2 csp

MASTER

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION • NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL - TM - 3343

SUMMARY OF THE CAMPAIGN DURING FEBRUARY 1969 TO PROCESS
SIX IRRADIATED HFIR TARGETS IN THE TRANSURANIUM PROCESSING PLANT

L. J. King and E. D. Collins

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

SUMMARY OF THE CAMPAIGN DURING FEBRUARY 1969 TO PROCESS
SIX IRRADIATED HFIR TARGETS IN THE TRANSURANIUM PROCESSING PLANT

L. J. King and E. D. Collins

TRANSURANIUM PROCESSING PLANT STAFF

W. D. Burch, Group Leader

J. E. Bigelow	F. L. Peishel
F. R. Chattin	C. L. Shepherd
E. D. Collins	R. C. Shipwash
W. W. Evans	B. J. Strader
L. J. King	J. E. Van Cleve
E. J. Manthos	C. E. Waddell
J. L. Matherne	O. O. Yarbrow

AUGUST 1971

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1

2

3

4

5

6

7

CONTENTS

	Page
Abstract	1
1. Introduction	2
2. Summary of Results	3
3. Target Description	4
3.1 Americium-Curium Oxide.	4
3.2 Irradiation	6
3.3 Compositions of Irradiated Targets.	7
4. Processing	8
4.1 Target Dissolution.	9
4.2 Pubex Solvent Extraction.	14
4.3 Tramex Solvent Extraction	19
4.4 Separation of Transplutonium Elements	25
4.5 Cleanex Batch Extraction.	34
4.6 Berkelium Material Balance.	37
5. Behavior of Radioiodine.	38
6. References	43

SUMMARY OF THE CAMPAIGN DURING FEBRUARY 1969 TO PROCESS
SIX IRRADIATED HFIR TARGETS IN THE TRANSURANIUM PROCESSING PLANT

L. J. King and E. D. Collins

ABSTRACT

Six irradiated HFIR targets were processed in the Transuranium Processing Plant (TRU) to recover the transuranium elements. This was the first campaign in which recycle americium-curium targets were processed. Prior to irradiation, each of the targets contained approximately 4.38 g of ^{244}Cm , 0.34 g of heavier curium isotopes, and 0.78 g of ^{243}Am that had been recovered in TRU from irradiated plutonium targets. The six targets had been fabricated in the remote target fabrication equipment in TRU, using americium-curium oxide powder which had been prepared during development studies of the curium sol-gel process. Purified products contained about 0.3 g of ^{243}Am , 17 g of ^{244}Cm , 1.2 mg of ^{249}Bk , 9.2 mg of ^{252}Cf , 68 μg of ^{253}Es and 10^8 atoms of ^{257}Fm . Processing steps were: dissolution of the aluminum using caustic-nitrate solution, dissolution of the actinide oxides using concentrated hydrochloric acid, removal of radioiodine and recovery of 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. Newly-installed metal (tantalum) equipment for the LiCl -based anion exchange process performed satisfactorily. All product fractions were taken based on continuous in-line alpha monitoring of the column effluent line and on neutron and gamma scans of the tantalum column. Only 300 millicuries of ^{131}I (of 400 curies present in the targets) was released from TRU during the campaign. We confined most of the iodine-bearing off-gas to a 3-cfm stream, and installed an experimental iodine removal system in this small stream. The treatment system was composed of a caustic scrubber to remove acid vapors, a heater, a bed of oxidation catalyst (operated at 350°C), a cooler, and a bed of KI-impregnated charcoal. The 3-cfm off-gas stream was decontaminated from ^{131}I by a factor (DF) as high as 10^4 .

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 or ^{244}Cm 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 6 irradiated HFIR targets, which were the first recycle americium-curium targets processed in TRU. Prior to irradiation, each of the targets contained 4.38 g of ^{244}Cm , 0.34 g of heavier curium isotopes, and 0.78 g of ^{243}Am that had been recovered in TRU from irradiated plutonium targets. The six targets had been fabricated in the remote target fabrication equipment in TRU, using americium-curium oxide powder which had been prepared during developmental studies of the curium sol-gel process.

The processing steps used 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 of radioiodine and recovery of plutonium using the Pubex batch extraction process; (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 and in supporting shielded cave facilities.

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 campaign contained 0.3 g of ^{243}Am , 17 g of ^{244}Cm , 1.2 mg of ^{249}Bk , 9.2 mg of ^{252}Cf , 68 μg of ^{253}Es and 10^8 atoms of ^{257}Fm . The campaign was completed in three weeks. No major problems were encountered.

The use of 3 M NaOH--1.5 M NaNO_3 , half the caustic-nitrate concentration that we had used previously, for dissolving the aluminum from the targets and the installation of a larger filter than we had used previously increased by a factor of 10 the rate at which the dejacketing solutions were pumped from the dissolver. In the previous campaign about 20% of the total time required for processing had been spent transferring the dejacketing solutions.

Permanent tantalum equipment was installed for the LiCl-based anion exchange process for separating the transcurium elements from americium and curium. This was the first time this process step was not done in transparent (glass and plastic) equipment. All product fractions were made based on continuous in-line alpha monitoring of the column effluent line and on neutron and gamma scans of the column. Such indications as the green color from nickel during its elution and the red glow from the curium band on the column were clearly not needed.

An experimental off-gas treatment system was used successfully to limit the release of radioiodine from TRU. The targets contained approximately 400 curies of ^{131}I when processing was started: only 300 millicuries was released from TRU during the campaign.

The main feature of the treatment system is a bed of oxidation catalyst that converts organic vapors to CO_2 and H_2O and thereby protects a bed of KI-impregnated charcoal from being poisoned against iodine retention. Earlier attempts to trap radioiodine, using charcoal beds, were unsuccessful because organic vapors quickly poisoned the charcoal.

We confined most of the iodine-bearing off-gas to a 3-cfm stream, and installed the iodine removal system in this small stream. The treatment system was composed of a caustic scrubber to remove acid vapors, a heater, a bed of oxidation catalyst (operated at 350°C), a cooler, and the charcoal bed. The 3-cfm off-gas stream was decontaminated from ^{131}I by a factor (DF) as high as 10^4 .

3. TARGET DESCRIPTION

The configuration of the HFIR target element is shown in Fig. 3.1. Details of fabrication have been published.¹ In each target, the 20-in.-long active column contained approximately 4.38 g of ^{244}Cm , 0.34 g of heavier curium isotopes, and 0.78 g of ^{243}Am in the form of americium-curium oxide, dispersed in aluminum powder (Alcoa grade 101, type 1100), in 34 to 36 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 curium oxide particles in an aluminum matrix, were pressed to 80% of theoretical density.

The 0.249-in.-diam pellets (nominally 0.571-in.-long) were pressed separately and then loaded into the finned, aluminum X-8001 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 accommodate any fission product gases released from the pellets 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 Americium-Curium Oxide

The americium-curium oxide was produced during developmental studies of the curium sol-gel process.^{2,3} Although the details of some of the process steps varied, essentially the same procedure was used throughout.

Fig. 3.1. HFIR Target Rod

The feed material was a nitrate solution of americium and curium (14% ^{243}Am , 80% ^{244}Cm , 6% higher curium isotopes) which had been recovered in TRU from irradiated plutonium targets. Metallic impurities, especially zirconium, were removed using single- or double-cycle oxalate precipitations. Americium-curium hydroxide was precipitated by adding a dilute solution of the americium-curium nitrate to a large excess of 8 M NH_4OH . The precipitate was washed with water, either by collection on a filter followed by washing on the filter, or by using a fluidized-bed technique in an inverted-cone washer. The precipitate was allowed to settle and was converted to a sol by digesting it 2 hr at 85°C. The sol was converted into gel microspheres using a conical, fluidized-bed drying column containing a two-fluid nozzle. The gel microspheres were washed with ethyl alcohol and allowed to dry overnight. The oxide product was heated slowly to 450°C and then calcined 4 hr at 1100°C.

3.2 Irradiation

Calorimetric measurements indicated that targets K11, K12, K14, K19, K20, and K21 contained 4.35, 4.36, 4.42, 4.42, 4.23, and 4.50 g of ^{244}Cm , respectively, prior to irradiation. The americium contained 99.96 atom % ^{243}Am and 0.04 atom % ^{241}Am ; the curium contained 92.27, 0.58, 6.83, 0.146, and 0.175 atom % of ^{244}Cm , ^{245}Cm , ^{246}Cm , ^{247}Cm , and ^{248}Cm , respectively.

The targets were irradiated 9 reactor fuel cycles (cycles 22 through 30) in ring 4 in the flux trap of the High Flux Isotope Reactor. The total reactor power multiplied by the thermal flux factor (the ratio of average thermal flux in the ring to the volume averaged thermal flux) was 19677 Mwd. The average thermal neutron fluence was 4.78×10^{22} n/cm². The targets were discharged from the reactor February 5, 1969; processing (12-DS-1) was started February 17, at which time the targets had cooled 12 days.

3.3 Compositions of Irradiated Targets

Tables 3.1 and 3.2 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.

Table 3.1. 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.

Target Numbers	K11, K12, K14, K19, K20, K21		
	Grams per Target	Grams per 10 g of Initial actinides	Atom % of Each element
^{243}Am	$\leq 5.7 \times 10^{-2}$	$\leq 9.9 \times 10^{-2}$	
^{244}Cm	2.16	3.77	80.33
^{245}Cm	1.86×10^{-2}	3.25×10^{-2}	0.69
^{246}Cm	4.68×10^{-1}	8.17×10^{-1}	17.41
^{247}Cm	1.40×10^{-2}	2.44×10^{-2}	0.52
^{248}Cm	2.82×10^{-2}	4.92×10^{-2}	1.05
^{249}Bk	3.50×10^{-4}	6.11×10^{-4}	
^{250}Cf	1.69×10^{-4}	2.95×10^{-4}	10.67
^{251}Cf	4.73×10^{-5}	8.25×10^{-5}	2.99
^{252}Cf	1.35×10^{-3}	2.36×10^{-3}	85.22
^{253}Cf	1.65×10^{-5}	2.88×10^{-5}	1.05
^{254}Cf	1.29×10^{-6}	2.25×10^{-6}	0.08
^{253}Es	6.93×10^{-6}	1.21×10^{-5}	
Fission products (calculated from ^{137}Cs)		2.32	

Table 3.2. Probable Amounts of Fission Products and
Activation Products in the Targets
When They Were Discharged from the Reactor

Target Numbers	K11, K12, K14, K19, K20, K21	
	Curies per Target	Curies per 10 g of Initial actinides
^{65}Zn	3.5	6.1
$^{95}\text{ZrNb}$	150	262
^{103}Ru	207	361
$^{110\text{m}}\text{Ag}$	3.7	6.5
^{131}I	109	190
^{134}Cs	3.7	6.5
^{137}Cs	5.2	9.1
$^{140}\text{BaLa}$	325	567
^{141}Ce	9.0	15.7

4. PROCESSING

The aluminum in the targets was dissolved using 3 M NaOH--1.5 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. Iodine was extracted and plutonium was recovered using the Pubex batch extraction process. There was no valuable plutonium in the irradiated targets; however, about 1.2 g of ^{242}Pu was found to be contained in the dissolver solution. We concluded that the ^{242}Pu had been left in the dissolver, T-70, from the previous campaign,⁴ in which irradiated plutonium targets had been processed. The transplutonium product from the Pubex step was decontaminated using the Tramex solvent extraction process. Americium and curium were separated from the transcurium elements using the LiCl-based anion exchange process and the transcurium elements were separated from each other and purified using a high-pressure chromatographic ion exchange column. The entire campaign was completed in three weeks, the same amount of time required for the previous campaign.

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 aluminum, coolant-flow shroud tube was mechanically removed from each of the targets. The remaining aluminum (jacket and matrix material) was dissolved from the 6 targets in two groups of three. For each group, one target was put into the Zircaloy-2 dissolver (T-70) and a solution of approximately 3 M NaOH--1.5 M NaNO₃ was added and 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 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 second group of targets was dejacketed in the same way as the first group, using a fresh batch of caustic-nitrate solution.

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 caustic solutions had been difficult to pump in the previous campaign in which the solution was 6 M NaOH--3 M NaNO₃; about 20% of the total time required for processing had been spent transferring the dejacketing solutions. In this campaign we used 3 M NaOH--1.5 M NaNO₃, half the caustic-nitrate concentration we had used previously. In laboratory tests the more dilute solution had been found to have adequate capacity for dissolving aluminum, to be less dense and, most importantly, to be much less viscous. We also used a larger filter than we had used in previous campaigns to retain the oxide during caustic

Fig. 4.1. Processing Diagram

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

Run Number	Purpose and Comments
12-DS-1	Dissolved 6 targets using caustic-nitrate and 6 M HCl.
12-PU-1	Removed radioiodine from dissolver solution. Also recovered plutonium which had been left in the dissolver heel from the previous campaign. This run was done in three parts which were separated by about one week.
12-TR-1	Decontaminated the transplutonium elements (from 12-PU-1 solution) from fission products using the Tramex process.
12-CM-1	Separated most of the curium from the transcurium elements using LiCl-based anion exchange. Feed was the Tramex product.
12-DS-2	Dissolved the oxide heel left in dissolver T-70 from run 12-DS-1, using 6 M HCl.
12-CL-1	Removed sodium and corrosion products from process condensate collected during runs 12-DS-1, 12-PU-1, 12-TR-1 and 12-DS-2 to recover actinides which had been entrained during some of these runs.
12-CM-2	Separated curium from the transcurium elements using LiCl-based anion exchange. Feed was (1) tank heels from run 12-CM-1; (2) tank heels from run 12-TR-1; and (3) transuranium elements recovered in run 12-CL-1.
12-CM-3	Reduced the lithium content in the transcurium product solutions from runs 12-CM-1 and 12-CM-2 by loading the transcurium elements from strong LiCl solution onto anion exchange resin and eluting them using HCl.
12-CM-4	Separated curium from the transcurium elements using LiCl-based anion exchange. Feed was tank heels from run 12-CM-2, equipment flush solutions from runs 12-CM-2 and 12-CM-3, and the plutonium-berkelium product solution from run 12-PU-1.

transfers and flushes. The net effect was that in this campaign the caustic-nitrate was pumped at more than 10 times the rate at which we had been able to pump the more concentrated solution through the smaller filter in previous campaigns. About 0.07% of the curium was lost to the dejacketing waste.

Table 4.2. Run Conditions for Dissolving the Targets

Run Number	12-DS-1	12-DS-2 ^a
Dates Covered	2/17/69 - 2/19/69	2/27/69 - 2/28/69
Target Numbers	K11, K12, K14, K19, K20, K21	None ^a
Equipment Used (Tank Numbers)	T70, T71, T72	T70
Run Conditions		
Aluminum Dejacketing	<u>b</u>	<u>c</u>
Dissolvent composition,		
NaOH, <u>M</u>	3	3
NaNO ₃ , <u>M</u>	1.5	1.5
Volume, liters	12.6	12.8
Dissolution temperature, °C	106	106
Digestion period, hours	0.5	0.5
Dejacket solution flushes,		
H ₂ O	none	3 x 3 liters
Acid Dissolution		
Dissolvent composition,		
HCl, <u>M</u>	6 ^d	6
Initial volume, liters	24.9	12.0
Evaporation time, hours	2	0.5
Final temperature, °C	108	109
Final volume, liters	22.1	11.5
Final composition, HCl, <u>M</u>	5.4	

^aRun 12-DS-2 was a heel dissolution.

^bAluminum was dissolved from K11, K12, and K21, successively, in the first batch of caustic-nitrate solution.

^cAluminum was dissolved from K14, K19, and K20, successively, in the second batch of caustic-nitrate solution.

^dActinides from all six targets were combined for dissolution in HCl.

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

Run Number	12-DS-1		12-DS-2
	Caustic Dejacketing Solution	Acidic Dissolver Solution	Acidic Dissolver Solution
Actinides			
²⁴² Pu, g		1.2	0.03
²⁴³ Am, g		0.3	
²⁴⁴ Cm, g	0.01	15.6	0.75
²⁴⁹ Bk, mg		2.01	
²⁵² Cf, mg		8.25	0.47
²⁵³ Es, µg		61.5	
²⁴⁴ Cm, % of ²⁴⁴ Cm in dissolver product	0.06		
Ionic contaminants			
Ni, g		2.14	
Zr, g		0.38	1.3
Radioiodine (¹³¹ I), Ci	91		
Other fission product γ activity, Ci			
⁶⁵ Zn	22.1		
⁹⁵ ZrNb	72.6	878	
¹⁰³ Ru	34.1	976	
^{110m} Ag	22.0		
¹³⁴ Cs	29.7		
¹³⁷ Cs	18.4	22	
¹⁴⁰ BaLa	18.1	1085	
¹⁴¹ Ce	53.5		
Gross alpha/gross gamma activity ratio		1.7	

^aAt the time of dissolution (February 17, 1969 for 12-DS-1 caustic dejacketing; February 19, 1969 for 12-DS-1 acid dissolution and; February 27, 1969 for 12-DS-2 dissolution).

The dissolver was flushed three times with 3 liters of water to remove residual sodium, and the actinide oxide particles were slurried in water by air-sparging and were jetted to a tantalum-lined vessel. The excess water was evaporated, and concentrated HCl was added and gently boiled two hours to dissolve the actinide oxides. The dissolver product contained 0.3 g of ^{243}Am , 15.6 g of ^{244}Cm , 2 mg of ^{249}Bk , 8.25 mg of ^{252}Cf and 61.5 μg of ^{253}Es . Later, we added 6 M HCl to the Zircaloy-2 vessel from which the oxide slurry had been transferred to determine if the transfer had been complete. We found 0.75 g of ^{244}Cm , which indicates that the slurry transfer had been only 95% complete. This heel dissolution did not cause excessive corrosion because the radiation level was low.

4.2 Pubex Solvent Extraction

The Pubex processing step was performed primarily to remove iodine from the acid solution of actinides prior to the Tramex step. The tanks used for preparing feed solutions and for performing the Pubex extraction were vented through an off-gas treatment system which removed iodine; however, the Tramex equipment was vented to the main VOG header in a way that by-passed the treatment system.

We used the usual Pubex procedure. Run conditions for the Pubex run 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.

The acidic solution was adjusted to feed specifications (5.5 M HCl, 0.05 M HNO_3) and contacted, by air sparging, with 1 M di(2-ethylhexyl) phosphoric acid (HDEHP) in diethylbenzene (DEB) to which 0.1 M Adogen (a trialkyl amine) had been added. Laboratory tests had shown that an amine such as Adogen improved the extraction of some species of iodine and it was felt that the amine might form stable complexes with the iodine and reduce its volatility in the organic. After the extraction

Table 4.4. Run Conditions for Plutonium Recovery Using Batch Extraction

Run Number	12-PU-1		
Dates ^a	2/19/69--2/21/69		
Equipment Used	T-72, T-73		
Feed Material Source	12-DS-1 dissolver product solution		
Volume after evaporation, liters	9.0		
Final boiling point, °C	108		
Approximate acid concentration, HCl, <u>M</u>	6		
Feed Adjustment Conditions			
Oxidant added, HNO ₃ , <u>M</u>	0.5		
Volume added, liters	1.1		
Sparging time, minutes	15		
Adjusted Feed Solution			
Acid concentration	5.5 <u>M</u> HCl--0.05 <u>M</u> HNO ₃		
Volume, liters	10.1		
Alpha power density, w/liter	4.35		
²⁴² Pu, g/liter	0.12		
Extraction			
Extraction solution	1 <u>M</u> HDEHP--0.1 <u>M</u> Adogen·HCl in DEB		
Volume used, liters	13.5		
Sparging time, hours	8		
Temperature, °C	25--35		
Scrubbing			
Scrub solution	6 <u>M</u> HCl--0.02 <u>M</u> HNO ₃		
Number of scrubs	3		
Volume used for each scrub, liters	10		
Sparging time for each scrub, hours	1		
Washing ^a			
Wash solution	<u>A</u>	<u>B</u> ^b	<u>C</u>
Acid concentration, HCl, <u>M</u>	6	3.5	5
Number of washes	1	1	2
Volume used for each wash, liters	15	21	10
Sparging time for each wash, hours	none	1	0.25
Stripping ^a			
Organic-phase reductant solution	0.2 <u>M</u> DBHQ in 2-ethylhexanol		
Volume, liters	7.5		
Aqueous stripping solutions	<u>A</u>	<u>B</u>	
HCl, <u>M</u>	5	5	
HONH ₂ , <u>M</u>	0.1		
Volume, liters	26.5	10	
Sparging time, hours	2	1	

^aThe washing and stripping steps were performed from 2/28/69 to 3/14/69.

^bThe 12-DS-2 product solution was used for this wash.

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

Run Number	12-PU-1			
	Feed	Product	Raffinate ^a	Waste Organic
Measured Stream Components ^b				
²⁴² Pu, g	1.2	0.84		
²⁴³ Am, g	0.3			
²⁴⁴ Cm, g	15.6	0.0021	14.5	0.0004
²⁴⁹ Bk, mg	2.01	0.093		
²⁵² Cf, mg	8.25		7.85	0.0005
²⁵³ Es, μ g	61.5			
Zr, g	0.38		0.026	
Ni, g	2.14		2.2	
⁹⁵ ZrNb, Ci	866	2.5		
¹⁰³ Ru, Ci	943	15.3		
^{110m} Ag, Ci		0.37		
¹²⁵ Sb, Ci		1.3		
¹³¹ I, Ci	109	1.7	1.3	
¹³⁷ Cs, Ci	22	<1.3		
¹⁴⁰ BaLa, Ci	966			
Gross gamma, cts/min	2.40×10^{15}	9.27×10^{12}	1.72×10^{15}	

^aPrimary raffinate only; does not include scrub raffinate.

^bOn February 19, 1969.

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

Run Number	12-PU-1	
	^{242}Pu	^{244}Cm
Input		
Feed, g	1.2	15.6
Output		
Transplutonium Product, g		14.5
Plutonium Product, g	1.3	
Measured losses, g		0.6
Total Measured Output	1.3	15.1
Output/Input, %	108	96.8

Table 4.7. Decontamination Factors
During Plutonium Recovery (Pubex)

Run Number	12-PU-1	
	Plutonium ^a	Curium
Product Solution		
^{244}Cm	5×10^3	
Zr		14
Gross gamma	180	1.3
$^{95}\text{ZrNb}$	242	
^{103}Ru	43	
^{131}I	45	78
^{137}Cs	>12	

^aBased on analysis of the first strip only.

contact was made, the solvent was scrubbed using 6 M HCl--0.02 M HNO₃ to recover small amounts of transplutonium elements, and the combined aqueous phase was transferred through a filter to another tank where it was adjusted to Tramex feed specifications. We did not collect any solids on the filter during the transfer as we had done at this step in the previous campaign.

The solvent, which contained the extracted plutonium, was stored 8 days during the main effort to recover the transplutonium elements. A solution of 3.5 M HCl (21 liters), which had been used to dissolve and flush the residue of actinides from the dissolver (run 12-DS-2), was contacted with the Pubex organic to remove zirconium from the dissolver solution. The aqueous phase, which contained 0.75 g of ²⁴⁴Cm and 0.47 mg of ²⁵²Cf, plus two 10-liter batches of 5 M HCl scrub solution were combined with other actinide-bearing solutions for feed to the second LiCl-based anion exchange run, 12-CM-2.

The plutonium in the six irradiated curium targets was essentially all ²⁴⁰Pu; it was not worth recovering as a product. However, we had planned to strip the plutonium for process evaluation to study the behavior of iodine and berkelium. In previous campaigns in which there was no amine in the solvent, iodine had been released during the stripping procedure. Also, in the previous campaign, we had found that more than 10% of the berkelium that had been measured in the dissolver solution had been extracted and stripped along with the plutonium. When ²⁴²Pu was discovered, which had been left in the dissolver in the previous campaign, recovering plutonium became a primary objective.

After the treatment of the 12-DS-2 solution, we added 25 liters of 5 M HCl to the tank containing the Pubex solvent and left it undisturbed for seven days while we concentrated on other processing. Then, we added 1.5 liters of 1.7 M hydroxylamine hydrochloride as a holding reductant in the aqueous phase, added 3.5 liters of an organic-phase reductant in a phase modifier (0.2 M di-tert-butylhydroquinone in 2-ethylhexanol) to the solvent, and contacted the phases by air sparging. We found that we had stripped from the solvent about 6% of the berkelium which had been

measured in the dissolver solution and about one gram of ^{242}Pu . We added an additional 4 liters of organic-phase reductant in phase modifier and contacted the phases again, because three days had elapsed since the original stripping contact. The aqueous phase was removed from the tank and 10 liters of 5 M HCl strip solution was added, contacted with the solvent and combined with the first strip raffinate. The ^{242}Pu DF from gross gamma was 188. The waste solvent contained <0.003% of the ^{244}Cm and <0.006% of the ^{252}Cf which had been measured in the dissolver solutions.

4.3 Tramex Solvent Extraction

The transplutonium product solution from the Pubex run was adjusted to feed specifications for solvent extraction processing and was decontaminated using the Tramex process. About 4% of the actinides was expelled from an evaporator while the transplutonium product was being concentrated prior to feed adjustment. This was recovered later (run 12-CL-1). Feed adjustment data and the operation summary for the Tramex run are given in Table 4.8. Table 4.9 lists the compositions of non-radioactive process streams, and flow rates and volume balances for all process streams. Compositions of radioactive streams are listed in Table 4.10.

Tramex Process Flowsheet.— The flowsheet for the Tramex solvent extraction process is shown in Fig. 4.2. 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)— 0.3 ± 0.01 M free HCl— 0.05 M DBHQ, 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

Table 4.8. Feed Adjustment Data and Operation Summary
for Tramex Solvent Extraction Processing (Run 12-TR-1)

Dates	2/20/69--2/26/69
Equipment Used	T-73A, T-20, T-21, T-60, T-65, and Cub. 7 Solvent Ext. Rack
Feed Material Source	Transplutonium Product from 12-PU-1
Initial volume, liters	13.4
Initial HCl concentration, <u>M</u>	~6
Feed Adjustment Conditions	
LiCl added, moles	60
Concentration	
Final boiling temperature, °C	137
Volume after evaporation, liters	5.8
Acid adjustment solution	8.1 <u>M</u> HCl--5.5 <u>M</u> LiCl
Volume added, liters	1.0
Digestion temperature, °C	120
time, minutes	20
Adjusted Feed Solution	
Volume, liters	6.3
HCl concentration, <u>M</u>	0.11 ^a
LiCl concentration, <u>M</u>	~11
²⁴⁴ Cm concentration, g/liter	2.3
Alpha power density, w/liter	6.5
Length of Operation (including feed tank flushes), hours	63.4
Feed Time, hours	41.4
Down Time, hours	22
Number of Shutdowns	2
Operating Temperature, °C	60

^aHCl concentration was adjusted to 0.2 M before feed was introduced into the columns.

Table 4.9. Compositions of Nonradioactive Streams and
Average Flow Rates and Volume Balances for all Process Streams
for Tramex Solvent Extraction (Run 12-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, 0.3.
	± 0.01 M	HCl, 0.05 M DBHQ in Diethylbenzene
Average Flow Rates, liters/hour		
Inlet streams		
Feed	0.25	
Aqueous scrub	0.64	
Strip	0.47	
Organic extractant	1.7	
Outlet streams		
Aqueous raffinate	0.93	
Aqueous product	0.43	
Waste organic	1.7	
Volume Balances, %		
Extraction-scrub column aqueous	104.5	
Strip column aqueous	91.5	
Total aqueous	100.0	
Organic	100.0	
Total	100.0	

Table 4.10. Contents of Radioactive Streams During
Tramex Solvent Extraction (Run 12-TR-1)

All values are adjusted to the start of the run, February 24, 1969.

Process Stream	Feed	Product	Raffinate	Waste Organic
^{242}Pu , g	$\leq 0.06^a$			
^{243}Am , g		0.29		
^{244}Cm , g	14.5	14.0	0.073	0.03
^{249}Bk , mg		1.28		
^{252}Cf , mg	7.85	7.45	<0.03	0.004
^{253}Es , μg		54.4		
Li, g		8		
Zr, g	0.026	<0.10		
Ni, g	2.2	1.9		
Gross γ , cts/min	1.59×10^{15}	2.83×10^{13}	7.9×10^{14}	2.6×10^{14}
$^{95}\text{ZrNb}$, Ci				11
^{103}Ru , Ci		39.6		516
$^{110\text{m}}\text{Ag}$, Ci		5.78^b		7.4
^{131}I , Ci	0.29			<2
^{137}Cs , Ci				<3
$^{140}\text{BaLa}$, Ci			550	<3
^{141}Ce , Ci		6.40		

^aBased on analysis of Pubex (12-PU-1) raffinate in T-72.

^bAlso contained ^{111}Ag .

ORNL DWG. 69-4979

Fig. 4.2. Flowsheet for the Tramex Process

liter/hr to the top of the scrub column in which 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 $8.0 \pm 0.2 \text{ M HCl}$ which is fed to the top of the strip column at $0.5 \pm 0.05 \text{ liter/hr}$. 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.

Tramex Feed Adjustment. - The solution of transplutonium elements from the Pubex extraction step was evaporated to a volume of about 5 liters, 60 moles of LiCl was added, and the solution was evaporated until the boiling temperature was 137°C (about 12 M LiCl). The solution was made 1 M in HCl by addition of 0.5 liter of 12 M HCl , and the addition line was flushed with 0.5 liter of an 11 M LiCl -- 0.2 M HCl solution (cold feed). 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 6.3 liters of solution that was 0.11 M HCl and about 11 M LiCl . It contained 2.3 g/liter of ^{244}Cm which made the solution power density (from alpha decay) 6.5 w/liter.

The Tramex Run. - The run lasted a total of 63.4 hours from the time radioactive feed was introduced until the feed tank was completely flushed. The run was interrupted twice for a total of 22 hours because of a plugged feed pump; a piece of teflon was found in the pump. The average feed rate (0.25 liter/hr) was only half of the nominal process rate. About 0.7% of the curium, which was left in the feed tank heel, was combined with other rework streams and included in the feed solution for the second LiCl-based anion exchange run (12-CM-2). About 97% of the curium was recovered as product. The material balance for ^{244}Cm was 99%. Gross gamma decontamination factor was 54. This value was higher than in the previous campaign (about 26) but was still low compared with Tramex runs for feeds which had been cooled longer. The major contaminants in the product were $^{110\text{m}}\text{Ag}$ and ^{103}Ru . The Ru DF was only 21.

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. This was the first time this processing step was done using an ion exchange column that had been fabricated from metal (tantalum) instead of glass. All product cuts were made based on in-line alpha monitoring of the column effluent and on neutron and gamma scans of the resin column. Such indications as the green color from nickel during its elution and the red glow from the curium band on the column were not needed.

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.

4.4.1 Ion-Exchange Equipment

The equipment that is used for the LiCl-based anion exchange process is shown in Fig. 4.3 and 4.4. Some equipment for precipitation purification is on the same equipment rack, which is located in cubicle 6. The major pieces of ion-exchange equipment are: (1) a 4-liter-capacity glass feed tank, (2) a column which was fabricated from a 2-in.-diam by 30-in.-long tantalum tube, and (3) five 7.5-liter-capacity tantalum tanks for product collection. An in-line alpha monitor is located in a jack leg in the column outlet line which contains a manifold of valves to permit quick switching of flow into one of the five product tanks.

4.4.2 Process Flowsheet

The flowsheet for the LiCl-based anion exchange process is shown in Fig. 4.5. The resin is pretreated with 6 M HCl to ensure that it is in the chloride form, and then is washed free of excess acid with water.

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

Run Number	12-CM-1	12-CM-2	12-CM-3	12-CM-4
Dates	2/25/69 - 2/26/69	3/6/69 - 3/8/69	3/17/69	3/18/69 - 3/19/69
Equipment Used	T-65, T-635, T-61, T-604, T-631, T-630, T-634	T-65, T-635, T-61 T-604, T-630, T-631	T-65, T-635, T-61, T-632	T-65, T-635, T-61, T-630, T-631
Ion Exchange Column	C-636	C-636	C-636	C-636
Material	Tantalum	Tantalum	Tantalum	Tantalum
Diameter, cm	4.9	4.9	4.9	4.9
Ion Exchange Resin	Dowex 1-X10	Dowex 1-X10	Dowex 1-X10 ^a	Dowex 1-X10 ^b
Size, mesh	~250 ^c	~250 ^c	~250 ^c	~250 ^c
Volume, liters	1.45	1.45	1.45	1.45
Column Temperature, °C	70 - 80	70 - 80	70 - 80	70 - 80
Column Pretreatment Solution				
LiCl, M	12.0 ± 0.2	12.0 ± 0.2	11.0 ± 0.2	12.0 ± 0.2
HCl, M	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05
HONH ₂ ·HCl, M	0.1	--	0.1	0.1
CH ₃ OH, Volume %	2.5	2.5	2.5	2.5
Volume used, liters	4	~3.5	4	3.9
Feed Material Source	12-TR-1 Product	Miscellaneous Rework Solutions ^d	12-CM-1 and 12-CM-2 Am-Cm Product	Miscellaneous Rework Solutions ^e
Initial volume, liters	2	11.5	9.6	23.7
Initial LiCl conc., M	0.6	4.4	5.4	1.0
Feed Adjustment Conditions				
LiCl added, moles	15.5	None	None	12
Final boiling point, °C	142.5	142.5	142.5	142.5
Final volume, liters	1.3	3.9	4.0	2.85
Acid adjustment solution				
Volume added, liters	0.370	0.445	0.640	0.320
HCl, M	5.5	9.3	8.2	6.7
LiCl, M	7.3	3.0	4.3	8.3
Digestion temperature, °C	120	120	120	120
Digestion time, minutes	10	10	10	10
Adjusted Feed				
Volume, liters	2.1 ^f	4.3	4.6	4.1 ^g
HCl, M (estimated)	~0.1	~0.1	~0.1	~0.1
LiCl, M	12.1	12.0	11.9	12.6
²⁴⁴ Cm, g/liter	8.8	0.87	3.4	0.17
Alpha power density, w/liter	24.8	2.5	9.5	0.50

^aResin used previously for run 12-CM-2.

^bResin used previously for runs 12-CM-2 and 12-CM-3.

^cMiddle fraction from classification of 200 - 300 mesh resin.

^d12-DS-2 product solution, 12-CL-1 product, 12-TR-1 heels, and 12-CM-1 heels and rework solutions.

^e12-FU-1 plutonium product, 12-CM-2 and 12-CM-3 heels and rework solutions.

^fIncludes 0.5 liter feed flush solution (12.0 M LiCl, 0.1 M HCl, 0.1 M HONH₂·HCl, 2.5% CH₃OH).

^gIncludes 1.0 liter feed flush solution (12.0 M LiCl, 0.1 M HCl, 0.1 M HONH₂·HCl, 2.5% CH₃OH).

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

Run Number	12-CM-1	12-CM-2	12-CM-3	12-CM-4
Feed Loading Rate, $\text{ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$	1.8	1.5 ^a	1.1	1.6
Rare Earth Elutriant Solution				
LiCl, $\underline{\text{M}}$	10.0 ± 0.1	10.0 ± 0.1		10.0 ± 0.1
HCl, $\underline{\text{M}}$	0.1 ± 0.05	0.1 ± 0.05		0.1 ± 0.05
$\text{HONH}_2 \cdot \text{HCl}$, $\underline{\text{M}}$	0.1	0.1		0.1
CH_3OH , volume %	2.5	2.5		2.5
Volume used, liters	4.2	2.3	None	5.0
Rate, $\text{ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$	0.63 ^b	1.0		0.7
Americium-Curium Elutriant	(First Portion)	(Second Portion)		
LiCl, $\underline{\text{M}}$	9.0 ± 0.1	8.0 ± 0.1	9.0 ± 0.1	9.0 ± 0.1
HCl, $\underline{\text{M}}$	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05	0.1 ± 0.05
$\text{HONH}_2 \cdot \text{HCl}$, $\underline{\text{M}}$	0.1	0.1	0.1	0.1
CH_3OH , volume %	2.5	2.5	2.5	2.5
Volume used, liters	1.55	1.17	3.1	2.2
Rate, $\text{ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$	0.43 ^b	0.38 ^b	0.82	0.95
Transcurium Elutriant				
HCl, $\underline{\text{M}}$	8.0 ± 0.2	8.0 ± 0.2		8.0 ± 0.2
Volume used, liters	2.55	1.3	None	1.85
Rate, $\text{ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$	0.95	1.3		1.8
Column Flush				
HCl, $\underline{\text{M}}$	0.8	0.8	0.8	0.8
Volume used, liters	4.0	4.0	3.7	3.1
Rate, $\text{ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$	1.5	1.0	2.0	1.3

^aAverage rate for first 60% of feed solution was $0.2 \text{ ml} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$. Column inlet screen plugged completely at this time. All succeeding flow into the column was routed through resin inlet line, by-passing screen.

^bRate lower than desired because column inlet screen was becoming plugged.

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

Run Number	12-CM-1					12-CM-2					12-CM-3				12-CM-4				
Process Solution	Feed	Transcurium Product	Am-Cm Product	Waste Solution	Rework Solutions	Feed	Transcurium Product	Am-Cm Product	Waste Solution	Rework Solutions	Feed	Am-Cm Product	Waste Solution	Rework Solutions	Feed	Transcurium Product	Am-Cm Product	Waste Solution	Rework Solutions
²⁴³ Am, g	0.29		0.19	<0.012		0.1		0.13			0.32								
²⁴⁴ Cm, g	14.0	0.15	12.7	0.0009	2.0	4.0	0.25	2.6	0.0007	0.46	15.5	14.1	0.001	0.13	0.73	0.26	0.40	0.0011	0.03
²⁴⁹ Bk, mg	1.28	0.83	0.001		0.002	0.65	0.31	0.013			0.014				0.09	0.07	0.0002		0.26
²⁵² Cf, mg	7.45	5.38	0.006	0.0002	2.0	3.37	3.23	0.002	0.0021	0.64	0.008				0.67	0.53	0.001	0.001	0.08
²⁵³ Es, μ g	54.4	40.3			1.6	23.7	22.7			1.8						2.9			0.3
Li, moles	1.2					51					52	5.7			25				
Ni, g	1.9					8.5													
Zr, g	<0.1																		
Gross gamma, cts/min	2.8×10^{13}	5.4×10^{11}	8.4×10^{11}	7.0×10^{12}		3.3×10^{14}	4.2×10^{11}	1.0×10^{12}			1.9×10^{12}	6.6×10^{11}			4.3×10^{13}		2.0×10^{11}		
⁹⁵ ZrNb, Ci			≤ 0.1	≤ 1.2		≤ 20		≤ 0.1			≤ 0.1								
¹⁰³ Ru, Ci	39.6	Present	≤ 0.06	≤ 0.4		462	Present	0.8--0.9			0.89					0.0002			
^{110m} Ag, Ci	5.8		0.57	3.4		≤ 10		0.05			0.64								
¹³⁷ Cs, Ci			≤ 0.1	≤ 0.9		≤ 20		≤ 0.1			≤ 0.1								
¹⁴⁰ BaLa, Ci			≤ 0.06	≤ 0.9		27.6		0.1--0.3			0.23								
¹⁴¹ Ce, Ci	6.4		≤ 0.03	4.2		74.5	Present	0.9--1.0			0.97								

^aAt date of start of run.

Table 4.14. Material Balances for Some Actinides Plus Americium-Curium
Product Decontamination Factors During Actinide Partitioning Using LiCl-Based Anion Exchange

Material Balances	12-CM-1				12-CM-2				12-CM-3	12-CM-4			
	²⁴⁴ Cm	²⁴⁹ Bk	²⁵² Cf	²⁵³ Es	²⁴⁴ Cm	²⁴⁹ Bk	²⁵² Cf	²⁵³ Es	²⁴⁴ Cm	²⁴⁴ Cm	²⁴⁹ Bk	²⁵² Cf	²⁵³ Es
Input													
Feed	14.0 g	1.28 mg	7.45 mg	54.4 μg	4.0 g	0.65 mg	3.37 mg	23.7 μg	15.5 g	0.73 g	0.09 mg	0.67 mg	
Output													
Transcurium product	0.15	0.83	5.38	40.3	0.25	0.31	3.23	22.7		0.26	0.07	0.53	2.9 μg
Am-Cm product	12.7	0.001	0.006		2.6	0.013	0.002		14.1	0.40	0.0002	0.001	
Waste	0.0009		0.0002		0.0007		0.002		0.001	0.0011		0.001	
Rework	2.0	0.002	2.0	1.6	0.46		0.64	1.8	0.13	0.03	0.26	0.08	0.34
Total Out	14.85	0.83	7.38	41.9	3.31	0.32	3.87	24.5	14.23	0.69	0.33	0.612	3.2 μg
Output/Input, %	106.1	65	99.1	77	82.8	49.7	114.8	103.4	91.8	94.7	367	91.3	
Decontamination Factors for Am-Cm Product													
Gross γ DF		31				214			2.6		118		
¹⁰³ Ru DF		>600				330							
^{110m} Ag DF		10											
¹⁴⁰ BaLa DF						60							
¹⁴¹ Ce DF		>200				48

Fig. 4.3. Equipment Rack for LiCl-Based Anion Exchange.

Fig. 4.4. Back View of LiCl-Based Anion Exchange Equipment

ORNL Dwg 69-3931
 R-1

Fig. 4.5. Flowsheet for the LiCl-Based Anion Exchange Process

The adjusted feed (12 M LiCl--0.1 M HCl) is transferred to the feed tank on the equipment rack by vacuum and is pumped through the column, which contains about 1.5 liters of Dowex 1-X10 resin (200 to 300 mesh). The actinides and some of the contaminants are sorbed on the resin. Most of the nickel and rare earths are eluted from the resin using 10 M LiCl--0.1 M HCl--0.1 M HONH₂·HCl--2.5 vol % CH₃OH. The hydroxylamine (HONH₂·HCl) is used to maintain cerium in the trivalent state, and the methanol is used to suppress the formation of radiolytic gases. Elution with this solution is continued until an increase in alpha activity (due to ²⁴⁴Cm) is noted in the effluent. The lithium concentration in the elutriant solution is then reduced to 9 M, and elution is continued until 90 to 95% of the curium is eluted. At this point, the elutriant is changed to 8 M HCl and the transcurium elements are stripped off the resin. Finally, the resin is washed with 0.8 M HCl solution to remove sorbed contaminants. The points at which elutriant solutions are switched and the points at which the product cuts are directed to the various catch tanks, are based on alpha activity levels in the column effluent, and neutron and gamma profiles of the column.

4.4.3 Feed Adjustment

The solution that contains the actinides to be purified and separated is concentrated, if necessary, by evaporation. LiCl brine (13 M Li) is added, if needed, to give a final feed solution that is 12 M LiCl. The solution is then evaporated to a final temperature of 142.5°C (13 M LiCl). The solution is cooled, and concentrated HCl (12 M) is added to adjust the concentration of the solution to 1 M. This also dilutes the solution to 12 M LiCl. The 12 M LiCl solution is then heated to 120°C and held at that temperature for 10 min. The 1 M acid redissolves any zirconium that might have precipitated during the first evaporation step and the heating to and holding at 120°C removes excess acid (to about 0.1 M).

4.4.4 Anion Exchange Runs

Four runs were made. In the first run (12-CM-1) the bulk of the actinides, which were contained in the Tramex (12-TR-1) product solution, were processed. The second run (12-CM-2) was made to process: (1) tank

heels and rework solutions from the first ion exchange run (12-CM-1) and from the Tramex run (12-TR-1); (2) the actinides contained in the dissolver heel dissolution (12-DS-2); and (3) the actinides that were recovered from a variety of rework solutions generated during previous process steps and subsequently purified in a Cleanex run (12-CL-1) to remove corrosion product impurities. In the third run (12-CM-3) the americium-curium products from the first two runs were loaded onto the column and eluted using 8 M HCl to reduce the lithium content. The fourth run (12-CM-4) was made to process tank heels and rework solutions from runs 12-CM-2, 12-CM-3 and 12-PU-1.

4.5 Cleanex Batch Extraction

A batch extraction step was used to recover actinides which had been entrained into the condensate during various evaporation steps and had been collected in the process condensate. Processing was required to remove sodium and corrosion product impurities. Run conditions are listed in Table 4.15, the contents of the process solutions are given in Table 4.16, and the ^{244}Cm material balance is given in Table 4.17.

The rework solution, which was basic because the condensate collection tank contained a caustic heel solution to prevent corrosion, was acidified (to 0.04 M) using concentrated HCl. This solution (393 liters) was contacted with 50 liters of 1 M di(2-ethylhexyl) phosphoric acid (HDEHP) in Amsco 125-82 diluent, by air sparging, to extract the actinides. The solvent also contained 0.1 M Adogen 364-HP (Tramex solvent). The aqueous phase was removed and the solvent was contacted twice with 20 liters of 0.03 M HCl to dilute the aqueous heel in the tank and scrub impurities from the solvent. Then the actinides were stripped from the solvent using two 20-liter batches of 5 M HCl.

About 0.73 g of ^{244}Cm and 0.51 mg of ^{252}Cf were recovered and combined with the feed solution for LiCl-based anion exchange run 12-CM-2. Measured losses to the aqueous raffinate and scrub solutions included 0.17 g of ^{244}Cm and 6.8 μg of ^{252}Cf .

Table 4.15. Run Conditions for the Recovery of Curium from Aqueous Rework Solutions Using Batch Solvent Extraction (Cleanex)

Run Number	12-CL-1
Dates	3/1/69--3/4/69
Equipment Used	T-10, T-60, F-115
Feed Material Source	Process condensate collected during 12-DS-1, 12-PU-1, 12-TR-1, and 12-DS-2 plus 12-CM-1 column flush and recovery from floor spill
Feed Adjustment Conditions	
Acid adjustment solution, HCl, <u>M</u>	12
Volume added, liters	11
Adjusted Feed Solution	
Volume, liters	393
Acid concentration, HCl, <u>M</u>	0.04
Specific gravity, w/liter	0.006
^{244}Cm , g/liter	0.002
Extraction	
Extractant solution	1 <u>M</u> HDEHP--0.1 <u>M</u> Adogen·HCl in Amsco 125-82
Volume added, liters	50
Sparging time, hours	4
Temperature, °C	20--30
Raffinate ^{244}Cm conc., g/liter	0.0017
Scrubbing	
Scrub solution, HCl, <u>M</u>	0.03
Number of scrubs	2
Volume used for each scrub, liters	20
Sparging time for each scrub, hours	1
Stripping	
Strip solution, HCl, <u>M</u>	5
Number of strips	2
Volume of each strip, liters	20
Sparging time for each strip, hours	1 ^a
Berkelium Stripping ^b	
Reductant solution	0.2 <u>M</u> DBHQ in 2-ethylhexanol
Volume added, liters	12.5
Strip solution	5 <u>M</u> HCl--0.1 <u>M</u> $\text{HONH}_2\cdot\text{HCl}$
Number of strips	1
Volume of each strip, liters	~50
Sparging time for each strip, hours	2

^aFirst strip sparged for four hours.

^bWaste organic from 12-PU-1 was added to T-10 before berkelium was stripped.

Table 4.16. Amounts^a of Various Elements and Isotopes
in Process Streams During Curium Recovery (Cleanex)

Run Number Process Solution	12-CL-1				
	Feed	Product	Bk Product	Raffinate	Waste Organic
²⁴⁴ Cm, g	0.88	0.73	0.001	0.17	0.0002
²⁴⁹ Bk, mg			0.11		
²⁵² Cf, mg	0.57	0.51	0.001	0.007	0.01
Fe, g		<0.3			
Cr, g		<0.2			
Ni, g		9.3			
Mo, g		<0.2			
Na, g		3.5			
¹³¹ I, Ci	5.9	0.034		2.1	4.1

^aAt time of analysis.

Table 4.17. Material Balance for ²⁴⁴Cm
During Curium Recovery (Cleanex)

Run Number	12-CL-1
Input	
Feed, g	0.88
Output	
Curium Product	0.73
Berkelium Product	0.001
Measured loss	0.17
Total out	0.90
Output/Input, %	102.4

The waste solvent from Pubex run 12-PU-1 was added to the tank and a special process step was done to recover berkelium from the combined solvent. An organic-phase reductant in a phase modifier (12.5 liters of 0.2 M di-tert-butylhydroquinone in 2-ethylhexanol) was added and the berkelium was stripped into 50 liters of 5 M HCl which contained 0.1 M hydroxylamine hydrochloride as a holding reductant. About 112 μg of ^{249}Bk was recovered.

4.6 Berkelium Material Balance

Apparently, some losses of berkelium occurred during this campaign: essentially all of the americium, curium, californium and einsteinium measured in the dissolver solution were recovered.

Berkelium is difficult to trace through our processing steps because its radioactive emissions are a soft beta and low-yield alpha. An analytical procedure was developed just prior to our previous campaign,⁴ in which berkelium is separated from interfering actinides using a high-pressure butyrate column, and from europium by a TTA extraction, and then is assayed by beta counting. This technique is somewhat unwieldy for process control but is useful for post-run evaluation. Prior to the development of the technique, we were able to analyze only highly-purified berkelium products for berkelium content.

We found that during the Pubex processing step of the previous campaign more than 10% of the berkelium that had been measured in the dissolver solution had been extracted and stripped along with the plutonium. About 6% of the berkelium in this campaign followed that path.

We did not expect that any berkelium would be oxidized to the extractable Bk(IV) in HCl solution. However, this apparently did occur and we suppose it was because of the high concentration of alpha radiation. If this is true, we may be losing berkelium in other process steps and, indeed, we only accounted for 50 to 75 per cent of the berkelium measured in the dissolver solution. Of course, the analysis of the dissolver solution may not be correct.

5. BEHAVIOR OF RADIOIODINE

It is desirable to dissolve and process irradiated targets very soon after they are removed from the HFIR in order to recover the maximum possible amount of the short-lived ^{253}Es ($t_{1/2} = 20$ days). A major obstacle to processing after short cooling periods is the presence of about 200 curies of ^{131}I in each target when it is removed from the reactor.

In successive campaigns, beginning in 1967 (when we processed three SRP slugs containing 20 to 30 curies of iodine and merely observed the behavior of iodine), we have increased our efforts to study and control iodine in TRU. About 1.7 Ci of ^{131}I was released to the environment during the previous campaign, in which fourteen irradiated targets were processed which contained 460 Ci of ^{131}I when processing was started. During this campaign to process six curium targets, which contained a total of 400 curies of ^{131}I ; only 300 mc was released from TRU during the processing campaign. The special steps that were made to control the release of radioiodine are discussed below.

Plant piping was modified so that all process and waste solutions that would contain significant amounts of radioiodine would be handled and stored in tanks that were vented through the condensate collection system for the dissolver and the seven process evaporators. Thus, most of the iodine-bearing off-gas was confined to a 3-cfm stream instead of being spread throughout the 350-cfm vessel off-gas (VOG) stream. An experimental iodine-removal system, consisting of a caustic scrubber to remove acidic vapors, a heater, a bed of oxidation catalyst (Hopcalite) to protect the charcoal trap from organics by converting them to CO_2 and H_2O , a cooler, and a charcoal trap, was placed in the 3-cfm off-gas stream. Hopcalite (a proprietary material of the Mine Safety Appliances Company) is a CuO-MnO_2 mixture that has been treated to give a large surface area. A few tests indicated that it would decompose TRU organics at 300 to 350°C. Previous attempts to trap radioiodine, using beds of KI-impregnated charcoal, had been unsuccessful because organic solvents, which are used in various processing steps, were transported to off-gas

streams in amounts that quickly poisoned the beds against iodine retention. We did not study Hopcalite exhaustively; no other catalysts were tested.

The process for removing iodine from the condensate system off-gas is shown in Fig. 5.1. After the gas is scrubbed to remove HCl vapors, it is heated electrically and passed to the bed of catalyst, which is kept at 650°F (350°C). The effluent from the catalyst is cooled, passed through a 7-in.-thick bed of KI-impregnated charcoal, and then added to the main vessel off-gas. The charcoal bed is operated at about 120°F.

Sodium hypochlorite (NaOCl) was added to all waste caustic streams and to the makeup caustic for the scrubber in the iodine treatment system to oxidize the iodine to the nonvolatile iodate or periodate form. In the previous campaign, we had released radioiodine when we transferred radioactive caustic solutions. Apparently, volatile forms of iodine are present in aged radioactive caustic solutions. This is contrary to the behavior in nonradioactive caustic solutions in which iodine is found only in the nonvolatile forms (iodine and iodate).

The Pubex processing step was performed in this campaign merely to remove radioiodine from the feed solution prior to the Tramex processing step; there was no valuable plutonium in the targets. (We later discovered that some ^{242}Pu had been left in the dissolver from the previous campaign; however, we did not know that when this campaign was planned.) In the Pubex process, iodine reports almost quantitatively to the solvent. Adogen 364-HP (0.1 M) was added to the solvent because laboratory tests had shown that it improved iodine extraction; also, we had hoped that the amine might form stable complexes with the iodine.

Of the 300 mc of ^{131}I released during the campaign only 6 mc was released from the 3-cfm treatment system; the remainder bypassed the treatment system either from tanks that were not vented through the treatment system or by direct release from the processing cubicles.

Although iodine material balances were poor in many cases, we accounted for about 340 of the 400 curies of ^{131}I we had estimated to be present in the targets; 100 curies was in the caustic dejacketing

Fig. 5.5. Iodine-Removal Process for the Condensate-Collection System Off-Gas

waste, 220 curies was in the acid feed for the Pubex process, and 20 curies was in the condensate collection tank at the end of the feed adjustment step.

We did not notice any significant difference between the behavior of iodine in the Pubex steps in this campaign (with amine) and in the previous campaign (without amine). The amount of iodine extracted was the same in each case, and about 0.5 curie was left in the Tramex feed. A small amount of iodine was volatilized during the Pubex stripping step (when we added reductant to the solvent and air sparged).

The NaOCl that was added to the waste caustic streams was effective in keeping the iodine in nonvolatile forms. On one occasion, we tried to release about one curie of iodine from some of the caustic waste by acidifying the waste to 2 M HNO₃, adding some ferrous sulfamate as a reductant, and air sparging. However, essentially no iodine was evolved. This can be compared with our experience in the previous campaign in which, after about the same one-month aging period, almost 10% of the contained iodine was released from some dejacketing waste by merely pumping it from one tank to another.

Samples of the 3-cfm VOG stream were taken at two locations: between the scrubber and the heater, and following the charcoal bed. The total VOG stream, which included the 3-cfm condensate-collection system VOG, about 10 cfm of off-gas from other vessels, and 300 cfm of cubicle and shielded cave ventilation, was sampled between the main plant VOG caustic scrubber and the VOG system absolute filters. The gas samplers, which were similar to those described by Bennett, Hinds, and Adams,⁵ were connected to the VOG ducts by means of about 50 ft of 3/8-in.-diam stainless steel tubing. Although one might expect this much tubing to cause erratic sample results, the daily iodine content, as indicated by the sampler for the 350-cfm stream, agreed closely with the official HFIR stack monitoring results.

The 3-cfm condensate-collection system VOG stream was decontaminated from ¹³¹I by a factor (DF) of 4×10^3 to 1×10^4 during the dejacketing and acid dissolution steps. During the Pubex solvent extraction step,

the DF appeared to decrease to 30; however, condensate observed in the rotameter on the line sampling the inlet to the system at this time probably introduced errors into the data. For the next week, during Tramex processing, the stream was not sampled. When we returned the sampler to service (during cleanup operations following the Tramex run), the DF had increased to 500. The average DF for the entire campaign (except during Tramex processing) was about 400.

The only significant difficulty we experienced during the test was the tendency of the Hopcalite bed to overheat (from heat of combustion) when we sparged a tank containing organic materials. We had to balance sparging rates and power input to the heater very carefully in order to keep the bed at the proper temperature. This would not be a problem in a larger system in which the concentrations of organics in the off-gas would be lower.

After the campaign was essentially finished, we decided to determine the effects of varying the temperatures of the Hopcalite bed and the charcoal trap. We found that if we increased the temperatures to 800°F and 200°F, respectively, DF's approaching 5×10^3 were obtained and the iodine content in the effluent returned to the very low level (0.006 mc in two days) that we had observed at the beginning of the campaign. When we lowered the temperatures (the Hopcalite to 500°F, and the charcoal to 120°F) the DF decreased to about 100.

When we again increased the temperatures of the Hopcalite and the charcoal to 800°F and 200°F, respectively, the DF again increased to about 3×10^3 . Thus, it appears that we can vary the DF by varying these temperatures.

The results obtained during the campaign indicate that in future processing we can expect to maintain an iodine DF of 10^3 to 10^4 . This is certainly satisfactory for processing short-cooled targets. We are now investigating a larger system for installation in the total vessel and cubicle off-gas system (350 cfm).

6. REFERENCES

1. J. D. Sease, The Fabrication of Target Elements for the High-Flux Isotope Reactor, ORNL-TM-1712 (March 1967).
2. Chem. Technol. Div. Ann. Progr. Rept. May 31, 1968, ORNL-4252, pp 111-13.
3. Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969, ORNL-4422, pp 167-68.
4. L. J. King and E. D. Collins, Summary of the Campaign During July 1968 to Process Fourteen Irradiated HFIR Targets in the Trans-uranium Processing Plant, ORNL-TM-2434 (December 1969).
5. R. L. Bennett, W. H. Hinds, and R. E. Adams, Development of Iodine Characterization Sampler for Application in Humid Environments, ORNL-TM-2071 (May 1968).

1

2

3

4

5

6

INTERNAL DISTRIBUTION

1. R. D. Baybarz	35. L. O. Love
2. J. E. Bigelow	36. J. L. Matherne
3. R. E. Blanco	37. R. V. McCord
4. R. E. Brooksbank	38. H. C. Meyer
5. K. B. Brown	39. F. L. Moore
6. F. R. Bruce	40. J. P. Nichols
7. W. D. Burch	41. P. B. Orr
8. S. R. Buxton	42. D. B. Owsley
9. A. E. Cameron	43. J. R. Parrott
10. J. M. Chandler	44. F. L. Peishel
11. F. R. Chattin	45. C. L. Shepherd
12. J. M. Chilton	46. R. C. Shipwash
13. H. E. Cochran	47. E. M. Shuford
14. E. D. Collins	48. M. J. Skinner
15. J. H. Cooper	49. Martha Stewart
16. L. T. Corbin	50. B. J. Strader
17. D. A. Costanzo	51. D. A. Sundberg
18. J. A. Cox	52. D. B. Trauger
19. F. L. Culler	53. W. E. Unger
20. J. E. Cunningham	54. J. E. Van Cleve
21. F. L. Daley	55. V. C. A. Vaughen
22. W. W. Evans	56. C. E. Waddell
23. D. E. Ferguson	57. B. S. Weaver
24. H. B. Graham	58. M. E. Whatley
25. R. G. Haire	59. J. C. White
26. F. A. Kappelmann	60. L. C. Williams
27. O. L. Keller	61. R. G. Wymer
28. M. T. Kelley	62. O. O. Yarbro
29-30. L. J. King	63. Laboratory Records - RC
31. J. B. Knauer	64-66. Laboratory Records
32. R. E. Leuze	67-68. Central Research Library
33. M. H. Lloyd	69. Document Reference Section
34. A. L. Lotts	

EXTERNAL DISTRIBUTION

70. W. K. Eister (AEC-Wash)	73. D. M. Richman (AEC-Wash)
71. C. H. Ice (Savannah River)	74-75. DTIE
72. L. H. Meyer (Savannah River)	76. Laboratory and University
Division, ORO