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LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT, JULY 1, 1954 TO NOVEMBER 30, 1955

R. P. Wischow
R. G. Mansfield

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT, July 1, 1954 to November 30, 1955

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CONTENTS

		Page
1.0	ABSTRACT	1
2.0	INTRODUCTION	1
3.0	FLOWSHEET CHANGES	4
	3.1 Feed and Scrub Acidities in First Cycle	4
	3.2 Second Thorium Cycle	4
4.0	DISSOLUTION OF BONDED SLUGS	12
	4.1 Dissolution Studies	13
	4.2 Metallographic Studies	13
5.0	FEED PREPARATION AND ADJUSTMENT STUDIES	19
	5.1 Effect of Final Temperature on Acidity	19
	5.2 Specific Gravity of Thorex Feed	19
	5.3 Effect of Aging of Feed on Ruthenium A-Column Decontamination	21
	5.4 Corrosion in Thorex Feed System	24
6.0	FIRST-CYCLE CHEMICAL STUDIES	26
	6.1 Mercury and Fluoride Distribution in Thorex A- and B-Columns	26
	6.2 Effect of Strip Acidity on Uranium Refluxing	26
	6.3 Effect of AU Holdup on U-Th Separation Factor	28
	6.4 First-Cycle Thorium Product Plutonium Decontamination	28
	6.5 Fission Product Decontamination of First-Cycle Thorium Product	29
7.0	RADIATION DAMAGE TO SOLVENT	31
	7.1 Radiation Damage to Extractant	33
	7.2 Predicted Solvent Exposure due to Pa^{233} Activity	38
	7.3 Experimental Technics	39
8.0	APPENDIX	42
	8.1 Thorium Dioxide Studies	42
	8.2 Preliminary Values of U^{233} and Thorium Backgrounds in Thorex Samples	43
	8.3 Preparation of Acid-Deficient Aluminum Nitrate	54

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ORNL-1367, "Progress Report: Laboratory Development of the Thorex Process," by A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, and J. E. Savolainen (Dec. 17, 1952).

ORNL-1431, "Laboratory Development of the Thorex Process: Progress Report, September 30, 1952," by A. T. Gresky, M. R. Bennett, S. S. Brandt, K. L. Mattern, W. T. McDuffee, J. E. Savolainen, and R. P. Wischow (March 16, 1953).

ORNL-1518, "Laboratory Development of the Thorex Process: Progress Report, October 1, 1952 to January 31, 1953," by A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, B. G. Ryle, J. E. Savolainen, and R. P. Wischow (July 14, 1953).

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ORNL-1757, "Laboratory Development of the Thorex Process: Progress Report, August 1, 1953 to June 30, 1954," by A. T. Gresky, R. P. Wischow, M. R. Bennett, and J. E. Savolainen (Jan. 27, 1955).

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1.0 ABSTRACT

Changes made in the Thorex process flowsheet were a decrease in the extraction column acidity to decrease thorium losses and the addition of a second thorium solvent-extraction cycle to provide the increased decontamination required when thorium irradiated to 2000-4000 g of U^{233} per ton is processed. Bonded slugs could not be dissolved by the Thorex flowsheet procedure. Various laboratory-scale studies on feed preparation, first-cycle variables, and radiation damage to the solvent are reported.

2.0 INTRODUCTION

The Thorex process one-cycle flowsheet has operated satisfactorily in the Pilot Plant. Further laboratory studies were made to develop means of obtaining additional decontamination, which will be required when material irradiated to 2000-4000 g of U^{233} per ton is processed. The dissolution procedure, which was designed for unbonded aluminum-jacketed slugs, was tested with aluminum-silicon--bonded slugs. Minor laboratory development studies on various phases of the process were continued.

The control analyses for the studies were made by G. R. Wilson's group, the radiochemical analyses by E. I. Wyatt's group, and the special analyses for very low reducing normalities in the radiation damage studies by P. F. Thomason's group of the Analytical Chemistry Division.

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Table 3.1. Thorex Process Flowsheet Details

Stream	Composition
Dissolvent	13 M HNO_3; 0.04 M HF; 0.0025 M Hg^{++}; 0.04 M Al
MD	~1 M Th; 0.4 M Al; 6-6.5 M HNO_3; ~0.93 g U per liter
AF	1.5 ± 0.05 M Th; 0.6 M Al; 0.1 M HNO_3 to 0.15 M acid deficient; ~1.39 g U per liter
AS	0.50 ± 0.02 M Al; 0.15 ± 0.05 M acid deficient; 0.003 ± 0.001 M PO_4^{3-}; 0.005 M $FeSO_4$
AX and BS	42.5 ± 1.0 vol % TBP; 57.5 ± 1.0 vol % Special Naphtha No. 1[a]
AU	42.5 ± 1.0 vol % TBP; 57.5 ± 1.0 vol % Special Naphtha No. 1;[a] 67 g Th per liter; 0.27 g U per liter
AP	0.55 M Al; 0.1-0.2 M acid deficient; ~0.1-0.2 g Th per liter
BX	Demineralized water
CX	0.008 M HNO_3
B'X	0.24 M HNO_3
BU	42.5 ± 1.0 vol % TBP; 57.5 ± 1.0 vol % Special Naphtha No. 1;[a] 0.21 g U per liter; 0.002 M HNO_3; ≤0.010 g Th per liter
BT	0.25 M Th; 0.20 M HNO_3
CU	~1.03 g U per liter; ~0.015 M HNO_3
CW	42.5 ± 1.0 vol % TBP; 57.5 ± 1.0 vol % Special Naphtha No. 1[a]
IX	3.0 M ammonium acetate; 1.5 M acetic acid; 0.75 M ammonium citrate; pH 5.1 at 70°C
SRX	0.2 M Na_2CO_3
DF	1.5 M Th; 1.1-1.2 M HNO_3; ~0.001 g U^{233} per liter
DS	1 M Al; 1.2 M acid deficient; 0.002 M PO_4^{3-}
DX	42.5 vol % TBP; 57.5 vol % Special Naphtha No. 1[a]
DW	0.55 M Al; 0.0-0.1 M acid deficient; <0.1 g Th per liter
DP	42.5 vol % TBP; 57.5 vol % Special Naphtha No. 1;[a] 68 g Th per liter; $\leq 10^{-4}$ g U^{233} per liter; 0.0 M HNO_3
EX	0.008 M HNO_3
ET	0.01 M HNO_3; 96 g Th per liter; $\sim 10^{-5}$ g U^{233} per liter
ETC	2.0 M Th; 0.04 M HNO_3
EW	42.5 vol % TBP; 57.5 vol % Special Naphtha No. 1;[a] ~0.5 g Th per liter; $\leq 10^{-4}$ g U^{233} per liter

Flow ratios:

AF/AS/AX = 1/1/5
AU/BX/B'X/BS = 5.2/1.0/4.8/1.6
BU/CX = 6.6/1.32
CW/SRX = 6.6/1.32

[a]An oleum-pretreated aliphatic hydrocarbon diluent similar in chemical and physical properties to Amsco 125-82.

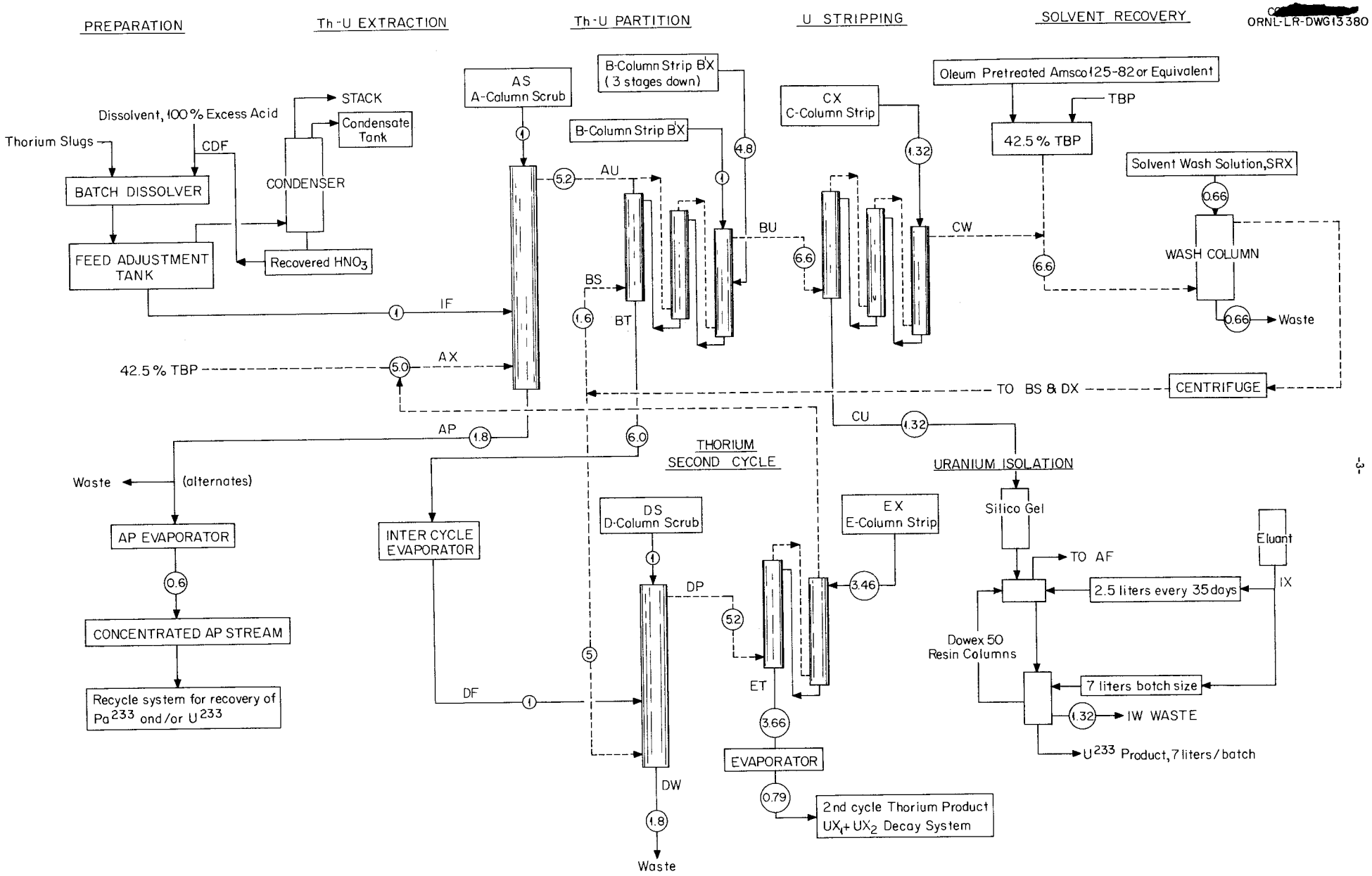

Fig. 3.1. Thorex Process Flowsheet Nov. 30, 1955. Basis 4000 g U^{233} per ton of thorium (3×10^{13} n/cm^2/sec flux, 180 days decay)

3.0 FLOWSHEET CHANGES

In the present Thorex flowsheet the acidity during the first-cycle extraction (Fig. 3.1 and Table 3.1) is lower than in the flowsheet published in the last progress report.* Laboratory studies indicated that this would decrease thorium losses in the extraction step. The new flowsheet also includes a second thorium cycle, which provides the additional decontamination needed when thorium irradiated to 2000-4000 g of U^{233} per ton is processed.

3.1 Feed and Scrub Acidities in First Cycle

Acid-deficient conditions appear necessary in the extraction column for satisfactory product decontamination.** Thorium losses are low under these conditions, being a minimum when the feed and scrub net acidity (i.e., the acidity of the aqueous effluent) is near neutrality (Table 3.2). Process thorium losses of about 0.1% can be realistically predicted if the feed acidity is kept in the range 0.1 M HNO_3 to 0.15 M acid deficiency and the scrub in the range 0.15 ± 0.05 M acid deficiency. With these limits, the net extraction section acidity cannot vary more than from neutrality to 0.02 M acid deficiency.

3.2 Second Thorium Cycle

The second thorium cycle (Fig. 3.1) for additional decontamination of the thorium product is a two-column system—the D-column for extraction and the E-column for stripping. The feed to the D-column is the concentrated thorium product of the first cycle. The E-column

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* ORNL-1757, Fig. 2.1.
** ORNL-1367, p. 64.

has no scrubbing section. Additional uranium stripping and solvent recovery facilities are avoided by recycling the organic stream from the E-column to the A-column as extractant. The D-column has been tested in the Thorex Pilot Plant, and the E-column has been evaluated in the laboratory. In preliminary tests decontamination factors appeared sufficient (Table 3.3).

Table 3.2. Effect of Acidity on Thorium Losses in First Extraction Column

Flowsheet conditions as shown in Fig. 3.1 except that feed and scrub acidities were varied; batch countercurrent experiments
Three volume changes for each set of conditions

HNO_3[a] (M)			Thorium Loss (%)
Feed	Scrub	Aqueous Effluent	
0.04	-0.04	-0.02	0.02
0.01	-0.20	-0.07	0.06
-0.09	-0.23	-0.18	0.11
-0.14	-0.36	-0.21	0.18
-0.30	-0.45	-0.37	0.56
-0.40	-0.10	-0.20	0.63

[a]Negative acidity signifies acid-deficient conditions.

Feed Preparation. The feed-preparation equipment for the second cycle is essentially the present first-cycle thorium product evaporators. The feed concentration is such that the feed/scrub/extractant flow ratios are the same as in the first cycle, i.e., 1/1/5.

Table 3.3. Decontamination Factors Obtained with Diban and Neutral Aluminum Nitrate Scrub Flowsheets

Flowsheets as shown in Fig. 3.2 and 3.3; batch countercurrent experiments; 5 volume changes

Contaminant	Decontamination Factor	
	With Diban Scrub	With Neutral $Al(NO_3)_3$ Scrub
Gross γ	123	30
Ru γ	17	2
Pa γ	128	50
Zr-Nb γ	210	186
Total rare earth β	2100	13,000

Extraction-Scrubbing (D-column). The extraction-scrubbing system is salted with aluminum nitrate. In one flowsheet (Fig. 3.2), diban (dibasic aluminum nitrate) is used as the scrub solution, and in an alternate (Fig. 3.3), neutral aluminum nitrate is used. The Thorex Pilot Plant has partially demonstrated the diban scrub flowsheet. The neutral aluminum nitrate scrub flowsheet has been evaluated only in the laboratory. In each flowsheet, 3 to 5 extraction stages are required as well as about 8 scrub stages. Losses of thorium to the waste are less than 0.1% with 5 extraction stages.

The main objection to the diban-scrub flowsheet is the higher thorium reflux which results from the high acid deficiency in the scrubbing section required to neutralize the acid contained in the feed. The ruthenium decontamination is about a factor of 10 higher than with the neutral aluminum nitrate—scrub flowsheet.

Stripping (E-Column). Three to 5 stages are required in the stripping column. The separation of thorium and uranium in the E-column can

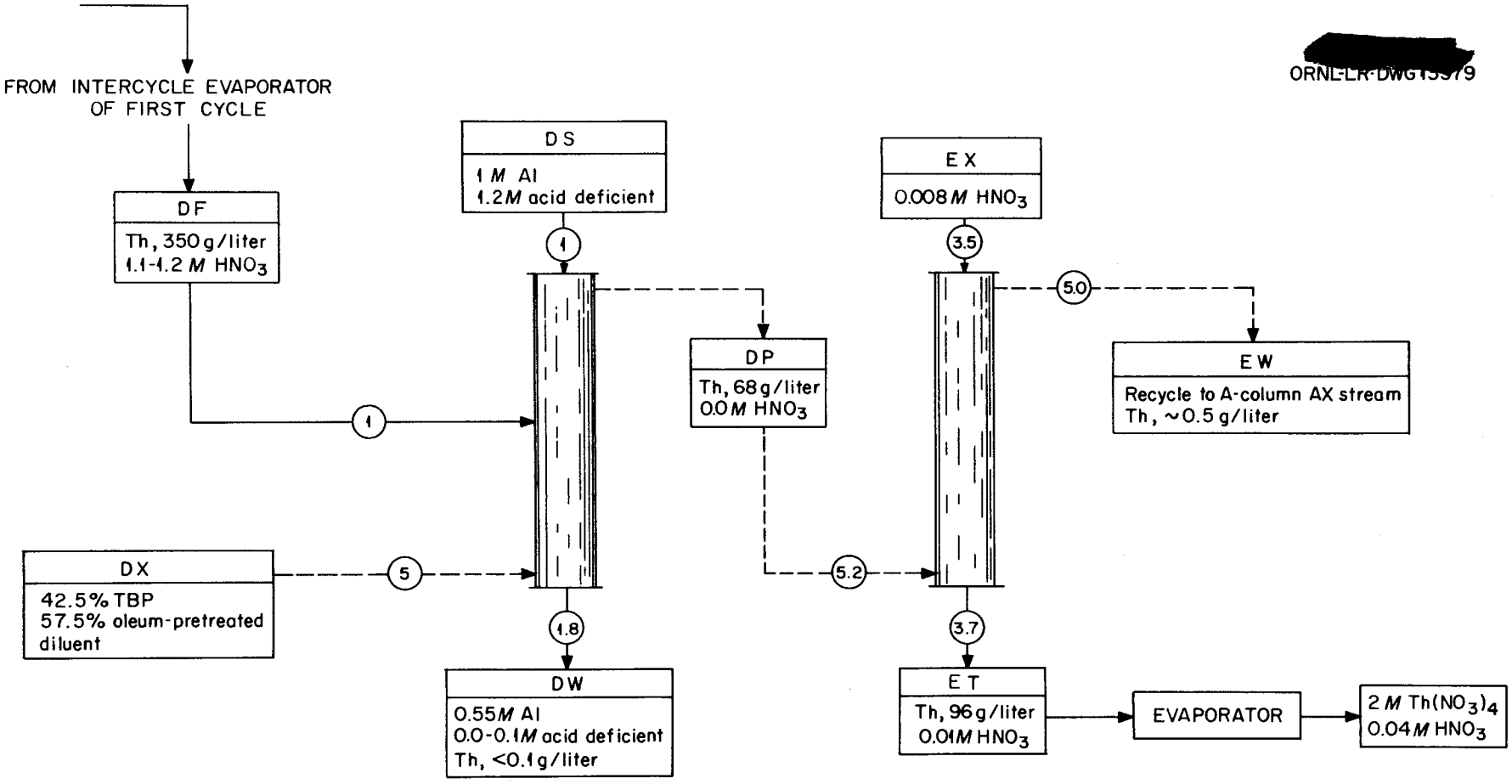

Fig. 3.2. Thorex Second Thorium Cycle Flowsheet, Dibasic Aluminum Nitrate Scrub. Circled numbers denote stream volume ratios based on a feed rate of one. Broken lines signify organic streams.

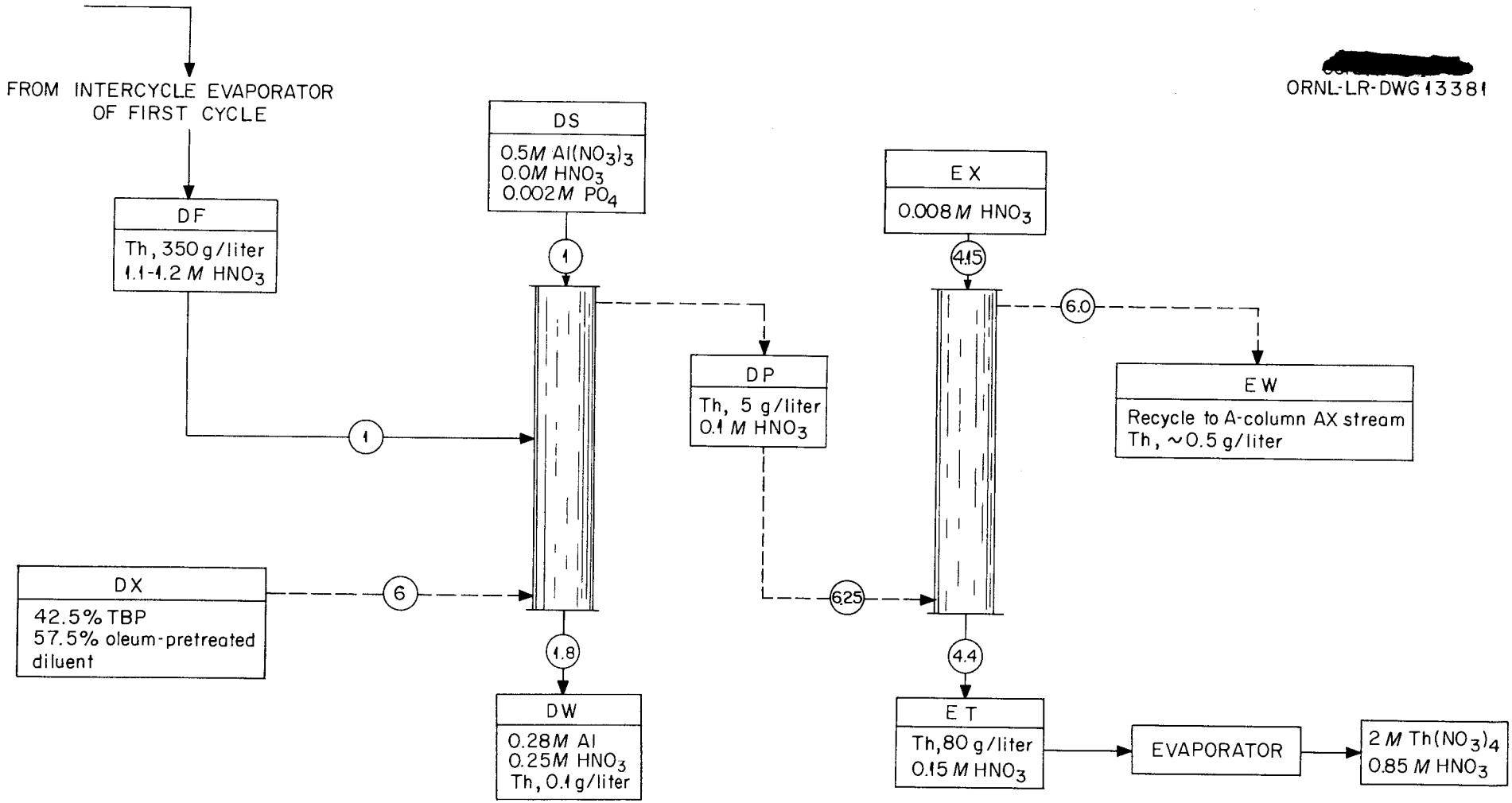

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Fig. 3.3. Thorex Second Thorium Cycle Flowsheet, Neutral Aluminum Nitrate Scrub. Circled numbers denote stream volume ratios based on feed rate of 1.0. Broken lines signify organic streams.

be optimized by proper choice of flow ratios. This permits considerable flexibility in the choice of column length. With 0.008 M HNO_3 as the stripping agent, the organic/aqueous flow ratios should be no greater than 1.5/1.0 for satisfactory stripping (Table 3.4). The thorium and uranium concentrations in the product can be controlled by varying the acidity of the strip solution (Table 3.5).

About 2% of the uranium entering the E-column will be stripped with the thorium; e.g., if the first-cycle uranium loss to the thorium product stream is 0.2%, the second-cycle loss to the thorium product stream would be 0.004% of the total processed. Concentration of the second-cycle thorium product for shipping and/or storage would be simpler than that of the first cycle because of the higher thorium concentration, i.e., about 100 g/liter as compared to approximately 60 g/liter in the first-cycle product.

Disposition of Used Solvent (EW). The EW stream is routed to the first cycle as the AX stream so that there is no need for a second-cycle uranium stripping column or solvent recovery system. Both thorium and uranium losses to the first-cycle aqueous effluent were low when recycled solvent was used as extractant (Table 3.6). It should be mentioned that if the EW thorium concentration is greater than about 2 g/liter, there is a possibility of saturating the organic phase with thorium in the first-cycle extraction column, which might result in a loss of thorium.

Waste. The diban-scrub flowsheet provides an acid-deficient waste which could be concentrated and stored in stainless steel tanks or tar pits. Waste from the neutral aluminum nitrate scrub flowsheet would require caustic neutralization prior to storage. The waste volume from either flowsheet would be 1040 liters/day for a plant with a capacity of 200 kg of thorium per day.

Table 3.4. Effect of Flow Ratio on Organic/Aqueous Distribution Coefficient

Batch countercurrent experiments
Solvent: 42% TBP, 58% Special Naphtha No. 1; Th, 71.6 g/liter; U^{233}, 2.07×10^4 α c/m/ml
Strip: 0.008 M HNO_3

Stage	Organic		Aqueous		D.C., O/A	
	Th (mg/ml)	U^{233} (α c/m/ml)	Th (mg/ml)	U^{233} (α c/m/ml)	Thorium	U^{233}
Organic/aqueous = 1.0/1.0						
5	<0.01	44	0.112	2.5×10^3	<0.09	0.018
3	0.56	3.44×10^4	14.5	2.35×10^4	0.039	1.46
1	37.5	1.51×10^4	65.0	1.28×10^3	0.58	11.8
Organic/aqueous = 1.5/1.0						
5	0.52	9.54×10^3	9.32	1.21×10^4	0.06	0.79
4	6.67	2.06×10^4	31.4	4.24×10^3	0.21	4.9
3	25.6	1.37×10^4	54.8	1.16×10^3	0.47	11.8
2	---	---	73.0	660	---	---
1	56.6	1.63×10^4	95.25	620	0.59	26.4
Organic/aqueous = 2.0/1.0						
5	13.0	9.33×10^3	36.8	980	0.36	9.5
4	33.9	1.38×10^4	60.8	580	0.56	24.0
3	46.0	1.40×10^4	80.9	700	0.57	20.0
2	54.3	1.63×10^4	94.0	620	0.58	26.4
1	63.4	1.55×10^4	109.0	640	0.58	24.4

Table 3.5. Effect of Strip Acidity on Organic Phase Thorium and U^{233} Concentrations

Batch countercurrent experiments
Solvent: 42.5% TBP, 57.5% Special Naphtha No. 1; Th, 71.6 g/liter; U^{233}, 2.07×10^4 α c/m/ml
Organic/aqueous = 1/1; 4 volume changes

Strip HNO_3 (M)	7th Stage (Organic)		5th Stage (Organic)		3rd Stage (Organic)	
	Th (mg/ml)	U^{233} (α c/m/ml)	Th (mg/ml)	U^{233} (α c/m/ml)	Th (mg/ml)	U^{233} (α c/m/ml)
0	0.004	5	0.004	5	0.70	3.1×10^4
0.009	0.01	5	0.01	44	0.56	3.4×10^4
0.10	0.014	1.2×10^3	0.10	9.7×10^3	2.8	2.4×10^4
0.20	0.052	8.8×10^3	0.22	1.2×10^4	8.5	1.1×10^4
0.24	0.054	5.7×10^3	0.33	1.1×10^4	9.8	1.0×10^4

Table 3.6. Utilization of EW by Recycling as AX

Batch equilibrations simulating bottom extraction stage of A-column
Organic/aqueous = 2.5/1.0; 1-min equilibration

EW Composition		First Cycle, 5th Extraction Stage					
		Organic		Aqueous		Loss[a] (%)	
Th (mg/ml)	U^{233} (α c/m/ml)	Th (mg/ml)	U^{233} (α c/m/ml)	Th (mg/ml)	U^{233} (α c/m/ml)	Thorium	U^{233}
0.52	9.5×10^3	0.49	9.5×10^3	0.09	200	7	0.84
0.56	3.4×10^4	0.74	3.4×10^4	0.18	360	12	0.42
2.75	2.3×10^4	3.8	2.2×10^4	0.08	220	1.1	0.38

[a]Based on EW thorium and/or uranium concentration.

Decontamination. Decontamination is obtained only across the D-column in either flowsheet. Separation of thorium from protactinium and all fission products with the exception of ruthenium was satisfactory for both flowsheets (Table 3.3). Efforts to obtain a ruthenium decontamination factor greater than 2 have met with little success for the neutral aluminum nitrate scrub flowsheet. The diban scrub flowsheet has consistently given a ruthenium decontamination factor of about 20.

An average process feed in these studies had the following composition: 350 g of thorium per liter; 1.3 M HNO_3; gross γ, 2×10^6 c/m/ml; Ru γ, 3×10^5 c/m/ml; Zr-Nb γ, 8×10^5 c/m/ml; TRE β, 3×10^7 c/m/ml; and Pa γ, 10^6 c/m/ml. Because of the low activity levels used, the reported decontamination factors may be low.

4.0 DISSOLUTION OF BONDED SLUGS

During the process of bonding the aluminum jacket to thorium slugs with aluminum-silicon alloy, an intermetallic layer of thorium silicide forms. This layer is very resistant to both acid and alkali attack, and single-dipped slugs that had already been dejacketed could not be dissolved in the mercury-catalyzed nitric acid used for unbonded slugs. Double-dipped slugs, which contain less of this layer because of a tin precoating used on the thorium before the bonding step, were dejacketed with caustic and then dissolved. However, a residue of aluminum-silicon and thorium silicide was left in the dissolver. This material must be separated from the dissolver solution before the solution is fed to the extraction columns. This would involve handling radioactive solids, and thorium and U^{233} would be lost in the separated material unless it was reprocessed. In addition, separate jacket

removal increases the cost of the process somewhat since the aluminum thus removed cannot be used as a salting agent in the extraction column, as it is when slug and jacket are dissolved together in acid.

4.1 Dissolution Studies

In laboratory studies the thorium silicide intermetallic layer of single-dipped bonded slugs was not dissolved by a 27-hr reflux in 13 M HNO_3 containing 0.01 M Hg^{++}, which is four times the amount of catalyst used in a nonbonded slug dissolution. It was not completely disintegrated in a caustic dejacketing step with hot 10% NaOH—20% $NaNO_3$ after refluxing for 24 hr, even when fresh caustic was charged to the dissolver. The intermetallic layer was so passive that the thorium metal in the centers of these dejacketed slugs, which had been sliced for convenience in handling, dissolved when submerged in fluoride-catalyzed nitric acid before the surface layer was significantly penetrated (Fig. 4.1).

Double-dipped slugs readily dissolved in fluoride-catalyzed nitric acid following caustic jacket removal. Here the dissolvent was able to penetrate the intermetallic layer, which is less thick than in the single-dipped slugs. The intermetallic compound was not attacked, and a residue of aluminum-silicon and thorium silicide was left in the dissolver.

4.2 Metallographic Studies*

The jacket of a longitudinal section of an aluminum-silicon—bonded, aluminum-jacketed slug was easily separated from the slug, with a smooth, bright finish on both surfaces (Fig. 4.2). This indicated little or no metallurgical bond between the jacket and the thorium. Metallographic examination confirmed the absence of a good bond. A transverse section showed a continuous fracture in one or the other of two intermetallic

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* Examinations were made by R. G. Gray of the Metallurgy Division, ORNL.

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Fig. 4.1. Aluminum-Silicon—Bonded Aluminum-Jacketed Thorium Slug That Has Been Partially Dissolved in $HNO_3 - HF - Hg^{++}$ Following Dejacketing in NaOH.

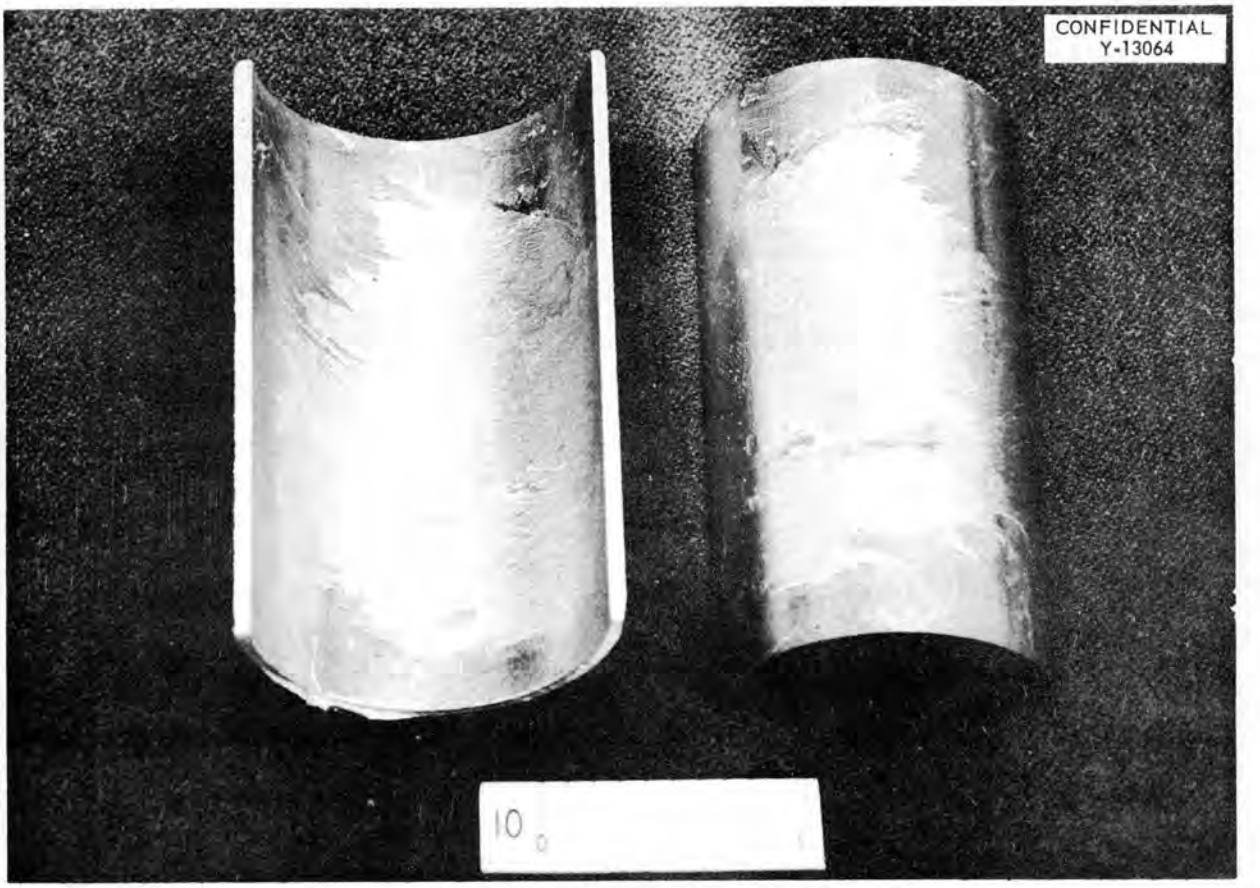

Fig. 4.2. Longitudinal Section of Aluminum-Silicon—Bonded (Single-dipped) Aluminum-Canned Thorium Slug, Showing Jacket Removed. The shiny surface of both jacket and slug are evidence of the poor bonding.

compound layers between the slug and the aluminum-silicon bonding alloy (Fig. 4.3). Such a fracture could have considerable effect on the thorium-to-aluminum heat-transfer properties. A transverse section (Fig. 4.4) of a slug that had been partially dissolved by refluxing in 13 M HNO_3—0.03 M NaF—0.0025 M $Hg(NO_3)_2$ showed a wide variation in the amount of dissolution. After the can had been partially dissolved, the slug was very resistant to further attack.

The intermetallic compounds developed on the thorium side of the aluminum-silicon alloy as a result of diffusion of silicon into the thorium. This grade of thorium has dark globular ThO_2 inclusions dispersed throughout the microstructure, and the same inclusions are present in a similar pattern within the compound layers. It was therefore assumed that the chief diffusion was into the thorium. Although the original aluminum-silicon alloy might have been of eutectic composition, there apparently was sufficient dilution by the aluminum can to make the alloy richer in aluminum and to result in some primary aluminum being present in the microstructure. The loss of silicon in the formation of $ThSi_2$ aided in making the aluminum-silicon alloy aluminum-rich; this silicon depletion is usual in ordinary bonding technics. Spectrophotometric analysis of the aluminum can showed it to be 2S grade aluminum.

The thickness of the intermetallic compound can be considered as the depth of aluminum-silicon diffusion into the thorium (Table 4.1); however, this is only approximate since there is probably a volume change in the formation of the compounds. There was considerable variation in the thickness of the aluminum-silicon alloy. This was undoubtedly due to the slug being out of center in the can when the aluminum-silicon alloy solidified, and has often been noted in slugs made by this process.

The outer surface of the aluminum-silicon—bonded slug was ground

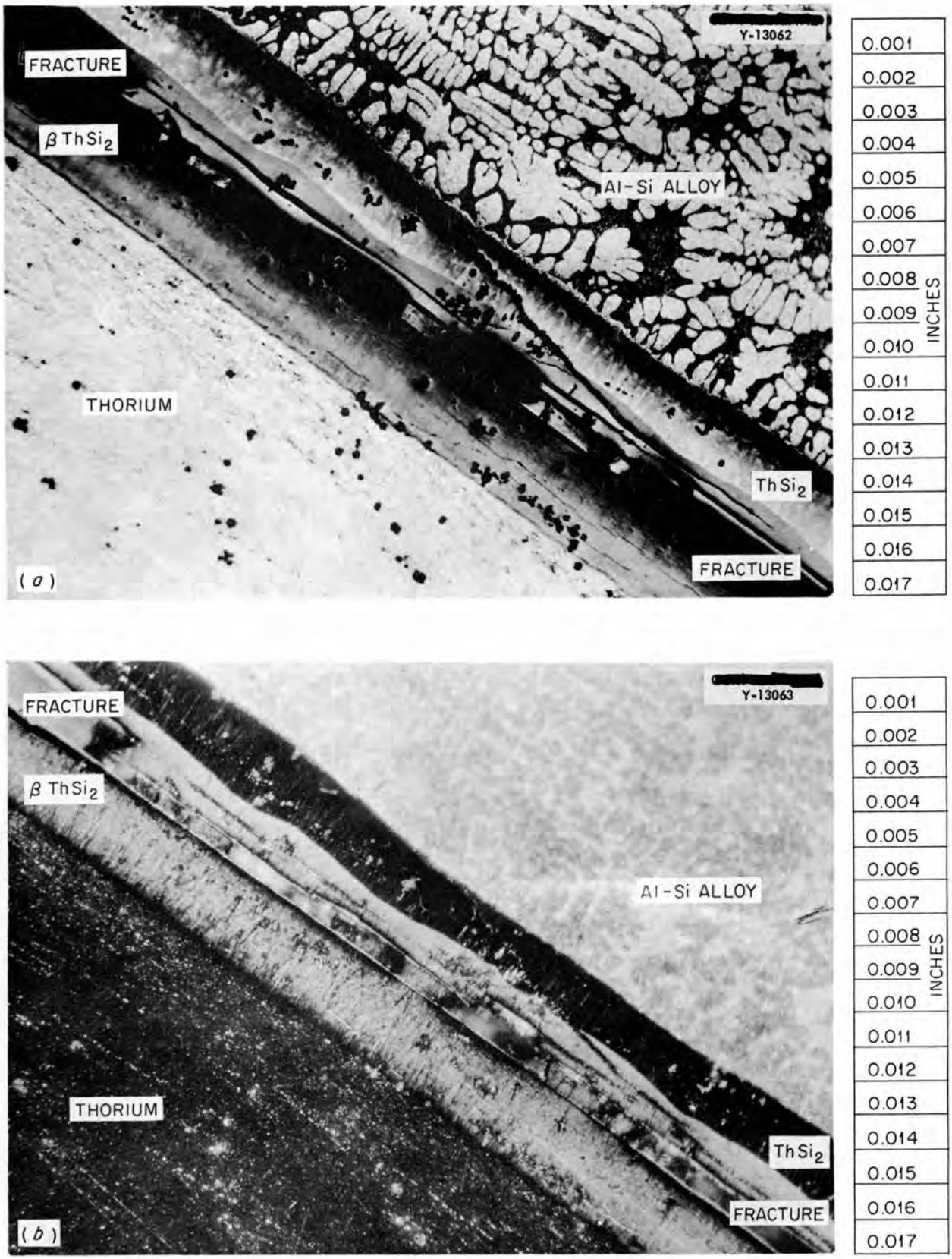

Fig. 4.3. Photomicrograph of Bond between Thorium and Aluminum-Silicon Alloy (Single-Dipped Slug). Transverse section Note continuous fracture in intermetallic compound layer. (*a*) bright field; (*b*) polarized light.

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Fig. 4.4. Aluminum-Canned (Single-dipped) Thorium Slug Partially Dissolved in 13 *N* HNO_3 – 0.03 *M* NaF – 0.0025 *M* $Hg(NO_3)_2$ at Approximately 100°C. Surface 1 still has β $ThSi_2$ on the thorium surface. Surface 2 shows partially dissolved aluminum-silicon alloy with some $ThSi_2$ on inner surface. Surface 3 shows some aluminum can and primarily aluminum-silicon alloy.

at a slight angle to increase the examination thickness of the intermetallic compounds, and the compound layers were analyzed by microspectrographic methods. The layer near the thorium was found to be primarily thorium and silicon, with a small amount of aluminum. X-ray analysis of scrapings from the compound adhering to the thorium slug were identified* as hexagonal crystals of β-$ThSi_2$; there were some unknown lines in the spectrum. Scrapings from the inner surfaces of the aluminum can and from the aluminum side of the continuous fracture were identified as the body-centered tetragonal $ThSi_2$. It was undoubtedly this $ThSi_2$ that retarded dissolution of the slug, since it is quite resistant to nitric acid.

The slugs were 1-7/16 in. in diameter and had been canned by the single-dip aluminum-silicon bonding technic. The longitudinal section was made at the end of the heliarc-welded cap, and the transverse sections were made at the centers of the slugs.

Table 4.1. Penetration of Aluminum and Silicon into Thorium Slugs

Measurements made in five different fields of a transverse section from the center of a canned slug

Thickness (in.)		
Intermetallic Compounds	Al-Si Alloy	Aluminum Can
0.006	0.005	0.039
0.007	0.022	0.034
0.005	0.030	0.032
0.006	0.024	0.034
0.005	0.016	0.034

* This compound is not found in the literature; conclusions were based on similarity to known lattice parameter measurements of uranium disilicide.

5.0 FEED PREPARATION AND ADJUSTMENT STUDIES

The dissolver solution is transferred to a feed adjustment tank, where nitric acid is removed by distillation. The solution is batch-concentrated until the liquid-phase temperature reaches 155°C, and the concentrate is refluxed at this temperature for 1 hr and subsequently diluted to feed conditions with water. This treatment increases the ruthenium decontamination factor 10-fold. In addition, the blue thoria present in irradiated thorium metal slugs is dissolved, interfacial precipitates and emulsion-forming impurities are dehydrated and partially eliminated, and the nitric acid is removed to produce an acid-deficient feed. The acid-deficient feed permits greater variation in column conditions without upsetting the extraction column.

5.1 Effect of Final Temperature on Acidity

For operational simplicity, it was desirable to relate the feed acidity after the adjustment cycle to the final temperature attained in the feed adjustment step. The acidity of the feed decreased curvilinearly as the final feed-adjustment liquid temperature increased (Fig. 5.1).

5.2 Specific Gravity of Thorex Feed

The specific gravity of acidic Thorex feed solution was reported* to be related to the major components of the feed by the formula

$$\text{Sp. gr. } (20^{\circ}\text{C}) = 0.373 \times \underline{M}\ \text{Th} + 0.126 \times \underline{M}\ \text{Al} + 0.0195 \times \underline{M}\ HNO_3 + 1.031.$$

Re-evaluation of the formula indicated it to be valid for the acid-deficient feeds if acid deficiency is assumed to be a negative acidity

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* ORNL-1367, p. 37.

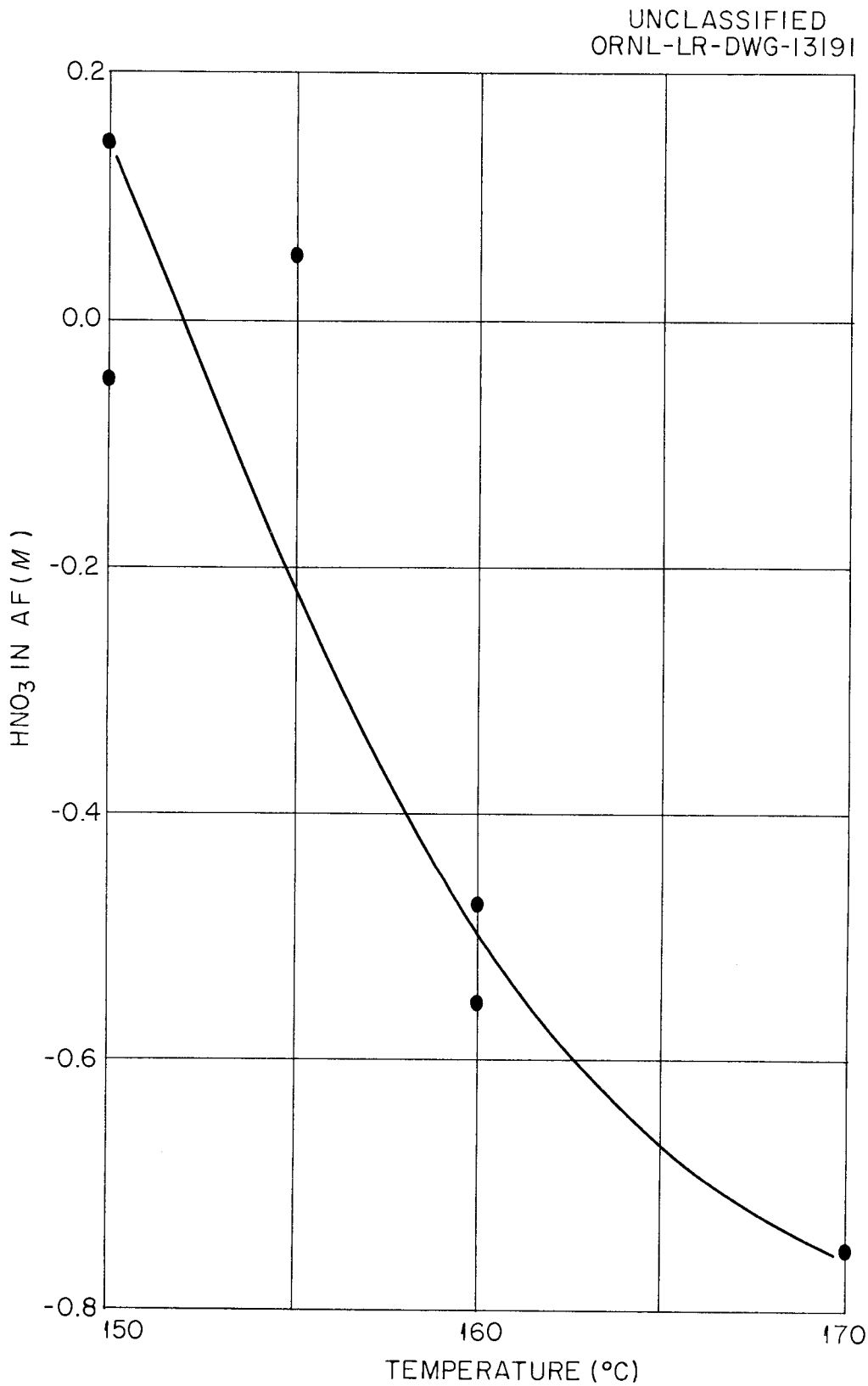

Fig. 5.1. Relation of Final Temperature of Feed Adjustment Cycle to Feed Acidity.

for calculation purposes. In the experiments, the feed solution specific gravity, as expected, was a linear function of the thorium concentration since the Th/Al ratio of 0.4 was essentially constant (Fig. 5.2). The deviation of the calculated from the experimental values was about ±0.01 specific gravity unit (Table 5.1). Greater deviations can be expected as the thorium concentration exceeds 400 g/liter since viscosity effects tend to increase experimental errors. The three feed solutions for which the calculations were made were chosen so that the acidity range would be covered from about 0.15 to 0.9 M acid deficiency; this range may be expected in the Thorex feed in experimental runs.

The specific gravity—temperature coefficient is -0.00104 specific gravity unit/°C of temperature rise (Fig. 5.3). Two feeds of different thorium concentration were used for the determination. From these data, recording instruments were set and calibrated for use in the Pilot Plant.

5.3 Effect of Aging of Feed on Ruthenium A-Column Decontamination

Experiments in which the same A-column feed was used over a period of several days indicated a progressive decrease in the A-column ruthenium decontamination with aging of the feed (Fig. 5.4). This effect is due to a disproportionation of the ruthenium species in the feed solution in favor of a tributyl phosphate—extractable species, which may be caused by the formation of ruthenium nitroso nitrate complexes. The loss in the ruthenium decontamination factor, about 4 in 13 days, is significant and suggests that the present type of feed should be processed as soon as possible after makeup.

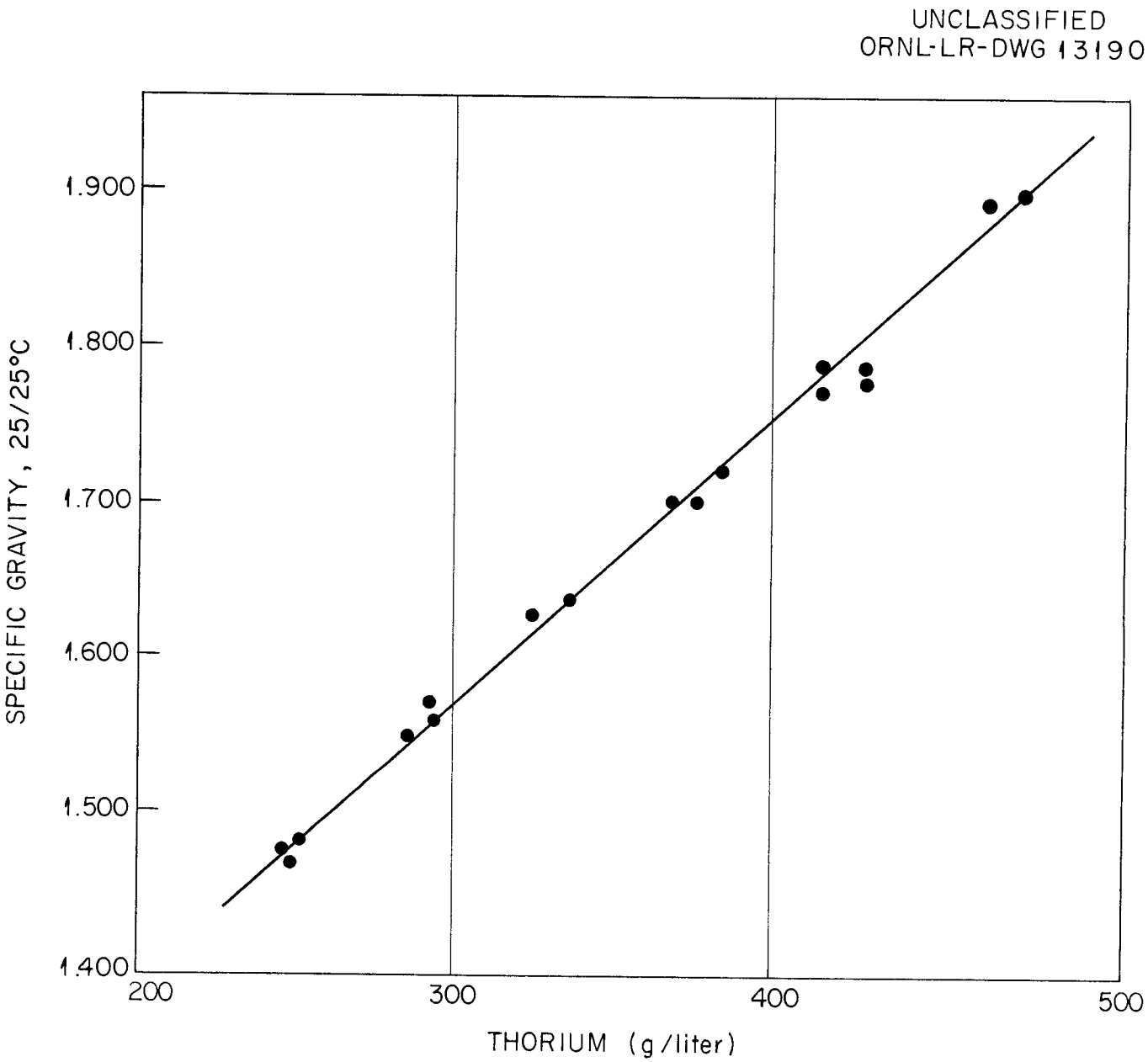

Fig. 5.2. Relation between Specific Gravity and Thorium Concentration of Thorex Feeds.

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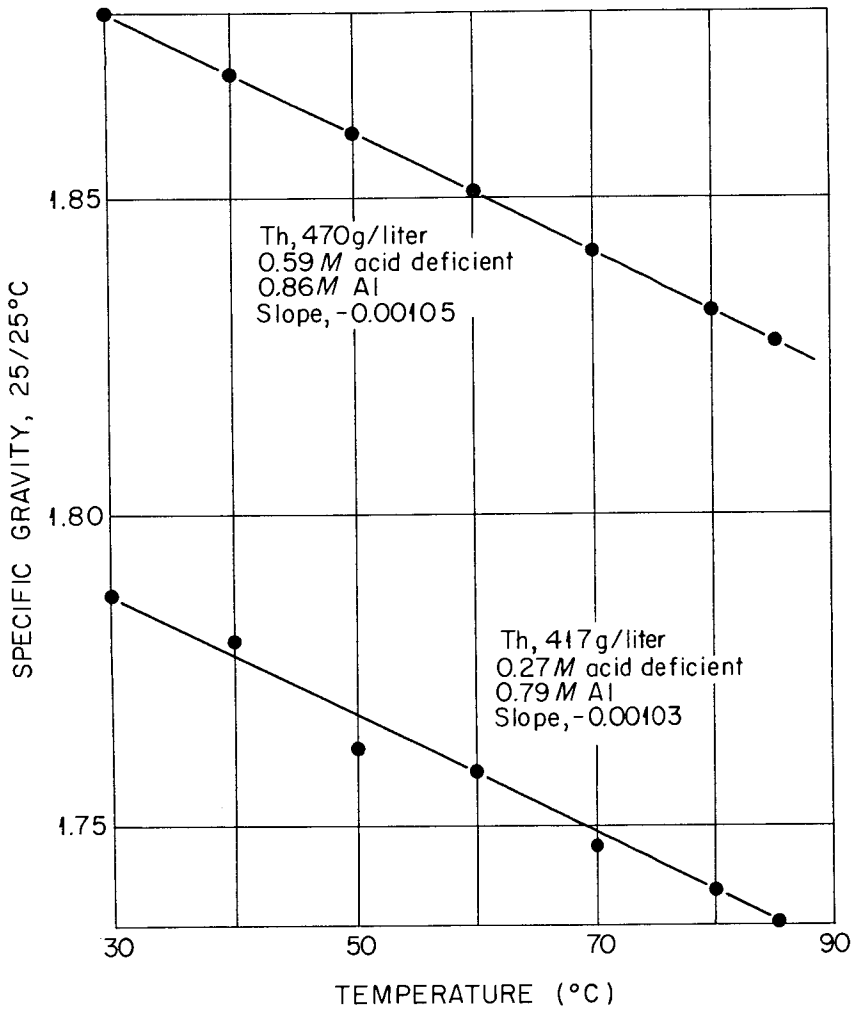

Fig. 5.3. Specific Gravity of Thorex Feed as a Function of the Temperature. Slope indicates Specific Gravity-Temperature Coefficient.

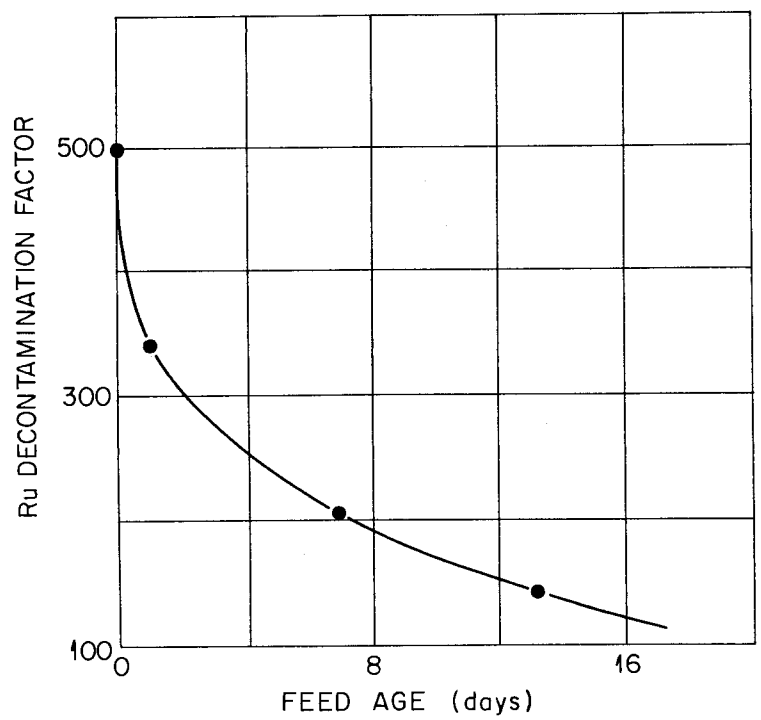

Fig. 5.4. Effect of Age of Feed on A-Column Ruthenium Decontamination Factor.

Table 5.1. Specific Gravity of Thorex Feeds

Batch No.	Th (g/liter)	Acid Deficiency (M)	Al (M)	Specific Gravity		
				Experimental	Calculated	Deviation
2-1	480	0.86	0.99	1.901	1.911	+0.010
2	430	0.76	0.82	1.786	1.811	+0.025
3	374	0.68	0.74	1.705	1.697	-0.008
4	324	0.61	0.67	1.628	1.626	-0.002
5	283	0.52	0.58	1.550	1.549	-0.001
6	246	0.44	0.47	1.468	1.475	+0.007
6-1	417	0.27	0.79	1.786	1.799	+0.013
2	368	0.24	0.68	1.702	1.705	+0.003
3	324	0.21	0.61	1.626	1.626	0.000
4	241	0.19	0.56	1.570	1.565	-0.005
5	248	0.16	0.46	1.481	1.486	+0.005
12-1	470	0.59	0.86	1.886	1.881	-0.005
2	430	0.52	0.77	1.780	1.826	+0.046
3	384	0.46	0.71	1.720	1.730	+0.010
4	334	0.42	0.62	1.639	1.638	-0.001
5	291	0.36	0.55	1.560	1.561	+0.001
6	244	0.30	0.47	1.473	1.477	+0.004

5.4 Corrosion in Thorex Feed System*

Laboratory tests with corrosion samples showed a peak corrosion rate of 30 mils/year for type 309SNb stainless steel under dissolution conditions (Table 5.2). In nonradioactive dissolution tests, involving six

* Reported by J. L. English of the Reactor Experimental Engineering Division, ORNL, at the Thorex Information Meeting, Oct. 19, 1954.

separate 7-hr dissolutions, the corrosion rate did not exceed 3 mils/year. In laboratory tests under feed adjustment tank conditions, a pitting attack at a peak rate of 55 mils/year was observed for type 309SNb stainless steel during the high-acid portion of the digestion cycle. Corrosion rates should not exceed 5 mils/year in other parts of the feed system. These rates are considered unduly high because they are based on continuous exposure of the specimens to process solutions in which the chromium concentration was 10-fold or more greater than that expected in the plant equipment. The high chromium concentration in these tests resulted from acid corrosion of the type 347 stainless steel beakers in which the specimens were exposed for 200-400 hr without replacement of the test solutions. High chromium concentrations have previously been reported to significantly increase stainless steel corrosion rates.

Table 5.2. Corrosion Rates of Type 309SNb Stainless Steel Observed in Laboratory Tests under Thorex Conditions

Vessel	Temperature (°C)	Corrosion Rate[a] (mils/year)
Dissolvent storage tank	25	2-5
Dissolver	105	30
Feed adjustment tank	105-140	55 max[b]
Acid recovery column	115	3-5
Lines to AP evaporator	25	0.03
Lines from AP evaporator	107	0.2

[a]Corrosion rates are for control specimens only.
[b]Pitting corrosion observed.

No corrosion data are yet available on thermally hot surfaces, but special corrosion-test steam coils were installed in the Thorex Pilot Plant along with sets of stress specimens; all these will be exposed in operation of the Thorex Pilot Plant with feed prepared from irradiated thorium.

6.0 FIRST-CYCLE CHEMICAL STUDIES

6.1 Mercury and Fluoride Distribution in Thorex A- and B-Columns

The thorium product from the present Thorex first-cycle flowsheet contains about 24 ppm of mercury and 650 ppm of fluoride, based on thorium. The distribution coefficients in the A- and B-columns are shown in Table 6.1. The mercury and fluoride decontamination factors are about 100 and 10, respectively, from the feed to the strip column thorium product.

6.2 Effect of Strip Acidity on Uranium Refluxing

If 0.005 M HNO_3 was used in the B-column for both BX and B'X streams instead of 0.24 M HNO_3 for the B'X, uranium reflux would be excessive (Table 6.2). Even after six countercurrent volume changes, the system is obviously not at a steady state. As demonstrated previously, an aqueous nitric acid concentration of 0.20 M is required to obtain a thorium-uranium separation factor of 10^3-10^4. Any significant decrease from the stipulated acidity will cause severe uranium refluxing at or slightly above the AU stream entry point.

Table 6.1. Mercury and Fluoride Distribution in A- and B-Columns

Thorex flowsheet conditions; feed contains 1.15 mg of mercury and 1.38 mg of fluoride per milliliter

Stage	Organic		Aqueous		D.C., O/A	
	Hg^{++} (mg/ml)	F^- (mg/ml)	Hg^{++} (mg/ml)	F^- (mg/ml)	Hg^{++}	F^-
A-8-Sc	1.7×10^{-3}	<0.01	0.001	<0.01	1.7	~1
A-1-Ex	3.4×10^{-3}	<0.01	0.58	1.01	6×10^{-3}	~0.01
A-5-Ex	2.1×10^{-3}	<0.01	0.33	0.9	6×10^{-3}	~0.01
B-10-St	4.1×10^{-3}	0.01	2.3×10^{-3}	0.16	1.8	0.06
B-8-St	3.2×10^{-3}	0.01	1.1×10^{-3}	0.02	2.8	1.5
B-1-Sc	3.2×10^{-3}	0.02	1.1×10^{-3}	0.02	2.8	1.0
B-5-Sc	2.3×10^{-3}	0.06	$<1.0 \times 10^{-3}$	0.02	2.2	3.0

Table 6.2. Effect of Using Only Dilute Acid (0.005 M in B-Column)

Batch countercurrent experiments
AU stream: 59 g of Th per liter; 0.26 g of U per liter
B'X: 0.005 M HNO_3
BX: neutral
BS: 42.5% TBP, Special Naphtha No. 1
Flow ratios: AU/BS/BX/B'X = 5.2/1.6/1.0/4.8
10 strip stages; 5 scrub; B'X entry at 8th scrub stage; 6 volume changes

Stage	Organic		Aqueous		D.C., O/A	
	Th (mg/ml)	U (mg/ml)	Th (mg/ml)	U (mg/ml)	Th	U
10 St	0.005	0.00016	<0.0001	0.00024	>50	0.67
8 St	0.005	0.00020	<0.0001	0.00024	>50	0.84
6 St	0.005	0.00013	<0.0001	0.0031	>50	0.04
4 St	<0.005	0.040	0.111	1.34	0.05	0.03
2 St	1.35	3.14	16.6	1.54	0.08	2.04
1 Sc	37.0	0.480	65.0	0.046	0.57	10.4
3 Sc	42.2	0.104	67.5	0.0075	0.63	13.9
5 Sc	38.8	0.0096	63.2	0.0013	0.62	7.4

6.3 Effect of AU Holdup on U-Th Separation Factor

The uranium-thorium separation tends to decrease as the holdup time of the AU stream is increased. The effect was appreciable when the AU solution was stored for several days before entry into the B-column (Table 6.3). At 336 hr the separation factor was only about 6% of the zero time value. At 20 hr the change was not appreciable. This effect is probably due to the formation of mono- and dibutyl phosphates as a result of the action of thorium nitrate on the tributyl phosphate.

Table 6.3. Effect of AU Holdup Time on Uranium-Thorium Separation Factor[a]

AU Holdup Time (hr)	U-Th Separation Factor
0	6.03×10^{3} [b]
20	1.07×10^{4} [b]
93	570
336	362

[a] U-Th separation factor = $\frac{Th/U^{233} \text{ in feed}}{Th/U^{233} \text{ in B-column U product}}$.

[b] Difference not significant because of low thorium content.

6.4 First-Cycle Thorium Product Plutonium Decontamination

The Thorex feed may contain plutonium as a result of the presence of U^{238} in the original raw materials and the subsequent conversion to plutonium by neutron irradiation. Assuming a U^{238} concentration in the thorium metal of 10 ppm, irradiation at 2×10^{13} n/cm^2/sec to a level

of 2000 g of U^{233} per 10^6 g of thorium would result in a total plutonium content of about 1 part in 10^8 parts of thorium.

With the present Thorex flowsheet (Fig. 3.1), in which the scrub solution contains ferrous sulfate, the plutonium decontamination factor is 165 across the A-column. Thus the A-column product has a plutonium concentration of 5 parts per 10^{11} parts of thorium in comparison to about 1 part per 10^8 parts of thorium in the A-column feed.* Without ferrous sulfate in the scrub solution, the plutonium decontamination factor is only 1.1. The plutonium distribution coefficients (O/A) were 0.21 and 3.3, respectively, at the eighth scrub stage for the flowsheets with and without ferrous sulfate in the scrub solution.

6.5 Fission Product Decontamination of First-Cycle Thorium Product

Further purification of the first-cycle thorium product by precipitation was investigated as an alternate to the second solvent extraction cycle (Sec. 3.2). Precipitation methods gave satisfactory decontamination, but the problem of handling radioactive solids makes such methods less attractive than the extraction method of purifying.

Thorium Oxalate Precipitation. The thorium product was decontaminated from ruthenium by a factor of 90 (Table 6.4) by precipitation as the oxalate. Uranium was separated by a factor of 20, the uranium remaining with the supernatant, which was treated as waste. Decontamination factors of 3 and 5 were obtained from Zr-Nb and Pa^{233},

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* The plutonium activity in a Thorex feed containing 350 g of thorium per liter would be ~250 α c/m/ml. With a plutonium decontamination factor of 165, the AU stream would contain about 0.3 α c/m/ml. This would yield about 4×10^{-3} Pu α c/m/mg Th in the B-column thorium product.

respectively, and there was no decontamination from rare earths. If the problem of handling radioactive solids could be decreased by remote operation, this method as a second or third Thorex decontamination cycle appears favorable.

Table 6.4. Decontamination of Thorium by Oxalate Precipitation

Contaminant	Activity (c/m/mg Th)		Decontamination Factor
	Feed	Product	
Gross γ	565	312	2
Ru γ	279	3	90
Zr-Nb γ	134	46	3
TRE β	79	77	1
U^{233} α	35	1.6	20
Pa γ	94	18	5

Thorium Fluoride Precipitation. Decontamination from ruthenium by a factor of 100-130 was obtained when ThF_4 was crystallized from the Thorex concentrated BT stream, but there was no decontamination from other fission products. The thorium product, which was about 2 M in $Th(NO_3)_4$ and 1.5 M in HNO_3, was heated to about 95°C, and 2-5% excess 48% HF was added. The mixture was digested and agitated for 10 min, and the precipitate was centrifuged and washed several times with water. The total thorium loss to the supernatant and wash was less than 0.01%.

Thorium Oxycarbonate Precipitation. Decontamination factors from the Thorex thorium nitrate product to the thorium oxycarbonate precipitate were insignificant: gross γ, 1.06; Ru γ, 1.05; Zr-Nb γ, 1.01;

and TRE β, 1.00. In the tests a nitrate solution, 10 wt % thorium, containing fission products was treated at 80°C with 7.5 wt % sodium carbonate solution. At a pH between 7.6 and 8.5 and a final temperature of 60°C, the precipitate that formed was allowed to settle 4-5 hr, after which the supernatant was decanted and the precipitate was thoroughly washed and filtered.

7.0 RADIATION DAMAGE TO SOLVENT

Radiation-induced physical and chemical changes could seriously affect the efficiency of the Thorex separation process as the radiation level increases and the fuel decay time decreases. Irradiation of Thorex solvent in the Co^{60} source in amounts greater than expected in the process did not seriously affect product decontamination from fission products except ruthenium. Stable emulsions formed under Thorex flowsheet A-column conditions with solvent that had been irradiated to 10.7 β watt-hr/liter; solvent irradiated to 6 β watt-hr/liter did not form emulsions.

Studies* of radiation damage to the Purex solvent (tributyl phosphate in Amsco) had indicated that the chief effects are due to the mono- and dibutyl hydrolysis products of tributyl phosphate and that damage was not serious until the exposure exceeded 2 watt-hr/liter. Calculations and laboratory data indicated that, in the Thorex process, Pa^{233}-induced solvent exposure at present reactor fluxes and irradiation levels is less than 0.6 β watt-hr/liter. Even in the extreme case (Fig. 7.1), with a calculated flux of 10^{15} n/cm^2/sec and irradiation to 4000 g of mass-233 isotope per ton, the fuel could be processed at or near the time of discharge without exceeding an exposure of 2 watt-hr/liter.

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* G. I. Cathers, "Radiation Effects in Chemical Processing," ORNL-CF-53-9-196 (Sept. 24, 1953).

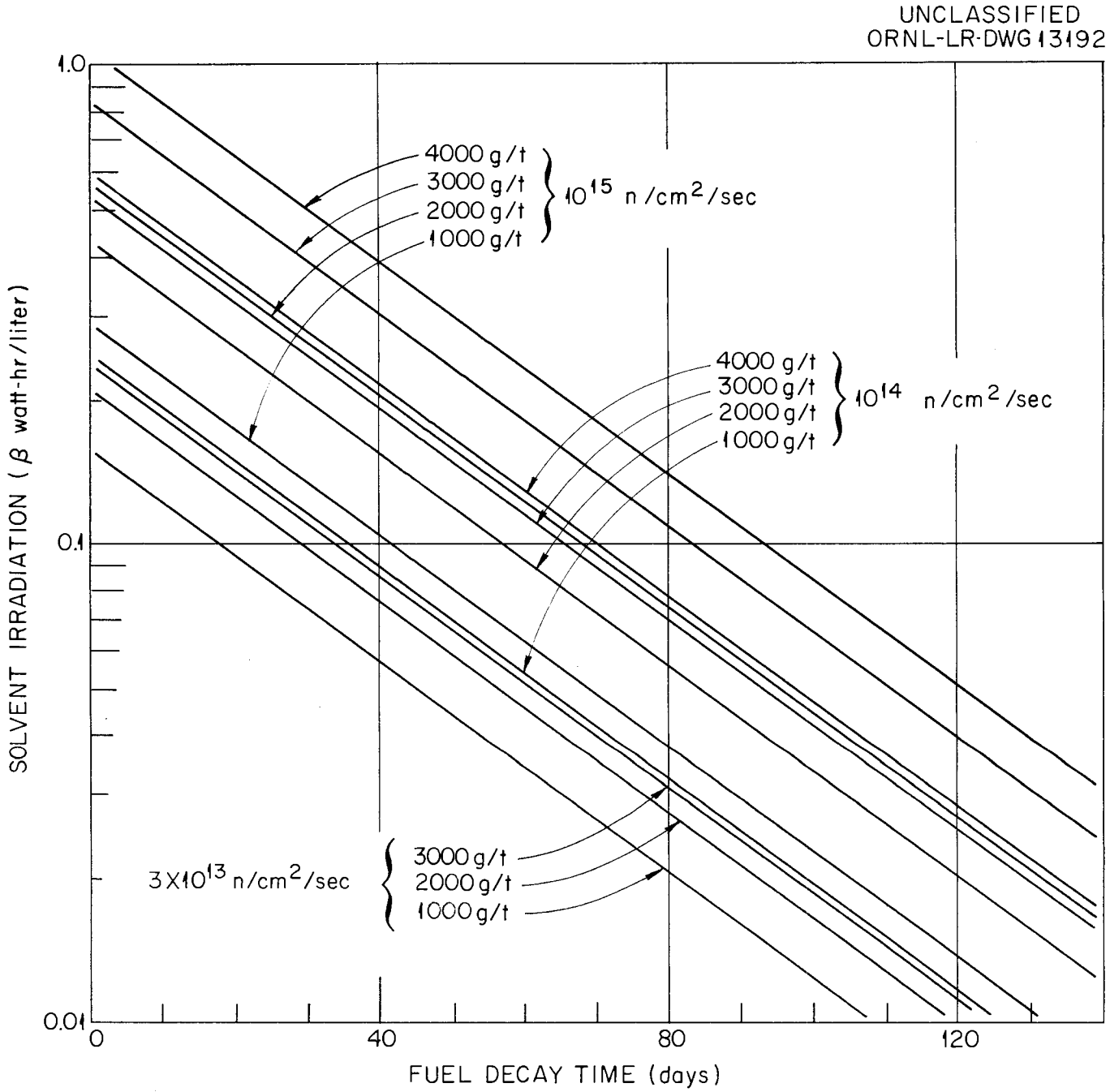

Fig. 7.1. Pa^{233}-Induced Solvent Irradiation as a Function of Flux, g/t Level, and Decay Time before Processing.

In order to evaluate the radiation damage that might be present during the processing of irradiated thorium, the following assumptions were made: (1) The major activity contributing to radiation damage is Pa^{233}; (2) the present Thorex flowsheet is indicative of future thorium processing flowsheets; and (3) the average time of contact of the solvent-diluent with the high activity zone is 5 min. The amount of Pa^{233} at the time of discharge of the fuel depends on the flux and irradiation time of the fuel.

7.1 Radiation Damage to Extractant

Fission Product Decontamination Factors. The decontamination of uranium and thorium from fission products other than ruthenium was not markedly affected by exposure of the solvent to irradiation up to 6 β watt-hr/liter of solvent (Table 7.1). The ruthenium decontamination factor decreased sharply with an increase in the radiation exposure from 0 to 1 β watt-hr/liter of solvent (Fig. 7.2). After an exposure of 1 β watt-hr/liter, the rate of decrease in the decontamination factor became less, and the present flowsheet is able to yield a decontamination factor of 50 up to 6 β watt-hr/liter solvent exposure.

Oxidizing Normality of Solvent. The present Thorex flowsheet provides a reducing scrub (0.005 M Fe^{++}) which eliminates extraction of chromate by tributyl phosphate. The Cr(VI) present is reduced to the nonextractable Cr(III). Irradiated solvent extracted chromium even when the 0.005 M Fe^{++} reducing scrub solution was used. The oxidizing normality of the irradiated solvent varied as a power function of the irradiation level (Table 7.2 and Fig. 7.3), although the experimental data may not warrant a rigorous mathematical treatment. Determination of the oxidizing normality of used solvent

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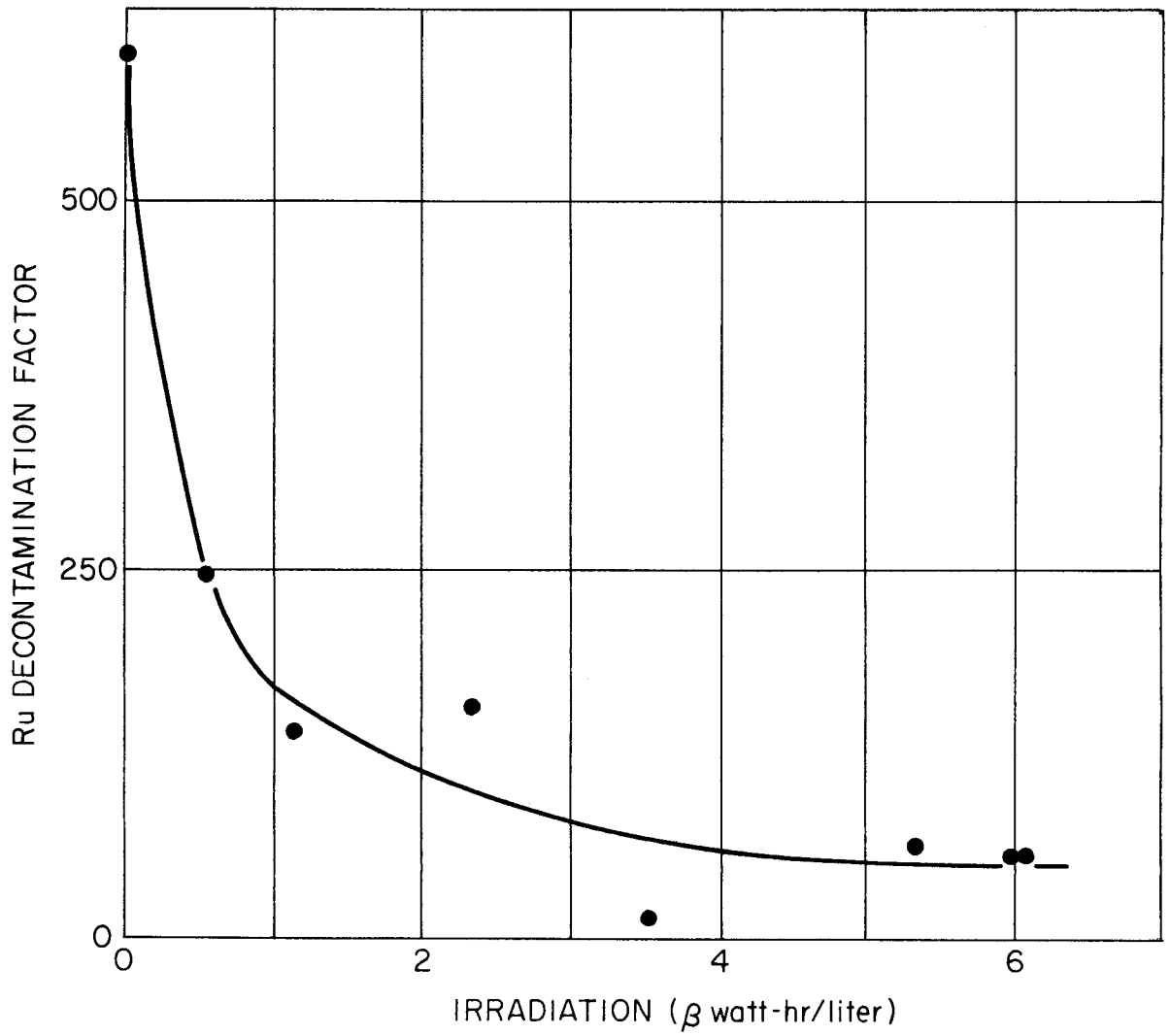

Fig. 7.2. Ruthenium Decontamination Factor across the A-Column as a Function of Radiation Exposure of the Solvent, 42% Tributyl Phosphate-58% Paraffinic Hydrocarbon.

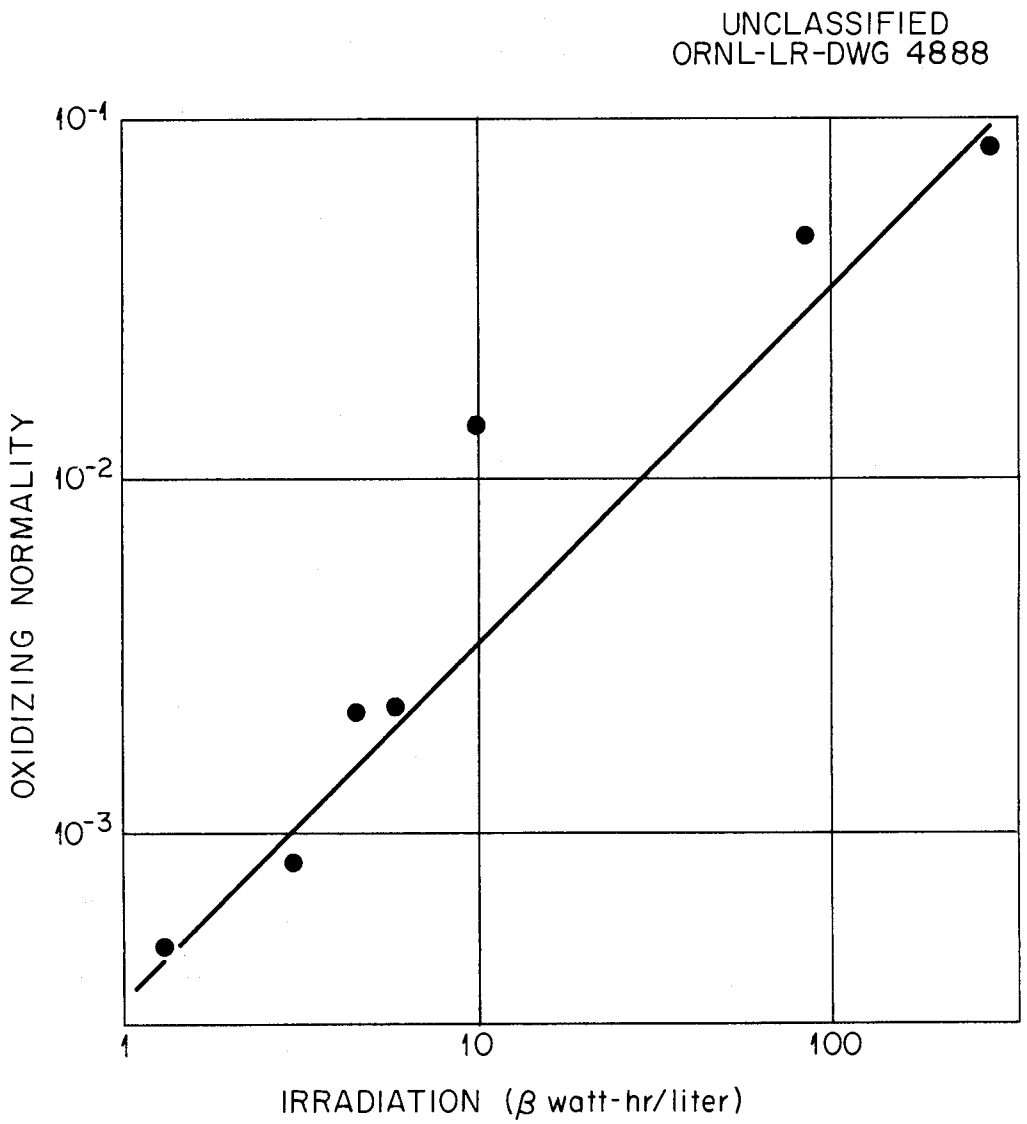

Fig. 7.3. Oxidizing Normality vs. Radiation Exposure of the Solvent Tributyl Phosphate - 58% Paraffinic Hydrocarbon.

may thus provide a means for evaluating the extent of radiation damage to an organic solvent. The analysis was based on the oxidation of standard ferrous sulfate, which was added in excess, shaken with the solvent, and back-titrated with standard ceric sulfate solution.

The increase in oxidizing normality of the solvent with an increase in radiation exposure is believed to be due to the formation of organic peroxides in the diluent. Since the A-column ruthenium decontamination factor decreased with increasing irradiation of the solvent, the extraction of chromate was taken as evidence that oxidation of the ruthenium in the feed by peroxides in the irradiated solvent could result in the formation of a TBP-extractable species of ruthenium.

Table 7.1. A-Column Decontamination Factors as a Function of Solvent Irradiation

Feed: 1.5 M Th; 0.6 M Al; 0.0-0.1 M H^+; fission product spike
Scrub: 0.6 M Al; 0.2 M acid deficient; 0.004 M PO_4^{3-}; 0.005 M Fe^{++}
Organic: 42.5% TBP, 58% Special Naphtha No. 1
Feed/scrub/organic ratio = 1/1/5

Solvent Irradiation (watt-hr/liter)	A-Column Decontamination Factors				
	Gross β	Ru β	Zr β	Nb β	TRE β
0	1.2×10^4	550	$>9.2 \times 10^3$	$>8.3 \times 10^3$	3.8×10^4
0.5	5.2×10^3	233	$>3.3 \times 10^4$	$>3.3 \times 10^3$	3.7×10^4
1	1.7×10^3	140	1.1×10^4	---	2.4×10^3
2	2.7×10^3	157	$>2 \times 10^4$	$>3.8 \times 10^3$	1.3×10^4
4	1.7×10^3	11	6.4×10^3	---	7.4×10^3
5	1.6×10^3	63	7.7×10^3	---	1.7×10^4
6	1.8×10^3	58	6.7×10^3	$>8.5 \times 10^3$	9.6×10^4

Table 7.2. Oxidizing Normality[a] of Irradiated Solvent

500 ml of 42% TBP—58% Special Naphtha No. 1 agitated with 100 ml of water while undergoing irradiation in Co^{60} source

Radiation Dose (β watt-hr/liter)	Oxidizing Normality	Radiation Dose (β watt-hr/liter)	Oxidizing Normality
0.0	<0.00005	6.1	0.0023
0.68	0.0003	10.7	0.014
1.35	0.0005	85.7	0.048
3.05	0.0008	286	0.086
4.7	0.0022		

[a]Analytical accuracy within 5%.

Emulsion Formation. Stable emulsions formed in countercurrent extraction with solvent that was irradiated to 10.7 β watt-hr/liter. No emulsions were observed at a solvent irradiation level of 6 β watt-hr/liter. With samples irradiated to 10.7 and 85.7 β watt-hr/liter, stable emulsions developed at the A-column third extraction stage. Evidence that the emulsion effect was not dependent on the presence of water during irradiation was given by an experiment with solvent that had received 10.7 β watt-hr/liter and was not agitated with water. A stable emulsion formed at the fourth A-column extraction stage under the same flowsheet conditions (Fig. 3.1). The maximum solvent exposure limit was therefore set at 5 β watt-hr/liter to avoid emulsion formation.

Exposure of Diluent Alone. An A-column countercurrent experiment was made with irradiated diluent (dosage, 12.4 β watt-hr/liter) that was mixed with nonirradiated tributyl phosphate after exposure in the Co^{60} source. No emulsions were formed in the column, indicating that

the emulsive effect was due to radiation damage to the tributyl phosphate. Chromate extraction was observed, however, and the A-column ruthenium decontaminating factor was only 2.3, indicating an oxidation and subsequent extraction of ruthenium.

7.2 Predicted Solvent Exposure due to Pa^{233} Activity

From the data in Fig. 7.1, and assuming that fission product activities may increase the exposure by 50%, solvent exposure in the Thorex process will still be below 2 β watt-hr/liter even with thorium irradiated at 10^{15} n/cm^2/sec to a 4000-g/t level and processed immediately after discharge. With thorium irradiated at 3×10^{13} n/cm^2/sec to 4000 g of U^{233} per ton, Pa^{233} was the controlling activity as far as solvent exposure was concerned. The total fission product activity in terms of the disintegration rate was a factor of about 20 below the Pa^{233} level.

The data were calculated by the equation

$$\frac{N_{13}}{N_{02}} = \frac{\phi\sigma_{02}}{\lambda_{13} + \phi\sigma_{13}} \left[1 - e^{-(\lambda_{13} + \phi\sigma_{13})t}\right]$$

where N_{13} = Pa^{233} produced, g
N_{02} = original Th^{232}, g
ϕ = reactor flux, n/cm^2/sec
σ_{02} = capture cross section of Th^{232} = 7.06 b
σ_{13} = capture cross section of Pa^{233} = 150 b
λ = decay constant
t = time, sec

For the derivation of Fig. 7.1, it was assumed that the present Thorex flowsheet was used with feed/scrub/extractant flow ratios of 1/1/5 with a 5-min contact time of the solvent with the intense radiation field.

Therefore, Fig. 7.1 was constructed so that any contact time other than 5 min may be obtained by multiplying by a factor.

7.3 Experimental Technics

Thorex solvent was irradiated in the Co^{60} source to an exposure equivalent to that expected in the Thorex A-column for different fuel irradiation and decay times. The irradiated solvent was tested in batch countercurrent experiments with the Thorex flowsheet. Non-irradiated solvent was used in control experiments.

The Co^{60} gamma radiation sources were shielded by 9 ft of water in the Bldg. 3001 canal. They were calibrated by the ceric ammonium sulfate reduction method, and the radiation intensity was calculated by the decay rate of the Co^{60} isotope. From the source intensity, the solvent exposure in watts per liter was calculated on the assumption that the solvent absorption was 93 ergs for each roentgen of source intensity. The total radiation exposure in watt-hours per liter of solvent was expressed by the product of the exposure time in hours and the rate of energy absorption in watts per liter for the two Co^{60} sources used (Table 7.3).

Table 7.3. Intensity of Co^{60} Sources and Rate of Energy Absorption by Solvent

Date	Co^{60} Source 1		Co^{60} Source 2	
	Intensity (r/hr)	Energy Absorption (watts/liter)	Intensity (r/hr)	Energy Absorption (watts/liter)
Oct. 1954	1.61×10^6	4.15	1.38×10^6	3.57
Nov. 1954	1.58×10^6	4.08	1.36×10^6	3.51
Dec. 1954	1.57×10^6	4.06	1.35×10^6	3.48

The apparatus (Fig. 7.4) was a stainless steel pressure vessel that fitted inside the ring of cylindrical Co^{60} source elements. The upper portion of the case was enlarged so that the flange rested on the source itself; this enlarged portion contained the electric stirring motor. A 32-oz glass bottle, which fitted loosely into the lower portion, held the samples. Electric wires to the agitator motor were sheathed in tygon tubing. A positive air pressure was applied via the tygon tubing to prevent canal water from entering the apparatus. A needle valve allowed a slow exit of the hydrogen gas formed by irradiation decomposition of water.

For experiments in which organic and aqueous phases were intimately mixed during irradiation, 500 ml of the organic phase was added to 100 ml of water or nonirradiated Thorex feed solution and put into the pressure case. The case was then sealed, 15 psi of air pressure admitted, the agitator started, and the case lowered into the source. A 600 ml volume was used when solvent or diluent samples were irradiated without an aqueous phase.

Preliminary experiments showed the necessity for a standardized feed preparation and solvent treatment so that results would be reproducible. The feed, 1 M $Th(NO_3)_4$—0.4 M $Al(NO_3)_3$—6.5 M HNO_3 was prepared by the dissolution of thorium and aluminum metal stock in nitric acid with mercury and fluoride catalysts and spiked to about 1×10^8 c/m/ml gross beta activity with a solution obtained by the dissolution of an irradiated thorium metal slug. This solution was evaporated with a slight negative pressure in the presence of type 309SNb stainless steel coupons to a liquid phase temperature of 157°C. After a 1-hr reflux period, the concentrated feed was diluted with water and adjusted to feed specifications, 1.5 M thorium—0.6 M aluminum—0.2 N acid deficiency to 0.1 N acid. The 42.5% tributyl phosphate in Special Naphtha No. 1 was pretreated by contacting it

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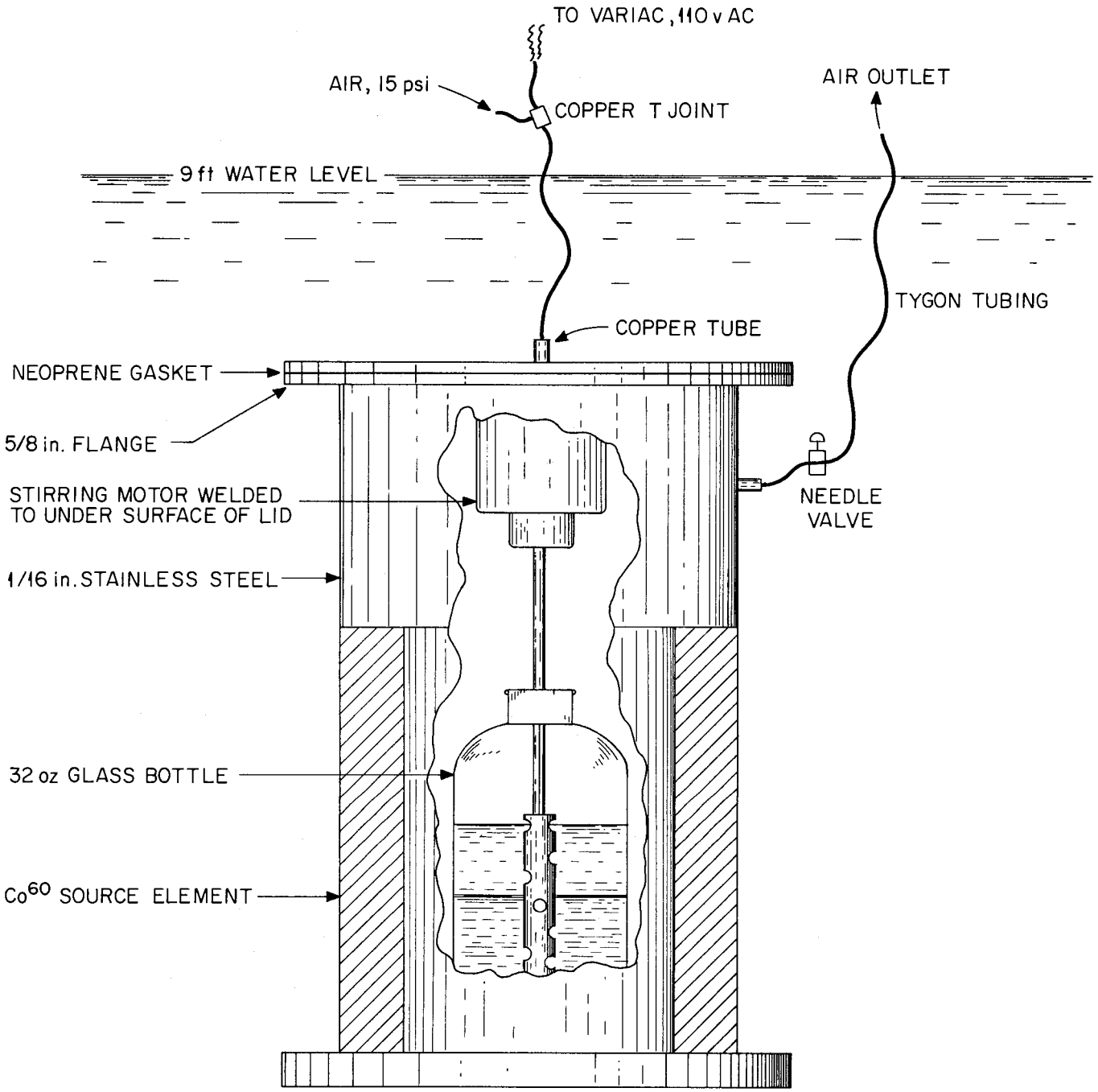

Fig. 7.4. Apparatus for Intimate Mixing of Two Liquid Phases in Co^{60} Source.

with a calcium hydroxide slurry* for 1 hr, filtering, and washing with water several times. The solvent received no washing or treatment after an irradiation exposure experiment.

8.0 APPENDIX

8.1 Thorium Dioxide Studies

Ratio of U^{233} to Thorium as a Function of ThO_2 Slug Radius. Several fragments of a ThO_2 slug were dissolved in an attempt to obtain data on the U^{233}/Th ratio as a function of the slug radius. The slugs dissolved very irregularly, leaving a pitted surface and cone-shaped ends. Because of this, no completely valid measurements could be made, but data (Table 8.1) indicate that the ratio does not vary significantly as a function of the slug radius.

Table 8.1. Determination of U^{233} Content as a Function of ThO_2 Slug Radius

Dissolvent: 13 M HNO_3--0.04 M HF; after each refluxing period the slug was rinsed, weighed, and measured with a vernier micrometer

Sample Wt (g)	Slug Radius (in.)	Length (in.)	Refluxing Time (hr)	Th in Solution (mg/ml)	U^{233} in Solution[a] (α c/m/ml)	g U^{233} / ton Th
169.0	0.562	1.188	7	119.5	1.29×10^6	981
104.5	0.469[b]	1.000	7	91.5	1.13×10^6	1123
54.5	0.372	---[c]	21	104.5	1.25×10^6	1087

[a]Counted at 52% geometry.
[b]Cone shaped; measurement only approximate.
[c]Pitted surface at end of slug; no measurement taken.

* 60 g of c.p. $Ca(OH)_2$ and 40 ml of distilled water per liter of solvent.

Heating of Irradiated ThO_2. Pellets of thorium oxide 1/8 and 1/4 in. in diameter were irradiated in the LITR at 5×10^{12} n/cm^2/sec for about 30 days. At the end of this time the pellets were blue-black in color. When the irradiated pellets were heated in an electric muffle furnace, the color changed from dark blue to the off-white color of the original ThO_2 pellet (Table 8.2). Allowing the pellets to cool did not change the color to blue again, showing that the original color transformation was a physical effect induced by neutron bombardment and did not result in a permanent physical change.

Blue thoria from an irradiated thorium metal slug was isolated and heated in the same manner as the ThO_2 pellets. The temperature required to restore the color was about twice that for the pellets.

Table 8.2. Heating of Irradiated Thoria

ThO_2 Pellets		Blue Thoria from Thorium Metal Slug	
Temperature (°C)	Color	Temperature (°C)	Color
25	Dark blue	25	Blue
140	Blue	140-380	Blue
160	Blue	400-440	Blue
180-200	Blue	480-515	Green
220-300	Off-white	540-600	Gray
25	Off-white	25	Off-white

8.2 Preliminary Values of U^{233} and Thorium Backgrounds in Thorex Samples*

The beta and gamma background activities of natural thorium and U^{233}

* Information in this section abstracted from ORNL internal memo CF-54-11-117, by S. A. Reynolds, Analytical Chemistry Division.

were estimated as an aid in evaluating thorium and U^{233} product specifications. Thorium^{232}, the parent of the thorium radioactive series,[a] has a very slight gamma activity.[b] Uranium^{233}, the parent of a number of radionuclides comprising the neptunium series,[c] emits alpha radiation accompanied by gamma radiation, x rays, and conversion electrons.[d] In Thorex samples containing appreciable quantities of Th^{232} or U^{233}, these nuclides and their active daughters contribute a noticeable background when gross or fission-product beta and gamma activities are measured. For example, in the analysis of a U^{233} product, it was found that U^{233} itself contributed most of the apparent gross beta activity.[e] It is important, therefore, to be able to correct observed beta and gamma activities for the presence of U^{233} or Th^{232} in determining fission product activity of a Thorex product.

The daughter activities regrow in freshly purified thorium, essentially from Th^{228}, approximately according to the relation[a]

$$A_{\beta,\gamma} = K(2e^{-\lambda_4 t} - 2.29e^{-\lambda_5 t} - 0.29e^{-\lambda_8 t})$$

where t = time after purification

λ_4 = decay constant for Th^{228}

λ_5 = decay constant for Ra^{224}

λ_8 = decay constant for Pb^{212}

The daughter activity reaches a maximum at ~30 days, decays slowly for ~3 years thereafter, then regrows to secular equilibrium in ~60 years.

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a. J. Fresco, E. Jetter, J. Harley, Nucleonics, 10, No. 8: 60 (1952).
b. J. M. Hollander, I. Perlman, G. T. Seaborg, Rev. Mod. Phys., 25: 602 (1953).
c. G. Friedlander, J. W. Kennedy, "Introduction to Radiochemistry," p. 15, Wiley, New York, 1949.
d. Hollander, Perlman, Seaborg, op. cit., p. 605.
e. T. H. Handley, Chem. Div. Quar. Prog. Rpt. for March 31, 1950, ORNL-686, Part II, p. 45 (May 18, 1950).

If the times of original purification of various lots of thorium differ considerably, there will be a substantial variation in daughter activity, but it is assumed that the histories of thorium slugs processed in the Thorex operation will be about the same, and also comparable to the thorium studied in this section.

The apparent beta and gamma activities of U^{233} would remain constant except for slow growth of daughters, governed by the 7×10^3-year half-life of Th^{229}. The known gamma-emitting daughters of U^{233} would grow in a pure preparation at the rate of ~ 10 d/m per month per million d/m of U^{233}. However, there may be other gamma emitters among the U^{233} daughters, and the presence of daughters of U^{232} and U^{234} would add to the gamma activity and increase its rate of growth.

Beta measurements were performed by evaporation of samples on 1-in. watch glasses, mounted in the usual way,[f] and counting by means of the standard Geiger-Mueller counter[g] with helium-organic vapor filling. For gamma measurements, 1-ml samples were placed in 10- by 75-mm culture tubes and counted in a standard well-type scintillation counter,[h,i] using a 5-g/cm^2 lead absorber. Uranium^{233} assays were made by a gross alpha technic,[j] i.e., evaporation of aliquots on stainless steel disks and counting by means of a proportional alpha counter at about 51% geometry.[k] Results were expressed in alpha counts per minute; 1 mg of U^{233} is equivalent to 1.07×10^7 α c/m.

The activities grew after separation approximately as predicted

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f. ORNL Master Analytical Manual, Method No. 9002302.
g. Ibid., Method No. 200355.
h. S. A. Reynolds, W. S. Lyon, Anal. Chem. Div. Quar. Prog. Rpt. for Sept. 26, 1952, ORNL-1423, p. 14 (Feb. 11, 1953).
i. ORNL Master Analytical Manual, Method No. 200365.
j. Ibid., Method No. 9002301.
k. Ibid., Method No. 200351.

by the equation (Figs. 8.1 and 8.2). The values for short-term maximum beta and gamma activities ~30 days after purification are given in Table 8.3, and the factors calculated from the theoretical equation to evaluate the beta or gamma activity at various times after separation in Table 8.4. Each value in Table 8.3 represents the average of several experimental results; the uncertainties are observed mean deviations. If the weight of thorium mounted for beta counting does not exceed 20 mg, the average of the first three beta values, 6.0 c/m/mg, can be taken as a fair approximation of the maximum beta activity.

Table 8.3. Maximum Daughter Activities of Thorium 30 Days after Purification

Activity	Wt of Thorium (mg)	(c/m/mg)
β	6.5	5.9 ± 0.3
β	13	6.2 ± 0.3
β	19.5	5.9 ± 0.4
β	26	5.5 ± 0.3
γ	75	14 ± 1

Thoron escapes from thorium samples during and after evaporation for gross beta measurement. The initial beta activity was observed to decay at a rate governed by the 10.6-hr half-life Pb^{212}. The activity later regrew, but did not reach the original counting rate (Fig. 8.3). It is therefore necessary to count thorium-bearing gross beta samples soon after drying if the background value of 6.0 c/m/mg is to be used.

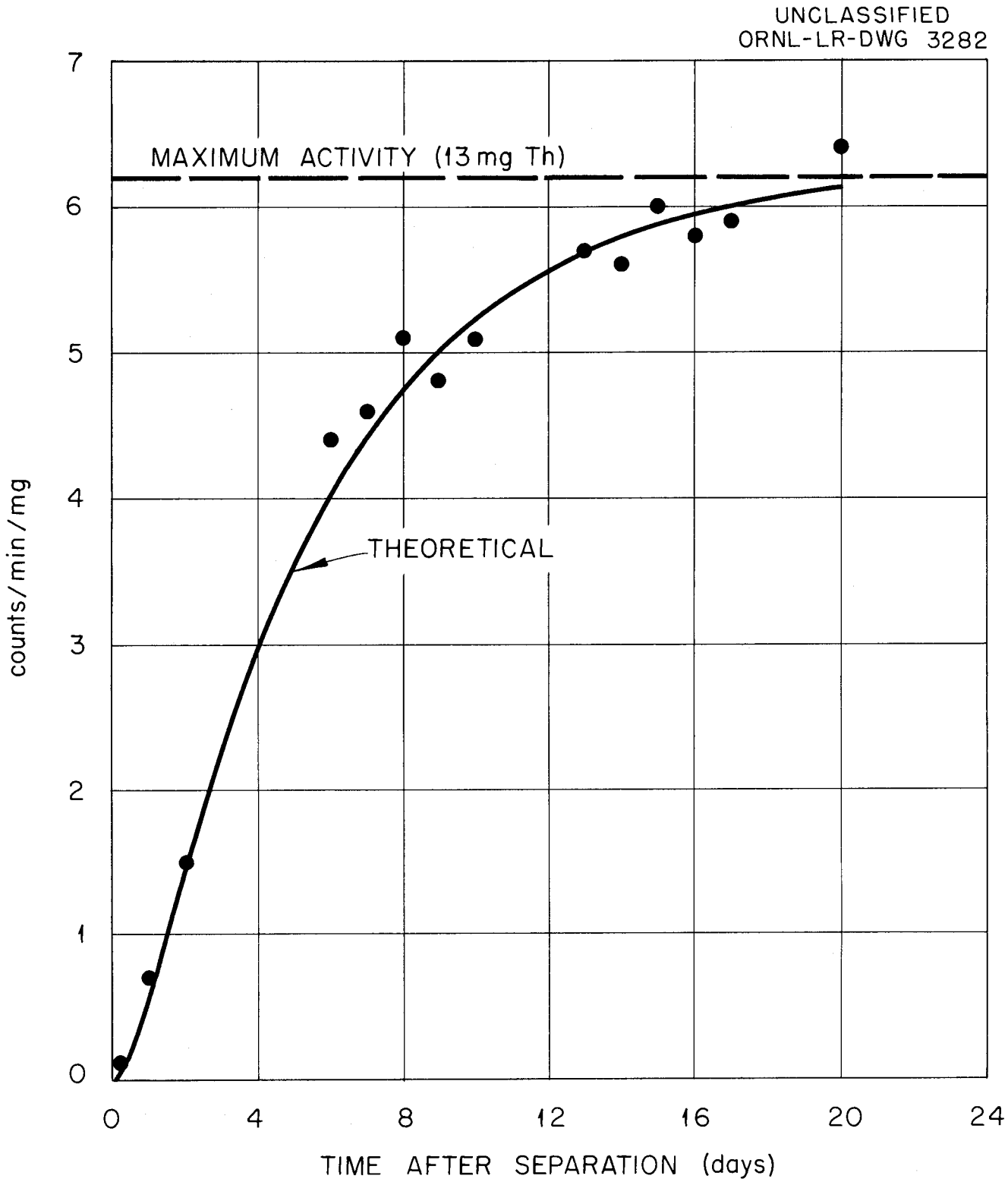

Fig. 8.1. Typical Growth of Beta Activity in Thorium.

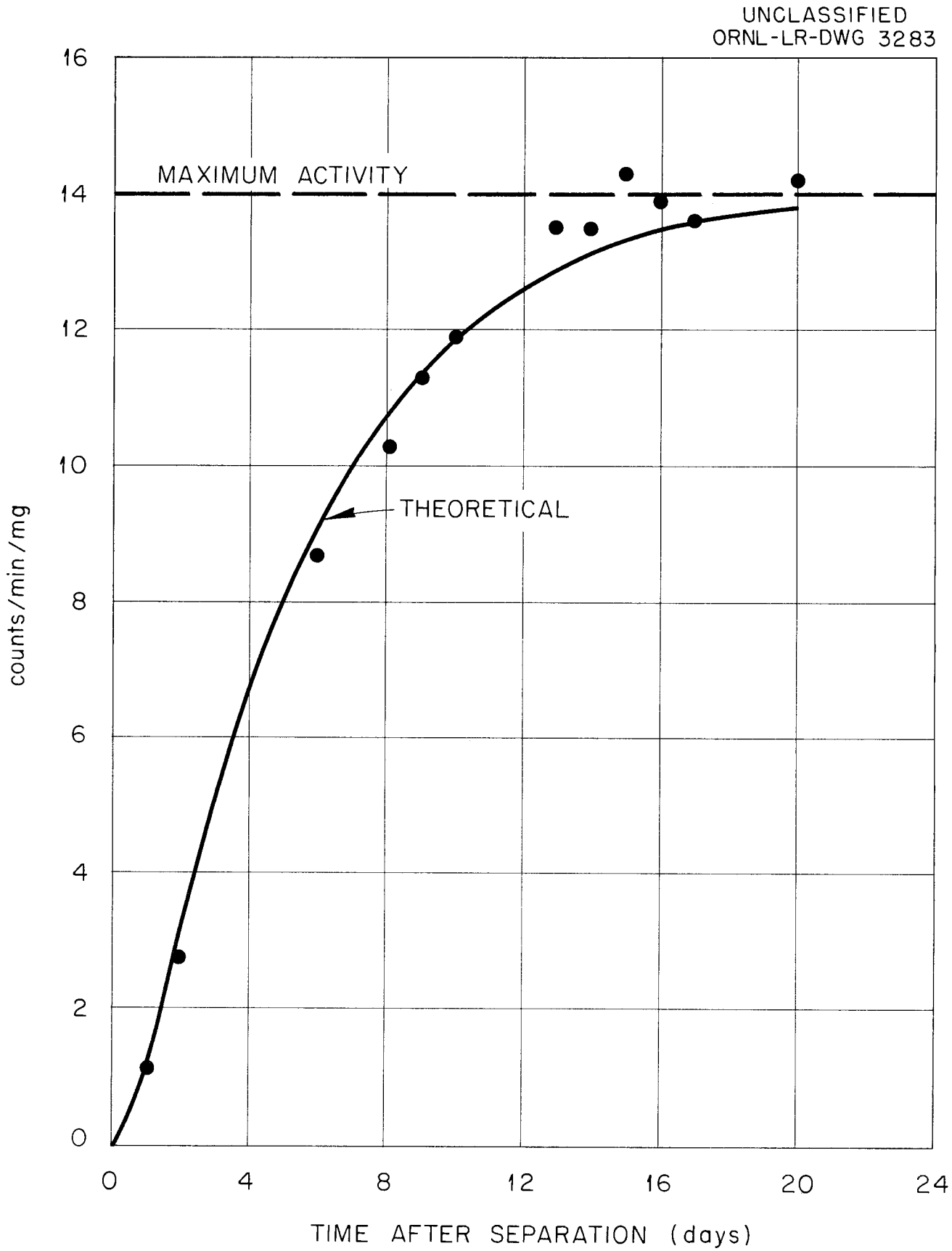

Fig. 8.2. Growth of Gamma Activity in Thorium.

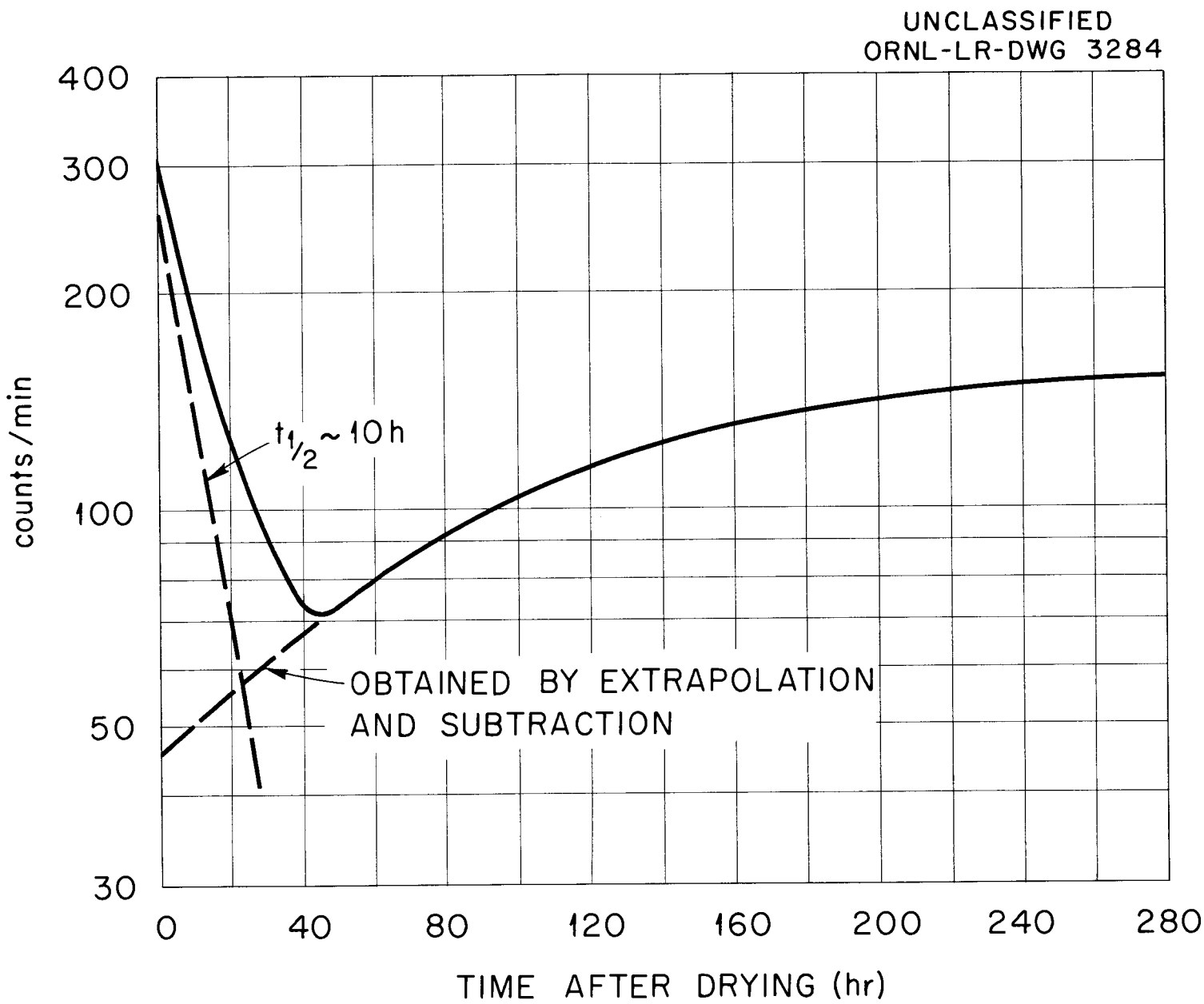

Fig. 8.3. Decay of Thorium Beta Activity.

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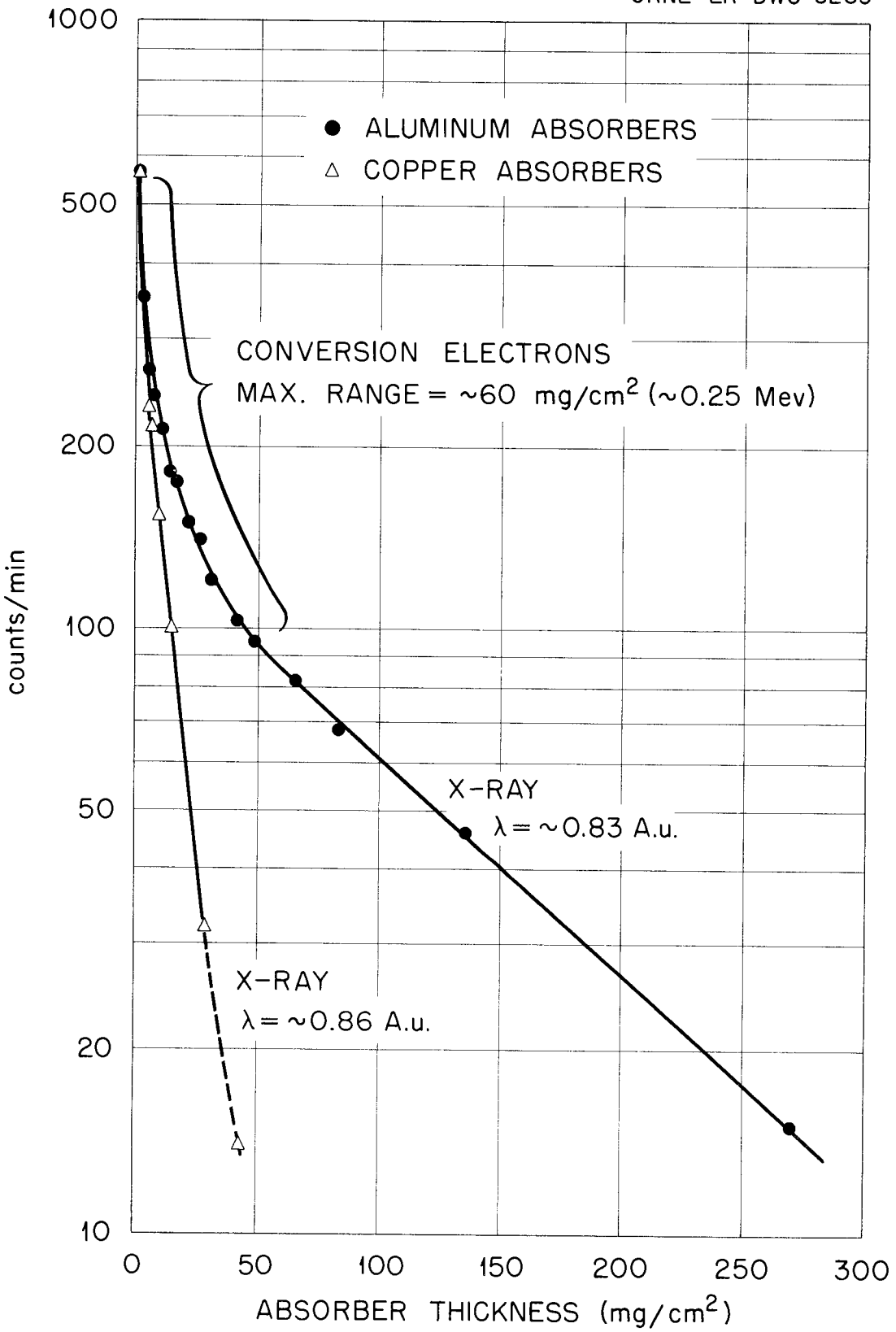

Fig. 8.4. U^{233} Absorption Curves.

Table 8.4. Growth of Thorium Daughters

Time after Separation (days)	Fraction of Maximum Activity	Time after Separation (days)	Fraction of Maximum Activity
0.5	0.025	6	0.649
1	0.085	8	0.766
2	0.229	10	0.848
3	0.362	12	0.901
4	0.476	14	0.937
5	0.571		

In studying U^{233} backgrounds, it was necessary to obtain very pure U^{233}. The material available, which was an Interim-23 process product, contained traces of fission products and possibly Pa^{233}.[ℓ] Additional purification was effected by two successive methylisobutyl ketone extractions of uranium from aluminum nitrate solutions[m] containing hydroxylamine hydrochloride to reduce the ruthenium.[n]

The absorption of electrons and x rays from U^{233} in aluminum and copper is shown in Fig. 8.4. The x-ray wavelength indicated is that characteristic of L radiation from elements in the thorium-uranium region; the K and M x rays are not easily detected by a Geiger-Mueller counter.

From gross beta measurements on U^{233} of known alpha activity, it was found that the apparent beta activity associated with 10^6 U^{233}

ℓ. E. I. Wyatt, H. P. Raaen, W. S. Lyon, Anal. Chem. Div. Quar. Prog. Rpt. for Jan. 10, 1953, ORNL-1474, p. 5 (March 11, 1953).

m. B. F. Rider, "Selected Analytical Methods for Purex Process Control," KAPL-890, p. 112 (April 30, 1953).

n. F. L. Moore, R. H. Powell, Chem. Div. Quar. Prog. Rpt. for Dec. 31, 1949, ORNL-607, p. 201 (March 7, 1950).

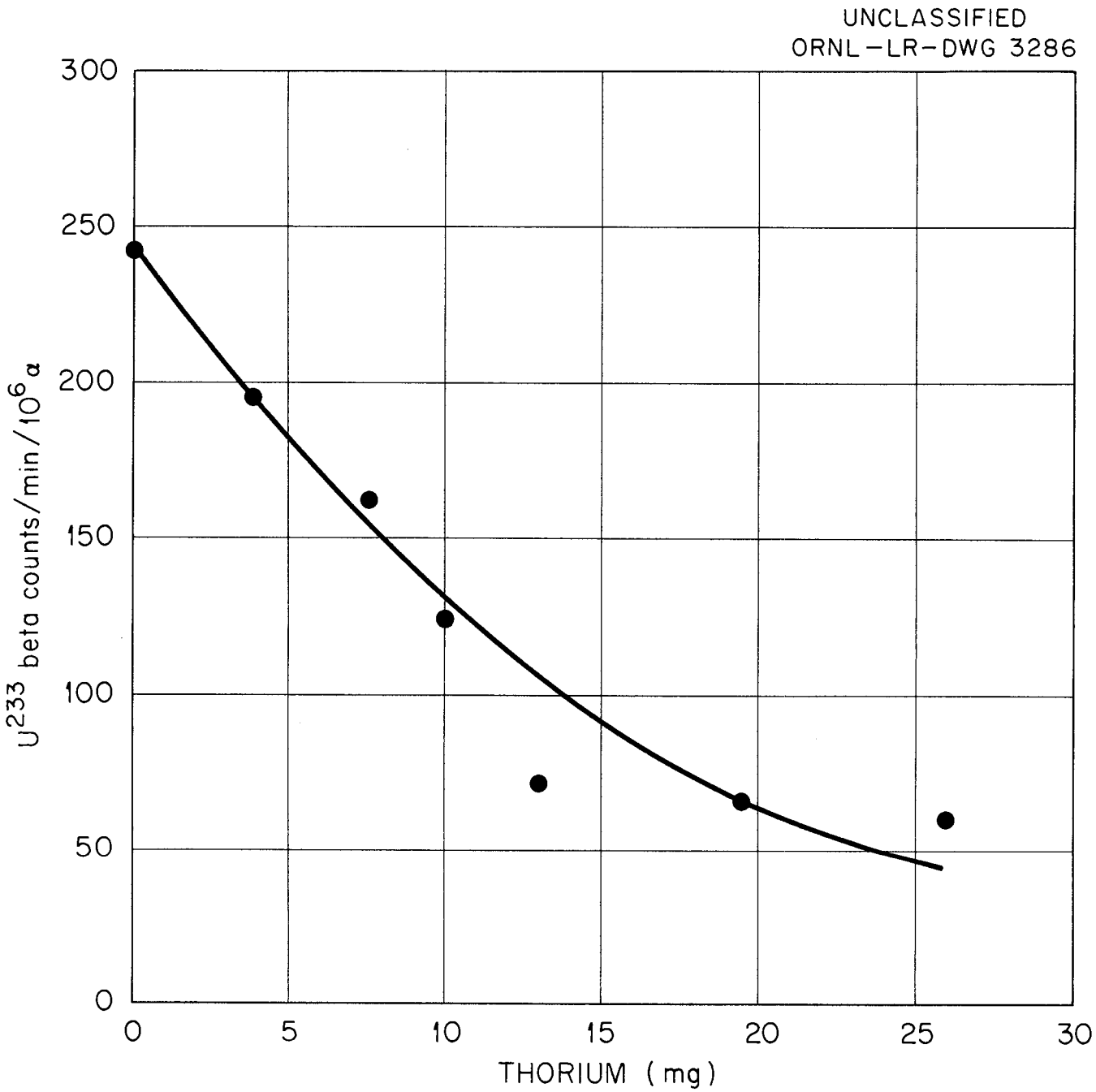

Fig. 8.5. Self-Absorption in Thorium Nitrate.

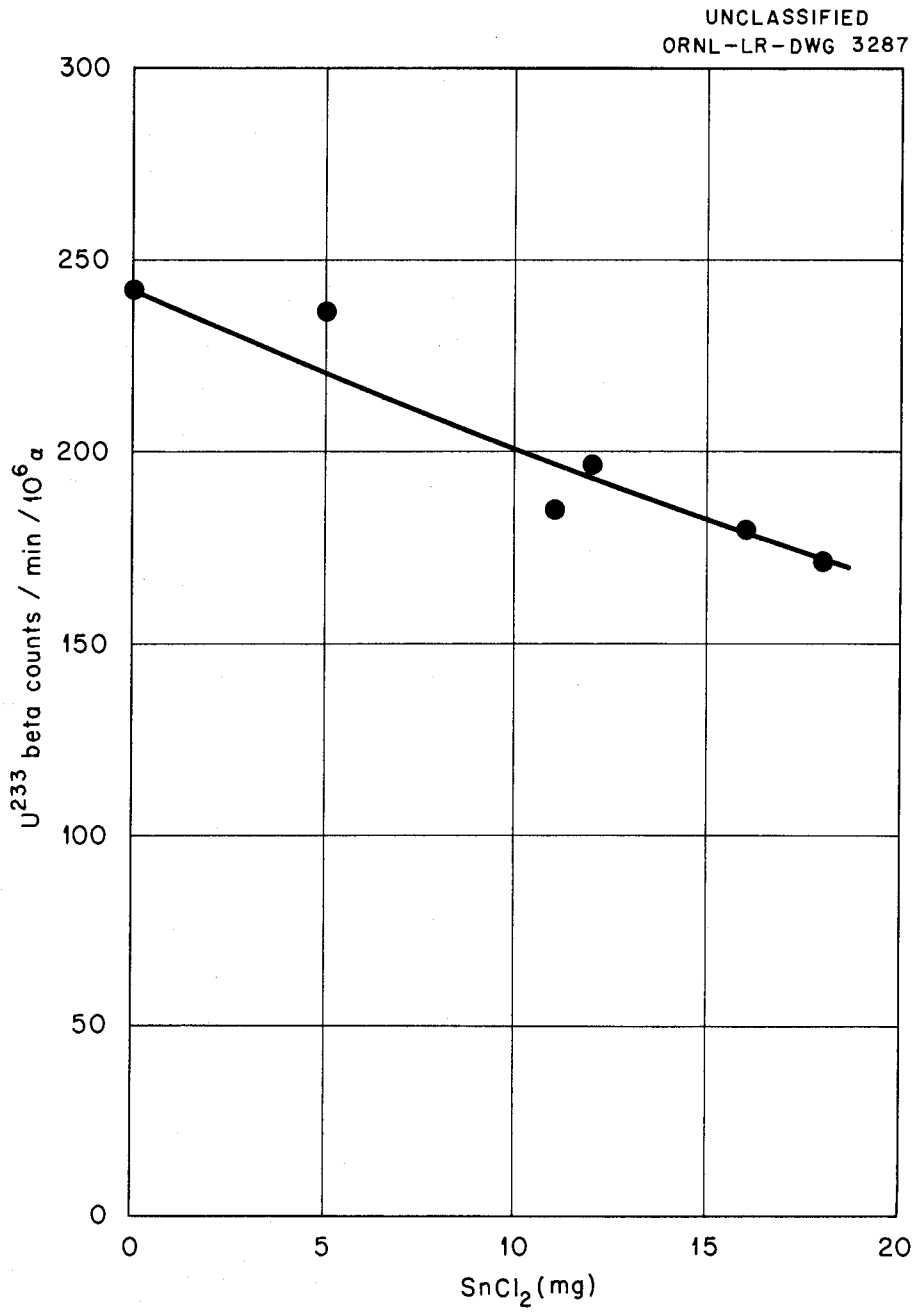

Fig. 8.6. Self-Absorption in Stannous Chloride.

alpha counts was 242 counts. The gamma activity equivalent to 10^6 U^{233} alpha counts was initially 33 ± 4 counts. The gamma activity increased after 50 days to 65 ± 9 counts. Measurements of gamma activity were difficult because of the high background, ~500 c/m, of the scintillation counter.

Since the radiations of U^{233} are strongly absorbed by matter, a considerable self-absorption correction[o] must be made if the gross beta samples contain solids. The absorption of electrons is roughly independent of the atomic number of the absorbing material,[p] but the absorption of x rays depends strongly on the absorber.[q] Therefore the self-absorption corrections for U^{233} were determined in thorium nitrate, which is present in some Thorex samples, and stannous chloride, which is added to gross beta mounts containing small amounts of solids. The data of Tables 8.5 and 8.6 were obtained by preparing solutions containing known amounts of U^{233} and absorbing material, either thorium nitrate or stannous chloride. It was necessary to correct for the thorium activity by preparing solutions containing the same amount of thorium and no U^{233}; the thorium activity was then subtracted from the corresponding thorium-U^{233} activity to obtain each self-absorption value. It is apparent from Figs. 8.5 and 8.6 that self-absorption in thorium nitrate is more pronounced than in stannous chloride.

8.3 Preparation of Acid-Deficient Aluminum Nitrate

Distillation of 2 M $Al(NO_3)_3$ solution at atmospheric pressure gave a residue which was determined to be monobasic aluminum nitrate. No

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o. G. Friedlander, J. W. Kennedy, op. cit., p. 229.
p. Ibid., p. 160.
q. Ibid., p. 168.

precipitates formed in the solution either during distillation or after standing several weeks. From distillate and feed concentrations and the respective volumes, the plot shown in Fig. 8.7 was developed.

Table 8.5. Self-absorption in Thorium Nitrate

Based on 10^6 U^{233} α c/m

Wt of Th (mg)	U^{233} β Activity (c/m)
0	242
3.8	195
7.5	162
10	124
13	72
19.5	66
26	60

Table 8.6. Self-absorption in Stannous Chloride

Based on 10^6 U^{233} α c/m

Wt of $SnCl_2$ (mg)	U^{233} β Activity (c/m)
0	242
5	236
11	185
12	197
16	180
18	172

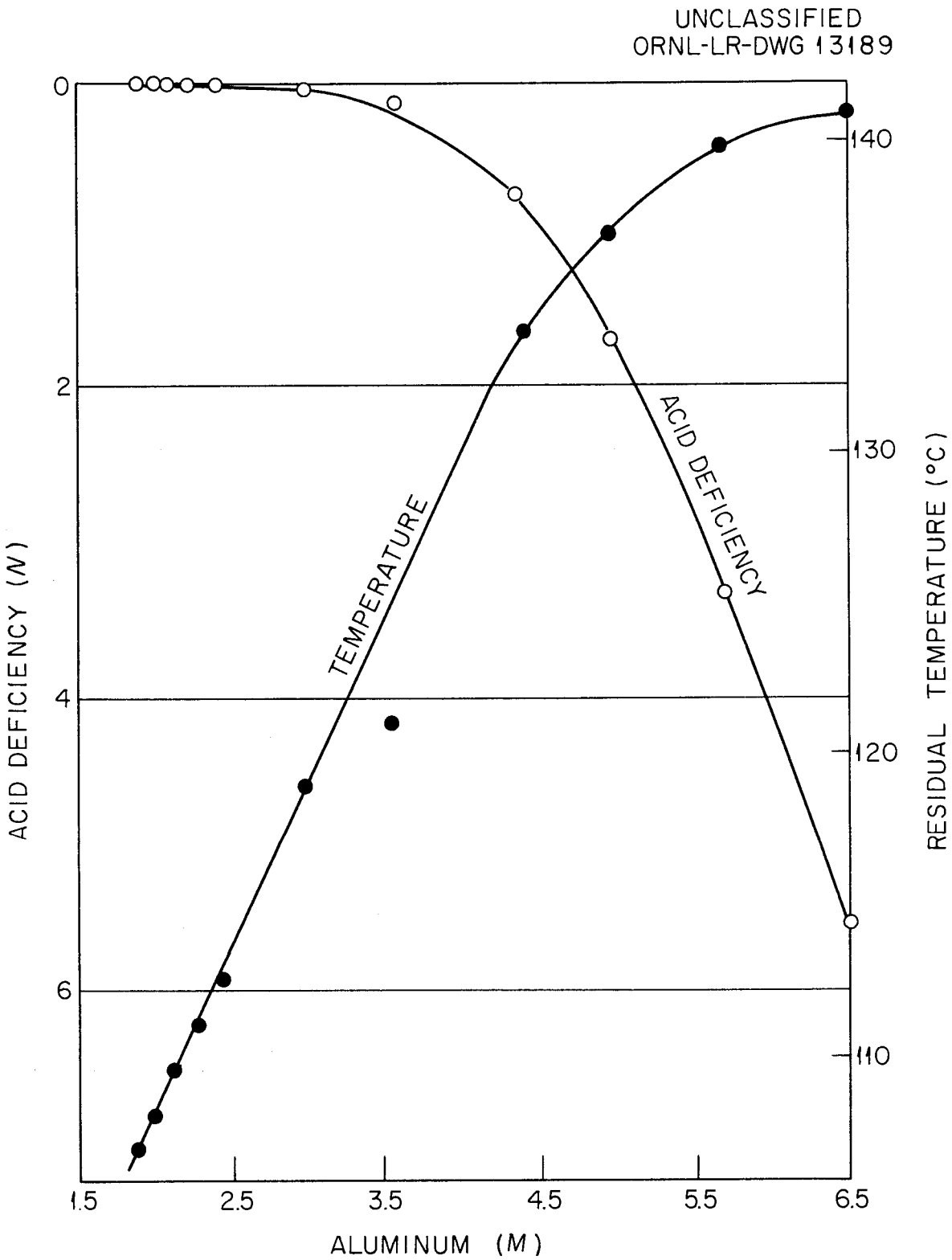

Fig. 8.7. Preparation of Acid-Deficient Aluminum Nitrate by Distillation-Evaporation of Neutral Aluminum Nitrate.