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LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT

August 1, 1953, to June 30, 1954

[redacted]

J. E. Savolainen

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT, August 1, 1953, to June 30, 1954

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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).

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CONTENTS

		Page No.
1.0	ABSTRACT	1
2.0	INTRODUCTION	1
3.0	EVAPORATION-DIGESTION STEP	6
3.1	Acidity of Distillate and Residue	6
3.2	Specific Gravity of Thorex Feed Solution	9
3.3	Crystallization in Feed Solution	11
3.4	Corrosion of Equipment	14
3.5	Ionic Contaminants	16
3.6	Concentration Limits of Final Feed	17
3.7	Effect of Aluminum Nitrate on the Thorium Nitrate—Nitric Acid System	18
4.0	BEHAVIOR OF FISSION PRODUCTS	20
4.1	Effect of Feed Adjustment Cycle on Ruthenium Extraction in A-Column	23
4.2	Disproportionation of Ruthenium Species in Relation to Acidity and Residence Time in Feed Solution	25
5.0	PROTACTINIUM RECOVERY	28
5.1	Storage of the Protactinium-Containing Stream	29
5.2	Recovery of Pa^{233} by Adsorption Techniques	32
5.3	Solvent Extraction of Pa^{233} with 42.5% TBP	37
6.0	APPENDIX	40
6.1	Preconditioning of Diluent	40
6.1.1	Procedure for Preconditioning of Diluent	40

Page No.

6.1.2 Analytical Method for Evaluating the Extent of Preconditioning 41

6.1.3 Comparison of Commercial Diluents by the Chromyl Chloride Method 43

6.1.4 Justification for Diluent Preconditioning 46

TABLES

3-1 Composition of Residue and Distillate Fractions during Evaporation-Digestion Cycle 8

3-2 Specific Gravity of Thorex Feed Solution during the Evaporation-Digestion Cycle as a Function of Temperature 11

3-3 Specific Gravity of a Thorex Feed Solution as a Function of Composition 13

3-4 Results of Crystallization Tests on Thorex Feed Solutions 14

3-5 Ionic Contaminants of Thorex Feed Solution 17

4-1 Fission Products in Distillate from Feed Adjustment Cycle 22

4-2 Change in Ruthenium Activity Level of Feed Adjustment Cycle Distillates at Various Fuel Processing Times after Discharge from Reactor 23

4-3 Decontamination Factors and Distribution Coefficients Obtained in Extraction Column as a Result of Feed Adjustment Step 24

5-1 Distribution of Uranium between Aqueous and TBP Solutions of Various Concentrations 31

5-2 Adsorptive Characteristics for Pa^{233} of Various Substances 33

Page No.

5-3 Effect of Time on Percentage of Pa^{233} Adsorbed by a Chromate Precipitate 35

6-1 Consumption of CrO_2Cl_2 by Treated and Nontreated Amsco 125-82 46

FIGURES

2-1 Thorex Process Chemical Flowsheet, June 1954 2

2-2 Feed Preparation System for Thorex Process 5

3-1 Conditions during Evaporation-Digestion Step of Feed Preparation Cycle of Thorex Process when 100% Excess Acid Is Used 7

3-2 Specific Gravity of Several Feed Solutions as a Function of Temperature 10

3-3 Variation in Specific Gravity with Change in Composition in Typical Evaporation-Digestion Cycle 12

3-4 Corrosion of Stainless Steel under Conditions of Evaporation-Digestion Step 15

3-5 Effect of Aluminum Nitrate on Thorium Nitrate-Nitric Acid System during Feed Preparation 19

4-1 Cooling of Total Ruthenium after Thorium Irradiation at 10^{13} $n/cm^2/sec$ Flux 21

4-2 Ruthenium Distribution Coefficients as a Function of Time Elapsed before Equilibration of Feed with Organic Stream 26

4-3 Ruthenium D.C.(O/A) as a Function of Acid Concentration of Initial Aqueous Phase at Various Equilibrium Time Intervals 27

		Page No.
5-1	Preliminary Schematic Flowsheet for U^{233} Recovery from Extraction Column Protactinium Stream	30
5-2	Percentage of Pa^{233} Adsorbed as a Function of the Chromate Concentration	34
5-3	Schematic Flowsheet for Pa^{233} Recovery from a Concentrated AP System by Chromate Scavenging	36
5-4	Effect of Additives on Protactinium Distribution Coefficient	38
6-1	Consumption of CrO_2Cl_2 by Treated and Nontreated Amsco 125-82	44
6-2	Comparison of Reactivity of Various Commercial Diluents by the CrO_2Cl_2 Test	45

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1.0 ABSTRACT

The currently recommended feed preparation cycle consists of batch dissolution of thorium slugs in excess nitric acid; concentration of the resulting solution by evaporation; digestion; and dilution with water to yield an acid-deficient feed. The solvent diluent (Amsco 125-82) is preconditioned with oleum. Protactinium will not be recovered; instead, when short-cooled fuel is processed, the extraction column aqueous waste will be stored and allowed to decay to U^{233}, which will eventually be recovered by an ion exchange process. A processing rate of 200 kg of thorium per day is planned for the pilot plant.

2.0 INTRODUCTION

In the current flowsheet (see Fig. 2-1) the aluminum-clad thorium slugs are dissolved batchwise in a 100% excess of 60% nitric acid, with mercuric and fluoride ions as catalysts, according to the reaction

$$\mathrm{Th} + 0.41\ \mathrm{Al} + 13.1\ \mathrm{HNO_3} \xrightarrow{\Delta,\ Hg^{++},\ F^-} \mathrm{Th(NO_3)_4} + 0.41\ \mathrm{Al(NO_3)_3} + 6.45\ \mathrm{HNO_3} + \text{nitrogen oxides.}$$

The excess nitric acid materially increases the thorium metal dissolution rate.

The advantages of the evaporation-digestion step are: (1) siliceous materials that might cause emulsions in the extraction column are dehydrated and rendered non-surface-active; (2) blue thorium contained in the slugs is dissolved completely, thereby lessening the thorium and associated uranium losses; (3) ruthenium decontamination factors in the extraction column are increased to 100-1000 in contrast to the 5-15

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APPROXIMATE STREAM COMPOSITIONS

Dissolvent	~13 M HNO_3, 0.04 M F^-, ~0.0025 M Hg^{++}, 0.04 M Al
MD	1.0 M Th, 0.4 M Al, 6.5 M H^+, ~0.2 g of U per liter
AF	1.5 M Th, 0.6 M Al, 0.2 M acid deficient, ~0.3 g of U per liter
AS	0.6 M Al, 0.4 M acid deficient, 0.002 M PO_4^{3-}, 0.005 M Fe^{++}
AX	42% TBP, 58% oleum-pretreated Amsco 125-82, 0.0 M H^+
AU	42% TBP, 0.29 M Th, 0.06 g of U per liter, 0.0 M HNO_3
BS	42% TBP, 58% oleum-pretreated Amsco 125-82, 0.0 M H^+
BX	0.005 to 0.01 M HNO_3
B'X	0.24 M HNO_3
BU	42% TBP, 0.045 g of U per liter, ~0.002 M HNO_3
BT	0.25 M Th, 0.20 M HNO_3
Thorium product	2.0 M Th, 1.4 M HNO_3
AP	0.6 M Al, 0.3 M acid deficient
Concentrated AP	~2.0 M Al, ~1.0 M acid deficient
CX	0.005 to 0.01 M HNO_3
CU	0.22 g of U per liter, 0.015 M HNO_3
CW	42% TBP, ~0.001 M HNO_3
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

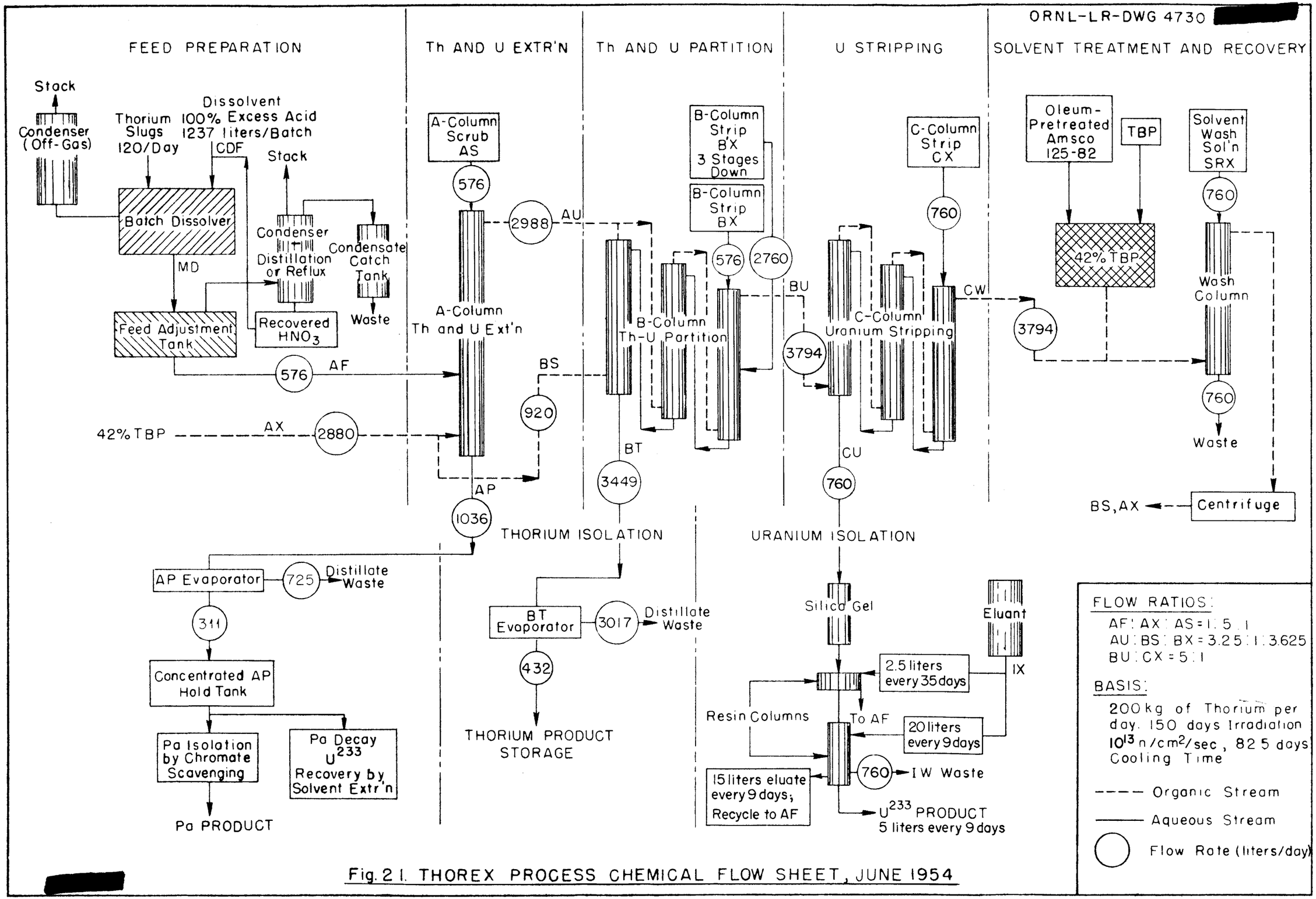

Fig. 2.1. THOREX PROCESS CHEMICAL FLOW SHEET, JUNE 1954

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previously obtained; and (4) the acid-deficient feed to the extraction process permits greater variations in the A-column solutions without disruptions in steady-state operation.

The silica can be dehydrated in 50, 75, and 100% excess acid dissolutions, but the rate of dehydration is increased with increased excess of acid. It is not necessary to remove the dehydrated silica prior to solvent extraction processing since silica in this form does not affect the extraction column efficiency.

About a 4-hr reflux-digestion period is required for complete dissolution of the blue thorium oxide. The ease of dissolution of this material is probably related to the length of the reactor irradiation or to the magnitude of the reactor flux. Short-term-irradiated (two weeks) thorium metal from the ORNL graphite reactor dissolves completely in the presence of a 50% excess of acid, but long-term-irradiated thorium metal from the Hanford reactors (containing approximately 1000 g of U^{233} per ton of thorium) dissolves incompletely even in the presence of a 75% excess of acid, leaving a blue thorium oxide residue. Based on these results, a 100% excess of acid is recommended to assure rapid and complete dissolution of the slugs.

The dissolver volume should be sufficient to contain a 10% metal heel from the previous dissolving and when fully charged should leave 200% freeboard.

The solution resulting from dissolution of the thorium slugs is discharged to the feed adjustment tank, where the excess acid is removed by fractional distillation, the feed adjustment tank serving as a reboiler (Fig. 2-2). The desired quantity of water is removed before the more concentrated nitric acid is distilled off. An obvious advantage of this system is the immediate concentration of the nitric acid distillate to 13 M by the addition to the existing equipment of only a small

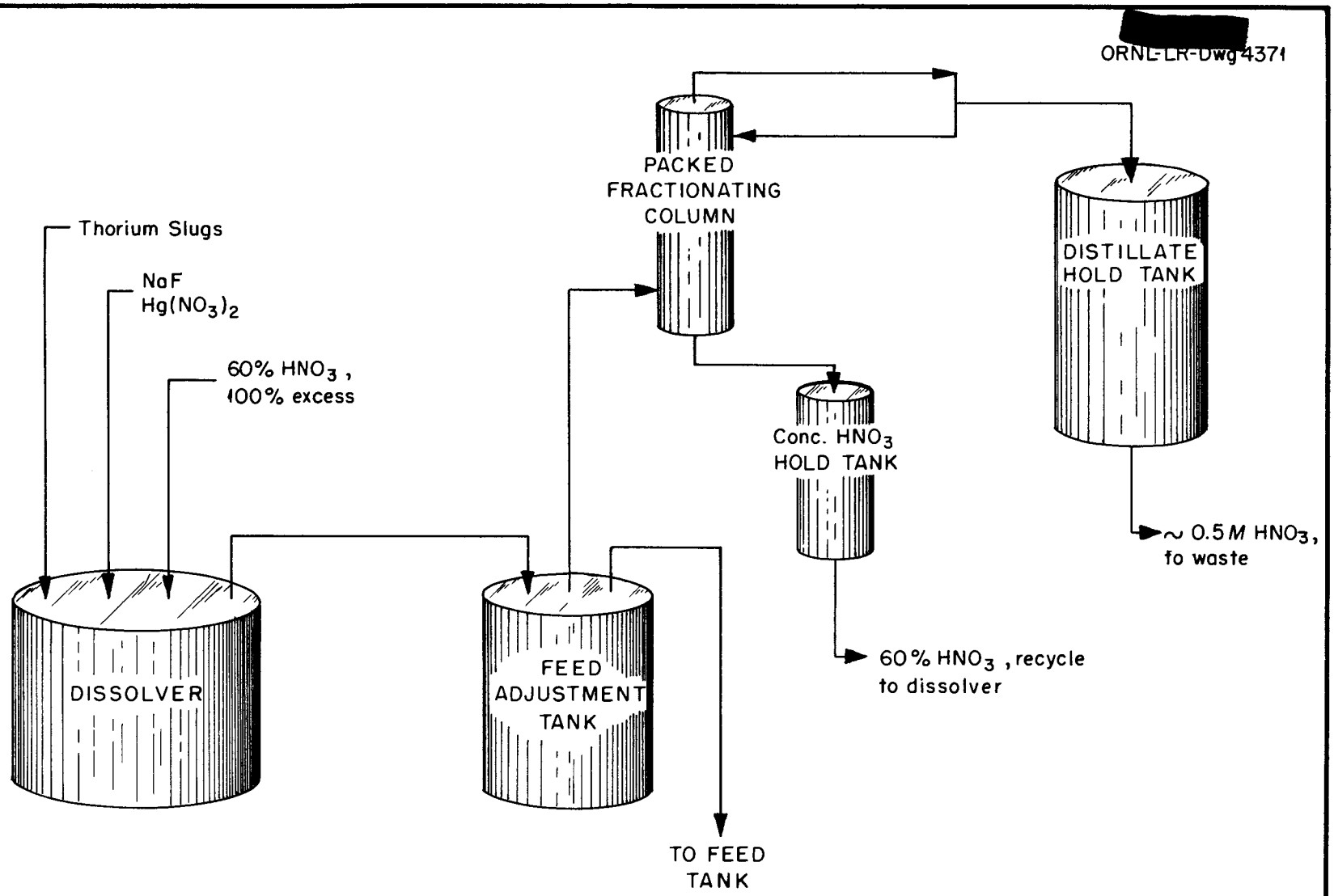

Fig. 2-2. Feed Preparation System for Thorex Process.

packed column.

The evaporation-digestion step was introduced into the process as a result of experiments reported in ORNL-1610. Further work was done on determining the effect of variables on the solution and equipment used in the process. Studies were also made of reagents for preconditioning the solvent diluent.

3.0 EVAPORATION-DIGESTION STEP

3.1 Acidity of Distillate and Residue

The acidity of the distillation residue rapidly reaches a maximum of 6.75 M at a thorium concentration of 1.33 M and then decreases almost linearly with increasing thorium concentration (see Fig. 3-1). This maximum value may be thought of as a region in which no "free water" is present, with only water of hydration remaining.

Variations in the acidity of the distillate and residue during the evaporation-digestion cycle were determined by taking distillate cuts of known volumes throughout a complete cycle and analyzing these cuts for nitric acid. From the data obtained (see Table 3-1) the acid and thorium concentrations of the pot residues were calculated.

During the distillation the major components of the solution apparently undergo a stepwise dehydration. First the nitric acid is dehydrated and distilled; then the aluminum nitrate is dehydrated until Al_2O_3 is formed. The thorium nitrate appears to have a stronger bonding force, and it is postulated that throughout the range of the experiment no thorium nitrate dehydration or denitration occurred. The regions in which these phenomena may occur are indicated in Fig. 3-1. The change

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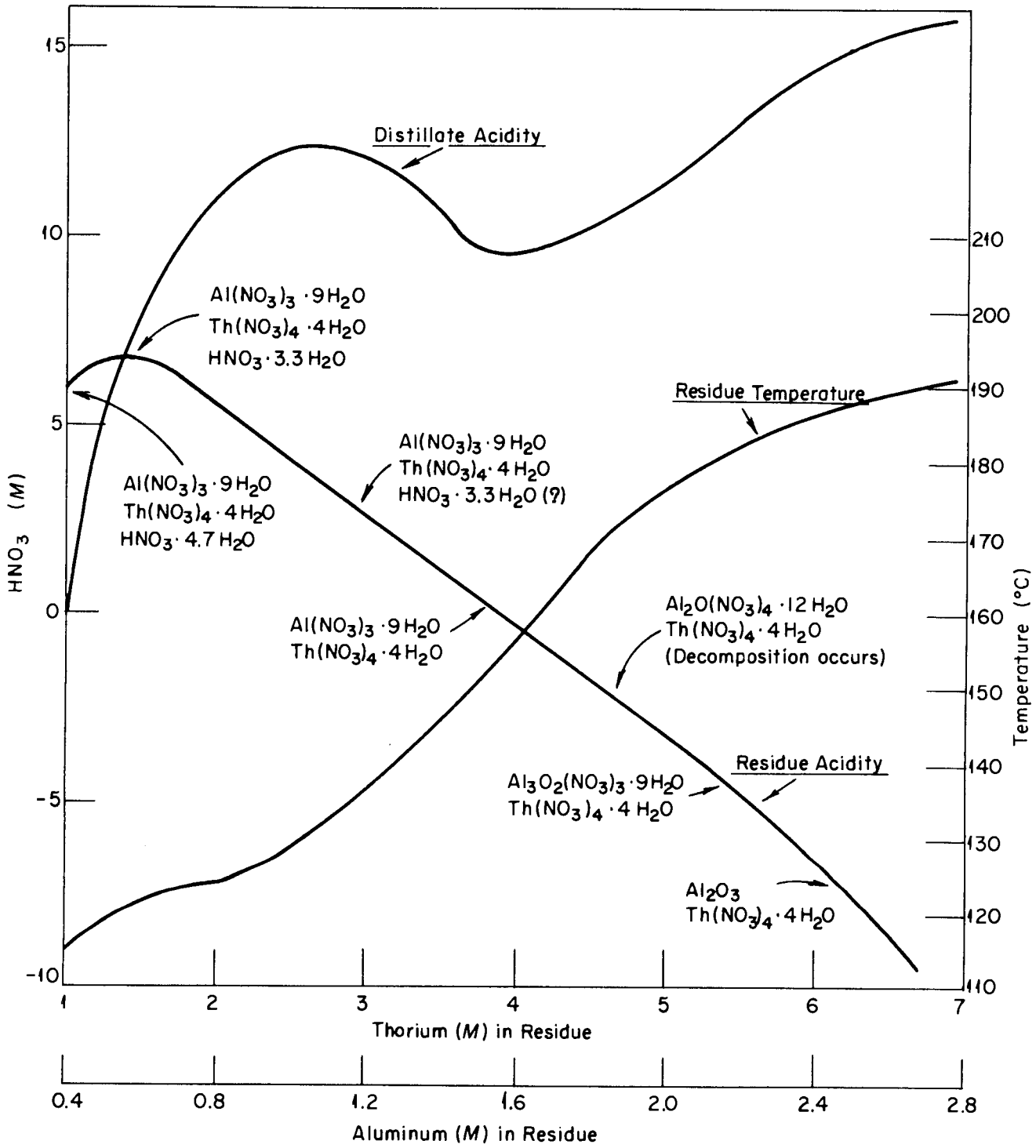

Fig. 3-1. Conditions during Evaporation-Digestion Step of Feed Preparation Cycle of Thorex Process when 100 % Excess Acid Is Used.

Table 3-1

Composition of Residue and Distillate Fractions during Evaporation-Digestion Cycle

100% excess acid; 10-ml distillate cuts

Distillate Acidity (M)	Calculated Residue Concentrations (M)		Liquid Temperature (°C)
	Thorium	HNO_3	
	1.01	6.07	115
1.66	1.05	6.30	116
3.4	1.11	6.47	117
4.2	1.18	6.60	118
5.0	1.25	6.70	119
6.0	1.33	6.75	120
7.0	1.43	6.72	120
8.2	1.54	6.60	121
9.2	1.67	6.40	122
10.35	1.82	6.02	123
11.1	2.00	5.52	124
11.9	2.22	4.82	126
12.25	2.50	3.88	129
12.3	2.86	2.68	134
11.2	3.33	1.25	142
9.9	3.64	0.47	149
9.6	4.0	-0.45	157
10.3	4.45	-1.65	167
11.6	5.0	-3.30	177
14.0	5.72	-5.75	185
15.5	6.66	-9.30	190

in nitric acid concentration in the distillate and the temperature of the pot residue are also plotted in Fig. 3-1 as functions of the thorium concentration of the residue.

3.2 Specific Gravity of Thorex Feed Solution

Data on the specific gravity changes during the evaporation-digestion step are important for design of control instruments. It was found that the specific gravity increased as the $[H^+]/[Th^{4+}]$ ratio decreased during the feed adjustment cycle. The specific gravity of any feed solution representative of the initial stages of the evaporation linearly decreased as the temperature increased.

For the temperature studies three solutions were used which were similar to those normally expected during the initial stages of the evaporation, i.e., from 1 to 1.8 M thorium. When the specific gravity was plotted against the temperature, each of the straight lines obtained was equidistant from the preceding one (see Fig. 3-2), indicating that the only effect was concentration. The temperature coefficients for the three systems were very close, the average being -0.00118 specific gravity units per degree centigrade (see Table 3-2). No data were obtained for systems more concentrated than 1.8 M thorium, 0.7 M aluminum, 6 M nitric acid since such solutions crystallize at about 70°C; however, it can be assumed that the temperature coefficient is approximately the same, since the only component depleted is nitric acid.

For the concentration studies a typical dissolver solution of concentration 1.0 M thorium, 0.4 M aluminum, and 6.5 M nitric acid was evaporated in stages, and the specific gravity was recorded by a hydrometer at intervals. The specific gravity was plotted against the ratio of hydrogen ion concentration to thorium ion concentration at

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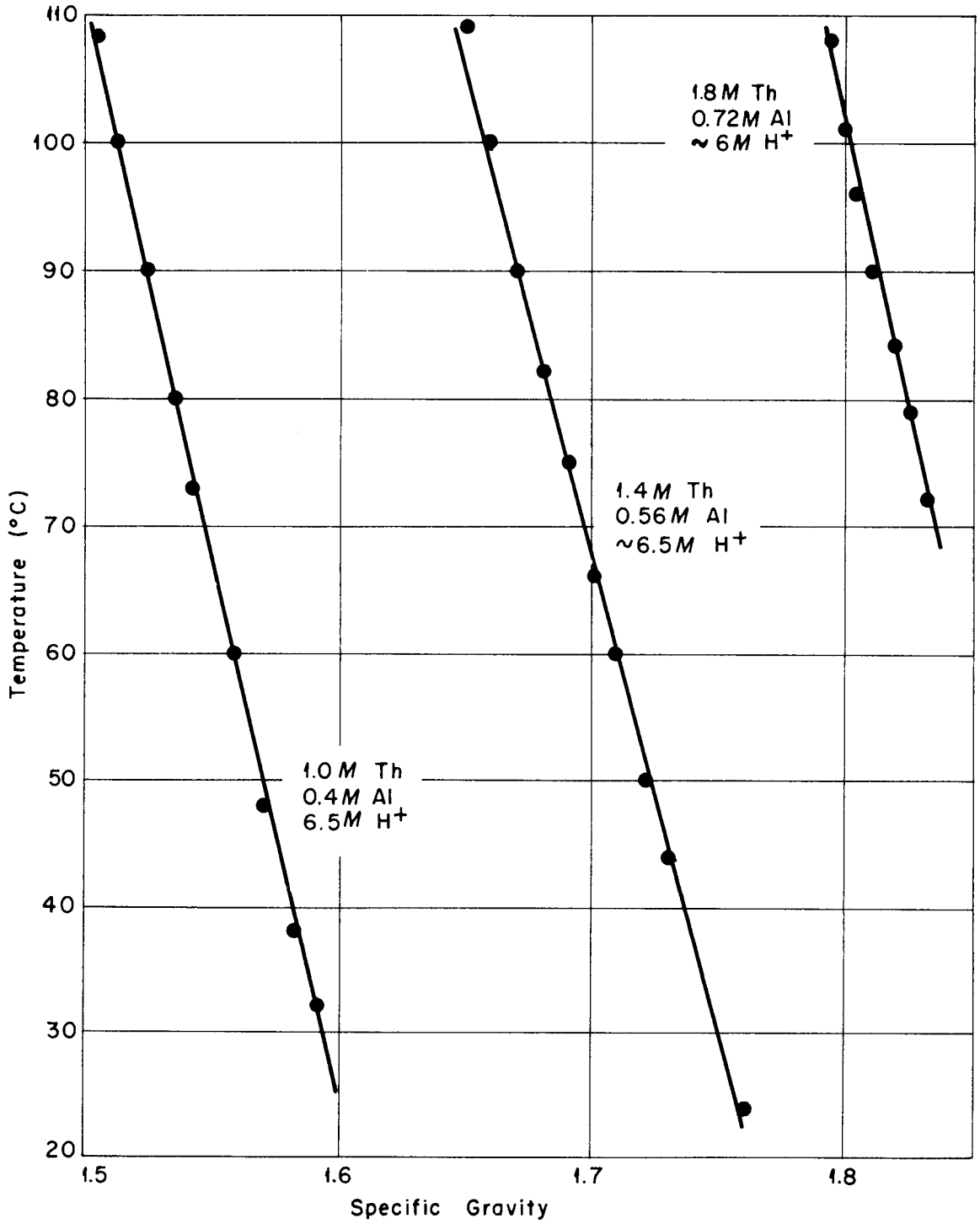

Fig. 3-2. Specific Gravity of Several Feed Solutions as a Function of Temperature.

103°C except for the $[H^+]/[Th^{4+}]$ zero value (see Fig. 3-3). Since a solution of this composition crystallized at about 130°C when cooled from the reflux temperature (see Table 3-3), this value was obtained by weighing a known volume of the solution and calculating the specific gravity at 103°C.

Table 3-2

Specific Gravity of Thorex Feed Solution during the Evaporation-Digestion Cycle as a Function of Temperature

Temperature (°C)	Th (M)	Al (M)	HNO_3 (M)	Specific Gravity	Sp. Gr. Units per °C
80	1.0	0.4	6.0	1.536	-0.00114
80	1.4	0.6	6.7	1.682	-0.00122
79	1.8	0.72	6.0	1.822	-0.00119
					-0.00118 (avg.)

3.3 Crystallization in Feed Solution

Results of crystallization tests on synthetic Thorex feed solutions (see Table 3-4) indicated that it will be possible to discharge the concentrated feed, i.e., 2 to 2.3 M thorium, 0.67 to 0.77 M aluminum, 0.33 to 0.38 M acid deficient, without crystallization at 40 to 50°C into a tank or drum containing dilution water. Feed solution of these

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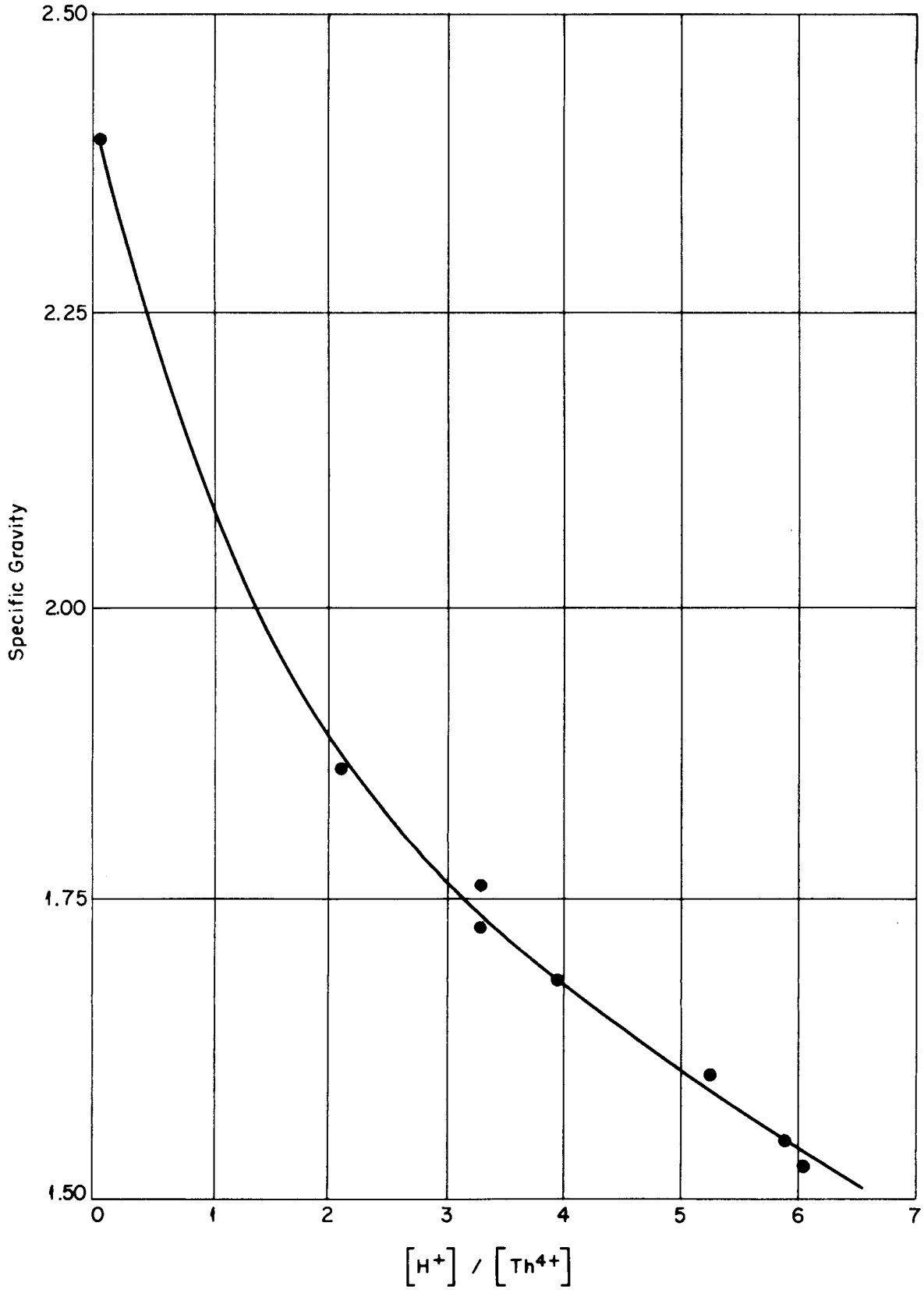

Fig. 3-3. Variation in Specific Gravity with Change in Composition in Typical Evaporation–Digestion Cycle. Temperature = 103 °C.

Table 3-3

Specific Gravity of a Thorex Feed Solution as a Function of Composition

Reflux Temperature (°C)	Temperature of Specific Gravity Determination (°C)	Specific Gravity	Thorium (M)	Nitric Acid (M)	Aluminum (M)	$[H^+]/[Th^{4+}]$
115.0	102	1.523	0.965	5.80	0.386	6.01
117.5	102	1.545	1.03	6.05	0.412	5.87
120.0	103	1.600	1.21	6.35	0.484	5.25
122.5	102	1.680	1.52	6.00	0.608	3.95
123.5	103	1.725	1.71	5.60	0.684	3.27
124.0	103	1.760	1.71	5.60	0.684	3.27
126.0	103	1.910	1.94	4.30	0.776	2.21
155.0	Calc. to 103	2.35 ± 0.05	~4	~0	~1.6	0

concentrations left in lines or pipes for an extended period of time would probably crystallize slowly.

Table 3-4

Results of Crystallization Tests on Thorex Feed Solutions

Approximate Solution Composition	Comments
2 M Th 0.67 M Al 0.33 M acid deficient	No crystallization at lowest temperature observed, 18°C; no crystallization when solution was seeded with thorium nitrate crystals
2.2 M Th 0.73 M Al 0.37 M acid deficient	No crystallization at lowest temperature observed, 18°C; when solution was seeded with a thorium nitrate crystal, small crystals appeared overnight; crystals redissolved at about 50°C
2.3 M Th 0.77 M Al 0.38 M acid deficient	No crystallization at lowest temperature observed, 18°C; when solution was seeded with a thorium nitrate crystal, small crystals appeared in 1 to 2 hr; crystals redissolved at 50 to 60°C

3.4 Corrosion of Equipment

Five different types of stainless steels were corroded at a rate higher than that normally considered satisfactory, i.e., 4 to 10 mils/year, under conditions simulating four different stages during the evaporation-digestion cycle. Type 309SNb, with a corrosion rate of about 25 mils/year, was the best specimen of those tested (see Fig. 3-4). The

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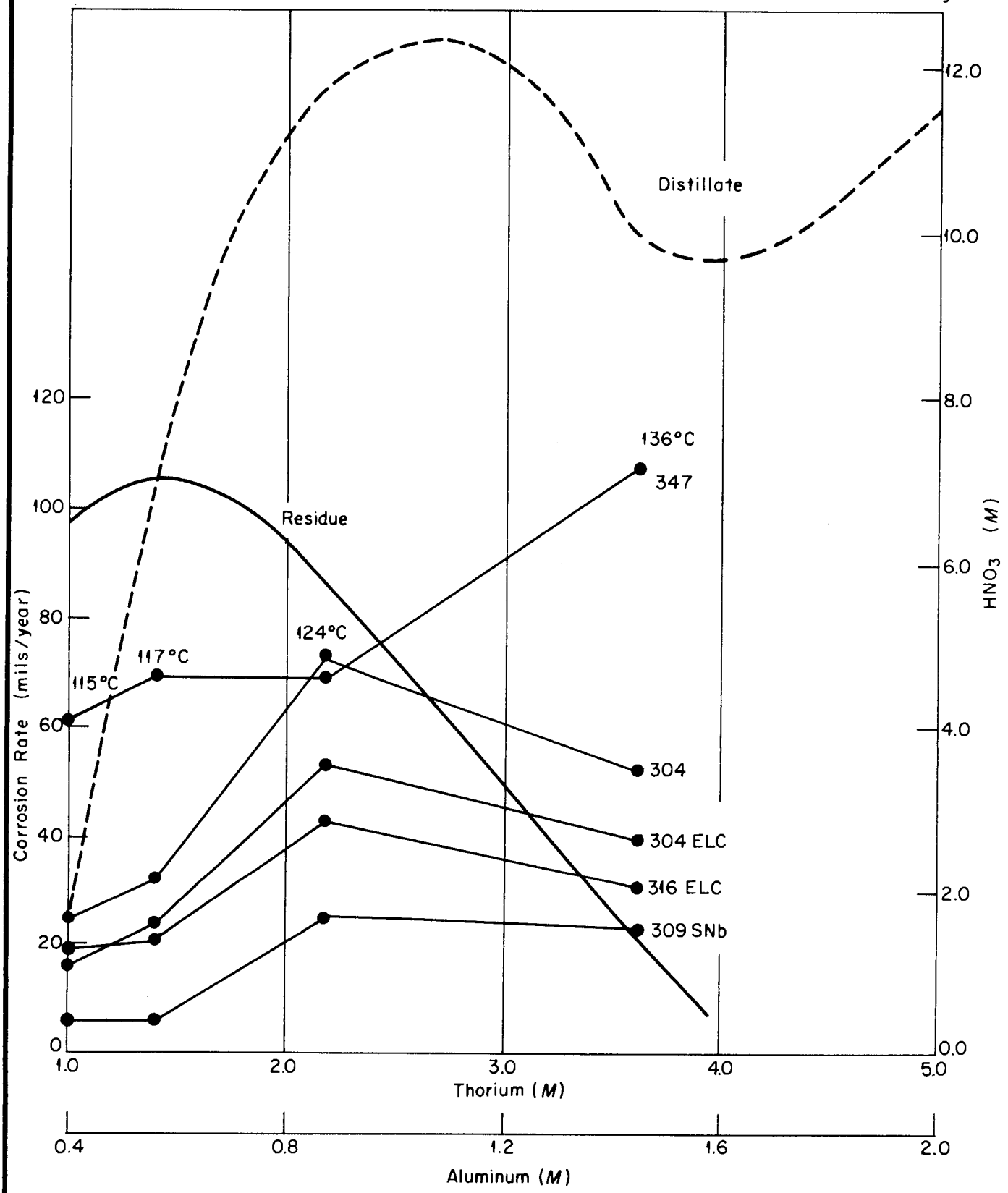

Fig. 3-4. Corrosion of Stainless Steel under Conditions of Evaporation-Digestion Step. Temperatures = boiling points of solutions.

tests were conducted for 100 hr under total reflux at the boiling temperature of the solutions. Corrosion rates were determined for each type of steel in the liquid phase, in the vapor phase, and at the liquid-vapor interface. The rate was essentially the same at the three positions. An acid concentration maximum of 12 M was apparent at approximately the same pot residue composition at which the maximum corrosion occurred. As the acid concentration of the distillate decreased, so did the corrosion rate of the stainless steel. It is expected that this region of high corrosion will exist for only a short period of time and that the overall corrosion will not be excessive. Type 309SNb stainless steel is used in the feed adjustment tank.

3.5 Ionic Contaminants

Of the several ionic contaminants (see Table 3-5) present in the Thorex dissolver solution, chromium is the chief element whose compounds are changed during the feed preparation. The chromium species are oxidized to the higher valence state, presumably chromic acid, as indicated by the yellow color of the feed after digestion. The yellow compounds would normally be extracted* by the organic stream in the A-column but are effectively prevented from being extracted by addition of a reducing agent, such as ferrous sulfate in the A-column scrub solution, which reduces the chromium to the tripositive valence state and thus prevents its extraction. The oxidizing normality of the digested feed was found to be ~0.077 meq/ml.

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* Drastic oxidation of the yellow organic-extracted species by hydrogen peroxide causes a bluish color in the organic phase, which is indicative of perchromic acid formation and chromate extraction. The chromic acid extraction in the absence of a reducing medium may correspond to the nitric acid extraction; e.g., the extraction may be written as $H_2CrO_4 + xTBP \rightleftharpoons H_2CrO_4 \cdot xTBP$.

Table 3-5

Ionic Contaminants of Thorex Feed Solution

Element	Approximate Concentration (ppm)	Approximate Concentration (M)
Fe	360	0.006
Nb	240	0.0025
Ni	60	0.001
Cr	56	0.001
Zr	9	---
Si	6	---

3.6 Concentration Limits of Final Feed

Extraction column feed prepared by the evaporation-digestion method may vary more than previously thought permissible. Since the thorium/aluminum ratio is constant with a batch dissolution, the acid deficiency is the only major ionic variable, and this has a wide range of operable concentrations. Operable feed concentrations are in the range 1.4 ± 0.1 M thorium, 0.55 ± 0.05 M aluminum, and 0.2 ± 0.1 M acid deficiency. Any large deviation in the acid deficiency of the feed could, if necessary, be compensated for by a corresponding change in the scrub acidity. Observations from countercurrent experiments indicate that column operation is satisfactory with any acid-deficient feed conforming to the specified thorium and aluminum concentrations. In addition, indications from laboratory countercurrent experiments on feed from a feed preparation

cycle where acid deficiency was not attained are that any feed which conformed to the above thorium and aluminum concentrations and is (1) slightly acid (approximately 0.1 M), (2) neutral, or (3) acid deficient (not over 0.5 M) will perform satisfactorily as far as column operation and decontamination are concerned.

3.7 Effect of Aluminum Nitrate on the Thorium Nitrate—Nitric Acid System

The overall effect of the presence of aluminum nitrate on the curve of nitric acid concentration vs. thorium concentration during the evaporation-digestion step is to shift the entire curve to the left on the thorium concentration axis (see Fig. 3-5). The two curves are similar in both the residue and distillate phases, the distillate acidity showing a distinct maximum and minimum in each case and the maximum occurring at the most severe corrosion conditions for the majority of the stainless steels tested (see Fig. 3-4). The vapor acidity minimum in each case occurred at the same thorium concentration as did the neutral point of the residue, i.e., the point at which no free acid was present. It is thought that after the neutral point of the residue or the minimum point of the distillate acidity is passed, the aluminum nitrate and/or thorium nitrate is denitrated to form an acid-deficient compound. Empirical calculations suggest that the denitration and dehydration proceed by stages and that in an aluminum nitrate—thorium nitrate solution the aluminum nitrate probably decomposes first.

If the evaporation of the thorium nitrate solution is carried to a high temperature, i.e., 230°C, and the resulting product is slurried with water, an acid-deficient water-insoluble thorium nitrate compound is formed. The compound has been tentatively calculated to be $Th_2(OH)(NO_3)_7 \cdot 7H_2O$.

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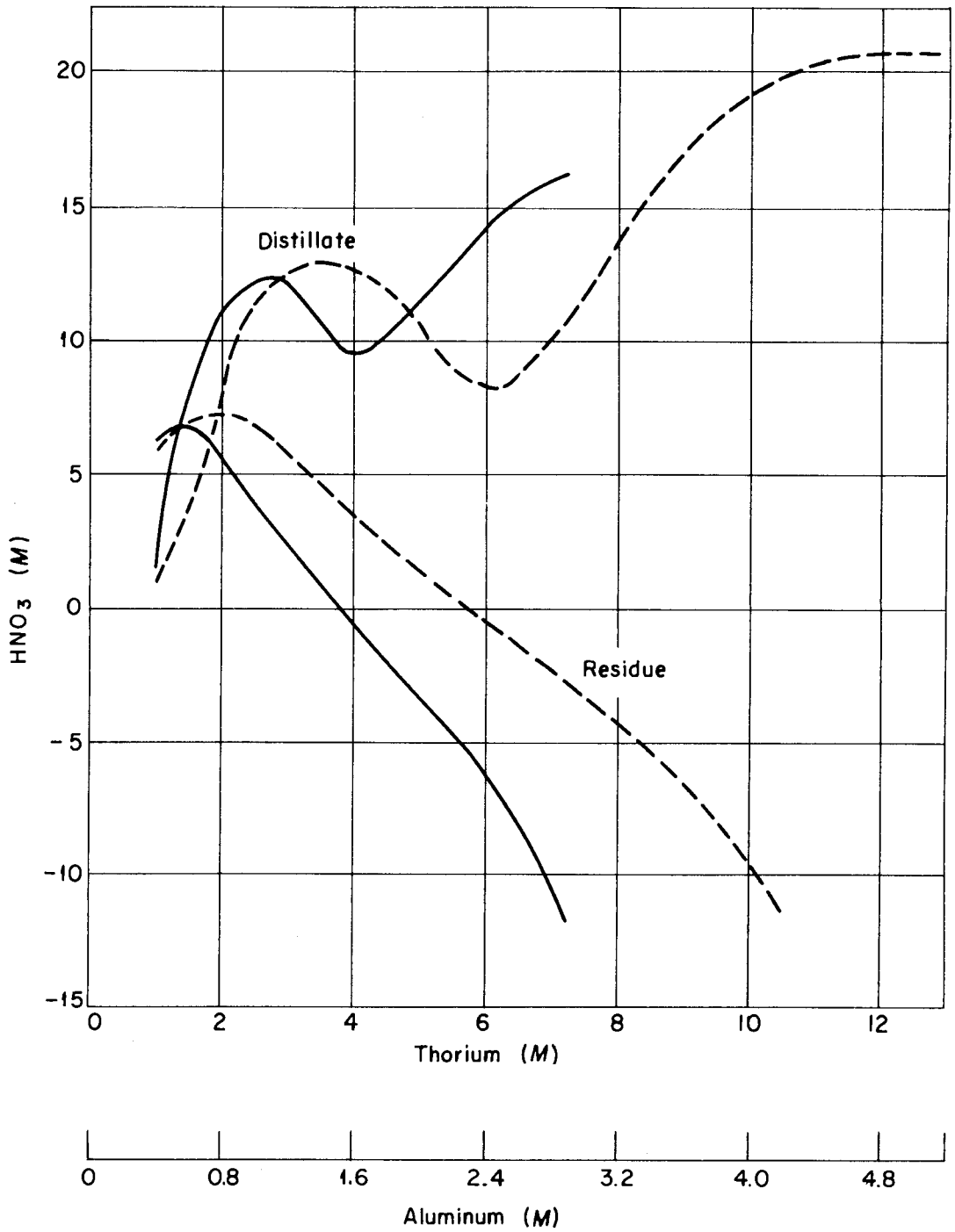

--- Thorium nitrate-nitric acid
—— Thorium nitrate-aluminum nitrate-nitric acid

Fig. 3-5. Effect of Aluminum Nitrate on Thorium Nitrate-Nitric Acid System during Feed Preparation.

4.0 BEHAVIOR OF FISSION PRODUCTS

The nitric acid that distilled off during the evaporation and digestion of feeds with activity representative of Thorex AF contained some beta and gamma activity, principally ruthenium. It is expected that in plant operation the bulk of the activity appearing in the distillate will result from ruthenium volatilization and from vapor entrainment of protactinium and rare earths. Vapor entrainment, however, should be materially reduced by the addition of the acid fractionation column to the feed adjustment cycle; no system for fractionation of the acid was used in the laboratory demonstrations.

As shown in Table 4-1, the bulk of the distillate activity was ruthenium when the distillation was carried out in laboratory-scale glass equipment. From 0.1 to 0.2% of the total ruthenium activity in the Thorex AF was volatilized and collected in the distillates. The Thorex AF used was dissolved thorium metal that had been irradiated at 2.8×10^{13} n/cm^2/sec for 83 days in the MTR to yield ~1000 g of U^{233} per ton of thorium; cooling time before processing was about 480 days.

Table 4-2 indicates the probable level of ruthenium activity in the distillates from the feed adjustment cycle after various cooling times of fuel elements containing 1000 g of U^{233} per ton of thorium. These values were calculated from data given in Fig. 4-1. The ruthenium volatilization to the distillate was assumed to be 0.2% of the feed activity, based on the experimental data given in Table 4-1. Therefore, even at 60 days' cooling time and assuming 0.2% volatilization, the distillate ruthenium activity should be of the order of 5×10^4 β c/m/ml. Carryover of this amount of activity should not be detrimental since the acid distillates will be reused as dissolving acid.

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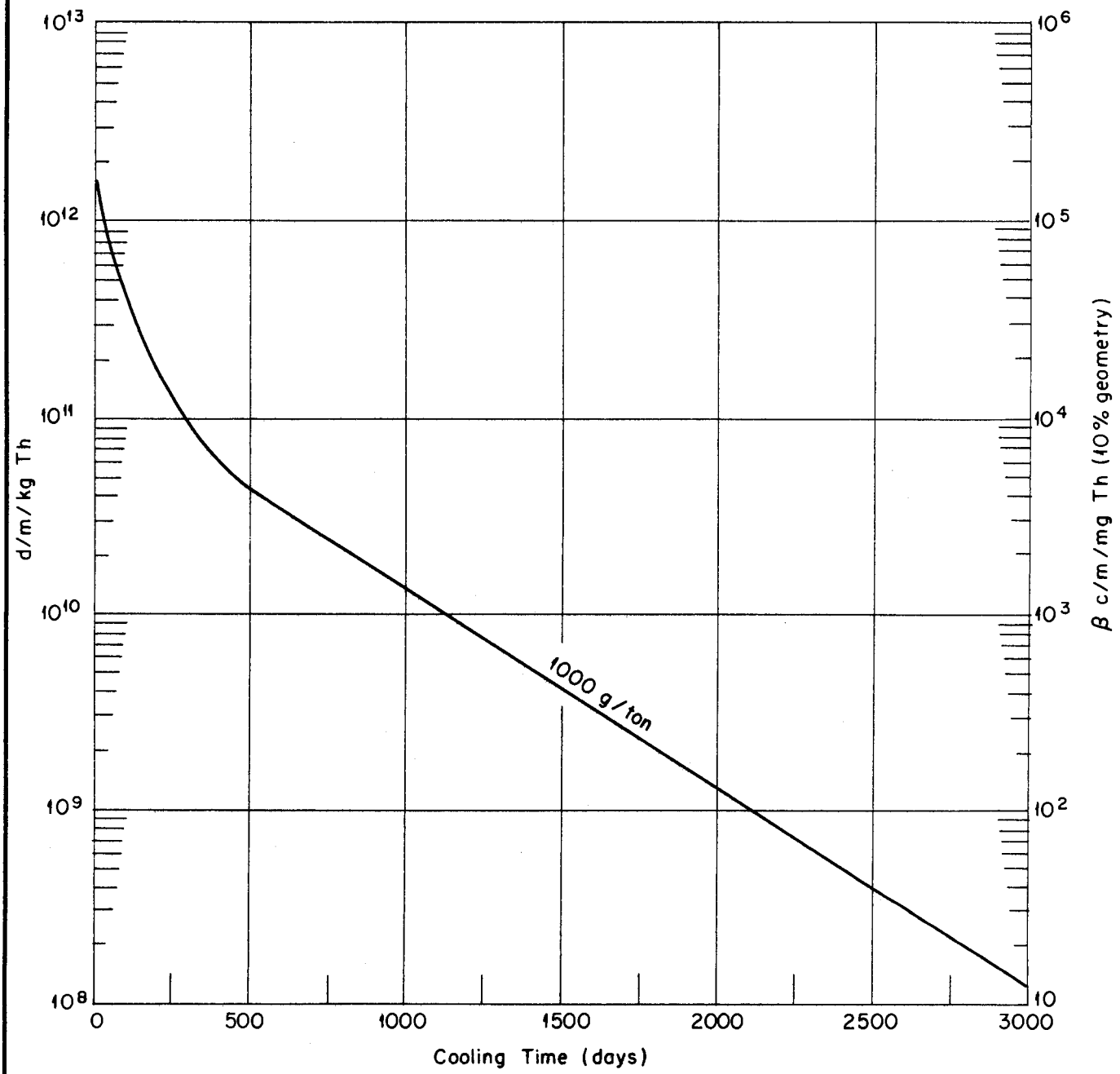

Fig. 4-1. Cooling of Total Ruthenium after Thorium Irradiation at 10^{13} n/cm^2/sec Flux.

Table 4-1

Fission Products in Distillate from Feed Adjustment Cycle

Run No.	Fission Product Activity (β c/m/ml)[a]						% Ru Volatilized during Acid Adjustment Cycle[b]
	In Thorex Dissolver Solution			In Feed Adjustment Step Distillate			
	Gross β	Ru β	Total Rare Earth β	Gross β	Ru β	Total Rare Earth β	
X-267	3.12×10^7	1.08×10^6	---	3.08×10^3	2.83×10^3	---	0.205
X-268	3.56×10^7	1.13×10^6	---	4.3×10^3	3.88×10^3	---	0.270
X-271	4.48×10^7	1.18×10^6	---	3.42×10^3	3.06×10^3	---	0.205
X-272	3.62×10^7	1.21×10^6	---	2.33×10^3	1.64×10^3	---	0.106
X-275	3.76×10^7	1.28×10^6	3.13×10^7	4.65×10^3	2.8×10^3	1.5×10^3	0.172
X-277	4.24×10^7	1.23×10^6	3.8×10^7	2.25×10^4	2.72×10^3	1.43×10^4	0.173
X-279	4.05×10^7	1.29×10^6	2.87×10^7	4.2×10^3	2.85×10^3	1.28×10^3	0.173
X-278	4.12×10^7	1.22×10^6	3.00×10^7	4.6×10^3	3.3×10^3	1.16×10^3	0.213

(a) Counted at 11% geometry.

(b) Based on feed activity before feed adjustment step.

Table 4-2

Change in Ruthenium Activity Level of Feed Adjustment Cycle Distillates at Various Fuel Processing Times after Discharge from Reactor[a]

Time Cooled after Discharge (days)	Ru (β c/m/ml)[b]	
	Thorex AF	Distillate from Feed Adjustment Cycle
60	2.5×10^7	5×10^4
90	1.8×10^7	3.6×10^4
120	1.0×10^7	2.0×10^4
180	7.0×10^6	1.4×10^4
280	3.5×10^6	7.0×10^3
360	2.5×10^6	5.0×10^3
400	2.1×10^6	4.2×10^3
540	1.4×10^6	2.8×10^3
660	1.1×10^6	2.2×10^3

(a) Calculated from values given in Fig. 4-1.

(b) Values calculated to 11% geometry.

4.1 Effect of Feed Adjustment Cycle on Ruthenium Extraction in A-Column

The feed adjustment cycle permits consistent and reproducible A-column decontamination factors for ruthenium of 200 or more (see Table 4-3). The ruthenium distribution coefficients in the extraction section of the A-column are of the order of 3×10^{-4} with this cycle as opposed

Table 4-3

Decontamination Factors and Distribution Coefficients Obtained in Extraction Column as a Result of Feed Adjustment Step

Run No.	Decontamination Factors		Ruthenium D.C.'s		HNO_3 in Feed (M)	Remarks
	Gross β	Ru β	8th Scrub Stage	5th Extraction Stage		
X-90	127	8	0.86	2×10^{-3}	0.56	Acid feed; no feed adjustment
X-169	96	8	1.03	0.016	0.60	Acid feed; no feed adjustment
X-199	2.8×10^{3}	238	0.74	3×10^{-4}	~0.15	Acid-deficient feed; feed adjusted
X-207	2.2×10^{3}	244	0.58	2×10^{-4}	~0.44	Acid-deficient feed; feed adjusted
X-208	1.5×10^{3}	160	0.62	3×10^{-4}	~0.46	Acid-deficient feed; feed adjusted
X-266	1.33×10^{4}	740	0.74	5×10^{-4}	~0.14	Feed adjustment in presence of 0.01 M Fe^{++}
X-268	1.31×10^{4}	823	0.84	6×10^{-4}	~0.20	Feed adjustment in presence of 0.01 M Fe^{++}
X-275	1.77×10^{4}	875	0.79	4×10^{-3}	~0.28	Feed adjustment in presence of 0.005 M Fe^{++}
X-279	1.03×10^{4}	940	1.37	5×10^{-4}	~0.06	Feed adjustment in presence of 0.0025 M Fe^{++}
X-278	1.68×10^{4}	1010	1.04	3×10^{-4}	~0.45	Feed adjustment in presence of type 309SNb stainless steel

to 0.02 - 0.002 obtained with the former flowsheet, using an acidic feed. A fraction of the ruthenium is extracted and is not scrubbed out as shown by the fact that the distribution coefficient at the eighth scrub stage or the top of the A-column ranges from $\sim$0.6 to greater than 1.0.

A definite beneficial effect upon the ruthenium decontamination factor was noticed when either ferrous sulfate was added to the dissolver solution before the feed was adjusted or the adjustment was carried out in a stainless steel vessel. As indicated in Table 4-3, the use of ferrous sulfate during the adjustment increased the ruthenium decontamination factor from about 200 to 740 - 940, and adjusting the feed in the presence of stainless steel gave a decontamination factor of $\sim 10^3$.

4.2 Disproportionation of Ruthenium Species in Relation to Acidity and Residence Time in Feed Solution

Previous studies (ORNL-1610, p. 46) indicated that changes in the acidity of and time of residence in an aqueous medium affect the distribution coefficients of the ruthenium species in the Thorex feed solution. Data obtained in recent experiments (see Fig. 4-2) showed that the ruthenium species in the feed were essentially at equilibrium after about 8 hr. Before this time, the ruthenium species' distribution coefficients apparently changed in a random manner, with the most marked deviations occurring in the period up to 5 hr. Acid-deficient conditions caused the least fluctuation of distribution coefficients throughout the time interval studied.

The maximum distribution coefficient was observed when the feed plate acidity was neutral to 0.5 M acid (see Fig. 4-3). The minimum values were found in the acid-deficient and high-acid ranges. From these experiments, the present Thorex conditions, i.e., 0.2 $\pm$ 0.1 M acid-deficient feed and

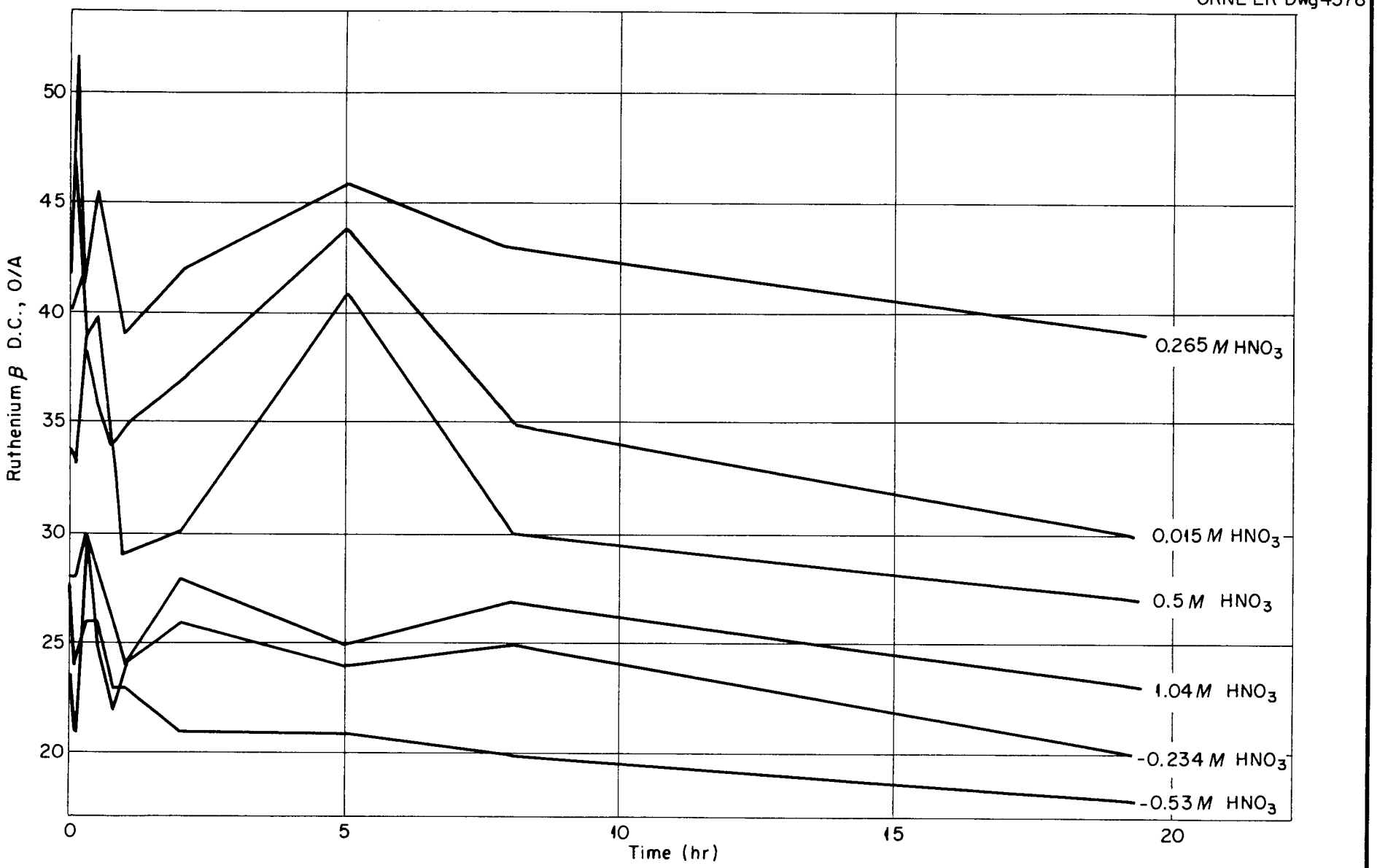

Fig. 4-2. Ruthenium Distribution Coefficients as a Function of Time Elapsed before Equilibration of Feed with Organic Stream. Feed plate conditions; single contact.

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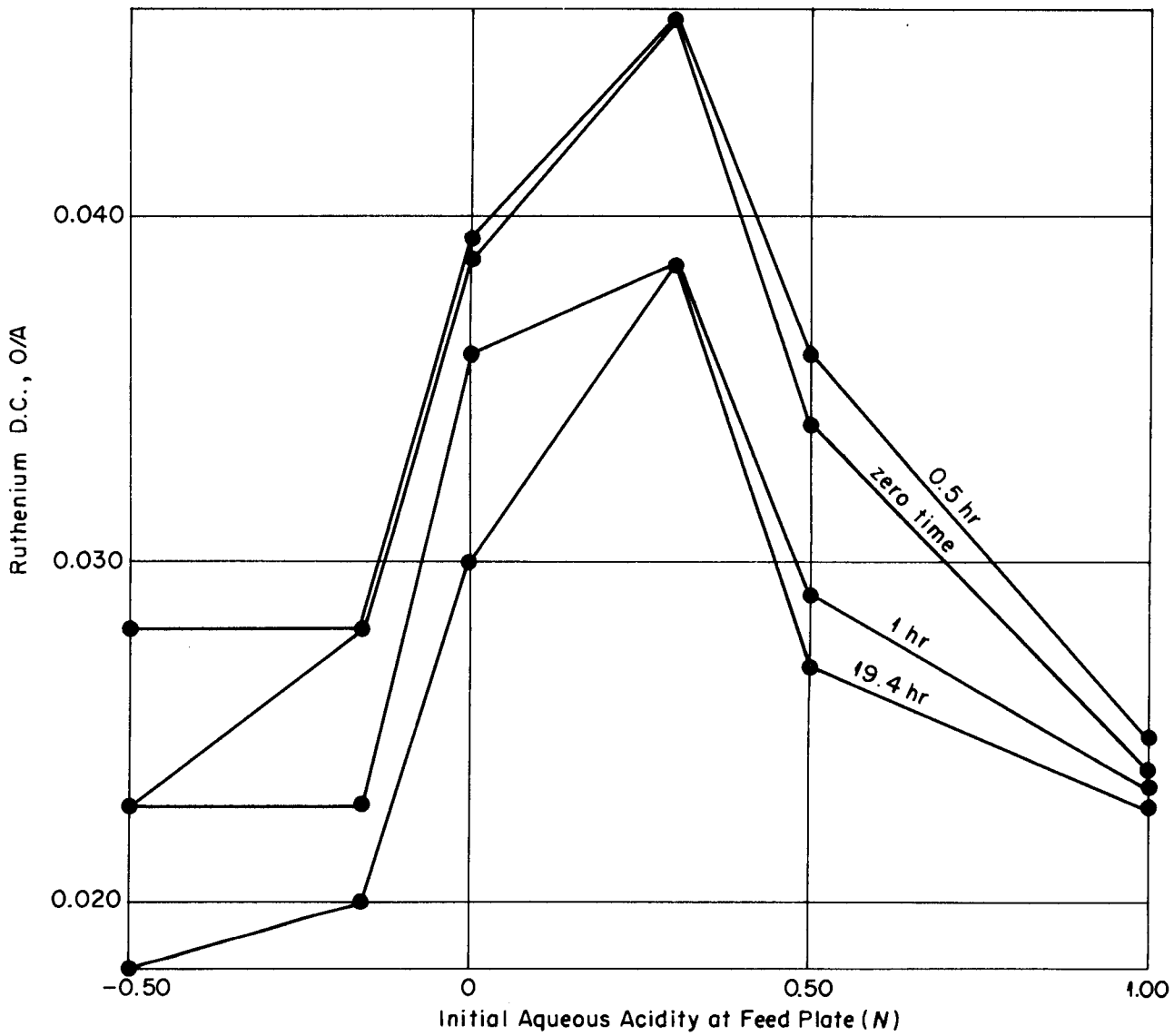

Fig. 4-3. Ruthenium D.C. (O/A) as a Function of Acid Concentration of Initial Aqueous Phase at Various Equilibrium Time Intervals.

0.25 ± 0.1 M acid deficiency at the feed plate and in the extraction section are the optimum for a low ruthenium organic-aqueous distribution coefficient and the resulting high (greater than 100) A-column decontamination factor.

The feed for the experiments was prepared by (1) evaporating and digesting acidic Thorex AF to attain acid deficiency; (2) neutralizing to zero acidity with dibasic aluminum nitrate; (3) spiking with Purex feed to give a sizable fraction of ruthenium activity; and (4) allowing the system to equilibrate overnight. This feed was made up to approximate the Thorex feed plate conditions, i.e., 0.75 M thorium, 0.6 M aluminum, 0.001 M phosphate ion, with a gross beta activity of 6.12×10^7 β c/m/ml (counted at 11% geometry in a Geiger-Mueller counter) at six acid concentrations, -0.53 to 1.04 M. The six solutions were prepared at essentially the same time to standardize the disproportionation effect. Immediately after being made up, the feeds were equilibrated for 1 min with 42.5% TBP in an aqueous/organic ratio of 1/2.5. This was arbitrarily taken as zero time. Additional samples were equilibrated at intervals up to about 20 hr.

5.0 PROTACTINIUM RECOVERY

Recovery of the Pa^{233} isotope in the Thorex process appears to be of minor interest at the present time. The advantages of a protactinium recovery process are (1) the decay product of separated Pa^{233} would provide isotopically pure U^{233} for physical and nuclear measurements; (2) the processing of short-cooled fuel elements would be possible without excessive losses of U^{233} as Pa^{233} in the raffinates; and (3) the long

term storage of large quantities of irradiated thorium, necessary to decrease the U^{233} losses in a program that does not allow for Pa^{233} recovery, would be eliminated.

Present indications are that storage of the protactinium solution from the extraction column and eventual recovery of the U^{233} formed by decay will be the most satisfactory method of recovering the U^{233}. A satisfactory but more complicated system of Pa^{233} recovery is the chromate adsorption technique. Solvent extraction of Pa^{233} has not been successful, and results have been extremely erratic.

5.1 Storage of the Protactinium-Containing Stream

This scheme involves concentrating the AP stream to about one third its volume, storing the concentrate, and recovering the U^{233} by a solvent extraction process after allowing a period for protactinium decay (see Fig. 5-1). It is expected that, in the dilute TBP system proposed, better decontamination will be obtained than in a more concentrated TBP system, although the uranium distribution coefficient (O/A) would be greater with higher percentages of TBP (see Table 5-1). The use of spray columns and aqueous-to-organic flow ratios of 10/1 or 100/1 should give concentration factors of 30 to 300 for the U^{233} from the dilute AP solution to the final strip volume before ion exchange. The stripped uranium solution can be put through ion exchange columns without additional treatment since this stream has about the same composition as the Thorex CU stream.

The obvious disadvantages are (1) storage facilities during the protactinium decay period must be provided; (2) TBP of a different concentration from that used in the Thorex process proper is used, which entails

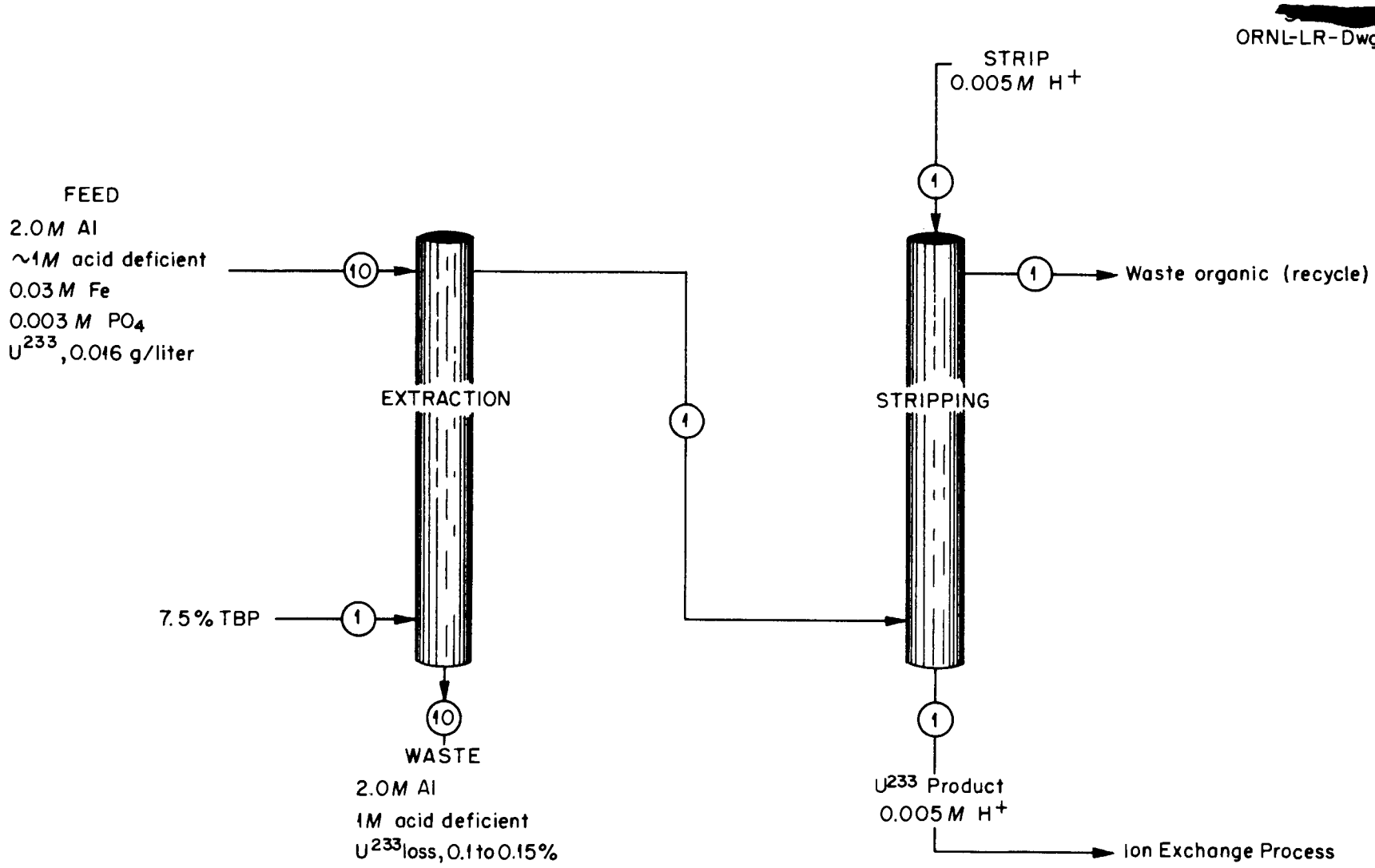

Fig. 5-1. Preliminary Schematic Flowsheet for U^{233} Recovery from Extraction Column Protactinium Stream. Circled numbers are volume flow ratios.

providing a separate solvent makeup and recovery system; and (3) this system will not recover isotopically pure U^{233} if it should be desired at a future date. Some of the advantages of this scheme are (1) higher thorium and uranium losses can be tolerated in the A-column since essentially a second cycle is involved; (2) U^{233} recovery from a stream less radioactive than that from which the protactinium would be recovered reduces the shielding requirement; and (3) U^{233} recovery is essentially complete.

Table 5-1

Distribution of Uranium between Aqueous and TBP Solutions of Various Concentrations

Feed: aluminum, 2 M; acid deficiency, 1 M; uranium, 56 μg/ml
Aqueous/organic flow ratio: 1/1

TBP (%)	Uranium (μg/ml)		Uranium Distribution Coefficient, O/A
	Organic	Aqueous	
1.7	33	1.3	25.4
3.5	43	0.32	135
7.5	42	0.09	467
22	43	0.03	1390
31	43	0.03	1430
44	45	0.03	1550

5.2 Recovery of Pa^{233} by Adsorption Techniques

As an alternate to the method discussed in Sec. 5.1, several adsorptive agents in common use were checked for their Pa^{233} adsorption characteristics. The combination of silica gel and 0.06 M chromate and that of bentonite clay and 0.06 M chromate recovered about 80% of the Pa^{233} from a Thorex process solution of the composition 0.6 M aluminum, 0.17 M acid deficient, and corrosion products representative of thorium metal slugs dissolved in a type 347 stainless steel dissolver. Recovery of Pa^{233} with 0.06 M chromate alone was slightly less than either combination, but all other agents tested recovered considerably less (see Table 5-2). Recovery of Pa^{233} from the actual process solution with silica gel was essentially zero. The 99% recovery values by silica gel adsorption reported earlier (ORNL-1431, p. 39) were obtained with synthetic solutions containing no corrosion products or other impurities representative of dissolved metal slugs.

The amount of Pa^{233} adsorbed increased with the length of time the chromate precipitate remained in contact with the AP solution (see Table 5-3). The data indicate that the chromate adsorbent that formed in the AP solution required 4 to 6 hr for 85 to 95% adsorption and at least 1 hr for 80% adsorption. The solution used for the experiments was a process AP solution, 0.6 M aluminum, 0.25 M acid deficient, to which was added variable amounts of sodium chromate. The precipitate was allowed to form and then centrifuged.

The composition of the chromate precipitate has not been completely determined, but the compound is tentatively thought to have the formula $Al_2(CrO_4)(NO_3)_4 \cdot 12H_2O$. It is noncrystalline and its formation is dependent upon the acid deficiency of the aluminum nitrate solution since it does not form in an acidic or neutral aluminum nitrate system.

Table 5-2

Adsorptive Characteristics for Pa^{233} of Various Substances

Process AP solution; 0.6 M Al; 0.18 M acid deficient
Additive agitated for 10 min, centrifuged 15 min
Supernatant analyzed for Pa β c/m/ml; percentage adsorbed based on original solution

Substance	Pa^{233} Adsorbed (%)	Substance	Pa^{233} Adsorbed (%)
Alumina	0.0	Silica gel + 0.1 M Na_2CrO_4	39.8
Silica gel	0.0	0.06 M Na_2CrO_4	72.4
$Zr_3(PO_4)_4$	0.0	0.06 M Na_2CrO_4 + bentonite	81
$Zr(OH)_4$	2.0	0.06 M Na_2CrO_4 + silica gel	82
$Al(CrO_4)NO_3$	7.3		
Bentonite	36.2		

If the A-column raffinate is concentrated by a factor of 3 and the concentration adjusted to 0.1 to 0.5 M sodium chromate, more than 90% of the Pa^{233} will be adsorbed on the chromate precipitate. As shown in Fig. 5.2 (curve A), the percentage of Pa^{233} adsorbed increased in a curvilinear manner as the chromate concentration increased. An adsorption maximum through a narrow chromate concentration range did not exist in this system, as was observed in the dilute AP chromate adsorption procedure described above and shown as curve B in Fig. 5-2 and also as Fig. 4-10, ORNL-1610, p. 53.

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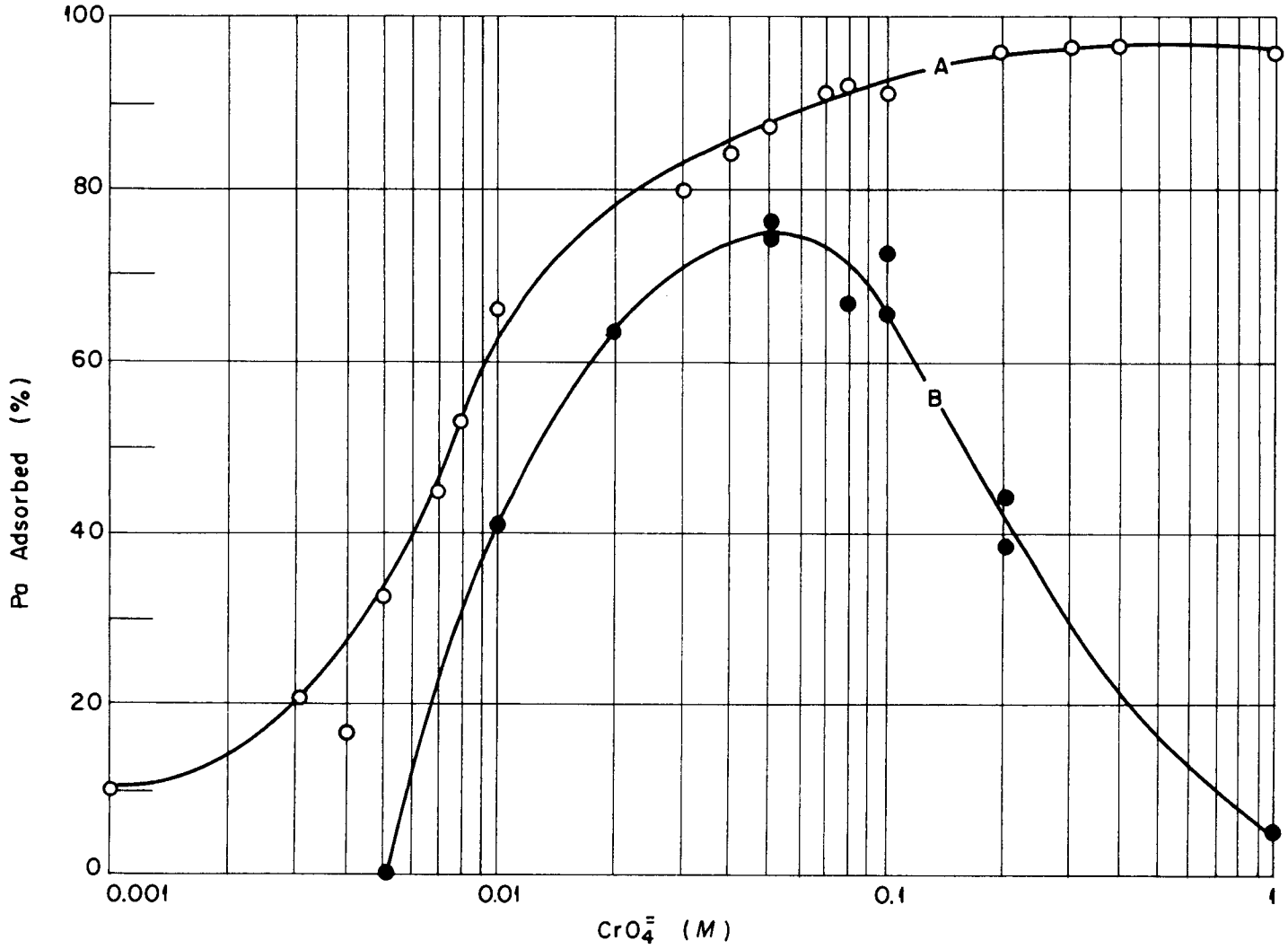

A: AP solution, concentrated 3.3 times; 2.0 *M* Al, 1.1 *M* acid deficient; digested 2 hr at 95°C, centrifuged 0.5 hr.

B: AP solution; 0.6 *M* Al, 0.25 *M* acid deficient

Fig. 5-2. Percentage of Pa^{233} Adsorbed as a Function of the Chromate Concentration. Comparison of dilute and concentrated systems.

Table 5-3

Effect of Time on Percentage of Pa^{233} Adsorbed by a Chromate Precipitate

Synthetic AP solution, 0.6 M in aluminum, 0.057 M acid deficient; 0.06 M $CrO_4^{=}$
Chromate precipitate was allowed to form and then centrifuged; supernatant analyzed for Pa β c/m/ml

Chromate Residence Time (min)	Pa Remaining in Supernatant (c/m/ml)	Adsorption (%)
Feed	3.80×10^5	---
10	1.14×10^5	70.0
20	1.78×10^5	53.2
30	1.05×10^5	72.4
60	7.04×10^4	81.7
120	5.20×10^4	86.4
180	6.96×10^4	82.0
240	6.80×10^4	83.8
300	3.30×10^4	91.4
360	2.62×10^4	93.3

The flowsheet for Pa^{233} recovery from a concentrated AP solution is shown in Fig. 5-3. The A-column raffinate, 0.6 M aluminum, 0.3 M acid deficient, is adjusted to 0.03 to 0.1 M sodium chromate and concentrated by a factor of about 3. The chromate precipitate which forms is

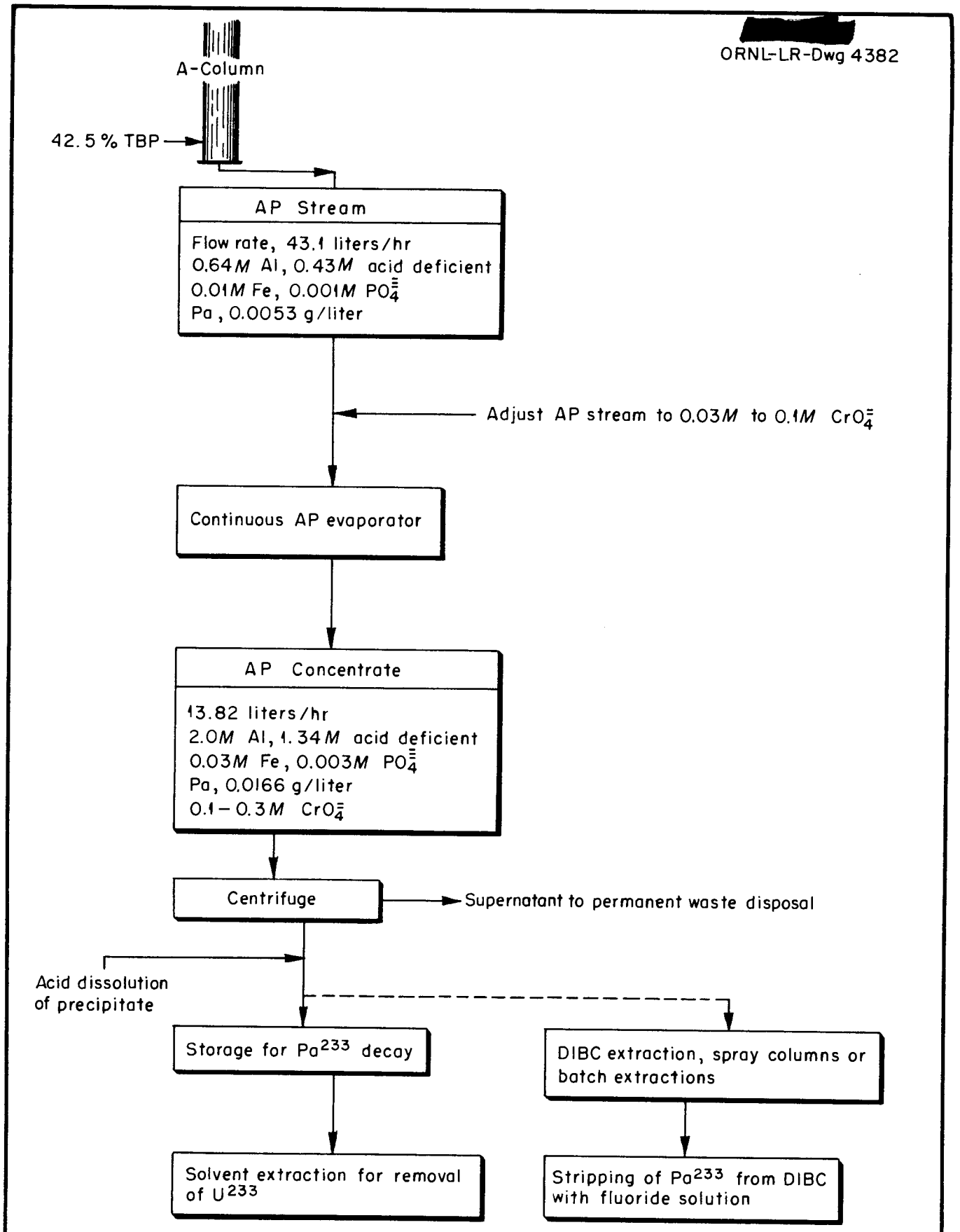

Fig. 5-3. Schematic Flowsheet for Pa^{233} Recovery from a Concentrated AP System by Chromate Scavenging.

centrifuged away from the supernatant, which will be disposed of as permanent storage wastes. The precipitate can be readily dissolved in acid for more convenient storage or handling.

The protactinium can be purified by a small-scale diisobutyl carbinol solvent extraction process, for example, that described in ORNL-1518, p. 53. Large aqueous-to-organic flow ratios may be utilized and final stripping accomplished with an aqueous sodium fluoride solution.

As an alternate to the DIBC solvent extraction procedure, the solution resulting from the dissolution of the chromate precipitate may be stored until the Pa^{233} has decayed and provisions made for subsequent recovery of U^{233}. This step would involve addition of Diban (dibasic aluminum nitrate) or aluminum nitrate to provide a sufficient salting strength, reduction of the chromate to the chromic ion to prevent chromate extraction, and then utilization of a solvent extraction technique with high aqueous-to-organic flow ratios in a dilute TBP system to obtain satisfactory fission product decontamination. The uranium can be satisfactorily stripped from the organic phase by dilute acid.

5.3 Solvent Extraction of Pa^{233} with 42.5% TBP

Recovery of protactinium by solvent extraction methods has not been successfully demonstrated. The behavior of Pa^{233} in an organic-aqueous system is very erratic, with changeable distribution coefficients. Two additives, chromic acid and titanous trichloride, were used to obtain drastic oxidizing and reducing conditions, respectively, and to observe their effect upon the extraction behavior of protactinium. As shown in Fig. 5-4, the distribution coefficient remained essentially constant after two batch equilibrations with 42.5% TBP saturated with nitric acid. The

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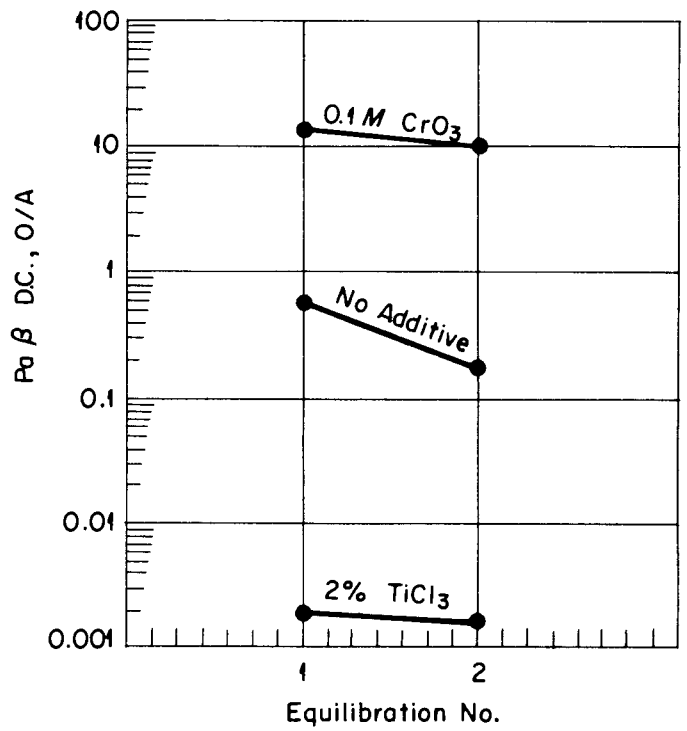

Aqueous phase: 1.7 *M* Al, 2.0 *M* HNO_3
Organic phase: 42.5 % TBP, saturated with HNO_3
Flow ratio: O/A = 1/1
2 min contacting time; two equilibrations

Fig. 5-4. Effect of Additives on Protactinium Distribution Coefficient.

addition of 0.1 M chromic acid caused about a 24-fold increase in the distribution coefficient in a control run in which no chromic acid was present, as constrasted to about a 275-fold decrease when the system was adjusted to 2% titanous trichloride. These experiments utilized 42.5% TBP saturated with nitric acid, contacted for 2 min with an aqueous phase of the composition 1.7 M aluminum, 2.0 M HNO_3, in a volume ratio of 1 to 1.

6.0 APPENDIX

6.1 Preconditioning of Diluent

Any hydrocarbon diluent considered satisfactory for making up 42.5% TBP for use in the Thorex process should be free from acid, alkali, suspended material, olefins, and aromatics. A typical analysis of untreated Amsco 125-82 is:

Color, Saybolt	+30
Doctor	Sweet
Corrosion	Passes
Odor	None
Distillation range, 760 mm Hg	
IBP	178°C
10%	181°C
50%	184°C
90%	194°C
EP	202°C
Flash point, Tag closed cup	53.3°C
API gravity, 15.6/15.6°C	55.5
Specific gravity, 15.6/15.6°C	0.7567
Density, lb/gal, 15.6/15.6°C	6.3
Kauri butanol value	26.2
Straight aniline point	85°C
Amount of unsaturated compounds present	~ 0.6 vol %

6.1.1 Procedure for Preconditioning of Diluent

Pretreatment of the diluent is aimed at removing impurities, principally unsaturated organic compounds, in order (1) to decrease the carryover, from the solvent extraction column, of fission product activity by the diluent, and (2) render the diluent more stable to radiation and/or chemical action. Laboratory demonstrations of the Thorex thorium-uranium extraction system indicate that iodine decontamination factors of 200 or higher are possible when preconditioned Amsco 125-82 diluent is used

whereas factors of perhaps 2 to 8 are obtained with the untreated diluent. Strong oxidizing agents have been found to remove the unsaturated compounds from the hydrocarbon.

Pretreatment with Oleum. The Amsco 125-82 is intimately agitated with a 1/10 or 1/5 volume of fuming sulfuric acid, technical grade, for 1 hr, the phases are separated, and the diluent is washed with water, neutralized with 0.1 to 1.0 M sodium carbonate solution, and washed with water again. Because of the obvious difference in specific gravity between the two phases, intimate dispersion is rather difficult and necessitates high speed agitation, efficient sparging, or a countercurrent mechanism. Additional contacting of the diluent with acid does not appear beneficial; the first contacting removes essentially all the unstable constituents.

Nontreated Amsco 125-82 reduces approximately 0.155 meq of Cr^{6+} per milliliter of diluent. Amsco 125-82 treated by the oleum procedure reduces not more than 0.02 meq of Cr^{6+} per milliliter of diluent.

Pretreatment with Chromyl Chloride. Contacting a hydrocarbon diluent such as Amsco 125-82 with 1/100 volume of chromyl chloride removes all the unstable components. The treated mixture is filtered, washed with caustic, and then with water. Although a highly stable hydrocarbon diluent is obtained, the method is too hazardous because of the corrosive nature of the chromyl chloride and too expensive for large-scale usage. Therefore, as a more economical approach, the oleum pretreatment is recommended.

6.1.2 Analytical Method for Evaluating the Extent of Preconditioning

Methods in common use for determining the quantity of unsaturated compounds present, such as the iodine or bromine number, were considered

to be too insensitive for determining the extent of the Amsco 125-82 diluent preconditioning treatment. The fundamental principles of the Etard reaction for preparing benzaldehyde from toluene,

$$3C_6H_5CH_3 + 6CrO_2Cl_2 \longrightarrow \overset{\text{Intermediate}}{3[C_6H_5CH_3 \cdot 2CrO_2Cl_2]} \longrightarrow H_2O + 3C_6H_5CHO + 2H_2CrO_4 + 4CrCl_3,$$

can be applied to the degradation of unstable components in a hydrocarbon diluent. Since chromyl chloride oxidizes double bonds as well as aromatic components, the amount of CrO_2Cl_2 consumed provides a measure of the amount of unstable constituents present.

The analytical procedure developed for accurately determining the quantity of unstable constituents present in a hydrocarbon diluent is 1 or 2 ml of a standardized chromyl chloride solution in carbon tetrachloride (~1 meq/ml) is accurately pipetted into each of five glass-stoppered cone tubes. One milliliter of the hydrocarbon whose unstableness is to be determined is carefully layered on the surface of the chromyl chloride in each tube. After the chromyl chloride and diluent are added, the tubes are shaken at essentially the same time, termed "zero" time. The reaction is stopped by the addition of 5 ml of standardized ferrous sulfate solution (~0.2 meq/ml) at time intervals such as 10, 20, 30, 60, and 90 min. The samples are then titrated with a Beckman Model K automatic titrimeter with a standardized sodium dichromate solution (~0.1 M) to obtain the excess ferrous ion present; thus, the amount of chromyl chloride consumed and the amount of unstable material that reacted in that time interval can be calculated. The change in potential at the end point is ~200 mv when platinum and calomel electrodes are used. The data are plotted so that the logarithm of the Cr^{6+} concentration remaining, expressed as milliequivalents, is represented as a function of the reaction time in minutes. A straight line is drawn through the majority of the points after about the

10-min time interval and projected to intersect the ordinate at zero time. This value, read from the plot, subtracted from the original milliequivalents of Cr^{6+} present yields the milliequivalents of unstable constituents present per milliliter of diluent. Analysis of the diluent before and after a specific pretreatment will show the extent of the removal of unstable constituents.

In evaluating a nonreactive diluent, an extrapolation to zero time of the data plotted as milliequivalents of Cr^{6+} remaining as a function of the reaction time should terminate at the original chromyl chloride concentration, indicating that the diluent did not contain any unstable constituents.

The reactivity of the diluent with chromyl chloride is independent of the amount of chromyl chloride present, provided, of course, that chromyl chloride in excess of that required to oxidize unstable components is present (see Table 6-1 and Fig. 6-1).

6.1.3 Comparison of Commerical Diluents by the Chromyl Chloride Method

For comparison with the Amsco 125-82 hydrocarbon diluent to be used in the Thorex pilot plant, other commercial diluents were analyzed by the chromyl chloride method (Sec. 6.1.2). The Amsco was much less reactive than Atlantic Ultrasene or Shell Sol 72 (see Fig. 6-2). The chromyl chloride reaction in the case of Amsco is believed to be with unstable organic impurities present in the hydrocarbon, and with the bulk constituents in the case of the other two. This theory is substantiated by the fact that a plot of the chromyl chloride reaction with Phillips diluent, which is a normal, straight-chain paraffin, is a line of less slope than that of Ultrasene, which is known to have a high aromatic and unsaturated aliphatic content.

[redacted]

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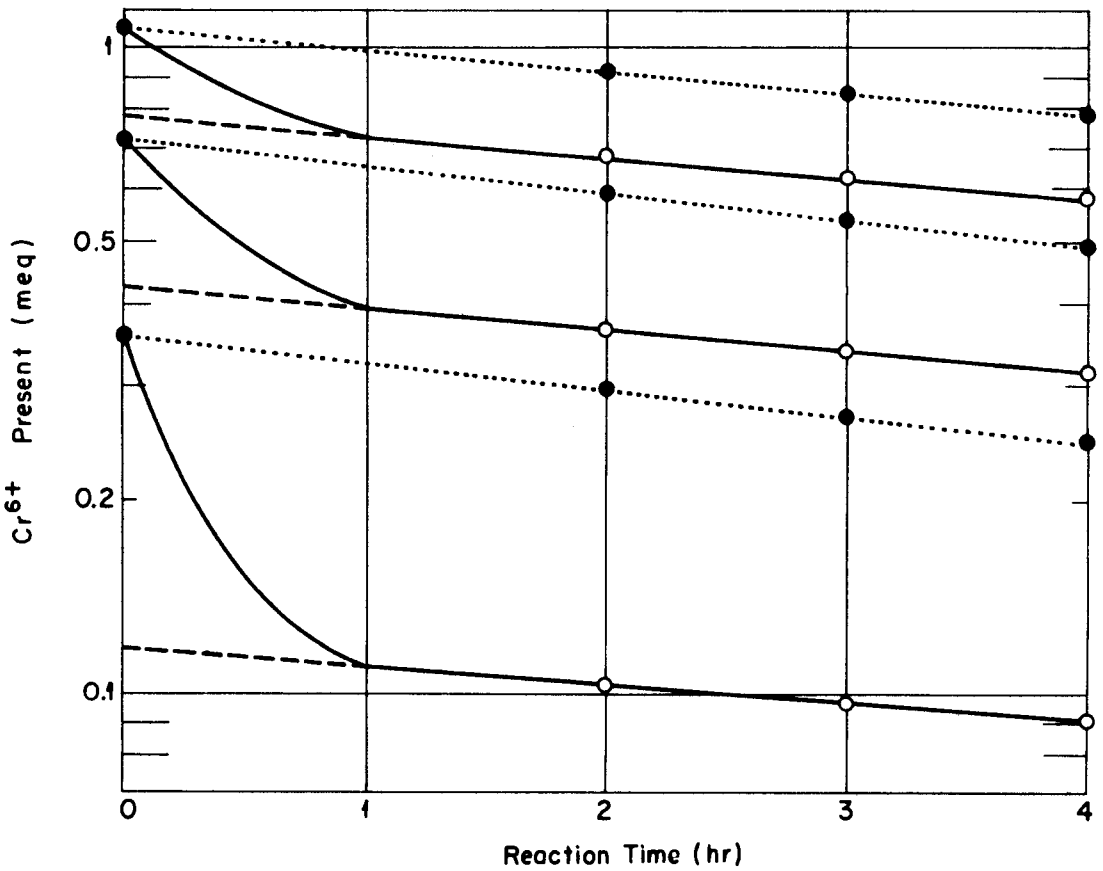

——— Nontreated Amsco 125-82

····· Amsco 125-82 pretreated with 1 part of CrO_2Cl_2 per 100 parts Amsco 125-82

Fig. 6-1. Consumption of CrO_2Cl_2 by Treated and Nontreated Amsco 125-82.

[redacted]

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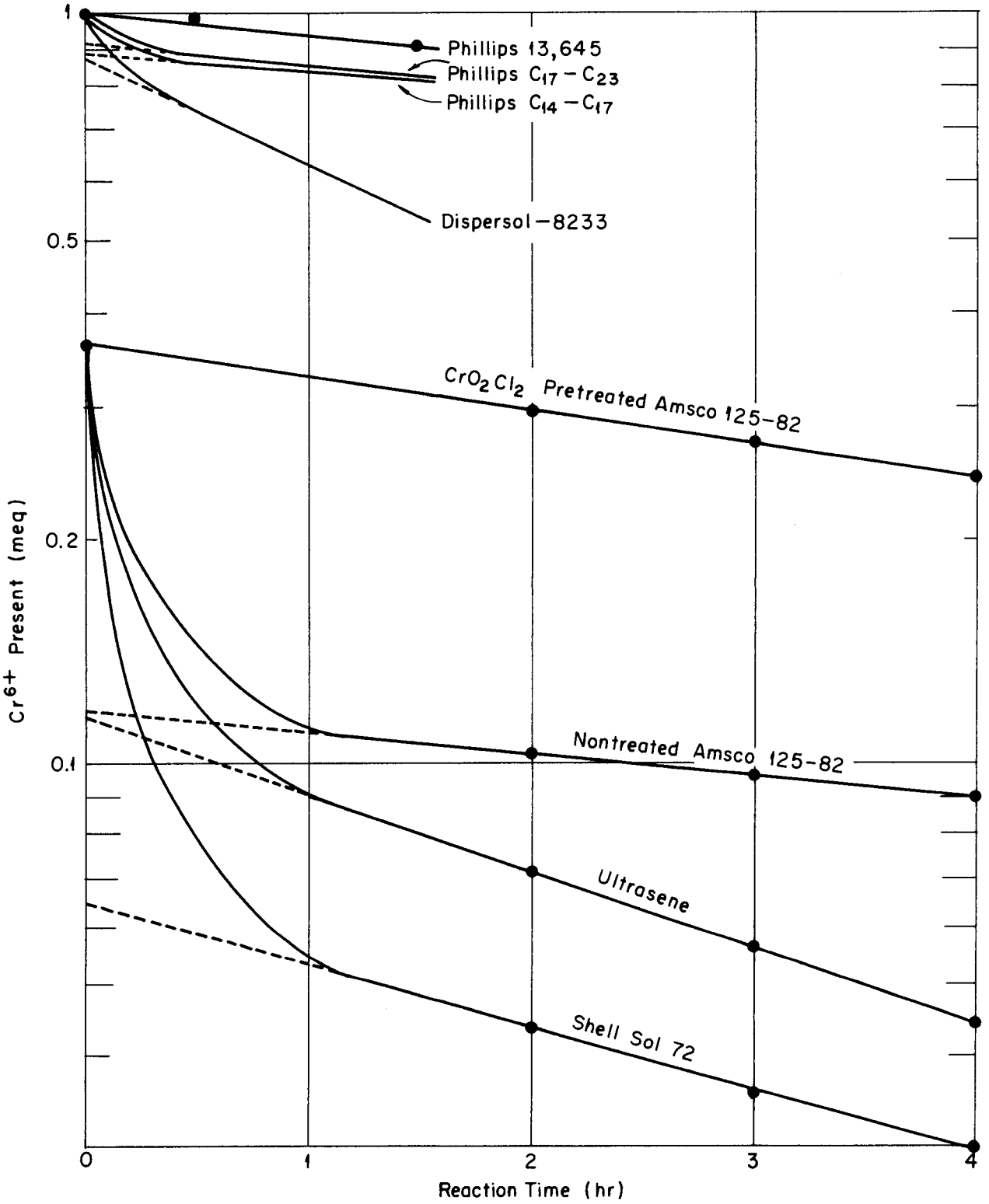

Fig. 6-2. Comparison of Reactivity of Various Commercial Diluents by the CrO_2Cl_2 Test.

Table 6-1

Consumption of CrO_2Cl_2 by Treated and Nontreated Amsco 125-82

2 ml of Amsco treated with varying amounts of CrO_2Cl_2; at time intervals indicated, an excess of $FeSO_4$, 0.185 meq/ml, added and back-titrated with $KMnO_4$, 0.0250 meq/ml

CrO_2Cl_2 Originally Present (meq)	Reaction Time (hr)	CrO_2Cl_2 Remaining (meq)	
		Amsco Preconditioned with CrO_2Cl_2[a]	Nontreated Amsco
0.361	2	0.295	0.102
0.361	3	0.267	0.097
0.361	4	0.243	0.090
0.722	2	0.607	0.368
0.722	3	0.550	0.349
0.722	4	0.495	0.312
1.082	2	0.905	0.689
1.082	3	0.860	0.633
1.082	4	0.790	0.586

(a) CrO_2Cl_2/Amsco 125-82 volume ratio = 1/100.

6.1.4 Justification for Diluent Preconditioning

Calculations indicated that preconditioned Amsco 125-82 could be used for 700 to 1000 passes at a Pa^{233} concentration of 0.15 g/liter and about 10^4 passes at a Pa^{233} content of 9.6×10^{-3} g/liter before returning to the state of containing 0.6% unstable constituents. The unstable

constituents are assumed to be double bonds since aromatics presumably would not form. If short-cooled material is to be processed and iodine decontamination is to be a problem, the use of a diluent preconditioning procedure appears highly desirable. Iodine activity is readily taken up by any unsaturated organic molecules, thus raising the residual activity of the organic stream. This activity, since it combines chemically with the organic unsaturates, cannot be removed by a caustic washing method. Also, the presence of unstable constituents causes the formation of interfacial precipitates, increases the carryover of other fission product activities into product streams, and possibly causes undesirable column operation such as slow coalescence, abnormal settling rates, and emulsions. Activities such as ruthenium, zirconium, protactinium, and niobium are particularly attracted to this type of interfacial material, thereby significantly increasing the health hazard to personnel who would normally be in a low-level or nonradioactive area.

The calculations were made as follows:

<u>Case 1</u>:

Pa^{233} concentration in feed = 0.15 g/liter
Pa^{233} specific power = 19 watts/g
Pa^{233} specific power per liter = (0.15)(19) = 3 watts/liter

Assuming a 5-min contact time for the solvent and Pa^{233}-containing aqueous phase, the exposure per liter of solvent = 0.25 watt-hr/liter.

There is 3.74×10^{-4} mole conversion per watt-hour. Therefore, the mole conversion per liter of solvent = 9.35×10^{-5}. Assuming that 5% of the conversions are olefin formations in the diluent, 4.7×10^{-6} mole of olefins formed per liter of solvent per pass.

Nontreated Amsco 125-82 contains 0.6% unstable constituents. If an

average molecular weight of 180 is assumed for the diluent ($\sim C_{13}H_{28}$), there is 3.4×10^{-3} mole of unstable components per liter. Therefore, 723 passes are required for the organic phase to reach the same unsaturated state as before treatment. The 723 passes are equivalent to 1080 days of operation.

Case 2:

Pa^{233} concentration in feed = 0.0096 g/liter
Pa^{233} specific power = 19 watts/g
Pa^{233} specific power per liter = 0.1824 watt/liter

Assuming a 5-min contact time for the solvent and Pa^{233}-containing aqueous phase, the exposure per liter of solvent = 0.015 watt-hr/liter.

If, as in Case 1, the mole conversion per watt-hour is assumed to be 3.74×10^{-4}, then there is 5.61×10^{-6} mole conversion per liter of solvent. If 5% of the conversions are olefin formations in the diluent, then 2.8×10^{-7} mole of olefins is formed per liter per pass.

From Case 1, the nontreated diluent has 3.4×10^{-3} mole of unstable components per liter; therefore, approximately 10^4 passes would be possible before the diluent is degraded to the same composition as before the pretreatment. The 10^4 passes would be equivalent to about 1.5×10^4 days of operation.