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for Plutonium and Uranium

Cf. 4

LABORATORY DEVELOPMENT OF THE THOREX PROCESS

PROGRESS REPORT

DECEMBER 1, 1955 TO JANUARY 1, 1958

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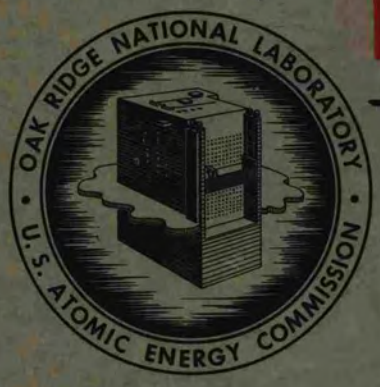

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Chemical Development Section A

LABORATORY DEVELOPMENT OF THE THOREX PROCESS

PROGRESS REPORT, DECEMBER 1, 1955, TO JANUARY 1, 1958

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ABSTRACT

The Thorex process has been modified to increase decontamination so that thorium irradiated to more than 2000 g U-233 per ton thorium and decayed less than 180 days may be recovered. Modifications include the conversion to a codecontamination flowsheet, sweep of I-131 from the dissolver with iodine carrier, improved ruthenium decontamination by addition of bisulfite to the feed, addition of a U-233 third-cycle solvent extraction, and improved solvent recovery by use of 0.2 M NaOH treatment. Activity remaining in products from pilot plant experiments processing thorium irradiated to 4000 g U-233 per ton of thorium, decayed 27 days, by this modified process, exceeded tentative specifications by about a factor of two.

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1.0 INTRODUCTION

This report gives the modifications in the Thorex chemical flowsheet to provide for increased decontamination for thorium irradiated to 4000 g of mass 233 per ton of thorium and decayed less than 90 days. The original Thorex process was developed[1] for the decontamination and recovery of thorium and U-233 from thorium which had been irradiated to 1000 g of mass 233 per ton and allowed to decay nine months for the conversion of the protactinium to U-233 before separation. In both the laboratory and pilot plant this material was satisfactorily processed in one solvent extraction cycle, but the process would not satisfactorily decontaminate thorium which had been more highly irradiated, or decayed less than 90 days.

Only a summary of the laboratory development during the period has been given. The work has been reported in somewhat more complete form.[2,3] Only the experimental values needed to substantiate the conclusions have been included. A few references have been made to pilot plant data to give a comparison with laboratory results.

The original Thorex flowsheet[4,5,6,7,8,9] was developed to recover U-233 and thorium for further research evaluations. The interest in the use of thorium and U-233 in breeder power reactors has put additional emphasis on the fuel processing. Longer periods of irradiation of thorium decrease the frequency of processing and processing after short decay periods decrease the storage charges for fissionable material in inventory, improving the economics of this type of reactor. These more severe requirements imposed conditions which were beyond the scope of the original Thorex development.

Chemical analyses for the laboratory development reported in this paper were made by G. R. Wilson's group, the radiochemical analyses were made by E. I. Wyatt's group and J. H. Cooper, and valuable advice on methods of analytical control and interpretation of data were given by P. F. Thomason and S. A. Reynolds, all of the ORNL Analytical Chemistry Division. Dr. James R. Oliver, Southwestern Louisiana Institute, assisted in the development of the third uranium cycle as a summer research participant. John C. Ganchoff, Jr., Marquette University, contributed to the solvent recovery program as a summer employee.

2.0 FLOWSHEETS

2.1 Thorium Second Solvent Extraction Cycle

Two proposed[9] second thorium cycle flowsheets used 1.0 M dibasic aluminum nitrate and 0.5 M $Al(NO_3)_3$, respectively, in the extraction column scrub. The first was found to be inoperable in pilot plant tests because of the formation of a precipitate in the extraction column; the second did not give sufficient decontamination in engineering-scale tests. The precipitation difficulties seemed to be associated with the high, 1.2 M, acid deficiency of the scrub, which is required to neutralize the 1.2 M HNO_3 in the concentrated feed. This acid originated from the intercycle evaporation of the thorium from the partitioning column which is stripped with 0.24 M HNO_3. A laboratory investigation of the partitioning column operation demonstrated that partitioning with either neutral or acid-deficient 0.1 M aluminum nitrate was satisfactory; 0.05% of the thorium remained in the U-233 product and 0.04% of the U-233 remained in the thorium product. This nonacidic partitioning solution caused a larger percentage of the fission products to accompany the thorium, which was desirable. After concentration of the stripped thorium, the second-cycle feed composition was the same as that of the first cycle except for the absence of U-233 and a lower activity level. Engineering-scale extraction of thorium that had been partitioned with 0.1 M $Al(NO_3)_3$ was satisfactory except for a slightly higher thorium loss than had been common in the first cycle (0.2% instead of 0.1%). Since the co-decontamination flowsheet had been developed in the meantime, the second thorium cycle was not tested in the Pilot Plant.

The possibility of using second-cycle extraction column waste as first-cycle extraction column scrub and a partition column strip was investigated in the laboratory and appeared promising, but no engineering-level experiments were made with this recycle.

2.2 Co-decontamination Flowsheet

A co-decontamination flowsheet was developed for the solvent extraction of thorium and U-233 from solutions of thorium that had been irradiated to more than 1000 g of mass 233 per ton or decayed less than 180 days (Fig. 2.1). In this flowsheet the thorium and uranium are extracted and stripped together in the first cycle and partitioned in the second cycle. Since all columns except the two strip columns were the same as those used in the original flowsheet, little laboratory data was needed to adapt this flowsheet for pilot plant use. Use of this flowsheet in the pilot plant to process thorium irradiated to 3000-4000 g of mass-233 per ton and decayed about 500 days gave both thorium and uranium products that met specifications. The uranium product from thorium irradiated to 3500 g of mass-233 per ton and decayed 72 days met tentative specifications for all fission products except ruthenium, which was high by a factor of about 2. The thorium met specifications

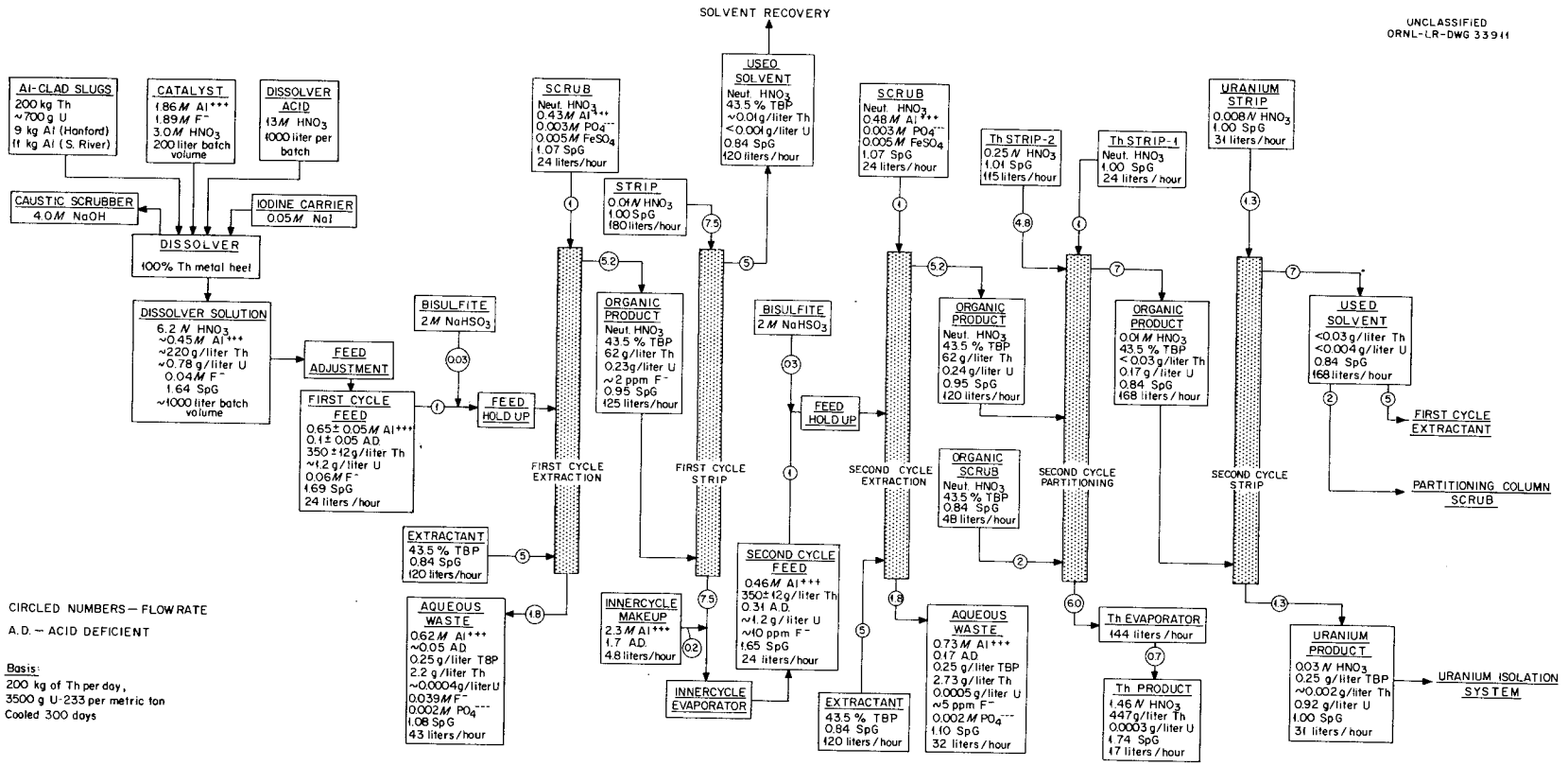

Fig. 2.1. Co-Decontamination Flowsheet Materials Flow Diagram.

at the time of separation for total rare earths but not for ruthenium, zirconium-niobium, or protactinium:

	Decontamination Factors					
	1st Cycle		2nd Cycle		Overall*	
Activity	Th	U	Th	U	Th	U
Gross	760	940	15	160	3.0×10^4	1.3×10^7
Pa	1.1×10^4	1.4×10^4	280	160	1.8×10^6	1.9×10^{10}
Ru	2	4	23	150	77	1.5×10^6
Zr-Nb	2300	2900	20	230	5.7×10^4	3.3×10^6
I-131	--	--	--	---	1.3×10^5	5.1×10^7
Rare earths	1.1×10^4	2.5×10^4	20	1200	6.6×10^5	3.4×10^8

* Includes two solvent extraction cycles of the co-decontamination flowsheet plus silica gel treatment of the thorium and ion exchange and third uranium cycle for the uranium.

When the development of the co-decontamination flowsheet began in the laboratory, equipment for a second thorium solvent extraction cycle had already been added to the Thorex pilot plant. Flowsheet conditions therefore were chosen so that no major change would be needed in existing equipment. This condition placed severe limitations on the two strip columns which did not have sufficient stages for the co-decontamination flowsheet and therefore decreased the throughput of the plant.

The strip first-cycle solution was changed from 0.008 M HNO_3 to 0.008 M $Al(NO_3)_3$ to improve column operation. This substitution decreased the phase disengaging time by a factor of 2. The solubility of nitric acid in the solvent decreased the concentration at the bottom of the column, which lowered the ionic strength and caused the disengaging time to be longer then two minutes at the bottom of the column during startup and shutdown. The use of $Al(NO_3)_3$ eliminated this difficulty.

Since the extraction columns for the two cycles are essentially the same, the decontamination factors should be the same if the feeds are the same. In practice, the measured decontamination in the second cycle complemented that in the first. Decrease in decontamination in the first cycle resulted in an increase in the second so that the product of the two was very nearly a constant. This characteristic not only greatly increased the consistency of the product compositions but also added to the flexibility of the operation, minimized recycle and decreased plant downtime. Since a second cycle does not greatly increase either capital or operating costs, its inclusion is probably warranted even though decontamination is satisfactory in a single-cycle plant under ideal operating conditions.

Partitioning of thorium from uranium was more difficult in the second than in the first cycle in the pilot plant. Laboratory experiments showed this difficulty to be due to heating of entrained and dissolved organic phase in the intercycle evaporator. In the laboratory experiments, when first-cycle strip solution was carefully freed from the organic phase before concentration, no difficulty was encountered in the partitioning step.

2.3 Third Uranium Cycle

A flowsheet for a third solvent extraction cycle to follow the ion exchange step was developed[10] for further purification of uranyl nitrate production solutions (Fig. 2.2). The feed is nitric acid eluate from the ion exchange columns adjusted to 50 g of uranium per liter, 0.7 M in $Al(NO_3)_3$, 0.5 M in HNO_3. The extractant is 10% TBP in Amsco and the scrub 0.5 M $Al(NO_3)_3$. The feed/scrub/extractant flow ratio is 1/0.3/1.5. Laboratory experiments under these conditions gave decontamination factors from ruthenium of 600 and from zirconium-niobium of 400. The decay daughters from U-232 were decreased to nondetectable concentrations. The uranium extraction loss was 0.01%. Phase-disengaging times throughout the countercurrent batch extraction were less than 1 min.

When thorium that was irradiated to between 3000 and 4000 g of U-233 per ton was processed through the co-decontamination flowsheet after less than 60 days' decay, the U-233 product failed to meet specifications.* The high activity is due both to fission products and the daughters of U-232 and U-233.

In a flowsheet for the solvent extraction[11] from acetate-citrate eluate[12] the feed contained high concentrations of aluminum nitrate and nitric acid to compensate for the formation of the inextractable complex of the uranium (Fig. 2.3). In the ion exchange flowsheet finally adopted, uranium is eluted with 6 M HNO_3.[13] The elimination of strong complexing ions in the solution provided an opportunity to redesign the third uranium cycle flowsheet to obtain maximum decontamination with an acceptable loss.

The fission product decontamination factors were determined in laboratory countercurrent batch experiments with natural uranium containing

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* The tentative U-233 specifications required that a shipping bottle containing 300 g of uranium in 1.5 liters of solution read less than 300 mr on a hard shell cutie pie gamma survey meter. The radiation reading was not correlated with the gross gamma count of the uranium product because of the variation of the energy of the various active contaminants. However, few products with more than 10^4 γ/min/ml met specifications.

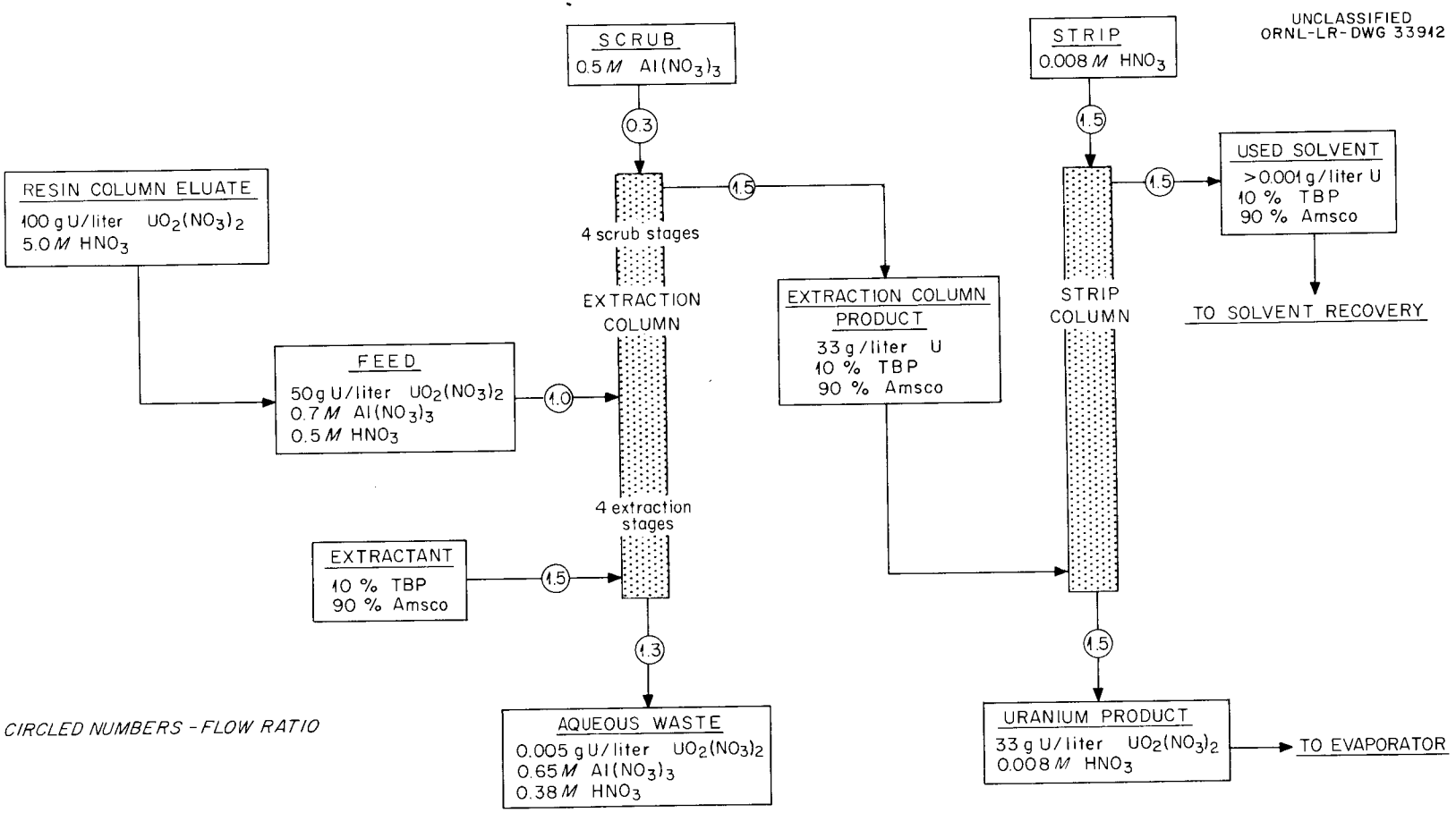

Fig. 2.2. Thorex Third Uranium Cycle No. 2 Chemical Flowsheet (Nitrate-Eluted Feed)

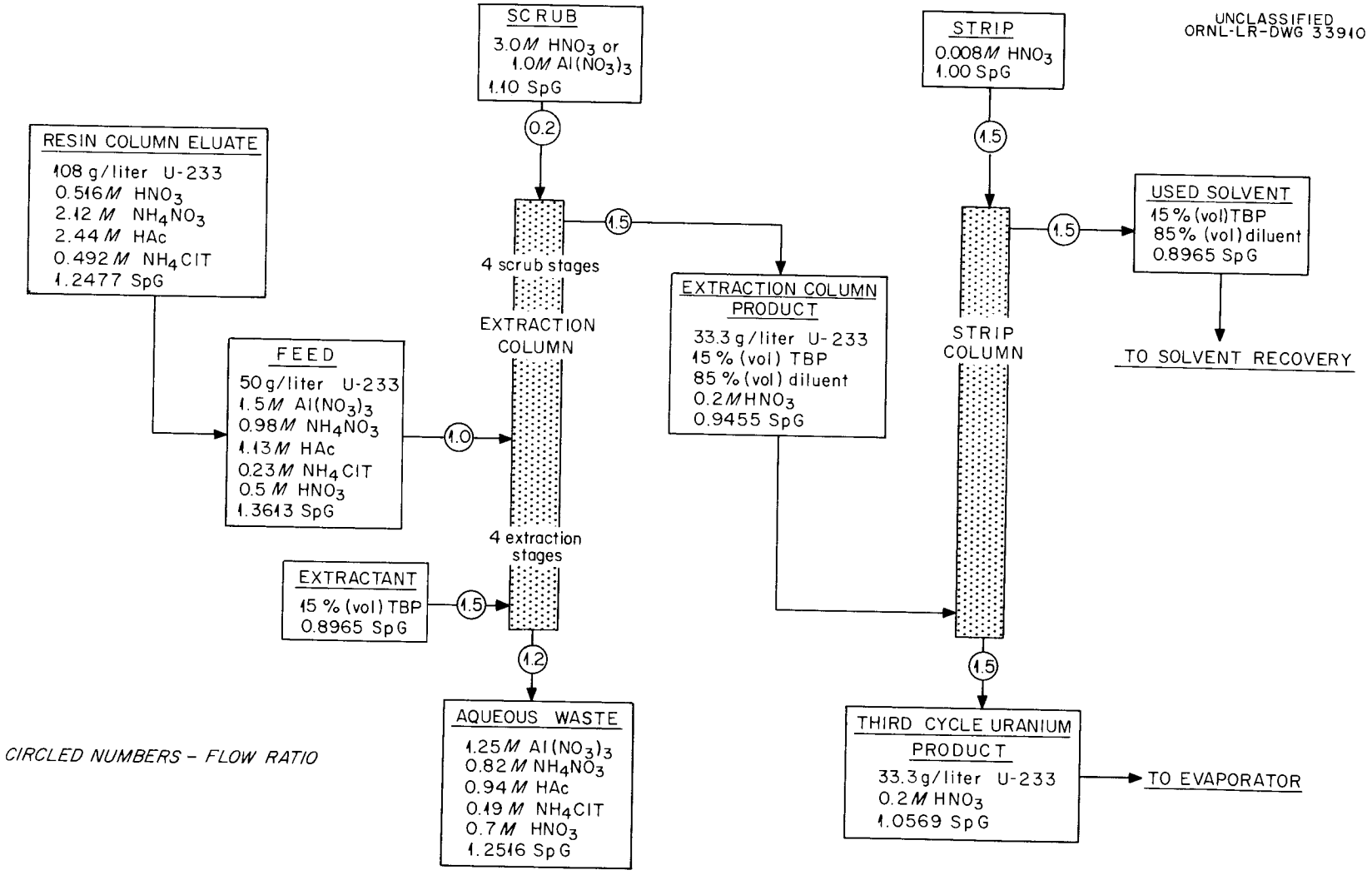

Fig. 2.3. Thorex Third Uranium Cycle No. I Chemical Flowsheet (Acetate-Citrate Eluted Feed) From CF 56-6-52.

highly contaminated pilot plant U-233 as a source of fission products and U-232 decay daughters.

The U-233 formed from Th-232 by neutron capture contains U-232 (see KAPL-1271, e.g., ORNL-1818, -1869). The U-232 daughter activities whose half-lives are sufficiently long to influence the gamma readings following extraction of the product are Th-228, Ra-224, and Pb-212 (Table 2.1). In laboratory tests with uranium from pilot plant ion exchange columns, plant extractant, and scrub, the third uranium cycle decreased these nuclides to an undetectable level. Gamma-energy scans of the feed showed that Th-228 contributed about 6.5×10^3 c/m/mg U, and Ra-224 and Pb-212 about 4×10^3 c/m/mg U. The Th-228 decontamination factor, considering the U-233 background, was not less than 10 and the Ra-Pb not less than 50. Because of the long half-lives of U-233 and Th-229 (Table 2.1) the growth of daughter activity from U-233 is much less rapid, and removal of Ra-225 and Ac-225 would assure rapid decay of the chain (Table 2.2).

The proposed flowsheet was adopted by the Pilot Plant, and the product met all specifications even when the plant processed U-233 from thorium that had been irradiated to 4000 g of mass-233 per ton and had decayed less than 45 days prior to solvent extraction. Because of the rapid buildup of radioactivity from the U-232 decay chain, the third cycle must be carried out shortly before the material is shipped to the consumer.

Successful decontamination includes the removal of thorium because of its Th-228 content (Table 2.1). Separation of the U-233 from thorium depends on maintaining high saturation of the organic phase with uranium. The Pilot Plant uranium product is collected from the pulsed-solvent extraction columns only when the columns are operating under equilibrium conditions. Nonequilibrium startup and shutdown material is recycled for later recovery. Careful column control is maintained to prevent the thorium, which refluxes in the bottom section of the extraction column, from passing up the column with the uranium.

Table 2.1. Nuclear Properties of U-232 Decay Chain

Nuclide	Mode of Decay	Half-life	Gamma Energy (Mev)	Occurrence* (%)
U-232	Alpha	74 y	0.058	32
			0.13	< 0.3
			0.27	Low
			0.33	Low
Th-228	Alpha	1.9 y	.084	28
			0.14	< 1
			0.17	< 1
			0.21	< 1
Ra-224	Alpha	3.64 d	0.241	5
			Others	< 1
Em-220	Alpha	54 sec	0.54	<1
Po-216	Alpha Beta(0.013%)	0.158 sec	None given	
Pb-212	Beta	10.6 hr	0.238	80
			0.299	5
			0.176	1
			0.249	Weak
Bi-212	Alpha(33.7%) Beta(66.3%)	60.5 min	0.040	--
			Others	--
Tl-208	Beta	3.1 min	2.62	100
			0.86	15
			0.58	80
			0.51	25
			0.28	10
Po-212	Alpha	3×10^{-7} sec	None given	
Pb-208	Stable			

* Compiled by B. H. Ketelle of the ORNL Chemistry Division.

Table 2.2 Nuclear Properties of the U-233 Decay Chain

Nuclide	Mode of Decay	Half-life	Gamma Energy (Mev)	Occurrence* (%)
U-233	Alpha	1.63×10^5 y	0.043 0.056 0.099	15 1.6
Th-229	Alpha	7×10^3 y	Questionable	
Ra-225	Beta	14.8 d	0.040	63
Ac-225	Alpha	10.0 d	None given	
Fr-221	Alpha	4.8 min	0.218	16
At-217	Alpha	0.02 sec	None given	
Bi-213	Alpha (2%) Beta (98%)	47 min	0.437	--
Tl-209	Beta	2.2 min	0.114 0.50 0.60 4 over 1 Mev	2 2 2
Po-213	Alpha	4.2×16^{-6} sec	None given	
Pb-209	Beta	3.3 hr	None	
Bi-209	Stable			

* Compiled by B. H. Ketelle of the ORNL Chemistry Division.

2.4 Comparison of KAPL and ORNL Thorex Flowsheets

A flowsheet for the recovery of U-233 and thorium from irradiated thorium metal was developed and tested through a small mixer settler pilot plant at Knolls Atomic Power Laboratory[17]. In contrast to the flowsheet developed at ORNL, the KAPL feed solution was highly acidic. In the Purex flowsheet, high acidity (as well as acid-deficient conditions) has been reported to increase the decontamination factors from ruthenium.[18] A comparison of the acid KAPL and acid-deficient ORNL flowsheet decontamination factors, made under laboratory conditions to determine which would be most useful for a second thorium solvent extraction cycle, indicated better decontamination from ruthenium and zirconium-niobium with the ORNL flowsheet (Table 2.3).

3.0 PRODUCT DECONTAMINATION FROM RUTHENIUM

3.1 Effect of Acidity

Early Thorex development work[4] demonstrated that ruthenium is much less extractable by 42% TBP from acid-deficient feeds than from neutral or slightly acidic feeds. In laboratory experiments reviewing this work, a synthetic Thorex feed that was 0.26 N acid deficient was decontaminated from ruthenium by a factor of 640 when 0.15 N acid-deficient scrub was used (0.15 M Al), as contrasted with a ruthenium decontamination factor of 14 when feed and scrub contained 4 N HNO_3 (Fig. 3.1). The variation in ruthenium decontamination as a function of feed acidity, with scrub maintained at 0.5 M Al $(NO_3)_3$, was determined. These values may be compared with those from a 0.15 M acid-deficient scrub in Fig. 3.2. The improvements to be obtained through increased acid deficiency in the feed and the benefit of acid deficiency in the scrub are evident. A slightly acid-deficient scrub was preferable to a neutral scrub for ruthenium decontamination over the feed acidity range 0.6 N acid deficiency to at least 0.8 N acid (Fig. 3.3).

In scouting tests, feeds containing the various ruthenium species at equilibrium at the stated acidity were stirred vigorously for 5 min with 5 vol of 42% TBP in Amsco. The phases were allowed to separate and placed in beakers, and the gamma activities were read by a standard technique, using a beta-gamma survey meter. The aqueous phase was discarded, and the organic phase was returned to a clean extraction cell, where it was stirred for 2 min with the scrub solution. The phases were separated and the activities read as before. After eight such scrubs the organic phase was analyzed for thorium and ruthenium and the decontamination factor computed. The tests were made in duplicate throughout.

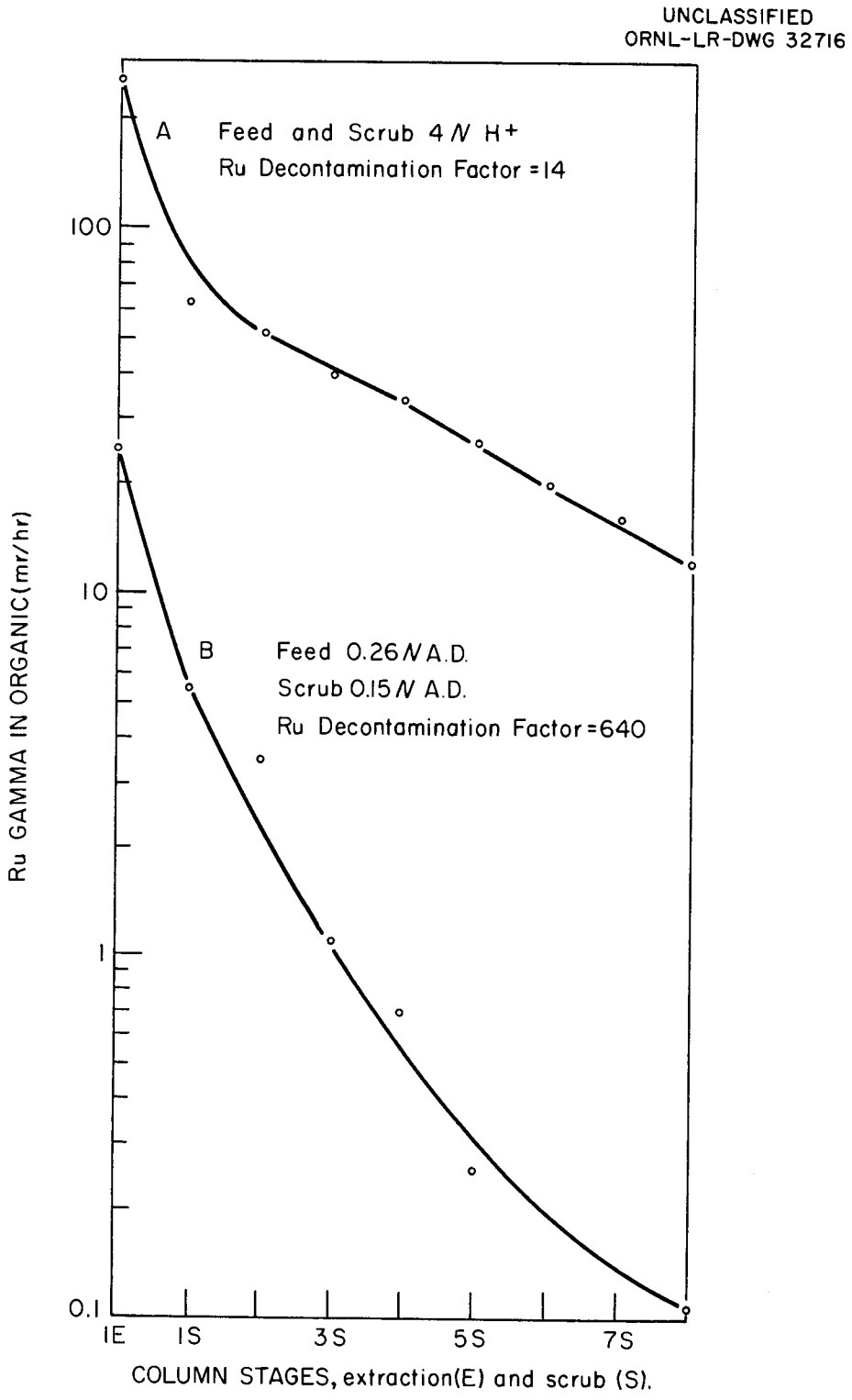

Fig. 3.1. Effect of Feed and Scrub Acidity on Thorex Product Decontamination from Ruthenium.

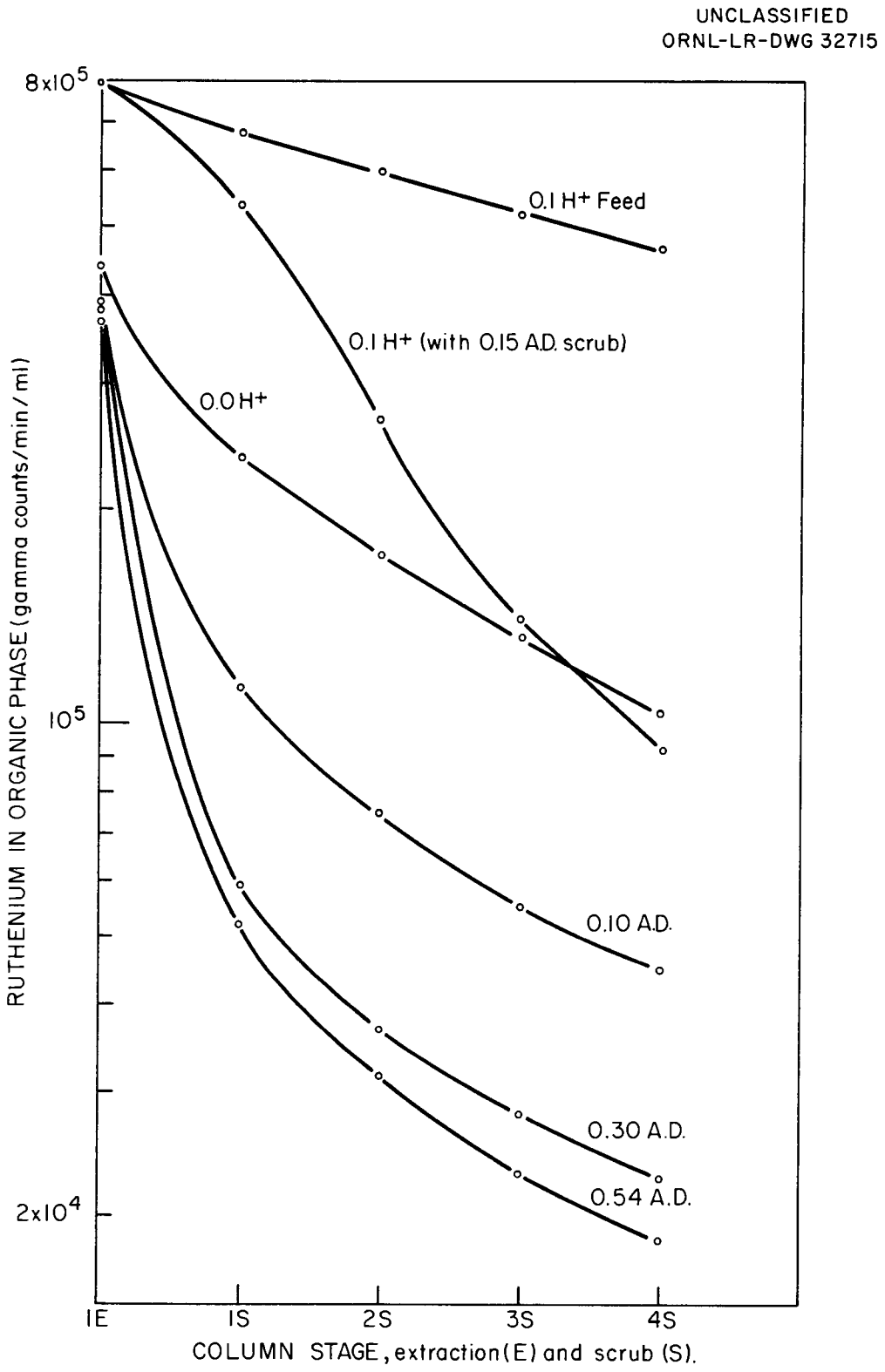

Fig. 3.2. Ruthenium Extraction vs. Feed Acidity (Neutral Scrubs).

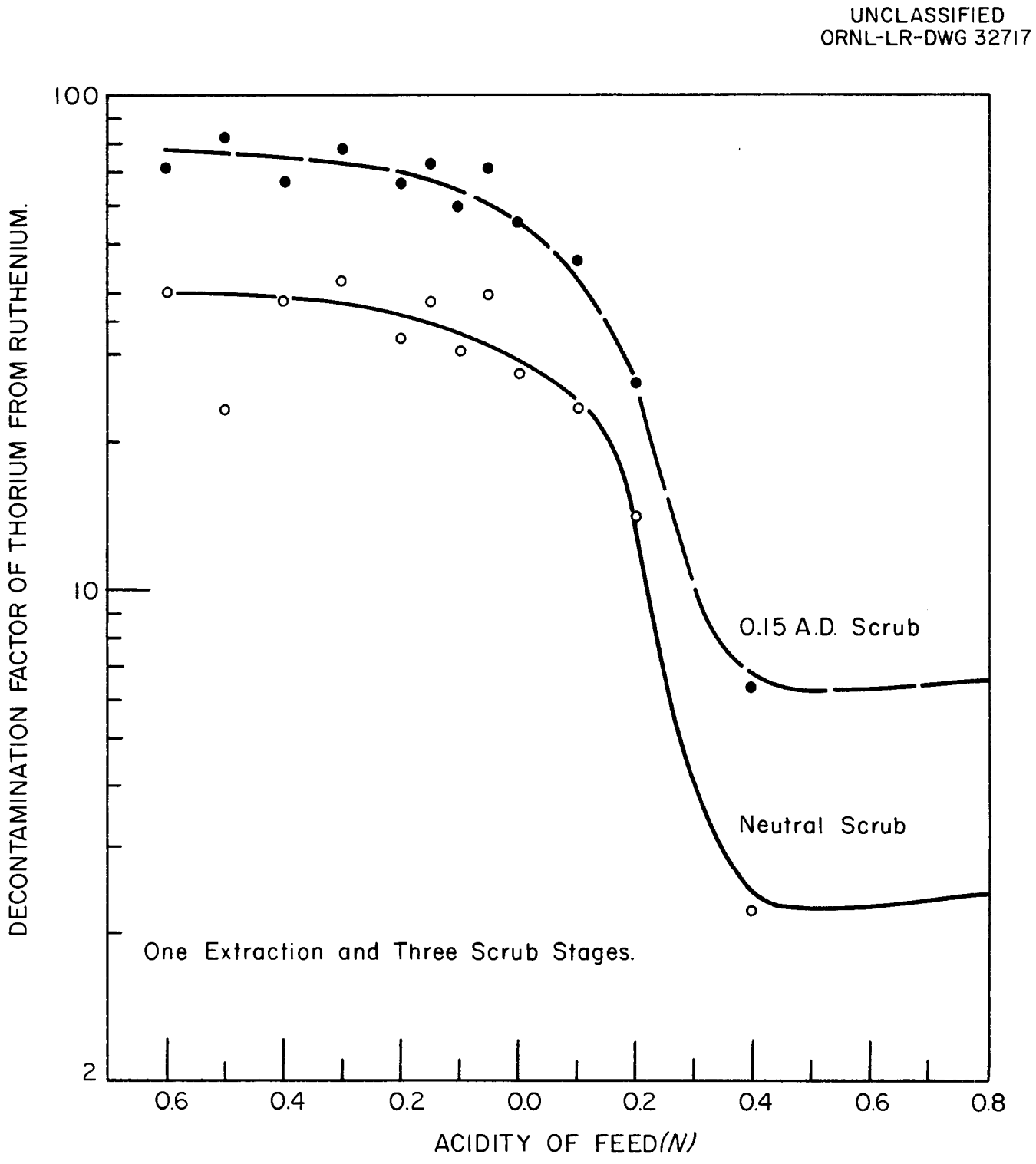

Fig. 3.3. The Effect of Neutral or Acid-Deficient Scrub Using Feeds of Varying Acidity on Ruthenium Decontamination in Synthetic Thorex Feed.

Table 2.3. Comparison of the Decontamination Factor Obtained with KAPL and ORNL Flowsheets

Run	Flowsheet	Decontamination Factors					
		Gross β	Gross γ	Pa γ	Ru γ	Zr-Nb γ	Total Rare Earths β
1	KAPL	7	5	20	25	41	1.1×10^4
	ORNL	66	74	180	37	410	1.6×10^3
2	KAPL	14	95	25	2.5	85	1.4×10^4
	ORNL	100	105	--	610	850	5×10^3
3	KAPL	--	29	--	70	200	4.6×10^4
	ORNL	--	2000	--	1300	3400	1.4×10^4
4	KAPL	--	1.5	--	1.8	2	1.5×10^3
	ORNL	--	750	--	850	580	3.6×10^2
5	KAPL	--	50	--	11	250	1.6×10^5
6	KAPL	--	1000	--	7.5	1700	9×10^4

The run conditions were:

1. First-cycle thorium product adjusted with aluminum and acid or dibasic aluminum nitrate for second-cycle feed.

2. Same as No. 1, simmered overnight at 85°C.

3. First-cycle feed, including ORNL feed adjustment followed by adjustment to proper acidity. KAPL feed simmered at 85°C overnight.

4. Same as No. 2 using spike which was mostly Ru.

5. First cycle feed without ORNL feed adjustment.

6. First cycle feed with "reverse strike" head-end.

In a limited number of tests, using highly acid-deficient feed which was partially neutralized by addition of acid downstream, the expected beneficial effect on ruthenium decontamination was not demonstrated. Further evaluation of the partial neutralization procedure, which was to include acid addition via acidified TBP, was not carried out because of the development of the bisulfite process (Sec. 3.4).

Thorium Losses. Although acid deficiency in the Thorex extraction column increased the decontamination from ruthenium, it also increased thorium losses to the waste stream (Fig. 3.4). When nitric acid was added near the bottom of the extraction column, while highly acid-deficient conditions were maintained at the feed plate, the thorium distribution coefficient was raised sharply at the stage at which acid was added (Fig. 3.5). Thorium loss was minimum with addition of acid to the next to the last stage. Laboratory countercurrent runs with five extraction and eight scrub stages confirmed these results. In a typical run, the feed was 0.61 N acid deficient and the equal volume of scrub was neutral, so that the aqueous phase in the extraction section was 0.3 N acid deficient. Without addition of acid, thorium loss was 1.9%. With addition of acid to 0.15 N acid deficiency at the second stage from the bottom, the thorium loss was 0.26%. In a control run at a feed acid deficiency of 0.24 N the thorium loss was 0.23%. Tests have not yet confirmed whether the thorium losses in acid-deficient extraction columns are due to the formation of a poorly extractable thorium salt (e.g., a hydroxy nitrate) or to a loss in salting strength of the aluminum nitrate.

3.2 Effect of Time

Tracer-level ruthenium in aqueous nitrate solution was changed from an extractable to a non-extractable form slowly in the cold, but rapidly when heated. A synthetic Thorex feed prepared from a ruthenium solution that had been aged in the slightly acidic state (and hence contained ruthenium that was solvent soluble), was divided into two parts. One part was made 4 N in nitric acid, and the other was made 0.1 N acid deficient with dibasic aluminum nitrate. Both contained 170 g of thorium and 0.56 M aluminum, as nitrates, per liter. Half of each part was heated to 100°C for 3.5 h. All four solutions were allowed to stand at room temperature for three days and were then extracted once with 42% TBP using the Thorex extraction conditions; the organic phase was scrubbed 11 times with 0.6 M $Al(NO_3)_3$ that was 0.5 N acid deficient. The ruthenium d.f. with the heated acidic feed was 1.5×10^3, vs 270 for the unheated, and with heated acid-deficient feed was 1.3×10^3, vs only 67 for the unheated. This high decontamination of organic extracts from strongly acidic feeds with acid-deficient scrubs was possible only when the feed acidity was maintained high during the extraction step. When acidic feed was mixed with acid-deficient scrub during the extraction to a final acidity of 0.7 N H,

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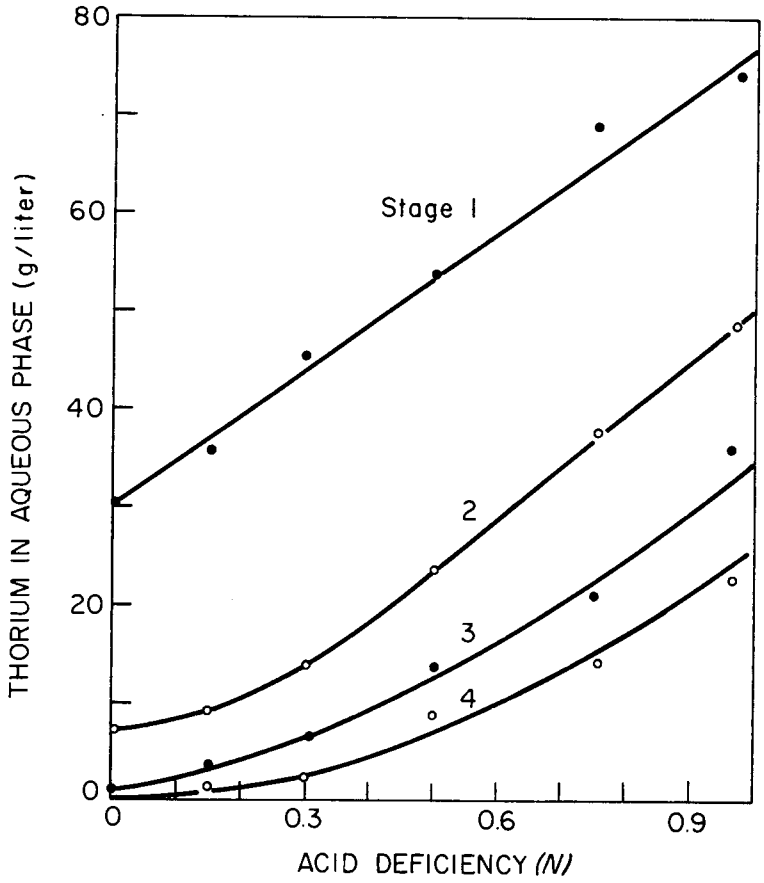

Fig. 3.4. Thorium Retained by Aqueous Phase in Extraction of Thorex Feed with 42.5% TBP as a Function of Column Acidity.

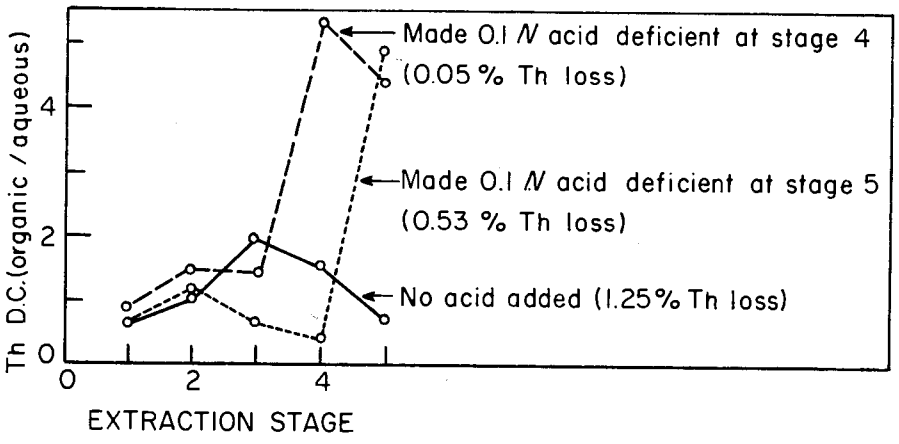

Fig. 3.5. Effect on Thorium Distribution Coefficient of Increasing Acidity in Lower Stages of Extraction Column. Aqueous 0.46 acid deficient at first stage.

decontamination after eight subsequent acid-deficient scrubs was decreased by factors of 2-3. This was probably due to the formation of some of the highly extractable ruthenium compound or compounds which are at equilibrium under slightly acid conditions (see previous section).

3.3 Effect of Thorium Concentration in Scrub

Ruthenium decontamination was increased by a factor of about 4 when 85 g of nonirradiated thorium per liter was added to the scrub. The purpose of thorium addition was to keep the organic phase nearly saturated with thorium (88-90 g/liter) at the top of the column, where normally the thorium is refluxed by the aqueous scrub. High thorium loading improves fission product decontamination by decreasing the uncombined TBP that is available for fission product extraction. However, this also introduces the possibility of third-phase formation. In two countercurrent experiments, one with 85 and the other with 40 g of thorium per liter in the scrub, no third phase formation occurred in 2.5 column changes. When aluminum was omitted from the scrub, a third phase formed in the scrub column, but the thorium loss was only 0.05%. Although third-phase formation prevents the efficient operation of pulse columns, its occasional formation in mixer-settlers might not be harmful because of its easy separation and its confinement to the scrub section.

3.4 Effect of Nitrite and Sulfite

Decontamination from Ruthenium. Product decontamination factors from ruthenium were 2-3 in the solvent extraction cycle of the first Thorex pilot plant run with short-decayed feed. Laboratory studies indicated that nitrite, formed by irradiation of the nitrate in the feed, converts ruthenium to a more extractable form. The flowsheet was therefore modified to include the addition of 0.06 M bisulfite to the feed prior to the extraction step to destroy the nitrite. In addition to the destruction of the nitrite, sulfite seems to have a specific reaction with ruthenium which decreases its extractability. Other reagents which would destroy the nitrite did not give as good decontamination factors as did sulfite. The presence of nitrite ion in the feed was not shown analytically, doubtless because of rapid destruction of unreacted nitrite by excess irradiation-produced hydrogen peroxide.

When nitrite was added to a synthetic feed solution containing ruthenium, the product decontamination factor in extraction with 42.5% TBP in Amsco was inversely proportional to the amount of nitrite added (Fig. 3.6). Irradiation likewise increased the ruthenium extractability, the decontamination factor being inversely proportional to the amount of irradiation (Fig. 3.6). When a Thorex feed solution containing nitrite was heated to 69°C for a few minutes with excess bisulfite, the ruthenium distribution coefficient (organic/aqueous) to 42.5% TBP in Amsco was 0.005 compared to 2 for a control. A similar synthetic

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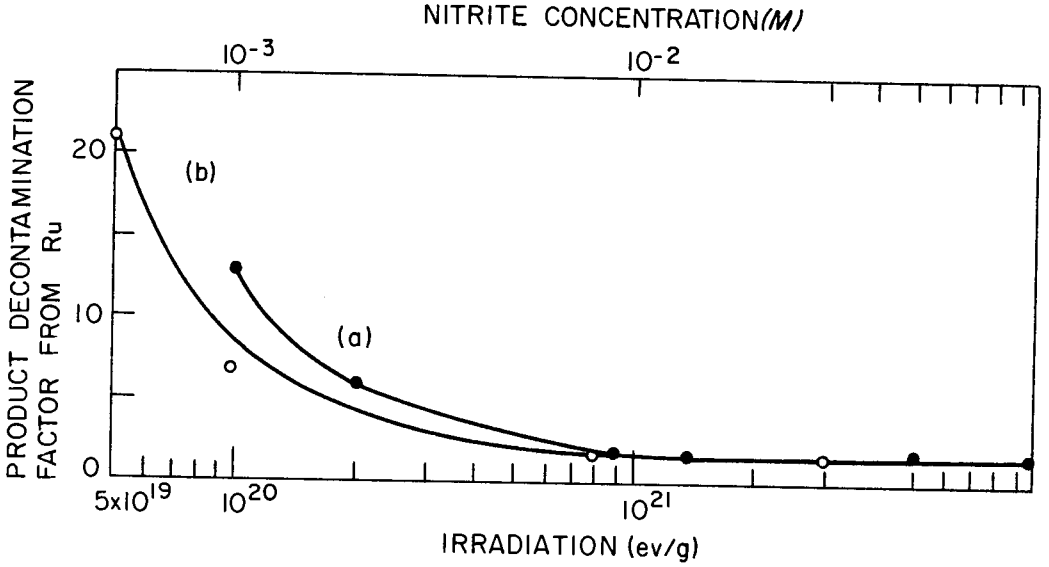

Fig. 3.6. Effect of (a) Nitrate Concentration and (b) Irradiation on Thorium Decontamination from Ruthenium.

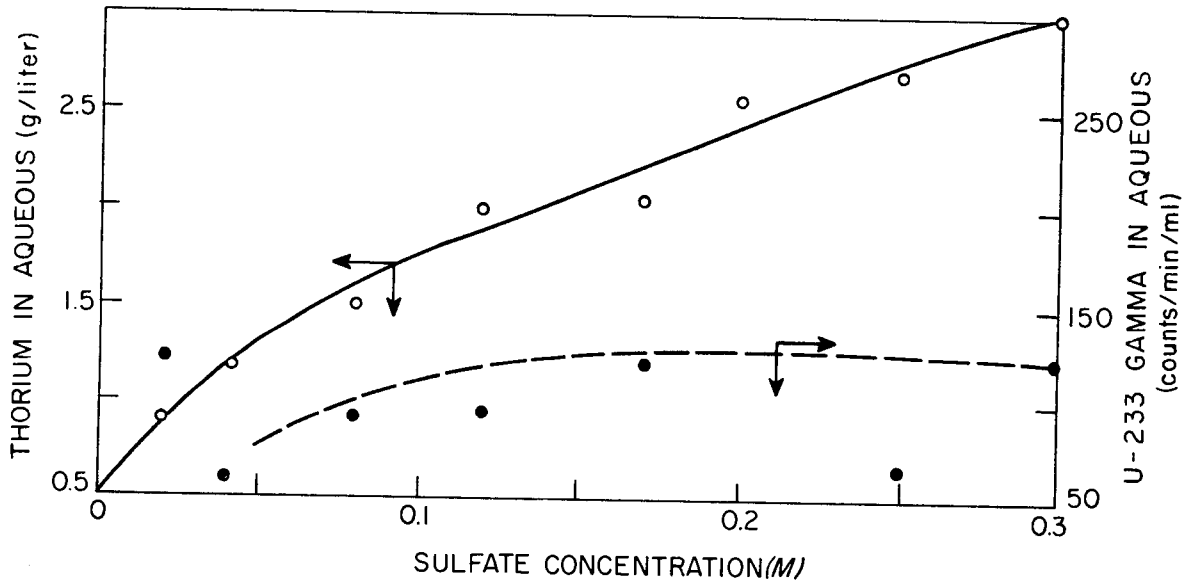

Fig. 3.7. Effect of Sulfate Concentration on Thorium and Uranium Remaining in Aqueous Phase after Four Extractions with 42.5% TBP. Synthetic thorex feed adjusted to proper sulfate with Na_2SO_4, equal volume of scrub added; 2.5 vol of extractant used per volume of feed for each extraction.

feed solution, 0.1 M in sodium bisulfite and heated to 85°C for 5 min and allowed to cool to 35°C before extraction, was decontaminated by a factor of at least 1.6×10^4. Controls without bisulfite were decontaminated by factors of ~ 100. In these experiments the feed had the composition 190 g of Th per liter, 0.3 M acid-deficient, 0.78 M $Al(NO_3)_3$, and a ruthenium activity of 5×10^6 gamma counts/ml/min. The product ruthenium activity was 42 gamma counts/ml/min. The extractions were carried out by agitating one volume of feed and scrub at high speed for 5 min with 5 vol of 42% TBP in Amsco. The phases were separated, and the organic phase was scrubbed with half-volume portions of 0.5 M $Al(NO_3)_3$ that was 0.15 N acid-deficient. A gross gamma count was made immediately on the scrubbed organic phase to avoid the growth of Th-228 daughters. Five days' standing at room temperature with as little as 0.002 M bisulfite gave a decontamination factor of 1100 as compared to 6.5 for an untreated control. Increasing the bisulfite concentration above 0.01 M did not further improve the decontamination factor (which was 2.3×10^3 for 0.01 M bisulfite and 2.8×10^3 for 0.06 M bisulfite) from solutions receiving irradiation only from the ruthenium tracer.

Sulfite also increased the decontaminations. At 0.5 N acid, the ruthenium decontamination factor was 10 with 0.01 M sulfite and 4 for the control after one extraction and four scrubs. There was no beneficial effect of sulfite in 3 N acid solutions. Bisulfite was preferable to sulfite because of its lower pH in aqueous solution. At 65 to 85°C, depending on the composition of the solution, either sulfite or bisulfite ion was decomposed by side reactions.

Sulfite or bisulfite in Thorex solutions reacts to sulfate, which increases thorium and uranium loss in the solvent extraction cycle (Fig. 3.7). In this experiment feeds containing varying quantities of sulfate were mixed with equal volumes of scrub solution and extracted with four separate portions of 5 feed volumes of 42.5% TBP.

3.5 Pilot Plant Application

The adaptation of the bisulfite-ruthenium reaction to Thorex pilot plant use was difficult. In addition to the expected instability of bisulfite in warm aqueous solutions of low pH, as a result of air oxidation and volatilization of sulfur dioxide, three other routes of bisulfite destruction were found:

1. The initial bisulfite consumption by equilibrium concentrations of irradiation products such as nitrite and peroxide was about 0.02 moles/liter. Oxidation by these products amounted to 0.02 to 0.03 moles/hr in small samples of short-decayed Thorex feed whose Pa activity was about 5×10^{11} gamma counts/ml/min. Oxidation in large volumes, such as in the feed storage tank, could be as high as 0.08 moles/hr because of increased gamma absorption in solution. The equilibrium value is kept at 0.02 M by the interaction of these degradation products. The bisulfite consumption

rate was determined by titrating sulfited feed solutions with standard iodine solution and by measuring the time for the appearance of a blue end-point in feeds to which had been added known amounts of bisulfite. Iodine starch was used as indicator.

2. Complete oxidation by the nitric acid formed in hydrolysis of thorium took place within a few seconds at elevated temperatures when the reaction temperature was reached. The reaction temperature was lower in more concentrated or more acidic solutions. For example, decomposition occurred at 85 $\pm$ 1°C for 0.4 N acid deficiency and 66 $\pm$ 1°C for 0.24 acid deficiency Thorex feeds which were both 7.6 N in nitrate ion. The reaction temperature of another synthetic feed was lowered from 89 to 77°C by changing from 0.4 N acid deficiency to neutral. Nitrite ion was produced in this reaction and reconverted part of the ruthenium to the extractable form. The reaction temperature was raised approximately 2°C for each percent of dilution by water. Reaction temperatures were measured by slowly heating sulfited synthetic Thorex feed in a water bath, and periodically withdrawing samples at known temperatures for titration by iodine solution.

3. Mercury salts also caused oxidation of the bisulfite. The mercury salts were first reduced to finely divided mercury, and at elevated temperatures the mercury was reconverted by the nitric acid of hydrolysis to the mercuric ion, which catalyzed the oxidation of sulfite by nitric acid. Concentrations and temperatures necessary for this reaction were not studied, because of the discontinuance of the use of mercury as a dissolution catalyst. (Sec. 4.0).

Since thorium losses in the extraction column increase with increasing sulfate concentration, it was not practical to treat the short-decayed pilot plant feed with enough bisulfite in one batch to ensure an excess during the run. Sulfite was therefore added continuously in the extraction column feed line. This treatment was begun at 0.01 M bisulfite, before all the modes of bisulfite destruction had been determined, and was later raised intermittently to 0.04 M. Bisulfite was added only while the feed stream temperature was below 50°C. During most of the run, 0.03 M sodium bisulfite was included in the scrub to help make up for inadequacies in feed treatment as well as to ensure reduction of iodine to iodide. In spite of the less-than-optimum bisulfite treatment, decontamination from ruthenium in the second short decay run averaged 18 for the first cycle. The decontamination factor was 280 for the thorium and 1800 for the uranium in the second cycle. This compared favorably with the one-cycle decontamination of 2-3 for thorium and uranium in the short-decayed pilot plant run made without bisulfite in July, 1956. The 1957 processing of short-decayed feeds in the Thorex pilot plant ended before the optimum bisulfite conditions were determined.

3.6 Laboratory Treatment of Short-decayed Feed

After processing of short-decayed feed ceased in the Thorex pilot plant, the sulfite method was further studied with short-decayed feed samples in the laboratory hot cell. The decontamination factor of thorium from ruthenium was 320, compared with 2.5 for an unsulfited control similarly treated. A sample of full-level short-decayed feed containing 0.06 M bisulfite was heated for 20 min at a temperature of 58 to 45°C. It was then diluted with an equal volume of 0.5 M $Al(NO_3)_3$ scrub, as is used in the solvent extraction column, and extracted with five times the feed volume of 42% TBP in Amsco. The organic phase was scrubbed six times with one-fifth its volume of 0.5 M $Al(NO_3)_3$ that was 0.15 N acid deficient, and its ruthenium activity measured by chemical separation and gamma counting.

The bisulfite-nitrate reaction temperature was measured on two short-decayed feed samples, each containing 325-350 g of thorium and 16 g of aluminum per liter. The measurement was made remotely by adding bisulfite to 0.06 M, with a trace of iodide-starch indicator, and immersing the sample into a beaker of nearly boiling water. Browning and gas evolution occurred at 73°C for a feed of approximately 0.2 N acid deficient, and had not yet occurred at 76°C, the maximum temperature reached, with a feed that was 0.44 acid deficient. Thus, it appeared that earlier fears of bisulfite decomposition by nitrate in the pilot plant between 50 and 60°C had been unjustified.

3.7 Bisulfite Treatment Recommended for Future Short-decayed Thorex Pilot Plant Runs

Ruthenium decontamination factors of 10^2-10^3 in the first cycle extraction column should be obtainable with 0.06 M sodium bisulfite and a contact time between 10 and 60 min at 50-65°C. Lower concentrations of bisulfite are apt to be ineffective owing to reaction with the products of irradiation. Higher concentrations begin to affect the extractability of the thorium. Feed temperatures below 50°C will need longer contact times than those necessary at higher temperatures. Feeds cooled to approximately room temperature need several hours to days of contact time, and thus introduce the problem of higher bisulfite requirements to match the disappearance by consumption by irradiation products. Temperatures higher than 65°C should not be used due to the danger of bisulfite decomposition by nitric acid, and of the introduction of nitrite.

4.0 ELIMINATION OF MERCURY FROM DISSOLVER CATALYST

The rate of penetration of the aluminum jackets on the thorium slugs in the Thorex dissolver solution without mercury is about 2.5 mils/hr. At this rate the 30-mil-thick aluminum jacket will dissolve more rapidly than the massive thorium slug. The elimination of mercury, besides decreasing the extractability of iodine, also precludes troublesome side reactions involving mercury, sodium bisulfite, and nitric acid.

Sheets of 2S aluminum were dissolved in boiling Thorex dissolver solution containing varying amounts of mercury. Typical penetration rates were:

Hg Conc.(M)	Penetration rate (mils/hr)	Hg Conc.(M)	Penetration rate (mils/hr)
0	2.5	0.0005	9.1
0.000025	2.7	0.0010	8.3
0.00005	2.5	0.0025	8.5
0.00025	6.5		

The rate of dissolution of aluminum in solutions containing acid, thorium, and aluminum at concentrations approximately those which would exist at the end of the dissolving step was about 2.0 mils/hr.

The dissolving procedure used in the pilot plant was as follows: A batch of irradiated slugs was loaded in the dissolver and the aluminum jackets were removed with caustic. A second batch was then loaded and acid dissolver solution was added. The dissolvent originally used contained nitric acid, fluoride, and mercury to increase the dissolution rates of thorium and aluminum, respectively. Dissolution progressed until the equivalent of one batch of thorium was in solution, a 100% heel being maintained throughout the run with a final heel dissolving to clear the tank. Elimination of mercury from the dissolver solution increases the dissolution cycle time only slightly, and would not increase it at all if the heel was slightly larger than 100%.

5.0 PROTACTINIUM RECOVERY

Present plans are to store the first-cycle solvent extraction column aqueous waste for decay of the protactinium to U-233, which will then be recovered. However, further laboratory studies were made on methods of recovering protactinium from the waste for possible future use. More than 99.8% of the protactinium coprecipitated with zirconyl phosphate, thorium iodate, or thorium hydroxide. About 99.4% of the protactinium coprecipitated with manganese dioxide.

5.1 Zirconyl Phosphate

Two coprecipitations with 0.06 M zirconyl phosphate removed 99.9967% (d.f. = 3×10^4) of the protactinium from pilot plant short-decayed waste, which had an initial protactinium activity of 4.3×10^9 gamma counts/ml/min. Preformed zirconyl phosphate adsorbed only 52% of the protactinium under the same conditions. In aged waste refortified with a Pa-233 tracer, protactinium adsorption by 0.06 M preformed zirconyl phosphate was only 66%. Only 20-90% of the protactinium from aged and spiked waste was adsorbed on a cation exchange column of zirconyl phosphate beads (RC-24, Minnesota Mining and Manufacturing Company).

The procedure for the coprecipitation of protactinium with zirconyl phosphate was: Zirconyl chloride (0.1 g) was added to 5 ml of feed at room temperature and was followed by 0.5 ml of 1 M H_3PO_4. The mixture was stirred for a few minutes and then centrifuged. The supernatant was separated, and the treatment repeated. The protactinium decontamination factor was computed as the ratio of protactinium activity in the feed to that in the second supernatant.

With synthetic waste solutions, the percent of protactinium adsorbed varied with the acidity. From 0.55 M $Al(NO_3)_3$, adsorption varied from 94% at 6 N HNO_3 to 99.98% at pH 2.7. Adsorption was at least 99% in the pH range 0.1-3.0, and 98-99.7% at a pH between 4 and 5, with a decrease to about 95% at pH 3.5. The inclusion of 0.02 M fluoride did not affect the adsorption. Increasing the zirconyl phosphate concentration from 0.06 to 0.3 M improved the protactinium adsorption only slightly. For second cycles with fresh zirconyl phosphate only 65-80% of the remaining protactinium was adsorbed. Adsorption of protactinium from 1.8 M $Al(NO_3)_3$, simulating threefold concentrated waste from the 1A column, was 98.4% from 6 N HNO_3 solution and 70% at pH 3.5.

Preformed zirconyl phosphate was precipitated from a boiling solution of zirconyl chloride by slow addition of ortho-phosphoric acid with stirring. The precipitate was centrifuged, and washed three times by resuspension in 5% HNO_3. The material was stored as a wet slurry, and portions were withdrawn for wet addition.

To determine the effect of pH, the synthetic feed solution of 500 ml of 0.55 M $Al(NO_3)_3$ was spiked to 10^6 counts/ml/min with Pa-233, 0.5 M preformed zirconyl phosphate (1.5% computed as dry weight) was added, and the solution was stirred for 10 min. The pH was read, from a pH meter with the electrodes immersed in the solution. A 5-ml sample was then withdrawn for centrifugation and protactinium determination in the supernatant. Ammonium hydroxide was then added, with continuous stirring, until another chosen pH had been reached. After 10 min of further stirring a second sample was withdrawn. This procedure was repeated for as many as 15 pH points, until the aluminum hydroxide began to thicken the solution. The pH range was then retraced by suitable additions of nitric acid. The % of protactinium adsorption was calculated from the relative gamma activities of the feed and sample supernatants, with suitable adjustments being made for volume changes.

The RC-24 zirconium phosphate cation exchange material adsorbed 99.9% of the protactinium from spiked 0.55 M $Al(NO_3)_3$ solution during the first six bed volumes, and 99.8-99.9% in the next six volumes. After 20 bed volumes, adsorption dropped to 93%. From spiked 1.8 M $Al(NO_3)_3$ solution adsorption was only 97% after six bed volumes, and about 90% after the second six volumes. Adsorption fluctuated between 87% and 95% thereafter, up to 24 volumes. In these experiments, the exchange column consisted of a 100-ml buret packed with 30 grams of zirconium phosphate. The feed rate was 0.8 ml/cm^2/min. Each 20 ml collected from the column was analyzed separately for protactinium by gamma counting.

5.2 Thorium Iodate

A single coprecipitation with thorium iodate removed 99.960% of the protactinium (decontamination factor = 2.5×10^3) from a short-decayed waste solution from the pilot plant first-cycle extraction column, containing 1.2×10^{10} protactinium gamma counts/ml/min and 0.38 g of Th per liter. The precipitation was made at room temperature by the addition of 0.1 M iodic acid, stirring, and centrifuging.

The average protactinium removal with thorium iodate from nine daily samples of longer-decayed waste solution withdrawn from the pilot plant on consecutive days with 4×10^6 to 2×10^8 protactinium gamma counts/ml/min and thorium concentrations from 0.1 to 1.6 g/liter was 99.898% (decontamination factor = 980). The iodate precipitate also carried about 66% of the fission products. Recovery from long-

decayed waste spiked with Pa-233 was 90-95% when the iodic acid concentration was 0.01 M, compared to 99.7-99.95% at 0.06-0.10 M from the same waste solution. Protactinium recovery at 0.1 M iodic acid dropped to 98.6-99.7% when the spiked pilot plant waste solution was concentrated by a factor of 3.

5.3 Thorium Hydroxide

Coprecipitation of protactinium on thorium hydroxide from the same lot of short-decayed waste (Sec. 4.2) was 99.86% (decontamination factor = 730), and with the nine pilot plant samples removed daily also previously described, coprecipitation of protactinium by the caustic method averaged 99.74% (decontamination factor = 655). The thorium hydroxide carried about 99% of the fission products in addition to the protactinium. The procedure consisted in adding enough solid sodium hydroxide to the solution to redissolve the aluminum hydroxide which first formed, stirring, centrifuging, and analyzing the supernatant for protactinium.

In spiked and threefold-concentrated synthetic waste solutions containing 7 g of Th per liter, the precipitate carried more than 99.99% of the protactinium. In spiked pilot plant waste, with thorium added in the range 0.4-50 g/liter, the protactinium coprecipitation did not seem to depend on thorium concentration, and ranged from 99.2-99.97%. The precipitate was not pure thorium hydroxide, since a typical precipitate prepared from cold solutions and washed to 0.013% sodium was analyzed as 69.2% Th, 3.74% Al, and 3.45% $CO_3^=$.

5.4 Other Carriers for Pa-233

Coformed manganese dioxide adsorbed 99.4% of the protactinium from aged pilot plant waste spiked with protactinium. However, the use of a MnO_2 headend treatment decreases ruthenium decontamination in the solvent extraction column unless care is used in assuring complete destruction of the potassium permanganate. Thorium oxalate, precipitated over a range of concentrations, adsorbed 27-94% of the protactinium. Coformed aluminum hydroxide adsorbed 80-93% of the protactinium. Other carriers briefly tried, and their resulting protactinium adsorptions were: preformed sodium bismuthate, 52%; ferrous sulfamate, 35%; calcium hydroxide, 10%; mercuric nitrate, 89%; ferrous sulfate, 62%; and formic acid, 83%.

6.0 RADIOLYTIC GASES FROM SHORT-DECAYED AQUEOUS WASTE

The aqueous waste from the short-decayed Thorex runs is stored for about nine months for decay of protactinium. The U-233 formed is recovered by reprocessing by a 6% TBP-Amsco flowsheet similar to that used in the 25-TBP Process.[19] Concern has been expressed regarding the possibility of an explosion resulting from the radiolytic production of hydrogen and oxygen from water during storage.

In a series of experiments in which synthetic Thorex waste solutions, containing a small amount of TBP-Amsco but not fission products, irradiated by Co-60, ~ 1 ml (STP) of gas was produced for each watt-hour of energy absorbed. The failure of the gas to ignite with a hot platinum filament indicates less than 1% hydrogen. Chemical analysis of the gas showed 5% H_2, 11% O_2, 5% NO, 3% NO_2, 8% CO, and 31% CO_2.

Table 5.1 Analysis of Gas from Tank Containing Short-decayed Aqueous Waste

Gas	Analysis (%) Uncorrected	Corrected for Air Content [a]
H_2	0.5%	2%
O_2	18.6%	24%
NO	0.5%	2%
NO_2	0.5%	2%
CO [b]	14.9%	55%
CO_2	4.1%	15%
N_2	61%	—

[a] Correction based on nitrogen in sample.

[b] Gas combustible to CO_2 with oxygen; probably chiefly Amsco.

Based on these values, the rate of air sparge of the decay tanks was regulated to maintain less than 1% hydrogen in the off-gas.

In order to obtain an analysis of the radiolytic gas from the pilot plant decay tank (Table 5.1), the sparge gas was discontinued for 18 hr and a sample of gas removed from an off-gas line. After correction for the air content, this analysis showed less hydrogen than the analysis from laboratory experiments.

7.0 SOLVENT RECOVERY

In laboratory experiments, solvent from short-decayed Thorex runs could not be satisfactorily decontaminated with the carbonate treatment but could be recovered by treatment with a lime slurry or with 0.2 M potassium hydroxide.

The solvent recovery system for the Thorex plant is designed to remove solvent degradation products solids and fission products. The fission products may be present as suspended solids, dissolved in the solvent, or chemically reacted with the solvent. The carbonate treatment provides for about 5 stages of countercurrent contact with 1/10 volume of 0.2 M Na_2CO_3 in a pulsed column and gives a decontamination factor of approximately 10. This treatment decreases the solubility of both degradation products and fission products or promotes their solubility in the aqueous phase. Other methods of solvent treatment have been investigated in an attempt to improve the decontamination.

A slurry of lime in the solvent consistently decontaminated used solvent by a factor of 2-10 more than did the sodium carbonate treatment. The lime particles act as nuclei for the adsorption of very fine solids and colloids. An early lime-organic contactor[20] had difficulty removing lime fines from the organic solution. A water wash removes the bulk of the lime. Treatment with 0.1 M HNO_3 polishes the solvent and completes the decontamination.

Slurrying with activated alumina (80-200 mesh) gave high decontamination but 10-20 mesh alumina in a packed column failed to show sufficient capacity for use.

Treatment with 0.2 M NaOH or KOH gave decontamination factors about twice those obtained with 0.2 M Na_2CO_3. The addition of ammonium hydroxide did not improve decontamination. There was no difference between the sodium hydroxide and potassium hydroxide in decontamination but the solids from the potassium hydroxide treatment were less viscous and could be handled more easily in pilot plant equipment.

Good decontamination was obtained by dissolving potassium permanganate, which was slowly reduced to MnO_2 and precipitated. This process has not been adapted for pilot plant use due to the difficulties involved in removal of the solids.

When the first short-decayed thorium was processed, the solvent became contaminated with I-131 and Ru-103 in addition to larger quantities of other fission products than previously encountered. The standard sodium carbonate treatment gave higher decontamination factors than had been previously measured; however, the solvent remained excessively active and could not be satisfactorily decontaminated by any of the processes previously investigated. It was shown that the persisting contaminants were I-131 and ruthenium. Some of the iodine was dissolved in the solvent and could be removed by first adding I-127 carrier then scrubbing with $Na_2S_2O_4$. This process also removed most of the ruthenium. Some of the I-131 was apparently chemically reacted with the solvent and no method for removal has been found. A method for preventing contamination of the solvent is discussed in Sec. 8.1.

For a new installation separate solvent recovery systems for the two cycles would be recommended in order to prevent cross contamination. Of the various solvent recovery processes that seem to be adaptable to pilot plant use, the lime slurry treatment gives the best consistent decontamination.

8.0 EFFECT OF IODINE IN SHORT-DECAYED THORIUM SOLUTION

8.1 Removal of Iodine from Feed Solutions

In early experiments on dissolution of short-decayed thorium or uranium, only 30-60% of the I-131 was volatilized in the dissolution. Part of the I-131 that remained in the solution was extracted by the TBP-Amsco and was recycled in the solvent resulting in increasing the radioactivity of the solvent with each pass (Sec. 7.0). In laboratory experiments, the continuous addition of 0.01 M KI to the dissolver during dissolution of the short-decayed thorium slugs resulted in the volatilization and removal of approximately 99% of the I-131 as elemental iodine. The addition of 0.01 M KI — 0.005 M Na_2SO_3 to the extractant column scrub solution converted the isotopically diluted I-131 that remained to unextractable iodide. In the short-decayed pilot plant runs the continuous addition of potassium iodide solution during slug dissolution, to a final concentration that would be 0.001 M if I_2 volatilization was neglected, resulted in an overall I-131 decontamination factor of at least 10.[7] Bisulfite, but no iodide, was used in the scrub in these runs.

In tracer concentrations, I-131, even when reduced to iodide by sulfite, was distributed about equally between the aqueous and organic phases in solvent extraction. The addition of as little as 0.001 M KI as an isotopic diluent raised the decontamination factor of I-131, as iodide, to over 200. However, the highly oxidative slug-dissolution and feed-preparation cycles of the Thorex Pilot Plant produced oxidized iodine in small proportions which did not exchange isotopically with nonradioactive iodine, iodate, or periodate and was not reduced to iodide with bisulfite. Isotopic dilution of these oxidized forms, and subsequent easy handling was accomplished only by addition of nonradioactive iodide prior to an oxidation cycle.

8.2 Reactions with Mercury

Mercury reacts with the iodide in the solvent extraction feed solution to give simple and complex iodides soluble in TBP-Amsco. The extractability of iodine from a solution containing .05 M iodide was proportional to the mercury concentration.

Hg in Feed (M)	I-131 in Organic (gamma counts/min/ml)
0.001	1.28×10^5
0.004	4.38×10^5
0.010	1.28×10^6

When isotopically diluted I-131 was extracted by TBP in the absence of mercury, scrubbing with sulfite removed most of the iodine. When mercury was present, iodine could not be removed by a sulfite scrub.

I-131 in Organic Feed	I-131 in Organic (gamma counts/min/ml)
No scrubbing	2.07×10^5
After 2 scrubs with 0.005 M sulfite	1.69×10^5
After 4 scrubs with 0.005 M sulfite	1.43×10^5
After 6 scrubs with 0.005 M sulfite	1.31×10^5
After 8 scrubs with 0.005 M sulfite	1.14×10^5

The addition of iodide to the scrub resulted in a tenfold decrease of the amount of I-131 in the organic phase, apparently by isotopic exchange:

I-131 in Organic Feed	I-131 in Organic (gamma counts/min/ml)
No Scrub	6.3×10^4
After 2 scrubs with .01 M iodide - .005 M sulfite	3.9×10^3
After 4 scrubs with .01 M iodide - .005 M sulfite	1.8×10^3
After 6 scrubs with .01 M iodide - .005 M sulfite	2.5×10^3
After 8 scrubs with .01 M iodide - .005 M sulfite	1.7×10^3

The feed for the second series was the material that had been scrubbed in the first series. The difference in initial activity was a result of several days' decay between runs. Dissolving-rate studies (Sec. 4.0) led to the elimination of mercury as a dissolver catalyst in the Thorex Pilot Plant.

8.3 Corrosion of Stainless Steel by Iodine Crystals

A trial use of 0.01 M KI in Thorex pilot plant feed, followed by a boildown cycle of the aqueous waste, resulted in actual puncture of stainless steel piping by wet iodine crystals in the off-gas system. No further trouble was encountered with corrosion when iodine crystals were not permitted to form. This was accomplished by dropping the KI concentration to 0.001 M, keeping the off-gas lines hot, and using an adequate flow of purge gas.

In a single laboratory experiment to determine the corrosion rate of 1/32-in.-thick coupons of stainless steel (309 SNb, 304 ELC, and 347) in synthetic Thorex feed solution containing thorium nitrate, aluminum nitrate, mercury, iodide, and sulfite at 87°C, 6-8% of the metal dissolved in 1 hr. Duplicate experiments and several other combinations of the reagents failed to produce any measurable attack on the same coupons.

9.0 DILUENT STUDIES

9.1 Comparison of Amsco and Decalin

The decontamination of thorium from fission products is critically dependent on the concentration of the thorium in the solvent (Fig. 9.1). A solution of 42.5% TBP in Amsco 125-82 will dissolve ~86 g of thorium per liter as the thorium-TBP complex without the separation of a second organic phase.[1] The formation of the second organic phase limits the thorium concentration in the Thorex extraction colums. If Decalin (decahydronaphthalene) is used as the diluent, the second organic phase is not formed until the concentration reaches ~125 g of thorium per liter. Under pilot plant conditions the flowsheet must be designed so that the thorium concentration does not exceed 90% of these saturation values, to allow for control. The use of Decalin as a diluent, therefore, could markedly increase the solvent capacity and the fission product decontamination.

Since Decalin has a specific gravity at 20°C of 0.885-0.890 where Amsco 125-82 has a specific gravity at 15°C of 0.7620 (Fig. 9.2) pulse column operation is somewhat more difficult to control with Decalin as a diluent than with Amsco. The density of TBP-in Decalin containing thorium nitrate is about 0.08 g/l greater than that for 41% TBP-Amsco containing the same concentration of thorium. (Fig. 9.3). In order to obtain a higher saturation of the thorium in the TBP without greatly increasing the density of the organic phase, a 35% solution of TBP in Decalin was chosen to maintain the present plant capacity.

In countercurrent batch extractions made under standard extraction column conditions except for a substitution of 35% TBP-Decalin for 42.5% TBP-Amsco, there were no mechanical difficulties. However, in engineering scale studies[21] using synthetic feed solutions the substitution of 35% TBP-Decalin for 42.5% TBP-Amsco increased the height equivalent to a theoretical stage of the pulsed column from ~2.5 ft to 5.6 ft and therefore increased the thorium loss (Fig. 9.4) to the aqueous waste stream. No engineering studies were made of the effect of solvent concentration on the height equivalent to a theoretical stage, and the variation due to Decalin therefore could not be evaluated. Time did not permit engineering-scale investigation of a simple substitution of 42.5% TBP-Decalin for 42.5% TBP-Amsco. In the batch extractions, synthetic feed solution contained 9×10^3 Pa gamma counts/m/mg of Th, 6×10^2 Zr-Nb gamma counts/m/mg of Th, 20 Ru gamma counts/m/mg of Th, and 3×10^3 total rare earth beta counts/m/mg of Th. Activity in the product stream was too low for accurate analysis but was less than 1 Pa gamma counts/m/mg of Th, 0.5 Zr-Nb gamma counts/m/mg of Th, 2 Ru gamma counts/m/mg of Th, and 3 total rare earth beta counts/m/mg of Th.

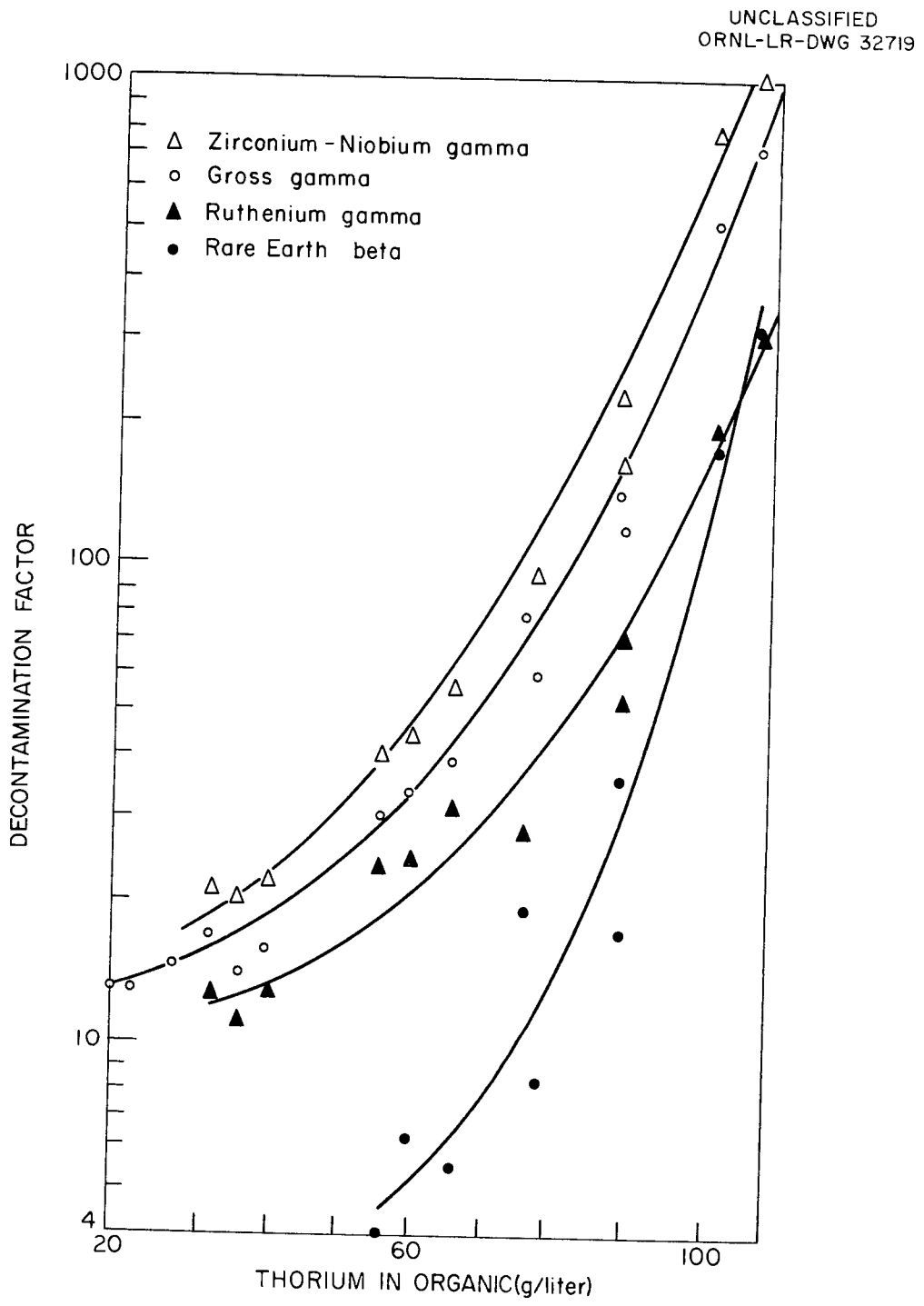

Fig. 9.1. Decontamination Factor of Thorium Product as a Function of Thorium Concentration in Organic Phase. Solvent: 42.5% tributyl phosphate-57.5% Decalin; aqueous phase: 0.5 M $Al(NO_3)_3$ containing thorium nitrate.

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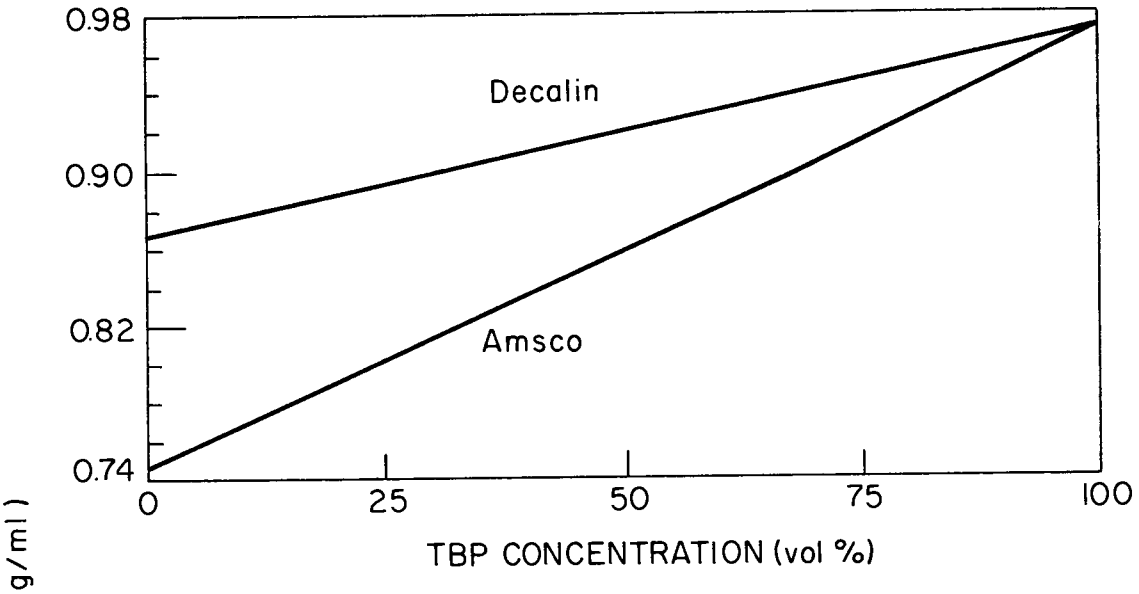

Fig. 9.2. Density of TBP-Amsco and TBP-Decalin Solutions as a Function of TBP Concentration.

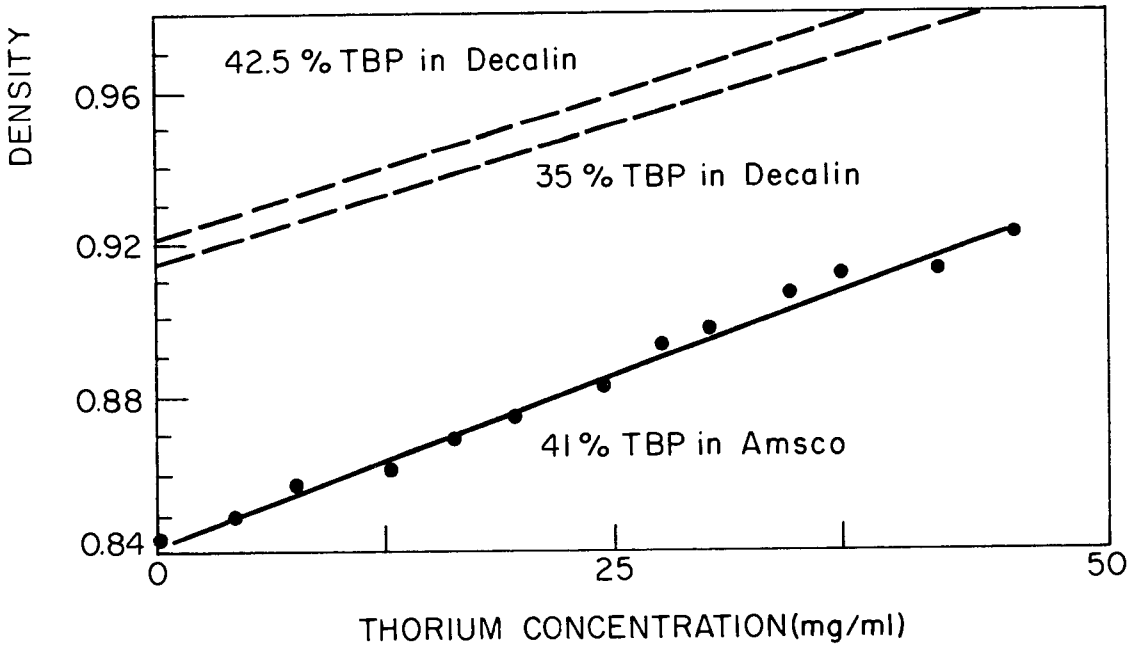

Fig. 9.3. Density of TBP-Diluent Solutions of Thorium Nitrate as a Function of Thorium Nitrate Concentration.

Table 9.1 $G_{I_2}^{*}$ Values for Amsco and Decalin

Irradiation Time (min)	G_{I_2}	
	Amsco	Decalin
2	0.88	0.96
6	0.70	0.88
15	0.64	0.86

* Molecules of I_2 reacting with degradation products per 100 ev.

The radiation stabilities of Amsco 125-82 and Decalin were compared by irradiation of air-saturated solvent containing dissolved iodine in a Co-60 source. The radical formation was measured by the reaction with the iodine which contained I-131 tracer.[22] The G_{I_2} value (number of molecules of I_2 reacted with degradation products per 100 ev) of the solvents showed slightly more irradiation degradation of the Decalin than Amsco. The irradiation exposure of the Amsco was 5.6×10^{15} kev/m/ml and of the Decalin 6.8×10^{15} kev/m/ml. After irradiation the excess iodine was removed from the organic by repeated washing with thiosulfate. The iodine that had reacted with the organic varied from 0.2 to 1% of the total iodine present.

9.2 Gas Chromatographic Study of Amsco*

Gas chromatographic analyses of Amsco 125-82 have shown the presence of possibly 14 components (Fig. 9.4) including about five low boilers which are possibly olefins. Treatment of the Amsco with concentrated sulfuric acid or oleum removed four of the low boilers and produced an additional peak (No. 4). Treatment with 0.5 M Na_2CO_3 solution or a lime slurry changed the shape of one peak (No. 2) and flattened another (No. 4). The program was not extended to the identification of the various components.

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* Analytical study by J. G. Surak, Prof. of Chemistry, Marquette University, summer employee Analytical Chemistry Division, ORNL.

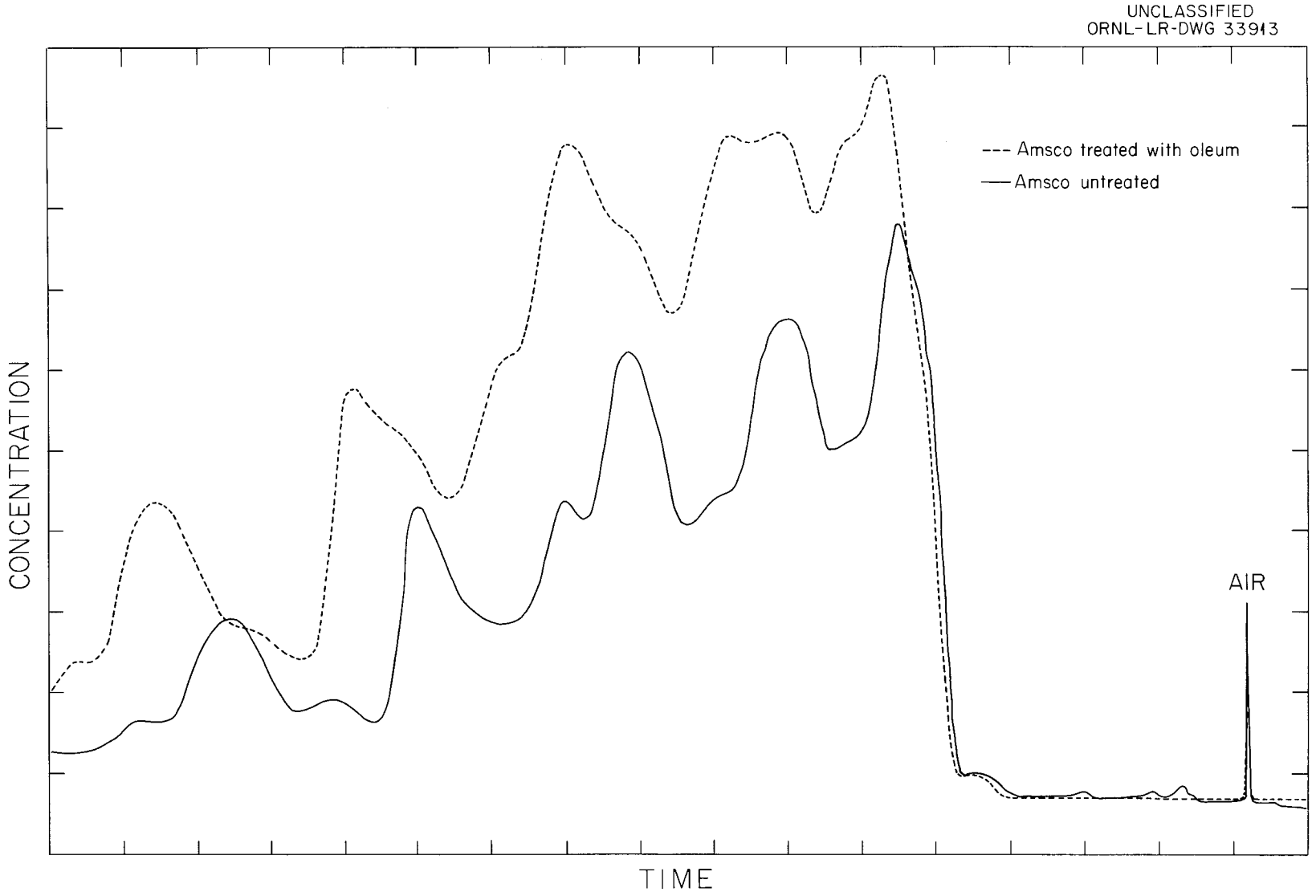

Fig. 9.4. Gas Chromatograph Analysis of Amsco 125-82.

10.0 PHYSICAL CONSTANTS OF FEED SOLUTIONS

10.1 Variation of Density with Uranium and Nitric Acid Concentrations

The specific gravity of an aqueous solution of uranyl nitrate containing 300 g of uranium per liter at 25°C and nitric acid may be calculated from the equation

$$\text{Sp gr}_{25} = 1.400 + 0.033\ \underline{M}_{HNO_3}$$

where $\underline{M}_{HNO_3}$ = molarity of the nitric acid. Known values selected from the handbook differed from the values obtained from this equation less than 2%. For temperatures above 25°C, the specific gravity varies at the rate of 0.0008 unit per degree of temperature change. After the specific gravity at 25°C is found from the above equation, the value at any temperature may be found from

$$\text{Sp gr}_t = \text{Sp gr}_{25^\circ} - 0.0008\ (t-25)$$

where t is the temperature in degrees centigrade.

10.2 Variation of Boiling Point with Uranium and Nitric Acid Concentrations

A plot of uranium and nitric acid concentrations vs boiling point of the solution is shown in Fig. 10.1. The data for this curve were obtained from a solution initially containing 33 g of uranium per liter and 0.2 $\underline{M}$ HNO_3, which is the expected composition of the solvent extraction product to be concentrated in the falling film evaporator used to concentrate the third uranium cycle product. With a different nitric acid/uranium ratio the curve may be slightly different. The solution was boiled in a system fitted with a condenser so that the condensate could be collected. The volume of the condensate was measured and titrated with standard sodium hydroxide, so that the amount of nitric acid that boiled off could be determined. The acid concentration was plotted against the observed boiling point, which was read at the time of removal of each sample.

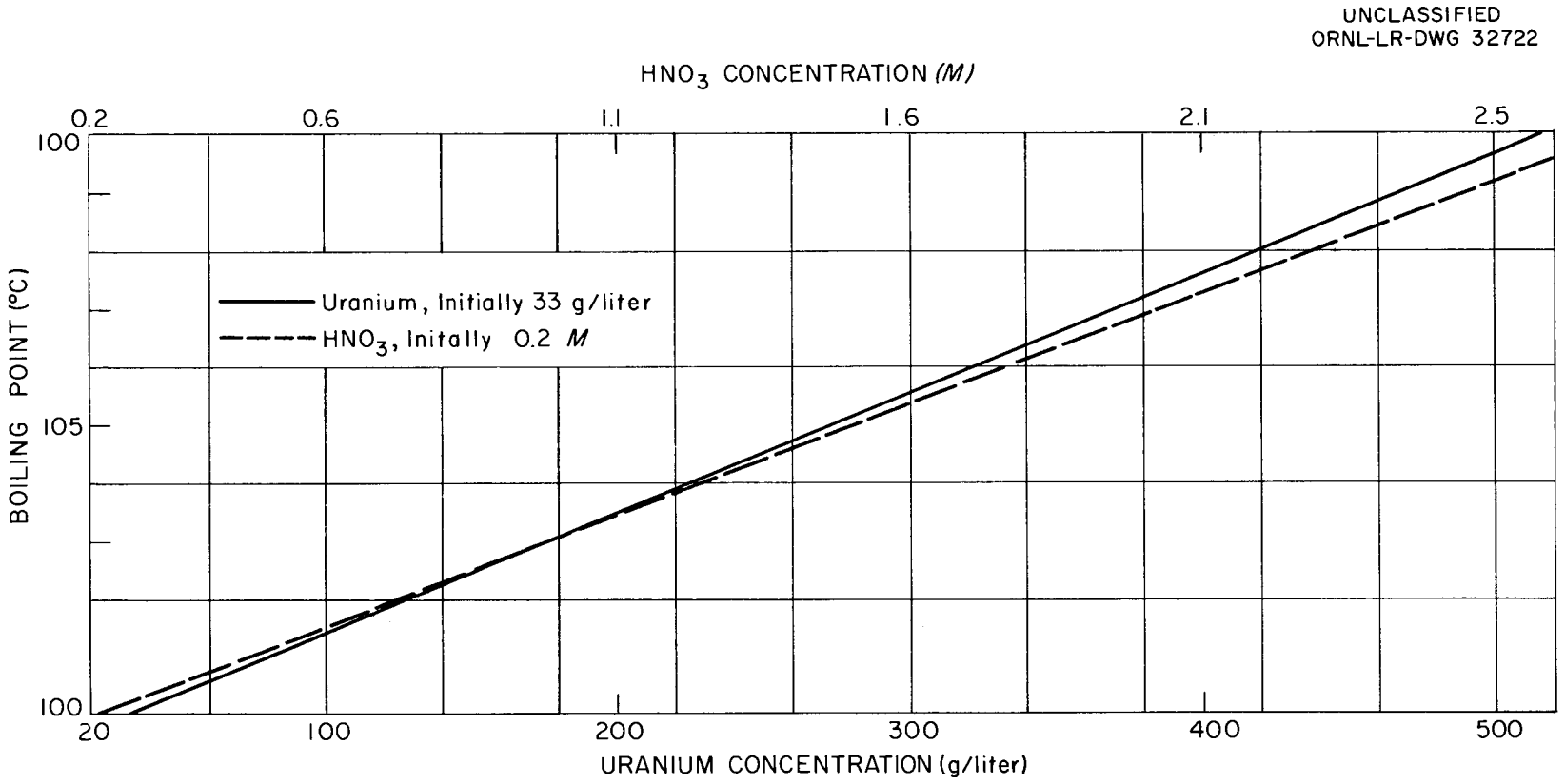

Fig. 10.1 Boiling Point vs Concentration of Uranium and HNO_3.

11.0 ELUTION OF URANIUM FROM DOWEX-50 RESIN WITH ACIDIFIED TBP

Approximately 97% of the uranium on a Dowex-50 ion exchange resin column was eluted in 2.3 volume changes of acidified 42.5% TBP giving uranium product at 30 g of uranium per liter with a decontamination factor from fission products of more than 10^3. The remaining 3%, which was eluted in an additional 1.7 volume change, was decontaminated by a factor of over 300. No difficulty was encountered in making the transition between aqueous and organic phases.

An ion exchange column containing 50-100 mesh Dowex-50W resin was loaded to 30% of its capacity with uranyl nitrate containing 4×10^3 each of beta and gamma counts/m/mg of U. Only 1% of the fission product activity failed to sorb on the resin. The column was then eluted with 42.5% TBP-Amsco which had previously been saturated with nitric acid. About 97% of the uranium was downflow eluted in the first 2.3 volume changes of the resin. This uranium had less beta and gamma activity than normal uranium. The remaining 3% of the uranium was eluted in an additional 1.7 volumes. The activity on the ion exchange column remained at the top of the column during the elution. After the uranium elution about 75% of the activity was removed from the column with four volume changes of an acetate-citrate solution.

Although this process had interesting features, it was not considered applicable to the Thorex Pilot Plant. Clean separation of the organic phase from the aqueous is not simple in engineering equipment. The uranium would have to be stripped from the organic. The existing resin columns were therefore modified to provide for downflow adsorption then upflow elution with nitric acid.[7] A third uranium cycle was added to provide additional decontamination (Sec. 2.3).

12.0 EXTRACTION OF ALUMINUM BY 42.5% TBP-AMSCO

The amount of aluminum extracted by 42.5% TBP-Amsco as a function of the concentration of aluminum nitrate concentration is approximated by the equation:

$$\log (\mu g \text{ Al in 1 ml organic phase}) = 1.66(\underline{M} \text{ Al}(NO_3)_3 \text{ in aqueous phase}) - 0.35$$

Equal volumes of 42.5% TBP-Amsco and aqueous aluminum nitrate were equilibrated at room temperature. The organic phase was removed, centrifuged, and analyzed by spectrographic techniques.* The concentration of aluminum in the organic phase is greatly increased by increasing the concentration in the aqueous phase (Fig. 12.1).

The pilot plant has found an almost constant small amount of aluminum present in the thorium product stream. The source of the aluminum could be accredited either to aluminum solubility in the TBP or to entrainment of aqueous from the extraction column. The experiment strongly indicates that the solubility of aluminum in TBP is responsible and that de-entrainment equipment is not warranted.

13.0 "GREASE" IN THOREX PILOT PLANT

The Thorex Pilot Plant has found that the tendency of the pulse columns to flood became progressively more pronounced with time, owing to the formation of a thorium-organic complex on the plates in the column. This material has been referred to as "Thorex grease" and has the appearance of heavy petroleum. It is not soluble in Amsco, tributyl phosphate, or in common mineral acids, but is highly soluble in trichloroethylene and acidified tributyl phosphate. Analytical methods have not been developed to identify the complex which is suspected to be thorium dibutyl phosphate.

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* Marvin Murray, Analytical Chemistry Division, ORNL.

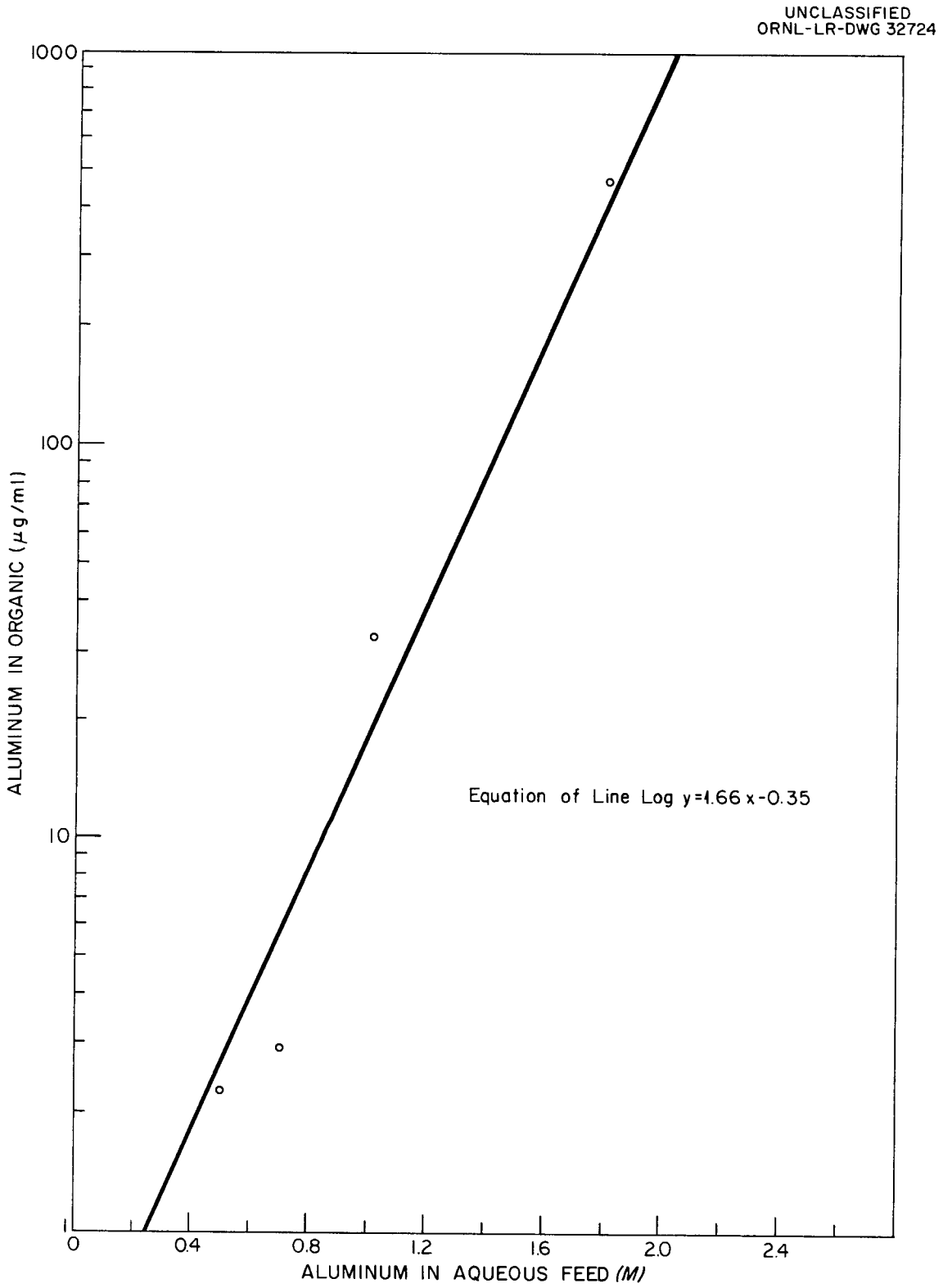


Fig. 12.1. Extraction of Aluminum by 42.5% TBP-Amsco. Feed contains only $Al(NO_3)_3$

The rate of hydrolysis of tributyl phosphate to dibutyl phosphate is increased with elevated temperatures or with the amount of irradiation. The principal source of the hydrolysis is probably the dissolved and entrained tributyl phosphate which is heated in the interstage evaporator or in the feed adjustment cycle.

The largest accumulation of the complex was in the second cycle strip column, but, since the stripped solvent from this column was used in the first cycle without treatment, the first-cycle strip column also accumulated the complex at a slower rate. A procedure developed for removing the grease consisted in washing the columns with ~ 6 $\underline{M}$ HNO_3 and then with Amsco. Apparently the strong acid displaces the thorium, converting the organic salt to an acid which is soluble in Amsco. This removed the bulk of the complex but did not leave the surfaces completely wettable by aqueous solution. The use of various soaps and detergents did not give noticeable improvement in operation. In the laboratory, a wash with trichloroethylene followed by a wash with nitric acid left the plates wettable by water. There was considerable hesitancy about the use of chlorine-containing compounds in pilot plant equipment for fear of corrosion of the stainless steel.

14.0 APPENDIX

The data from countercurrent batch extractions or strippings may be mathematically approximated by a graphical method which simulates conditions existing in each stage after each equilibration or at equilibrium conditions. The agreement with experimentally determined concentrations of thorium in a strip column after five volume changes is:

	Thorium Concentration (mg/ml)					
	Organic			Aqueous		
	After 5 vol chgs.		Calculated	After 5 vol chgs.		Calculated
Stage	Expl.	Calc.	Equilibrium	Expl.	Calc.	Equilibrium
1	58.3	57	62	98.0	99	108
2	46.1	45	54	79.5	82	94
3	31.2	29	45	60.4	60.5	82
4	15.5	13	35	42.8	40.8	68
5	1.08	0.80	23	17.6	16.8	54

In this experiment 1.5 volumes of 42.5% TBP-Amsco containing 71.3 g of thorium per liter was batch-countercurrently stripped with 1 vol of 0.008 $\underline{N}$ HNO_3. After 5 column changes, both phases of each stage were analyzed for thorium. The thorium concentrations were calculated by the method described below.

The graph consists of two lines plotted on coordinate paper of some convenient scale. The line OB (see Fig. 14.1) is the quantity of solute in the feed phase plotted versus the total quantity of solute in the combined organic and aqueous phases. These data are determined by simple batch equilibrations of the two phases and taking into consideration the flow rates of the organic and aqueous phases. Line OA is a line of slope 1 drawn through the origin and can be thought of as representing the case where the solute is soluble only in the feed phase. An extraction factor of 1 is represented by a slope of 0.5 on the graph. Therefore, a system is not operable if the slope of the tangent to the OB curve is greater than 0.5 at any point which might be encountered in the operation.

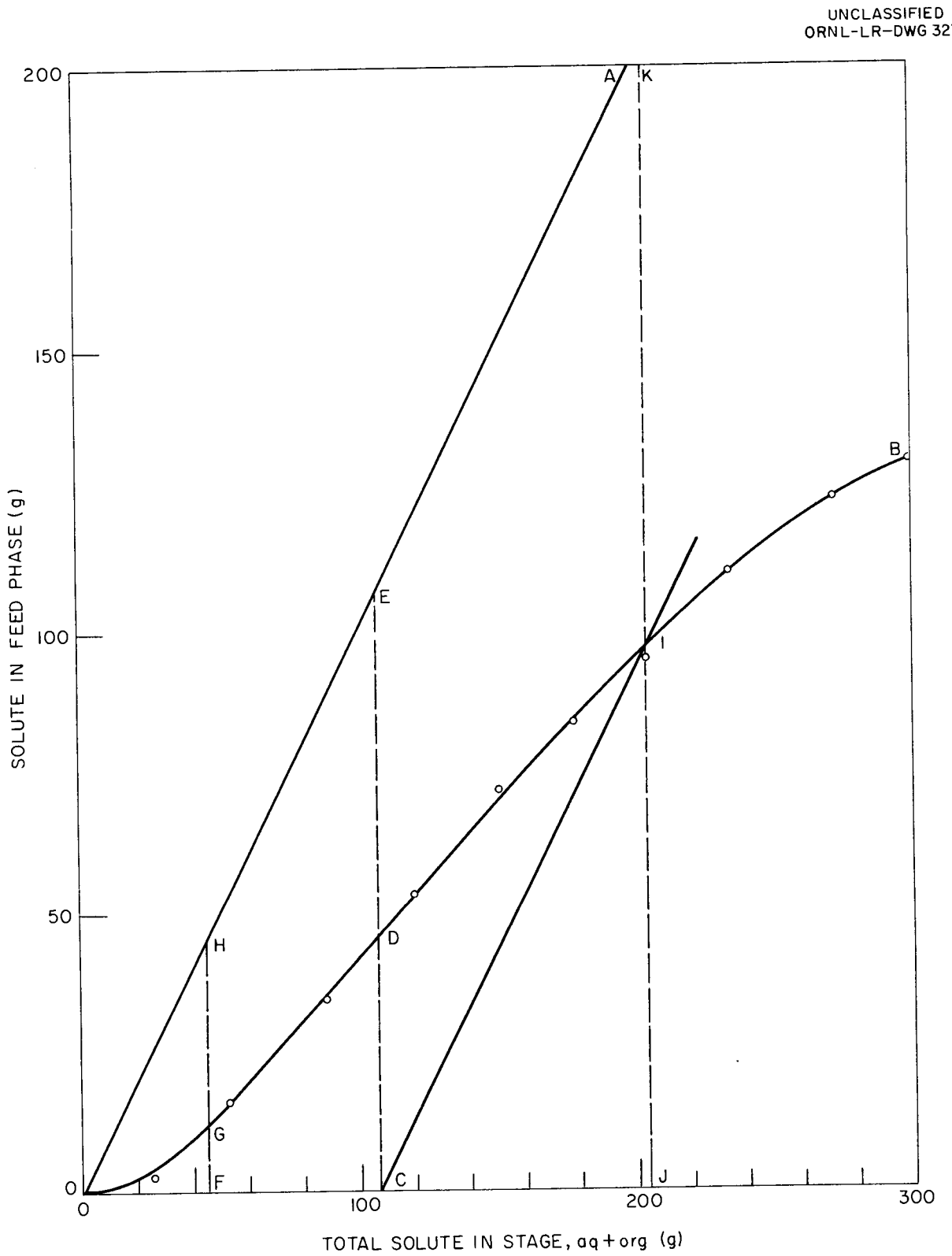
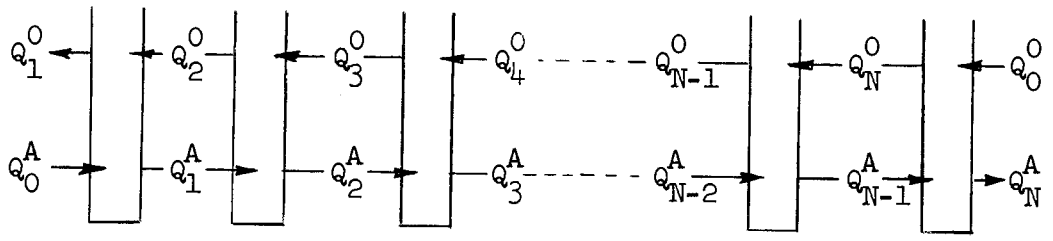


Fig. 14.1. Graph for Calculating Countercurrent Batch Extraction Data.

A similar calculation may be made on extraction column. By using two sets of graphs, a compound column simulating extraction and scrub sections may be made.

The nomenclature of the solvent extraction system is indicated by the following sketch:



The amount of solute in a given stream, Q, is equal to the volume (or flow rate) times the concentration of solute at that point. The superscript designates the phase and the subscript the stage from which the solution came. If the equilibrium number is to be used as well, it may be hyphenated in the subscript; e.g. (Q^A_{2-3} is the aqueous phase from third equilibration of the second stage, or $Q^O_{(N-1)-4}$ is the organic phase from the 4th equilibration of the N-1 stage).

14.1 Graphical Calculations of Material Balance

For Nonequilibrium Conditions. To calculate the distribution of the solute at the end of the first equilibration of the first stage, a vertical line is drawn from the point C on the abscissa which is equivalent to the amount of solute in the feed. This line intersects OB at D and OA at E. By construction DE is equivalent to the amount of solute which transfers to the new phase Q^A_{1-1} and CD the amount remaining in the feed phase Q^O_{1-1}. In the illustration, there are 1.5 volumes of feed containing 71.3 g of thorium per liter, equivalent to 107 g in the feed. After equilibration the thorium is distributed so that 62 g is in the aqueous phase and 45 g remains in the organic. In like manner, a second equilibration is simulated by drawing a vertical line at 45, intersecting OB at G and OA at H. As before, GH is the amount in the aqueous phase, Q^A_{2-1}, and is equal to 34 g and FG is the amount remaining in the organic phase, Q^O_{2-1}, or 11 g. This process is continued for as many stages as desired. As the lines approach the apex, new graphs with smaller scales may be used to maintain the desired accuracy.

In the second equilibration of the first stage, the quantity of solute in the stage is the amount in the feed (107 g) plus the amount in the aqueous phase, (34 g) Q^{A}_{2-1}, 141 g. The procedure is repeated adding the amount entering the stage in the organic phase from the previous equilibration; for example, Q^{A}_{3-1} is added to Q^{O}_{1-2} before the second equilibration of the second stage.

This procedure may be continued for as many equilibrations as desired.

For Equilibrium Conditions. When the column has reached equilibrium the quantity of solute leaving the column must be equal to the amount entering. Since the assumption is made that no solute leaves in the feed phase, Q^{O}_{o} equals Q^{A}_{1}.

In order to determine the equilibrium material balance about the first stage, a line with a slope of 1 is drawn through C, intersecting OB at I. A vertical line is drawn through I, intersecting the abscissa at J and OA at K. The line IK represents Q^{A}_{1}, the amount of solute leaving the column, and is equal to OC, the feed to the column. By construction IJ represents the organic phase in equilibrium with IK and, therefore, is equivalent to Q^{O}_{1}.

In the illustration the feed, and therefore Q^{A}_{1}, also contains 107 g of thorium. The 1.5 volumes of Q^{O}_{1} contains 93 g of thorium or 62 g of thorium per liter. In like manner, a material balance around the second stage may be determined by drawing a line with a slope of 1 from 93 on the abscissa. This procedure is repeated for the number of stages desired. The Q^{O}_{N} will closely approximate the loss from the column at equilibrium.

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