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GLOSSARY

Abbreviations and Codes Used in the Thorex Process

S-1	Dissolver
S-2	Feed adjustment tank
S-4	Feed tank for A-column
A-column	Extraction column
B-column	Partitioning column
C-column	Uranium strip column
T-column	Solvent recovery column
AX	A-column organic extractant solution
AS	A-column aqueous scrub solution
AF	A-column feed solution
AU	A-column organic exit stream, bearing thorium and uranium
AP	A-column waste stream
APC	AP composite from A-column
BT	B-column aqueous thorium product stream
BTC	BT evaporator thorium product composite
BTW	BT evaporator waste condensate
BX	B-column water strip solution
B'X	B-column partitioning strip solution
BS	B-column organic scrub solution
BU	B-column uranium-bearing organic exit stream
CX	C-column strip solution
CU	C-column uranium-bearing aqueous exit stream
CW	C-column organic waste stream
CWC	Spent solvent from C-column
TX	T-column extractant solution
TWA	T-column aqueous waste stream
TWC	T-column aqueous waste stream composite
TWO	T-column clean solvent exit stream
RS	Recovered solvent
RCS	Recovered solvent composite
-C or -C-	Composite stream
RA	Recovered nitric acid
LA	Lean acid from acid recovery column
RCA	Radiochemical analysis (for Ru, Nb, Zr and TRE)
Sc γ	Scintillation gamma

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1.0 INTRODUCTION

The ORNL Thorex Pilot Plant was constructed to develop and demonstrate a solvent extraction flowsheet for the separation of uranium-233, thorium, and fission products (including protactinium-233) from reactor irradiated metal and to recover the uranium-233 and thorium as aqueous solutions suitable for further direct handling. The development program is directed toward obtaining the necessary chemical and mechanical data for the design and construction of a thorium processing plant. The Thorex flowsheet includes dissolution of the irradiated metal in nitric acid; adjustment and acid recovery; solvent extraction, partitioning, and stripping; continuous solvent recovery; and semi-continuous isolation of uranium-233 by sorption on Dowex-50 resin. This run

was made to demonstrate the chemical flowsheet and the equipment that had been designed on laboratory data.

Specific objectives of this run were to:

1. Continue the evaluation of the ORNL Thorex Flowsheet No. 1.2-7.
2. Continue to determine the effects of acid-deficient aging time on ruthenium decontamination.
3. Determine the loss of uranium and thorium to extraction column waste as a function of the extraction column effective extraction length.
4. Continue to determine the effects of the metal heel and the catalyst concentration on dissolution rate.
5. Determine the effect of A-column scrub solution ferrous ion concentration on ruthenium decontamination.
6. Determine the effect of free phosphate in the extraction column scrub solution on protactinium-233 decontamination.
7. Evaluate a revised extraction column shutdown-startup procedure.
8. Continue the evaluation of uranium loss to thorium product as a function of B-column effective scrub length.

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2.0 SUMMARY

In operating according to ORNL Thorex Flowsheet, No. 1.2-7 conditions, thorium was decontaminated from protactinium-233 and fission product activity by a factor of 1.6×10^4 with a thorium recovery of 98.7 per cent. The Th-234 (UX_1 - UX_2) content of the thorium product averaged 272 beta cts/min/mg thorium; after 35 days this would decay to 100 cts/min/mg thorium. Ruthenium contributed 3 per cent and protactinium-233 contributed 41 per cent of the gamma activity of the thorium product. Approximately 0.03 per cent of the ruthenium in the A-column feed was found in the thorium product and less than 0.01 per cent in the uranium product. The phosphate content of the thorium product averaged 15 ppm.

The U-233 product was decontaminated from Pa-233 and fission product gamma activity before sorption by a factor of 3.3×10^4 with a recovery of 97.8 per cent. The solvent extraction product stream, which averaged 0.082 g of U-233 per liter, was sorbed on Dowex-50 ion exchange resin. Additional decontamination from fission product and ionic impurities is obtained in the sorption step. The uranium will be eluted after the resin column has been loaded to approximately 50% capacity.

The feed material for this run was prepared from thorium irradiated slugs.

The slugs were dissolved in 100 per cent excess 13 N nitric acid; the dissolver solution was concentrated to approximately 4 M thorium nitrate, 0.4 N acid deficient, and was diluted to 1.5 M thorium nitrate for extraction column feed. After adjustment to flowsheet A-column feed conditions, the acid-deficient mixture was processed through one solvent extraction cycle at a thorium throughput of 200 kg/day. The uranium and thorium were separated in a partitioning column. The thorium was stripped into the aqueous phase, and after the aqueous phase was steam-stripped to remove entrained solvent, the thorium was concentrated in a continuous evaporator to approximately 450 g/liter. The uranium was stripped into dilute nitric acid in a third column, and the aqueous uranium solution was passed through a silica gel column to obtain additional niobium and zirconium decontamination.

The feed solution contained less than normal background of iodine-131.

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Active contaminants remaining in the spent solvent from C-column were principally niobium, zirconium, and ruthenium. The solvent recovery system removed these and reduced the gross gamma count to 200 gamma cts/min/ml---a decontamination factor of 11.

The acid recovery system was operated during the feed adjustment of Run HD-8-A dissolver solution for 15 hr; 99 per cent of the excess nitric acid used in the dissolution of thorium slugs was recovered, while 0.17 per cent was lost to the lean acid. Gross gamma decontamination factors of 2.3×10^4 and 7.1×10^4 were obtained for the recovered acid and the lean acid fractions, respectively. The principal contaminants in the recovered acid were ruthenium and niobium, and in the lean acid was niobium.

Conclusions from this run are:

1. Reducing the acid-deficient feed aging time increased the ruthenium decontamination. Halving the feed acid-deficient aging time used in Run HD-7 increased the ruthenium decontamination by a factor of five.
2. Increasing the effective extraction section length of the extraction column reduced the thorium and uranium extraction losses.
3. The size of the undissolved thorium metal heel exerts a greater effect on the thorium dissolution rate than the combined effects of nitric acid and catalyst concentration.
4. Maintaining ~~reducing conditions (Run 2)~~ in the extraction column scrub section gave ruthenium decontamination results that were masked by the effect of acid-deficient aging of the feed solution.
5. Maintaining the phosphate-ion concentration in the extraction column scrub solution in excess of the ferric-ion concentration increased the protactinium-233 decontamination.
6. Shutting down the solvent extraction columns according to a revised procedure (final flushing of the solvent from the extraction column to prevent prolonged contact with radioactive material) prevented surges of contaminated solvent from the extraction column to the partitioning column during start-up of the following run.
7. Increasing the effective length of the scrub section of the partitioning column reduced the uranium loss to thorium product. An increase of 2 ft in the effective length of the scrub section in

this run resulted in uranium losses to thorium product of 0.44 per cent as compared to 0.59 per cent observed in the previous runs.

Other conclusions are:

1. A reduction in the effective length of the A-column scrub section resulted in lower thorium product TRE decontamination.
2. Maintaining the solvent tributyl phosphate concentration at 42-44 per cent resulted in stable A-column operation.
3. Substituting water for 0.008 N nitric acid in the B-column strip solution reduced the acid concentration of the B-column uranium-bearing stream to 0.01 N.
4. Reducing the aluminum concentration in the A-column scrub solution did not result in any observable effect on decontamination or thorium and uranium losses to waste.

3.0 CONDENSED TABULATION OF RESULTS

This section contains a condensed tabulation of losses, decontamination factors, radioactivities, and ionic impurities of the thorium and uranium product streams. Detailed analyses of all product streams are presented in Section 13.0. Gamma activity balances are low for thorium and uranium product streams because of the pronounced tendency of protactinium, niobium, and zirconium to plate out of neutral or weak acid solutions.

3.1 Product Recovery and Decontamination Factors

Various data obtained on product recovery and decontamination are given in Tables 3-1 through 3-3. The decontamination factors for thorium are for the concentrated (approximately 2.0 M) solution; those for uranium are for the solvent extraction product stream prior to sorption on the resin column.

Table 3-1
Equilibrium Solvent Extraction Losses

Stream	Thorium Loss, %	Uranium Loss, %
AP	0.1200	0.066
BT	-----	0.442
CU	0.0003	-----
CW	0.0018 ^(a)	0.150
BTW ^(b)	0.0020	-----
Total	0.1241	0.658

(a) Below limits of accuracy for the analytical method.

(b) Calculated from analysis of the composite solution.

Table 3-2
Over-All Material Balance

Product	Thorium, %	Uranium, %
Composite	105.3	99.3
Equilibrium	102.9	100.2

Table 3-3

Over-All Decontamination Factors for Thorium and Uranium Products

Constituent	Product Stream			
	Thorium		Uranium ^(a)	
	Run HD-8-A	Run HD-8-B	Run HD-8-A	Run HD-8-B
Gross γ	2.0×10^4	1.2×10^4	4.0×10^4	2.7×10^4
Pa γ	3.6×10^4	3.0×10^4	1.4×10^5	2.4×10^4
Ru γ	2.8×10^3	3.5×10^3	9.3×10^3	1.5×10^4
Zr-Nb γ	5.6×10^6	3.0×10^3	5.4×10^4	4.6×10^3 (b)
TRE β	2.4×10^4	2.9×10^3	5.4×10^5	2.0×10^6

(a) Before sorption on the resin column.

(b) This discrepancy is not understood; succeeding runs will be studied to see whether a trend is indicated.

3.2 Thorium Product

3.21 Radiochemical and Ionic Analyses

The radiochemical and ionic analyses of the thorium product are shown in Table 3-4.

Table 3-4

Radiochemical Analysis and Ionic Composition of Thorium Product

Constituent	Radiochemical Analyses			
	Run HD-8-A		Run HD-8-B	
	cts/min/ml	% of Total	cts/min/ml	% of Total
Gross γ	1.3×10^5	100	1.6×10^5	100
Ru γ	4.0×10^3	3	2.5×10^3	2
Zr-Nb γ	3.4×10^4	27	5.7×10^4	35
TRE β	3.7×10^3	---	4.2×10^4	---
UX ₁ -UX ₂ β	1.3×10^5	---	1.1×10^5	---
Pa γ	6.2×10^4	48	5.4×10^4	33
Iodine β	None detected	---	None detected	---
	Ionic Analyses			
	Run HD-8-A		Run HD-8-B	
Thorium, g/liter	445		427	
Uranium, ppm of Th	3.1		2.1	
HNO ₃ , N	2.28		1.77	
PO ₄ ³⁻ , ppm of Th	10		22	

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3.3 Uranium Product

3.31 Radiochemical and Ionic Analysis of Uranium Product Before Sorption

The radiochemical and ionic analyses of uranium product are shown in Table 3-5.

Table 3-5

Radiochemical Analysis and Ionic Composition of Uranium Product Before Sorption

Constituent	Radiochemical Analyses			
	Run HD-8-A		Run HD-8-B	
	cts/min/ml	% of Total	cts/min/ml	% of Total
Gross γ	1.5×10^4	100	3.4×10^4	100
Ru γ	287	2	285	1
Zr-Nb γ	8.3×10^3	55	1.7×10^4	51
TRE β	50	---	28	---
UX ₁ -UX ₂ β	600	---	17	---
Pa γ	3.9×10^3	26	3.2×10^3	10
I β	None detected	---	None detected	---
	Ionic Analyses			
	Run HD-8-A		Run HD-8-B	
Uranium, g/liter	0.075		0.123	
Th, wt %	1.3		0.08	
HNO ₃ , N	0.01		0.013	

3.4 Ruthenium Distribution and Decontamination Factors

3.41 Ruthenium Distribution in the Process Streams

The distribution of ruthenium in the Thorex process streams is shown in Table 3-6.

Table 3-6

Ruthenium Distribution in the Process Flowing Streams

Stream	Ruthenium Activity, γ cts/min/ml	
	in Run HD-8-A	in Run HD-8-B
AU	1.2×10^3	1.1×10^3
AP	4.4×10^6	4.0×10^6
BU	635	640
BT	677	1000
CU	480	620
CW	470	395
TWO	216	360
TWA	2.7×10^3	3.1×10^3
RS	---	108

3.42 Ruthenium Decontamination Factors

The ruthenium decontamination factors, calculated from flowing stream sample analyses, are given in Table 3-7.

Table 3-7

Ruthenium Decontamination Factors
(corrected for flow ratios)

Run No.	Decontamination Factors			
	A-column	B-column		C-column
	AF/AU	AF/BU	AF/BT	AF/CU
HD-8-A	1.5×10^3	2.1×10^3	1.9×10^3	2.8×10^3
HD-8-B	1.2×10^3	1.8×10^3	1.1×10^3	1.5×10^3

3.5 Solvent Recovery Decontamination and Radiochemical Analysis

Decontamination factors are listed in Table 3-8 for the solvent recovery system, which includes the sodium carbonate contacting column (T-1) and a Sharples Super-Centrifuge (T-3). Radiochemical analysis of the solvent system is shown in Table 3-9.

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Table 3-8

Solvent Recovery System Decontamination Factors

Run No.	Decontamination Factors					
	Solvent Recovery Column			Centrifuge		
	CW/TWO			TWO/RS		
	Gross γ	Ru	Nb-Zr	Gross γ	Ru	Nb-Zr
HD-8-A	2.7	2.8	2.3	6.3	1.1	12.5
HD-8-B	3.9	1.6	1.6	1.2	1.0	5.8

Table 3-9

Radiochemical Analysis of Solvent Recovery System Streams

Run No.	Radioactivities, cts/min/ml								
	in the CW Stream			in the TWO Stream			in the RS Stream		
	Gross γ	Ru γ	Nb-Zr γ	Gross γ	Ru γ	Nb-Zr γ	Gross γ	Ru γ	Nb-Zr γ
HD-8-A	3.4×10^3	470	1.8×10^3	1.4×10^3	216	680	218	---	65
HD-8-B	4.8×10^3	395	1.4×10^3	1.4×10^3	360	875	1.1×10^3	108	150

3.6 Acid Recovery

3.61 Fission Product Distribution in Recovered Acid and Lean Acid

The gross gamma activity level in the recovered acid averaged 1.2×10^5 cts/min/ml and that of the lean acid averaged 1.3×10^3 cts/min/ml. The fission product distribution in the recovered acid and the lean acid for HD-8-A is shown in Table 3-10. The acid recovery system was not operated throughout in HD-8-B, but was discontinued after approximately 50 per cent of the lean acid had been removed from the dissolver solution.

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Table 3-10

Average Fission Product Distribution in Recovered Acid and Lean Acid

Run HD-8-A	Gross γ	Ru γ		Nb γ		Zr-Nb γ		TRE β	
	cts/min/ml	cts/min/ml	% (a)	cts/min/ml	% (a)	cts/min/ml	% (a)	cts/min/ml	% (a)
Recovered Acid	1.2×10^5	3.6×10^4	0.20	4.4×10^4	0.02	4.6×10^4	0.02	1950	0.001
Lean Acid	250	65	0.006	---	---	270	0.001	100	0.0002

(a) Based on dissolver solution = 100%.

3.62 Decontamination Factors Across the Acid Recovery System

Average decontamination factors are presented in Table 3-11 for the 10.6 N recovered acid and the lean acid.

Table 3-11

Average Decontamination Factors Across the Acid Recovery System

Solution	Decontamination Factors for Run HD-8-A				
	Gross γ	Ru γ	Nb γ	Zr-Nb γ	TRE β
Recovered Acid	2.3×10^4	289	4.8×10^3	6.2×10^3	5.8×10^4
Lean Acid	7.0×10^4	5.3×10^4	---	3.4×10^5	3.7×10^5

4.0 FLOWSHEET AND EQUIPMENT MODIFICATIONS

4.1 Flowsheet Modifications

The run was operated under ORNL Thorex Flowsheet No. 1.2-7 conditions. The pump rates of the AX and BS metering pumps were adjusted to compensate for pump and pulser leakage, which was measured at intervals throughout the run. The flow ratios were maintained at flowsheet conditions. The ferrous ion concentration of the AS was determined by analysis, and adjusted when required.

4.2 Equipment Modifications

(1) The AS and AF entry points into A-column were at the 33.25-ft and 11.25-ft levels, respectively.

(2) The acid recovery rectifying tower was operated without reflux during the last half of the adjustment of HD-8-B feed. No fractionation occurred during this phase. Because most of the water had already been removed as lean acid, 10 M nitric acid was collected in the lean acid catch tank during this portion of the run.

5.0 PROCEDURE

5.1 Feed Preparation and Acid Recovery

Irradiated thorium slugs were dissolved in 100 per cent excess of approximately 13 N nitric acid to a specific gravity of 1.52 at 110°C, 1.0 M thorium and a 6.0 N nitric acid concentration. The dissolver solution was cooled to 40°C, sampled, and transferred to the feed adjustment tank. The amounts of uranium and thorium transferred from the dissolver to the feed adjustment tank were calculated by comparing the analyses and the volume depletion in the dissolver to the volume buildup in the feed adjustment tank. Dissolver heel determinations were made after each run by making a material balance around the dissolver.

The solution in the feed adjustment tank was heated to 150°C, distilling off the excess nitric acid present in the feed solution. The nitric acid vapors from distillation of Run HD-8-A were rectified in the acid recovery tower, producing a 10.6 N recovered acid fraction (7,500 moles) and a 0.01 N lean acid fraction. During the distillation of Run HD-8-B, the acid recovery system was operated without reflux and no nitric acid was recovered.

The feed adjustment step produced a feed solution 0.1 to 0.2 N acid deficient, dissolved any existing "blue" thorium, and dehydrated soluble silica, ruthenium, zirconium, and niobium. The feed adjustment step provides improved decontamination factors for zirconium, niobium, and ruthenium and elimination of emulsion-forming soluble silica.

The temperature of the concentrated solution in the feed adjustment tank was cooled to 135°C and diluted with demineralized water to bring the solution to approximately the final feed conditions. Final feed adjustment to flowsheet specifications was made in the feed head tank.

5.2 Column Operation

The columns were started from the stand-by conditions established in the revised shutdown procedure followed in Run HD-7.

The revised shutdown procedure for A-column began with the exhaustion of radive feed and continued with feed prepared from acid-digested mantle grade thorium nitrate (TNT), until the U-233 was substantially exhausted from A-column. The entering streams were stopped, and the solvent in the column was pulsed to the top of the column. The column contents above the suction level of the interface jet (all organic) was transferred to the rework-recycle system. The interface in the column was raised to several inches above the interface jet suction

with AS, and a second transfer of the column interface contents was made. The pressure on the pressure pot was removed and the column allowed to stand until the next run began. The B-, C-, and T-columns were operated, after A-column had been shut down, until the thorium and uranium were substantially exhausted from them, and then all streams were stopped.

The startup procedure began with the startup of the solvent recovery column. When a supply of recovered solvent was available, the B- and C-columns were started from the standby condition in which they had remained during shutdown. A-column was started up last, using cold feed until thorium equilibrium was established. When thorium equilibrium was established, the radive feed was turned on, and equilibrium with respect to the radioactive constituents of the feed was established.

After total equilibrium had been established in the system, the data in this report were recorded and analyzed.

Flowing stream samples were taken from all process streams at 8-hr intervals, and composite samples were taken from the catch tanks prior to disposal of the solutions.

The columns were operated with feed to A-column for 131 hr. The detailed schedule of feed preparation and operating time is presented in Sect. 11.0, Table 11-1.

6.0 FEED PREPARATION

The process feed was prepared by dissolving two batches of aluminum jacketed, 6-inch Hanford reactor irradiated thorium slugs in nitric acid, catalyzed with fluoride and mercury. Feed for Run HD-8-A was prepared by dissolving 178 slugs in the presence of a 240-slug heel. Feed for Run HD-8-B was prepared by dissolving the 240-slug heel. The aluminum content was adjusted by adding aluminum metal to the dissolver. The heel dissolving was carried to approximately 97 per cent completion.

The slugs for HD-8-A and -B were dissolved in 100 per cent and 110 per cent excess nitric acid, and to 130 per cent and 3 per cent metal heel, respectively. Sufficient stock catalyst solution containing $\text{Hg}(\text{NO}_3)_2$, NaF and $\text{Al}(\text{NO}_3)_3$ was added to the dissolver at the beginning of each dissolving to yield final mercuric and fluoride ion concentrations in the final dissolver solutions of 73 per cent and 100 per cent, respectively, of flowsheet catalyst concentration.

HD-8-A slugs were dissolved in a less concentrated nitric acid than usual, because 150 liters of recovered acid previously added to cover the metal heel had been diluted to half the usual acid concentration owing to a steam leak into the dissolver. The dilute acid contained 96 g. thorium per liter at the beginning of the run, and this also retarded the dissolution rate.

The average unit weight of the thorium slugs processed in HD-7 and HD-8 runs was 1,618 g; the lot previously processed averaged 1,653 g per slug.

6.2 Slug Dissolution

Dissolving to a definite metal heel was approximately controlled by conducting the reaction to a definite specific gravity, while limiting the quantity of nitric acid fed to the dissolver. The times for dissolving 178 slugs to approximately 130% heel and 232 slugs to approximately 3% heel were 32 and 15 hr, respectively.

The acid requirements, moles of nitric acid per mole of dissolved thorium and aluminum, averaged 4.7 and 4.0, respectively. The final thorium concentration in the dissolver solutions averaged 215 g per liter in 5.15 N nitric acid, and the specific gravity averaged 1.57. Approximately 20 per cent of the nitric acid used in slug dissolution was recovered from the previous feed adjustment step.

The metal heel remaining in the dissolver was calculated after each run. A running inventory was maintained by subtracting the amount of material leaving the dissolver in solution from the amount added to the dissolver. The volume of the dissolver solution was corrected for the volume occupied by the thorium metal heel.

After each dissolving was completed, the solution was transferred to the feed adjustment tank. The thorium metal heel in the dissolver was covered with approximately 150 liters of recovered nitric acid and allowed to stand at ambient temperature in the absence of catalyst until the beginning of the next dissolution.

The data for Run HD-8 slug dissolution are shown in Table 6-1.

6.3 Feed Adjustment

The excess nitric acid was removed from the dissolver solution by evaporation to a temperature of 150°C. This procedure dehydrated the soluble silica, ruthenium and zirconium compounds, and produced an acid-deficient feed solution. The acid-deficient, concentrated feed solution was diluted to approximately A-column feed conditions and transferred to the A-column feed head tank, where final adjustment was made.

6.4 Radiochemical Analysis and Ionic Composition of Final Feed

The radiochemical analysis and ionic composition of the final feed solution are shown in Table 6-2.

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Table 6-1

Thorium Slug Dissolution

Dissolver Data	Run HD-8-A	Run HD-8-B
Dissolver Metal		
Number of slugs	178	259
Thorium, kg	387	418
Uranium-233, g	174.4	260.0
Heel, Thorium, kg	418.49	18.50
Heel, Uranium-233, g	260.00	11.4
Nitric Acid Added		
Recovered, moles	9,575	12,745
Fresh, moles	6,951	2,480
Total acid added, moles	16,526	15,225
Dissolver solution, liters	1,715 ^(a)	1,990 ^(a)
Thorium concentration, g/liter	231.0	200.5
Thorium dissolved, kg	246	400
Uranium dissolved, g	159.3	258.5
Nitric acid utilization, %	84	84 ^(b)
Catalyst used, % of flowsheet concentration	73	100
Dissolution time, hr	32	15
Acid recovered, % of excess in dissolver solution	99.8	--- ^(b)
Acid lost to lean acid, %	0.17	---

(a) 650 liters of HD-8-A dissolver solution was left in the dissolver for HD-8-B to simulate a 178 and 240 slug dissolution.

(b) The acid vapors were allowed to go to waste for the last half of this run due to lack of recovered acid storage space.

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Table 6-2

Radiochemical Analysis and Ionic Composition of Final Feed

Constituent	Radiochemical Analyses			
	Run HD-8-A		Run HD-8-B	
	cts/min/ml	% of Gross	cts/min/ml	% of Gross
Gross γ	2.0×10^9	100	1.6×10^9	100
Ru γ	8.8×10^6	0.4	7.3×10^6	0.5
Pa γ	1.7×10^9	87	1.4×10^9	87
Nb-Zr γ	1.4×10^8	7	1.4×10^8	9
TRE β	8.9×10^7	---	1.0×10^8	---
UX ₁ -UX ₂ β	1.7×10^5	---	1.4×10^5	---
I β	Not detected	---	Not detected	---
Ion chamber, mv/ml	1.9×10^6	---	1.1×10^5	---
	Ionic Analyses			
	Run HD-8-A		Run HD-8-B	
Th, g/liter	348		356.5	
HNO ₃ , N	0.03		0.12 acid deficient	
U, g/liter	0.245		0.214	
Al, g/liter	18.6		17.0	

6.5 Feed Aging Time

The feed preparation time cycles in Run HD-8 consisted of the following aging times, expressed in hours, as shown in Table 6-3.

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Table 6-3

Feed Aging Time for Run HD-8

Run No.	Acid Add., ^(a) hr	Dissolution Time, ^(b) hr	Acid Aging Heel Pres., ^(c) hr	Acid Aging No Heel, ^(d) hr	Feed Adj., ^(e) hr	Acid Def. Aging, ^(f) total hr
HD-8-A	2.7	32.2 ^(g)	2.4	16.6	15.4	133.8
HD-8-B	4.1	15.3	8.5 ^(g)	22.0	21.2 ^(h)	115.0
HD-8-B ^(h)	---	---	---	---	---	142.1

- (a) The acid addition time began when the catalyst was added and continued until all acid had been added.
- (b) The dissolution time began at the end of the catalyst addition and ended when a specific gravity of 1.52 at 110°C was reached.
- (c) Acid aging in presence of metal heel began when the specific gravity reached 1.52 at 110°C and continued until the solution was transferred to the feed adjustment tank.
- (d) Acid aging in absence of metal heel began when the dissolver solution was transferred to the feed adjustment tank and ended when the temperature in the feed adjustment reached 150°C.
- (e) Time for feed adjustment began when steam was turned on to the jacket of the feed adjustment tank, and ended when the feed adjustment temperature reached 150°C.
- (f) Total acid deficient aging began when the temperature in the feed adjustment tank reached 150°C and ended when the last of the feed solution was pumped to the extraction column. This period includes the acid deficient time both in S-2 and in S-4.
- (g) Approximately 396 kg of thorium was dissolved in HD-8-A but only 252 kg was transferred for feed adjustment. The remainder was left in the dissolver to become a part of HD-8-B; approximately one-third of HD-8-B feed had been aged in acid environment in 6 N nitric acid for approximately 90 hr.
- (h) The second transfer of HD-8-B to the feed head tank.

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7.0 DECONTAMINATION

The decontamination factors for HD-8-A were based on analyses of flowing stream samples taken at about 24-hr intervals throughout the equilibrium portion of the run. The feeds for HD-8-A and -B were pumped to the columns for 28.2 and 45.8 hr, respectively. The composition of the A-column scrub solution (AS) averaged 0.48 M Al, 0.08 N acid deficient, 0.006 M Fe and 0.003 M PO_4^{-3} for the run. The Fe^{+2} content averaged 0.005 M throughout the run.

7.1 Decontamination Factors

The decontamination factors obtained for A-, B-, C-, and T-columns are shown in Tables 7-1 through 7-4.

Table 7-1

A-column Decontamination Factors

Basis: AF/AU

Run No.	Decontamination Factors				
	Gross γ	Pa	Ru	Zr-Nb	TRE
HD-8-A	5.1×10^4	1.2×10^5	1.5×10^3	2.0×10^4	5.7×10^4
HD-8-B	2.1×10^4	3.5×10^4	1.2×10^3	8.0×10^3	3.1×10^4

Table 7-2

B-column Decontamination Factors

Basis: AU/BU and AU/BT

Run No.	Decontamination Factors									
	Gross γ		Pa		Ru		Nb-Zr		TRE	
	BU	BT	BU	BT	BU	BT	BU	BT	BU	BT
HD-8-A	1.10	1.90	2.48	1.13	1.50	1.30	2.03	3.40	1.05	1.21
HD-8-B	2.20	1.80	2.60	1.20	1.60	1.30	2.00	3.10	1.10	1.25

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Table 7-3

C-column Decontamination Factors

Basis: BU/CU

Run No.	Decontamination Factors				
	Gross γ	Pa	Ru	Nb-Zr	TRE
HD-8-A	1.60	3.96	3.78	1.23	3.12
HD-8-B	1.58	1.90	3.50	2.10	3.20

Table 7-4

T-column Decontamination Factors

Basis: CW/TWO

Run No.	Decontamination Factors			
	Gross γ	Ru	Nb-Zr	TRE
HD-8-A	2.70	2.80	2.30	2.50
HD-8-B	3.90	1.60	1.60	---

7.2 Ruthenium Distribution in the System

The distribution of ruthenium in the solvent extraction system is shown in Table 7-5.

7.21 Ruthenium Distribution in B-column

The distribution of ruthenium into the BU and BT streams is shown in Table 7-6.

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Table 7-5

Ruthenium Distribution in the Solvent Extraction System

Basis: AF Ru = 100%

Run No.	AU		AP		BT	
	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total
HD-8-A	1.2×10^3	0.068	4.4×10^6	90.0	677	0.048
HD-8-B	1.1×10^3	0.078	4.0×10^6	98.8	1.0×10^3	0.083
Run No.	BU		CU		CW	
	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total
HD-8-A	635	0.046	480	0.001	470	0.033
HD-8-B	640	0.059	620	0.011	395	0.033
Run No.	TWO		TWA		RS	
	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total
HD-8-A	216	0.013	2.7×10^3	0.029	---	---
HD-8-B	360	0.033	3.1×10^3	0.040	108	0.007

Table 7-6

Ruthenium Distribution in B-column Product Streams

Basis: BU and BT Ru γ = 100%

Run No.	BU		BT	
	γ cts/m/ml	% of Total	γ cts/m/ml	% of Total
HD-8-A	635	50.8	677	49.2
HD-8-B	640	41.0	1010	58.9

7.3 Decontamination Factors for Thorium and Uranium Product

7.31 Thorium Decontamination

Listed in Table 7-7 are decontamination factors based on analyses of flowing stream samples taken before boildown. The UX_1 - UX_2 beta (Th-234) levels were 292 and 254 beta cts/min/mg Th, respectively, for HD-8-A and -B.

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Table 7-7
BT Decontamination Factors

Run No.	Gross γ	Pa	Ru	Nb-Zr	TRE
HD-8-A	3.3×10^4	6.8×10^4	1.9×10^3	5.2×10^3	4.5×10^4
HD-8-B	3.6×10^4	6.4×10^4	1.1×10^3	1.0×10^4	3.0×10^4

7.32 Uranium Decontamination

Listed in Table 7-8 are decontamination factors based on the analyses of flowing stream samples taken during the equilibrium portion of the run.

Table 7-8
CU Decontamination Factors

Run No.	Gross γ	Pa	Ru	Nb-Zr	TRE
HD-8-A	2.2×10^4	1.4×10^5	2.8×10^3	2.5×10^3	5.9×10^5
HD-8-B	1.6×10^4	2.0×10^4	1.8×10^3	2.8×10^3	7.6×10^5

7.33 Discrepancies in Decontamination Factors for Flowing Stream and Composite Samples

The discrepancies in decontamination factors calculated from analyses of flowing stream samples (Tables 7-7 and 7-8) and samples of composites (Table 3-3) are thought to be caused by two things: (1) plating out of activities, and (2) collection of solids at the extraction column interface.

Protactinium, niobium, and zirconium precipitate from weak acid solution and plate out on glass surfaces, making rapid withdrawal, delivery, stabilization and analysis of samples containing these ions necessary for reliable analytical results. The use of polythene sample bottles or plastic-coated glass sample bottles in the future will assist in eliminating discrepancies due to sampling and analytical technique.

The collection of finely divided solids, consisting of refractory oxides of thorium, silica, calcium, and magnesium, at the interface of the extraction column during runs has been noted. Isolation and analysis of such matter has revealed that protactinium, niobium and zirconium were the principal contaminants absorbed on the interfacial solids.

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In glass columns, the interfacial film layers have been observed to increase in depth to several inches over a period of 6-24 hr and then collapse to depths of 1 to 2 in. with the simultaneous release of small agglomerants of the solids into the product-carrying organic layer. This process was observed to repeat itself over and over again. The agglomerants would remain suspended in the organic layer for some time and a portion would be carried into the partitioning column and into the products. As such solid material exhibits no true solubility in either phase in the partitioning column, it distributed randomly across the interface of this column, thereby contaminating both the thorium product in the aqueous phase and the uranium in the stripping column.

Because the flowing streams may be sampled during, just before, or just after the collapse of the interfacial film, a contaminated sample may or may not be obtained. Likewise, one composite sample may contain the contaminants that had accumulated on the interfacial film during early periods of the run, but because of the collapse of the film layer, these solids found their way into a single composite, thereby yielding misleading results as to decontamination.

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8.0 PRODUCT LOSSES

8.1 Thorium Losses

Thorium losses to the various waste streams are given in Table 8-1. These losses are based on average analyses of flowing stream samples taken at 8-hr intervals during the equilibrium portion of the run.

Table 8-1
Equilibrium Thorium Losses

Stream	Thorium Loss % of AF Thorium
AP	0.1200
BTW ^(a)	0.0020
CU	0.0003
CW	0.0018 ^(b)
Total	0.1241

(a) Calculated from composite samples

(b) Limit of accuracy

8.2 Uranium Losses

Listed in Table 8-2 are the uranium losses to the various process streams. The losses were based on average analyses of flowing stream samples taken at 8-hr intervals throughout the equilibrium portion of the run.

Table 8-2
Equilibrium Solvent Extraction
Uranium Losses

Stream	Uranium Loss % of AF Uranium
AP	0.066
BT	0.442
CW	0.150
Total	0.658

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9.0 SOLVENT RECOVERY

The solvent used in the Thorex Run HD-8 consisted of a mixture of 42.5 volume per cent solution of tributyl phosphate in Special Naphtha No. 1, an oleum treated hydrocarbon diluent. This organic mixture undergoes chemical and radiative degradation in the Thorex process forming butyl alcohol, mono and dibutyl phosphates and compounds reactive to fission products. The mono and dibutyl phosphates and butyl alcohols are found also as impurities in freshly prepared tributyl phosphate but, after one pass through the solvent recovery system, are present only as formed by the hydrolysis of tributyl phosphate in the solvent. Mono and dibutyl phosphates (MBP and DBP) form stable thorium and uranium compounds, some of which are difficultly stripped from solvents, resulting in high losses. Iodine is chemically reactive to the degraded diluent, forming compounds which are not stripped from the solvent with dilute nitric acid.

Most of the organic impurities were removed from the organic solvent by contacting the solvent with a 0.1 volume of 0.2 M sodium carbonate solution. The necessary contacting time, required for the fission products contained in the spent solvent to react with Na_2CO_3 , was obtained by operating the solvent recovery column organic continuous. The reaction rate was increased by maintaining the temperature at 45-50°C.

The solvent recovery column is 25 ft long and 6 in. I. D. It was pulsed 53 cycles per minute at an amplitude of 0.75 in. It has been found⁽¹⁾ that at frequencies greater than 55 cycles per minute stable emulsions formed that were slow to separate and were responsible for entrained activity being carried from the contacting column in the treated solvent. Entrained solids and aqueous droplets were removed from the treated solvent by passing the carbonate-treated solvent through a Sharples Super-Centrifuge operated continuously at 15,000 revolutions per minute. A water purge was continuously added to the centrifuge with the feed to move the entrained aqueous carbonate solution and solids material from the centrifuge bowl. The removal of entrained carbonate solution and solids material improved the gross gamma decontamination of the recovered solvent by a factor of 4. The recovered solvent contained less than 50 alpha cts/min/ml,

(1) C. V. Ellison, "Continuous Solvent Recovery Process Using Pulse Contacting Column," ORNL-1224, (Mar. 14, 1952)

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400 beta cts/min/ml, and averaged 42.5 per cent tributyl phosphate.

The first solvent which passed through the solvent recovery system after the five-day shutdown period contained higher activity than freshly processed solvent. This above-average-contamination of solvent that has remained in contact with process solutions is attributed to the degradation of the solvent to form substances reactive toward fission products that are difficult to strip from the solvent with dilute nitric acid.

The principal solvent contaminants were niobium and ruthenium. Each has previously been found to behave in organic solvents as if it was partly insoluble; i. e., polymeric, and did not exhibit a true distribution coefficient, but distribute into the two phases randomly.

9.1 Solvent Recovery Decontamination and Activity Distribution

Shown in Tables 9-1 and 9-2 are the decontamination factors and the fission product distribution for the solvent recovery system.

Table 9-1
Solvent Recovery Decontamination Factors

Run No.	Activity	Solvent Column CW/TWO	Centrifuge TWO/RS	Over-All CW/RS
HD-8-A	Gross γ	2.7	6.3	17.3
	Ru	2.8	1.1	3.1
	Nb-Zr	2.3	12.5	28.5
	TRE	2.5	---	2.5
HD-8-B	Gross γ	3.9	1.2	4.8
	Ru	1.6	1	1.6
	Zr-Nb	1.6	5.8	9.4

The average recovered solvent fission product activity was 650 gamma cts/min/ml. The over-all decontamination factors reported probably are correct only to within a factor of 2 or 3 due to the low precision of analyses at these activity levels.

Table 9-2
Fission Product Distribution in the Solvent Recovery System

Run No.	CW							
	Gross γ	Ru γ		Nb γ		Nb-Zr γ		TRE β
	cts/min/ml	cts/min/ml	% of Gross	cts/min/ml	% of Gross	cts/min/ml	% of Gross	cts/min/ml
HD-8-A	3.4×10^3	470	14	2.0×10^3	59	1.9×10^3	53	35
HD-8-B	4.8×10^3	395	8	1.4×10^3	29	1.4×10^3	29	10
TWO								
HD-8-A	1.4×10^3	216	16	50	4	680	50	50
HD-8-B	1.4×10^3	360	27	---	---	875	65	---
RS								
HD-8-A	218	---	---	---	---	65	30	---
HD-8-B	1.1×10^3	108	9	---	---	150	14	---

9.2 Solvent Inventory and Losses

A solvent loss of 172 liters from an inventory of 2,833 liters occurred during 184 hr of continuous column operation. The total solvent throughput during this period was 22,632 liters, equivalent to 8 passes through the system. The over-all solvent loss was 6.07 per cent for 8 passes, equivalent to 0.76 per cent per pass. A 0.69 per cent loss per pass was observed in Run HD-7.

The solvent inventory and losses are summarized in Table 9-3.

Table 9-3
Solvent Inventory and Losses

Solvent Data	Volume, liters	%
Inventory	2833	---
Total pumped	22,632	---
<u>Losses</u>		
Total	172	6.07
Per pass	21.5	0.76
Per kg Th processed	0.27	---
Per g U ²³³ processed	0.42	---

9.3 Solvent Recovery Equipment Performance

The solvent recovery column was operated organic continuous for 184 hr. The solvent leakage rate from the pulser averaged 46 ml per minute.

The Sharples Super-Centrifuge was operated continuously at 15,000 rpm. Approximately 30 per cent of the gross gamma contamination in the spent solvent was removed by centrifuging the solvent after carbonate treatment. The principal fission products removed by centrifugation were niobium and zirconium. The radive solids accumulated in the centrifuge bowl, increasing the activity level to 430 mr/hr at the surface of 0.5-in. lead shielding surrounding the frame.

10.0 ACID RECOVERY

10.1 Summary

During the feed adjustment step, the nitric acid vapor from the dissolver solution was rectified in the acid recovery unit. Nitric acid, 10.6 N, was removed continuously from the reboiler of the rectifying column and lean acid, approximately 0.01 N, was collected as an overhead fraction. The recovered acid was cooled continuously in a shell and tube heat exchanger and stored for use in a subsequent slug dissolution. The acid vapors from HD-8-B were not rectified for approximately the last half of HD-8-B, but were allowed to go overhead to the lean acid catch tank.

The feed adjustment step completely removed the nitric acid, and partially denitrated a small fraction of the aluminum nitrate, rendering the feed solution acid deficient. The over-all nitric acid recovery for Run HD-8-A feed adjustment step was 99 per cent based on the free nitric acid that remained in the dissolver solution. The nitric acid loss to waste as lean acid was 0.17 per cent. In the Run HD-8-A feed adjustment step, 4,583 moles of nitric acid was recovered which averaged 10.6 N, while 8 moles (0.01 N) was lost to waste.

The recovered acid was decontaminated from gross gamma activity by a factor of 3.0×10^4 , TRE by a factor of 7.8×10^4 , ruthenium by a factor of 3.7×10^2 , and niobium-zirconium by a factor of 7.7×10^3 . The decontamination factors for Run HD-8-B were less than half those for HD-8-A, indicating that proper operation of the acid recovery column within design ranges at reflux ratios of approximately 4:1 is a controlling factor in lean acid decontamination. Thorium concentration and gamma activity in the acid streams varied with column operation and normality of the acid stream. The gross gamma activity in Run HD-8-A recovered acid was 1.2×10^5 cts/min/ml.

Run HD-8-A lean acid averaged 1.3×10^3 gross, 65 ruthenium, 270 niobium-zirconium gamma cts/min/ml and 2×10^3 TRE beta cts/min/ml. Operating the acid recovery column without reflux resulted in an average increase in the lean acid TRE concentration by a factor of 10.

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10.2 Procedure and Operation of the Acid Recovery Column

The nitric acid vapors from the feed adjustment tank passed into an 18-in. O. D. stainless steel tower packed with 1-in. Raschig rings. The tower consists of 5.5 ft of stripping section and 1.5 ft of rectifying section. The reboiler is equipped with a steam jacket containing 25 sq ft of heat transfer area. The heat input to the reboiler was controlled by an automatic flow regulator in the 125 psig steam supply line. The recovered acid was cooled in a 22-sq ft shell and tube condenser and air-lifted to the recovered acid storage tank.

A boil-up rate of 325 liters/hour was determined in preoperational testing, based on the boil-up rate from the feed adjustment tank. The acid recovery tank has operated successfully at 80 per cent of flooding.

The reflux ratio of the acid recovery rectifying column was controlled manually at 4-5:1 by maintaining the desired build-up rates in the recovered acid head tank and lean acid catch tank and maintaining the reboiler and overhead temperatures at 120° and 102°C, respectively. The over-all heat transfer coefficient was 143 BTU/hr-sq ft-°F.

During HD-8-B, when the reflux was reduced to a minimum, the lean acid fraction, although containing higher nitric acid concentrations than usual, was sent to waste.

10.3 Decontamination Factors in the Acid Recovery System

Decontamination factors for the recovered acid and lean acid streams are given in Table 10-1.

Table 10-1
Decontamination Factors ^(a) for Recovered Acid and Lean Acid

Sample Number	Decontamination Factors for Recovered Acid				
	Gross γ	Ru γ	Nb γ	Zr-Nb γ	TRE β
RA-200-3	2.3×10^4	289	4.8×10^3	6.2×10^3	5.8×10^4
RA-300-3	1.2×10^4	90	7.7×10^3	8.0×10^3	4.1×10^4
RA-400-3	6.1×10^3	---	---	5.7×10^3	9.3×10^3
	Decontamination Factors for Lean Acid				
RA-200-3	7.1×10^5	5.3×10^4	---	3.4×10^5	3.7×10^5
LA-300-3	1.2×10^6	8.3×10^4	---	7.6×10^5	1.4×10^6
LA-400-3	1.6×10^3	---	---	2.4×10^3	974

$$(a) \text{ Decontamination Factors} = \frac{c/m/ml \text{ in S-2}}{c/m/ml \text{ in S-5 (or S-12)}} \times \frac{N \text{ HNO}_3 \text{ in S-5 (or S-12)}}{N \text{ HNO}_3 \text{ in S-2}}$$

Purposely operating the acid recovery column outside of design conditions allowed the acid concentration in HD-8-B to become equal to that of the recovered acid.

10.4 Activity Levels and Nitric Acid Concentrations

The nitric acid concentrations and activity levels in the recovered acid and lean acid solution are given in Tables 10-2 and 10-3. These data were taken during HD-8-A and -B feed adjustment steps.

Table 10-2
Recovered Acid Molarity and Radiochemical Analysis

Sample Number	HNO_3 , M	Activity, cts/min/ml				
		Gross γ	Ru γ	Nb γ	TRE β	Nb-Zr γ
RA-200-3	9.7	1.2×10^5	3.6×10^4	4.4×10^4	2.0×10^3	4.6×10^4
RA-300-3	10.8	2.2×10^5	1.2×10^5	2.7×10^4	2.8×10^3	3.5×10^4
RA-400-3	11.9	4.4×10^5	1.7×10^5	4.5×10^4	1.2×10^4	4.9×10^4

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Table 10-3

Lean Acid Molarity and Radiochemical Analysis

Sample Number	HNO ₃ M	Activity, cts/min/ml				
		Gross γ	Ru γ	Nb γ	TRE β	Nb-Zr γ
LA-200-3	3.25	1.3×10^3	65	---	100	270
LA-300-3	9.83	2.0×10^3	125	---	80	360
LA-400-3	0.45	7.7×10^4	513	5.2×10^3	5.2×10^3	9.6×10^3

Table 10-4

Fission Product Distribution in the Acid Recovery System

Basis: Dissolver Solution = 100%

Solution	Gross γ , %	Ru γ , %	Nb γ , %	TRE β , %	Zr γ , %	Volume, liters
RA	3×10^{-3}	2×10^{-1}	2×10^{-2}	1×10^{-3}	---	396
LA	5×10^{-5}	6×10^{-3}	---	2×10^{-4}	---	566
AF	0.7×10^2	1×10^2	0.7×10^2	1×10^2	0.8×10^2	685
MD-100	1×10^2	1×10^2	1×10^2	1×10^2	1×10^2	1065

10.5 Operational Data

Operational data collected during the two feed adjustment runs HD-8-A and -B are shown in Table 10-5.

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Table 10-5

Acid Recovery System Data

Run No.	Feed Adjustment		Boil-up Rate, liters/hr	Reflux Ratio Avg	Pressure Drop Across Column, in. of water	Reboiler Temp, °C
	Tank, S-2					
	Temp, °C	Sp Gr				
HD-8-A: Initial	113	(a)	----	4:1	3.0	113
Final	151	(a)	62.5	4:1	7.0	120
HD-8-B: Initial	114	(a)	----	---	1.5	115
Final	149	2.28	71.8	---	10.0	121

(a) The density instrument was out of service in this portion of the run.

The feed adjustment time cycles for HD-8-A and HD-8-B were 15.5 and 21.2 hr, respectively. HD-8-A feed was split, approximately 65 per cent being processed as HD-8-A and the remainder along with HD-8-B feed.

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11.0 OPERATING SCHEDULE

Given in Table 11-1 is the schedule of operating dates for run HD-8.

Table 11-1
Date and Duration of Run HD-8

Process Step	Date	Time
<u>Feed Preparation</u>		
Slug dissolving - HD-8-A, 178 slugs	4/22-23/55	32.2 hr
HD-8-B, Heel	4/24-25/55	15.3 hr
<u>Feed adjustment - HD-8-A, Total</u>		
HD-8-B, Total	4/24-25/55	15.4 hr
	4/25-26/55	21.2 hr
<u>Solvent Extraction</u>		
Start-up began with cold feed	4/28/55	0200
Run began	4/28/55	0644
HD-8-A began	4/28/55	0644
Cold feed began	4/29/55	1430
HD-8-B began	4/30/55	1004
Run ended	5/2/55	1152
Shutdown feed ended	5/3/55	1300
Duration of equilibrium, hr		74

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12.0 METHODS OF COUNTING AND CALCULATING ACTIVITIES

12.1 Counting Methods

12.11 Gamma Counting

All gamma activities were counted using a gamma scintillation counter, Model SU-1 built by Nuclear Measurements Corp. The detector was comprised of a thallium-iodide-activated sodium iodide crystal detector coupled with a photomultiplier tube, the output of which was amplified to energize a scaling unit. All counting was through approximately a 4.5 gm/cm^2 lead absorber. No geometry factor was applied to the results, but corrections for background and instrument deviation were applied.

12.12 Alpha Counting

All alpha counting was with an alpha methane proportional counter at 52% geometry. Corrections for background and instrument error were applied to the results.

12.13 Beta Counting

Beta counting was done with a beta Geiger-Mueller counter at 10.18% geometry corrected for background, coincidence loss, and beta instrument factor.⁽¹⁾

12.14 Ionization Chamber

Ionization chamber determinations were made at 100% geometry using a gamma ionization chamber filled with argon gas at 30 atmospheres pressure. Results were corrected to a 10^{11} scale and reported as millivolts per milliliter of solution.

12.2 Calculating Methods

No corrections have been made in the Th product for UX_1 - UX_2 (Th-234) content. All decontamination factors were calculated from gamma activities, except TRE, which were calculated from beta activities.

(1) C. G. Goss, "Temporary Instructions for Checking and Using Mica Window Geiger Tube with Q-762 Scales."

Decontamination factors across the acid recovery system were based on the activity levels found in the recovered acid and the condensate streams compared to the corresponding activity level in the evaporator, i. e., the feed adjustment tank and the S-9 reboiler, multiplied by the average acid concentration ratio in the respective streams.

$$\text{Recovered Acid Decontamination Factor} = \left[\frac{\gamma \text{ cts/min/ml (in S-2)}}{N \text{ HNO}_3} \right] \left[\frac{N \text{ HNO}_3 \text{ (in S-5)}}{\gamma \text{ cts/min/ml}} \right]$$

$$\text{Lean Acid Decontamination Factor} = \left[\frac{\gamma \text{ cts/min/ml (in S-2)}}{N \text{ HNO}_3} \right] \left[\frac{N \text{ HNO}_3 \text{ (in S-12)}}{\gamma \text{ cts/min/ml}} \right]$$

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13.0 DISTRIBUTION OF ACTIVITIES IN FEED AND PRODUCT STREAMS

The activities listed in Table 13-1 were obtained from analyses of flowing stream samples taken during the equilibrium portions of the run. A flow diagram showing the sampling points in the process is shown in Figs. 16-1 through 16-7.

Table 13-1
Distribution of Activities in Feed and Product Streams

Run No.	Stream	Radioactivities												Total γ , %
		Gross γ		Ru γ		Nb γ		Nb-Zr γ		Pa γ		TRE β		
		cts/min/ml	%	cts/min/ml	% ^a	cts/min/ml	% ^a	cts/min/ml	% ^a	cts/min/ml	% ^a	cts/min/ml	% ^a	
HD-8-A	AF	2.0x10 ⁹	100	8.8x10 ⁶	0.4	1.2x10 ⁸	6	1.4x10 ⁸	7	1.7x10 ⁹	87	8.9x10 ⁷	--	94
-B	AF	1.6x10 ⁹	100	7.3x10 ⁶	0.5	1.0x10 ⁸	7	1.4x10 ⁸	9	1.4x10 ⁹	87	1.0x10 ⁸	--	97
-A	AU	5.1x10 ³	100	1.2x10 ³	23	760	15	1.3x10 ³	26	2.9x10 ³	57	305	--	106
-B	AU	1.4x10 ⁴	100	1.1x10 ³	8	1.6x10 ³	11	3.3x10 ³	24	7.2x10 ³	53	610	--	85
-A	AP	4.7x10 ⁸	100	4.4x10 ⁶	0.9	3.3x10 ⁷	7	7.5x10 ⁷	16	3.9x10 ⁸	83	1.4x10 ⁶	--	100
-B	AP	4.9x10 ⁸	100	4.0x10 ⁶	0.8	2.6x10 ⁷	5	8.4x10 ⁷	15	3.9x10 ⁸	79	2.6x10 ⁶	--	95
-A	BU	4.5x10 ³	100	635	14	---	--	2.4x10 ³	47	1.5x10 ³	33	23	--	94
-B	BU	4.9x10 ³	100	640	13	600	12	1.1x10 ³	22	3.1x10 ³	64	25	--	99
-A	BT	8.7x10 ³	100	677	8	3.4x10 ³	38	4.0x10 ³	45	3.8x10 ³	43	290	--	96
-B	BT	6.5x10 ³	100	1.0x10 ³	16	---	--	2.1x10 ³	32	3.2x10 ³	49	494	--	97
-A	CU	1.4x10 ⁴	100	480	3	8.7x10 ³	62	8.7x10 ³	62	2.5x10 ³	18	23	--	83
-B	CU	1.5x10 ⁴	100	620	4	8.7x10 ³	58	7.8x10 ³	52	3.2x10 ³	21	20	--	77

(a) Percentage of radioactive constituents is given as per cent of the gross gamma activity.

14.0 COLUMN DATA AND VOLUME CHANGES

14.1 Column Data

The pertinent data for the columns in run HD-8-A and -B are shown in Tables 14-1 through 14-4.

Table 14-1
Column Pulse Plate Data

Plate Data	A-column Extraction	B-column Partitioning	C-column Strip	T-column Solvent Recovery
Plate diameter, in.	5	5	5	6
Hole diameter, in. (a)	0.125	0.125	0.125	0.125
Open area, %	23	23	23	23
Plate spacing, in.	2	2	2	2
Supports for plates (b)	3	3	3	3
Number of plates in column	200	275	225	125

(a) Holes were drilled on an equilateral triangular pattern, 1/4 in. apart.

(b) Supports were spaced equilaterally 120° apart.

Table 14-2
Average Column Temperatures, °C.

Run No.	A-column	B-column	C-column	T-column
HD-8-A	33	32	31	47
HD-8-B	33	32	31	47

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Table 14-3
Column Dimensions and Capacities

Column	Type	Extraction Height, ft	Scrub Height, ft	Partitioning Height, ft	Stripping Height, ft	Throughput, gal/ft ² /hr	Flooding Rate, gal/ft ² /hr	% Flooding
A	Vertical	11.25	22	---	---	315	810	39
B	Concatenated ^(a)	---	18.3	19.5	11	614	1000	61
C	Concatenated ^(b)	---	---	---	36	359	790	45
T	Vertical, inverted	---	---	---	19.25	228	600	38

(a) Consists of three 5-in. diameter sections, 17.8 ft, 19 ft and 11 ft in effective length.

(b) Consists of two 5-in. diameter sections, 20.3 ft and 17.5 ft in length.

Table 14-4
Column Pulsing Data

Column	Type	Frequency, cycles/min, avg	Amplitude, in., avg	Pulser Leakage, ml/min, avg
A	Vertical	40	0.75	134
B	Concatenated	52	0.75	36
C	Concatenated	52	0.90	28
T	Vertical	53	0.75	46

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14.2 Column Volume Changes

The volume changes of the two phases in each column that occurred during the equilibrium portion of the run are given in Table 14-5. These values were obtained by dividing the flow rate of the stream under consideration (either organic or aqueous) by the volume of the plate-filled section (i. e., the effective length) of the column and multiplying the result by the duration of the run in hours.

These are calculated values and represent the minimum number of volume changes occurring during the run. In actual operation, the presence of two phases limits the volume available for either phase and serves to increase the actual number of changes per hour by approximately 20 per cent for the continuous phase and a few hundred per cent for the dispersed phase.

Table 14-5
Column Volume Changes

Column	Column Volume, liters	Run Duration, hr		No. of Volume Changes per Run			
				Run HD-8-A		Run HD-8-B	
				Continuous phase, aqueous	Dispersed phase, organic	Continuous phase, aqueous	Dispersed phase, organic
		HD-8-A	HD-8-B				
A-column	128	28.2	45.8	10.4	26.1	16.9	42.4
B-column	184	28.2	45.8	21.7	24.1	35.3	39.2
C-column	139	28.2	45.8	6.4	31.9	10.4	51.8
T-column	107	28.2	45.8	4.2 ^(a)	41.5 ^(a)	6.78 ^(a)	67.3 ^(a)

(a) T-column was operated organic continuous.

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15.0 CHEMICAL FLOWSHEET

15.1 Composite Volumes and Compositions

The volumes and compositions of various composite streams are given in Tables 15-1 and 2.

Table 15-1
Composite Volumes and Compositions of Entering Streams

Stream	Composition	Relative Volumes	
		AF = 100	
		HD-8	Flowsheet
AF	353 g/liter Th, 0.6 M Al, 0.08 N acid deficient	97 ^(a)	100
AS	0.48 M Al, 0.08 N acid deficient, 0.003 M PO_4^{-3} 0.006 M total Fe (0.005 M Fe^{+2})	99.8	100
AX	42.5% TBP in Special Naphtha No. 1	494	500
BX	Demineralized water	101	100
B'X	0.24 N HNO_3	490	480
BS	42.5% TBP in Special Naphtha No. 1	162	160
CX	0.008 N HNO_3	133	132
TX	0.2 M Na_2CO_3	65	66

(a) Cold AF rate was 99.9.

Table 15-2
Composite Volumes and Compositions of Exit Streams

Stream	Composition	Relative Volumes	
		AF = 100	
		HD-8	Flowsheet
AP	0.63 M Al, 0.13 N acid deficient	182	180
BT	52.8 g/liter Th, 0.2 N HNO_3	668 ^(a)	600
CU	0.12 g/liter U, 0.02 N HNO_3	133	132
CW	42.5% TBP in Special Naphtha No. 1	656	660
TWA	0.14 M Na_2CO_3	129 ^(b)	94

(a) Calculated from the thorium concentration at equilibrium.

(b) Includes the centrifuge purge and the T-column interface controller instrument purge streams as well as the TX stream.

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15.2 Flowing Stream Compositions

The compositions of various flowing streams are given in Table 15-3.

Table 15-3
Flowing Stream Compositions

Stream	Thorium, g/liter		U-233 Activity, α cts/min/ml	γ Activity, cts/min/ml	Pa γ Activity, cts/min/ml
	HD-8	Flowsheet			
AF	352	350	2.5×10^6	1.7×10^9	1.5×10^9
AU	66.9	67.3	3.9×10^5	4.7×10^4	4.2×10^3
AP	0.24	0.01	918	4.4×10^8	---
BU	0.03	< 0.01	3.9×10^5 (a)	2.8×10^4	2.5×10^3
BT	52.8	58.3	1.6×10^3	1.6×10^4	4.0×10^3
CU	< 0.001	< 0.01	1.1×10^6 (a)	9.5×10^4	6.8×10^3
CW	0.05	< 0.01	554	1.0×10^4	---
TWO	----	< 0.01	< 50 (a)	1.7×10^3	---
TWA	< 0.001	< 0.01	1.5×10^3	2.4×10^5	---
RS	< 0.001	< 0.01	55 (a)	4.77	---
IWU	< 0.001	< 0.01	649	3.2×10^4	---

(a) Gross α .

16.0 APPENDIX

16.1 Equipment and Sampling Flowsheet

Figs. 16-1 through 16-7 show the Thorex equipment flowsheet and the sampling points.

16.2 ORNL Thorex Process Chemical Flowsheet

Shown in Fig. 16-8 is the ORNL Thorex Process Chemical Flowsheet, No. 1.2-7.

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Fig. 16-2
THOREX PROCESS
EXTRACTION SYSTEM

No.	Service
M-5	CP Acid Storage
M-6	B'X Makeup Tank
M-7	B'X Head Tank
M-8	BX, CX Makeup Tank
M-35	BX Head Tank
P-1-A	B Column
P-1-B	
P-1-C	
P-9	Pressure Pot
P-12	BS Head Pot
P-13	Sample Pot
T-5	Rec. Solv. Catch Tank

—LEGEND—	
●	Flowing Stream Sample
■	Composite Sample
—	Th
—	U, or U& Th

Fig. 16-3
THOREX PROCESS
PARTITIONING SYSTEM

No	Service
T-4	CW Catch Tank
M-8	BX, CX Make-Up Tank
M-9	CX Head Tank
N-8	Rework Catch Tank
N-16	Aqueous Waste Catch Tank
R-1-A	C Column
R-1-B	
R-2	CU Catch Tank
R-3	CU Head Tank
R-4	Sample Pot
R-5	Silica Gel Column
R-6	Head Pot
R-7	Pressure Pot
R-8	Phase Separator
R-10	Head Pot
R-11	BU Stand Pipe
R-13	Separator

—LEGEND—

- Flowing Stream Sample
- Composite Sample
- Th—
- U, or U&Th—

Fig. 16-4
THOREX PROCESS
STRIPPING SYSTEM

No	Service
P-2	Vapor Scrubber
P-3	Concentrated Thorium Catch Tank
P-4	
P-5	B.T. Stripper & Surge
P-6	B.T. Condensate Catch
P-7	B.T. Evaporator Heater
P-8	Evaporator Condenser
P-10	Phase Separate
P-15	Evaporator Loop
P-16	Concentrated Thorium Decay Tanks
P-17	
P-18	
P-19	Drum Loading Head Tank

— LEGEND —	
●	Flowing Stream Sample
■	Composite Sample
— Th —	Th

Fig. 16-5
THOREX PROCESS
THORIUM RECOVERY SYSTEM

No	Service
M-13	AX Make-Up Tank
M-14	BX Make-Up Tank
M-15	Solvent
M-25	TX Make-Up Tank
T-1	T Column
T-2	Preheater
T-3	Centrifuge
T-4	CW Catch Tank
T-5	Recovered Solv. Catch
T-6	Pressure Pot
T-7	Sample Pot
T-9	Flow Checker
T-10	TWC Catch Tank
T-11	Sample Pot

—LEGEND—

- Flowing Stream Sample
- Composite Sample

Fig. 16-7
THOREX PROCESS
SOLVENT RECOVERY SYSTEM

SOLVENT TREATMENT AND RECOVERY

Oleum-
Pretreated
Special
Naphtha #1

TBP

Solvent
Wash
Sol'n
TX

42% TBP

Wash
Column

BS/AX ← Centrifuge

Rev 5-27-55

FLOW RATIOS
 AF' AX' AS=1 5 1
 AU BS BX=3 25 1 3 625
 BU CX=5 1

BASIS.
 200 kg of Thorium per
 day 150 days irradiation
 10^{13} n/cm²/sec, 82.5 days
 Cooling Time

--- Organic Stream
 — Aqueous Stream
 ○ Flow Rate (liters/day)

U STRIPPING

C-Column
Strip
CX

760

C-Column
Uranium Stripping

CU

760

URANIUM ISOLATION

Silica Gel

Eluant

25 liters
every 35 days

IX

Resin Columns

20 liters
every 9 days

To AF

15 liters eluate
every 9 days;
Recycle to AF

760

IW Waste

U²³³ PRODUCT
5 liters every 9 days

Th AND U PARTITION

B-Column
Strip
BX
3 Stages
Down

B-Column
Strip
BX

576

2760

B-Column
Th-U Partition

BT

3449

Th AND U EXTR'N

A-Column
Scrub
AS

576

A-Column
Th and U Ext'n

2988

AU

BS

920

AP

1036

THORIUM ISOLATION

To Waste

BT
Evaporator

432

THORIUM PRODUCT
STORAGE

FEED PREPARATION

Stack
Condenser
(Off-Gas)

Dissolvent
Thorium Slugs
120/Day
100% Excess Acid
1237 liters/Batch
CDF

Batch Dissolver

MD
Feed Adjustment
Tank

Stack

Condenser
Distillation
or Reflux

Recovered
HNO₃

AF

AX

42% TBP

Condensate
Catch Tank

To Waste

Fig 16-8. THOREX PROCESS CHEMICAL FLOW SHEET... MAY 1955