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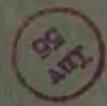
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LABORATORY DEVELOPMENT OF  
THE THOREX PROCESS

PROGRESS REPORT - SEPTEMBER 30, 1952

AEC RESEARCH AND DEVELOPMENT REPORT



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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT,

SEPTEMBER 30, 1952

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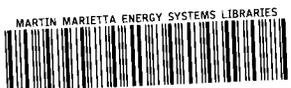
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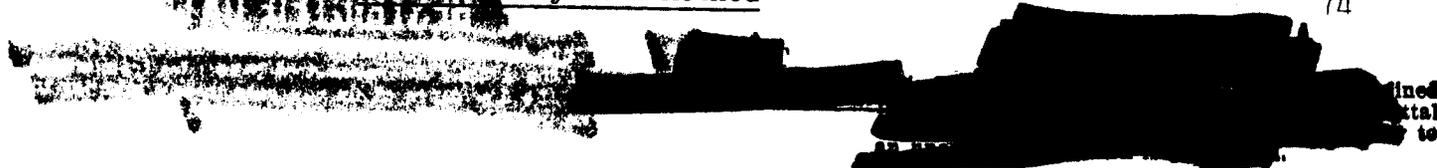


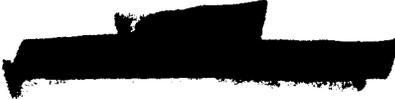
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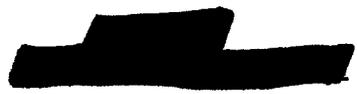


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0.0 ABSTRACT

This report, a supplement to ORNL-1367, records progress in the laboratory development of the Thorex process. Related chemical studies and revisions in the chemical flowsheet are described.



## 1.0 INTRODUCTION

The Thorex process No. 2 has been officially adopted by the Thorex Committee of the Chemical Technology Division as the most feasible process for the separation of Th<sup>232</sup>, U<sup>233</sup>, Pa<sup>233</sup>, and fission products from irradiated thorium slugs. In this and in future reports this process will be called simply the "Thorex process." The work reported here by the Chemical Development Section is a continuation of that reported in ORNL-1367, and the experimental results reflect a laboratory development phase of chemical process improvement, physical evaluation of process solutions, and determination of data needed for the pilot plant and preliminary full-scale-plant design, construction, testing, and operation. Progress made in other sections of the Chemical Technology Division is not discussed in this report, but is summarized in the following paragraphs.

The Unit Operations Section has developed the following: (1) a continuous procedure for nitric acid dissolution of slugs, which is proposed to produce a consistent product solution composition at a constant flow rate that can be controlled and measured by the acid addition rate; (2) a continuous dissolver, which has the advantages, compared to a conventional batch dissolver, that the radioactive feed flow rates to the A-column can be controlled by measurement of the nonradioactive dissolver feed rate, time-consuming feed preparation procedures are eliminated, and the number and frequency of radioactive sampling operations are reduced; and (3) concatenated pulse-column contactors, which make use of relatively short column sections connected in series by a system of check valves and actuated by a single pulse generator and are proposed to permit variable and essentially unlimited total contact lengths in a low overall height. Progress has been made in the testing of chemical process units and all associated equipment and in the studies on corrosion of structural materials.

The Design Section has proceeded with (1) equipment and procedural diagrams, (2) material balance surveys and economic evaluation, (3) pilot plant design, and (4) preliminary full-scale-plant design.

The Pilot Plant Section is currently charged with responsibility for (1) consultation in pilot plant design, and (2) pilot plant construction.

## 2.0 SUMMARY

Process steps in the previously published (ORNL-1367) Thorex Flowsheet No. 2, now known officially as "The Thorex Flowsheet," include: (1) nitric acid dissolution of the irradiated thorium slugs and aluminum jackets, catalyzed by fluoride and mercuric ions; (2) extraction of the  $U^{233}O_2(NO_3)_2$  and  $Th(NO_3)_4$  from the aqueous nitrate solution by the use of 41% tributyl phosphate (TBP); (3) silica gel adsorption of  $Pa^{233}$  from the aqueous aluminum nitrate raffinate, followed by elution with oxalic acid; (4) scrubbing of the organic extract containing the thorium and uranium with acid-deficient aluminum nitrate solution to remove fractions of the protactinium and fission products; (5) preferential stripping of the thorium from the extract into 0.2 N  $HNO_3$ , followed by evaporation and concentration; and (6) stripping of the uranium into 0.02 N  $HNO_3$ , followed by absorption on Dowex-50 resin. Provisions are also included for concentration and/or recovery of aqueous and organic waste streams.

Material balances that have been made for this flowsheet indicate that the process is economically feasible.

The following changes that have been made in the flowsheet are discussed in this report:

1. Small changes were made in the composition of certain cold streams, principally to expand and define the limits of operability, in order to permit fairly wide variations in process control of the hot feed composition and solution flow rates.

2. B-column AU/BX/BS flow ratios were changed from 5.2/5.2/1.0 to 5.2/5.8/1.6 to permit more efficient partition from  $U^{233}$  and more efficient extraction of the  $U^{233}$ .

3. The solvent recovery procedure was changed from the caustic washing method to a calcium hydroxide slurry treatment in order to reduce aqueous waste production and to provide for a more efficient cleanup of the solvent.

Further investigation of fission product decontamination in the Thorex extraction system has indicated that ruthenium may possibly be a limiting factor in radioactive decontamination of the thorium product stream. Protactinium recovery by adsorption on silica gel appears to be the most favorable process technique studied to date for handling the highly radioactive  $Pa^{233}$  product.

3.0 THOREX FLOWSHEET

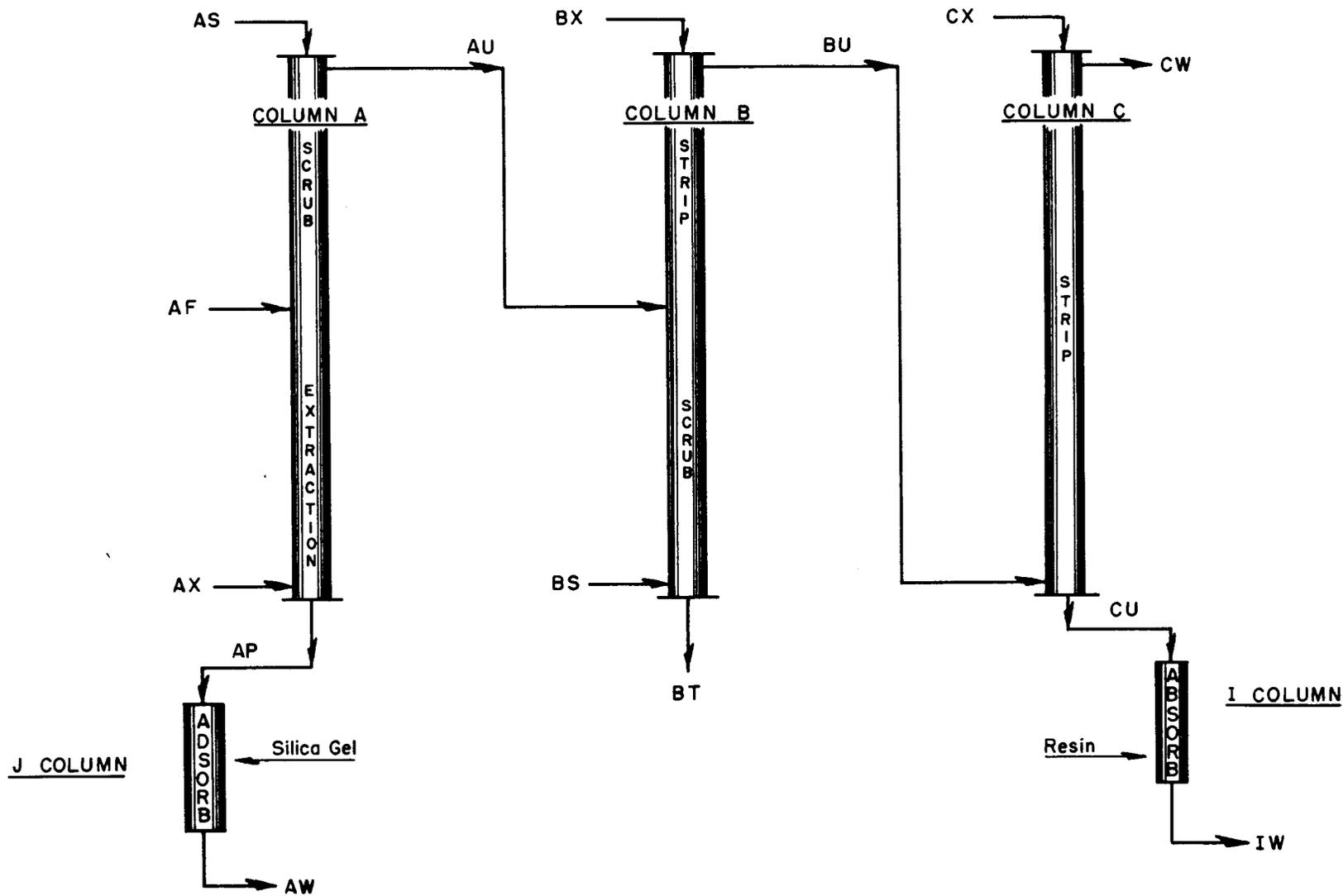
3.1 Nomenclature

In order to simplify discussion and recording of Thorex process information, the following terminology has been agreed upon by the ORNL Thorex Committee (see Fig. 3.1):

- A: A-column — column for separation of thorium and U<sup>233</sup> from fission products and Pa<sup>233</sup>; lower portion termed the "extraction" section; upper portion, the "scrub" section.
- AF: A-column Feed — aqueous product stream from the dissolution of aluminum-jacketed thorium slugs, adjusted to conditions necessary for process feed.
- AX: A-column extractant — virgin organic solvent, e.g., 42% TBP in a mixture of the kerosene diluent Amsco 125-90W, used to extract thorium and U<sup>233</sup>.
- AS: A-column Scrub — nitric acid-deficient solution of aluminum nitrate used to scrub fission products and Pa<sup>233</sup> from the organic product stream.
- AU: A-column, Uranium stream — organic effluent of 42% TBP containing both U<sup>233</sup> and thorium; cascaded as feed stream to the B column.
- AP: A-column, Protactinium stream — aqueous effluent of nitric acid-deficient aluminum nitrate containing Pa<sup>233</sup> and fission products.
- AW: A-column Waste — continuation of the AP stream following the removal of Pa<sup>233</sup> by adsorption on the silica gel column.
- B: B-column — partition of thorium from U<sup>233</sup> by preferential stripping; upper portion termed "strip" section; lower portion, the "scrub" section.
- BX: B-column extractant — 0.2 N HNO<sub>3</sub> solution used to strip, or extract, the thorium from the AU stream.
- BS: B-column Scrub — organic solvent identical to the AX stream, used in this case to scrub U<sup>233</sup> from the aqueous stream containing thorium.

Figure 3.1  
STREAM NOMENCLATURE IN THE THOREX PROCESS

Dwg No 16926



- BT: B-column, Thorium stream — aqueous effluent of dilute nitric acid containing the thorium product.
- BU: B-column, Uranium stream — organic effluent containing U<sup>233</sup>.
- C: C-column — stripping of U<sup>233</sup>; made up of strip section only.
- CX: C-column eXtractant — 0.02 N HNO<sub>3</sub> solution used to strip, or extract, the U<sup>233</sup> from the BU stream.
- CU: C-column, Uranium stream — aqueous effluent of very dilute nitric acid containing the uranium product.
- CW: C-column Waste — organic effluent freed of nearly all extractables; cascaded as feed to solvent decontamination and recovery process.
- IW: Ion-column Waste — continuation of the CU stream, following the removal of U<sup>233</sup> by absorption in the resin column.

3.2 Summary of Flowsheet Changes

In order to permit a degree of variation in flow rate control, the continuous dissolving operation, and the resultant AF composition, the following tentative limits for critical components have been set for the AF, AS, and AX streams:

<u>AF</u> :	Thorium	1.43 ± 0.07 M
	Aluminum	0.5 ± 0.1 M
	Nitric Acid	0.5 ± 0.1 M
<u>AS</u> :	Aluminum	0.6 ± 0.02 M
	Nitric Acid	- 0.75 ± 0.02 M
<u>AX</u> :	TBP	42.5 ± 0.5% by volume.

In order to reduce the number of contacting stages required to strip thorium from the AU stream as well as to scrub U<sup>233</sup> from the BT stream, the following stream flow ratios have been adopted: AU/BX/BS = 5.2/5.8/1.6. The narrow limits of the specification for the nitric acid concentration in the BX, i.e., 0.2 ± 0.01 N, indicate the close control needed on this stream. Lower concentrations would permit considerable U<sup>233</sup> reflux in the B-column, whereas higher concentrations would increase the BU and/or CU acidity to levels that could interfere with stripping efficiency in the C-column.

An increase in the flow ratio of the CX stream may become necessary to accommodate the 10% increase in the BU flow ratio; however, this seems undesirable in consideration of U<sup>233</sup> isolation problems, since an increasing flow ratio, an increasing acidity, or a decreasing U<sup>233</sup> concentration in the CU stream would have adverse effects on absorption efficiency, resin saturation, and resin capacity.

### 3.3 Material-Balance Flowsheet

K. L. Mattern

The Chemical Development Section, in conjunction with the Design and Pilot Plant Sections, has issued an overall tentative chemical flowsheet for the Thorex process. This flowsheet (ORNL - CF drawings D-9163 and D-9184) is a preliminary material-balance flow diagram based on a through-put of 100 kg of thorium per day, the thorium having been irradiated for 150 days at  $10^{13}$  n/cm<sup>2</sup>/sec and cooled for 60 days.

A summary of the material balances in the primary extraction steps of the process is shown in Fig. 3.2. A materials analysis of the (1) slug dissolution, (2) solvent recovery, and (3) U<sup>233</sup> isolation steps is given in Table 3.1.

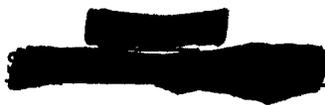
### 3.4 Fission Product Decontamination

W. T. McDuffee

Contrary to information presented in the previous progress report (ORNL-1367), results of recent studies indicate that the fission product ruthenium may constitute a limiting activity in Thorex decontamination. This was discovered when an activity spike from irradiated uranium (Purex dissolver solution) was included in the studies to eliminate protactinium interference observed in previous radiochemical analyses. The following decontamination factors have been obtained: gross  $1.2 \times 10^2$ ; Ru, 8.6; TRE,  $6.8 \times 10^5$ ; Zr,  $>3.0 \times 10^4$ ; Nb,  $>1.6 \times 10^4$ . The low ruthenium decontamination factor was the result of a fraction in the extraction system, about 5 to 10% of the total, which has a distribution coefficient (organic/aqueous) greater than 1.0. The remaining 90 to 95% of the element, which was an inextractable species, exhibited a D.C. of about 0.001.

Since ruthenium had not been observed as a limiting fission product contaminant when activity spikes from dissolved irradiated thorium were used, it has been assumed that the observed fractionation of the ruthenium species is a function of dissolving conditions. Digestion for 3 hr at 100°C in the presence of AF concentrations of F<sup>-</sup> and Hg<sup>++</sup> was found to increase the Ru D.F. from 8.6 to 38. Studies are underway to determine (1) the nature of the extractable ruthenium species and (2) whether its decontamination can be controlled under the actual conditions of the Thorex process.

Characteristic data from countercurrent runs demonstrating the A-, B-, and C-columns are presented in Tables 3.2 through 3.5. A reflux of rare earth activities, up to 1000%, has been observed in the A-column; however, rare earth decontamination is accomplished because of the thorium saturation of the solvent in the scrub section. Most of the ruthenium fractionated in the A-column followed the thorium product stream in the B-column. Most of the activity fractions in the BU stream followed the CW stream, and it has been determined that this activity can be completely removed by the calcium hydroxide slurry treatment (see Sec. 4.5) of the solvent. Removal of 95% of this activity on silica gel has also been demonstrated.

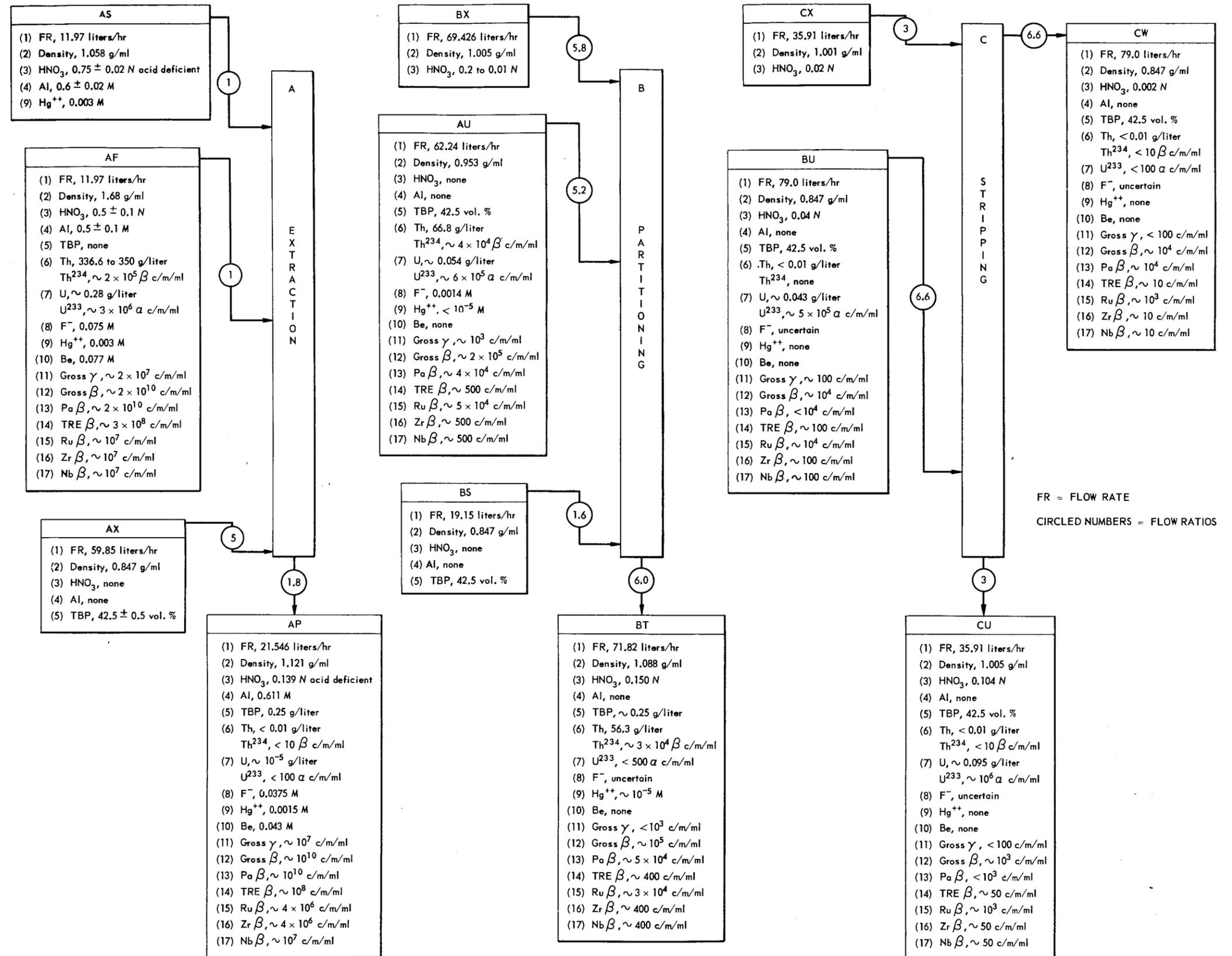



Fig. 3.2

Thorex Flowsheet, October 1952.  
Basis: 100 kg of thorium per day; slugs irradiated at 10<sup>13</sup> n/cm<sup>2</sup>/sec for 150 days, cooled for 60 days.

Table 3.1

Materials Analysis of Process Units

- 1. Dissolution -- assuming 95% recovery and reuse of the NO<sub>2</sub> and NO gaseous products of the dissolving step:

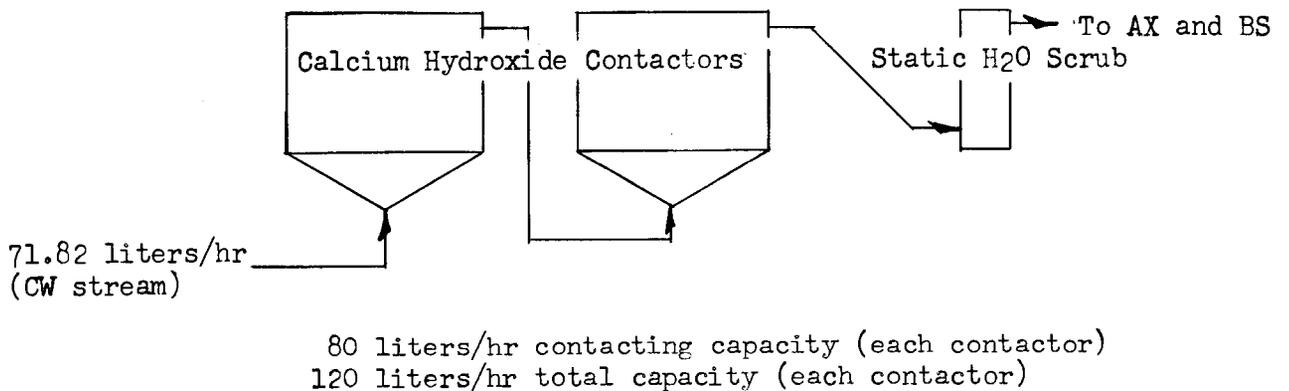
	<u>A-Column Feed Preparation</u>			<u>A-Column Scrub Preparation</u>	
Th	100 kg/day	13 N HNO <sub>3</sub>	277.367 kg/day	Al (metal)	4.649 kg/day
Al	3.89 kg/day	NaF <sup>-</sup>	0.904 kg/day	6 N HNO <sub>3</sub>	67.808 kg/day
Be	200 g/day	Hg(NO <sub>3</sub> ) <sub>2</sub> · ½H <sub>2</sub> O	0.288 kg/day	Hg(NO <sub>3</sub> ) <sub>2</sub> · ½H <sub>2</sub> O	0.288 kg/day
U <sup>233</sup>	80 g/day	H <sub>2</sub> O (makeup)	100.917 kg/day	H <sub>2</sub> O (makeup)	231.481 kg/day
Pa	4.9 g/day				
FP's	1.7 g/day				

Total weight\* of off-gases, water saturated at 50°C and 28/30 atmosphere, equals 44.754 kg/day.

Total weight\* of off-gases under same conditions equals 4.553 kg/day.

\*Note: Weight quoted on basis of NO<sub>2</sub> and NO being oxidized by oxygen from air inleakage to dissolver. With oxygen fed into the off-gas recovery (RAGS) system, these values will drop to 5.636 kg/day (AF) and 0.729 kg/day (AS).

- 2. Solvent preparation (basis of daily throughput):  
 TBP ----- 572.846 kg/day or 588.924 liters/day (replenish with 735 g/day)  
 Amsco 125-90W - 638.997 kg/day or 847.476 liters/day  
 Ca(OH)<sub>2</sub>, for solvent pretreatment, equals 4.3 kg per contactor per 17-day charge.



- 3. U<sup>233</sup> isolation:

35.91 liters/hr of CU (92.8 mg of U<sup>233</sup> per liter) passed through a Dowex-50W 8% cross-linked resin column at the rate of 5 to 15 ml/m/cm<sup>2</sup>. In order to maintain a column capacity equal to the CU output, a 4.86-, 3.43-, or 2.8-in. column would be needed for flow rates of 5, 10, or 15 ml/m/cm<sup>2</sup>, respectively.

The U<sup>233</sup> elutriant is 0.0057 unit volume, or 1.64 liters/day, of 2.0 M ammonium acetate with 0.2 to 1.0 M acetic acid. The elution step is carried out at 70°C, and concentrations of up to 130 g of uranium per liter have been attained. (With 2.0 M ammonium acetate and 1.0 M acetic acid and a 4-in. ion exchange column, a 300-g batch of uranium has been eluted in approximately 1.5 hr.)

Table 3.2

Fission Product Decontamination in Thorex A-Column,  
Using Spike from Irradiated Uranium Dissolver Solution

Feed: 1.47 M Th, 0.62 M Al, 0.56 N HNO<sub>3</sub>; Gross β 1.1 x 10<sup>8</sup> c/m/ml;  
TRE β 7.9 x 10<sup>7</sup>; Ru β 7.3 x 10<sup>6</sup> c/m/ml; Zr β 1.05 x 10<sup>7</sup> c/m/ml;  
Nb β 1.35 x 10<sup>6</sup> c/m/ml (90-day cooled, Purex AFU spike) (in 1EX, out 5EX)

Scrub: 0.6 M Al; 0.8 N HNO<sub>3</sub> deficient (in 8Sc, out 5EX)

Organic: 41% TBP in preconditioned Amsco 125-90W; NaOH-H<sub>2</sub>O washed  
(in 5EX, out 8Sc)

F/S/O flow ratio = 1/1/5; 5 extraction, 8 scrub stages; 1.5 vol. changes

Stage	Determination	Organic	Aqueous	D.C. (O/A)	E.F. (O/A)	D.F.
8Sc	Th (mg/ml)	57.0	62.0	0.92	4.6	-
	Gross β (c/m/ml)	1.5x10 <sup>5</sup>	1.8x10 <sup>5</sup>	0.83	4.1	120
	Ru β (c/m/ml)	1.5x10 <sup>5</sup>	1.7x10 <sup>5</sup>	0.87	4.5	8.6
	Nb β (c/m/ml)	16*	20	-	-	>1.6x10 <sup>4</sup>
	TRE β (c/m/ml)	23*	220	-	-	>6.8x10 <sup>5</sup>
	Zr β (c/m/ml)	72*	200	-	-	>2.9x10 <sup>4</sup>
4Sc	Th (mg/ml)	78.0	103.3	0.75	3.8	-
	Gross β (c/m/ml)	3.3x10 <sup>5</sup>	1.7x10 <sup>6</sup>	0.19	0.95	67.0
	Ru β (c/m/ml)	2.9x10 <sup>5</sup>	1.5x10 <sup>6</sup>	0.19	0.95	5.0
	Nb β (c/m/ml)	31*	2.3x10 <sup>3</sup>	0.01	0.05	9x10 <sup>3</sup>
	TRE β (c/m/ml)	1.4x10 <sup>3</sup>	7.6x10 <sup>4</sup>	0.02	0.1	1.1x10 <sup>4</sup>
	Zr β (c/m/ml)	7.3x10 <sup>2</sup>	2.2x10 <sup>4</sup>	0.03	0.15	2.9x10 <sup>3</sup>
1EX	Th (mg/ml)	77.0	80.0	0.96	2.4	-
	Gross β (c/m/ml)	3.8x10 <sup>6</sup>	1.3x10 <sup>8</sup>	0.03	0.08	5.3
	Ru β (c/m/ml)	7.7x10 <sup>5</sup>	5.7x10 <sup>6</sup>	0.13	0.32	1.9
	Nb β (c/m/ml)	1.2x10 <sup>4</sup>	5.5x10 <sup>5</sup>	0.02	0.05	22.5
	TRE β (c/m/ml)	2.2x10 <sup>6</sup>	1.1x10 <sup>8</sup>	0.02	0.05	10.0
	Zr β (c/m/ml)	2.3x10 <sup>5</sup>	5.1x10 <sup>6</sup>	0.07	0.18	9.1
5EX	Th (mg/ml)	0.02	0.23**	0.09	0.22	-
	Gross β (c/m/ml)	2.4x10 <sup>5</sup>	5.1x10 <sup>7</sup>	0.005	0.013	-
	Ru β (c/m/ml)	5.6x10 <sup>3</sup>	2.3x10 <sup>6</sup>	0.002	0.005	-
	Nb β (c/m/ml)	94	9.8x10 <sup>5</sup>	0.001	0.0005	-
	TRE β (c/m/ml)	1.5x10 <sup>5</sup>	3.1x10 <sup>7</sup>	0.005	0.013	-
	Zr β (c/m/ml)	1.8x10 <sup>2</sup>	6.6x10 <sup>6</sup>	0.00003	0.00007	-

\*Low values are questionable.

\*\*Apparently a loss due to high acid deficiency (0.32 N) in extraction section.

Table 3.3

Fission Product Decontamination in Thorex A-Column:  
Effects of Feed Digestion in Presence of F<sup>-</sup> and Hg<sup>++</sup>

Feed:\* 1.54 M Th; 0.64 M Al; 0.55 N HNO<sub>3</sub>; U, 1.42 mg/ml; Be, 0.7 mg/ml;  
 0.075 N F<sup>-</sup>; 0.005 M Hg<sup>++</sup>; gross β 1.1 x 10<sup>7</sup> c/m/ml; TRE β 7.9 x 10<sup>6</sup>  
 c/m/ml; Ru β 7.3 x 10<sup>5</sup> c/m/ml; Zr β 1.05 x 10<sup>6</sup> c/m/ml; Nb β 1.4 x 10<sup>5</sup>  
 c/m/ml (Purex AFU spike) (in 1EX, out 5EX)

Scrub: 0.62 M Al, 0.84 N HNO<sub>3</sub> deficient (in 8Sc, out 5EX)

Organic: 41% TBP in preconditioned Amsco 125-90W; NaOH-Na<sub>2</sub>CO<sub>3</sub> washed  
 (in 5EX, out 8Sc)

F/S/O flow ratio = 1/1/5; 5 extraction, 8 scrub stages; 3.5 vol. changes

Stage	Determination	Organic	Aqueous	D.C. (O/A)	E.F. (O/A)	D.F.
8Sc	Th (mg/ml)	63.6	51.5	1.23	6.2	-
	Gross β (c/m/ml)	3.9x10 <sup>3</sup>	5.6x10 <sup>3</sup>	0.7	3.5	570
	Ru β (c/m/ml)	3.4x10 <sup>3</sup>	4.6x10 <sup>3</sup>	0.73	3.6	43
	Nb β (c/m/ml)	7***	12***	-	-	-
	TRE β (c/m/ml)	24***	-	-	-	>6.5x10 <sup>4</sup> **
	Zr β (c/m/ml)	42***	-	-	-	>5.0x10 <sup>3</sup> **
2Sc	Th (mg/ml)	79.6	87.2	0.91	4.6	-
	Gross β (c/m/ml)	4.0x10 <sup>4</sup>	1.3x10 <sup>6</sup>	0.03	0.15	-
	Ru β (c/m/ml)	2.2x10 <sup>4</sup>	3.3x10 <sup>5</sup>	0.07	0.35	-
	Nb β (c/m/ml)	16***	2.8x10 <sup>3</sup>	0.006	0.03	-
	TRE β (c/m/ml)	1.4x10 <sup>4</sup>	8.5x10 <sup>5</sup>	0.02	0.1	-
	Zr β (c/m/ml)	43.0	5.4x10 <sup>4</sup>	0.008	0.04	-
1EX	Th (mg/ml)	74.6	48.0	1.65	3.9	-
	Gross β (c/m/ml)	6.8x10 <sup>5</sup>	3.5x10 <sup>7</sup>	0.02	0.05	-
5EX	Th (mg/ml)	-	0.02	-	-	-
	Gross β (c/m/ml)	5.2x10 <sup>5</sup>	2.5x10 <sup>6</sup>	0.2	0.5	-
	Ru β (c/m/ml)	3.2x10 <sup>3</sup>	2.6x10 <sup>5</sup>	0.01	0.025	-
	Nb β (c/m/ml)	4.6x10 <sup>1</sup>	1.5x10 <sup>4</sup>	0.003	0.008	-
	TRE β (c/m/ml)	5.0x10 <sup>5</sup>	-	-	-	-
	Zr β (c/m/ml)	1.3x10 <sup>2</sup>	4.0x10 <sup>5</sup>	0.0003	0.0008	-

\*Feed was refluxed at 105°C for 3 hr.

\*\*D.F. values were limited by initial activity levels.

\*\*\*Low values are questionable.

Table 3.4

Fission Product Distribution in Thorex B-Column,  
Using Activities Fractionated by A-Column Extraction

Feed: 41% TBP from countercurrent extraction shown in Table 3.3;  
Th, 60.8 mg/ml; 0.01 N HNO<sub>3</sub>; U, 0.225 mg/ml; gross β 2.7 x 10<sup>3</sup>  
c/m/ml (~87% Ru) (in 1Sc, out 8St)

Strip: 0.2 N HNO<sub>3</sub> (in 8St, out 6Sc)

Scrub: 41% TBP in Amsco 125-90W (in 6Sc, out 8St)

F/St/Sc flow ratio = 1/1/0.2; 8 strip, 6 scrub stages; 4.0 vol. changes

Stage	Determination	Organic	Aqueous	D.C. (O/A)	E.F. (O/A)	D.F.
8St	Th (mg/ml)	0.04*	0.021	2.0*	2.4*	-
	U (mg/ml)	0.27	0.165	1.64	1.96	-
	H <sup>+</sup> (N)	0.05	0.20	0.25	0.3	-
	Gross β <sup>-</sup> (c/m/ml)	505	155	3.25	3.9	~5
4St	Th (mg/ml)	3.7	14.0	0.26	0.3	-
	U (mg/ml)	0.36	0.1	3.6	4.3	-
	H <sup>+</sup> (N)	-	-	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	270	70	3.75	4.5	-
1Sc	Th (mg/ml)	46.4	71.2	0.65	0.13	-
	U (mg/ml)	0.27	0.026	10.0	2.0	-
	H <sup>+</sup> (N)	-	0.16	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	415	880	0.47	0.09	-
3Sc	Th (mg/ml)	48.2	-	-	-	-
	U (mg/ml)	0.073	-	-	-	-
	H <sup>+</sup> (N)	-	-	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	410	680	0.60	0.12	-
5Sc	Th (mg/ml)	45.9	-	-	-	-
	U (mg/ml)	0.02	-	-	-	-
	H <sup>+</sup> (N)	-	-	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	315	1210	0.26	0.05	-
6Sc	Th (mg/ml)	-	62.2	-	-	-
	U (mg/ml)	-	0.0008	-	-	-
	H <sup>+</sup> (N)	-	0.1	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	-	1970	-	-	~1.3

\*Questionable value.

Table 3.5

Fission Product Decontamination in Thorex C-Column,  
Using Activities Fractionated by A- and B-Columns

Feed: 41% TBP from preferential stripping shown in Table 3.4; Th, 0.019 mg/ml; U, 0.22 mg/ml; 0.1 N HNO<sub>3</sub>; gross β 352 c/m/ml (in 1St, out 5St)

Strip: 0.02 N HNO<sub>3</sub> (in 5St, out 1St)

F/S flow ratio = 2:1; 5 stages; >2 vol. changes

Stage	Determination	Organic	Aqueous	D.C. (O/A)	E.F. (O/A)	D.F.
5St	U (mg/ml)	0.01	0.066	0.152	0.3	-
	Th (mg/ml)	< 0.01	-	-	-	-
	H <sup>+</sup> (N)	-	0.023	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	305	180	1.8	3.6	-
3St	U (mg/ml)	0.067	0.300	0.23	0.46	-
	Th (mg/ml)	-	-	-	-	-
	H <sup>+</sup> (N)	-	0.028	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	340	60*	5.7	>3.0	-
1St	U (mg/ml)	0.275	0.45	0.61	1.21	-
	Th (mg/ml)	-	0.037	-	-	-
	H <sup>+</sup> (N)	-	0.093	-	-	-
	Gross β <sup>-</sup> (c/m/ml)	370	242	1.53	3.0	3.0

\*Questionable value.

## 4.0 GENERAL PROCESS STUDIES

4.1 The A-Column4.1.1 Electrical Conductivity of Dissolver Solutions

J. E. Savolainen

Conductivity measurements on a series of synthetic dissolver solutions showed that the conductivity decreases with increasing  $\text{Th}(\text{NO}_3)_4$  or  $\text{Al}(\text{NO}_3)_3$  and increases with increasing nitric acid concentration (see Table 4.1 and Figs 4.1 through 4.3). At constant nitric acid concentrations, the conductivity decreases as the total nitrate concentration increases (see Fig. 4.4). With proper instrumentation, conductivity measurements may be used in conjunction with density measurements to monitor and control the degree of utilization of the nitric acid in the continuous dissolver or to indicate the amount of free acid in the dissolver solution.

The conductivity measurements were made with an Industrial Instrument, Inc., conductivity bridge, model RC-16, used with a dipping conductivity cell. The concentration of the thorium nitrate was varied from 1.2 to 2.0 M, of the aluminum nitrate from 0.2 to 0.8 M, and of the nitric acid from 0.756 to 1.5 M.

4.1.2 Removal of Silica from Mantle Grade Thorium Nitrate Tetrahydrate

W. T. McDuffee

Off-standard thorium nitrate tetrahydrate can be purified sufficiently for use as a Thorex feed in pilot plant cold runs by refluxing it at 125 to 130°C in concentrated nitric acid. This treatment dehydrates any soluble silica present and thus considerably reduces the emulsification encountered with the untreated product. The dehydrated silica coagulates and may be filtered off, but this is not necessary since the extraction process in pulse columns can be carried out satisfactorily in the presence of the dehydrated material.

The time required for the pretreatment is 22 hr with a proportion of 1 ml of 16 N  $\text{HNO}_3$  per 25 g of thorium nitrate tetrahydrate, which is the molecular proportion proposed for use in preparation of Thorex feeds. However, satisfactory dehydration can be obtained in 6 hr if the amount of 16 N  $\text{HNO}_3$  is increased to 1 ml per 8 g of the thorium salt, and this is the proportion recommended for pretreating the thorium nitrate hexahydrate that is to be used for cold runs in the pilot plant.



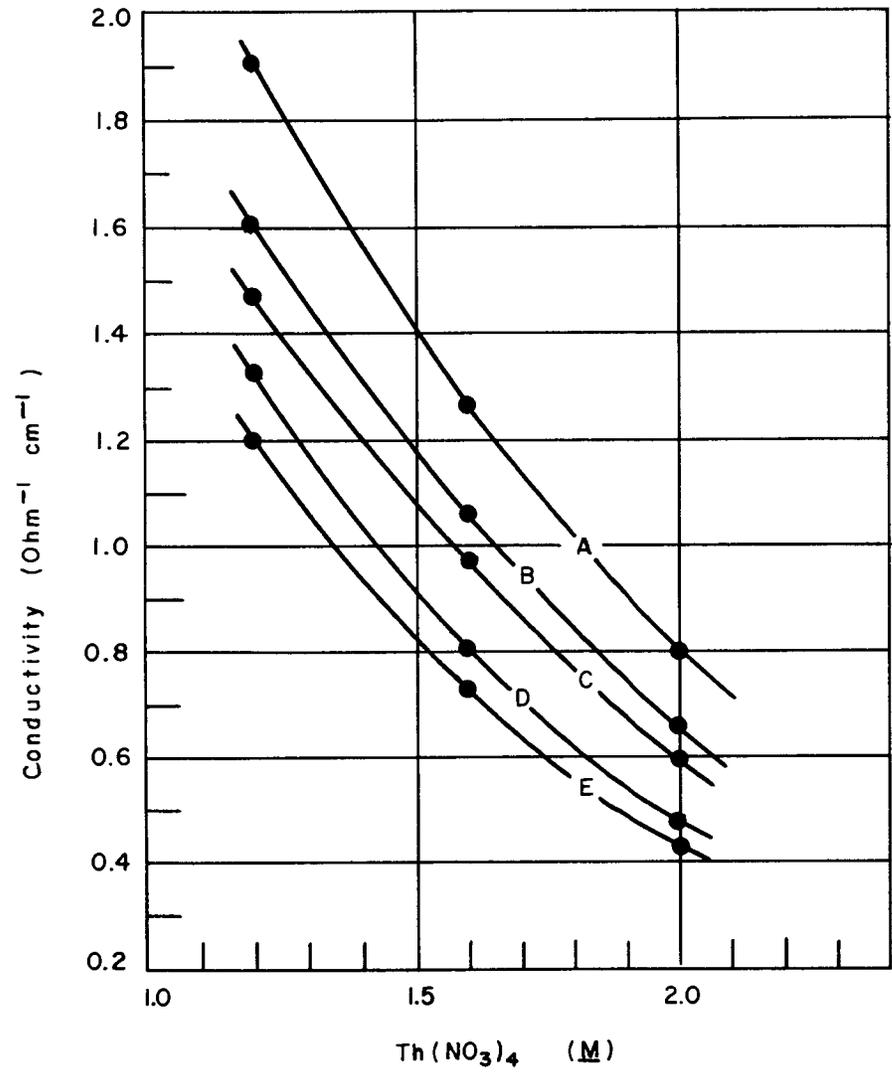


Figure 4.1  
CONDUCTIVITIES OF SYNTHETIC DISSOLVER SOLUTIONS AS FUNCTIONS OF THORIUM CONCENTRATION MEASURED AT 25 °C.

Curve	Al(NO <sub>3</sub> ) <sub>3</sub> (M)	HNO <sub>3</sub> (M)
A	0.50	0.756
B	0.50	1.00
C	0.20	0.756
D	0.20	1.00
E	0.20	1.50

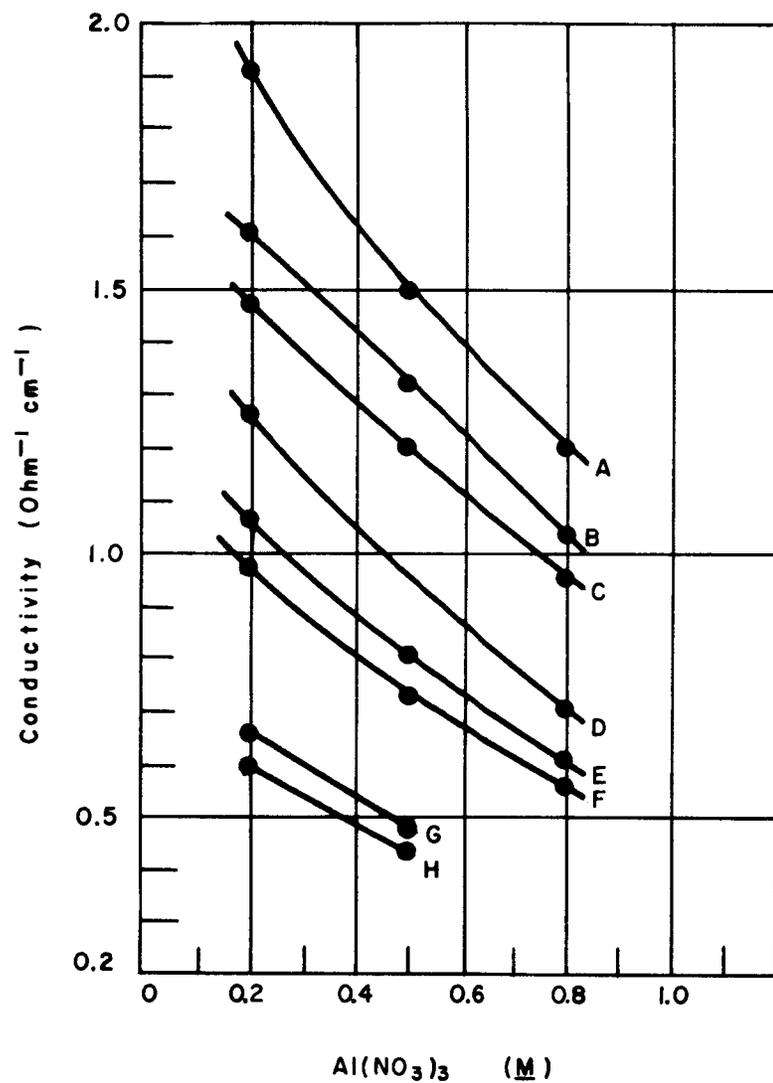


Figure 4.2  
 CONDUCTIVITIES OF SYNTHETIC DISSOLVER  
 SOLUTIONS AS FUNCTIONS OF ALUMINUM  
 CONCENTRATION MEASURED AT 25°C.

Curve	Th(NO <sub>3</sub> ) <sub>4</sub> M	HNO <sub>3</sub> M
A	1.2	1.50
B	1.2	1.00
C	1.2	0.756
D	1.6	1.5
E	1.6	1.00
F	1.6	0.756
G	2.0	1.00
H	2.0	0.756

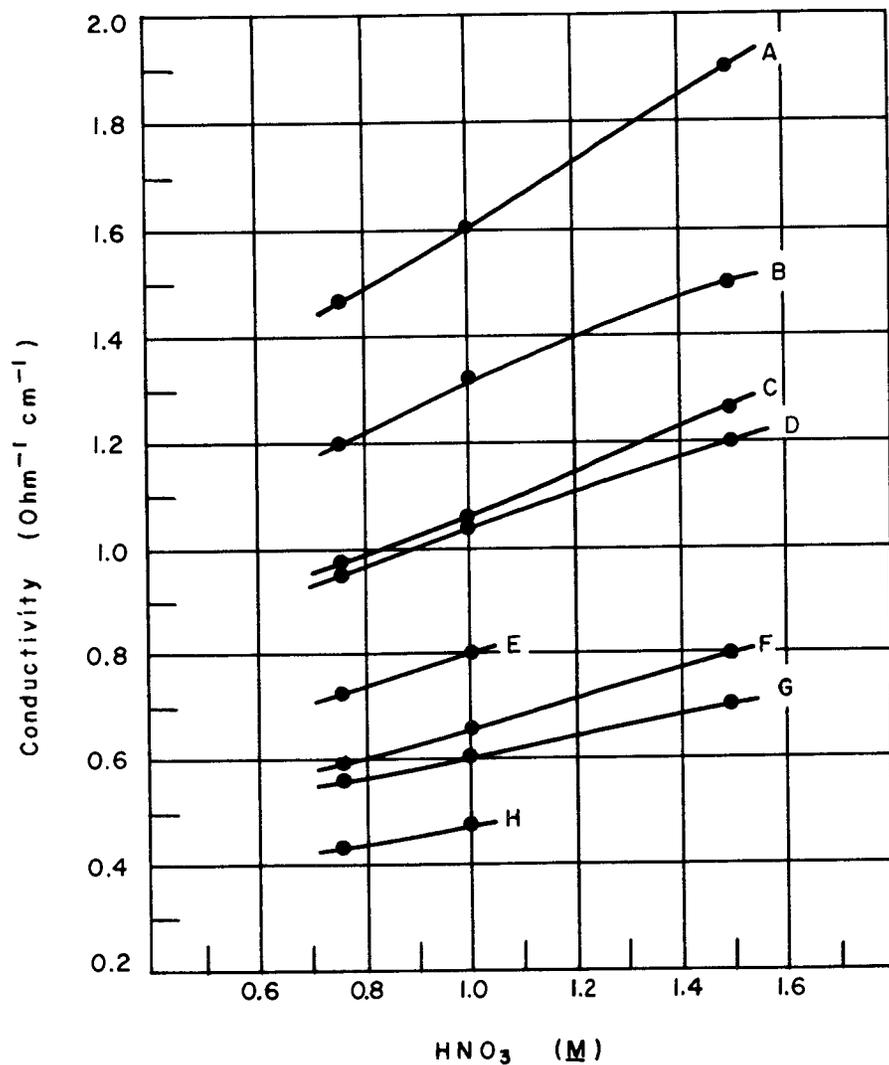


Figure 4.3  
 CONDUCTIVITIES OF SYNTHETIC DISSOLVER  
 SOLUTIONS AS FUNCTIONS OF NITRIC ACID  
 CONCENTRATION MEASURED AT 25°C.

Curve	Th(NO <sub>3</sub> ) <sub>4</sub> M	Al(NO <sub>3</sub> ) <sub>3</sub> M
A	1.2	0.2
B	1.2	0.5
C	1.6	0.2
D	1.2	0.8
E	1.6	0.5
F	2.0	0.2
G	1.6	0.8
H	2.0	0.5

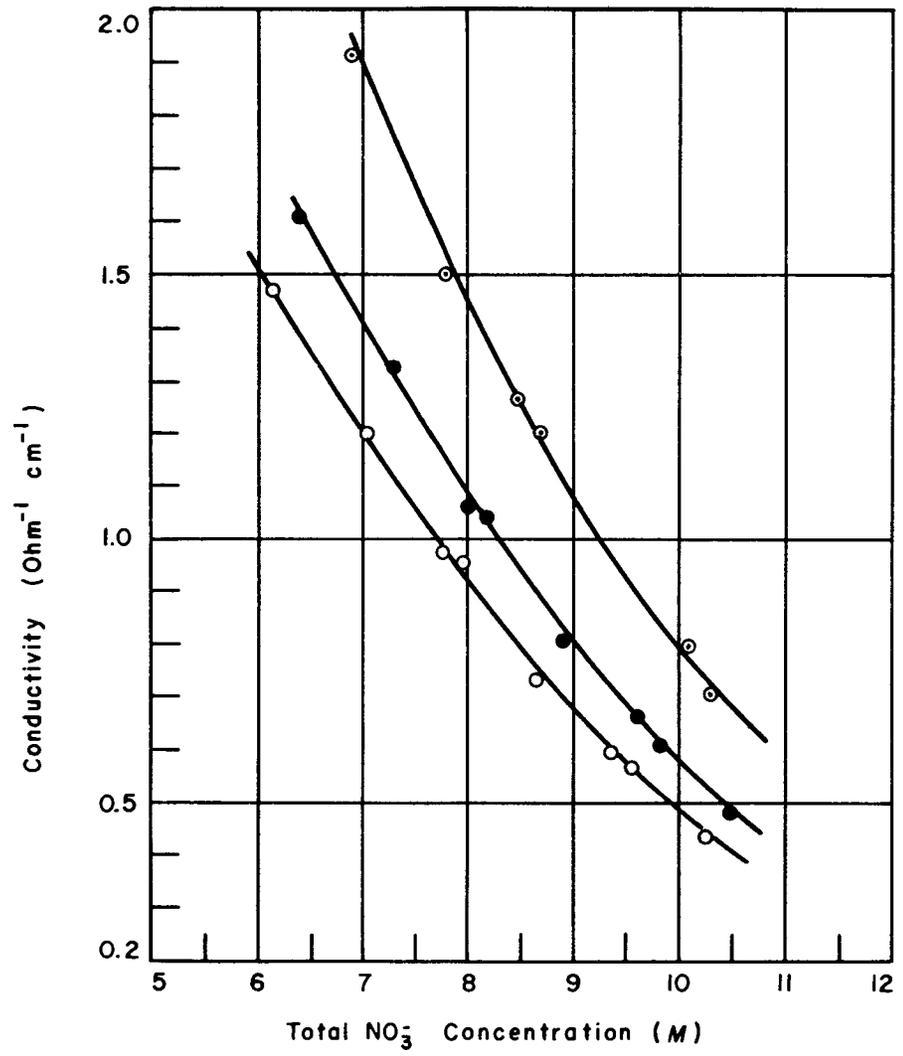


Figure 4.4  
CONDUCTIVITIES OF SYNTHETIC DISSOLVER  
SOLUTIONS AS FUNCTIONS OF TOTAL NITRATE  
ION CONCENTRATION MEASURED AT 25° C.

- ⊙ 1.50 M HNO<sub>3</sub>
- 1.00 M HNO<sub>3</sub>
- 0.756 M HNO<sub>3</sub>

Table 4.1

Conductivities of Synthetic Dissolver Solutions

Measured at 25°C; cell constant = 1.125

Concentration (M)				Resistance (ohms)	Conductivity (ohm <sup>-1</sup> cm <sup>-1</sup> )
Th(NO <sub>3</sub> ) <sub>4</sub>	Al(NO <sub>3</sub> ) <sub>3</sub>	HNO <sub>3</sub>	Total NO <sub>3</sub> <sup>-</sup>		
1.2	0.8	0.756	7.956	11.8	0.955
		1.00	8.2	10.8	1.04
		1.50	8.7	9.4	1.20
	0.5	0.756	7.056	9.4	1.20
		1.00	7.3	8.5	1.33
		1.50	7.8	7.5	1.50
	0.2	0.756	6.156	7.65	1.47
		1.00	6.4	7.00	1.61
		1.50	6.9	5.9	1.91
1.6	0.8	0.756	9.556	20.0	0.564
		1.00	9.8	18.6	0.605
		1.50	10.3	16.0	0.705
	0.5	0.756	8.656	15.4	0.73
		1.00	8.90	14.0	0.805
	0.2	0.756	7.756	11.55	0.975
		1.00	8.00	10.6	1.06
		1.50	8.50	8.9	1.26
	2.0	0.5	0.756	10.256	26.0
1.00			10.5	23.6	0.477
0.2		0.756	9.356	18.9	0.596
		1.00	9.6	17.1	0.659
		1.50	10.1	14.1	0.799

#### 4.1.3 Solubility of Mercuric Nitrate

W. T. McDuffee

The practical limit of solubility of mercuric nitrate at 25°C appears to be 6 M  $\text{Hg}(\text{NO}_3)_2$  in 3 N  $\text{HNO}_3$ . The nitric acid is necessary to prevent hydrolysis of the mercuric nitrate and the attendant precipitation of the basic mercury salts. Nitric acid in 0.1 N concentration is not sufficient to prevent the hydrolysis. Concentrated mercuric nitrate solutions will be stored at the pilot plant for use in adjusting dissolver feeds to the proper  $\text{Hg}^{++}$  catalyst content.

#### 4.1.4 Diluent Studies

W. T. McDuffee

Purex pilot plant experience with regard to cumulative radioactivity in the process solvent (30% TBP in Amsco 123-15) indicated a need to consider the use of other diluents. Laboratory data presented in the last progress report (ORNL-1367) indicated that activity retention by the process solvent was associated primarily with nitration products of the diluent Amsco 123-15, and the degree of nitration appeared to be a function of aromatic content.

Preliminary investigation of Amsco 125-90W has indicated that it is considerably more stable than Amsco 123-15 to nitric acid. The aromatic content of this diluent is less than 1.0%, and its physical properties appear favorable for use in the Thorex process (see Table 4.2 and Fig. 4.5). Although availability of Amsco 125-90W is somewhat limited, assurances have been given that sufficient quantities can be obtained to satisfy presently conceived demands of the Thorex program, and this material has been tentatively chosen as the diluent for Thorex process studies. Nitric acid pre-conditioning and a silica gel treatment of the diluent as described in ORNL-1367 are recommended to ensure generally high stability to Thorex process conditions.

The low aromatic content of the diluent has certain disadvantages in the process; for example, the viscosity of thorium-saturated TBP increases with decreasing aromatic content of the diluent and the saturation point at which a "two-phase" formation can occur is decreased. Batch counter-current runs have indicated that neither of these effects will prevent good operability. Effects on decontamination have not been investigated completely.

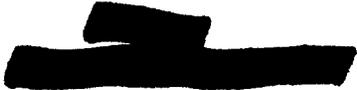


Table 4.2

Comparison of the Properties of Amsco 123-15 and 125-90W

Property	Amsco 123-15	Amsco 125-90W
Density at 25°C	0.7879	0.7570
Refractive index at 25°C	-	1.4226
Viscosity at 25°C (millipoises)	-	14.1
Kauri butanol value (ml)	32.1	25.1
Aniline cloud point (°F)	148.5	186
Flash point, Tag closed cup (°F)	143.0	133
Distillation range (°C)	186.7-204	186-199
Midpoint (°C)	190.5	190
Aromatics (%)	11	<1
Napthenes (%)	5.8	-
Paraffins (%)	83.2	-
Iodine number	-	0.49

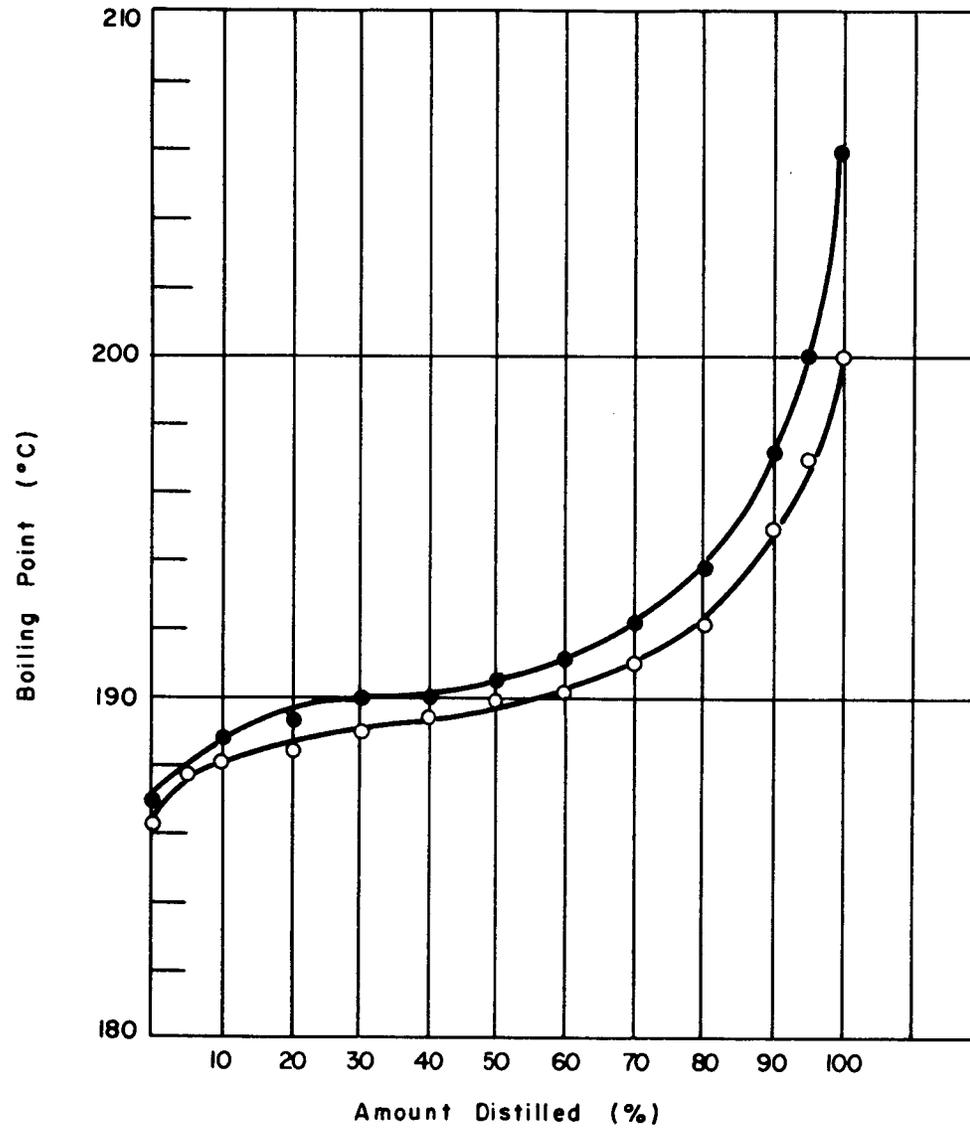


Figure 4.5  
BOILING RANGES OF AMSCO 123-15  
AND AMSCO 125-90W

- 123-15
- 125-90W

#### 4.1.5 Densities of the TBP Phase

J. E. Savolainen

The densities of solutions of TBP in the Amsco 125-90W diluent were determined (see Table 4.3). A plot of the data (Fig. 4.6) shows that the density is almost a linear function of the volume percentage of TBP.

The effect of the extracted thorium nitrate in 41% TBP-Amsco diluent is given in Table 4.4 and plotted in Fig. 4.7. The density appears to be a linear function of the thorium nitrate concentration.

#### 4.1.6 Hydrolytic Reactions of the Aluminum Ion

R. P. Wischow

A form of aluminum nitrate can be made in aqueous solutions in which the nitrate ions do not satisfy the sum of all the charges of the aluminum ion. Such a solution is termed "acid deficient" even though its pH is low. This low pH can presumably be explained by the hydrolysis and formation of complex aluminum-hydroxyl ions. Studies have been made in an attempt to determine the mechanism involved in the reaction, but data are too incomplete for final conclusions to be drawn.

The pH's of solutions of 0.167 M  $\text{Al}(\text{NO}_3)_3$  and 1.0 M  $\text{Al}(\text{OH})_2\text{NO}_3$  were determined by a titration method, the concentrations being chosen to give ionic strengths of about 1.0. This ionic strength would be relatively constant if polymerization did not occur.

The experimental data plotted in Fig. 4.8 show the pH of the solution as a function of the bulk OH/Al concentration ratio. The bulk hydroxyl concentration was calculated by subtracting the bulk nitrate ion concentration from three times the bulk aluminum concentration. The pH was observed to increase rapidly with apparent changes in slope at OH/Al ratios of 0.25 and 1.3. At ratios of 1.7 and above, the pH remained constant at 3.56.

Hypothetical reactions have been worked out, but as yet the evaluation of constants for the most probable mechanism has not been completed. Complications involving the evaluation and calculation are: (1) the actual number of complex ionic species in the system; (2) the probable variation in the ionic strength; (3) the evaluation of the concentrations of the ionic species present; and (4) the complexing nature of the nitrate ion.

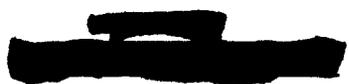


Table 4.3

Density of TBP-Amsco 125-90W

TBP (vol. %)	Density (mg/ml)		
	At 20°C	At 25°C	At 35°C
0	0.7455	0.7429	0.7395
10	0.7736	0.7703	0.7631
20	0.7928	0.7908	0.7858
30	0.7150	0.8117	0.8049
40	0.8380	0.8359	0.8270
50	0.8575	0.8570	0.8500
60	0.8820	0.8795	0.8724
70	0.9064	0.9043	0.8980
80	0.9310	0.9272	0.9200
100	0.9755	0.9710	0.9648

1 = 7(1,000) - 1(7)10,000



Figure 4.6  
SPECIFIC GRAVITY OF TBP-AMSCO 125-90W  
SOLUTIONS MEASURED AT 25° C.

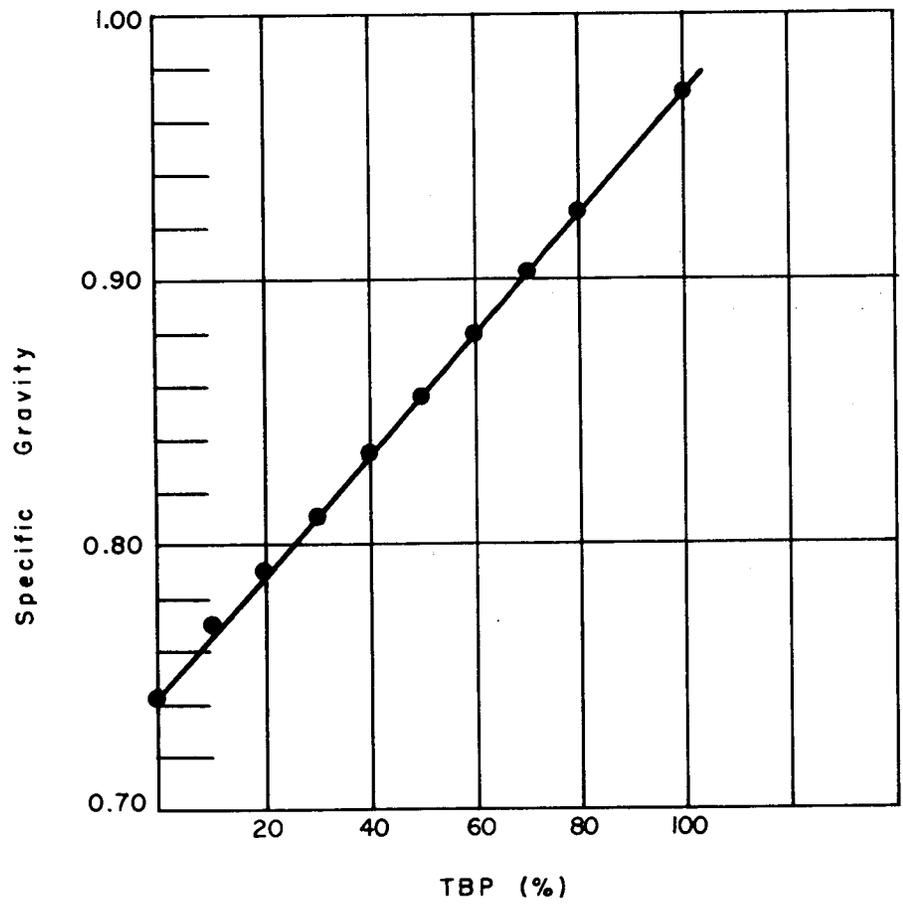


Table 4.4

Density of 41% TBP in Amsco 125-90W Containing Thorium Nitrate

Thorium		Density (mg/ml)		
(mg/ml)	(M)	At 20°C	At 25°C	At 35°C
0	0	0.8423	0.8392	0.8328
4.05	0.0175	0.8482	0.8440	0.8374
7.80	0.0336	0.8553	0.8530	0.8440
12.05	0.052	0.8592	0.8570	0.8513
16.32	0.0704	0.8689	0.8649	0.8596
20.52	0.0884	0.8753	0.8716	0.8649
24.64	0.106	0.8827	0.8783	0.8730
27.4	0.118	0.8903	0.8865	0.8795
30.8	0.133	0.8963	0.8919	0.8865
34.4	0.148	0.9025	0.8991	0.8920
27.5	0.162	0.9096	0.9049	0.8976
42.3	0.182	0.9147	0.9107	0.9055
46.3	0.199	0.9222	0.9170	0.9111



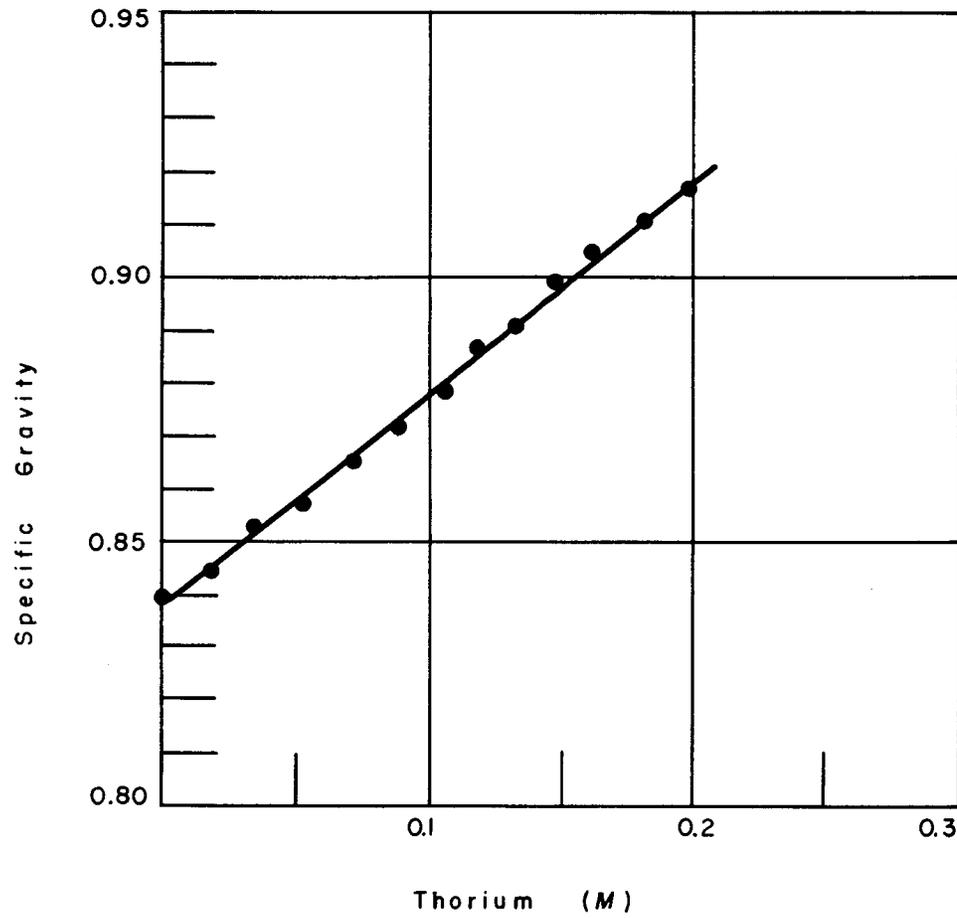


Figure 4.7  
SPECIFIC GRAVITY OF 41% TBP IN  
AMSCO 125-90W CONTAINING EXTRACTED  
THORIUM NITRATE MEASURED AT 25°C.

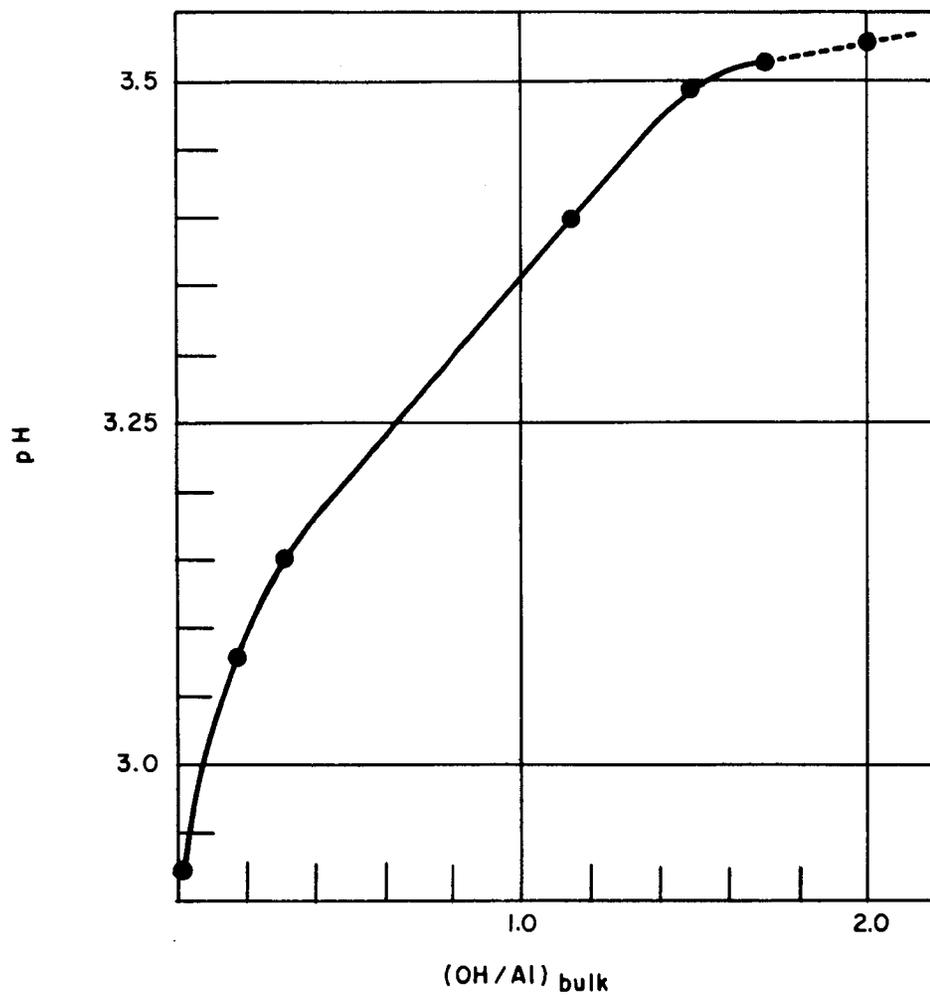


Figure 4.8  
HYDROLYSIS OF ALUMINUM NITRATE;  
pH vs OH/Al RATIO IN A SYSTEM OF  
CONSTANT IONIC STRENGTH

CONDITIONS:

0.167 M  $\text{Al}(\text{NO}_3)_3$  titrated with 1.0 M  $\text{Al}(\text{OH})_2 \text{NO}_3$ .

#### 4.1.7 Effect of Variable Acid Deficiency on pH of A-Column Scrub Section

R. P. Wischow

In the acid-deficient extraction column, equilibrium is attained among the components of the aqueous scrub, organic, and thorium feed solutions. For the decontamination of protactinium and fission products and for the recovery of thorium, it is necessary to maintain narrow acid-deficiency limits. To define the nature of the scrubbing section of the A-column, as proposed for the Thorex process, the pH of a system analogous to that in the scrub section was experimentally determined as a function of the bulk hydroxyl concentration over the anticipated operational range. The solution investigated was 0.405 M in  $\text{Th}(\text{NO}_3)_4$ , 0.61 M in aluminum, and 0.0 to 1.2 N acid deficient.

The results (plotted in Fig. 4.9) suggest a curvilinear relation in that the pH increases sharply in the less basic region but increases more slowly as the solution becomes more basic. The slope changes at approximately 0.4 M  $\text{OH}^-$ , and the curve becomes almost a straight line from 0.6 to 1.2 M  $\text{OH}^-$ . This indicates that the solution in the latter region is less sensitive to pH change than in the region 0 to 0.6 M  $\text{OH}^-$ . The proposed scrub section will operate in the hydroxyl range 0.6 to 0.8 M, which will permit the higher pH's preferred for promoting protactinium hydrolysis.

#### 4.1.8 Protactinium Extraction in TBP as a Function of Acid Deficiency and Digestion

W. T. McDuffee

Initial acid deficiency in Thorex feeds to limit protactinium extractability has been considered as a possible alternate approach to a separation scheme for use in the A-column. For example, a feed 1.5 M in thorium, 0.6 M in aluminum, and 0.2 N  $\text{HNO}_3$  deficient might be used in conjunction with a scrub solution that is 0.5 M in aluminum and 0.2 N  $\text{HNO}_3$  deficient, under which conditions the TBP extraction of thorium and uranium would be feasible.

To approximate column conditions in such a system, a solution 0.78 M in thorium, 0.67 M in aluminum, and 0.2 N  $\text{HNO}_3$  deficient was spiked with 0.5 vol. % of an acidic Interim-23 feed solution and used as the aqueous phase in extraction tests with 41% TBP. In one series of batch counter-current experiments, the solution was allowed to digest at 28°C for intervals of 0.1 to 16.0 hr prior to extraction. In another series a similar digestion was carried out at 100°C.

A change in the distribution coefficient occurred between the first and third stages (see Table 4.5), which indicates the existence of at least two different species of protactinium. In the experiment at 28°C the rise in distribution coefficient during the first hour and the subsequent decrease between the 1- and 4-hr period presumably implies a changing equilibrium



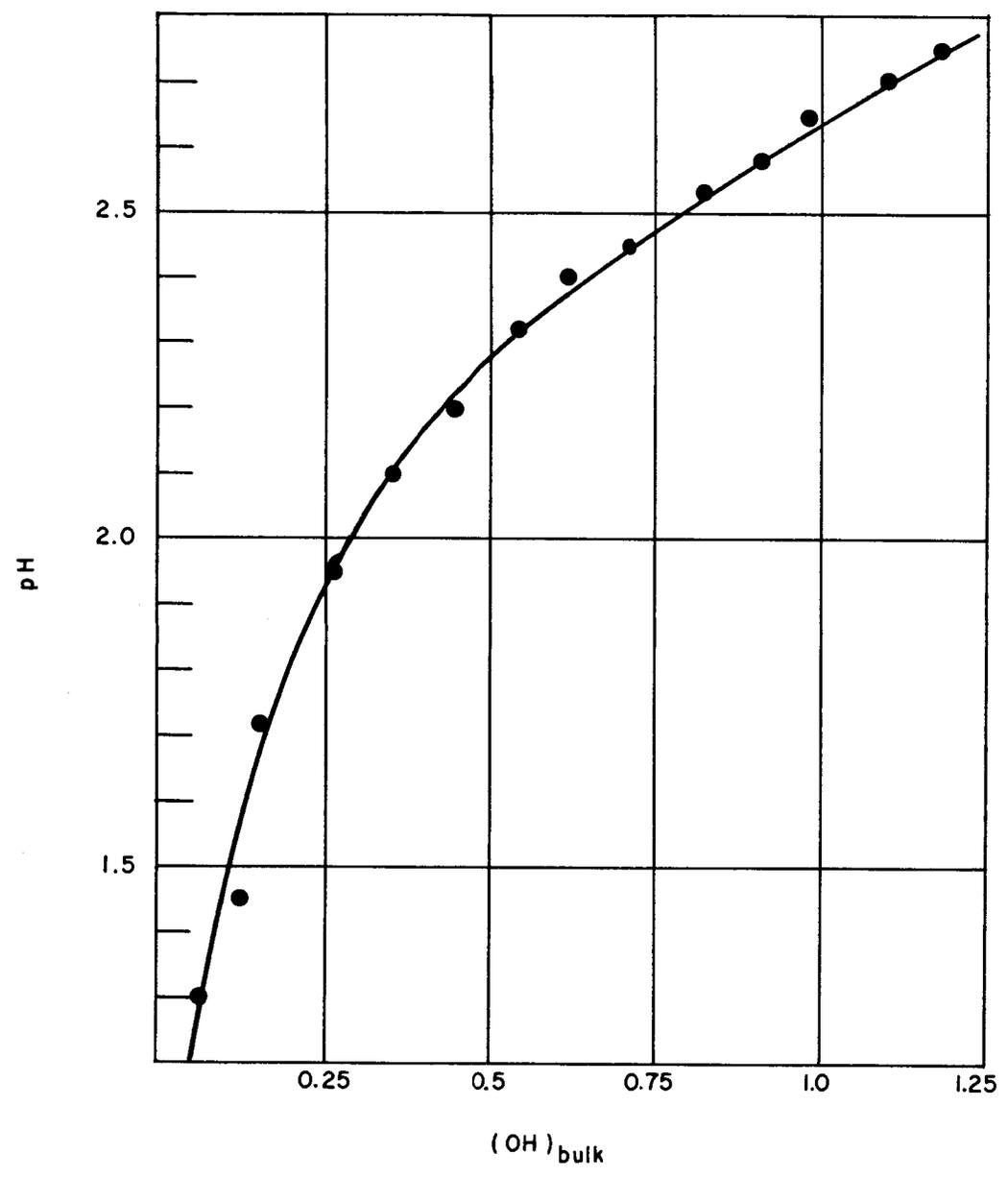


Figure 4.9  
pH OF A-COLUMN SCRUB SECTION AS  
A FUNCTION OF BULK  
HYDROXYL CONCENTRATIONS.

Table 4.5

Protactinium Distribution Coefficients as Functions of Digestion Time in Acid-Deficient Solutions

Feed: 0.78 M Th, 0.67 M Al, 0.2 N HNO<sub>3</sub> deficient;  
5.0 x 10<sup>7</sup> Pa β c/m/ml; digested at 25 and 100°C

Organic: 41% TBP in Amsco 123-15

Batch countercurrent operation; 3 extraction stages;  
3 vol. changes; O/A flow ratio = 5; data taken at first and third stages

Digestion Temperature (°C)	Digestion Time (hr)	Pa D.C.'s (O/A)	
		First Stage	Third Stage
28	0.1	0.018	0.0024
	0.5	0.025	0.004
	1.0	0.051	0.001
	2.0	0.041	0.001
	4.0	0.008	0.0009
	16.0	0.006	0.0004
100	0.1	0.026	0.0002
	0.5	0.031	0.003
	1.0	0.028	0.0008
	2.0	0.042	0.0007
	4.0	0.04	0.0002
	20.0*	0.06	0.0002

\*About 30% of the original activity was apparently "plated out" on the equipment, as calculated by difference.

of the most extractable species. In the experiment at 100°C the protactinium distribution coefficient did not decrease during the 1- to 4-hr period. Very little plating of protactinium onto the glass vessels or stainless steel stirrers was observed at 28°C, but it was calculated that at 100°C about 20% of the activity was plated out during the 0.1-hr digestion period, and it was observed that about 30% had plated out at the end of the 20-hr period.

#### 4.1.9 Distribution of Fluoride Ion in Thorex Extraction System

W. T. McDuffee

The distribution coefficients and extraction factors of the fluoride ion in the A-column were investigated (see Table 4.6). About 90% of the fluoride was observed to follow the aqueous stream (AP), and about 10%, by difference, can be expected to follow the organic extract (AU). The higher fluoride distribution coefficient observed in the scrub section, 0.18, as opposed to the value of 0.07 in the extraction section, may indicate that part of the fluoride exists as a thorium complex.

In countercurrent process demonstrations starting with A-column feeds that contained 0.075 M fluoride, the proposed Thorex-feed concentration, the BT stream was observed to contain about 120 ppm of fluoride and the CU stream about 40 ppm. More extensive data will be obtained to confirm the latter.

#### 4.2 Protactinium Adsorption Column

##### 4.2.1 Protactinium Adsorption Studies

S. S. Brandt

Protactinium adsorption behavior in the presence of thorium was found to be the same as in the absence of thorium within the limits studied. In these experiments protactinium was adsorbed on silica gel from an acid-deficient AP stream containing thorium in concentrations up to 1 M. The silica gel column was washed with 0.5 N HNO<sub>3</sub> to remove any thorium, which would form an insoluble precipitate in contact with the protactinium elutriant, and the protactinium was then eluted with 4% oxalic acid. Protactinium losses were less than 0.1% in the nitric acid wash.

In view of these results, it is thought that, if any thorium or uranium should be present, they can be preferentially removed with dilute nitric acid without appreciable loss of protactinium. However, large variations in the thorium content of the AP stream may complicate the use of a Higgins type contactor (see Fig. 4.10), which is based on a continuous adsorption, washing, and elution scheme.

Table 4.6

Extraction of Fluorides in the Thorex A-ColumnFeed: 1.5 M Th; 0.5 M Al; 1.0 N HNO<sub>3</sub>; F<sup>-</sup>, 1.9 mg/ml

Scrub: 1.0 M Al, 1.4 N acid deficient

Organic: 41% TBP

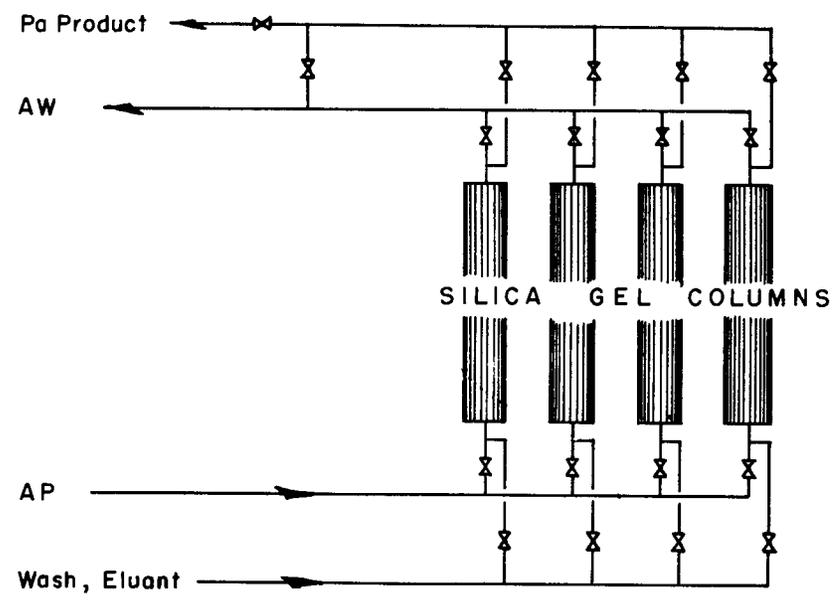
F/S/O flow ratio = 1/1/5

7 extraction, 8 scrub stages; data taken after  
1 vol. change

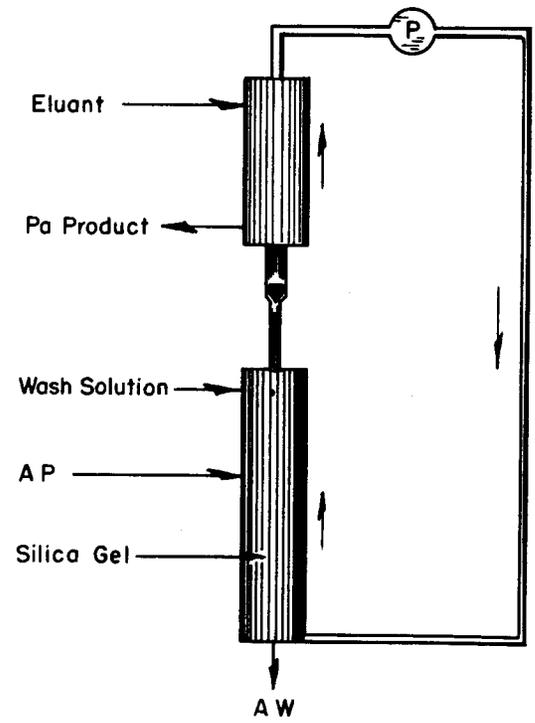
Stage No.	Fluoride Concentration (mg/ml)		D.C. (O/A)	E.F. (O/A)
	Organic Phase	Aqueous Phase		
2Sc	0.036	0.20	0.180	0.9
1Ex	0.057	0.85	0.067	0.167
3Ex	0.033	0.80	0.041	0.102
7Ex	0.036	0.87*	0.041*	0.102

\*When this aqueous stream (AP) was adjusted from 0.15 N HNO<sub>3</sub>-deficient to 0.2 N HNO<sub>3</sub>, the fluoride distribution coefficient increased to 0.09.

Figure 4.10  
SCHEMES FOR PROTACTINIUM ADSORPTION  
ON SILICA GEL



BATCH (CARTRIDGE) COLUMNS



CONTINUOUS HIGGINS COLUMN

Consideration is being given to adsorption schemes in which cartridge type silica gel units would be used for protactinium adsorption. Such units would be in process service for only about 24 hr, and washing or elution steps could be well controlled by batch treatment. Washed columns containing protactinium could also be stored to allow for any degree of  $\text{Pa}^{233}$  decay prior to elution. After 27.4 days, one half of the adsorbed  $\text{Pa}^{233}$  would be converted to  $\text{U}^{233}$ . Holdup of the  $\text{Pa}^{233}$  product on the columns would presumably permit controlled emphasis on either  $\text{Pa}^{233}$  or pure  $\text{U}^{233}$  production; e.g., the protactinium might be eluted only if and when it was desired for radiological warfare usage, following a relatively simple  $\text{U}^{233}$  "milking" operation.

#### 4.3 The B-Column

##### 4.3.1 Removal of TBP from BT Stream by Amsco Washing

M. R. Bennett

The BT stream at equilibrium with 41% TBP contains about 0.25 g of TBP per liter. It is desirable to remove this TBP prior to the BT concentration by evaporation since its degradation to phosphoric acid during evaporation would create problems in any subsequent extraction operations. One method for its removal consists in scrubbing the BT stream with Amsco.

Economic factors of organic waste handling have limited the consideration of such a procedure in previous separations processes. Laboratory studies have indicated that by virtue of high TBP D.C.'s (O/A) in the Amsco-aqueous BT system, countercurrent extractions utilizing very low O/A flow ratios are feasible and will thus permit reasonably low organic waste volumes.

TBP distribution coefficients in such a system are presumably a function of TBP concentration in the organic phase. Although analytical data presently obtained in the laboratory studies are somewhat doubtful, owing to the limitations of detecting extremely low TBP concentrations, it is apparent that the TBP D.C.'s (O/A) will be in the range 150 to >200. These high values permit TBP extractability in a system with low O/A ratios; for example, at the lower value of 150 an O/A ratio of 0.01 would allow an E.F. (O/A) of 1.5, which is ample to permit high TBP separation in a multi-stage system.

TBP D.C.'s were measured by spiking known quantities of TBP into liter portions of synthetic BT solution (0.25 M Th, 0.2 N  $\text{HNO}_3$ ) and extracting with 10 ml of Amsco 125-90W. TBP was analyzed in the organic phase by the nitric acid saturation method and was calculated by difference in the aqueous phase. Results are recorded in Table 4.7. Countercurrent studies, using five "static" stages and overall O/A flow ratios of 0.01 and 0.001 were also carried out to demonstrate a possible process system. Twenty

Table 4.7

Distribution Coefficients (O/A) of TBP in the Amsco 125-90W-BT System

System: Amsco 125-90W-0.25 M Th(NO<sub>3</sub>)<sub>4</sub> spiked with TBP

O/A volume ratio = 10 ml/1000 ml

Contact time: 5 min

Settling time: 8 min

Specific Gravity <i>Control</i>	TBP (aq before extraction)		TBP (org after extraction) ( <u>M</u> )	D.C. (O/A)	E.F. (O/A)	TBP Extracted (%)
	(g/liter)	( <u>M</u> )				
1	0.2440	0.00092	0.061	187	1.87	66.3
2	0.0970	0.00036	0.025	233	2.33	69.4
3	0.0240	0.00009	0.006	233	2.33	69.4
4	0.0097	0.00004	0.005		-	100

50-ml passes of BT solution containing about 0.001 M TBP (0.03% TBP), were equilibrated countercurrently in five tubes containing 10 ml each of Amsco so that the final A/O contact ratios were 100, 95, 90, 85, and 80, respectively. The contents of the organic phases were then determined, by analysis, to be 3.16% in the first tube, 0.57% in the second tube, etc. Figure 4.11 is a plot of the molarity of TBP found in successive stages following experiments as described above, when using overall O/A volume ratios of 0.01 and 0.001. The data indicate that the 0.01 ratio is feasible for a high degree of TBP removal by countercurrent extraction, whereas the 0.001 ratio does not appear feasible.

Potential use of an extraction process utilizing flow ratios of the above order would require contactor equipment development. Whether pulse columns or concatenated columns can be adopted to allow reasonable HETS values and stage efficiencies will be considered by the Unit Operations Section.

#### 4.3.2 Concentration of the Thorium Product

M. R. Bennett

It is tentatively planned that the BT stream, which is about 0.25 M in  $\text{Th}(\text{NO}_3)_4$  and 0.2 M in  $\text{HNO}_3$ , will be evaporated to a concentration of about 2.0 M thorium and 1.5 M  $\text{HNO}_3$  for storage during the decay period of  $\text{Th}^{234}$  and/or the  $\text{Pa}^{233}$  not separated in the extraction column. The evaporation is planned as a continuous operation.

The boiling-point curve, shown in Fig. 4.12, of a batch evaporation of the BT stream indicates the change of boiling point that occurs during concentration and the degree of nitric acid distillation when the operation is carried out at atmospheric pressure. Under these conditions, most of the TBP that is soluble in the BT stream, i.e., about 0.25 g of TBP per liter (0.001 M TBP) will be decomposed according to the reaction



The degradation to  $\text{H}_3\text{PO}_4$  appears to be essentially complete, so that the final concentrated solution would be of the order of 0.01 M in  $\text{PO}_4^{3-}$ .

In consideration of the event of BT recycle, these concentrated solutions were adjusted to conditions of the AF solution and used in demonstrations of the countercurrent A-column operation. Although no stable emulsion occurred in the contacting units, very copious precipitates of thorium phosphates formed in the extraction section. The presence of small concentrations of DBP was indicated by some colloidal dispersion in the organic product stream. It is not known whether the proposed pulse columns would operate under these conditions.

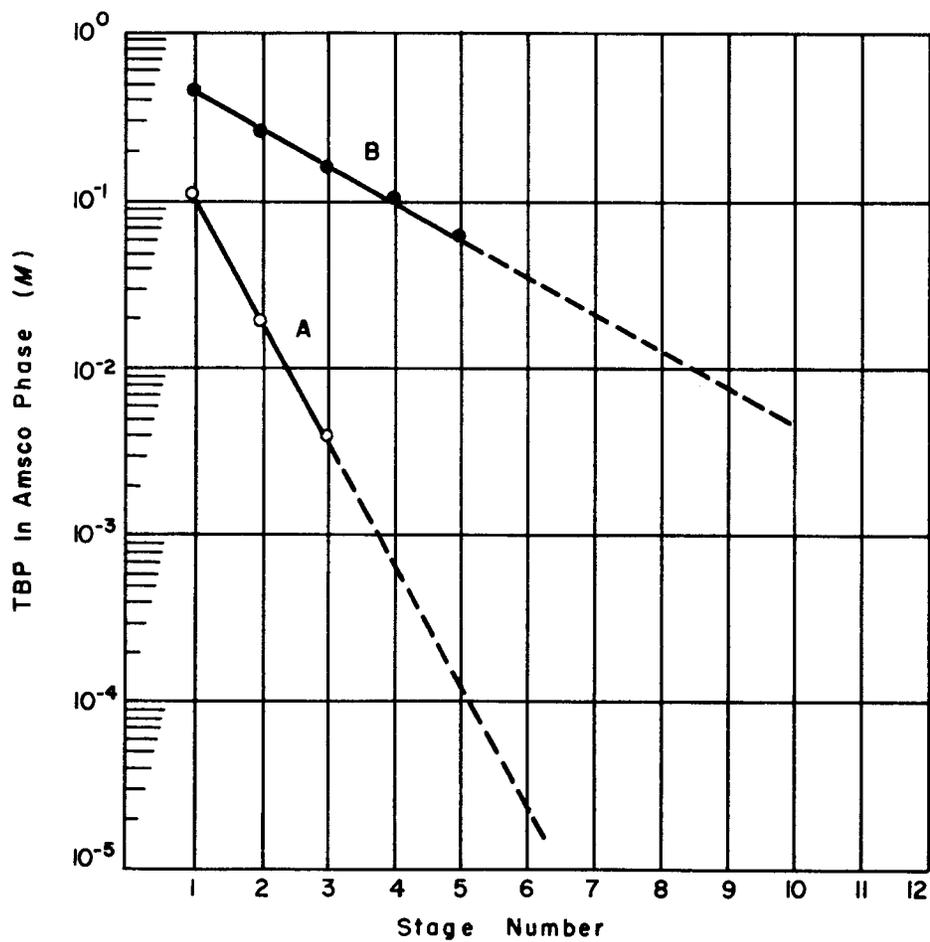


Figure 4.11  
AMSCO WASHING OF THE AQUEOUS  
BT STREAM

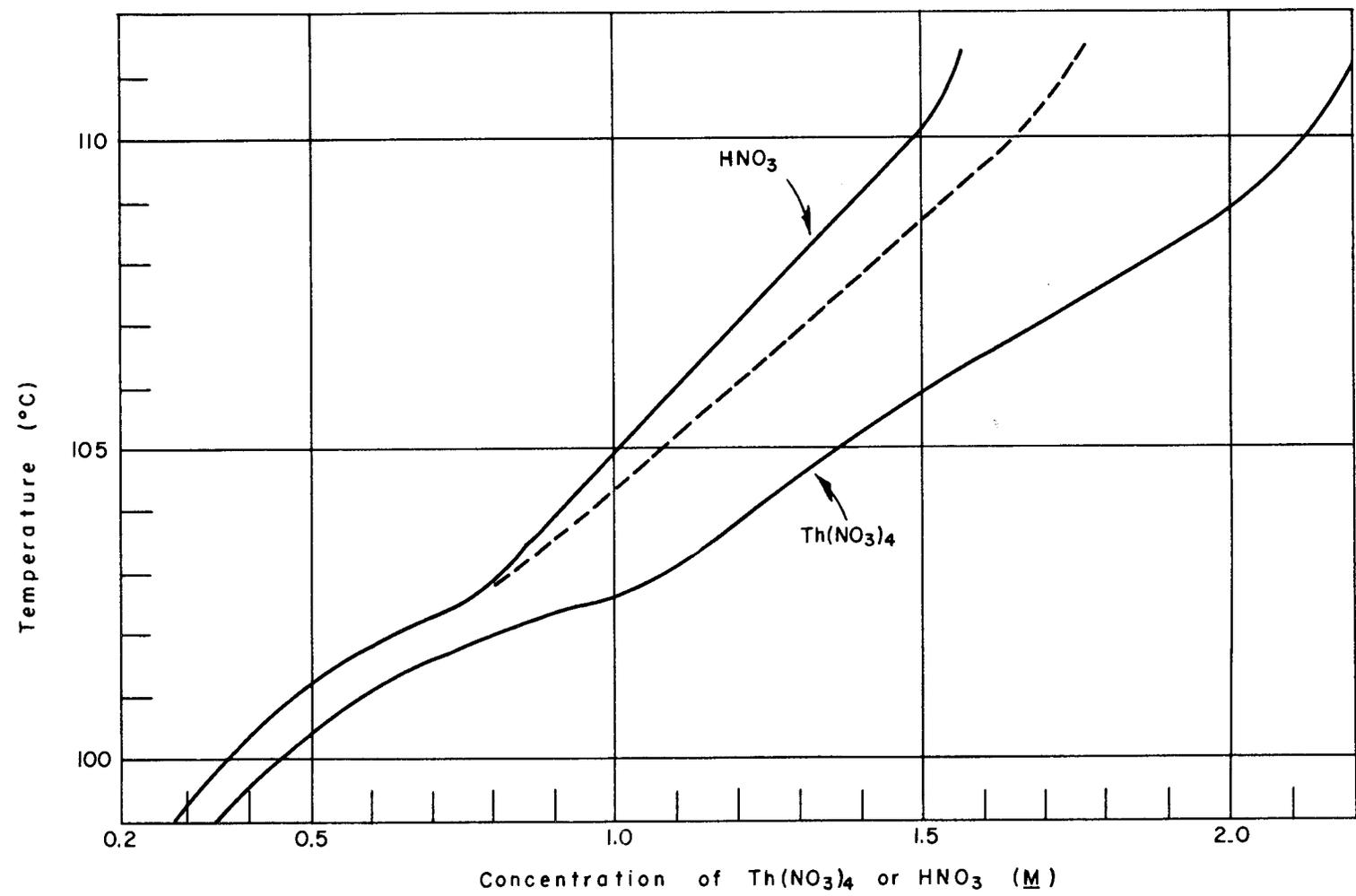
Molarity of TBP in the Amsco phase following extractions at flow ratios (O/A) of:

- A = 0.01
- B = 0.001

**CONDITIONS:**

0.245 M Th, 0.185 N HNO<sub>3</sub> solution was concentrated to 2.1 M Th, 1.47 N HNO<sub>3</sub> by evaporation at atmospheric pressure. Difference between solid and broken lines for HNO<sub>3</sub> indicates effect of HNO<sub>3</sub> distillation.

Figure 4.12  
EVAPORATION OF THE BT STREAM  
BOILING POINTS vs Th(NO<sub>3</sub>)<sub>4</sub> AND  
NITRIC ACID.



An economical procedure for removing the soluble TBP from the BT stream is desirable. Possible methods include (1) washing with Amsco, (2) distillation with steam, and (3) evaporation of the BT solution at low temperatures and pressures. An Amsco-washing method has been investigated briefly and appears to allow very high removal of the TBP under conditions which limit any degradation by hydrolysis. Steam distillation, which has been studied by other investigators, will be surveyed by the Chemical Development Section since it appears to have certain engineering advantages. Evaporation of TBP-saturated BT solutions at low temperatures and pressures, e.g., 22 to 28°C and 19 mm Hg, was found to concentrate the TBP so that a two-phase system could be observed in the concentrated solution. This method seems promising since it would permit adjustment to AF conditions without TBP degradation.

If removal of the TBP should not prove feasible, it would be desirable to remove its degradation products from the BT concentrate prior to any extraction operation. Possible methods for this include (1) precipitation and filtration of some insoluble phosphate, or (2) purification by preferential crystallization of hydrates of the thorium nitrate. No suitable precipitant has been found for the first method. The latter method appears to offer some promise and will be investigated further.

#### 4.3.3 Thorium Nitrate Crystallization

W. T. McDuffee

Crystallization of thorium nitrate from solutions of mantle grade thorium nitrate tetrahydrate, or from the BT stream, may offer a means of purifying the salt. Crystals of the dodecahydrate, obtained by slow crystallization from a concentrated solution of impure commercial thorium nitrate tetrahydrates, were found to contain only small amounts of the silicates and phosphates that normally produce severe emulsions in the TBP extraction process. Crystals of the tetrahydrate, obtained by evaporating the BT stream to 6% of its original volume, were found to be decontaminated by a factor of about 10 from the ruthenium activity that was present in the original solution.

Thorium nitrate crystallizes as a mixture of the tetra- and hexahydrates at higher temperatures and as the dodecahydrate at lower temperatures. The tetrahydrate is nonhygroscopic, the hexahydrate is slightly hygroscopic, and the dodecahydrate is very hygroscopic.

Owing to the limitations on radioactive decontamination of the thorium product imposed by the presence of the active  $\text{Th}^{234}$ , it may become desirable during the decay period to store the product in the form of crystals in order to realize minimum storage volumes; the tetrahydrate would be the preferable form. However, the handling of radioactive solids may be an undesirable operation.

#### 4.3.4 Impurities in the Product Streams

W. T. McDuffee

Preliminary analysis of the product streams has been carried out to determine the extent of contamination by certain probable impurities. Principal consideration was given to beryllium, iron, and mercury from the AF, and aluminum and iron from the AS. Results are recorded in Table 4.8.

#### 4.4 The C-Column

##### 4.4.1 Study of TBP Hydrolysis and Its Effect on U<sup>233</sup> Stripping Step

M. R. Bennett

Tributyl phosphate hydrolyzes under certain conditions to form principally dibutyl phosphate, monobutyl phosphate, butanol, and orthophosphoric acid. Other more complex derivatives can supposedly be formed by interaction of these primary products. Rates and forms of hydrolysis as functions of acidity, alkalinity, and temperature have been studied previously and were reported in the last progress report (ORNL-1367).

Since the alkyl phosphoric acid products DBP and MBP apparently form rather stable compounds with heavy metals ions, such as Th<sup>4</sup>, Pu<sup>4</sup>, or UO<sub>2</sub>, the degree and rate of TBP hydrolysis is important in Thorex process considerations. In addition to the previously reported (ORNL-1367) emulsifying properties of the DBP and MBP reaction products with thorium nitrate, the distribution of similar products of U<sup>233</sup> in the stripping step was a matter of concern. The amount of U<sup>233</sup> in the 41% TBP-Amsco solvent will be small, e.g., 0.05 g per liter, or 0.00013 mole of U<sup>233</sup> per mole of TBP, and low concentrations of the very reactive MBP or DBP may cause marked changes in distribution coefficients. It is suspected that the MBP salt will be more soluble than the DBP in aqueous solutions. The latter may presumably cause nonstrippability of the U<sup>233</sup>, as has been observed in similar cases with plutonium in the Purex process.

An empirical study has been made of (1) the hydrolysis of freshly purified TBP as a function of time and (2) its effect on U<sup>233</sup> distribution coefficients and strippability. Exposure of the solvent to air and/or light, possible catalysts of the hydrolysis, was also investigated. Both the Amsco 123-15 and the TBP mixture were meticulously pretreated to reduce possible catalytic effects of organic impurities, such as nitro compounds or tars, formed by nitration of diluent fractions.

A test solution of Amsco was washed thoroughly with one-half volume of 8.0 M HNO<sub>3</sub> for 1/2 hr and was then used as diluent in making up a 54% solution of TBP. The mixture was carefully washed with a 1.0 M solution

Table 4.8  
Impurities in the Product Streams

Impurity Sought	AF Stream		Simulated AS Stream*		BT Stream		CU Stream	
	Spectro-graphic (ppm)	Ionic (mg/ml)	Spectro-graphic (ppm)	Ionic (ppm)	Spectro-graphic (ppm)	Ionic (ppm)	Spectro-graphic (ppm)	Ionic (ppm)
Al	-	-	-	-	~ 3	-	0.8	-
Be	-	0.39	-	-	< 0.03**	-	< 0.03**	-
Ca	-	-	< 5	-	-	-	-	-
Cr	-	-	8	-	0.76	-	None	-
Cu	-	-	4	-	-	-	-	-
F	-	1.2	-	-	-	114***	-	38***
Fe	-	-	78	-	3.2	-	0.8	-
Hg	-	1.0	None	1*	None	4***	None	< 1*
Mn	-	-	None	-	None	-	None	-
Ni	-	-	None	-	None	-	3.2	-
P	-	-	None	-	Trace	-	Faint trace	-
Si	-	-	Faint trace	-	Trace	-	None	-

\*Prepared by reaction of 2S aluminum metal with HNO<sub>3</sub>-Hg.

\*\*Lower limit of detection.

\*\*\*Questionable; to be rechecked.

of NaOH followed by three successive washes with 0.1 M Na<sub>2</sub>CO<sub>3</sub>, each for 1/2 hr. U<sup>233</sup> tracer was extracted into the TBP to give an  $\alpha$  activity level of  $1.08 \times 10^5$  c/m/ml. The TBP was then divided into three equal portions: (I) which was placed in a dark bottle and blanketed with dry nitrogen, (II) which was exposed only to air, and (III) which was exposed to both air and light as a "control." Countercurrent extractions, using 0.025 M HNO<sub>3</sub> as strip solution and a constant O/A ratio of 1/1, were then carried out at intervals over a period of two months. Five contacting stages and more than two volume changes were used in all runs. Results may be summarized as follows:

1. The nonstrippable U<sup>233</sup> at the end of two months was <0.05% for each test solution, which indicated that DBP, if present, had not become limiting.
2. Noticeable decreases, i.e., factors of about 2.0, occurred in the D.C.'s (A/O) for U<sup>233</sup> at the end of 15, 23, and 40 days, respectively, for TBP solutions Nos. III, II, and I (see Table 4.9).
3. At the end of two months the D.C.'s (O/A) for U<sup>233</sup> had decreased by factors of 2, 4, and 4, respectively, for TBP solutions I, II, and III.
4. Results of the tests indicate that keeping light and air from TBP solutions may have some retarding effect on hydrolysis rates.

#### 4.4.2 Beta Decontamination of the CW Stream

W. T. McDuffee

Residual activity that is not stripped from the organic solvent in the C-column is readily removed by treatment of the stream with calcium hydroxide [60 g Ca(OH)<sub>2</sub> per liter of solvent]. An alternate method equally effective consists in washing the solvent with 1.0 M sodium hydroxide which contains 0.3 g of 18- $\mu$  silica gel per liter and then removing the alkali with successive water washes. The use of a silica gel column resulted in the removal of ~95% of the activity. Table 4.10 summarizes the results.

The data indicate that a silica gel column would be effective for localizing entrained activities in the solvent recovery stream, thus limiting the build-up of radiation in the calcium hydroxide contactors. Solvent leaving the recovery system should be decontaminated prior to storage in cold areas.

Table 4.9

Stripping of U<sup>233</sup> from 54% TBP Solvent: Effect of Storage Time and/or TBP Hydrolysis on Distribution Coefficients

Solution No.                      Treatment  
I                                      Blanketed with N<sub>2</sub> in dark bottle  
II                                      Exposed to air only  
III                                     Exposed to light and air

Time (days)	U <sup>233</sup> D.C. (O/A)			Nonstrippable U <sup>233</sup> (%)
	No. I	No. II	No. III	
0	33.7	32.0	33.8	0.001
5	25.4	27.6	29.3	0.06
6	29.0	31.0	30.0	0.01
7	31.0	32.0	32.5	0.01
12	34.8	32.0	30.0	0.01
15	25.0	24.8	17.0	0.01
23	24.6	13.0	11.9	0.01
33	26.5	14.3	13.4	0.01
40	15.0	8.4	13.1	0.01
51	14.0	9.6	12.2	0.01
61	15.0	8.6	9.5	0.05

Table 4.10

Beta Decontamination of the CW Stream

CW stream: 41% TBP in Amsco 125-90W, containing  $1.79 \times 10^3$  c/m/ml

Treatment of CW Stream	Final Activity (c/m/ml)	Activity Removed (%)
60 g of $\text{Ca}(\text{OH})_2$ per liter of solvent		
1 hr contact	10	99.4
Two successive treatments	0	100
Silica gel column (bed volume 10 ml, cross-sectional area $1.23 \text{ cm}^2$ ; flow rate 0.5 ml/m)		
Vols. of feed put through bed:		
1	85	95.3
2	75	96.3
3	105	94.0
4	85	95.3
1.0 M NaOH (containing 0.3 g of 18- $\mu$ silica gel per liter); two 0.2-vol. washes, followed by three 0.2-vol. washes with $\text{H}_2\text{O}$	0	100

## 4.5 Solvent Treatment

### 4.5.1 With Calcium Hydroxide

J. E. Savolainen

Owing to the large aqueous waste volumes produced in a previously described (ORNL-1367) solvent recovery system, which utilized sodium hydroxide or sodium carbonate washing, a new approach to this system appeared desirable. The use of a calcium hydroxide slurry treatment of the 41% TBP has shown considerable promise with respect to (1) the removal of MBP, DBP, and certain unidentified surface-active impurities, and (2) low solid and liquid waste production.

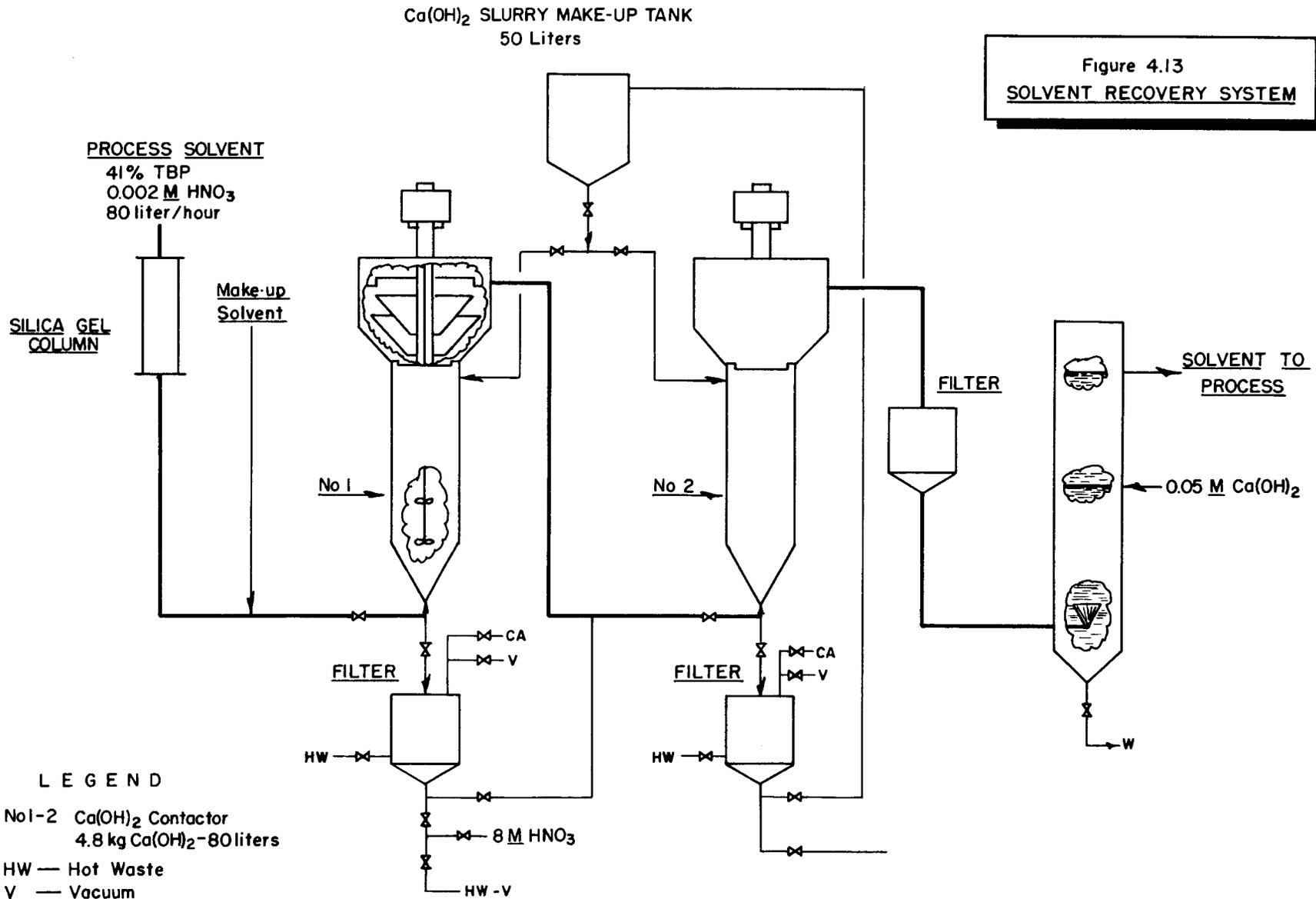
The process consists in agitating anhydrous calcium hydroxide for 1 hr with water-saturated 41% TBP at a constant ratio of 60 g of  $\text{Ca}(\text{OH})_2$  per liter of solvent. The water-wetted particles are allowed to settle for about 30 min, after which the supernatant solvent is decanted through a medium-porosity filter. Means of carrying out this kind of treatment on a continuous basis required study of an aqueous-slurry contactor system, which would be designed to allow particle coagulation, settling, and filtration.

Figure 4.13 indicates the nature of the treatment process and features of design which were recommended for engineering study. A silica gel column, to permit a certain degree of radioactive decontamination of the entering solvent stream, has been recommended for reducing contamination of the calcium hydroxide contactors. The first contactor will be designed for a 1-hr solvent holdup in the mixing section; continuous operation of the system will be carried out until the  $\text{Ca}(\text{OH})_2$  is 50% neutralized by the nitric acid in the solvent; and rapid settling rates of the slurry will be obtained by use of 60-deg conical baffles in a disengaging section. The clarified solvent will pass through a similar second contactor to ensure a high degree of purification. The solvent will finally pass through a filter and then through a glass column containing 0.05 M (saturated)  $\text{Ca}(\text{OH})_2$  which will serve as a visual indicator of the efficiency of the recovery system. Provisions for periodic unloading and recharging of the contactors include (1) filters for the used slurry, (2) valving for nitric acid addition and removal of neutralized slurry, and (3) a slurry make-up tank. Aqueous waste volumes in the proposed system will be of the order of 1 liter of 1 M  $\text{Ca}(\text{NO}_3)_2$  for 250 liters of treated solvent.

The relative rates of settling of the slurry in the  $\text{Ca}(\text{OH})_2$  contactors were investigated briefly by studying the coagulation and settling times as functions of angles of inclination in 100-ml graduates. Typical data are given in Table 4.11.



Figure 4.13  
SOLVENT RECOVERY SYSTEM



LEGEND

- No 1-2 Ca(OH)<sub>2</sub> Contactor  
4.8 kg Ca(OH)<sub>2</sub>-80liters
- HW — Hot Waste
- V — Vacuum
- CA — Compressed air

Table 4.11

Settling of Calcium Hydroxide Slurry in 41% TBP-Amsco Solvent

60 g of  $\text{Ca}(\text{OH})_2$  per liter of water-saturated\* 41% TBP in Amsco 125-90W shaken in 100-ml graduates; settling rates served as functions of "angle of tilt" of the graduates; diameter of graduates was about 1 in.

Settling Time (min)	Vol. of Clarified Liquid in 100 ml of Slurry		
	Vertical	30 deg from vertical	45 deg from vertical
0	0	0	0
0.5	1.1	3.6	3.2
1.0	2.7	6.7	6.3
1.5	4.7	8.6	7.8
2.0	5.7	9.6	8.6
2.5	8.1	10.1	8.8
3.0	8.8	10.6	8.9
3.5	9.7	10.7	
4.0	10.7	10.9	
4.5	11.5	11.1	
5.0	12.1	11.2	
5.5	12.8		
6.0	12.8		
0.0			

\*In batch operations 5 to 10% by volume of water appeared optimum for good settling characteristics and efficient TBP clean-up.

## 5.0 GENERAL INVESTIGATIONS

### 5.1 Relative Dissolution Rates of Thorium Oxide as a Function of Calcination Temperatures

M. R. Bennett

Three samples of  $\text{ThO}_2$  crystals, in the form of pellets, which had been prepared at temperatures of 700, 1200, and 1630°C, respectively, were studied with regard to relative dissolution rates in nitric acid. Rates as a function of actual crystal surface area were not determined.

Since the samples were limited in size, dissolvings were carried out in a very small glass reactor with a finger condenser. Heat was supplied by means of an oil bath. Two grams of the  $\text{ThO}_2$  samples and the nitric acid were charged for each dissolving at a ratio of 4.5 moles of  $\text{HNO}_3$  per mole of  $\text{ThO}_2$ , calculated to provide a product at a 0.5  $\text{M H}^+$  excess. Dissolution characteristics and rates were determined as functions of nitric acid concentration, temperature, and amount of fluoride catalyst.

Results of the various experiments (see Table 5.1) may be summarized, as follows:

1. The dissolvability of  $\text{ThO}_2$  was found to decrease with increasing preparation temperatures.
2. The use of concentrated nitric acid alone at 115°C permitted dissolution of only small fractions of the crystals, from 3 to 10<sup>-4</sup>%.
3. Decreasing the reaction temperature from 115 to 23°C caused a decrease in dissolvability by a factor of about 50.
4. Decreasing the  $\text{HNO}_3$  concentration from 15.8 to 8.0  $\text{N}$  caused very little change in dissolvability.
5. The pellets from the 700 and 1200°C samples disintegrated rapidly to a very fine powder as soon as the reaction was begun; the 1630°C samples maintained the pellet form throughout the dissolvings.
6. The addition of 0.075  $\text{M F}^-$  in 15.8  $\text{M HNO}_3$  gave complete dissolution in all tests. The length of the overall dissolution period increased as the calcination temperature increased.
7. Dissolving in presence of the fluoride ion was found to produce early disintegration of even the 1630°C samples.

Table 5.1

Dissolvability of Heat-Treated Thorium Oxide Crystals in HNO<sub>3</sub> and HNO<sub>3</sub>-HF

2.0 g of ThO<sub>2</sub> charged at a HNO<sub>3</sub>/Th mole ratio of 4.5 in all runs; agitation of dissolvings effected by thermal means alone; % of crystals remaining in the larger pellet size during dissolution was estimated

Run No.	Calcination Temp. of Sample (°C)	HNO <sub>3</sub> (M)	Dissolution Temp. (°C)	Fluoride Ion (M)	Dissolution Time (hr)	ThO <sub>2</sub> Reacted (g)	% Dissolution	Pellet Form Remaining	
8	700	15.8	23	0	1.0	0.001	0.05	None	
11		15.8	23	0	1.0	0.0008	0.04	30%	
1		15.8	115-118	0	1.0	0.077	3.85	None	
2		15.8	115-118	0	1.0	0.057	2.80	None	
5		15.8	115-118	0.075	1.5	2.0	100	None	
9		13.0	115-118	0	1.0	0.066	3.3	None	
10		8.0	115-118	0	1.0	0.047	2.35	None	
12		1200	15.8	23	0	1.0	0.00012	0.006	75%
3			15.8	115-118	0	1.0	0.0024	0.11	Few
6			15.8	115-118	0.075	2.6	2.0	100	None
13	1630	15.8	23	0	1.0	< 0.0001	0.0016	98%	
4		15.8	115-118	0	1.0	< 0.001	< 0.0001	98%	
7		15.8	115-118	0.075	5.0-5.5	2.0	100	None	

5.2 Dissolution of Aluminum Metal in Thorium Nitrate Solutions

W. T. McDuffee

Highly acid-deficient and stable solutions of aluminum and thorium nitrate may be prepared by dissolving aluminum metal in thorium nitrate solutions containing mercuric ion. A solution of the composition 2.0 M thorium, 1.9 M aluminum, 7.0 N HNO<sub>3</sub>-deficient has been prepared by this method, which indicates an equivalent composition of Th(NO<sub>3</sub>)<sub>2</sub>·4(OH)1.6·0.95 Al(NO<sub>3</sub>)(OH)<sub>2</sub>. This solution was clear and stable for longer than one week. When extracted with five volumes of 41% TBP, the aqueous phase solidified into a gelatinous state.

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ATG:MRB:SSB:KLM:WTM:JES:RPW:ig

Appendix

ANALYTICAL METHODS

To define the status of analytical requirements of the Thorex process the following summary of analytical requirements and procedural principles is presented.

A1. Estimates of Sample Compositions and Required Analyses

In Fig. A1.1 are summarized the presently conceived solution compositions and anticipated requests for analyses from the pilot plant operation.

A2. Summary of Analytical Procedures for Thorex Solutions

K. L. Mattern

1. Thorium (5 to 80  $\mu\text{g}$  in 10 ml), in the presence of uranium, iron, and aluminum (less than 1000  $\mu\text{g}$  each in 10 ml), is determined by the spectrophotometric measurement of the specific red complex<sup>(1,2)</sup> (absorption maximum at 545  $\text{m}\mu$ ) formed with Thoron, 1-(o-arsenophenylazo)-2-naphthol-3, 6-disulfonic acid, in hydrochloric acid solution. Limits of error are reported to be less than 5% by this procedure.

2. Uranium may be separated from many other elements and activities by extraction of uranyl nitrate into hexone<sup>(3)</sup> or ether.<sup>(4)</sup> An aliquot of the organic phase is then plated and counted for alpha activity. The hexone extraction method has been altered by increasing the aluminum nitrate reagent concentration from 1.6  $\text{M}$ <sup>(3)</sup> to 2.4  $\text{M}$ , 0.4  $\text{N}$  acid deficient.

3. Protactinium is extracted with diisopropyl- (or diisobutyl-) carbinol<sup>(3)</sup> from a chloride and nitrate solution, plated on glass, and counted for beta activity.

4. Zirconium is precipitated as the mandelate<sup>(5)</sup> and ignited to the oxide, which is weighed and counted. No interference was observed in the presence of 1.3  $\text{M}$   $\text{Al}(\text{NO}_3)_3$ , 0.5  $\text{M}$   $\text{HNO}_3$ , 2  $\text{M}$   $\text{UO}_2(\text{NO}_3)_2$  or tracer amounts of barium, lanthanum, ruthenium, rhodium, cerium, or praseodymium activities. More reproducible results have been obtained with this method of analysis than have been found with the other precipitation procedures in current manuals.

Zirconium (1 to 7  $\mu\text{g}$  in 10 ml) is precipitated with pararsonic acid<sup>(6)</sup> in hydrochloric acid and filtered, and the precipitate is washed free of excess reagent. The precipitate is metathesized with ammonium hydroxide, thereby liberating ammonium pararsonate while leaving the zirconium on the filter as zirconium hydroxide. The filtrate is analyzed spectrophotometrically and the concentration of the associated zirconium is determined.

Fig. A1.1 GOLD AND RADIVE ANALYSES - - - - - THOREX PROCESS

Process Steps →	Thorex feed stream.	Pa product and FP's.	AP stream after silica gel treatment to remove Pa.	Th - "23" extract (Pa, FP's removed).	Th-free "23" extract.	Th product stream.	"23" product stream.	Stripped solvent for pretreatment and recycle.		Slug dissolving solution.	Acid Deficient Scrub for stripping Pa from organic, A-column.	Th - "23" extractant, A-column.	"23" reextractant, B-column.	Th stripping solution.	"23" stripping solution.
STREAM →	AF (aq.) <sup>H</sup>	AP (aq.) <sup>H</sup>	AW (aq.) <sup>H</sup>	AU (org.) <sup>H</sup>	BU (org.) <sup>H</sup>	BT (aq.) <sup>H</sup>	CU (aq.) <sup>H</sup>	CW (org.) <sup>H</sup>		GDF (aq.) <sup>C</sup>	AS (aq.) <sup>C</sup>	AX (org.) <sup>W</sup>	BS (org.) <sup>W</sup>	BK (aq.) <sup>C</sup>	CX (aq.) <sup>C</sup>
Density	1.68 I	1.121 I	1.121 I	0.953 I	0.849 I	1.088 I	1.005 I	0.847 I		1.27 I	1.058 I	0.847 I	0.847 I	1.005 I	1.001 I
M HNO <sub>3</sub>	0.4-0.6 I	0.1-0.15AD <sup>I</sup>	0.1-0.15AD <sup>I</sup>	0.00 I	0.04 I	0.150 I	0.104 I	0.002 I		8.8 I	0.75±0.02AD	-----	-----	0.2±0.01 I	0.02±0.005 I
M NaF	0.075 I	0.0375 I	0.0375 I	0.0014 I	( ) I	( ) I	( ) I	nil		0.072 I	-----				
M Hg(NO <sub>3</sub> ) <sub>2</sub>	0.003 I	0.0015 I	0.0015 I	<10 <sup>-5</sup> I	nil I	<10 <sup>-5</sup> I	nil I	nil		0.0029 I	nil I	1 I			
mg Al/ml	11-16 I	15-20 I	15-20 I	nil I	nil I	nil I	nil I	nil I			16.2				
mg Be/ml	0.7 I	0.35 I	0.35 I	nil I	nil I	nil I	nil I	nil I							
mg Th/ml	330-350 I	<0.010 I	<0.010 I	65-70 I	<0.010 I	55-60 I	<0.010 I	<0.010 I							
Th <sup>234c</sup> /m/ml <sup>a</sup>	1-3x10 <sup>5</sup>	<10	nil	2-6x10 <sup>4</sup>	nil R	2-5x10 <sup>4</sup> R	nil R	nil							
mg "23"/ml	0.2-0.3 I	2-3x10 <sup>-5</sup> I	2-3x10 <sup>-5</sup> I	0.038-.0581 I	0.03-.045 I	4-6x10 <sup>-5</sup> I	0.06-0.09 I	~2x10 <sup>-5</sup> I							
"23" c/m/ml <sup>b</sup>	2-3x10 <sup>6</sup> IR	<10 <sup>2</sup> IR	<10 <sup>2</sup> IR	~5x10 <sup>5</sup> IR	~4x10 <sup>5</sup> IR	<500 IR	~9x10 <sup>5</sup> IR	1-2x10 <sup>2</sup> IR							
Σα <sup>a</sup> /m/ml	1-3x10 <sup>10</sup> IR	0.5-1.5x10 <sup>8</sup> IR	0.8-3x10 <sup>8</sup> IR	1-2x10 <sup>5</sup> IR	~10 <sup>4</sup> IR	1-2x10 <sup>5</sup> IR	~10 <sup>3</sup> IR	~10 <sup>4</sup> IR							
Paβ <sup>a</sup> /m/ml	1-3x10 <sup>10</sup> R	0.5-1.5x10 <sup>10</sup> R	0.3-1x10 <sup>8</sup> R	2-6x10 <sup>4</sup> R	~10 <sup>4</sup> R	~5x10 <sup>4</sup> R	<10 <sup>3</sup> R	<10 <sup>4</sup> R							
ΣREβ <sup>a</sup> /m/ml	1.5-4x10 <sup>8</sup> R	0.7-2x10 <sup>8</sup> R	0.7-2x10 <sup>8</sup> R	3-8x10 <sup>2</sup> R	~10 <sup>2</sup> R	~4x10 <sup>2</sup> R	~50 R	~10 R							
Zrβ <sup>a</sup> /m/ml	0.5-1.5x10 <sup>7</sup> R	2-7x10 <sup>6</sup> R	3-5x10 <sup>6</sup> R	3-8x10 <sup>2</sup> R	~10 <sup>2</sup> R	~4x10 <sup>2</sup> R	~50 R	~10 R							
Nbβ <sup>a</sup> /m/ml	0.7-2x10 <sup>7</sup> R	0.4-1x10 <sup>7</sup> R	3-5x10 <sup>6</sup> R	3-8x10 <sup>2</sup> R	~10 <sup>2</sup> R	~4x10 <sup>2</sup> R	~50 R	~10 R							
Ruβ <sup>a</sup> /m/ml	0.4-1x10 <sup>7</sup> R	2-5x10 <sup>6</sup> R	2-5x10 <sup>6</sup> R	3-6x10 <sup>4</sup> R	~10 <sup>4</sup> R	~3x10 <sup>4</sup> R	~10 <sup>3</sup> R	~10 <sup>3</sup> R							
Σγ <sup>c</sup> /m/ml	1-3x10 <sup>7</sup> IR	~10 <sup>7</sup> IR	~10 <sup>5</sup> IR	~10 <sup>3</sup> IR	~10 <sup>2</sup> IR	<10 <sup>3</sup> IR	<10 <sup>2</sup> IR	<10 <sup>2</sup> IR							
% TBP	-----	-----	-----	42.5	42.5	-----	-----	42.5				42.5±0.5 I	42.5±0.5 I		
mg TBP/ml	-----	0.25	0.25	-----	-----	0.25	0.25	-----				-----	-----		
% Amsco	-----	-----	-----	57.5	57.5	-----	-----	57.5				57.5±0.5 I	57.5±0.5 I		

Sample Code:

Frequency of sampling:

- a) 11% geometry for β counting
- b) 52% geometry for α counting
- c) Ion Chamber analyses

1.1 x 10<sup>7</sup> c/m/mg "23" @ 52% geometry.  
 ("23" analyses based on total alpha, for all but BT.)

H--Hot Radive Streams  
 W--Warm Radive Streams  
 C--Cold Streams  
 AD--Acid Deficient

Ionic Lab  
 Radive Lab

Samples to be analyzed for cold runs, only.

Samples to be analyzed for hot or cold runs.

I  
 R

Zirconium is precipitated, after separation from UX, thorium, strontium, and rare earths by  $\text{LaF}_3$  precipitation, as the insoluble barium fluozirconate.<sup>(4)</sup> The zirconium is redissolved, and the barium is removed by precipitation as sulfate. The zirconium is reprecipitated as the cupferrate for ignition to  $\text{ZrO}_2$ , which is weighed and counted.

Zirconium (10 to 160  $\mu\text{g}$  in 50 ml of sample) content of thorium-free\* and uranium-free acetic acid solutions is determined colorimetrically by observing the light absorption at 335  $\text{m}\mu$ , the absorption maximum of the zirconium complex formed with chloranilic acid (0.0026 to 0.0034 M), 2,5-dichloro-3,6-dihydroxyquinone. No interference due to fluoride (up to 150  $\mu\text{g}$  in 50 ml of sample) was observed, although nitrate and ammonium ion tolerances are low. In the presence of uranium (up to 300  $\mu\text{g}$  in 50 ml of sample), the analyses are run in 2 M  $\text{HClO}_4$ . Since uranium absorbs strongly at the 335- $\text{m}\mu$  maximum, the spectrophotometric measurements are less sensitive to the zirconium complex concentration; however, good results are obtained by measuring the light absorption at 355  $\text{m}\mu$ . Reference solutions, identical except for the zirconium content, are measured at the same wavelengths, and appropriate corrections are applied to the sample readings. This analytical procedure is presently being written up, as an ORNL report, by O. Menis of the Analytical Chemistry Division.

5. Niobium is separated from other activities and process constituents<sup>(9)</sup> by the precipitation of niobium oxalate.<sup>(4)</sup> This is converted to the hydrous oxide by destruction of the oxalate with bromic acid, dissolved in hydrofluoric acid, and the zirconium removed as barium fluozirconate. The niobium is reprecipitated as the hydrous oxide, filtered, ignited, weighed as  $\text{Nb}_2\text{O}_3$ , and counted. Erroneous results obtained in analyses performed in the presence of soluble orthophosphates have required that the initial sample be precipitated in high iodate concentration<sup>(9)</sup> to prevent the coprecipitation of phosphate. Ruthenium interference has been successfully removed by pretreatment of the sample with hydroxylamine.<sup>(1)</sup>

6. Ruthenium is separated cleanly from other fission products by distillation, as  $\text{RuO}_4$ , from perchloric acid solution.<sup>(4,8)</sup> Iodide carrier is added, and sodium bismuthate is included to oxidize iodine to the nonvolatile iodate or periodate. The presence of phosphate prevents the volatilization of small amounts of molybdenum. The  $\text{RuO}_4$  distillate is caught in aqueous sodium hydroxide, and the ruthenium is precipitated as a mixture of  $\text{Ru}_2\text{O}_3$  and  $\text{RuO}_2$  by reduction with ethanol. The ruthenium oxide precipitate is dissolved in hydrochloric acid, and the ruthenium is reprecipitated in a weighable form by reduction with powdered magnesium metal, filtered, dried, weighed, and counted.

7. The rare earths are separated from thorium, uranium, protactinium, and other fission product activities by precipitation with hydrofluoric acid

\*Thorium interferes strongly; this method is also used for the analysis of thorium in zirconium-free solutions or of fluoride in thorium-free solutions.

in acidic solution containing zirconium holdback carrier. The major contaminating activities in the fluoride precipitation are zirconium, alkaline earths, and UX. The fluoride precipitate is dissolved in nitric and boric acids; the remaining zirconium and UX are removed by hydroxide precipitations, and a final precipitate of the rare earths, as the carbonate-free, hydrated oxalates,<sup>(8)</sup> is dried, weighed, and counted.

8. Cerium is separated from the bulk of fission product activities and other elements, as are the total rare earths. The cerium is purified by precipitation of the insoluble ceric iodate,<sup>(4,8)</sup> to remove it from the rare earths, then reduced. The zirconium and UX activities are removed on a zirconium iodate scavenger-precipitate while the cerium is held in the trivalent state. Hydroxide precipitations of the cerium separate it from the alkaline earth activities, and the cerium is converted to the oxalate for weighing and counting.

9. Free acid in solutions containing thorium and aluminum is determined by titration with standard alkali, after complexing the polyvalent metal ions with oxalate (see Sec. A3.1).

10. Aluminum in Thorex feed solutions is determined in the presence of thorium nitrate and excess nitric acid. The concentrations of the thorium and free acid are determined by separate analyses. An aliquot of the feed solution is passed through a Dowex-50 12% cross-linked cation-exchange resin, and the total liberated acid is titrated to the methyl red end point (see Sec. A3.2). The aluminum content is equal to the difference between the total liberated acid and the liberated acid due to thorium and free acid.

A rapid volumetric aluminum analysis is made by titrating a thorium-free solution with barium hydroxide to the phenolphthalein end point, metathesizing the aluminum hydroxide precipitate, with fluoride, to the complex fluoride of aluminum and potassium, and titrating the liberated hydroxyl ion with standard hydrochloric acid solution (see Sec. A3.3). The aluminum is equivalent to the hydrochloric acid used.

11. Macro-beryllium,<sup>(9)</sup> in thorium nitrate solutions, is determined gravimetrically as the oxide, after extracting the thorium with 2% TTA in carbon tetrachloride from an aqueous phase at a pH of approximately 2.5.

Micro-beryllium,<sup>(10)</sup> in the absence of aluminum, is determined colorimetrically in an acetate-acetic acid buffer of pH approximately 5.5, using aurintricarboxylate (aluminon) as the indicator. Thorium is first removed by precipitation with excess ammonium hydroxide (beryllium hydroxide is soluble in excess alkali).

In the spectrographic beryllium analysis of aqueous solutions by the porous cup spectrochemical method, a cobalt spike is used as an internal standard.

Radio-beryllium<sup>(1)</sup> is precipitated from a chloride solution as the hydroxide, converted to the anhydrous acetate, extracted with anhydrous chloroform, and plated, counted, and weighed as BeO.

12. Phosphorus, in the form of orthophosphate, may be determined by extracting the ammonium phosphomolybdate complex with n-butyl alcohol, reducing the nitrate-free complex, with stannous chloride, to molybdenum blue, and measuring the absorption at 735 m $\mu$  with a Beckman spectrophotometer (see Sec. A3.4).

13. Silicon is determined in a manner similar to phosphorus (see Sec. A3.5). A lower acidity is maintained in the extraction step, to permit the ammonium silicomolybdate to be extracted. The reduced complex is measured at 800 m $\mu$  for the silicon analysis.

14. Fluoride (greater than 50 g/ml) is determined as fluosilicic acid by steam distillation,<sup>(11)</sup> at 135  $\pm$  1°C, from a sulfuric acid solution of the sample. The fluosilicic acid is collected in a slightly alkaline solution, buffered with monochloroacetic acid, and titrated with thorium nitrate using alizarin sulfonate as the indicator. Sample preparation, ionic interference,<sup>(15)</sup> details of the procedure, and the precautions to be observed are described in the formal laboratory procedure in use by the Analytical Chemistry Division and will be presented in an ORNL report in the near future.

Inorganic fluorides (0 to 50  $\mu$ g/ml) are determined colorimetrically,<sup>(4)</sup> using Thoron as an indicator. This procedure is also used as an analysis for thorium, as previously mentioned in this report.

15. The tributyl phosphate concentration<sup>(12)</sup> in Amsco 125-90W diluent is determined by equilibration with an equal volume of a nitric acid solution of concentration (approximately 9 N HNO<sub>3</sub>) such that the aqueous equilibration concentration will be 8 N HNO<sub>3</sub>, and titration of the TBP-HNO<sub>3</sub> complex, in the organic solution, with standard alkali.

Determinations of the TBP content of a TBP-Amsco solution by measurement of the dielectric constant<sup>(1)</sup> have proved to be reproducible and to agree to  $\pm$ 2% with results obtained by the complete decomposition of TBP<sup>(13)</sup> and subsequent phosphate analysis (see Sec. A3.4). A calibration chart was prepared from measurements of standard solutions of known composition, and the dielectric-constant meter reading was translated directly into concentration.

16. A method for roughly estimating the amount of crud-forming impurities in TBP-Amsco solutions has been devised (see Sec. A3.6). The organic sample is contacted with a saturated aqueous calcium hydroxide solution, agitated, and allowed to settle. The amount of impurities in the sample is obtained by visual comparison of the turbidity and interfacial crud in the two-phase sample system with a set of standard solutions made with clean TBP and Amsco and spiked with a DBP-MBP-H<sub>3</sub>PO<sub>4</sub> mixture.

17. Specific gravity measurement by the Westphal method<sup>(4,14)</sup> is used only on cold makeup solutions. The specific gravity is obtained by comparing the weight of a solid object in air to the weight of the same object in the solution to be analyzed. The specific gravity balance is calibrated to read specific gravity units directly.

Density measurements of radioactive aqueous solutions<sup>(4)</sup> are obtained by measuring the time required for a drop of the sample to fall a fixed distance in an immiscible organic medium, the density being found by reference to a calibration curve.

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- (10) M. T. Kelley, "Analytical Chemistry Division Quarterly Progress Report for Period Ending June 26, 1951," ORNL-1113 (Dec. 12, 1951).

- (11) M. T. Kelley, "Analytical Chemistry Division Quarterly Progress Report for Period Ending September 10, 1951," ORNL-1129 (Feb. 26, 1952).
- (12) F. L. Steahly, "Chemical Technology Division Progress Report for Period August 1, 1952 to February 10, 1952," ORNL-1311 (Oct. 13, 1952).
- (13) J. A. Swartout, "Chemistry Division Quarterly Progress Report for Period Ending September 30, 1949," ORNL-499 (Dec. 6, 1949).
- (14) W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., New York, 1939.
- (15) F. E. McKenna, "Methods of Fluorine and Fluoride Analysis. I," Nucleonics, 8, No. 6, p. 24 (1951); "Part II," Nucleonics, 9, No. 1, p. 40 (1951).

### A3. Specific Analytical Procedures for Thorex Solutions

#### A3.1 Free Acid

Free acid in solutions containing thorium and aluminum is determined by titration with standard alkali, after complexing the polyvalent metal ions with oxalate.

#### Reagents:

Saturated potassium chromate solution.

0.1 N NaOH, standardized against potassium acid phthalate.

0.1 N HCl, standardized against the above sodium hydroxide.

#### Procedure:

1. Pipet an aliquot of sample into the titration vessel and place in the vessel a small magnetic stirring bar. If less than 5 ml of a 0.1 N NaOH solution will be required to neutralize the estimated acidity of the sample, pipet an HCl spike into the titration vessel.
2. Pipet 10 ml of saturated potassium chromate solution into the titration vessel.
3. Buffer the Beckman automatic titrator and set the pH dial to read 7.0.
4. Titrate with standardized sodium hydroxide.

Calculations:

$$\begin{aligned} & (\text{ml of base} \times \underline{N} \text{ of base}) - (\text{ml of spike} \times \underline{N} \text{ of spike}) \\ & = \text{total meq of free acid (or of acid deficiency) in sample} \end{aligned}$$

A3.2 Indirect Determination of Aluminum Using a Cation Exchange Resin

P. F. Thomason

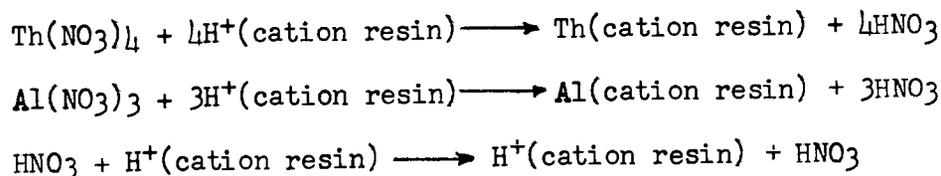
Scope:

This method was developed for a fast "shotgun" estimation of aluminum in feed solutions for the Thorex process.

Principle:

The feed solution of the Thorex process contains thorium nitrate, aluminum nitrate, and excess nitric acid. Since the concentrations of thorium and free nitric acid are known from previous analyses, the aluminum concentration is easily found by passing an aliquot of the feed solution through Dowex-50 12% cross-linked cation exchange resin, and titrating the total liberated nitric acid to the methyl red indicator end point. The acid liberated by thorium plus the original free acid is subtracted from the total acid found. The remainder of the liberated acid is due to the aluminum present. The capacity of Dowex-50 is approximately 4.5 meq/g.

Equations:



Status:

The fact that Dowex-50 resin has been used for the determination of sulfate<sup>(1)</sup> in uranyl sulfate solutions suggested the use of this resin for the determination of aluminum.

This indirect method depends upon accurate determinations of free acid and thorium, since Dowex-50 gives the total cation absorption. With optimum conditions, an accuracy of  $\pm 5\%$  should be obtained.

Radioactive solutions are easily handled by this procedure since the fission products are also absorbed by the resin column. The acid liberated by the fission products can usually be ignored since, chemically, they are present in small amounts.

Solutions are passed slowly (approximately 5 ml per minute) through the resin and a wash with 50 volumes of distilled water per volume of sample is sufficient to remove all the liberated acid.

Sampling:

The usual precautions involving the handling of radioactive solutions should be observed. It is convenient to pipet samples with a remote pipettor, using delivery pipets.

Reagents:

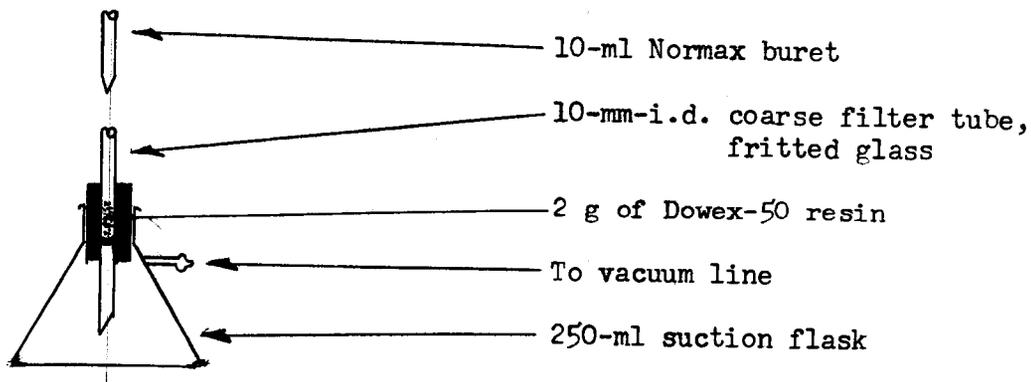
0.1 N NaOH made up by diluting carbonate-free 1 N NaOH with distilled water and standardizing against potassium acid phthalate.

0.1% methyl red indicator made by dissolving 0.1 g of the sodium salt of methyl red in 100 ml of distilled water.

Dowex-50, 12% cross-linked, cation exchange resin.

Apparatus:

The resin column is set up as follows:



Procedure:

1. Place filter-resin apparatus behind barricade for radioactive samples.
2. Pipet, with a delivery pipet, 1 ml of feed solution onto the resin bed.

3. Rinse down the sides of the tube with distilled water.
4. Apply gentle vacuum so that approximately 5 ml of liquid per minute drips into the suction flask.
5. Continue washing with distilled water until a volume of 50 to 100 ml is in the filter flask.
6. Add 1 drop of methyl red indicator solution to the filter flask.
7. Titrate with standardized 0.1 N NaOH to the yellow end point.

Calculations:

ml of NaOH x N of NaOH = total meq of acid liberated

millimoles of thorium x 4 = meq of acid due to thorium

meq of original free acid is known

(total meq of liberated acid) - (meq of acid due to thorium and free acid)  
= (3 x millimoles of aluminum present in original sample)

If sample is acid deficient, add meq of original acidity to the total meq of liberated acid instead of subtracting. The resin bed may be used on repeated samples until nearly exhausted and then can be regenerated with sulfuric acid. However, it is easier to replace the resin after it has absorbed approximately 3.0 meq of cations per gram of resin, since it has become radioactive.

Reference:

- (1) H. O. Day, J. S. Giel, E. B. Jones, W. L. Marshall, "A Search for a Reliable Sulfate Analysis of Uranyl Sulfate: The Ion Exchange Method," ORNL CF-52-2-50 (February 7, 1952).

A3.3 Rapid Volumetric Method for Aluminum(1)

Reagents:

Ba(OH)<sub>2</sub>: saturated solution.

HCl: 0.3 N, standardized with reference to a known AlCl<sub>3</sub> solution.

AlCl<sub>3</sub>: 0.3 N; weigh 2.5-2.7 g of pure aluminum and dissolve in 200 ml of 1 N NaOH (NH<sub>3</sub> and CO<sub>2</sub> free, to prevent buffering and low results); make the solution just acidic with 6 N HCl, boil slowly to remove CO<sub>2</sub>, and dilute to 1 liter.

Sodium potassium tartrate: 30% solution, neutral to phenolphthalein.

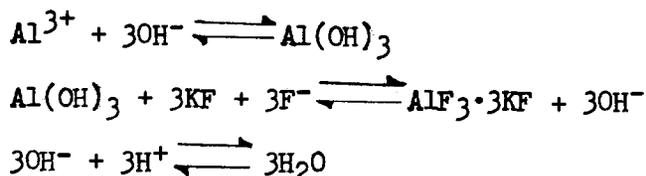
KF: 45% solution, neutral to phenolphthalein; store in wax or plastic bottle.

Procedure:

1. Pipet a sample containing 5 to 25 mg of ammonium-free aluminum per milliliter into an erlenmeyer flask.
2. Titrate with Ba(OH)<sub>2</sub> until the free acid is just neutralized, as shown by a slight precipitate of Al(OH)<sub>3</sub>.
3. Add 30 ml of the tartrate solution and a few drops of phenolphthalein.
4. Continue to titrate with the Ba(OH)<sub>2</sub> to the phenolphthalein end point.
5. Add 30 ml of the fluoride solution (use at least a 100% excess, over the theoretical amount of KF, to prevent low results) and titrate with 0.3 N HCl to the disappearance of the red color; the end point is considered permanent when the color does not return for 30 sec.

Calculations:

- a. The standard Ba(OH)<sub>2</sub>, used through step (4), gives the total meq of free acid and aluminum present.
- b. The standard HCl, used in step (5), is equivalent to the aluminum present.
- c. The total free acid equals (a) minus (b).



Accuracy:

Analyses of pure aluminum chloride samples were accurate to  $\pm 0.1$  mg. At an aluminum/impurity mole ratio of 100, only phosphate, sulfate, and silicate interfered. (Ca<sup>++</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Cr<sup>3+</sup>, Cu<sup>++</sup>, Fe<sup>3+</sup>, Mg<sup>++</sup>, and Mn<sup>++</sup> did not.) Sulfate caused results to be of the order of 1% high, and silicate approximately 15% high. At a mole ratio of 2, all ions interfered except Na<sup>+</sup>, K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, and Cl<sup>-</sup>. With Zn<sup>++</sup>, results were 1% low; with Cu<sup>++</sup>, 1% low; with Mg<sup>++</sup>, 2.5% low; with Fe<sup>3+</sup>, 4.5% low; with Mn<sup>++</sup>, end point was obscured; with Cr<sup>3+</sup>, 8% low; with PO<sub>4</sub><sup>3-</sup>, 32% low; with SO<sub>4</sub><sup>2-</sup>, 1% low; with SiO<sub>3</sub><sup>2-</sup>, 38% high.



40% SnCl<sub>2</sub>: Dissolve 40 g of stannous chloride in 100 ml of concentrated HCl.

0.2% SnCl<sub>2</sub>: Dilute 1 ml of 40% SnCl<sub>2</sub> to 200 ml with 1 N H<sub>2</sub>SO<sub>4</sub> (make up fresh daily).

Amyl acetate: Reagent Grade Baker's Analyzed (poor results have been obtained with some brands).

Spectrophotometer: Beckman or Coleman.

Orthophosphate solution: 0.1433 g of KH<sub>2</sub>PO<sub>4</sub> dissolved in 100 ml of distilled water; this contains PO<sub>4</sub> in a concentration of 1 mg/ml; 10 ml of this, diluted to 1 liter, gives a solution with PO<sub>4</sub> concentration of 10 µg/ml.

Procedure:

1. Add 10 ml of 1 N H<sub>2</sub>SO<sub>4</sub> to a 125-ml separatory funnel.
2. Add sample containing 1 to 30 µg of PO<sub>4</sub><sup>3-</sup>. If sample is alkaline, it should be made slightly acid with H<sub>2</sub>SO<sub>4</sub>.
3. Shake well and add 2 ml of 6.25% (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>; shake, and allow to stand for 5 min.
4. Pipet 10 ml of n-butyl alcohol into the funnel, shake well for 2 min, and allow layers to separate. If the organic layer is a pronounced yellow color, too much phosphate is present and a smaller sample must be used.
5. Discard aqueous (lower) phase, and then pipet 5 ml of 1 N H<sub>2</sub>SO<sub>4</sub> into the funnel; shake for 2 min and allow layers to separate.
6. Discard aqueous phase, and pipet 15 ml of 0.2% SnCl<sub>2</sub> in 1 N H<sub>2</sub>SO<sub>4</sub> into the funnel; shake for 2 min and allow layers to separate.
7. Discard lower layer and the first few drops of the n-butyl alcohol layer, and drain the remainder into the spectrophotometer cell. The sacrifice of this small volume of the butyl alcohol layer, which may be needed for the larger Coleman cuvettes, is to ensure elimination of water; if the stems of the funnels are dried this may not be necessary.
8. Read the absorption at 735 mµ and determine the PO<sub>4</sub><sup>3-</sup> from a standard calibration curve, which can be made by carrying out this procedure with the standard phosphate solution.

References:

- (1) D. F. Boltz and M. G. Mellon, "Spectrophotometric Determination of Phosphorus as Molybdic Acid," Anal. Chem., 20, 749 (1948).
- (2) D. F. Boltz and M. G. Mellon, "Determination of Phosphorus, Germanium, Silicon, and Arsenic by the Heteropoly Blue Method," Anal. Chem., 19, 873 (1947).
- (3) P. L. Kirk and R. E. Curtis, "HEW Analytical Development Program," CN-1791 (June 1, 1944).
- (4) I. Berenblum and E. Chain, "Studies on the Colorimetric Determination of Phosphate," Biochem. J., 32, 286 (1938); "An Improved Method on the Colorimetric Determination of Phosphate," Ibid., p. 295.

A3.5 Spectrophotometric Determination of Silicon<sup>(1,2)</sup>

Discussion:

See Spectrographic Determination of Phosphorus, Sec. A3.4.

Range: 0 to 20  $\mu\text{g}$ .

Reagents:

- 1 N  $\text{H}_2\text{SO}_4$ : 27.8 ml of concentrated  $\text{H}_2\text{SO}_4$  per liter.
- 6.25% ammonium molybdate: 6.25 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  per 100 ml of solution.
- 0.2%  $\text{SnCl}_2$ : 0.5 ml of 50%  $\text{SnCl}_2$  diluted to 100 ml with 1 N  $\text{H}_2\text{SO}_4$ .
- 0.4 N  $\text{H}_2\text{SO}_4$ : 8.3 ml of concentrated  $\text{H}_2\text{SO}_4$  per liter.

Procedure:

1. Pipet sample containing 2 to 20  $\mu\text{g}$  of silicon, but not over 2 ml in volume, into a small separatory funnel.
2. Add 2 ml of 6.25% ammonium molybdate solution and 1 ml of 1 N  $\text{H}_2\text{SO}_4$  and mix well. If by this time a precipitate has formed, try adding the 1 ml of  $\text{H}_2\text{SO}_4$  first, then the 6.25% ammonium molybdate slowly and with shaking. If the precipitate still forms, add concentrated  $\text{H}_2\text{SO}_4$  until it disappears. Avoid an excess of  $\text{H}_2\text{SO}_4$ .
3. Allow to stand for 5 min; then add 5 ml of n-butyl alcohol and shake for 2 to 3 min.

4. Discard aqueous (bottom) layer, and wash butyl alcohol layer twice with 3 ml of 0.3 N H<sub>2</sub>SO<sub>4</sub>.
5. Add 5 ml of 0.2% SnCl<sub>2</sub> solution and shake for 30 sec.
6. Discard aqueous layer, and transfer alcohol layer to a 25-ml volumetric flask; rinse separatory funnel with 5 ml of 95% ethyl alcohol, and transfer this rinsing to the 25-ml volumetric flask.
7. Make up to the mark with ethyl alcohol.
8. Measure transmittancy at 800 mμ.

References:

- (1) D. F. Boltz and M. G. Mellon, "Determination of Phosphorus, Germanium, Silicon, and Arsenic by the Heteropoly Blue Method," Anal. Chem., 19, 873 (1947).
- (2) H. C. Davis and A. Bacon, "A Study of Some Chemical Reactions Employed in Photometric Analysis," J. Soc. Chem. Ind., 67, 316 (1948).

A3.6 Qualitative Test for Crud-Forming Impurities in TBP

Reagents:

Prepare standards (10 to 500 ppm of impurity spike) using:

- a. 40 ml of 41% TBP—59% Amsco 125-90W, freshly washed twice with 0.2 volume of 1 M NaOH and three times with 0.2 volume of water.
- b. impurity spike consisting of DBP-MBP-H<sub>3</sub>PO<sub>4</sub> (in a mole ratio of 60/30/<1).

Make up a saturated Ca(OH)<sub>2</sub> solution (approximately 0.05 N at room temperature). Filter immediately before using.

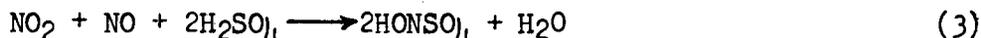
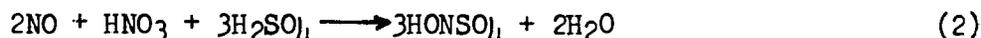
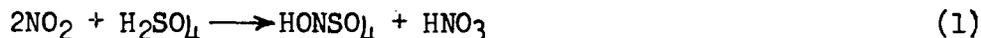
Procedure:

To the sample to be tested (41% TBP—59% Amsco diluent) and to the prepared standards (40 ml of the organic solution), add 0.2 volume of the freshly filtered, saturated calcium hydroxide solution. Shake each vigorously for at least 1 min and allow the two phases to separate. By visual comparison of the turbidity and interfacial crud in the sample solution with the standard solutions, the approximate concentration of crud-forming impurities can readily be estimated.

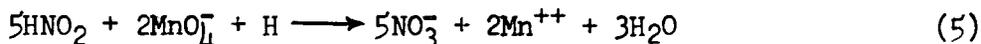
### A3.7 Off-Gas Analytical Method

The off-gases, generated by the dissolution steps in the preparation of the feed and scrub solutions for the Thorex A-column, are a mixture of any or all of the following:  $N_2$ ,  $N_2O$ ,  $NO$ ,  $NO_2$ ,  $O_2$ ,  $CO_2$ ,  $CO$ , and  $H_2$ . In order to determine the dissolution mechanism, the composition of the off-gas mixture was studied. The analytical method is based on the use of small amounts of reagents to absorb preferentially constituents of the mixture, both as received from the dissolver and after intermediate combustions.

First, the nitric oxide and nitrogen dioxide are absorbed in concentrated sulfuric acid containing: (1) sodium sulfate to reduce the solubility of carbon dioxide and nitrous oxide and (2) concentrated nitric acid to oxidize the nitric oxide, in excess of an equimolar mixture with nitrogen dioxide.

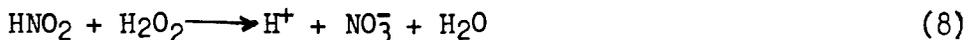
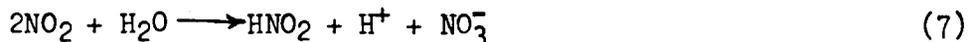
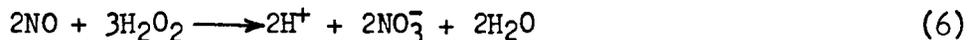


The nitrosylsulfuric acid is titrated with a standard potassium permanganate solution, according to the following equations:



From Eqs. (1) and (2), it may be seen that three times as many titratable species are formed from the oxidation of each nitric oxide as from the reduction of nitrogen dioxide; hence, this titer is a measure of the quantity ( $3 \times$  mmols of  $NO$  + mmols of  $NO_2$ ) of titratable species.

A separate off-gas sample is absorbed in a neutral 3%  $H_2O_2$  solution and titrated with standard alkali, to determine the quantity (mmols of  $NO$  + mmols of  $NO_2$ ) of titratable species. The following equations show that the same number of titratable species are formed per nitric oxide as per nitrogen dioxide:



The amounts of nitric oxide and nitrogen dioxide are readily calculable from the two quantities obtained in these two analyses:

$$\begin{array}{rcl}
 (3NO + NO_2) & = & \underline{X} \text{ mmols as nitrosylsulfuric acid} \\
 \text{minus } (NO + NO_2) & = & \underline{Y} \text{ mmols as hydrogen ion} \\
 \hline
 (2NO) & = & (\underline{X} - \underline{Y}) \text{ mmols}
 \end{array}$$

The NO<sub>2</sub> content is then determined by substitution.

After the nitric oxide and nitrogen dioxide have been absorbed into the concentrated acid mixture, the residual gases, now free of acidic components, are expanded into an evacuated gas-sample tube, saturated with water vapor, and analyzed in a modified Fisher gas-analysis apparatus. The total millimoles of residual gases in the sample are calculable from experimental pressure, temperature, and volume observations.

The carbon dioxide is absorbed by 50% KOH solution; oxygen is absorbed by potassium pyrogallate solution; and nitrous oxide is burned with an added, known excess of hydrogen. If this combustion takes place in the presence of carbon monoxide, a more powerful reducing agent than hydrogen gas at these temperatures, some of the carbon monoxide will be oxidized to carbon dioxide. This product material is absorbed and measured as previously discussed.

The amount of residual hydrogen and carbon monoxide in the combustion tube is determined by burning with a known excess of oxygen and individually absorbing and measuring the carbon dioxide product and the residual oxygen, as above.

The amounts of nitrous oxide, carbon monoxide, and hydrogen are calculated and the nitrogen and rare gas content are obtained by difference from the total amount of residual gases run through the modified Fisher apparatus.

The known limitations of this procedure are the following:

1. The initial sample must be free of hydrogen sulfide, ammonia, and liquid water. If a condensable quantity of water is present initially, the gas mixture that is analyzed will not be a truly representative sample.
2. The recommended sample size for a mixture of all the gases discussed is three to four times as large as that recommended for a sample free of nitric oxide and nitrogen dioxide.
3. It is essential that the analysis of the residual gases, in the Fisher analyzer, be carried out as rapidly as possible in order to minimize the effects of leakage in the equipment.

This analytical procedure is currently being used by the ORNL Pilot Plant and the Eastern Laboratory of the Explosives Department, E. I. du Pont de Nemours and Company, Inc., at Gibbstown, New Jersey.

The estimated precision of the individual analyses is  $\pm 1\%$ , or better.

Reagents:

Sulfuric acid, 99.5 to 100% by weight: prepared by adding concentrated sulfuric acid (92%) to fuming sulfuric acid, until the fuming ceases.

NO-NO<sub>2</sub> absorption mixture: prepared by dissolving 20 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> in 100 ml of sulfuric acid (99.5 to 100%) and adding 5 ml of fuming nitric acid (97 to 100%) to it.

Potassium hydroxide solution for absorbing the carbon dioxide: prepared by dissolving 59 g of 85% KOH pellets in 41 ml of water.

Potassium pyrogallate: prepared by dissolving 90 g of KOH in 60 ml of water, cooling solution, and adding 10 ml of pyrogallic acid, C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub>. It is stored in a full, tightly stoppered bottle for one month before using, in order to avoid the liberation of CO while in the apparatus. It is transferred to smaller bottles for individual analyses.

Neutral hydrogen peroxide solution: prepared by diluting the 30% reagent tenfold and neutralizing with dilute NaOH and an external indicator. This reagent should not be used if it has stood for more than three days.

The following stopcock lubricants are advocated:

- (a) Dow-Corning Hi-Vac silicone grease (Dow Corning Corp.) or Halocarbon stopcock grease (Halocarbon Products Co.) for use in the gas-sample tubes containing NO and NO<sub>2</sub>.
- (b) Cello-Grease (Fisher Scientific Co.) for the stopcocks on the Fisher Analyzer and for the stopcocks on the gas-sample tubes ( $> 60^{\circ}\text{F}$ ) when NO and NO<sub>2</sub> are absent.
- (c) Lubriseal (A. H. Thomas Co.) for gas-sample stopcocks when a temperature of less than  $60^{\circ}\text{F}$  prevents the use of Cello-Grease.