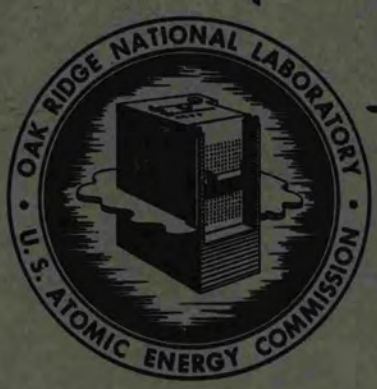
ORNL-2473
Chemistry - Separation Processes
for Plutonium and Uranium

THOREX PROCESS: THIRD URANIUM CYCLE STUDIES

J. R. Oliver



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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

THOREX PROCESS: THIRD URANIUM CYCLE STUDIES

J. R. Oliver

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1.0 ABSTRACT

Laboratory studies indicated that a Thorex third cycle uranyl nitrate feed containing 50 g of uranium per liter should be 0.70 M in $Al(NO_3)_3$ and 0.50 M in HNO_3; the scrub, 0.50 M in $Al(NO_3)_3$; the extractant, 10 vol % tributyl phosphate (TBP) in Amsco; and the feed/scrub/extractant flow ratios, 1/0.3/1.5. With these conditions the uranium loss was 0.005 g/liter, or 0.01%, in laboratory tests. Decontamination factors were about 600 for ruthenium and 400 for zirconium-niobium.

2.0 INTRODUCTION

This report recommends conditions for the Thorex third uranium solvent extraction cycle, based on single and multiple extractions and batch countercurrent runs. The third cycle was added to the process in order to increase the uranium decontamination from fission products when highly irradiated, short-decayed thorium is processed. Uranium losses to the aqueous raffinate should be less than 0.01%.

In the Thorex Pilot Plant, the third cycle uranium product is concentrated in a falling film evaporator, and specific gravity measurements will be used to determine the uranium concentration of the residual solution. Since this solution will contain nitric acid at a concentration that will increase as the uranium concentration increases, although not necessarily at the same rate, the relation between the solution density and the uranium and nitric acid concentrations was determined. The relation between the boiling point of the solution and the uranium and nitric acid concentrations was also determined.

The writer acknowledges the assistance of R. H. Rainey whose suggestions were very helpful in the course of this investigation. Thanks are due also for the analytical work performed by Ed Wyatt and G. R. Wilson and their groups. J. H. Groover assisted with many of the laboratory experiments.

3.0 EXTRACTION CONDITIONS

In developing a flowsheet for the third uranium cycle, the following equilibriums must be considered:

$$UO_2(NO_3)_2 \rightleftharpoons UO_2^{++} + 2NO_3^-$$

$$2TBP + UO_2(NO_3)_2 \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP$$

The first equation indicates that the addition of a source of nitrate ion, such as aluminum nitrate, will cause the formation of more un-ionized uranyl nitrate, the extractable species. Similarly, the use of a higher concentration of TBP will facilitate the formation of the complex, which is responsible for its extraction. However, increasing the concentrations of the above components will also enhance the extractability of the fission products that have persisted to the third cycle. Conditions must therefore be chosen to effect a suitable compromise between uranium loss and decontamination from fission products.

3.1 Single Batch Extractions

Synthetic third cycle feed, containing aluminum nitrate, nitric acid, uranyl nitrate, and fission products, was extracted with tributyl phosphate in Amsco in preliminary tests.

Effect of Feed Aluminum Nitrate Concentration. Under the conditions of the experiment, increasing the $Al(NO_3)_3$ concentration up to 0.7 M increased the uranium distribution to the organic phase (Table 3.1), but further increase in the $Al(NO_3)_3$ gave little increase in uranium extraction. The extractability of the fission products continued to increase with higher concentration of $Al(NO_3)_3$ (Fig. 3.1), thereby decreasing the separation factor of uranium from fission products. With any particular set of conditions, the amount of $Al(NO_3)_3$ used as salting agent should be the minimum required to prevent excessive uranium loss.

Effect of Feed Acidity. This was the only variable measured which gave both an increase in uranium extractability and decontamination factor at the same time. Increasing the HNO_3 concentration from 0 M to 3.5 M in the presence of 0.5 M $Al(NO_3)_3$ increased the uranium extraction slightly (Table 3.2). The feed uranium concentration was 0.5 g/liter. The 0.5 M HNO_3, which was used in most of the extraction work, seemed satisfactory.

Decontamination from ruthenium increased with increasing acidity (Fig. 3.2). Total rare earths were badly scattered, but decontamination generally increased with acidity. The Zr-Nb data were also badly scattered, but decontamination decreased with acidity.

Effect of Uranium Concentration. The concentration of uranium influences its distribution coefficient in two ways. First, uranium acts as a self-salting agent. The self-salting of the uranium is high near the feed plate where the concentration is high, but the effect rapidly vanishes when additional extraction stages are added. Second, the extracted uranium complexes the TBP, decreasing the solvent available for further extraction. This effect is greatest at the feed plate and somewhat compensates for the self-salting effect. Satisfactory uranium distribution coefficients were maintained throughout the range of 0.005-50 g/liter by using 1.0 M $Al(NO_3)_3$ and 10% TBP (Tables 3.3 and 3.4).

Effect of Aluminum Nitrate/Nitric Acid Ratio. Varying the ratio of aluminum nitrate to nitric acid while keeping the nitrate ion concentration constant at 4.7 M affected the uranium distribution. Extraction was best with a low concentration of nitric acid and a high concentration of aluminum nitrate (Table 3.5).

Since nitric acid is extracted by TBP, the uranium and acid compete for the TBP. Also, the cation being trivalent in the case of aluminum nitrate, it is likely that the difference in ionic strength, even with the same nitrate ion concentration, affects the salting ability of the electrolytes.

Table 3.1. Distribution of Uranyl Nitrate to TBP-Amsco as a Function of Aluminum Nitrate Concentration

HNO_3 concentration of feed: 0.5 M
Uranium concentration of feed: 2 g/liter
TBP concentration: 15%

$Al(NO_3)_3$ Concentration, M	Distribution Coefficient (O/A)	$Al(NO_3)_3$ Concentration, M	Distribution Coefficient (O/A)
0.08	2	0.72	40
0.16	4	0.80	50
0.24	7	0.88	70
0.32	10	0.96	15
0.40	14	1.04	60
0.48	20	1.12	120
0.56	30	1.20	50
0.64	40	1.28	80

Table 3.2. Distribution of Uranyl Nitrate to 15% TBP Amsco as a Function of Nitric Acid Concentration

$Al(NO_3)_3$ concentration of feed: 0.5 M
Uranium concentration of feed: 2 g/liter
TBP concentration: 15%

HNO_3, M	Distribution Coefficient (O/A)	HNO_3, M	Distribution Coefficient (O/A)
0	30	2.0	50
0.5	35	2.5	40
1.0	40	3.0	45
1.5	50	3.5	50

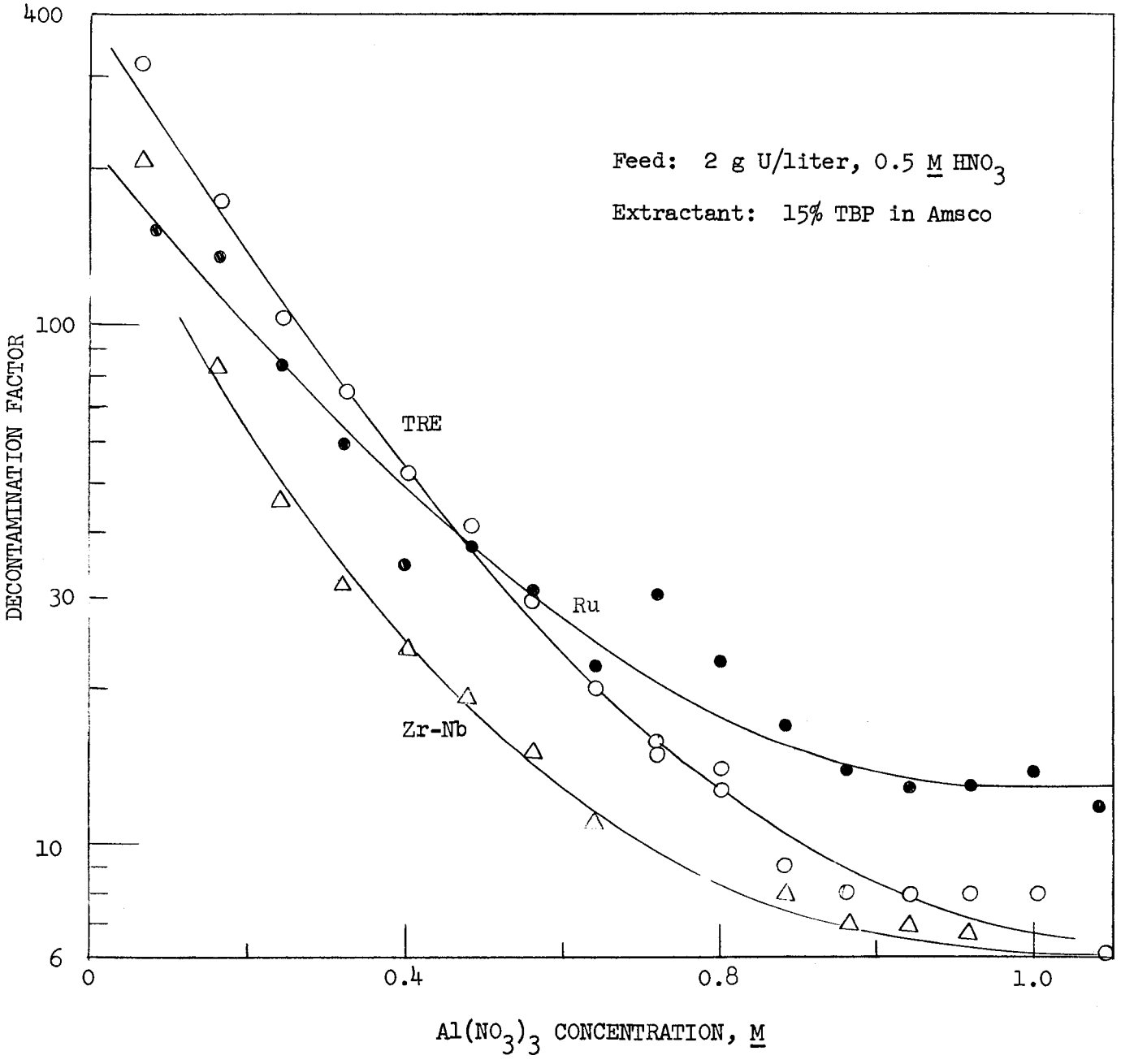

Fig. 3.1. Decontamination of Uranium from Fission Products with Varying Concentrations of Aluminum Nitrate.

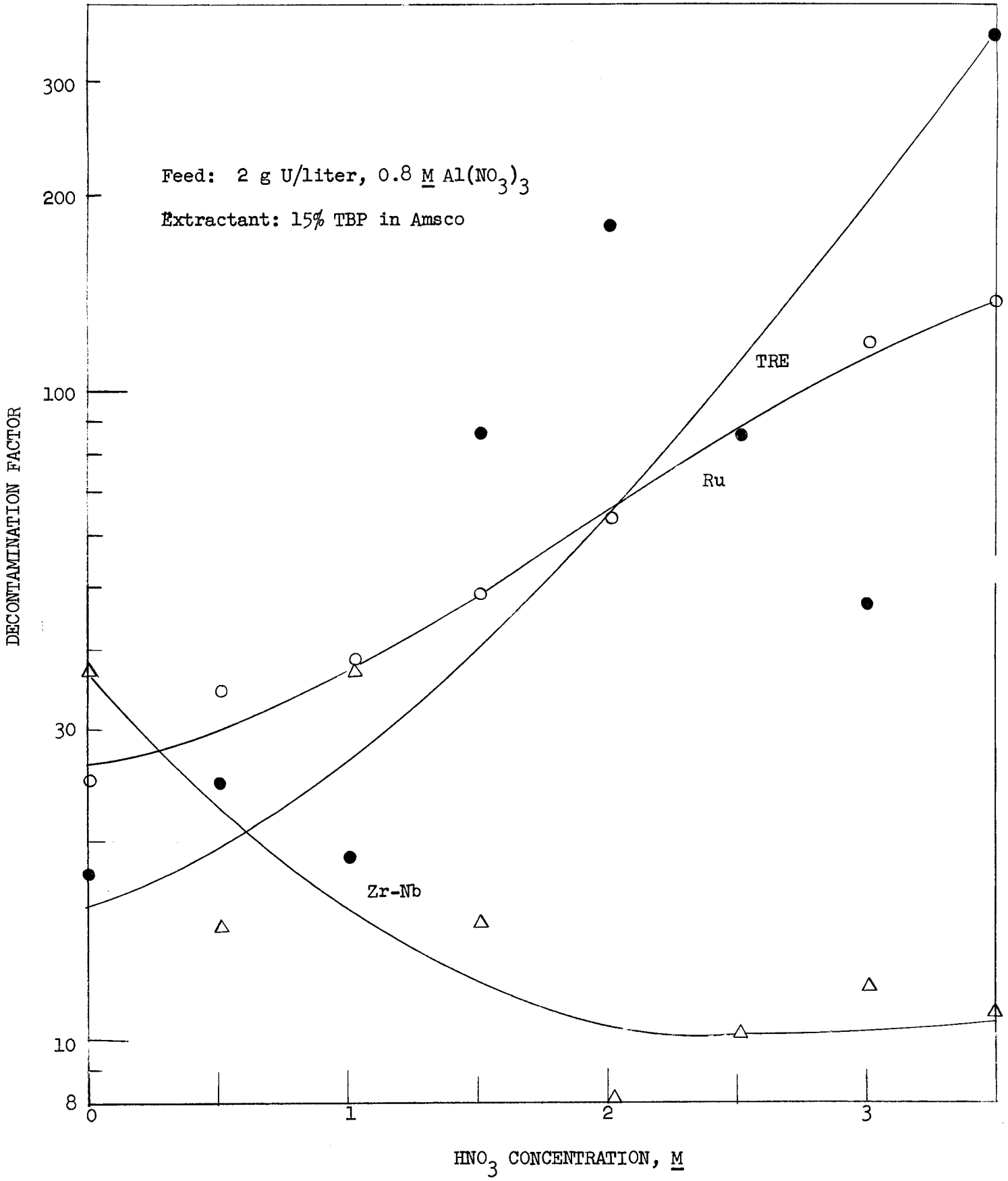

Fig. 3.2. Decontamination of Uranium from Fission Products as a Function of Feed Acidity.

Table 3.3. Distribution of Uranyl Nitrate to 15% TBP-Amsco as a Function of Aluminum Nitrate and Uranyl Nitrate Concentration of Feed

HNO_3 concentration of feed: 0.5 M

U in Feed, g/liter	U Distribution Coefficient (O/A)			
	0.2 M-- $Al(NO_3)_3$	0.5 M-- $Al(NO_3)_3$	1.0 M-- $Al(NO_3)_3$	1.4 M-- $Al(NO_3)_3$
50	1.5	3	8	30
40	2	4	20	70
30	3	6	30	80
20	3	8	300	400
10	4	13	90	300
5	4	14	100	600
2	8	20	110	700
0.5	4	20	110	500
0.2	3	20	130	700
0.05	5	20	50	400
0.005	5	20	70	250

Table 3.4. Distribution of Uranyl Nitrate to TBP-Amsco as a Function of Feed Uranyl Nitrate Concentration and Extractant TBP Concentration

Feed $Al(NO_3)_3$, 1.4 M; feed HNO_3, 0.5 M

U in Feed, g/liter	U Distribution Coefficient (O/A)			
	4% TBP	6% TBP	10% TBP	15% TBP
50	0.4	1	2	35
40	1.1	2	12	70
30	1.4	4	50	80
20	2	8	60	400
10	24	80	120	300
5	24	60	200	600
2	45	85	250	700
0.5	50	115	250	500
0.2	45	100	300	700
0.05	50	140	---	400
0.005	5	70	150	250

Table 3.5. Distribution of Uranyl Nitrate to 15% TBP-Amsco as a Function of Aluminum Nitrate/Nitric Acid Ratio

Total nitrate ion concentration in feed: 4.7 M

U in feed, g/liter	Distribution Coefficient (O/A)		
	3.2 M HNO_3-- 0.5 M $Al(NO_3)_3$	1.7 M HNO_3-- 1.0 M $Al(NO_3)_3$	0.5 M HNO_3-- 1.4 M $Al(NO_3)_3$
50	4	10	35
40	8	17	70
30	13	30	80
20	17	45	400
10	26	60	300
5	26	70	600
2	28	400	700
0.5	150	50	500
0.2	18	70	700
0.005	1	4	250

Table 3.6. Distribution of Uranyl Nitrate to Extractant with Varying TBP Concentrations

Feed: 0.8 M $Al(NO_3)_3$, 0.5 M HNO_3, 2 g uranium/liter

TBP, %	Distribution Coefficient (O/A)	TBP, %	Distribution Coefficient (O/A)
3	3	15	100
6	18	18	100
9	40	21	150
12	150	24	200

Effect of TBP Concentration. Increasing the TBP concentration from 3% to 24% increased the uranium extraction (Table 3.6). Fission product decontamination decreased with increasing TBP concentration (Fig. 3.3).

At lower TBP concentrations, the extractant became saturated with uranium, and, as the organic phase approached saturation, the uranium distribution coefficient decreased rapidly. Decontamination factors from fission products were higher under near saturation conditions; therefore a compromise must be made between the uranium distribution coefficient required and the decontamination desired. A concentration of 10% TBP showed 75% uranium saturation under the proposed flowsheet conditions, and this value was selected for process use.

3.2 Multiple Batch Extractions

Multiple batch extractions were made under conditions chosen as a result of the single extractions discussed above. After five extractions, with 10% TBP, from feed containing 31.9 g of uranium per liter, only 0.004% of the original uranium remained in the aqueous phase:

Extraction	DC	Uranium, g/liter	
		Organic	Aqueous
1	2.3	27.9	12.2
2	9.5	11.6	1.22
3	14.9	1.31	0.088
4	21.0	0.147	0.007
5	13.0	0.013	0.001

The aqueous phase was contacted with fresh organic in each extraction.

3.3 Countercurrent Batch Extraction

From the above data, flowsheet conditions were selected as follows: feed, 50 g U/liter, 0.5 M HNO_3, 0.7 M $Al(NO_3)_3$; extractant, 10% TBP in Amsco; scrub, 0.5 M $Al(NO_3)_3$ with a feed/scrub/extractant flow ratio of 1/0.3/1.5. In a countercurrent batch extraction with synthetic feed under the recommended conditions, the uranium in the aqueous waste was 0.005 g/liter, a loss of 0.01%. The decontamination factor for ruthenium was > 600 and for zirconium-niobium, 400. If the uranium concentration varies in the feed, the desired extractant/feed volume ratio may be calculated by dividing the feed concentration (in g/liter) by 33, within the limits 1/1 to 5/1. The scrub/organic ratio should be constant at 1/5.

The batch countercurrent run, simulating operation of a pulsed column, used four extraction and four scrub stages. The feed was spiked with fission products to a gross gamma activity of 6.2×10^5 c/m/ml. The extraction was run to 20 equilibrations to ensure equilibrium in the various stages.

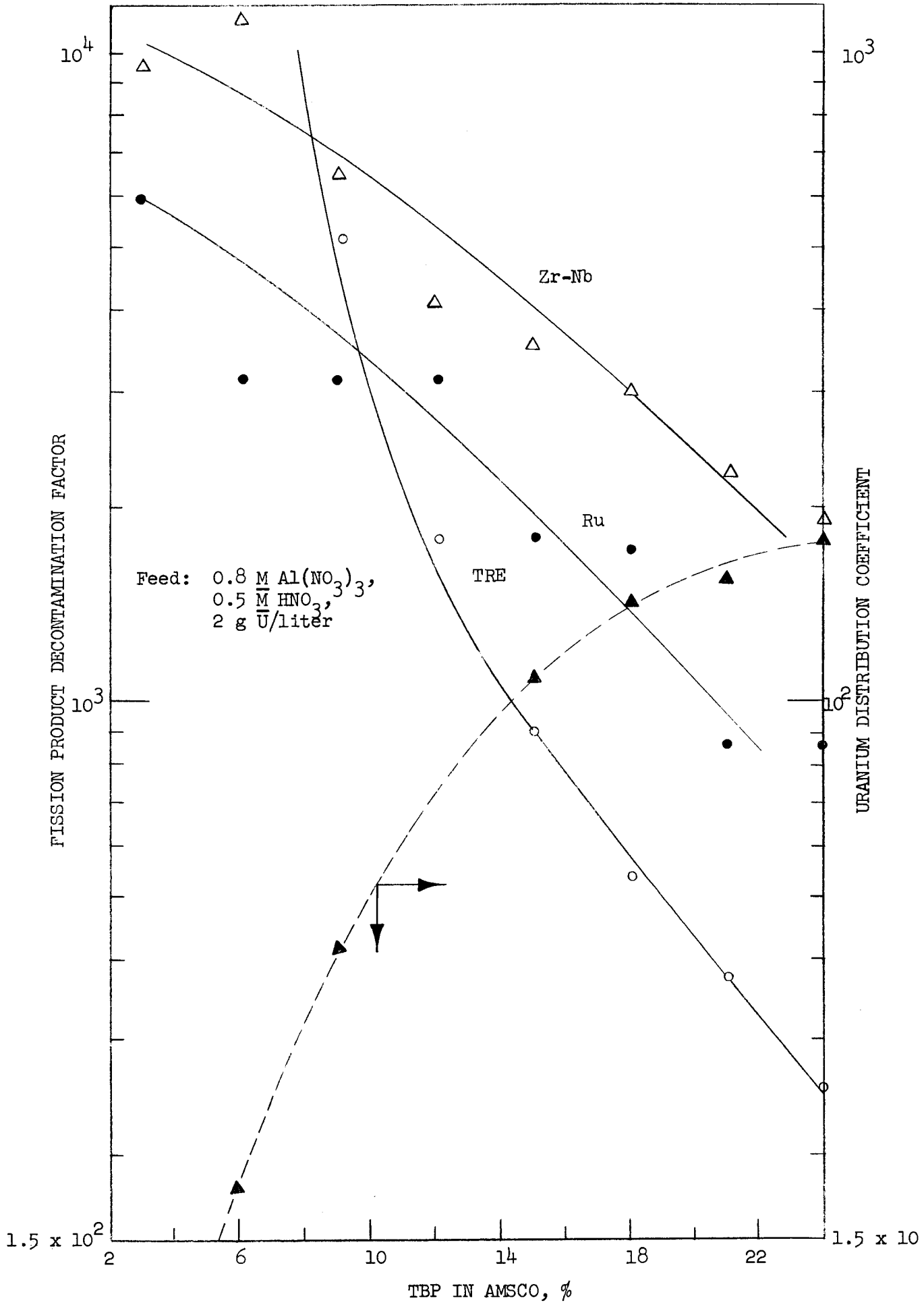

Fig. 3.3. Uranium Distribution and Fission Product Decontamination as a Function of TBP Concentration.

3.4 Laboratory Test Using Pilot Plant Solutions

U-233 formed from Th-232 by neutron capture contains U-232 (see 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 3.7). In laboratory tests with uranium from pilot plant ion exchange columns and plant extractant and scrub, the third uranium cycle decreased these nuclides to an undetectable level. Gamma energy scans of the feed used in the experiment showed Th-228 contributing 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, 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 3.8).

For this experiment U-233 solution from ion exchange columns was adjusted to 46 g of uranium per liter, 0.7 M Al, and 0.8 M H^+. The extractant was 10% TBP-Amsco and the scrub 0.5 M Al. The feed/scrub/extractant volume ratio was 1/0.3/1.5. Four extraction and four scrub stages were used. The disengaging time throughout the column was less than 1 min.

3.5 Pilot Plant Testing*

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. The tentative specifications for U-233 product require that a shipping bottle containing 300 g of uranium in 1.5 liters of solution shall not show more than 300 mr/hr on a gamma survey meter. Because of 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 3.7).

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. This type of problem is much more easily controlled in batch operation.

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* This test was made after this document was written. It is reported here for convenience.

Table 3.7. Nuclear Properties of U-232 Decay Chain

Nuclide	Mode of Decay	Half-life	Gamma Energy, Mev	Occurrence,[a] %
U-232	Alpha	74 yr	0.058	32
			0.13	< 0.3
			0.27	Low
			0.33	Low
Th-228	Alpha	1.9 yr	0.084	28
			0.14	< 1
			0.17	< 1
			0.21	< 1
Ra-224	Alpha	3.64 days	0.241	5
			Others	< 1
Em-220	Alpha	54 sec	0.54	< 1
Po-216	Alpha (0.013% beta)	0.158 sec	None listed	
Pb-212	Beta	10.6 hr	0.238	80
			0.299	5
			0.176	1
			0.249	Weak
Bi-212	33.7% alpha 66.3% beta	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 listed	
Pb-208	Stable			

[a] Compiled by B. H. Ketelle of the ORNL Chemistry Division.

Table 3.8. Nuclear Properties of U-233 Decay Chain

Nuclide	Mode of Decay	Half-life	Gamma Energy, Mev	Occurrence,[a] %
U-233	Alpha	1.63×10^5 yr	0.043	15
			0.056	1.6
			0.099	
Th-229	Alpha	7×10^3 yr	Questionable	
Ra-225	Beta	14.8 days	0.040	63
Ac-225	Alpha	10.0 days	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	2
			0.50	2
			0.60	2
			4 over 1 Mev	
Pa-213	Alpha	4.2×16^{-6} sec	None given	
Pb-209	Beta	3.3 hr	None	
Bi-209	Stable			

[a] Compiled by B. H. Ketelle of the ORNL Chemistry Division.

4.0 VARIATION OF DENSITY WITH URANIUM AND NITRIC ACID CONCENTRATIONS

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

$$\text{Sp. gr.}_{25} = 1.400 + 0.033\ M_{HNO_3}$$

where 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.

5.0 VARIATION OF BOILING POINT WITH URANIUM AND NITRIC ACID CONCENTRATIONS

A plot of uranium and nitric acid concentrations against boiling point of the solution is shown in Fig. 5.1. The data for this curve were obtained from a solution initially containing 33 g/liter of uranium and 0.2 M HNO_3, the expected composition of the solvent extraction product to be concentrated in the falling film evaporator. 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 at the condensate so collected was measured and titrated with standard sodium hydroxide, so that the amount of nitric acid which 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.

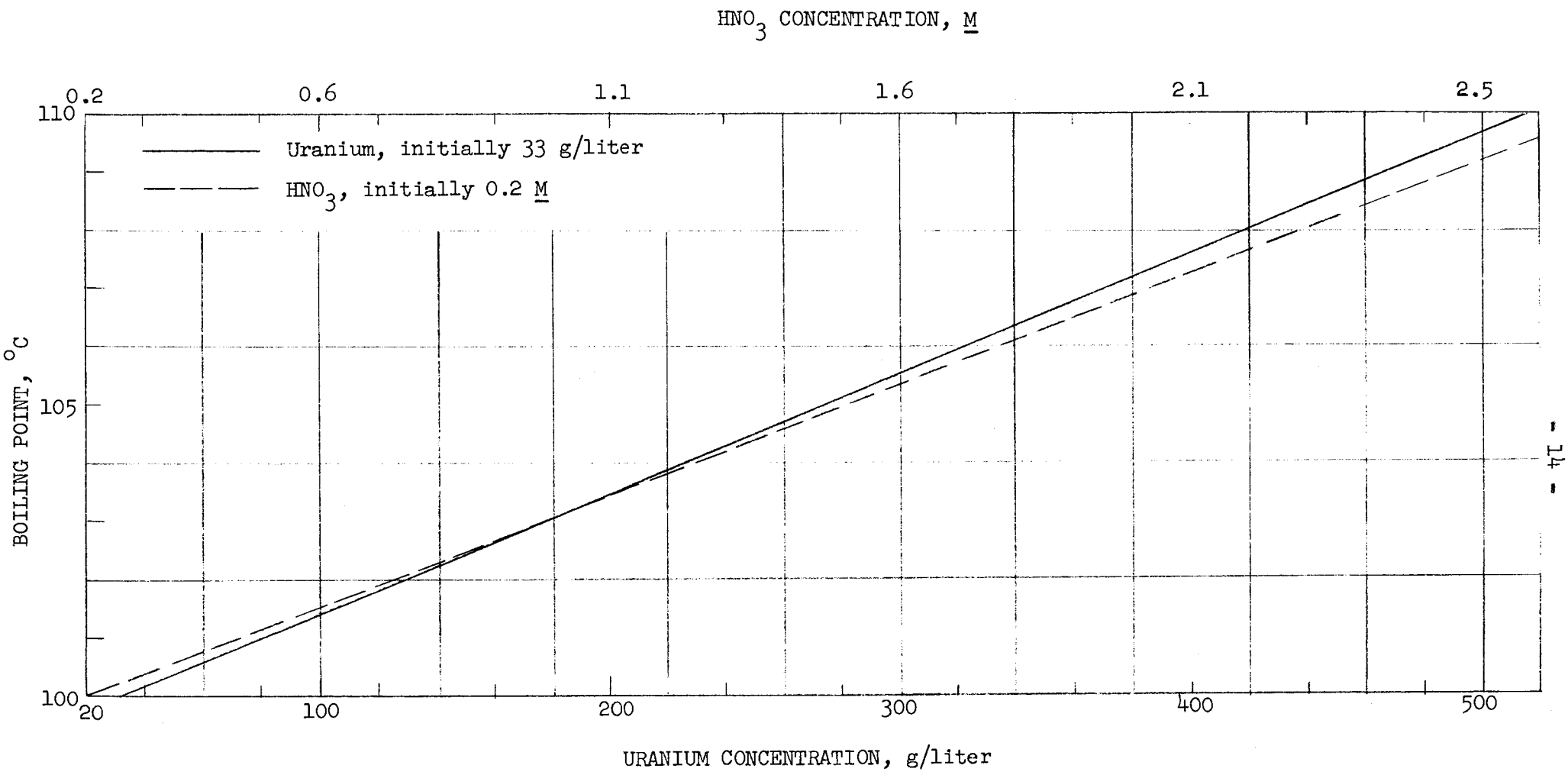

Fig. 5.1. Boiling Point Vs. Concentrations of Uranium and HNO_3.

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