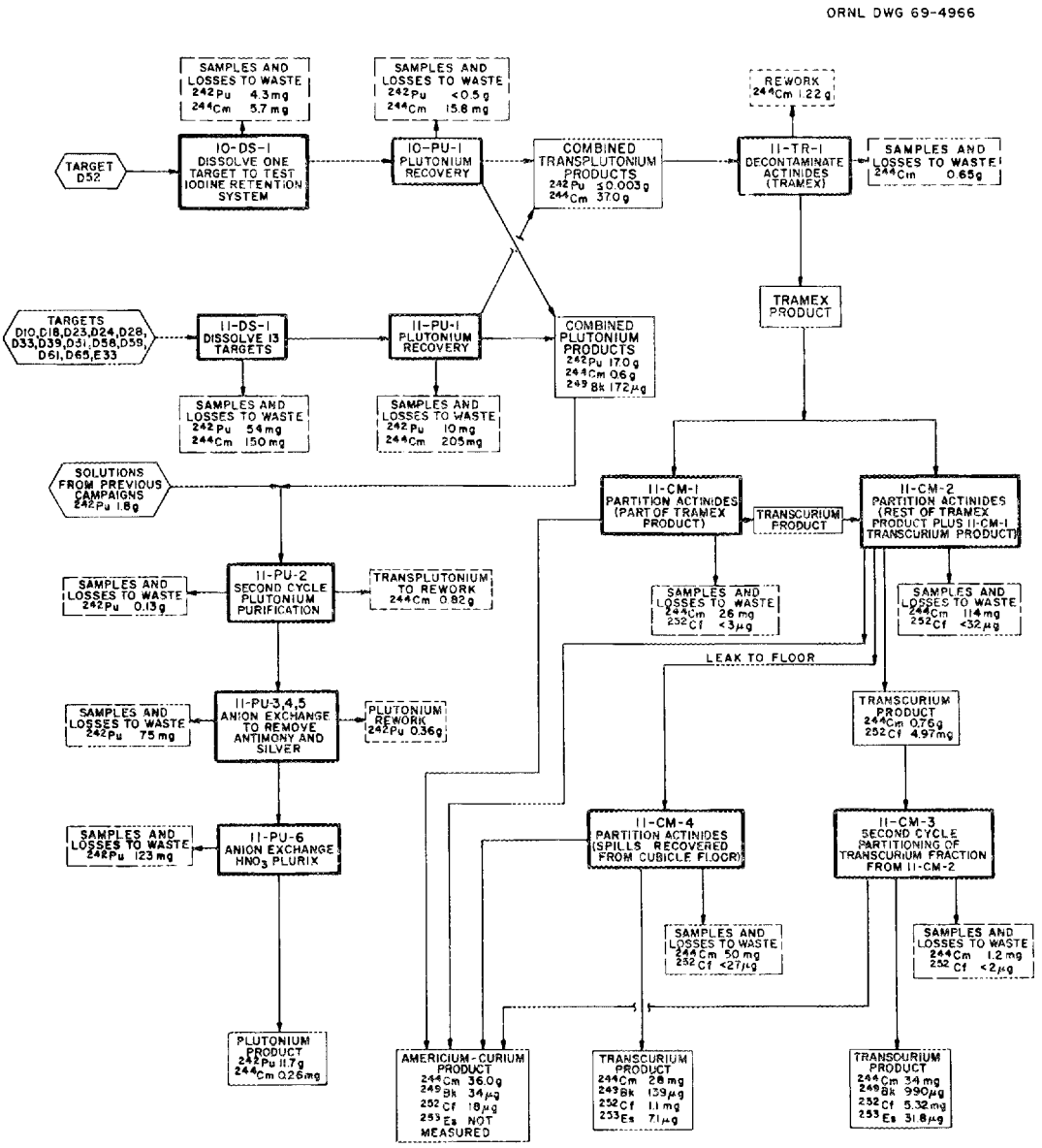

Fig. 4.1. Processing Diagram.

Table 4.1. List of Individual Runs Made in TRU to Recover Transuranium Elements from Fourteen HFIR Targets

Run Number	Purpose and Comments
10-DS-1	Dissolved target D52 to test iodine retention system.
10-PU-1	Recovered plutonium from 10-DS-1, using the Pubex batch extraction process, to test iodine retention system.
11-DS-1	Dissolved 13 targets using caustic-nitrate and 6 M HCl.
11-PU-1	Recovered plutonium from the 11-DS-1 solution using the Pubex batch extraction process.
11-TR-1	Decontaminated transplutonium elements (from 10-PU-1 and 11-PU-1) from fission products using the Tramex process.
11-CM-1	Separated most of the americium and curium from the transcurium actinides using LiCl-based anion exchange. Feed was first portion of the Tramex product.
11-CM-2	Separated all of the transcurium elements from the americium and curium using LiCl-based anion exchange. Transcurium actinides from 11-CM-1 were added to the feed for this run.
11-CM-3	Second cycle of purification of the transcurium elements (from 11-CM-2) from americium and curium using LiCl-based anion exchange.
11-CM-4	Recovered and purified transcurium elements that had leaked from the equipment during 11-CM-2.
11-PU-2	Second cycle of purification of the plutonium products from 10-PU-1 and 11-PU-1 using the Pubex process.
11-PU-3 11-PU-4 11-PU-5	Anion exchange treatment of 11-PU-2 product to remove $^{124,125}Sb$. Three attempts were required because of feed adjustment difficulties and limited capacity of the resin column for the contaminants.
11-PU-6	Plurix anion exchange treatment to remove ^{59}Fe from 11-PU-5 product. Plutonium was decontaminated sufficiently to permit removal from the cells to a glove box for final purification.

Table 4.2. Run Conditions for Dissolving the Targets

Run No.	10-DS-1	11-DS-1		
Dates Covered	6/28/68--6/30/68	7/8/68--7/14/68		
Target Numbers	D52	D10, D18, D23, D24, D28, D33, D39, D51, D58, D59, D61, D65[a], E33		
Equipment Used (Tank Numbers)	T70, T71, T72	T61, T70, T71, T72		
Run Conditions				
Aluminum Dejacketing		[b]	[c]	[d]
Dissolvent Composition, NaOH, M	5.8	5.8	5.5	5.7
$NaNO_3$, M	2.9	2.9	2.7	2.9
Volume, liters	11.5	13.0	17.7	17.5
Dissolution temperature, °C	100	100	100	100
Hold times, hours	0.5	0.5	0.5	0.5
Dejacket solution flushes	1 x 4 liters 2 M NaOH 2 x 3 liters 0.05 M NaOH	None	None	1 x 3 liters 2 M NaOH 2 x 3 liters 0.05 M NaOH
Actinide Dissolution				
Dissolvent composition, HCl, M	4		4[e]	
Initial volume, liters	42.7		33.7	
Evaporation time, hours	5		2	
Final temperature, °C			108.5	
Final volume, liters	25.2		24.1	
Final composition, HCl, M	4.9		3.9	

[a]About one-half pellet representing 1.4% of the active material was removed from D65 before it was dissolved.
[b]Aluminum was dissolved from D24, D59, D51 and D28, successively, in the first batch of caustic-nitrate solution.
[c]Aluminum was dissolved from D65, D10, D33 and D23, successively, in the second batch of caustic-nitrate solution.
[d]Aluminum was dissolved from D61, D39, D58, D18 and E33, successively, in the third batch of caustic-nitrate solution.
[e]Actinide oxides from all thirteen targets were combined for dissolution in HCl.

Table 4.3. Concentrations[a] of Various Components in Dejacketing Solutions and Dissolver Product Solutions

	Caustic Dejacketing Solutions		Acidic Dissolver Solutions	
Run Number	10-DS-1	11-DS-1	10-DS-1	11-DS-1
Actinides				
^{242}Pu, g			1.44	11.0
^{243}Am, g				
^{244}Cm, g	0.00073	0.0124	1.40	38.9
^{249}Bk, μg			9.2	957
^{252}Cf, μg			30	8620
^{253}Es, μg			0.25	49.2
^{244}Cm, % of ^{244}Cm in dissolver product	0.03	0.04		
Ionic contaminants				
Al, g			0.37	
Zr, g			0.35	5.1
Radioiodine (^{131}I), Ci	3.62	144	2.48	139
Other fission product gamma activity, Ci				
^{65}Zn		44		
$^{95}ZrNb$	9.71	159	37-45	2208
^{103}Ru	9.74	516	67.3	1581
^{110m}Ag		≤ 5		118
^{134}Cs		63.6	1.56	55.0
^{136}Cs		455	2.07	551
^{137}Cs	1.42	67.8	1.13	56.8
$^{140}BaLa$	1.14	34	24	927
^{141}Ce		1.85		1749
^{144}Ce	≤ 2.3	2.10	291	1197
Gross γ/Gross α Activity Ratio			0.727	0.988

[a]At the time of the aluminum dissolution (June 28, 1968 for 10-DS-1; July 8, 1968 for 11-DS-1).

was probably due in part to the high viscosity and in part to the silicon that was present. Backflushing the filter with water resulted in a temporary increase in the pumping rate but also added to the total amount of solution that had to be pumped. Transferring the aluminum-bearing dejacketing solutions consumed about 20% of the time that was required for the entire processing campaign.

The actinide oxide particles were slurried in demineralized water by vigorous air sparging and the slurry was jetted to a tantalum-lined vessel. Eight 5-liter flushes were required to transfer the solids. We considered the transfer of solids to be completed when the level of beta-gamma radiation at the top of T-70, which is located in cubicle 7, was not reduced by subsequent flushes to the receiving vessel, which is in the tank pit.

The use of two separate vessels (a Zircaloy-2 vessel for the aluminum dissolution using caustic-nitrate and a tantalum-lined vessel for the actinide dissolution using 6 M HCl) minimizes corrosion. Tantalum will not handle caustic solutions and previously we experienced high corrosion rates while dissolving targets in 6 M HCl in the Zircaloy-2 dissolver.

Excess water was evaporated from the tantalum-lined dissolver vessel, and concentrated HCl was added and gently boiled 2 hours to dissolve the actinide oxides. The dissolver product contained about 11 g of ^{242}Pu, 39 g of ^{244}Cm, 944 μg of ^{249}Bk, 6 mg of ^{252}Cf and 42 μg of ^{253}Es.

4.2 Plutonium Recovery

The plutonium was separated from the transplutonium actinides using the Pubex batch solvent extraction process. The plutonium that was contained in target D52 was separated immediately following the dissolution of the target. This was run 10-PU-1. The procedure that was used was identical to the one described below for separating the plutonium that was contained in the 13 targets (run 11-PU-1).

Following the separation and purification of the transcurium elements, the plutonium products from the two first-cycle Pubex runs were combined and the plutonium was purified further using a second cycle of

the Pubex process (run 11-PU-2), 3 cycles of anion exchange to remove $^{124,125}Sb$ and ^{110m}Ag (runs 11-PU-3, 11-PU-4, and 11-PU-5), and one cycle of the nitrate-based Plurix anion exchange process to remove ^{59}Fe (11-PU-6). We experienced considerable difficulty during nearly every step of additional purification, and material balance data fluctuated as much as 30% from step to step.

The transplutonium product solutions from runs 10-PU-1 and 11-PU-1 were combined for subsequent purification using the Tramex process (see Sect. 4.3).

4.2.1 Pubex Solvent Extraction Runs

Run conditions for the Pubex runs (including the second-cycle run, 11-PU-2) are given in Table 4.4. Amounts of various elements and isotopes in Pubex process solutions are listed in Table 4.5. Transuranium element material balances and process decontamination factors are given in Tables 4.6 and 4.7.

First-Cycle Runs (10-PU-1 and 11-PU-1). - The major first cycle run, 11-PU-1 is described below. Minor differences between it and run 10-PU-1, such as different solution volumes and concentrations, or different numbers of scrubbing or stripping contacts, may be noted in the tables. However, because of the similarity between the runs, 10-PU-1 will not be described here.

The dissolver solution from run 11-DS-1 was adjusted to feed specifications (4.5 M HCl and 0.05 M HNO_3) and the plutonium was extracted using 1 M di(2-ethylhexyl) phosphoric acid (HDEHP) in diethylbenzene (DEB). About 10 liters of feed solution and 10 liters of solvent were mixed by air sparging for about 8 hours. The solvent was scrubbed to remove small amounts of transplutonium elements using three 10-liter batches of 5 M HCl--0.02 M HNO_3, each of which was sparged with the solvent for about one hour. Each batch of aqueous, which contained the transplutonium elements, was transferred to an evaporator in which the combined aqueous phase was concentrated and adjusted to Tramex feed. The aqueous phase contained a large amount of dark gray solids which continually plugged the filter and

Table 4.4. Run Conditions for Plutonium Recovery Using Batch Extraction (Pubex)

Run Number	10-PU-1	11-PU-1	11-PU-2[a]	
Dates	6/30/68--7/4/68	7/14/68--7/25/68	7/26/68--8/10/68	
Equipment Used	T40, T72, T73	T40, T72, T73	T33, T40, T54, T604, T73	
Feed Material Source	10-DS-1 dissolver product solution	11-DS-1 dissolver product solution	Combined plutonium product solutions from 10-PU-1 and 11-PU-1 plus plutonium heels from previous campaigns	
Volume after evaporation, liters	9.2	9.0	5.8	
Final boiling point, °C		109	125	
Approximate acid concentration	6 M HCl	6 M HCl	16 M HNO_3[b]	
Feed Adjustment Conditions				
Reductant added	None	None	0.9 M $Fe(SO_3NH_2)_2$	
Volume added, liters			1.25	
Oxidant added	0.5 M HNO_3	0.5 M HNO_3	0.2 M KNO_2	
Volume, liters	1.0	1.0	1.0	
Sparging time, minutes	15	15	40[c]	
Adjusted Feed Solution				
Acid concentration				
HCl, M	5.5	4.5	None	
HNO_3, M	0.05	0.05	8	
Volume, liters	10.6	10.2	11.7	
Alpha power density, w/liter	0.5	10.8	0.2	
^{242}Pu, g/liter	0.31[d]	1.37[d]	1.6	
Extraction				
Extraction solution	1 M HDEHP in DEB	1 M HDEHP in DEB	1 M HDEHP in DEB	
Volume used, liters	10	10	10	
Sparging time, hours	8	8	8	
Temperature, °C	25-35	25-35	25-35	
Scrubbing				
Scrub solution			Solution 1	Solution 2
HCl, M	5	5	None	None
HNO_3, M	0.02	0.02	5	0.1
Number of scrubs	3	3	1	2
Volume used for each scrub, liters	10	10	10	5
Sparging time for each scrub, hours	1	1	1	1
Washing				
Wash solution	5 M HCl	5 M HCl	5 M HCl	
Volume, liters	10	10	5	
Number of washes	1	1	1	
Sparging time, hours	1	1	1	
Stripping				
Organic-phase reductant solution	0.2 M DBHQ in 2-ethylhexanol	0.2 M DBHQ in 2-ethylhexanol	0.2 M DBHQ in 2-ethylhexanol	
Volume, liters	2.5	5[e,f]	7.5[g]	
Aqueous stripping solution				
HCl, M	5	5	5	
$HONH_2$, M	0.1	0.1	0.1	
Number of strips	3	6[e,f]	8[g,h]	
Volume used for each strip, liters	10	10	10	
Sparging time for each strip, hours[i]	1	1	1	

[a]Second cycle run.
[b]Diluted to 10 M HNO_3 after evaporation was completed.
[c]Sparged 10 minutes after KNO_2 addition then heated to 55-65°C and sparged 30 minutes.
[d]Based on plutonium product solution measurements.
[e]After the wash was completed, aqueous strip solution was added but the addition of the organic-phase reductant and the first stripping contact were delayed seven days.
[f]Added 2.5 liters of reductant solution before the first strip and before the fourth strip.
[g]Added 2.5 liters of reductant solution before the first, fourth and seventh strips.
[h]Organic was entrained into the product catch tank, T-54; therefore, 2.5 liters of reductant solution and 2.5 liters of DEB were added to T-54 and this solution was stripped four times with 3 liters of 2 M HCl.
[i]Sparging time was 4 hours for the strip following each addition of reductant solution.

Table 4.5. Amounts of Various Elements and Isotopes in Process Solutions During Plutonium Recovery (Pubex)

Run Number	10-PU-1			11-PU-1			11-PU-2[b]		
	Feed	Product	Raffinate	Feed	Product	Raffinate[a]	Feed	Product	Raffinate
Measured Stream Components[c]									
^{242}Pu, g	1.44	3.00	<0.04	11.0	14.0	<0.003	19.0	23.2	0.017[d]
^{244}Cm, g	1.40	0.11	1.64	38.9	0.49	37.0	0.97	0.035	0.82[d]
^{249}Bk, μg	9.2		2.7	1352	187		183	16.6	
Zr, g	0.35			5.2		0.064			
Al, g	0.37								
Fe, g		∿11.3							
Ni, g						22.9			
Mo, g						∿0.05			
Gross gamma cts/min	8.99×10^{13}	1.17×10^{12}	8.19×10^{13}	3.51×10^{15}	1.53×10^{13}		1.67×10^{13}	2.48×10^{12}	
^{59}Fe, Ci		0.33	NR					0.199	
^{95}Nb, Ci	36.8	≤0.039	≤4.2	1477			≤0.52		
^{95}Zr, Ci	≤6.3	≤0.067	≤3.6	507			1.04		
^{103}Ru, Ci	67.3	0.243	82.0	1396	72.1		11.0	0.595	
^{106}Ru, Ci			NR				22.7		
^{110m}Ag, Ci		0.050	NR	≤108	4.9		0.60	0.138	
^{124}Sb, Ci		0.007	NR		0.44			0.033	
^{125}Sb, Ci			NR		36.0			2.62	
^{131}I, Ci	2.27	0.007		85.2	0.21	0.9	≤0.21		
^{134}Cs, Ci	1.56		NR	54.5			0.95		
^{136}Cs, Ci	2.07		NR	259					
^{137}Cs, Ci	0.97	≤0.025	≤3.0	55.5			0.65	≤0.41	
^{140}BaLa, Ci	23.6	≤0.063	28.1	635			1.21		
^{141}Ce, Ci			NR	1510					
^{144}Ce, Ci	291	3.98	352	1182			11.9	≤0.55	
^{154}Eu, Ci		5.79	NR				7.69		

[a] Includes components from 10-PU-1.
[b] Second cycle run.
[c] At the start of the run.
[d] Primary raffinate only: does not include scrub raffinates.

Table 4.6. Material Balances for ^{242}Pu and ^{244}Cm During Plutonium Recovery (Pubex)

Run Number	10-PU-1		11-PU-1		11-PU-2[a]	
	^{242}Pu	^{244}Cm	^{242}Pu	^{244}Cm	^{242}Pu	^{244}Cm
Input						
Feed, g	1.44	1.4	11.0	38.9	19.0	0.97
Output						
Transplutonium product, g	<0.04	1.64	<0.003	35.36	0.017[b]	0.82[b]
Plutonium product, g	3.0	0.11	14.0	0.49	23.2	0.035
Total out	3.0	1.75	14.0	35.85	23.2	0.855
Output/Input, %	208	125	127	92.2	122	88.1

[a]Second cycle run.
[b]Primary raffinate only: does not include scrub raffinates.

Table 4.7. Decontamination Factors During Plutonium Recovery (Pubex)

Run Number	10-PU-1		11-PU-1		11-PU-2[a]	
Product Solution	Plutonium	Curium	Plutonium	Curium	Plutonium	Curium
^{242}Pu		≥ 40		$\geq 3.6 \times 10^3$		946
^{244}Cm	28		101		34	
Zr				77		
Gross gamma	160	No DF	292		8.2	
^{95}Nb	≥ 1960	>10				
^{103}Ru	576	No DF	25		22	
^{110m}Ag					5	
^{131}I	676		517	90		
^{137}Cs	≥ 80	No DF			≥ 2	
$^{140}BaLa$	≥ 780	No DF				
^{144}Ce	152	No DF			≥ 26	

[a]Second cycle run.

thereby impeded the transfers. Previous studies had shown this to be almost entirely silicon.

The first batch of strip solution (10 liters of 5 M HCl) was put into the tank which contained the plutonium in the solvent phase, but the addition of the organic phase modifier and the actual stripping was postponed one week. Nearly 400 mCi of ^{131}I had been released from the HFIR stack during the processing thus far, and we felt that the major cause had been air sparging to contact the phases during the extraction step. We elected to defer the stripping of the plutonium until after we finished the processing of the heavier actinides. We did not want to risk being forced to delay the recovery of the transcurium elements because of a continued high rate of iodine release.

After the processing of the transplutonium elements was completed, we added 2.5 liters of organic phase modifier, 0.2 M 2,5 di-*tert*-butylhydroquinone (DBHQ) in 2-ethylhexanol, to the solvent to strip the plutonium. After we made three stripping contacts, using 10 liters of fresh strip solution each time, we added an additional 2.5 liters of phase modifier to the solvent and made three more 10-liter stripping contacts. Evidently the plutonium was more difficult to strip after it was left in the organic phase for a week.

About 91.2% of the curium was recovered in the curium product along with less than 0.03% of the plutonium. The final plutonium product contained 140% of the plutonium that was measured in the feed and contained 1.3% of the curium. Losses to the waste organic were less than 0.03% for plutonium, curium, and californium.

Second-Cycle Run (11-PU-2). - The plutonium product solutions from 10-PU-1 and 11-PU-1 were combined with a nitrate solution that contained about 2 g of ^{242}Pu from previous campaigns, and the mixture was converted to a nitrate solution. Ferrous sulfamate was added to reduce all the plutonium to Pu(III) and then potassium nitrite was used to convert it all to Pu(IV). The final feed acidity was 8 M HNO_3. The plutonium was extracted into 1 M HDEHP in DEB by air sparging approximately equal volumes of feed solution (11.7 liters) and solvent (10 liters). The solvent was scrubbed with

10 liters of 5 M HNO_3 and two 5-liter batches of 0.1 M HNO_3, and was washed with 5 liters of 5 M HCl. This sequence removed the nitrate so that it would not interfere with the reductant in the subsequent step. Two and one-half liters of 0.2 M DBHQ in 2-ethylhexanol was added to the solvent to reduce the plutonium which was then stripped using 5 M HCl solution containing 0.1 M hydroxylamine. Stripping was difficult, as it had been in first cycle run 11-PU-1. After three 10-liter batches of strip solution had been used, the solvent still contained most of the plutonium. A second batch of reductant (DBHQ) was added and three more acid strips were made. The solvent still contained 0.9 g of ^{242}Pu which was stripped by adding still more reductant and making two more stripping contacts. Analysis of the product indicated that it contained 23.2 g of ^{242}Pu (122% of the amount indicated by analysis of the feed). The gross gamma DF was 8.

4.2.2 Anion Exchange

The plutonium had to be decontaminated further so that it could be removed from the cells for final purification in a glove box. The major radioactive contaminants that remained following 11-PU-2 were $^{124,125}Sb$, ^{110m}Ag and ^{59}Fe.

For removal of radioantimony the solution was adjusted to 2.3 M HCl and 0.15 M hydroxylamine, and was pumped through a column filled with Dowex 21K anion exchange resin and back into the feed tank. Pumping was continued until the radiation level on the column stopped increasing. Three runs were made: 11-PU-3, 11-PU-4 and 11-PU-5. After the first run only about 20% of the plutonium was found in the solution. Either the plutonium had precipitated during feed adjustment or had loaded on the resin column. Five liters of 6 M HCl was added to the tank, the column was flushed back to the tank with 0.1 M HCl and the solution in the tank was concentrated, by boiling, to 8.5 liters. This solution, which now contained the plutonium, was adjusted to feed specifications and pumped through the resin column. The solution still contained too much penetrating radiation to permit transfer to a glove box. We think that the column capacity had been exceeded. The resin was replaced and the solution was again adjusted to feed specifications and pumped through the

column. The gross gamma DF for the 3 runs was 6.7. Most of the ^{124}Sb and ^{125}Sb had been removed but the solution still contained more radioactivity (^{110m}Ag and ^{59}Fe) than could be handled conveniently in a glove box.

The solution was converted to a nitrate solution and adjusted to feed specifications for the nitrate-based Plurix anion exchange process,[2] and the plutonium was loaded on the resin column. The product of the first elution was decontaminated sufficiently for removal to the glove box (the major contaminant was ^{110m}Ag) but it contained only 75% of the plutonium. The other 25% was not in the raffinate so a second elution was made. No more plutonium was eluted but, instead, the product was recontaminated by radioactive isotopes (^{95}Zr and/or ^{95}Nb) that were eluted.

The level of penetrating radiation was low enough to permit handling of the plutonium in a glove box. Thus, no additional purification was attempted.

4.3 Tramex Solvent Extraction

The combined solution of transplutonium products from the first-cycle Pubex runs was adjusted to feed specifications for solvent extraction processing and was decontaminated using the Tramex process. Feed adjustment data and the operation summary are given in Table 4.8. Table 4.9 lists the compositions of nonradioactive process streams, and flow rates and volume balances for all process streams. Compositions of radioactive streams are listed in Table 4.10.

About 1.5% of the curium was pumped to a waste tank during attempts to unplug the outlet line from the phase separator on the strip column. Except for that plugged line, equipment operation was satisfactory. About 3% of the curium was recovered from feed tank heels, column flushes and flushes of the cubicle floor, and was stored in the rework tank. Gross gamma decontamination factor (DF) was 43, which is lower than usual. The material balance for ^{244}Cm was 94.4%.

Table 4.8. Feed Adjustment Data and Operation Summary for Tramex Solvent Extraction Processing (Run 11-TR-1)

Dates	7/16/68--7/20/68
Equipment Used	T-73A, T-20, T-21, T-60, and Cub. 7 Solvent Ext. Rack
Feed Material Source	Combined Transplutonium Fractions from 10-PU-1 and 11-PU-1
Initial volume, liters	2.9
Initial HCl concentration, M	~6
Feed Adjustment Conditions	
LiCl added, moles	160
Concentration	
Final boiling temperature, °C	137
Volume after evaporation, liters	15.1
Acid adjustment solution	12 M HCl
Volume added, liters	1.25
Flush solution	0.2 M HCl, 11 M LiCl
Volume added, liters	0.5
Digestion temperature, °C	120
time, minutes	20
Adjusted Feed Solution	
Volume, liters	16.0
HCl concentration, M	0.29
LiCl concentration, M	~11
^{244}Cm concentration, g/liter	2.3
Alpha power density, w/liter	6.5
Length of Operation (including feed tank flushes), hours	52.4
Feed Time, hours	52.4
Down Time, hours	0
Number of Shutdowns	0
Operating Temperature, °C	60

Table 4.9. Compositions of Nonradioactive Streams and Average Flow Rates and Volume Balances for all Process Streams for Tramex Solvent Extraction (Run 11-TR-1)

Cold Stream Compositions	
Aqueous scrub solution	11 ± 0.1 M LiCl, 0.20 ± 0.02 M HCl
Aqueous strip solution	8.0 ± 0.2 M HCl
Organic extractant solution	0.60 ± 0.025 M Adogen·HCl, 0.03 ± 0.01 M HCl, 0.05 M DBHQ in Diethylbenzene
Average Flow Rates, liters/hour	
Inlet streams	
Feed	0.45
Aqueous scrub	0.61
Strip	0.54
Organic extractant	1.75
Outlet streams	
Aqueous raffinate	1.14
Aqueous product	0.57
Waste organic	1.75
Volume Balances, %	
Extraction-scrub column aqueous	107.5
Strip column aqueous	105.6
Total aqueous	106.9
Organic	100.0
Total	103.3

Table 4.10. Contents of Radioactive Streams During Tramex Solvent Extraction (Run 11-TR-1)

All values are adjusted to the start of the run, July 16, 1968.

Process Stream	Feed	Product	Raffinate	Waste Organic
Stream Volume, liters	16.0	a	92.9	135
^{242}Pu, g/liter	<0.004			
^{244}Cm, g/liter	2.31	1.15	2.4×10^{-4}	2.4×10^{-5}
LiCl, M	11.7[b]	0.010		
HCl, M	0.29			
Zr, g/liter	0.004	0.01		
Ni, g/liter	1.44			
Mo, g/liter	<0.003			
^{60}Co, Ci/liter			0.46	0.123
^{95}Zr, Ci/liter	≤14.1	≤0.045	≤0.68	≤0.099
^{103}Ru, Ci/liter	109	4.64	≤0.68	7.61
^{110}Ag, Ci/liter		0.181	≤0.032	
^{131}I, Ci/liter	0.10	≤0.037	≤0.35	≤0.069
^{134}Cs, Ci/liter	≤14.1	≤0.032		
^{137}Cs, Ci/liter	≤14.1	≤0.067	≤0.68	≤0.099
$^{140}BaLa$, Ci/liter	77.6	≤0.049	3.8	≤0.03
^{144}Ce, Ci/liter	774	≤0.67	47.7	≤0.045
Gross γ/Gross α Ratio	1.074	0.0252	783	2440

[a] Evaporating during collection.
[b] Calculated from boiling temperature and volume.

Tramex Equipment. - The Tramex process equipment that was used in this campaign was new equipment that was designed to be operated with the organic phase continuous. The old equipment had been replaced because it had become difficult to operate because of corrosion, wear, and damage. Operation with the organic phase continuous eliminated the need for an organic backwash in the strip column and reduced problems we had had with overflow of organic from the columns. A major advantage of having Tramex equipment that will operate with the organic phase continuous is that the Hepex process (for partitioning the actinides) can be operated in the same equipment.

The new equipment rack is shown in Fig. 4.2. The major difference between equipment for operation with the organic phase continuous and equipment for operation with the aqueous phase continuous is that phase separators external to the columns are required for organic-continuous operation.

Tramex Process Flowsheet. - The flowsheet for the Tramex solvent extraction process is shown in Fig. 4.3. The adjusted feed is pumped to a pressurized feed pot and is allowed to overflow to the feed tank through a jack leg. The flowrate to the scrub column phase separator is adjusted to 0.5 ± 0.05 liter/hr by adjusting the air pressure on the pot. The extractant, which is 0.6 ± 0.025 M Adogen 364-HP (a high purity trialkyl amine), containing 0.03 ± 0.01 M free HCl, in diethylbenzene (DEB) diluent, is fed at 1.7 ± 0.1 liter/hr to the phase separator on the extraction column from which it is pumped to the bottom of the extraction column by means of the column pulser and appropriate flow restrictors in the column-phase separator circulating loop. The scrub solution, which is 11.0 ± 0.1 M LiCl--0.2 ± 0.02 M HCl, is fed at 0.6 liter/hr to the top of the scrub column where it flows countercurrent to the organic to scrub out small amounts of extracted or entrained rare earths before the extractant flows to the strip column. The actinide-bearing organic from the scrub column is fed to the strip column phase separator and then pumped through the column where the transuranium elements are back-extracted into 8.0 ± 0.2 M HCl which is fed to the top of the strip column at 0.5 ± 0.05 liter/hr. The rare earths and other contaminants are collected in the extraction column raffinate or in the waste organic from the strip column, both of which are discarded.

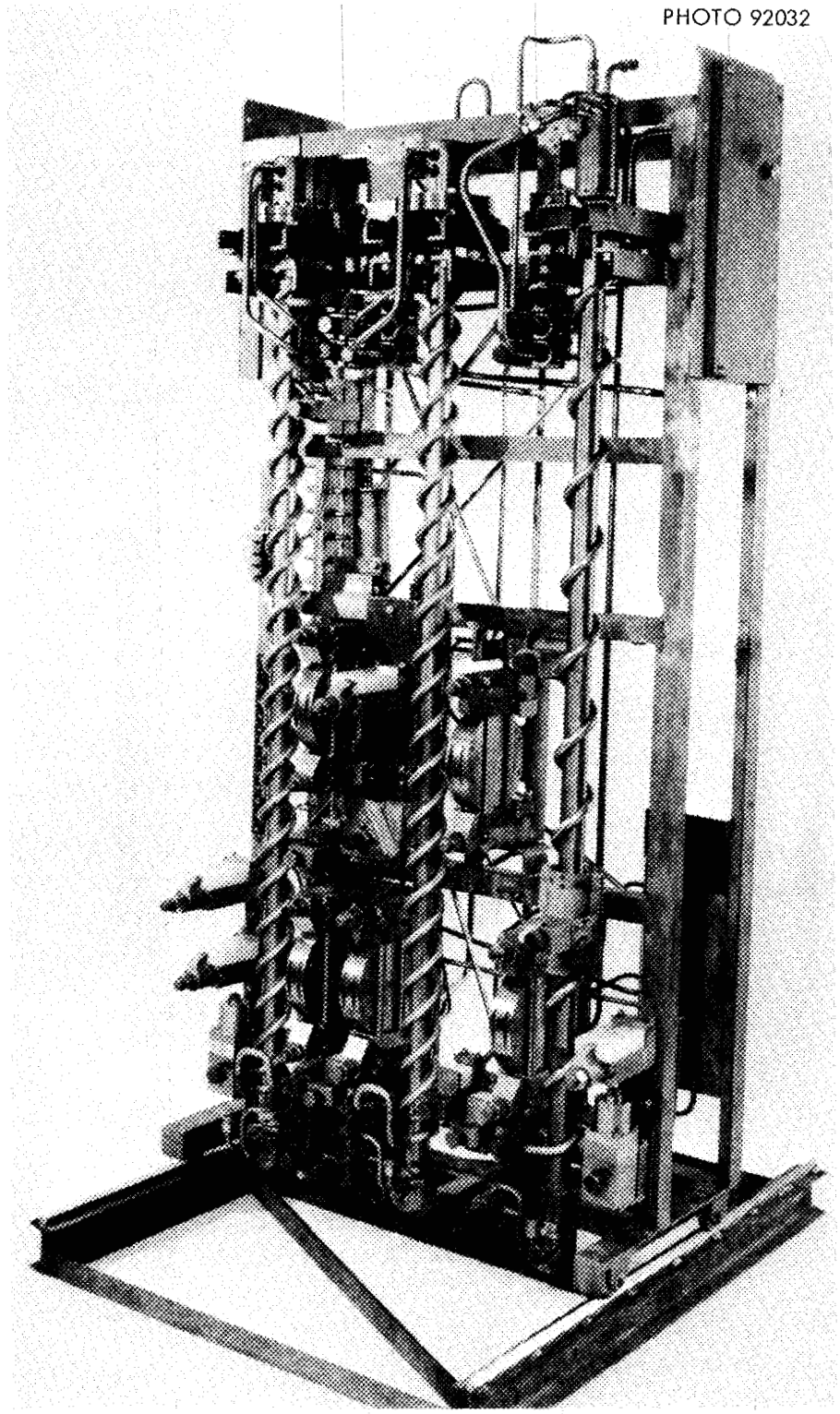

Fig. 4.2. Tramex Equipment (Organic Continuous).

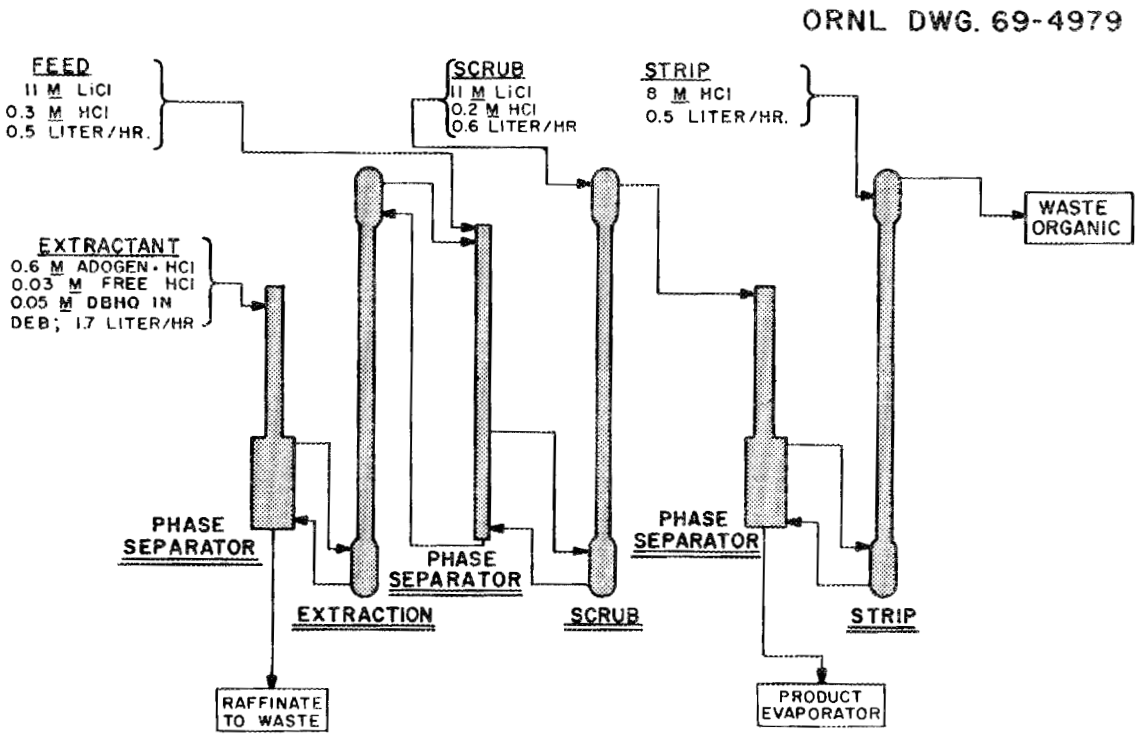

Fig. 4.3. Flowsheet for the Tramex Process.

Tramex Feed Adjustment. - The solution of transplutonium elements from the plutonium recovery step was evaporated to a volume of about 3 liters, 160 moles of LiCl was added and the solution was evaporated until the boiling temperature was 137°C (about 11.8 M LiCl). The solution was made 1 M in HCl by addition of 1.25 liters of 12 M HCl and the addition line was flushed with 0.5 liter of a solution of 11 M LiCl, 0.2 M HCl. The feed solution was then digested at 120°C for 20 min to assure dissolution of any zirconium that might have precipitated during the evaporation and to remove excess acid.

The adjusted feed was 16 liters of solution that was 0.29 M HCl and about 11 M LiCl. It contained 2.3 g/liter ^{244}Cm which made the solution power density (from alpha decay) 6.5 w/liter.

The Tramex Run. - The run lasted for a total of 52.4 hours on radioactive feed and feed tank flush solutions. The only significant operating difficulty was a plugged outlet line from the phase separator on the strip column. About 1.5% of the curium was pumped to a waste tank during attempts to unplug the line. About 3% of the curium was recovered from feed tank heels, column flushes and flushes of the cubicle floor and was stored in the rework tank. Less than 0.1% was lost to the extraction column raffinate. Gross gamma DF was 43, which is lower than usual for the Tramex process but which is adequate. The major radioactive contaminant in the product was ^{103}Ru which is not effectively removed in the Tramex process. The ^{103}Ru DF was 12.

It was not possible to make an exact material balance because part of the Tramex product was used without measurement as feed to LiCl-based anion exchange. The outlet streams from that ion exchange run, the remaining Tramex product and known losses and rework totaled 94.4% of the curium that was measured in the Tramex feed; at least 90% was recovered as product.

4.4 Separation of Transplutonium Elements

The Tramex product was contacted with 1 M HDEHP in DEB to remove zirconium and any residual organic that might interfere with the next processing step. Then, the Tramex product was decontaminated further, and the transcurium elements were separated from the americium and curium

using LiCl-based anion exchange. Four runs were made. Descriptions of the equipment that was used and feed adjustment data are given in Table 4.11. Table 4.12 lists compositions of elutriant solutions and solution flow rates. Amounts of various isotopes in process solutions are listed in Table 4.13 and material balances are listed in Table 4.14.

About half of the Tramex product solution was adjusted to feed specifications (12 M LiCl and 0.1 M HCl) and passed through an anion-exchange column of Dowex 1-X10 resin (200 to 300 mesh), on which the actinides and many of the contaminants were sorbed. The nickel and rare earths were eluted, using 10 M LiCl, and discarded. Most of the americium and curium was eluted, using 9 M LiCl, and stored as product. The elutriant was changed to 8 M HCl to remove the remaining actinides (berkelium, californium and einsteinium). All of the transcurium elements and about 7% of the curium were collected in this transcurium product fraction, which was added to the rest of the unprocessed Tramex product. This solution was adjusted to feed specifications and was processed using the LiCl-based anion exchange process. The americium-curium products from both runs were combined and stored. The transcurium product from this second loading-eluting of the ion exchange resin, which contained all of the transcurium elements and only 0.76 g of curium, was adjusted to feed and purified further using a third cycle of LiCl-based anion exchange. New resin was used for this part of processing. The final transcurium product fraction contained 5.2 mg of ^{252}Cf, 1 mg of ^{249}Bk, 32 μg of ^{253}Es and only 30 mg of ^{244}Cm.

During the second ion-exchange run, some of the transcurium product solution leaked from damaged plastic valves and lines. This solution was recovered from the cubicle floor and was combined with feed tank heels and column flushes, and a fourth LiCl-based anion exchange run was made to recover the transcurium elements. An additional 140 μg of ^{249}Bk, 1 mg of ^{252}Cf and 7 μg of ^{253}Es were recovered in a transcurium fraction that contained only 28 mg of ^{244}Cm. Material balances over the four runs were 109% for curium, 112% for berkelium, 96% for californium and 90% for einsteinium. The transcurium product solutions were transferred to cell 5 where the transcurium elements were separated and purified.

Table 4.11 Equipment Descriptions and Feed Adjustment Data for Actinide Partitioning Using LiCl-Based Anion Exchange

Run Number	11-CM-1	11-CM-2	11-CM-3	11-CM-4
Dates	7/18/68--7/20/68	7/20/68--7/21/68	7/21/68--7/22/68	7/24/68
Equipment Used	T65, T67, T604, T607 Ion Exchange Column	T65, T67, T604, T607 Ion Exchange Column	T65, T67, T604, T607 Ion Exchange Column	T65, T67, T607 Ion Exchange Column
Ion Exchange Column				
Material	Glass	Glass	Glass	Glass
Diameter, cm	5	5	5	5
Ion Exchange Resin	Dowex 1-X10	Dowex 1-X10	Dowex 1-X10	Dowex 1-X10
Size, mesh	200-300	200-300	200-300	200-300
Volume, liters	1.2[a]	1.2[b]	1.2	1.2[c]
Column Temperature, °C	70-80	70-80	70-80	30-40[d]
Column Pretreatment Solution				
LiCl, M	~12.0	~12.0	~12.0	~12.0
HCl, M	0.1	0.1	0.1	0.1
$HONH_2 \cdot HCl$, M	0.1	0.1	0.1	
CH_3OH, volume %	2.5	2.5	2.5	
Volume used, liters	4	4	4	4
Feed Material Source	Part of 11-TR-1 product	Rest of 11-TR-1 product plus transcurium product from 11-CM-1	Transcurium product from 11-CM-2	Material recovered from cubicle floor plus 11-CM-3 feed heel
Initial volume, liters	1.6	12.1	3.5	6.2
Initial HCl, M	6	6	2	0.5
Initial LiCl, M	0.1	0.5	1.5	
Feed Adjustment Conditions				
LiCl added, moles	14.0	7.5	5.0	6.0
Final boiling point, °C	142.7	142.0	142.5	142.5
Final volume, liters	1.1	1.1	0.8	0.6
Acid adjustment solutions				
HCl, moles	1.6	1.6	1.15	1.03
LiCl, moles	2.5	2.5	2.5	2.51
Volume added, liters	0.335	0.335	0.295	0.285
Digestion temperature, °C	120	120	120	120
Digestion time, minutes	10	10	10	10
Adjusted Feed				
Volume, liters	1.54	1.85	2.8	2.2
HCl, M	0.1	0.1	0.1	0.1
LiCl, M	12	12	12	12
^{244}Cm, g/liter	11.6	8.9	0.27	0.033
α power density, w/liter	33	25	0.84	0.11

[a] Resin was used previously for Run 7-CM-11 in which 10 g of ^{244}Cm was processed.
[b] Resin used previously for Run 7-CM-11 and Run 11-CM-1.
[c] Resin used previously for Run 11-CM-3.
[d] Leaking hot water line prevented heating of column.

Table 4.12. Compositions of Elutriant Solutions and Solution Flow Rates for Actinide Partitioning Using LiCl-Based Anion Exchange

Run Number	11-CM-1	11-CM-2	11-CM-3	11-CM-4
Feed Loading Rate, $ml \cdot min^{-1} \cdot cm^{-2}$	0.85	1.05	0.99	0.43
Rare Earth Elutriant Solution				
LiCl, M	10.0 ± 0.1	10.0 ± 0.1	10.0 ± 0.1	10.0 ± 0.1
HCl, M	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05
$HONH_2 \cdot HCl$, M	0.1	0.1	0.1	0
CH_3OH, vol. %	2.5	2.5	2.5	0
Volume used, liters	1.6	2.0	1.8	2.2
Rate, $ml \cdot min^{-1} \cdot cm^{-2}$	0.91	0.77	0.69	0.56
Americium-Curium Elutriant				
LiCl, M	9.0 ± 0.1	9.0 ± 0.1	9.0 ± 0.1	
HCl, M	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05	
$HONH_2 \cdot HCl$, M	0.1	0.1	0.1	
CH_3OH, vol. %	2.5	2.5	2.5	
Volume used, liters	3.0	3.5	5.2	
Rate, $ml \cdot min^{-1} \cdot cm^{-2}$	1.25	1.12	1.38	
Transcurium Elutriant				
HCl, M	8.0 ± 0.2	8.0 ± 0.2	8.0 ± 0.2	8.0 ± 0.2
Volume used, liters	2.7	1.1	1.1	0.88
Rate, $ml \cdot min^{-1} \cdot cm^{-2}$	1.56	1.43	1.40	1.12
Column Flush				
HCl, M	0.8	0.8	0.8	0.8
Volume used, liters	4.0	4.0	2.5	3.8
Rate, $ml \cdot min^{-1} \cdot cm^{-2}$	2.8	4.1	1.2	1.7

Table 4.13. Amounts of Various Isotopes in Process Solutions During Actinide Partitioning Using LiCl-Based Anion Exchange

Run Number	11-CM-1				11-CM-2					11-CM-3				11-CM-4		
Process Stream	Feed	Column Flush and Raffinate	Am-Cm Product	Feed Heel and Transcurium Product	Feed	Column Flush and Raffinate	Leak to Floor	Am-Cm Product	Feed Heel and Transcurium Product	Feed	Feed Heel and Column Flush	Am-Cm Product	Transcurium Product	Feed	Raffinate and Am-Cm Product	Transcurium Product
Measured Stream Components[a]																
^{244}Cm, g		0.026	16.7	1.22	16.4	0.089	0.033	18.6	0.76	0.76	0.040	0.70	0.030	0.073	0.050	0.028
^{249}Bk, mg			0.010	0.581	1.027			0.022	0.885	0.885		0.002	0.990			0.139
^{252}Cf, mg		0.026	0.004	3.30	6.68	0.031	0.68		5.13	5.13	0.26	0.014	5.32	0.94	0.026	1.10
^{253}Es, μg				19.6	39.9	0.2			27.6	27.6			31.8			7.1
^{95}Nb, Ci/g ^{244}Cm			$\leq$0.0076[b]		$\leq$0.15			$\leq$0.0076[b]				$\leq$0.0076[b]				
^{95}Zr, Ci/g ^{244}Cm	$\leq$0.039		$\leq$0.0091[b]		$\leq$0.22			$\leq$0.0091[b]				$\leq$0.0091[b]				
^{103}Ru, Ci/g ^{244}Cm	4.03		0.0052[b]		7.91			0.0052[b]				0.0052[b]				
^{110}Ag, Ci/g ^{244}Cm	0.157		0.0221[b]		0.275			0.0221[b]				0.0021[b]				
^{131}I, Ci/g ^{244}Cm	$\leq$0.028		0.0048[b]		$\leq$0.073			0.0048[b]				0.0048[b]				
^{134}Cs, Ci/g ^{244}Cm	$\leq$0.028		0.0021[b]		$\leq$0.11			0.0021[b]				0.0021[b]				
^{137}Cs, Ci/g ^{244}Cm	$\leq$0.058		0.012[b]		$\leq$0.15			0.012[b]				0.012[b]				
^{140}BaLa, Ci/g ^{244}Cm	$\leq$0.039		0.0021[b]		0.456			0.0021[b]				0.0021[b]				
^{144}Ce, Ci/g ^{244}Cm	$\leq$0.58		$\leq$0.021[b]		3.56			$\leq$0.021[b]				$\leq$0.021[b]				
Gross Neutrons/Gross Alpha		1.89×10^{-5}	8.59×10^{-7}	4.60×10^{-4}	8.54×10^{-5}	6.35×10^{-5}	3.89×10^{-3}		1.14×10^{-3}	1.14×10^{-3}	1.22×10^{-3}	9.03×10^{-7}[b]	1.20×10^{-2}	2.41×10^{-3}	9.91×10^{-5}	5.47×10^{-3}
Gross Gamma/Gross Alpha	2.52×10^{-2}		4.35×10^{-4}[b]		5.79×10^{-2}			4.35×10^{-4}[b]				4.35×10^{-4}[b]				

[a]At date of start of run.
[b]Based on analysis of composite Am-Cm product from 11-CM-1, 11-CM-2 and 11-CM-3.

Table 4.14. Material Balances for ^{244}Cm and Gross Neutron Activity During Actinide Partitioning Using LiCl-Based Anion Exchange

Run Numbers	11-CM-1		11-CM-2		11-CM-3		11-CM-4	
	^{244}Cm (g)	Gross Neutrons (neutrons/min)	^{244}Cm (g)	Gross Neutrons (neutrons/min)	^{244}Cm (g)	Gross Neutrons (neutrons/min)	^{244}Cm (g)	Gross Neutrons (neutrons/min)
Input								
Feed			16.4	1.25×10^{11}	0.76	8.35×10^{10}	0.073	1.62×10^{10}
Output								
Transcurium Product	1.22	5.25×10^{10}	0.76	8.35×10^{10}	0.03	8.53×10^{10}	0.028	1.88×10^{10}
Am-Cm Product	16.7	1.31×10^{9}	18.6	5.92×10^{8}	0.70	2.98×10^{9}	None	None
Rework Material	None	None	0.033	1.17×10^{10}	0.04	4.50×10^{9}	None	None
Measured Losses	0.026	4.53×10^{7}	0.089	5.20×10^{8}	< 0.01	2.97×10^{7}	0.050	4.51×10^{8}
Total Out	17.95	5.38×10^{10}	19.48	9.63×10^{10}	0.77	9.28×10^{10}	0.078	1.92×10^{10}
Output/Input %			119	77.0	101	111	107	119

5. BEHAVIOR OF RADIOIODINE

Einsteinium-253 was an important product of this campaign. Because it has a half life of only 20 days, the amount that can be recovered from a group of targets is limited by the need to allow the targets to cool to avoid the release of an excessive amount of ^{131}I to the environment. Each of the 13 targets contained 216 curies of ^{131}I at reactor shutdown. We assumed that one curie was an acceptable release during the campaign. If we released from 1 to 1-1/2%, as we had in previous campaigns, we would have had to wait 6 weeks to begin processing.

We installed an iodine trapping system consisting of a caustic scrubber and a bed of KI-impregnated charcoal in the condensate collection system which serves all of the process evaporators and the dissolver vessel, and we modified the piping so that all off gas from these vessels (about 3 cfm) passed through the scrubber and charcoal trap.

Dejacketing wastes were stored in two unused process vessels. These were not vented through the trapping system but, at least, there was no danger that the iodine-bearing caustic wastes would be acidified inadvertently. The instrument air purges were shut off as an additional safeguard.

To test the system we dissolved target D52, which contained 9.8 curies of ^{131}I, and separated the plutonium from the transplutonium actinides using the Pubex batch extraction process. About 0.15% (14 mCi) of the ^{131}I was released from the HFIR stack. That indicated that we could dissolve the 13 targets after a 3-week cooling period and process them without releasing more than one curie of radioiodine.

Processing was started after a 22-day cooling period: the targets contained a total of 460 curies of ^{131}I. Approximately 1.1 curie of ^{131}I was released to the environment during the 3-week processing period and 0.6 curie was released during the following 2 weeks when we were transferring waste solutions, consolidating rework material and concentrating products.

There were three times when the iodine release rate increased sharply. The first two were related to the Pubex process. When we sparged the tank that contained the adjusted feed (in 4.5 M HCl) and the Pubex extractant (1 M HDEHP in DEB) we by-passed the new charcoal trap to avoid loading it with organic vapors. The feed solution contained 135 curies of ^{131}I. The ^{131}I release rate jumped to 200 mCi the first day and was 160, 100, 40 and 20 mCi on successive days. Analyses showed that over 95% of the ^{131}I had been extracted along with the plutonium. We transferred (by steam jet) some neutralized condensate and caustic scrubber overflow solutions, which contained a total of 40 Ci, to our waste tank during this period. The HFIR stack iodine monitor indicated that this caused a release of iodine in addition to the release caused by Pubex process operations.

The next large iodine release occurred about 10 days later when we again by-passed the trap and started stripping the plutonium from the Pubex organic. The iodine release rate jumped from 6 mCi per day to 200 mCi per day and then dropped slowly (over a 2-week period) to 20 mCi per day. Clearly, by-passing the charcoal trap and/or sparging the Pubex solvent caused the release of a significant amount of radioiodine.

The third release occurred when we pumped about 50 liters of the caustic-nitrate dejacketing waste from a process vessel, in which it had been stored for a month, to our waste tank, F-126. This involved pumping a caustic solution containing about 5 Ci of radioiodine into a tank that contained a caustic heel. We had had no concern that this would release iodine. Cold and low-level tests had indicated that in caustic the iodine would be partly iodide and partly iodate with none as free iodine. However, the daily release rate from the HFIR stack jumped to 140 mCi and then dropped slowly to 5 mCi over a 5 day period. Subsequent analysis of the solution showed that all of the iodine was extractable into carbon tetrachloride; thus, none of it was in the iodide or iodate form.

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