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LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT

OCTOBER 1, 1952 TO JANUARY 31, 1953

A. T. Gresky
M. R. Bennett
S. S. Brandt
W. T. McDuffee
B. G. Ryle
J. E. Savolainen
R. P. Wischow

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LABORATORY DEVELOPMENT OF THE THOREX PROCESS: PROGRESS REPORT, OCTOBER 1, 1952 TO JANUARY 31, 1953

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0.0 ABSTRACT

Progress in the laboratory development of the Thorex Process from October 1, 1952 through January 31, 1953, is reported. Related chemical studies and revisions in the chemical flowsheet are described.

1.0 INTRODUCTION

Recent changes in the Thorex process and additional chemical evaluation of process units are recorded in this report.

The Thorex process has been frozen, in most part, for final pilot plant design and construction. As a result of close analysis of full plant considerations in preliminary plant design, certain conditions in the proposed process appear somewhat less than optimum, and some further laboratory investigation is indicated. However, in general, the Unit Operations Section's testing of such process units as continuous dissolving, thorium and uranium separation from protactinium, thorium separation from uranium, uranium stripping, scrub solution makeup, feed preparation, diluent preconditioning, and solvent recovery have been shown to be satisfactory; scaling and testing of equipment have been completed. Portions of the process flowsheet that remain to be optimized include the final isolation of the protactinium and U^{233} products.

In addition to considerations of plant size and attendant process philosophies, it is recognized that the future of thorium in nuclear reactors may involve the use of such materials as thorium oxide and thorium-zirconium alloys. Use of these materials would necessitate specific alterations in process steps, but would perhaps not involve changes in the basic concepts of the separation process.

The continuous dissolving operation appears most operable in a two-stage unit, and production of consistent AF conditions at reasonably consistent flow rates has been demonstrated. Provisions for possible continuous head-end treatment of the AF solution, e.g., reagent additions and/or digestion, are included in the dissolver system to permit control of decontamination.

2.0 SUMMARY

Primary engineering features of the Thorex process and recent revisions in the chemical flowsheet are indicated in the January, 1953 flowsheet (see Fig. 3-1).

Decontamination of the thorium-uranium stream from protactinium in the A-column was shown to be markedly dependent on the presence of phosphate ion. Inclusion of 0.002 M H_3PO_4 in the AS stream was found optimum both for control of protactinium separation and to permit insignificant thorium losses in the AP stream.

In order to improve conditions of the CU stream and to permit a more nearly optimum operation of the U^{233} ion exchange isolation step, inclusion of a neutralization column to remove nitric acid from the BU stream was shown to allow (1) lower CU (or CX) flow rates with (2) lower acidity and (3) higher uranium content of the product. In this column the BU stream is scrubbed with the AS stream at a BU/AS flow ratio equivalent to that prescribed by the flowsheet. The AS stream is provided initially with sufficient "HNO_3 deficiency" to absorb the nitric acid from the BU stream and leave the neutralization column at proper conditions for A-column use. Each of the three improved conditions enumerated above was known to promote higher efficiency in the isolation step.

The optimum system for protactinium recovery from the AP stream is undecided, and alternate procedures are being investigated and evaluated for preliminary plant design. Adaptation to efficient plant operation of the silica gel adsorption system described in previous reports (see p. 3 for list of previous reports) is considered doubtful. In addition, certain unknown variables adversely affecting protactinium adsorption have been encountered, and radiation instability of silica gel structures under prospective high exposures has caused uncertainties regarding its use as a "protactinium sponge." The solvent extraction scheme indicated in the January, 1953 flowsheet shows an alternate scheme that provides for high recovery of protactinium and large volume reduction factors of the product.

Final protactinium and/or U^{233} isolation techniques are realistically considered as problems requiring close laboratory control owing to the unique problems of handling extremely high activities.

Head-end treatments of the AF stream, which were considered vital to control of ruthenium decontamination in the A-column separation, were investigated. Increases in ruthenium decontamination factors of 10 and 100, respectively, were demonstrated by (1) refluxing the aqueous feed at 110°C for 3 hr in the absence of thorium metal and (2) successive digestion with about 0.001 M HIO_4 and with 0.01 M HCOOH present in the feed. Use of the latter treatment would provide one-cycle ruthenium decontamination factors of more than 10^3, which would ensure sufficient fission product decontamination of the thorium and uranium to meet proposed specifications.

3.0 THOREX FLOWSHEET

The chemical flowsheet for January, 1953 (see Fig. 3-1) reflects changes, based on additional laboratory information, which represent process improvements and revisions shown to be necessary by the results of a preliminary plant design study. Principal changes or additions were concerned with improvements in ruthenium decontamination, protactinium separation, U^{233} isolation, and protactinium isolation.

3.1 Revised Chemical Flowsheet

The revised chemical flowsheet, as presented in Fig. 3-1, includes the following changes:

1. A head-end treatment of the AF stream, which was considered vital to control of ruthenium decontamination in the A-column separation. Increases in ruthenium decontamination factors of 10 and 100, respectively, were demonstrated by (1) refluxing the aqueous feed at about 110°C for 3 hr in the absence of thorium metal and (2) digestion of the AF with 0.0005 to 0.005 M HIO_4 followed by digestion with 0.005 to 0.05 M HCOOH. Use of the second process would provide one-cycle ruthenium decontamination factors of greater than 10^3; this would ensure sufficient fission product decontamination of the thorium product to meet proposed specifications.
2. Addition of 0.002 M H_3PO_4 to the AS stream. This was found necessary to give high protactinium decontamination of the thorium-uranium stream from the A-column. Use of the phosphate ion should permit decontamination factors of greater than 10^6. The variable phosphate content of thorium sources (e.g., raw thorium nitrate tetrahydrate, thorium nitrate recovered from the BT stream and purified, and metal slugs) used in earlier process investigations was observed to be a factor governing the decontamination from protactinium.
3. A tentative alternate proposal (see Sec. 3.2) for solvent extraction of protactinium from the AP stream. This will be evaluated along with other schemes previously reported.

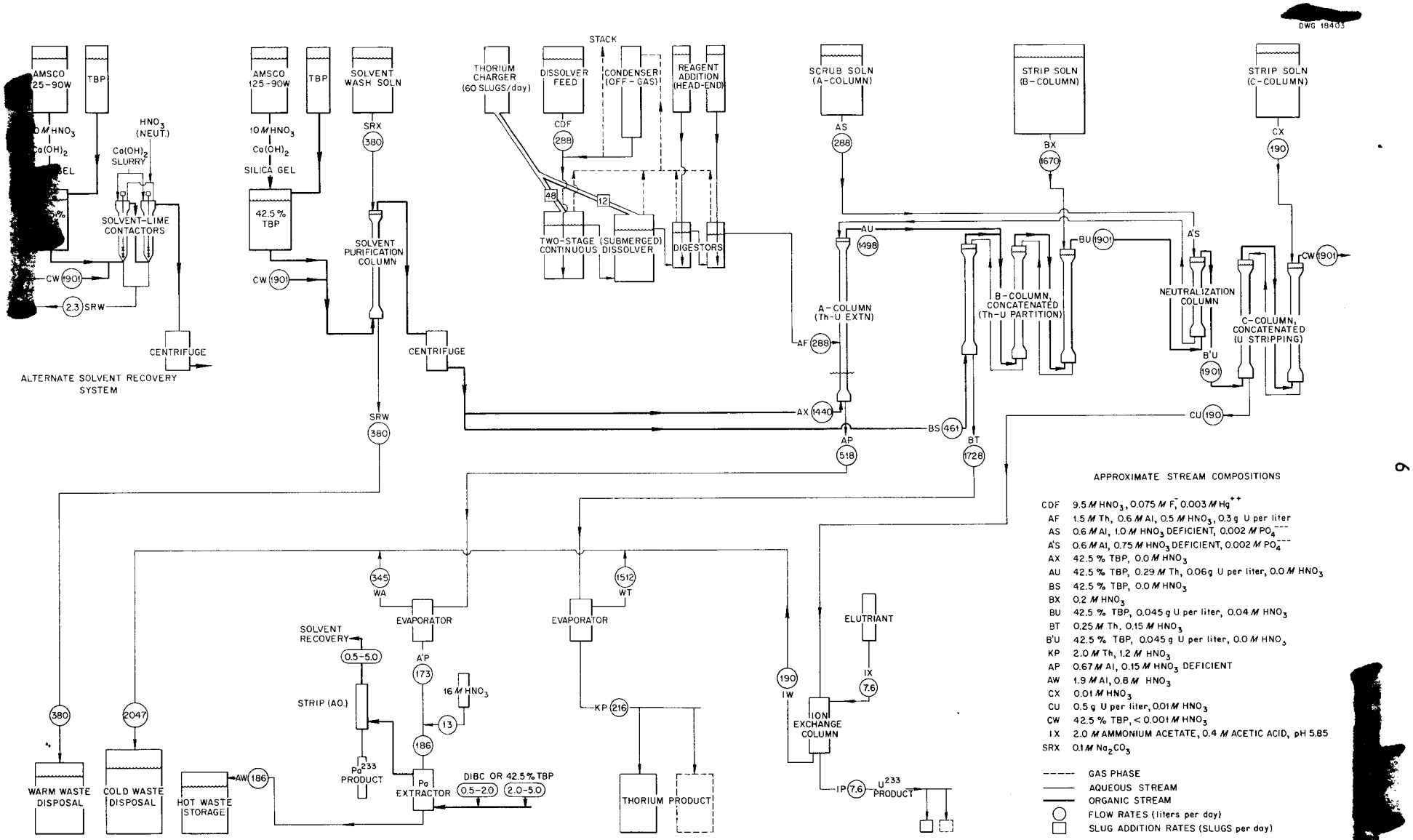

FIG. 3-1. THOREX PROCESS CHEMICAL FLOWSHEET, JANUARY 1953.

4. Introduction of a neutralization column (see Sec. 3.3) to remove nitric acid from the BU stream. This will permit removal of nitric acid from the BU stream so that it will have an optimum acidity for uranium stripping in the C-column and will permit more favorable use of the ion exchange isolation technique, which was developed during the Interim-23 program.

3.2 Protactinium Isolation

Use of the silica gel adsorption technique for protactinium recovery from the AP stream appears unattractive in preliminary plant design. On a basis of 99.9% recovery, the large volumes of silica gel required for batch type processes appear inefficient, and operating procedures appear difficult.

An alternate, untested concept of a "silica gel sponge" system, which would consist of a bed sufficiently large to retain Pa^{233} until it reached equilibrium with the daughter U^{233}, i.e., about 120 days, was considered favorable from the design viewpoint. This concept would depend on continuous desorption and re-extraction of the U^{233} formed during decay. It would satisfy the desirable ends of (1) the lowest possible inventory of fissionable material with (2) maximum availability of the short-lived Pa^{233}. The practical applicability of this concept remains doubtful owing to a multitude of complex problems concerning radiation stability, heat exchange, criticality, crud accumulation, and control of chemical variables affecting the adsorption characteristics of the gel. The last problem, associated with physical variables affecting protactinium adsorption efficiency, was shown during recent studies to be a serious one. The results of experiments in which adsorption has failed to take place, in some cases involving use of metal dissolver solutions, have not been satisfactorily explained. Variables associated with the presence of niobium, chromates, and phosphates are suspected.

Further study of solvent extraction methods for protactinium isolation and preliminary plant evaluations are underway. Development to date in use of the solvents DIBC and TBP is summarized in Sec. 4.2.2.

3.3 U^{233} Isolation

The use of a neutralization technique on the BU stream to permit lower flow rates, lower acidity, and higher uranium content of the CU stream is described in Sec. 4.4.1. These conditions were necessary to allow engineering validity of ion exchange for U^{233} isolation in a plant with a thorium capacity of 0.5 ton/day. In considerations of plants with higher capacity, e.g., 3 tons/day, feasibility of the ion exchange technique remains somewhat doubtful owing to problems of flow control, multiple valving, and criticality.

Although further development of the ion exchange method or criticality control might solve some of the unattractive engineering problems, it was felt desirable that an alternate isolation technique be investigated. Studies are currently underway on the conventional approach of CU evaporation followed by a second solvent extraction cycle. Problems associated with TBP degradation products, optimum feed conditions, process solvent, flow conditions, and decontamination will be evaluated.

4.0 GENERAL PROCESS STUDIES

Process improvement studies and data on certain chemical and physical properties of various process units are reported in this section.

4.1 The A-Column

The operability of a 2-in.-diameter vertical pulse A-column under flowsheet conditions has been thoroughly tested by the Unit Operations Section. Loss of less than 0.01% thorium and uranium have been demonstrated. Pulse conditions, column geometry, and stage heights in the extraction section have been defined. A vertical column has been recommended for installation in the pilot plant.

In this section are discussed methods for improving decontamination of the products from ruthenium, the effects of additives on decontamination from protactinium, and decontaminations from other fission products. Profiles of density, viscosity, pH, and conductivity, which were made to indicate possible control points for instrumentation of the A-column, are given. The determination of Th^{234} by scintillation spectrometry is discussed.

4.1.1 Decontamination of Products from Ruthenium
(W. T. McDuffee and A. T. Gresky)

Ruthenium appears to be the limiting contaminant of thorium and uranium streams in the Thorex process. Data obtained when using Purex dissolver spike in synthetic AF's indicate that at least two distinct species of ruthenium are present. Distribution coefficients (O/A) of about 0.003 and 1.0 were observed in the extraction and scrub sections, respectively. The concentration ratio of the 0.003 species to that of the 1.0 species was about 8. Addition of nitrite ion was observed to increase the amount of the fraction having a D.C. of 1.0. The bulk of the extractible ruthenium shows no obvious effects of colloidal nature and is not adsorbed from the BT stream by silica gel; however, it does show a reversibility of behavior when allowed to remain in the solvent phase (AU) for periods as short as 1 hr. Digestion of the AF for 3 hr at 110°C, in glass equipment, was observed to reduce the amount of the extractible fraction by about 90%.

The most promising techniques found to improve decontamination from ruthenium in the A-column are (1) digestion for 2 to 3 hr at >100°C in stainless steel equipment and/or (2) digestion with 0.0005 to 0.005 M HIO_4 followed by digestion with 0.005 to 0.05 M HCOOH. In investigations of the first process, digestion of feeds containing macro concentrations of ruthenium nitrate was observed to decompose significant amounts of the salt to insoluble oxides. In investigations of the second process, periodic acid addition caused immediate conversion of the ruthenium to the yellow tetroxide, RuO_4, and, upon subsequent addition of formic acid at room temperature, the color gradually ($\sim$15 min) changed to pink and finally to amber. Other organic materials were usually observed to reduce the tetroxide rapidly to insoluble compounds which were generally very surface-active. Typical data from countercurrent runs demonstrating the ruthenium problem are recorded in Tables 4-1 and 4-2.

The use of head-end treatments of the above type appear feasible in the process, but will considerably complicate the continuous dissolver design.

Table 4-1

Typical Data from a Countercurrent Run Demonstrating Fission Product Distribution in the A-Column

Feed: Thorex AF using thorium dissolver solution spiked with Purex AF;[a] treated with HIO_4 and HCOOH; in 1E, out 5E

Scrub: Thorex AS containing 0.002 M PO_4^{3-}; in 8S, out 5E

Organic: 42% TBP in preconditioned Amsco 125-90W; in 5E, out 8S

F/S/O = 1/1/5; 5 extraction, 8 scrub stages; 3 volume changes

Stage	F.P.	β Activity (c/m/ml)		D.C. (O/A)	E.F. (O/A)
		Organic Phase	Aqueous Phase		
8Sc	TRE	<50	<50	---	---
	Zr	~300	~300	---	---
	Ru	2.9×10^3	1.6×10^3	1.76	8.8
	Nb	<10	<30	---	---
6Sc	TRE	55	1.4×10^3	0.039	0.195
	Zr	306	2.8×10^3	0.11	0.55
	Ru	3.1×10^3	6.1×10^3	0.52	2.6
	Nb	<10	205	0.049	0.245
4Sc	TRE	1.8×10^3	6.3×10^4	0.029	0.146
	Zr	694	2.4×10^4	0.029	0.146
	Ru	3.9×10^3	1.6×10^4	0.25	1.25[b]
	Nb	40	1.7×10^3	0.024	0.12
2Sc	TRE	8.0×10^4	2.7×10^6	0.03	0.15
	Zr	3.7×10^3	1.9×10^5	0.02	0.10
	Ru	5.9×10^3	5.2×10^4	0.11	0.57
	Nb	270	1.26×10^4	0.02	0.10
1E	TRE	5.0×10^6	3.4×10^8[c]	0.014	0.037
	Zr	6.7×10^4	9.6×10^6	0.007	0.019
	Ru	1.6×10^4	1.1×10^6	0.014	0.037
	Nb	2.0×10^3	1.1×10^6	0.007	0.019
3E	TRE	4.4×10^7	7.3×10^7	0.62	1.67
	Zr	2.1×10^4	1.1×10^6	0.002	0.005
	Ru	6.8×10^3	1.3×10^6	0.005	0.014
	Nb	1.7×10^3	9.4×10^5	0.002	0.005
5E	TRE	8.3×10^6	1.5×10^7[d]	0.55	1.6
	Zr	3.2×10^3	9.0×10^5	0.003	0.008
	Ru	2.4×10^3	1.4×10^6	0.002	0.006
	Nb	15	1.0×10^6	---	---

(a) Activities (c/m/ml) as follows: gross β, 1.5×10^8; TRE β, 9.5×10^7; Zr β, 1.9×10^7; Ru β, 9.0×10^6; Nb β, 2×10^6. About 70% of ruthenium activity was "plated out" during HIO_4-HCOOH treatment.

(b) Permits no further ruthenium decontamination.

(c) About 700% TRE reflux.

(d) TRE not at equilibrium after 3 volume changes.

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Table 4-2

Decontamination from Fission Products in the A-Column, Using Purex Dissolver Spike

Feed: 1.5 M Th, 0.6 M Al, 0.5 N HNO_3; HIO_4 added and digested at room temperature for 15 min., then HCOOH added and digested

Scrub: 0.6 M Al, 0.7 N OH^-, 0.002 M PO_4^{3-}

Organic: 42% TBP in Amsco 125-90W

F/S/O = 1/1/5; 5 extraction, 8 scrub stages; 3 volume changes

Conditions of Feed Treatment					Decontamination Factors					
			Digestion							
Run No. X-	HIO_4 (M)	HCOOH (M)	Time (hr)	Temp. (°C)	Gross β	Ru β	Nb β	Zr β	TRE β	Remarks
90	---	---	---	---	127	8	1.32×10^4	2.44×10^4	5.16×10^4	Mantle grade thorium nitrate tetrahydrate as feed
141	---	---	---	---	365	20	3.14×10^4	9.01×10^5	5.3×10^5	Untreated slug solution as feed
142	---	---	3.0	110	852	63	2.9×10^4	6.54×10^3	8.1×10^5	Type 347 stainless steel turnings in digester
139	---	0.005	2.0	90	660	37	2.31×10^4	1.31×10^4	4.47×10^5	
137	0.0005	0.005	0.5	25	600	29	5.47×10^4	2.88×10^4	7.3×10^5	Iodine D.F. = 8
138	0.0005	0.005	2.0	90	1030	54	1.44×10^4	1.0×10^4	7×10^5	Iodine D.F. = 8
140	0.0005	0.005	2.0	90	770	68	7.54×10^4	8.59×10^4	6.53×10^4	Feed was 0.1 N acid defici[redacted]
134	0.005	0.05	0.5	25	840	43	3.2×10^4	3.9×10^4	3.78×10^5	Iodine D.F. = 9
136	0.005	0.05	2.0	50	860	51	5.6×10^4	2.93×10^4	3.68×10^5	Iodine D.F. = 57
143	0.005	0.05	3.0	110	7350	570	3.9×10^4	8.65×10^3	3.52×10^6	Type 347 stainless steel turnings in digester

[redacted]

4.1.2 Decontamination of Products from Protactinium

(A. T. Gresky and W. T. McDuffee)

During earlier studies of A-column conditions the synthetic feeds were prepared from mantle-grade thorium nitrate tetrahydrate crystals, and it now appears that phosphate impurities in those crystals contributed markedly to the observed nonextractibility of protactinium. When purified thorium nitrate, e.g., from the BT stream or from nitric acid dissolution of thorium, was used, marked decreases in decontamination from protactinium resulted. Studies of protactinium distribution in the A-column scrub section indicated that addition of iodate or phosphate ions caused significant reduction in the protactinium D.C. (O/A), with the latter showing the larger effect, i.e., x 10.

The distribution coefficients (O/A) were observed to decrease as a direct function of increasing phosphate concentrations in the scrub solution, AS. A log-log plot of the data was a straight line with a slope of -0.77 (see Fig. 4-1). In countercurrent runs in which phosphate was added to the AS, approximately stoichiometric amounts of thorium were lost in the AP stream, presumably as nonextractible $Th_3(PO_4)_4$. The latter observation led to the use of 0.002 M PO_4^{3-} in the AS as optimum with regard to both protactinium decontamination and thorium losses in the A-column.

During demonstrations of countercurrent operation of the A-column, protactinium D.C.'s (O/A) observed in the absence of phosphate ion were: extraction section, 0.003; scrub section, 0.25. Inclusion of 0.002 M H_3PO_4 in the AS permitted D.C.'s as follows: extraction section, 0.002; scrub section, 0.02. In experiments in which no phosphate was used in the AS, the concentration ratio of species 0.003 to species 0.25 varied from about 8 to 30, presumably indicating variable "normal" phosphate concentrations in the AF solutions. Inclusion of phosphates in the scrub solution apparently precluded protactinium fractionation to extractible species, thus permitting excellent decontamination of thorium from protactinium through the A-column.

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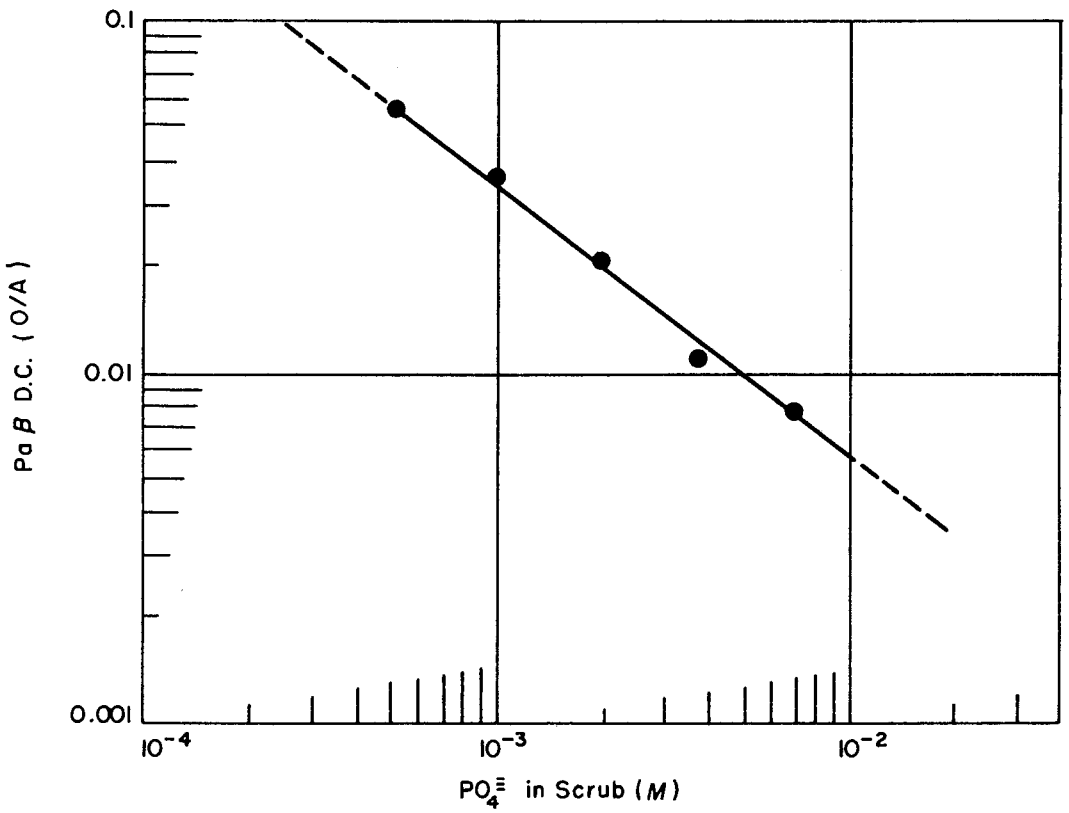

CONDITIONS:

Organic phase from the 8th stage of a countercurrent run using Interim-23 spiked feed was scrubbed with 0.2 volume of 0.6*M* $Al(NO_3)_3$, 0.7*N* acid deficient, to which Na_3PO_4 had been added.

Pa*β* D.C. at 8th stage, i.e., 0.0*M* phosphate, was 0.26.

Slope of curve = -0.768.

Fig. 4-I EFFECT OF PHOSPHATE ION ON EXTRACTABILITY OF PROTACTINIUM IN A-COLUMN.

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4.1.3 Decontamination from Other Fission Products

(W. T. McDuffee)

In general, decontamination from other fission products, e.g., rare earths, niobium, and zirconium, is sufficiently good to permit use of a single extraction cycle for decontamination of thorium and uranium (see Table 4-1). However, some concern about rare earth reflux (up to 1000%) in the A-column extraction section may cause the extraction length to be held to a minimum, i.e., as dictated by acceptable U^{233} and thorium losses.

Table 4-3 records the yields of fission products produced by fission of U^{233} as compared to that of U^{235}. The lower yields of Ru^{103}, and especially Ru^{106}, are important considerations in the Thorex process, where ruthenium constitutes the limiting contaminant of the thorium and uranium products.

4.1.4 Density, Viscosity, pH, and Electrical Conductivity Profiles of A-Column

(J. E. Savolainen and R. P. Wischow)

Physical properties of the aqueous and organic streams of the A-column are plotted in Fig. 4-2 as functions of stage number, i.e., as column "profiles," previously described in ORNL-1367. Additional data are recorded in Sec. A-1.

4.1.5 Determination of Th^{234} by Scintillation Spectrometry

(W. T. McDuffee)

Calculated values for the Th^{234} content and Th^{234}/Pa^{233} ratios in Hanford-irradiated thorium check closely with values obtained in determinations* made both by $UX_1 + UX_2$ method of analysis and by gamma scintillation spectrometer methods. The Th^{234} (UX_1) peak was observed at about 90 kev and the Pa^{234} (UX_2) peak at about 210 kev. Although Pa^{233} produces a coincident peak at 90 kev, the known relation to its other peak at 300 kev permits interpretation of activity differences due to the Th^{234} (see Figs. A-8, A-9, and A-10).

*S. A. Reynolds, ORNL, personal communication.

Table 4-3

[redacted] Yields of Fission Products Formed in Thermal-Neutron Bombardment of U^{233} and U^{235}(a)

Yields obtained by comparison, using the value 5.6×10^{-2} for La^{140} in U^{235} fission

Isotope	Half-Life	U^{233}	U^{235}
Br^{83}	140 m	---	2.0×10^{-3}
Br^{84}	30 m	---	6.0×10^{-3}
Sr^{89}	55 d	$4.1 \pm 0.6 \times 10^{-2}$	$3.2 \pm 0.3 \times 10^{-2}$
Sr^{90}	$\sim$ 25 y	$\sim 1.5 \times 10^{-2}$	$\sim 1.3 \times 10^{-2}$
Y^{91}	61 d	$4.1 \pm 0.4 \times 10^{-2}$	$4.0 \pm 0.3 \times 10^{-2}$
Zr^{95}	65 d	$7.0 \pm 0.3 \times 10^{-2}$	$5.7 \pm 0.3 \times 10^{-2}$
Mo^{99}	66 h	---	$5.3 \pm 0.3 \times 10^{-2}$
Ru^{103}	37 d	$2.1 \pm 0.6 \times 10^{-3}$	$8.4 \pm 2 \times 10^{-3}$
Ru^{106}	290 d	$6.4 \pm 1.3 \times 10^{-4}$	$1.5 \pm 0.1 \times 10^{-3}$
Ag^{111}	7.5 d	$1.5 \pm 0.1 \times 10^{-4}$	$1.6 \pm 0.1 \times 10^{-4}$
Sn^{122}	136 d	$2.5 \pm 0.4 \times 10^{-5}$	$6.5 \pm 1 \times 10^{-6}$
Sn^{125}	10 d	$2 \pm 0.4 \times 10^{-4}$	$3 \pm 0.5 \times 10^{-5}$
Sb^{127}	95 h	---	$8.8 \pm 0.5 \times 10^{-4}$
Te^{127}	95 d	$6.7 \pm 0.3 \times 10^{-4}$	$1.5 \pm 0.3 \times 10^{-4}$
Sb^{128}	$\sim$ 3 y	$\sim 1.7 \times 10^{-4}$	$\sim 3 \times 10^{-5}$
Te^{129}	32 d	$2.2 \pm 0.2 \times 10^{-3}$	$9 \pm 1 \times 10^{-4}$
I^{131}	8.0 d	$1.4 \pm 0.6 \times 10^{-2}$	$1.3 \pm 0.2 \times 10^{-2}$
Te^{132}	77 h	$4.9 \pm 1.2 \times 10^{-2}$	$4.8 \pm 1.2 \times 10^{-2}$
I^{134}	54 m		5.8×10^{-2}
Cs^{136}	$\sim$ 15 d	$\sim 2 \times 10^{-4}$	$\sim 2 \times 10^{-4}$
Cs^{137}	$\sim$ 37 y	$\sim 1.1 \times 10^{-2}$	$\sim 1.9 \times 10^{-2}$
Ba^{139}	86 m		6.1×10^{-2}
Ba^{140}	12.8 d	$5.2 \pm 0.4 \times 10^{-2}$	4.3×10^{-2}
La^{140}	40 h	$6.7 \pm 0.6 \times 10^{-2}$	5.6×10^{-2}
Ce^{141}	28 d		$6.4 \pm 0.3 \times 10^{-2}$
Ce^{144}	290 d	$2.2 \pm 0.2 \times 10^{-2}$	$2.9 \pm 0.3 \times 10^{-2}$
Pm^{147}	$\sim$ 3.7 y	$\sim 6 \times 10^{-3}$	$\sim 7 \times 10^{-3}$

(a) W. E. Grummitt and G. Wilkinson, "Thermal Neutron Fission Yields of U^{233} and U^{235}," CRC-470 (March, 1951).

[redacted]

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FLOW RATIO: F/Sc/O = 1/1/5

ORGANIC PHASE: 41 % TBP in Amsco 125-90W

FEED: Th, 346.4 mg/ml; U, 0.34 mg/ml; HNO_3, 0.44 *N*; $Al(NO_3)_3$, 0.6 *M*

SCRUB: Al, 0.6 *M*; HNO_3 deficiency, 0.7 *N*; NO_3^-, 1.1 *N*; $PO_4^{\equiv}$, 0.002 *M*

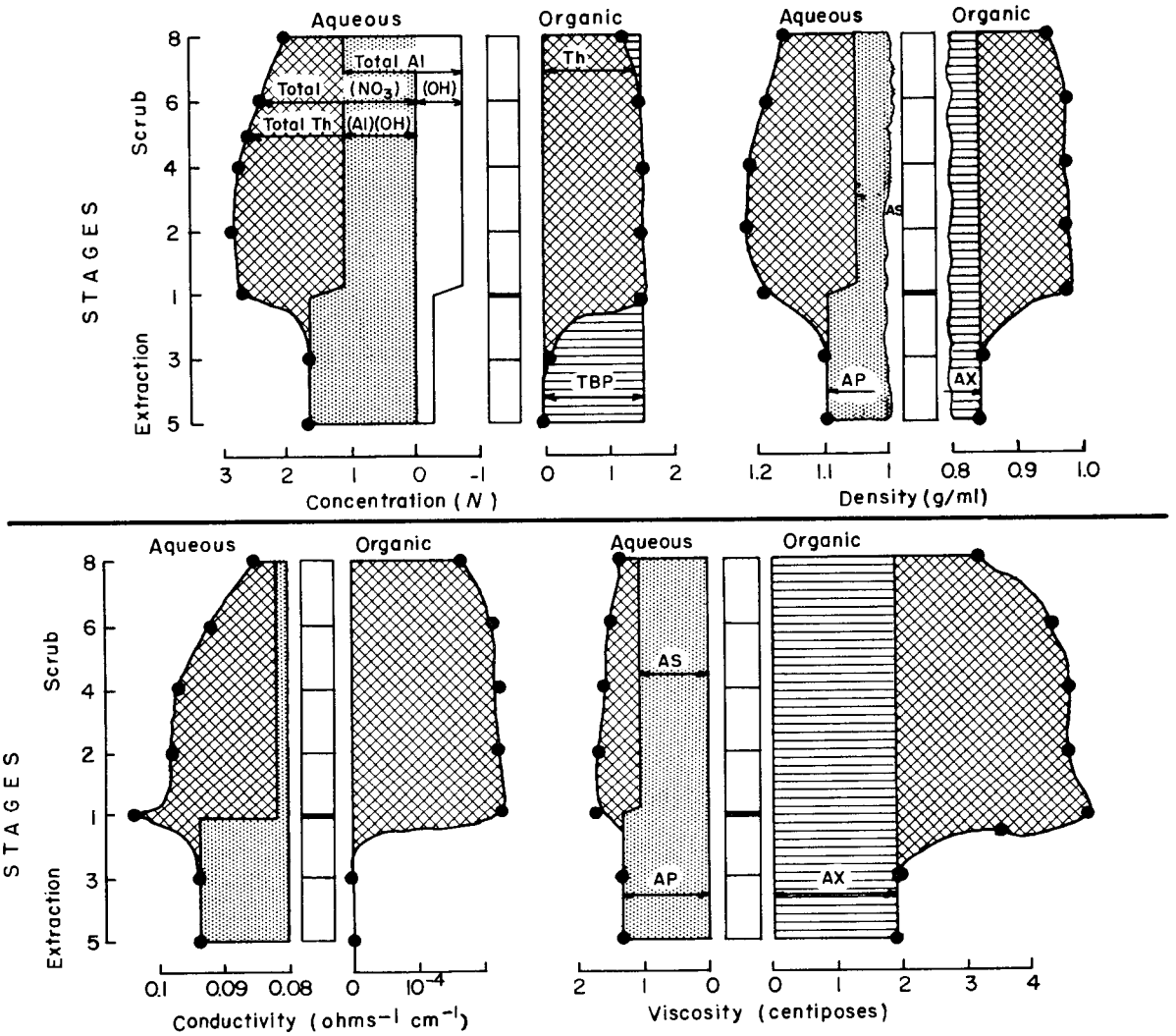

Fig. 4-2 PHYSICAL PROPERTY PROFILES OF A-COLUMN

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4.2 Protactinium Separation and Isolation

(S. S. Brandt and M. R. Bennett)

As indicated in Sec. 3, it has not yet been decided which is the most adaptable approach to protactinium separation and/or isolation. Further studies of protactinium behavior in silica gel adsorption and in solvent extraction with either DIBC or TBP are reported here.

4.2.1 Studies on Silica Gel Adsorption of Protactinium

In attempts to adsorb the protactinium from about 14 liters of an adjusted AW stream from the Interim-23 process, it was discovered that only 10% adsorption was obtained under conditions designed for greater than 95% recovery. Variables suspected of causing this behavior include (a) impurities contained in the various thorium sources, (b) feed insolubles, (c) corrosion products, and (d) chemical history of the protactinium. Results of preliminary investigations showed that phosphate, which is not present in the thorium metal but present in significant amounts in commercial thorium nitrate, increases protactinium adsorbability; chromate, which might be present as a result of corrosion of the stainless steel dissolver, decreases it; and protactinium tracers that have been treated differently before being passed through the silica gel are adsorbed in different amounts. However, no satisfactory resolution of the difficulty has been obtained to date.

The cruds found in Thorex dissolver solutions, and persisting in the AP stream, were observed to be adsorbed or filtered out by the gel, and could presumably cause plugging during extended operations. These difficulties indicate that operability of adsorption columns would be severely limited in the event that the feed was not filtered.

Effect of Impurities Contained in the Various Thorium Sources. Previous silica gel adsorption studies (ORNL-1367 and 1431) utilized synthetic AP solutions or actual AP streams from laboratory countercurrent tests in which AF's had been synthesized from commercial thorium nitrate tetrahydrate. In these cases, about 99.9% protactinium adsorption could

be realized. AP streams with significant thorium concentrations were similarly shown to permit greater than 85% protactinium adsorption. However, subsequent tests with similar solutions (Interim-23 AW's) produced from AF's containing dissolved thorium metal indicated that drastic changes in protactinium adsorbability had occurred. In some cases, less than 10% of the protactinium was strongly adsorbed by the silica gel. These discrepancies in behavior raised some very difficult questions as to whether protactinium adsorption was being (1) enhanced or limited by (2) either the absence or presence of (3) some impurities or combination of impurities, found in the various thorium sources used. The impurities occurring in several thorium sources are shown in Table 4-4.

In testing the effect of impurities, an acid-deficient Interim-23 AW solution containing protactinium was passed through a silica gel column. Fifty percent adsorption of the protactinium was observed up to a throughput of 20 column volumes but then a sharp breakthrough occurred and most of the protactinium was desorbed (see curve 1 in Fig. 4-3). Since the Interim-23 dissolver solution used in this experiment contained little or no phosphate, and since solvent extraction studies had indicated that the presence of phosphate ion changes the character of protactinium in such a way as to render it nonextractible in the Thorex A-column, an identical run was made with 0.005 M PO_4^{3-} in the feed. No breakthrough occurred in over 60 column volumes (see curve 2 of Fig. 4-3), and 27% of the protactinium was adsorbed. These data could be interpreted to mean either that the presence of phosphate ion favored conversion of part of the protactinium to a strongly adsorbable form or that the phosphate ion reduced the effectiveness of some constituent in the dissolver solution which interfered with strong protactinium adsorption.

Effect of Corrosion Products. The principal foreign ions in the dissolver solution, besides metallurgical products, are corrosion products of stainless steel. The dissolver in use was made of type 347 stainless steel, which contains 17 to 20% chromium, 8 to 12% nickel, and about 0.4% niobium. It is known that the presence of chromate ion produced erratic adsorption behavior with certain fission products, e.g., zirconium and niobium.

Table 4-4

Impurities in Various Thorium Sources

Orders of concentrations: Data obtained from available analytical values and/or listings of specifications

Impurity	Amount of Impurity (ppm of Th)		
	Mantle-Grade $Th(NO_3)_4 \cdot 4H_2O$ (a)	Ames Metal (b)	MTR Metal (Specs)
SO_4	16,650	---	---
Ca	2,100	< 50	---
Mg	900	< 20	---
Be	< 0.2	500	1000
Si	345	225	---
Fe	60	170	300
Al	28	70	100
Mo	108	---	---
Rare earths	110	50 to 100	23
Cu	36	---	---
P	< 40	---	---
Zr	< 30	< 20	---
Mn	< 1	< 20	---
B	12	0.5	---
Pb	3	---	---
Sb	< 5	---	---
Cd	< 0.2	< 0.2	---
Cs	2	---	---
U	---	10	5
Ba	< 5	---	---
V	< 5	---	---
Cr	4	---	---
Ni	< 1	---	---
Sn	< 2	---	---
Ge	< 2	---	---
C	---	1,000	---
O	---	500	---

(a) Mantle-grade thorium nitrate tetrahydrate is 40.6% Th, 42.4% NO_3.

(b) Ames produces metal slugs now in use at Hanford.

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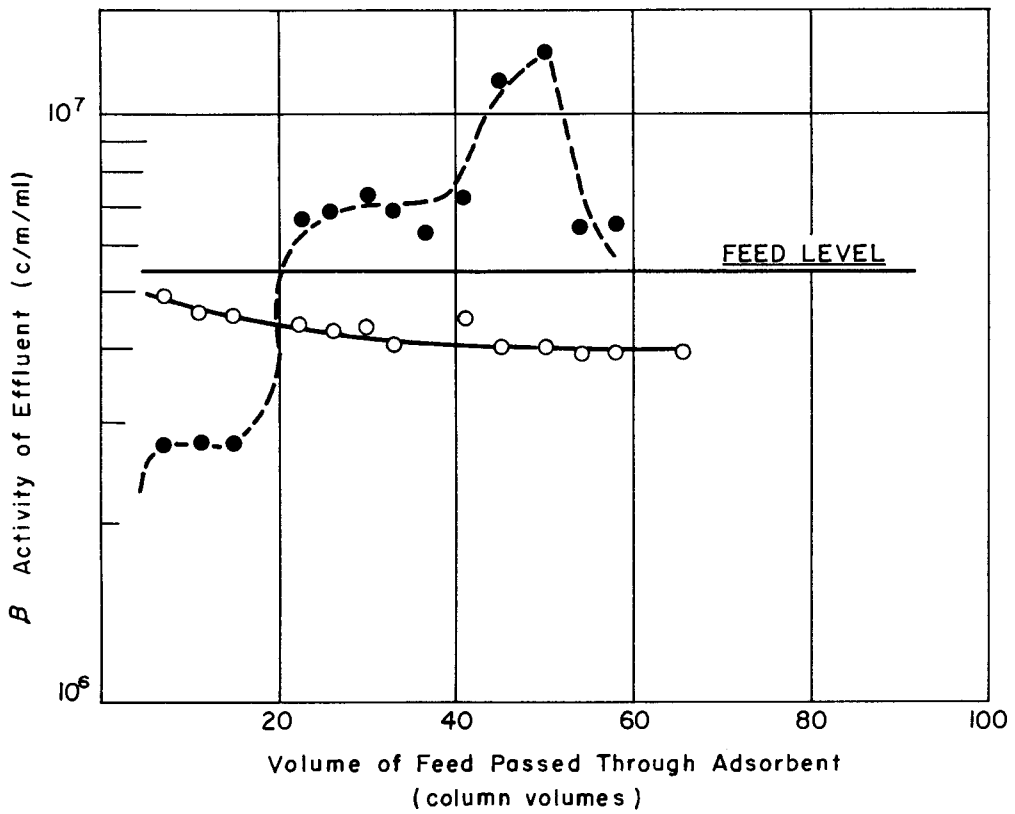

● Column Feed: 0.9 *M* Th, 1 *M* in Al, 0.3 *N* acid deficient, Pa tracer.
○ Column Feed: Same as ● with H_3PO_4 added.

Silica Gel: 30 to 40 mesh.
Column: 1 X 29.8 cm.
Flow Rate: 1.3 ml/m/cm^2.

Fig. 4-3 PROTACTINIUM ADSORPTION STUDY: EFFECT OF PHOSPHATE ION.

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Studies on protactinium adsorption in the presence of chromate ion were carried out with a feed solution 0.8 to 1.0 M in aluminum and 0.3 N acid deficient. The adsorbability of the protactinium decreased when the feed contained 0.05 M $CrO_4^{=}$ ion (see Table 4-5).

Other corrosion products, such as niobium (which is particularly suspect), iron, and nickel, will be investigated.

Effect of Feed Insolubles. Insoluble suspended matter in the dissolver solutions was observed to be adsorbed strongly, or filtered readily, in the silica gel columns. No correlation of insoluble content with poor adsorption was observable, but some slowing down of the flow rate was noted.

Effect of Chemical History of Protactinium. Protactinium solutions used in spiking synthetic AP solutions were either "hot" dissolver solutions of Interim-23 feed or protactinium obtained from Interim-23 feed by DIBC extraction followed by fluoride stripping. The protactinium from the DIBC extraction showed a marked tendency toward adsorption, while that from untreated feed did not (see Table 4-6). Whether or not the species or character of the protactinium is permanently changed during the extraction and/or stripping remains to be established.

Since the ratio of spike to synthetic feed in each case was about 0.001, it seems unlikely that minor constituents, such as corrosion products or DIBC, could exert such large effects on the behavior of the protactinium. At the present time, it is thought that a species difference between the "native" protactinium and the DIBC-extracted protactinium is responsible for the adsorption differences. Studies on this problem will continue.

4.2.2 DIBC and TBP Extraction of Protactinium from AP Concentrates

The January, 1953 Thorex flowsheet (Fig. 3-1) calls for a threefold volume reduction of the AP stream with subsequent recovery and decontamination of Pa^{233}. Primary considerations center on the use of either DIBC or 41% TBP as the organic extractant for protactinium. DIBC has been shown in recent work to give a high distribution coefficient with Pa^{233} and would

Table 4-5

Protactinium Adsorption Study: Effects of Chromate Ion

Feed: 0.9 M aluminum, 0.3 N HNO_3 deficient
Adsorption conditions identical for the two experiments

Column Volumes Passed through Silica Gel	Pa Retention (%)	
	Standard	0.05 M $CrO_4^=$ Added
7	96.77	41.7
12	97.13	79.4
16	96.72	75.7
22	97.13	77.7
26	96.53	74.6
30	96.70	70.5
33	95.83	69.9
	96.69 (avg.)	69.92 (avg.)

Table 4-6

Protactinium Adsorption Study: Effects of Tracer History

Feed: 0.8 to 1.0 M aluminum, 0.3 N HNO_3 deficient
Adsorption conditions identical for the two experiments

Column Volumes Passed through Silica Gel	Pa Retention (%)	
	Feed Spiked with Interim-23 AF	Feed Spiked with DIBC Tracer
7	58.8	96.77
12	44.5	97.13
16	24.5	96.72
26	18.9	96.53
30	12.6	96.70
	31.86 (avg.)	96.75 (avg.)

permit the highest protactinium concentration factors. On the other hand, TBP would be favorable from the standpoint of using a single solvent for the Thorex flowsheet and may be more adaptable to process use because of its ability to retain both protactinium and U^{233}. A process combining the use of both extractants would provide a more specific separation.

Organic-Aqueous Distribution of Pa^{233} (M. R. Bennett and S. S. Brandt). A synthetic test solution of concentrated AP was made up which was approximately 2.0 M in $Al(NO_3)_3$, spiked with Pa^{233} tracer and 0.003 M PO_4^{3-}, and saturated with TBP (approximately 1.0 g/liter). The resulting solution was divided into seven portions, and each was adjusted to 1.9 M $Al(NO_3)_3$ and the desired acidity or basicity. A volume of each portion was then contacted with DIBC and another volume with 41% TBP until equilibrium was reached. Samples of both phases were analyzed for Pa^{233} and/or gross β (see Table 4-7 and Fig. 4-4).

The high $Al(NO_3)_3$ salt strength in the aqueous phase provided generally high distribution coefficients (O/A), and the effect of free nitric acid in the concentration range 0.2 to 0.7 N permitted unusually high protactinium extractibility. The D.C.'s (O/A) obtained were $>10^3$ and $>10^2$ for DIBC and 41% TBP, respectively, which indicates that large protactinium concentration factors can be obtained by proper use of solvent extraction techniques. Under similar conditions, gross fission product D.C.'s are of the order of 10^0 in both DIBC and TBP. Uranium D.C.'s are also in the 10^0 range in DIBC but are of the same order as protactinium D.C.'s in TBP.

Separation of Protactinium from DIBC Extracts by Steam Distillation of the DIBC (J. E. Savolainen). Protactinium can be extracted with DIBC from a concentrated AP stream approximately 1.9 M in $Al(NO_3)_3$ and 1 N in HNO_3. The volume ratios can be made such that the nitric acid in the aqueous phase will not be depleted; the nitric acid concentration in the DIBC phase would be about 1.1 N. Results of experiments showed that the DIBC can be removed by steam distillation, leaving water-soluble, nonvolatile materials, including protactinium, in the aqueous residues in the still.

Table 4-7

Data on Distribution of Protactinium between $Al(NO_3)_3$-HNO_3 and DIBC or TBP

Aqueous:[a] 1.9 M $Al(NO_3)_3$, containing 0.003 M PO_4^{3-}

Volume ratio, O/A: 0.10

Portion No.	HNO_3 (N)	Pa^{233} (aq) (c/m/ml)	Gross β (c/m/ml) Aqueous	Gross β (c/m/ml) Organic	Pa^{233} D.C. (O/A)
		DIBC			
1	-0.20 (basic)	3.25×10^6	2.97×10^6	7.45×10^6	2.3
2	-0.08 (basic)	3.16×10^6	3.20×10^6	6.34×10^6	2.0
3	0.0	6.63×10^5	7.30×10^5	1.84×10^7	27.8
4	0.20	9.52×10^5	9.23×10^5	2.14×10^7	22.5
5	0.32	6.24×10^5	6.32×10^5	2.58×10^7	41.4
6	0.58	1.04×10^4	7.87×10^4 [b]	3.18×10^7	3060
7	0.86	4.88×10^3	6.15×10^4 [b]	3.31×10^7	6760
		41% TBP			
1	-0.20 (basic)	4.06×10^6	3.60×10^6	8.04×10^6	1.9
2	-0.08 (basic)	2.91×10^6	2.85×10^6	8.90×10^6	3.0
3	0.0	8.05×10^5	9.25×10^5	2.12×10^7	22.0
4	0.20 acid	7.27×10^5	7.77×10^5	2.64×10^7	36.4
5	0.32	1.85×10^5	3.64×10^5	2.50×10^7	135.0
6	0.58	1.69×10^5	1.21×10^5	2.80×10^7	166.5
7	0.86	3.77×10^5	2.51×10^5	2.71×10^7	73.0

(a) A sample of the synthetic AP was shown by analysis to have the following composition:

Activity	Amount (c/m/ml)
Gross β	2.90×10^6
Zr β	7.11×10^4
Nb β	6.53×10^3
Pa β	2.83×10^6
TRE β	2.50×10^2

(b) Bulk of activity due to zirconium.

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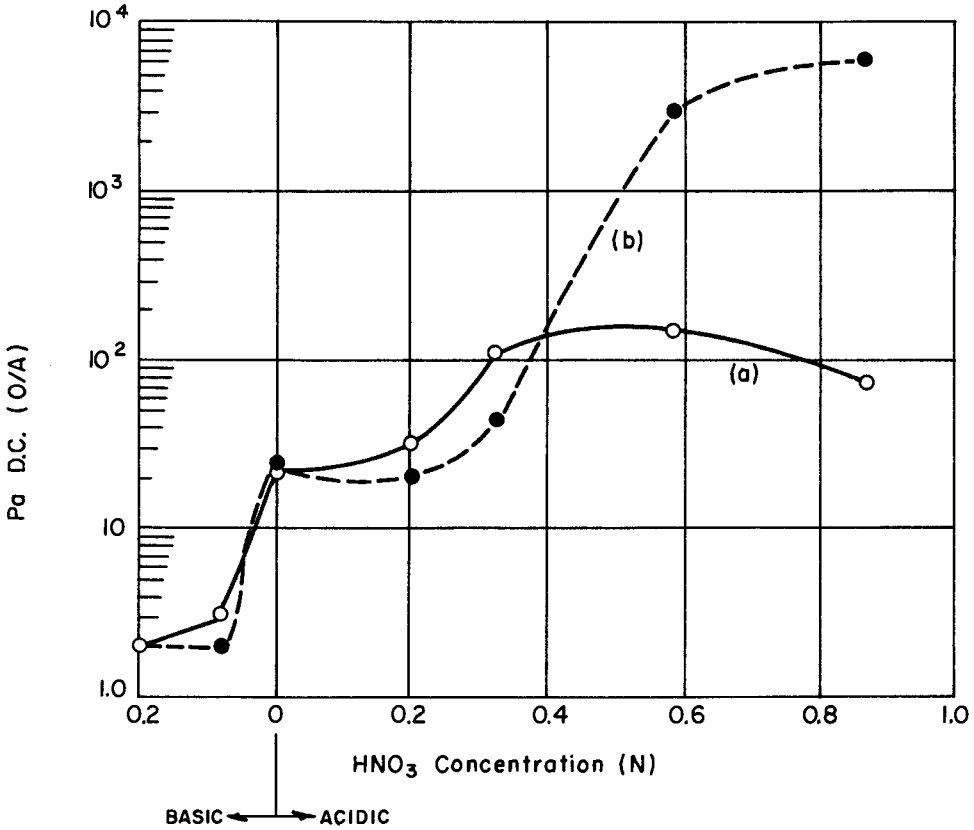

Fig. 4-4 DISTRIBUTION OF Pa^{233} AT 25°C, BETWEEN 1.9 *M* $Al(NO_3)_3$ AND (a) 41% TBP, (b) DIBC AS A FUNCTION OF NITRIC ACID CONCENTRATION.

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A distillation was carried out with 100 ml of DIBC and 300 ml of water containing 0.125 mole of HNO_3, approximately the amount of nitric acid that would be present in 100 ml of the DIBC extract of protactinium. (The use of 3 volumes of water for each volume of DIBC keeps the boiling temperature below 112°C and the acid concentration of the still residue below 1 N during most of the distillation.) For each volume of DIBC distilled, 2.37 volumes of water was also distilled. The nitric acid did not distill in appreciable amounts, and, as the acid concentration of the residue increased, the boiling temperature of the liquid in the still increased. However, the vapor temperature did not show a substantial increase until the DIBC was completely distilled (see Table 4-8). Less than 1% of the nitric acid was found in the distillates (see Table 4-9). Similar results were obtained when the distillation was carried out with a slightly higher acid concentration.

The composite of the distilled DIBC was treated with a 1/10 volume of 1 N NaOH solution to remove any organic acids. The caustic solution was separated, acidified with hydrochloric acid, and extracted with ethyl ether. When the ether was evaporated, a yellow liquid remained which had an odor indicative of isovaleric (3-methylbutanoic) or isobutyric (2-methylpropanoic) acid. These two organic acids would be expected to be the oxidation decomposition products of DIBC. Their boiling points, 176.3°C for isovaleric and 154.4°C for isobutyric, are in the same range as the boiling point of DIBC, 173.3°C, and they would be expected to be steam distilled along with the DIBC.

An extract of protactinium in DIBC was then made by extracting a 100-ml volume of 2 M $Al(NO_3)_3$ solution, 2.4 N in HNO_3 and containing protactinium, with 100 ml of DIBC. An initial nitric acid concentration of 2.4 N in the aqueous phase, which had a volume equal to that of the organic phase, was used so that the final acid concentration in the DIBC would be that proposed for process conditions (i.e., at equilibrium with an aqueous solution 1.9 M in $Al(NO_3)_3$ and 1 N in HNO_3. The 100 ml of DIBC extract of protactinium was then steam distilled, as before, over an initial volume of 300 ml of water to determine the behavior of protactinium in the process. Analyses of the

[redacted]

Table 4-8

Temperature of Distillation of DIBC and Water Containing Nitric Acid

Initial charge: 100 ml of DIBC, 300 ml of H_2O, 0.125 mole of HNO_3

Still Temp. (°C)	Vapor Temp. (°C)	Total Vol. H_2O + DIBC Distilled (ml)	Total Vol. DIBC Distilled (ml)
102	97.5	0	0
102.5	98.0	10	3.0
103	98.0	20	5.9
104	98.0	50	14.8
105	98.0	90	26.7
106	98.0	150	44.5
107	98.0	190	56.4
109	98.5	240	71.2
112	98.7	270	80.3
---	99.7	320	95.0
---	100.2	337	100.0

Table 4-9

Distribution of Nitric Acid on Distillation of DIBC and Water Containing Nitric Acid

Initial charge: 100 ml of DIBC, 300 ml of H_2O, 0.125 mole of HNO_3

Sample No.	Aqueous Distillate		DIBC Distillate		Still Residue	
	Vol. (ml)	HNO_3 (N)	Vol. (ml)	HNO_3 (N)	Vol. (ml)	HNO_3 (N)
1	34.9	0.005	15.3	<0.0025		
2	34.8	0.004	15.4	<0.0025		
3	35.5	0.005	14.5	<0.0025		
4	35.0	0.005	15.0	<0.0025		
5	35.3	0.005	14.7	<0.0025		
6	35.8	0.008	14.2	<0.0025		
7	29.0	0.015	7.8	<0.0025		
8	15.5	0.025	0.2	<0.0025		
					45.5[a]	2.74[a]

(a) Total amount of acid in residue was 0.1247 mole.

various distillate fractions and of the residue indicated that the bulk of the protactinium remained in the still, while most of the DIBC distilled over (see Table 4-10).

The activity in the DIBC distillate was below the level of accurate counting; the protactinium decontamination of the distilled DIBC was greater than 2.2×10^4. The aqueous distillate showed an increase in contamination near the end of the distillation. The concentration of the nitric acid in the still residue, which was 16 ml in volume, was estimated to be about 7.5 N.

Although decomposition of the DIBC by oxidation is expected to produce isovaleric and isobutyric acids, these are steam distilled with the DIBC and are thus removed from the protactinium product.

Further concentration of the protactinium product can be made by distillation of the water phase after the DIBC has been distilled. Most of the nitric acid will remain with the residue until a constant-boiling composition is reached. Explosion hazards would not be expected until the still residues approach dryness.

Table 4-10

Distribution of Protactinium Activity During Steam Distillation of DIBC Extract of Protactinium

Initial charge: 100 ml of DIBC, 1.3 N in HNO_3, 2.32×10^5 β c/m/ml; 300 ml of H_2O

Distillate Fraction No.	Volume (ml)		β Activity (c/m/ml)	
	Aqueous Phase	DIBC Phase	Aqueous Phase	DIBC Phase
1	67	33	10	10
2	69	31	10	10
3	72	28	10	15
4	26	---	10	---
5	25	---	40	---
6	28	---	700	---
Still Residue	16	---	1.5×10^6	---

4.3 The B-Column

The effects of flow ratios on thorium-uranium separation and uranium recovery, problems in evaporation of the BT solution, and physical properties of the aqueous and organic phases in the B-column are discussed.

4.3.1 Pulse Column Results (Unit Operations Section)

The B-column stream flow ratios found optimum with regard to both thorium-U^{233} separation and U^{233} recovery are AU/BX/BS = 5.2/5.8/1.6. Studies made in 2-in.-diameter columns have demonstrated uranium losses of about 0.01% and thorium-uranium separation factors of about 8×10^3. There is reasonable assurance, despite analytical difficulties of measuring thorium in the 1.0- to 10.0-μg range, that the thorium-uranium separation factor actually approaches 5×10^4. Operability in the concatenated columns appeared entirely satisfactory.

Observations have indicated that the degree of thorium-uranium separation is a function of aging of the AU stream. Significant hydrolysis of the TBP to DBP and MBP apparently can occur in periods as short as one to three days, which in turn effects formation of a detectable percentage of nonstrippable thorium in the BU stream. Most of this nonstrippable material appears to persist in the CW stream.

4.3.2 Determination of Thorium in the BU Stream (W. T. McDuffee)

The determination of the thorium concentration in the BU stream (41% TBP, thorium concentration 1.0 to 10 μg/ml) is difficult because of both (1) the failure of aqueous solutions to completely strip the thorium from the TBP and (2) the large uncertainty in the analytical methods for thorium at these low concentrations. Since values for the BU thorium were needed for calculating thorium-uranium separation factors in the B-column, brief studies were carried out on the effectiveness of (1) 0.1 N NaOH, (2) H_2O, and (3) 0.05 M $Al(OH)_2NO_3$ as stripping agents. The dibasic aluminum nitrate gave the best results (see Table 4-11).

Table 4-11

Thorium Analyses Using Various Stripping Solutions

Calcd. in 41% TBP (μg/ml)	Found in Aqueous Strip[a] (μg/ml)		
	0.1 N NaOH	H_2O	0.05 M $Al(OH)_2NO_3$
2	0.32	0.16	0.98
5	0.32	0.1	3.20
10	6.5	6.1	10.35
20	9.0	19.53	24.2
100	40.0	91.56	101.25

(a) Based on equal volumes of original organic phase.

A stock solution of 41% TBP, 0.04 N in HNO_3 and containing thorium at a concentration of 1 mg/ml, was diluted with 41% TBP of the same acidity to give solutions containing various low concentrations of thorium. The thorium was stripped from the organic solution with the three different aqueous solutions, and its concentration in the aqueous phase was determined colorimetrically.* All new glassware was used. Strip solutions whose thorium concentrations were calculated to be less than 10 μg/ml were boiled down before being analyzed.

The colorimetric method appears to retain its accuracy of ±3% down to a thorium concentration of 10 μg/ml, but below this concentration the uncertainty becomes large.

4.3.3 Evaporation of the BT Solution

(M. R. Bennett)

It has been demonstrated that the BT solution can be evaporated at atmospheric pressure to a thorium concentration of approximately 2.0 M without excessive decomposition of the soluble TBP present (see Table 4-12). It was shown that, at atmospheric pressure, 95% of the TBP can be steam distilled; however excessive decomposition of the TBP occurred when the vapor phase was exposed to equipment surfaces at temperatures significantly exceeding the boiling point of the solution. Evaporation at reduced pressure, to limit decomposition of the TBP, was also found successful as a process approach, but the soluble TBP was not removed and appeared as a light phase in the concentrates.

The behavior of the various evaporated BT solutions when they were recycled in the A-column is given in Table 4-13.

There was suspended material in some of the evaporated BT solutions, and this appeared to be correlated with the formation of emulsions when the material was recycled under A-column conditions in a batch countercurrent system (see Table 4-13). It is not known whether the type of Amsco present in the original BT solution affects the tendency toward emulsion formation.

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*The authors acknowledge the assistance of G. W. Wilson, and his group in the [redacted]cal Chemistry Division, for these analyses.

[redacted]

Table 4-12

Evaporation of BT Solution

[redacted]

Solution No.	Source[a] of BT	Vol. of BT (liters)	Method	Evaporator Conditions				Initial Th Conc. (M)	Final Th Conc. (M)
				Type of Heating[b]	Boiling Point (°C)	Pressure (mm Hg)	Time (hr)		
1	U. O.	0.50	Live steam	Mantle	100-101	~760	0.11	0.22	0.25
2	U. O.	0.45	Atmospheric	Mantle	100-107	~760	1.5	0.22	2.5
3	Synthetic	0.45	Atmospheric	Unit	100.5-106.5	~760	~1.5	0.25	2.5
4	U. O.	0.45	Atmospheric	Unit	100.5-106.5	~760	~1.5	0.24	2.5
5	U. O.	0.45	Atmospheric	Unit	100.5-106.5	~760	~1.5	0.24	2.5
6	U. O.	0.45	Atmospheric-reflux	Unit	100.5-106.5	~760	4.0	0.24	2.5
7	U. O.	0.45	Atmospheric-reflux	Mantle	100.5-106.5	~760	4.0	0.24	2.5
8	U. O.	0.45	Atmospheric-reflux	Mantle	100-107	~760	7.5	0.22	2.5
9	U. O.	0.45	Atmospheric-reflux	Unit	100.5-106.5	~760	18.0	0.24	2.5
10	Synthetic	0.45	Vacuum	Unit	29-32	30.5	~1.5	0.20	1.75
11	Synthetic	0.45	Vacuum	Unit	43-46	66.8	~1.5	0.20	1.75
12	Synthetic	0.45	Vacuum	Unit	49.5-52.5	96.5	~1.5	0.25	1.75
13	Synthetic	0.45	Vacuum	Unit	58-61	149.5	~1.5	0.25	1.75

(a) The Unit Operations (U. O.) solution had been equilibrated with TBP in Amsco 123-15, the synthetic with TBP in Amsco 125-90W. The U. O. solutions used in this study were obtained from the Unit Operations demonstrations of the 2-in. B-column.

(b) The use of a flask heating mantle involved boildown of the initial volume until the liquid surface dropped below the upper edge of the mantle, thus permitting high local surface temperatures to contact the vapor phase. The use of a small heating element, or unit, provided a point source of heat to the flask bottom and allowed good liquid heat transfer throughout the evaporation step.

[redacted]

[redacted]

Table 4-13

Behavior of Evaporated BT During A-Column Recycle

Solution No.[a]	Type[a] of Amsco in Original BT	Amt. of Suspension in AF	No. of Equilibrations	Emulsion Formation[b]	Phase Separation
1	123-15	Medium	6	Yes	Poor
2	123-15	Heavy	6	Yes	Poor
3	125-90W	None	20	No	Rapid
4	125-90W	None	22	No	Rapid
5	125-90W	None	20	No	Rapid
6	125-90W	None	19	No	Rapid
7	123-15	Heavy	8	Yes	Poor
8	123-15	Very heavy	4	Yes	Very poor
9	123-15	None	18	No	Rapid
10	125-90W	Very slight	26	No	Rapid
11	125-90W	Very slight	23	No	Rapid
12	125-90W	Very slight	26	No	Rapid
13	125-90W	Very slight	24	No	Rapid

(a) For source and evaporation conditions of these solutions, see Table 4-12.

(b) It is not known whether the type of Amsco affects the formation of emulsion.

4.3.4 Density, Viscosity, and Electrical Conductivity Profiles of [redacted] the B-Column

(J. E. Savolainen and R. P. Wischow)

Physical properties of the aqueous and organic streams of the B-column are plotted in Fig. 4-5 as functions of stage number, i.e., as column "profiles." A discussion and additional data are recorded in Sec. A.1. The profiles point out the best control points for instrumentation of the B-column operation.

4.4 The C-Column

C-column conditions indicated in the August, 1952 flowsheet were tested by the Unit Operations Section and found operable in 2-in.-diameter pulse columns. Thorium losses in the CW of less than 0.01% were demonstrated.

Changes shown in the January, 1953 flowsheet (see Fig. 3-1), i.e., the use of a neutralization column and reduced CX flow rates, have not yet been tested on this scale.

4.4.1 Effects on C-Column Operation of Nitric Acid Removal from the BU Stream

(A. T. Gresky and W. T. McDuffee)

The nitric acid, 0.04 N, in the BU stream limited the BU/CX flow ratio to 2.0 in the August, 1952 flowsheet, since this acid was transferred to the aqueous phase and provided sufficient "salt" strength to hold the uranium D.C. (O/A) at nearly limiting values with regard to stripping efficiency. It may be noted that a BU/CX flow ratio of 10, for example, with an HNO_3 concentration of 0.04 N in the BU, would predetermine an HNO_3 concentration of 0.4 N in the CU stream, which is prohibitive for either U^{233} stripping or sorption by the present ion exchange procedure.

Since the aqueous salting strength was limiting, the use of alkali in the stripping medium would not be allowed. However, prior to the entry of the BU stream into the C-column, it is permissible to neutralize the acid with acid-deficient aluminum nitrate solutions, and this process has been shown to be feasible.

[redacted]

[redacted]
Dwg No18981

FLOW RATIO: F/Sc/St = 5.2/1.6/5.8
STRIP: 0.19 N HNO_3
FEED: 42.4 % in Amsco 125-90W; U, 0.057 g/liter; Th, 71.6 g/liter
SCRUB: 42.4 % TBP in Amsco 125-90W

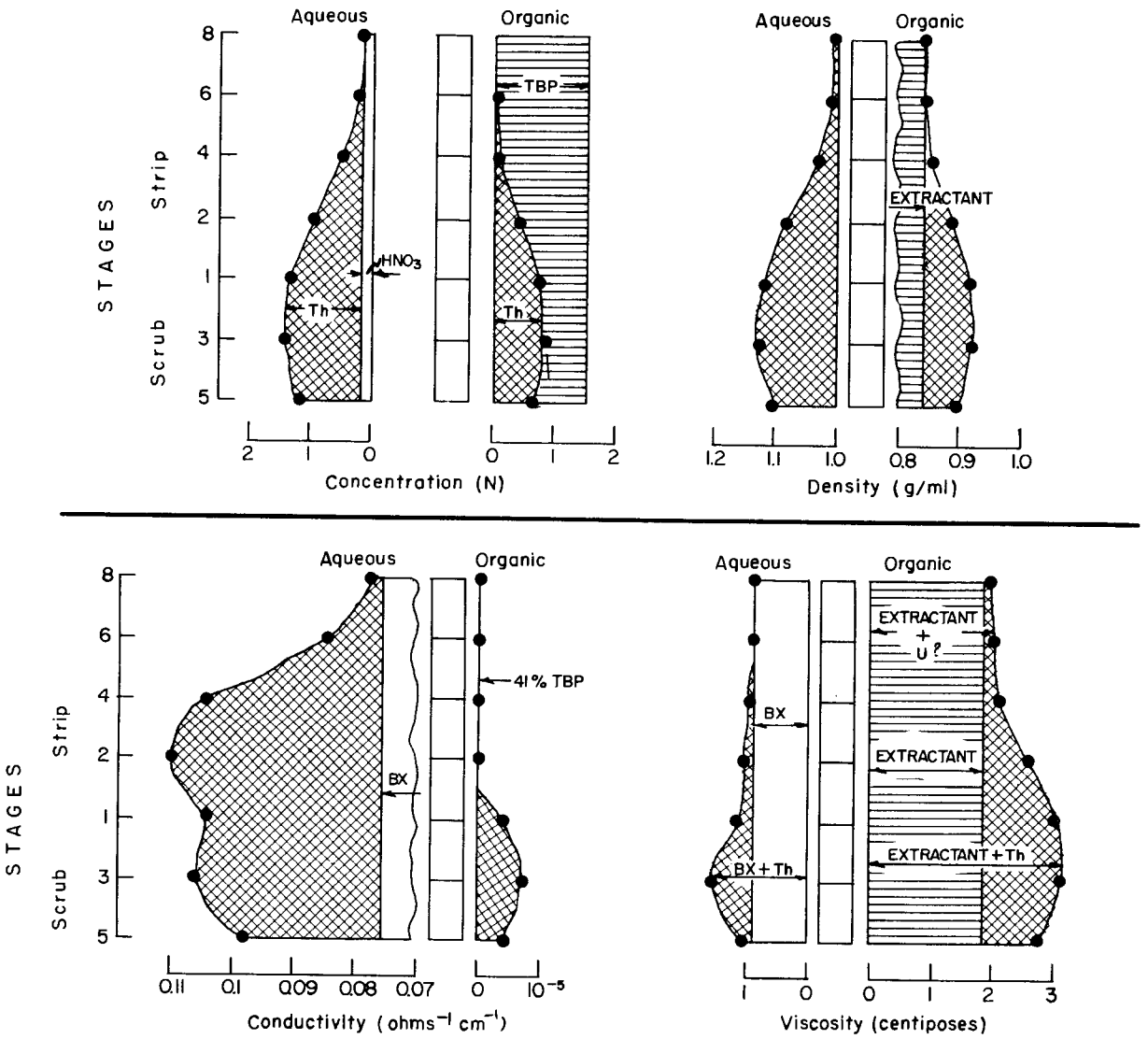

Fig. 4-5. PHYSICAL PROPERTY PROFILES OF B-COLUMN

[redacted]

When an essentially neutral BU stream is used, the only significant salting agent affecting the uranium distribution in the C-column is that added in the CX stream, i.e., 0.01 N HNO_3. Thus reasonably large BU/CX flow ratios, e.g., 10, become possible and permit significant volume reductions, which allow more favorable use of the ion exchange isolation step. The resulting CU stream will have an HNO_3 concentration lower than 0.05 N and will contain approximately 0.5 g of U^{233} per liter, and the flow rate will be only one-fifth of that when a BU/CX flow ratio of 2.0 is used.

Use of the AS Stream for BU Neutralization. By providing the AS stream (aqueous scrub solution in the A-column) initially with excess acid deficiency, i.e., by increasing the OH/Al ratio, neutralization of the BU acidity can be accomplished in a continuous cascading system with BU/AS flow ratios of 6.6, as prescribed by the flowsheet. Such a system requires only one effective contact stage for neutralization.

Experiments were carried out in a three-stage countercurrent run which demonstrated the above conditions and a subsequent uranium stripping (see Table 4-14). Sufficient thorium was added to the BU stream to permit its distribution in the system to be followed. Thorium was observed to be stripped into the aqueous phase, whereas uranium remained extractible. Slight uranium recycle to the A-column will result from such an operation.

Revisions in Flow Ratios. With the nitric acid removed from the BU stream and a CX HNO_3 concentration of 0.01 N, BU/CX flow ratios of 10 become feasible. With the currently considered thorium irradiation history, the concentration of U^{233} in the CU stream will be 0.5 g/liter, and the nitric acid concentration will be in the range of 0.01 to 0.02 N.

It may be noted that brief laboratory batch tests indicated that aqueous CX solution containing 0.0 N H^+, e.g., freshly distilled water, tended to emulsify on contact with the neutral organic BU stream. Nitric acid concentrations of 0.002 N or greater were required to reduce emulsification and permit rapid phase separation. In pulse-column studies it was

Table 4-14

Typical Data from Countercurrent Run Demonstrating BU Neutralization and Subsequent Uranium Stripping

Feed: BU stream; 42% TBP, 0.05 N HNO_3, 0.048 mg of U and 0.04 mg of Th per milliliter; in 3Sc, out 5St

Scrub: AS stream, adjusted; 0.58 M Al, 1.05 N HNO_3-deficient, 0.002 M PO_4; in 1Sc, out 3Sc

Strip: CX stream; 0.01 N HNO_3; in 5St, out 1St

Stages: 3 neutralization (or scrub), 5 stripping

Flow ratios: F/Sc/St = BU/AS/CX = 6.6/1.0/0.66

Stage	Determination	Organic	Aqueous	D.C. (O/A)	E.F. (O/A)
5St	Th (mg/ml)	0.008	0.000	---	---
	U (mg/ml)	0.00002	0.0045	0.004	0.04
	H^+ (N)	0.005	0.02	---	---
3St	Th (mg/ml)	0.008	0.010	---	---
	U (mg/ml)	0.001	0.150	0.006	0.06
	H^+ (N)	0.005	0.02	---	---
1St	Th (mg/ml)	0.008	0.05	---	---
	U (mg/ml)	0.027	0.553 (a)	0.05	0.5
	H^+ (N)	0.005	0.02 (a)	---	---
1Sc	Th (mg/ml)	0.005	0.190	---	---
	U (mg/ml)	0.054	0.002	27.0	178.0
	H^+ (N)	0.005	-0.82 (b)	---	---
3Sc	Th (mg/ml)	0.018	0.259 (c)	0.07	0.46
	U (mg/ml)	0.045	0.0015	30.0	198.0
	H^+ (N)	0.005	-0.86 (b)	---	---

(a) Compare with values for CU stream when BU stream is not neutralized, i.e., 0.1 mg of U per milliliter, 0.09 N HNO_3.

(b) Acid deficient.

(c) Observed thorium removal by AS stream.

observed that a CX acidity of at least 0.01 N was required to reduce flooding tendencies in the C-column.

Effects of Nitric Acid and Uranium Content on U^{233} Isolation by Ion Exchange. Uranium sorption coefficients, or distribution coefficients (U in resin/U in solution), in the Dowex 50—$UO_2(NO_3)_2$—HNO_3 cation exchange system have been observed[1] to increase with increasing uranium concentration and decreasing nitric acid concentrations, e.g., in the Thorex CU stream. These coefficients govern the percentage saturation of the resin and the uranium capacity in a given bed. Conditions of the CU stream in the August, 1952 flowsheet, i.e., 0.09 N HNO_3 and a uranium concentration of 0.1 g/liter, were considered unfavorable for the ion exchange isolation step because of the high flow rates and the low resin capacity prescribed by a low saturation value of about 25%. Low HNO_3 concentrations, e.g., 0.0 to 0.02 N, greatly increase the ability of the resin to concentrate uranium from very dilute solutions, since under such conditions column feed flow rates of 10 to 15 $ml/m/cm^2$ will permit about 85% saturation of the resin.

The above considerations were incentives for the use of the BU neutralization column and adjustment of the CX flow rates. Optimum plant design features for criticality control require that the columns not exceed 4 in. in diameter. Larger columns would presumably require the utilization of neutron "poisoning."

4.4.2 Studies of U^{233} Isolation by Evaporation and Solvent Extraction of the CU

(B. G. Ryle)

Isolation of U^{233} by ion exchange is considered optimum for the Thorex process; however, alternate methods will be evaluated before a final decision is reached as to the type of isolation process that will be used. Studies currently in progress indicate that evaporation of the CU and solvent extraction of the uranium from the concentrated solution may be a satisfactory method. Work is now being carried out on the factors that affect the degree of volume reduction and TBP decomposition.

Synthetic CU solutions of the August, 1952 flowsheet type, containing iron, chromium, and nickel in the concentrations that would be present in process solution (calculated from the observed corrosion of type 309 stainless steel), have been successfully concentrated by a factor of 90. Factors of this magnitude would permit a small-scale TBP extraction system of the Purex type for a uranium isolation step. About 97% of the soluble TBP was removed during the evaporation.

Fluoride ion carried over into the CU stream (see Sec. 5.1) will presumably contribute to significant corrosion rates and corrosion product concentrations by the evaporation step. Whether the initial CU stream is 0.1 N in HNO_3 and has a uranium concentration of 0.1 g/liter (August, 1952 flowsheet), or is 0.02 N in HNO_3 and has a uranium concentration of 0.5 g/liter (January, 1953 flowsheet), is naturally an important process consideration. A concentration factor of 100 would produce a solution approximately 10 N in HNO_3 and having a uranium concentration of 10 g/liter in the former case, and a solution 2 N in HNO_3 and having a uranium concentration of 50 g/liter in the latter case.

4.5 Solvent Treatment

Use of a solvent recovery system of the type now used in the Purex process, i.e., the sodium carbonate system including centrifugation, has been adopted for use in the Thorex pilot plant. Conditioning of the Amsco 125-90W diluent has been accepted by the Pilot Plant Section.

Further studies of the calcium hydroxide solvent recovery system are presented. This system will be used in the pilot plant only if the sodium carbonate system appears inadequate.

Additional studies have been carried out on evaluation of the diluent preconditioning method.

4.5.1 The Calcium Hydroxide Process

(J. E. Savolainen)

Testing of prototype lime contactors by the Unit Operations Section[2,3] has pointed out certain difficulties in maintaining the water content of

the slurry at optimum levels for good settling characteristics. On a weight basis, the $H_2O/Ca(OH)_2$ ratio of 6.0 has been found to allow the best operating characteristics. The use of a centrifuge to remove any entrained calcium hydroxide particles from the effluent solvent has been proposed to ensure purification.

Removal of used slurry from the contactor after neutralization and dissolution of the calcium hydroxide with 8 N HNO_3 has been shown to eliminate the necessity for filtration of the slurry, as proposed in the last progress report.[4] The new method involves the loss of small volumes of solvent, which would be removed along with the resulting calcium nitrate solution. Tests of this operation, following an extended operating period of the test unit, indicate that high proportions of the decomposition products of TBP and Amsco 123-15 are extracted into the residual solvent phase. In experiments now underway on this material, the attempt is being made to separate and identify the complex products of organic degradation. In contact with neutral and basic aqueous solutions, these degradation products exhibit marked surface action and permit extensive emulsion formation.

The large quantities of Amsco decomposition products collected in the calcium hydroxide slurry during the above tests point out the desirability of diluent preconditioning for the Thorex process. Prior removal of the more reactive components from the kerosene diluents, e.g., certain unsaturated and tertiary compounds, by "preconditioning" to nitric acid conditions, should increase the useful process life of the calcium hydroxide slurry.

The β,γ decontamination of TBP—Amsco 123-15 solvents by the lime method has been significant, but irreproducible. Iodine removal appeared to be incomplete, presumably owing to its reaction with unsaturated components of the diluent. No conclusive tests with contaminated solvent of the TBP—preconditioned Amsco 125-90 class have been carried out. However, batch tests on CW solutions from laboratory Thorex studies have indicated complete activity removal. Decontamination factors of >100 were characteristic of the low-activity-level tests.

4.5.2 Preconditioning of Diluent
(W. T. McDuffee)

The use of crude hydrocarbon diluents in solvent extraction processes is complicated by the fact that many of them contain organic fractions that are unstable in the presence of nitric acid or nitrate solutions of concentration 1.0 to 8.0 N. In fields of intense β,γ radiation, other side reactions may be expected to occur, the products of which are compounds that may be expected to cause such difficulties as emulsification and formation of nonstrippable fission product compounds. The radioactive impurities being separated from the uranium or thorium products are low in concentration but have been shown to be sensitive to the presence of exceedingly low concentrations of aqueous impurities; it is not unreasonable to expect them to be sensitive also to impurities native to the diluent or formed in it by decomposition. It was found possible to prepare a hydrocarbon diluent that is relatively inert to nitric acid of concentrations up to 10 N by removing the unstable constituents from Amsco 125-90W, a commercially available synthetic solvent naphtha of high purity (see Table 4-15). The most effective method of removing the impurities was pretreatment of the solvent with 10 N HNO_3 and calcium hydroxide, followed by adsorption of the nitrated impurities on silica gel. This treatment may be expected to remove initial sources of surface-active agents, or crud formers, and to prolong the life of the diluent, but does not guarantee a diluent completely inert to radiation decomposition.

A more detailed report of the preconditioning treatment can be found in ORNL CF-53-1-63[5] and CF-52-11-23.[6]

The following methods of treating Amsco 125-90W were evaluated qualitatively in order to determine a usable, inexpensive process for diluent purification and stabilization.

(1) Pretreatment with Silica Gel. The diluent was passed through a bed of refrigeration grade silica gel, 20 to 40 mesh, which was 1.25 in.^{2} in surface area and 12.75 in. deep, at a rate of 60 ml/min. The temperature

Table 4-15

Properties of Amsco 125-90W

Specific gravity, 25/4°C	0.7570
Refractive index, 25°C	1.4226
Aniline cloud point (°F)	186.5
Kauri butanol value (ml)	26.0
Viscosity (millipoises)	14.1
Boiling range (°C)	186-199
Midpoint (°C)	190
Flash point, Tag closed cup (°F)	133
Composition (%)	
Aromatics	1
Naphthenes	---
Paraffins	---
Iodine No.	0.49
Odor	Slight
Color	Water white

of the bed was maintained at 60 to 70°C for maximum capacity. It was estimated that after about 10 volume changes the impurities (such as aromatics) began to break through in prohibitive amounts. The adsorption bands on the bed were not sharply defined.

(2) Pretreatment with 10 N HNO_3 Followed by Silica Gel Adsorption. The raw diluent was contacted with 0.1 vol. of 10 N HNO_3 for a period of 2 hr and was then washed once with 0.1 vol. of H_2O to remove entrained acid from the organic phase. (The acid treatment appeared to nitrate and/or oxidize the unstable compounds, rendering them partially insoluble in either phase and more susceptible to removal by subsequent steps in the process. The insoluble material, blue-black in color, was somewhat resinous in character and accumulated at the interface. The acid-treated Amsco 125-90W was colorless, in contrast to the yellow color of acid-treated Amsco 123-15.) The diluent was then passed through a bed of silica gel as outlined in the above paragraph. The silica gel appeared to have about the same capacity as in case (1); however, the adsorption bands on the silica gel were sharper and more intense. It appeared that the acid treatment rendered a portion of the most unstable compounds easily adsorbable, and the more stable compounds were not strongly attacked. It was concluded that the acid treatment was beneficial in that the diluent was made more stable toward the expected nitric acid conditions imposed in the solvent extraction process.

(3) Pretreatment with 10 N HNO_3 and Calcium Hydroxide Followed by Silica Gel Adsorption. The raw diluent was pretreated with 10 N HNO_3 as in case (2) above, and was then washed with water and slurried with dry calcium hydroxide for 1 hr. Solids were then removed by decantation and filtration, yielding a colorless liquid.

Following the calcium hydroxide treatment, the diluent was passed through a silica gel bed as in case (1). The capacity of the adsorbent under these conditions was about 25 volumes of diluent per volume of silica gel. Sharp banding, of intense purple color, was obtained along the first 3 in. of bed depth, and the remainder shaded off to practically no color. This indicated very effective removal of the impurities which

remained in the diluent after the first two steps of the process. The deeply colored band represented only 25% of the bed depth, and possibly a band depth of 40% could have been tolerated before the impurities would break through the bed in sufficient concentration to limit further loading of the column. It was concluded that the calcium hydroxide treatment permitted an increased capacity of the silica gel to remove impurities.

The calcium hydroxide/diluent ratio may be varied over rather wide ranges without appreciably different results. The governing consideration in this step appears to be physical in nature rather than chemical. Proportions of as little as 2 g of $Ca(OH)_2$ to 1 liter of diluent may be required as arrived at from chemical considerations, while 20 g of $Ca(OH)_2$ per liter of diluent may be optimum from purely physical considerations. With the higher amounts of lime, filtration and settling were more rapid and the materials were, in general, easier to handle in batch operations. Other considerations that entered into the choice of proportions involved the varying composition of the acid-treated diluent which was delivered to the calcium hydroxide step. While the acid-treatment step and the subsequent water-washing steps saturated the diluent with moisture, the addition of more water, to the extent of 20 to 30 g per liter of diluent, improved the settling characteristics of the calcium hydroxide considerably. Proportions of water much in excess of this were observed to cause the calcium hydroxide to agglomerate into larger pellets and lumps, which stuck to the bottom and sides of the vessel and sharply reduced the reactive surfaces as well as capacity. There was also some tendency for the calcium hydroxide to stick to the agitator blades and shaft when excess water was used.

Some of the factors affecting the capacity of the silica gel bed are:

(a) Flow rate. Higher flow rates for a given silica gel bed lowers the capacity. The banding observed for a flow rate of 6 ml/min was sharp and occupied about 10% of the bed depth when 10 vol. of diluent were passed through 1 vol. of silica gel. At a flow rate of 60 ml/min, the band was less intense and extended through 25 to 30% of the bed depth.

(b) Temperature. Higher temperatures favored the capacity; an increase in capacity by a factor of 2 was obtained by raising the temperature from 25 to 65°C. Sharper and more intense banding was also obtained, indicating more effective adsorption of the impurities.

(c) Degassing. Degassing of the bed prior to passage of the diluent increases the capacity and effectiveness of the adsorption. Degassed silica gel was obtained by passing previously treated diluent over the bed of fresh silica gel at 70 to 80°C and allowing the gas to escape to the atmosphere. The bed, when allowed to cool to about 50 to 65°C, was observed to be uniform throughout in bulk density and porosity.

(d) Adsorbent surface area. The adsorptive capacity of adsorbent substances varies directly as the surface involved or inversely with the diameter of the particles.

The relative nitric acid stability of the diluents following treatment by methods (1), (2), and (3) above was investigated to evaluate the need for each proposed step in the finally adopted procedure.

(1) Test Following Silica Gel Treatment Alone. When the diluent product of this treatment was contacted with 0.1 vol. of 10 N HNO_3 for 2 hr, water-washed, and then passed over 0.04 vol. of silica gel at 70°C, intense blue-black banding was observed on the silica gel. This result was interpreted to mean that the silica gel treatment by itself had not removed all the substances that would be reactive to Thorex process conditions.

(2) Test Following Nitric Acid and Silica Gel Treatment. When the diluent product was contacted with 0.1 vol. of 10 N HNO_3 for 2 hr, water-washed, and then passed through 0.04 vol. of silica gel, a sharp yellow band appeared on the adsorbent. This band was of different character and lower intensity than that observed in the initial treatment. These results were interpreted to indicate that the most unstable compounds and the reaction products, i.e., the intense blue-black compounds, had been removed during the initial treatment. The yellow or less intensely colored products of the second "test" were probable products of the nitric acid attack on the

main diluent constituents, which react at a much slower rate and in lower yield. These latter compounds were probably nitro compounds for the most part and, although the initial contact with nitric acid had produced small amounts, the bulk of reaction products which had originated with the less stable substance in the raw diluent had masked their visible effects on the silica gel.

(3) Test Following Nitric Acid, Calcium Hydroxide, and Silica Gel Treatment. The diluent product when contacted with 0.1 vol. of 10 N HNO_3, water-washed, and passed through 0.04 vol. of silica gel gave a sharp but considerably less intense brown-yellow band. This was interpreted to show that the nitro compounds and the degradation products generated by the nitric acid in the first treatment had been effectively removed and that the yellow-brown substances were essentially all nitration products which had their origin in the attack of the nitric acid on the main, and more stable, constituents of the diluent.

5.0 GENERAL INVESTIGATIONS

This section presents data and conclusions from studies of general interest in the Thorex development program.

5.1 Fluoride Distribution in the Extraction System

(W. T. McDuffee)

Analytical difficulties and poor material balances are as yet unresolved; however, additional data indicate a significant fluoride extractibility throughout the A, B, and C columns. Analysis of critical extraction and scrub stages of the A-column (see Table 5-1) shows that fluoride ion is extracted at a higher rate than was originally anticipated.

Additional data from the B- and C-columns are also reported in Table 5-2.

Table 5-1

Fluoride Distribution in A-Column

Thorex flowsheet conditions; AF contained 1.1 mg of F^- per milliliter

Stage	Fluoride Conc. (mg/ml)		D. C. (O/A)	E. F. (O/A)
	Organic	Aqueous		
8S	0.3[a]	0.44	0.68	3.5
4S	0.43	0.56	0.77	4.0
1E	0.16	0.46	0.35	0.9
5E	0.08	0.43[a]	0.19	0.5

(a) Material balance over the A-column equals 210%. Discrepancies are as yet unexplained.

Table 5-2

Fluoride Distribution in Process Streams

Thorex flowsheet conditions; AF contained 1.1 mg of F^- per milliliter

Stream	Fluoride Conc. (mg/ml)	Total Fluoride[a] (mg)
AU	0.3	1.56
BT	0.14	0.84
CU	0.13	0.43
CW	0.001	0.007

(a) The fluoride concentration multiplied by the stream flow rate. The material balance through the B- and C-columns is about 82%.

5.2 Corrosion by the Continuous Dissolver Feed

(W. T. McDuffee)

The Unit Operations Section has made the observation that the continuous dissolver feed (CDF) solution, which is 9 to 10 M in HNO_3, 0.075 M in NaF, and 0.003 M in $Hg(NO_3)_2$, strongly attacked all stainless steels, permitting significant corrosion of feed lines, instruments, and dissolver components. It has been found that various combinations of CDF addition methods, e.g., adding the nitric acid and catalysts in separate streams, could be used to reduce corrosion in head tanks and feed lines to the dissolver (see Table 5-3). A report covering the studies of corrosion in the overall Thorex process is in preparation by the Unit Operations Section.

Table 5-3

Corrosion by CDF Feed: Effect of Separate Reactant Streams

Solution[a]	Solution Composition (M)			Corrosion Rate[b] of Stainless Steels (mils/year)		
	HNO_3	NaF	$Hg(NO_3)_2$	Type 309SCb	Type 347	Type 304ELC
1	8.0	0.075	0.003	3.0	15.0	15.0
2	15.8	---	0.005	0.12	0.05	0.11
3	---	0.13	---	0.01	0.05	0.19
4	0.5	0.13	0.005	0.25	1.45	1.44
5	15.8	---	0.005	0.06	0.15	0.13

(a) Various combinations of these approximate desired CDF conditions.

(b) All tests were made at room temperature.

5.3 Preparation of Dibasic Aluminum Nitrate

(A. T. Gresky, R. P. Wischow, and J. E. Savolainen)

Since the scrub solution used in the Thorex A-column is a somewhat unusual application of the hydrolytic behavior of aluminum nitrate solutions, additional development work on methods of producing dibasic aluminum nitrate,

"Diban," was carried out. Commercial sources of supply for this material may appear desirable in the event that large-scale and general application is indicated.

The Thorex pilot plant[16] will need about 1500 lb of aluminum in the form of the compound $Al(OH)_2NO_3$. This material will be acceptable in the form of either a 4 M $Al(OH)_2NO_3$ solution or a powder of the approximate composition $Al_6(OH)_{13}(NO_3)_5 \cdot 8H_2O$. This is thought to be a novel compound.

4 M $Al(OH)_2NO_3$ Solution. The solution should conform to the approximate composition 4 M Al^{3+}, 7 to 8 M OH^-, 5 to 4 M NO_3^-, and should have a specific gravity of from 1.343 to 1.333 and a pH of 1.8 to 2.0.

A material meeting these requirements may be produced by the straightforward reaction

$$8Al + 7Al(NO_3)_3 + 15H_2O \xrightarrow[\Delta]{Hg^{++}} 15Al(OH)_2NO_3 + 1.8NO\uparrow + 1.2N_2O\uparrow + 0.9N_2\uparrow$$

by a very simple technique. On a 1-liter basis, in a stainless steel vessel having 200% freeboard and provided with a reflux condenser and off-gas system, 2 moles (54 g) of 99.6% aluminum metal is added to 1 liter of aqueous 2 M $Al(NO_3)_3$, 0.005 M $Hg(NO_3)_2$, and the reaction is allowed to proceed for about 1 hr. The mixture is heated to complete the dissolution of the metal and is then filtered. The initial reaction may be violent and accompanied by foaming; however, the rates of reaction can be conveniently controlled by heat adjustment and/or metal addition rates.

A second method, having possible large-scale economic advantages, involves the use of a continuous dissolver (vertical pipe) with aluminum metal and nitric acid as the starting materials, and the two combined reactions

$$Al + 3.75HNO_3 \xrightarrow{Hg^{++}} Al(NO_3)_3 + 0.225NO\uparrow + 0.15N_2O\uparrow + 0.1125N_2\uparrow + 1.875H_2O$$

$$Al + 0.875Al(NO_3)_3 + 1.875H_2O \xrightarrow{Hg^{++}} 1.875Al(OH)_2NO_3 + 0.225NO\uparrow + 0.15N_2O\uparrow + 0.1125N_2$$

(see also Sec. A-2).

In this method the dissolver product composition is controlled by the initial concentration of the nitric acid and the flow rate, the excess of aluminum metal and the addition rate, and the overall dissolver length. Engineering information regarding equipment design, instrumentation, and operation has been obtained by the Unit Operations Section of the Chemical Technology Division.

The $Al(OH)_2NO_3$ is soluble up to a concentration of about 9 M at 40°C, but it gels at room temperature. The 4 M $Al(OH)_2NO_3$ solutions have shown stability for several months in the absence of air, but 6 M solutions have tended toward precipitation in a few weeks. The 4 M solution should be stored in stainless steel containers, instead of glass, to minimize light-metal contamination.

Preparation of Solid Diban. This material, which has the approximate composition $Al_6(OH)_{13}(NO_3)_5 \cdot 8H_2O$, can be prepared by precipitation in the presence of organic reagents. The method involves evaporation of the 4 M $Al(OH)_2NO_3$ solution to a concentration of 7 M, cooling, and adding it to an agitated methanol—diethyl ether mixture in an overall volume ratio of solution/methanol/ether = 1/5/6. The resulting precipitate is removed by filtration, washed with excess ether, and dried in an oven up to 105°C. The first marked instability of the compound occurs at about 140°C. It has the approximate composition of 19 to 20% Al, 26 to 27% OH, 37% NO_3, and 16 to 18% H_2O. The fine white material can be powdered to 400- to 500-μ particles and pelletized, if desired. The dust has been observed to irritate nasal membranes. The material gave no evidence of crystalline structure.

The methanol and ether can be separated and recovered efficiently from the aqueous residues and from each other by fractional distillation; the additional cost of purification should therefore not be excessive.

The residue from the solvent recovery step was viscous, had a yellow color, and represented about 2% of the initial solvent volume. After it had stood at room temperature for about 18 hr, fine yellowish crystals were observed to have formed. These were separated by centrifugation and

were found to be readily soluble in water or methanol but were insoluble in ether. They melted at about 73°C and decomposed at about 135°C. Analysis indicated the $Al/OH^-/NO_3^-$ mole ratio to be 1.55/1.8/3.1, approximately that of monobasic aluminum nitrate, $Al(OH)(NO_3)_2$.

With regard to impurity specifications of the Diban solution or solid, the following upper limits of elements (spectrographic estimation) should preferably not be exceeded:

Impurity	Amount (ppm of Al_2O_3)	Impurity	Amount (ppm of Al_2O_3)
B	50	Cr	700
Be*	2	Ni	30
Li*	200	Cu	20
Ca	20	Ga	300
Mg	100	Hg*	2000
P*	5000	Mn	1500
Si	2000	Ti	60
Fe	4000	V	600

*These elements have not been found in the inspected samples, but the amounts quoted represent the detection limits.

The light elements, e.g., lithium, beryllium, and boron, are particularly undesirable, and amounts higher than the quoted maximum would probably not be allowed.

5.4 Purification of Materials for Use as Experimental Standards

(J. E. Savolainen)

Data on the equilibrium distribution of thorium nitrate between the aqueous and the organic phases are required for evaluation of the operation of extraction columns. To obtain these data under reproducible conditions and to reduce the uncertainty introduced by the presence of impurities, the

thorium nitrate, the TBP, and the diluent were subjected to standard purification treatments. These treatments were also used in preparation for measurements of physical properties of process solutions.

TBP purification. The TBP as received was saturated with water. Each liter of TBP was contacted for at least 2 hr with 50 g of calcium hydroxide per liter. The calcium hydroxide was allowed to settle, and the supernatant was filtered through paper. The filtrate was distilled under reduced pressure to remove the dissolved water and small amounts of butanol; when these had distilled off, the temperature of the TBP in the retort was raised briefly to about 100°C to ensure that all water had distilled over. The aqueous distillate was removed from the system. The pressure was then lowered to 1 to 2 mm Hg, and the temperature of the retort was raised to 109 to 116°C to distill the TBP. The first portion of the TBP distillate was removed from the system since this could contain traces of the low-boiling constituents, and then the main bulk of the TBP was distilled. In the laboratory apparatus, complete distillation of the TBP was not attempted since this would lead to excessive heating of the retort walls and would promote decomposition of the TBP. A cold trap was used in the distillation apparatus to prevent water vapor from entering the vacuum pump.

The data obtained from two laboratory distillations are given in Table 5-4.

Thorium nitrate purification. The thorium nitrate was dissolved in water, and nitric acid was added to give a solution that was 2 M in thorium and 4 M in HNO_3. This solution was refluxed at its boiling point for 4 hr to precipitate the soluble silica, and was then filtered. The filtrate was evaporated slowly under reduced pressure at room temperature to crystallize $Th(NO_3)_4 \cdot 12H_2O$. The crystals were washed with nitric acid and dried.

Diluent pretreatment. The diluent was contacted with 0.1 vol. of 10 M HNO_3 for 2 hr, followed by a 1-hr treatment with 40 g of $Ca(OH)_2$ per liter. The calcium hydroxide was removed by decantation and filtration, and the filtrate was passed through a silica gel column to remove the final traces of nitration and oxidation products.

Table 5-4

Purification of TBP by Distillation at Reduced Pressures

	1st Run	2nd Run
Original volume of TBP (ml)	760	660
Removal of water by distillation:		
Temperature (°C)	23	25
Pressure (mm Hg)	15	20
Volume of H_2O distilled (ml)	33	31
Volume of H_2O in cold trap (ml)	11.5	9
Distillation of TBP		
Temperature (°C)	114 to 116	109
Pressure (mm Hg)	2	1.5
Volume distilled, 1st cut (ml)	64	115
Volume distilled, 2nd cut (ml)	383	370
Volume of residue in retort	266	130

5.5 Isolation of Isotopic U^{233}

(S. S. Brandt, M. R. Bennett, and A. T. Gresky)

U^{233}, as now separated from neutron-irradiated thorium, contains a significant amount (approximately 1.5%) of isotopic impurities, such as U^{238}, contained in the source material, as well as U^{234} and U^{232} formed by nuclear side reactions. However, if the parent Pa^{233} is initially separated from the thorium (Th^{232} and Th^{234}) and uranium (U^{232}, U^{233}, U^{234}, U^{235}, and U^{238}), its decay would produce essentially pure U^{233}.

A need for about 20 mg of pure U^{233} was the basis for a laboratory-scale production operation with Interim-23 aqueous raffinates as a Pa^{233} source.(7) Since 99.9% of the initial uranium content had been previously extracted, the primary isotopic impurity remaining was U^{234}, conforming roughly to the initial U^{233}/U^{234} ratio governed by the Th^{233}-Th^{234} equilibrium established by the neutron flux during irradiation. These raffinates had the approximate composition 1.0 M Th, 0.8 M Al, 0.7 M HNO_3.

It was initially considered that the operation could be feasibly carried out by use of a silica gel adsorption technique developed in synthetic tests by the Chemical Development Section. This included (1) the simple adjustment of about 14 liters of the raffinate, after about 90 days' cooling, to HNO_3-deficient conditions; (2) subsequent adsorption of about 50 mg of Pa^{233} onto a silica gel column; (3) extensive washing with dilute nitric acid to elute traces of uranium and thorium; after which (4) the adsorbed Pa^{233} would be allowed to decay for about one half-life. The U^{233} formed by decay would then be preferentially eluted with dilute nitric acid and isolated by appropriate techniques. As described in Sec. 4.2.1, the adsorption was incomplete owing to unpredicted Pa^{233} behavior under actual processing conditions. A significant delay was imposed on the proposed operation, owing to failure of this method.

An alternate method utilizing solvent extraction of Pa^{233} with diisobutyl carbinol was rapidly developed and installed in the thorium waste storage area to permit processing of rather large volumes of the AW solutions, imposed because of a very significant intervening Pa^{233} decay

period. This system involved recirculation of the AW solution from a waste tank through the DIBC in a continuous spray contactor (see Fig. 5-1). With a D.C. (O/A) of about 10.0, attainment of equilibrium permitted Pa^{233} concentration factors of 10.0 and significant thorium and uranium separation. Alternately, the extract was scrubbed with 7.0 N HNO_3 to effect further thorium and uranium separation, and was finally stripped into a 0.1 volume of 0.2 M NaF solution to afford further Pa^{233} concentration. After about 60 mg of Pa^{233} had been collected and an appropriate decay period had been permitted, the strip solution was adjusted to 2.0 M Al and 0.3 N HNO_3 deficiency, and the U^{233} daughter was preferentially extracted into a 0.03 volume of 41% TBP. Final decontamination and isolation were completed in the laboratory by a solvent extraction technique.

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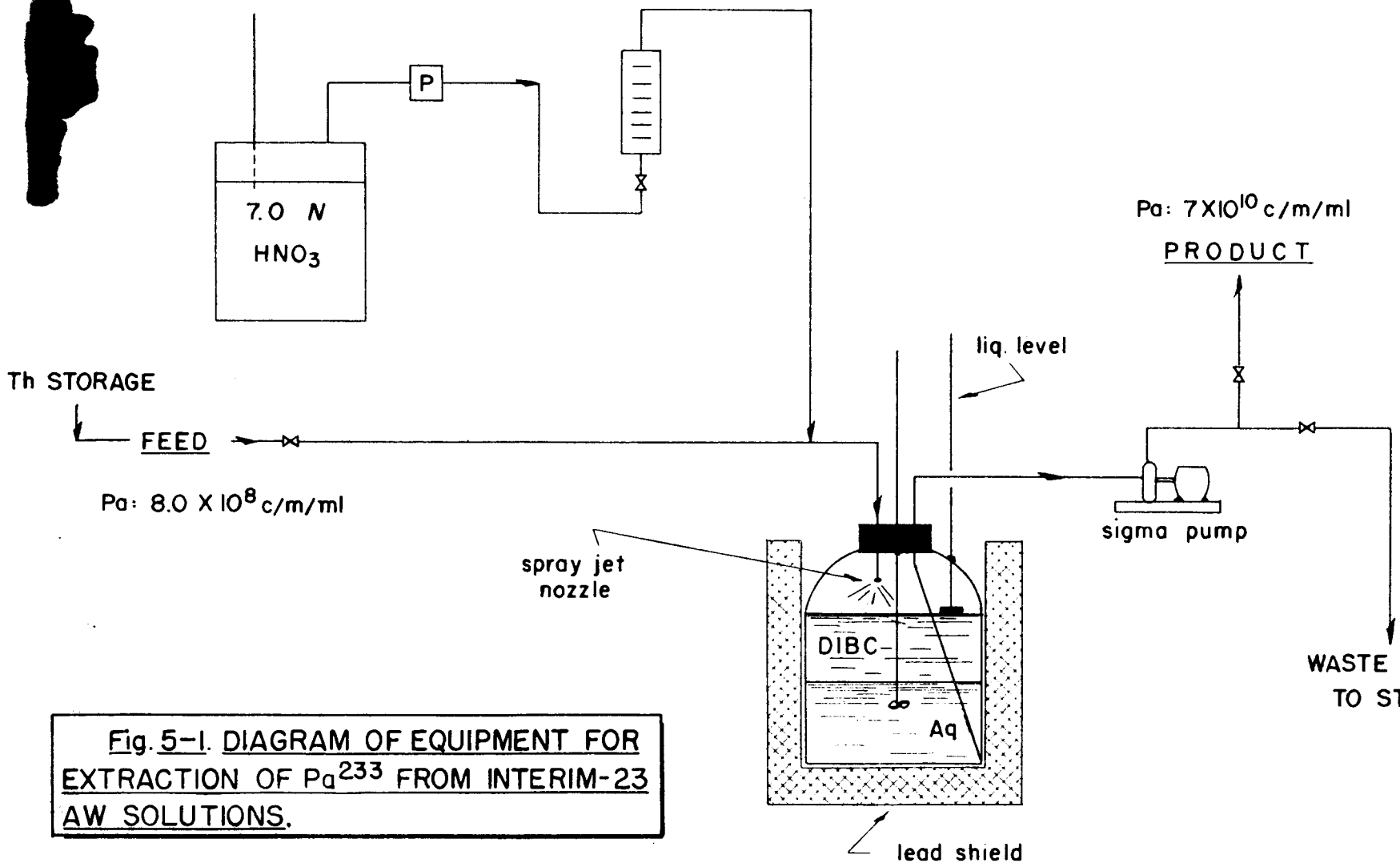

[redacted]

Fig. 5-1. DIAGRAM OF EQUIPMENT FOR EXTRACTION OF Pa^{233} FROM INTERIM-23 AW SOLUTIONS.

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Note: References 12 and 13, and certain other reports on the same subject, will be included in and superseded by an ORNL report, now in preparation, by A. C. Jealous and E. Lieberman.

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APPENDIX

A-1 Physical Properties of Process Solutions

(J. E. Savolainen)

Measurement of the physical property values of the streams in the Thorex process may afford a means of monitoring the process operation to control deleterious changes in stream flow rates or compositions. It is advantageous to monitor with the measurement of a property which is not influenced by a minor change of a secondary constituent of the stream. Automatic, continuous sampling and monitoring is most advantageous at those accessible points where the deleterious change has an immediate effect on the measured property before the overall process is interrupted.

The physical properties of the process solutions as they appear in laboratory batch countercurrent operations (representing the A, B, and C columns) were determined at 25°C. The viscosities were measured with Fenske-Cannon viscometers, pH's with a Beckman pH meter, densities with a Westphal balance, and electrical conductivities with a conductivity bridge (Industrial Instrument Company, model RC) using a dipping type conductivity cell.

The data recorded in Table A-1 show the properties of the liquid phases in the A column. A dense organic phase formed during the countercurrent batch extraction at the first extraction stage (sample 1E-O). It should be noted that, as an approximation, the calculated average density of the total organic phase can be used at this point as the effective density of the organic phase. However, the apparent viscosity of an intimate mixture of the two organic phases may be widely divergent from the average of the two individual organic phases, since the intimate mixture of the two phases would constitute an emulsion, and in an emulsion the effective viscosity is governed largely by the interfacial tension between the two phases. The formation of a dense organic phase was also observed at the second scrub stage sample (2S-O); however, when this sample was equilibrated at 25°C the dense phase disappeared.

Table A-1

Physical Properties of Phases in A-Column

Sample	Density	Viscosity (centipoises)	Conductivity ($ohms^{-1}$ cm^{-1})	pH	Concentration		
					H^+ (M)	U (g/liter)	Th (g/liter)
Aqueous Phase							
8Sc-A	1.1794	1.492	0.091	2.45	-0.80	0.0043	72.2
6Sc-A	1.2439	1.810	0.099	2.25	-0.80	0.0042	117
4Sc-A	1.2859	2.025	0.100	2.20	-0.70	0.0036	137
2Sc-A	1.3139	2.284	0.100	2.05	-0.80	0.0032	148
1E-A	1.2777	2.210	0.108	1.35	-0.20	0.00245	116
3E-A	1.0888	1.334	0.092	2.40	-0.15	0.00002	0.379
5E-A	1.0920	1.358	0.095	2.36	-0.15	0.00002	0.016
Aq. composite	1.0935	1.368	0.094	2.38	-0.14	0.00002	0.019
Scrub	1.0450	1.088	0.050	3.18	-0.73	---	(0.5 M Al)
Feed	1.6877	10.40	0.062	0.0	+0.44	0.34	346.4 (0.66 M Al)
Organic Phase							
8Sc-O	0.9515	4.090	1.41×10^{-5}	---	---	0.0570	71.6
6Sc-O	0.9816	5.756	2.33×10^{-5}	---	---	0.0445	89.6
4Sc-O	0.9896	6.538	2.75×10^{-5}	---	---	0.0520	94.4
2Sc-O	0.9949	7.445	2.62×10^{-5}	---	---	0.0520	97.6
1E-O (avg.)	(1.005)	---	---	---	---	(0.046)	(101.0)
3E-O	0.8472	1.985	---	---	---	0.00096	3.15
5E-O	0.8415	1.922	---	---	---	0.00025	0.019
Org. comp.	0.9474	3.933	1.22×10^{-5}	---	---	0.055	63.8
Org.	0.8382	1.808	---	---	---	(42.4% TBP)	---
1E-O, light phase (37.5 ml)	0.8528	2.257	---	---	---	0.0400	39.0
1E-O, (dense phase (64.5 ml)	1.0928	15.95	4.59×10^{-5}	---	---	0.0500	137

An interesting behavior of the three-phase system was indicated by the difference in distribution of uranium and thorium between the dense and light phases of sample 1E-0. The ratio of concentrations of the uranium is 1.25 while that of the thorium is 3.5. This dissimilarity may be interpreted as indicating the difference between the extracted complexes of thorium and uranium. The apparent polymerization reactions of the thorium complex in the organic phase are not duplicated by the uranium complex.

The properties of the aqueous and organic phases in the B-column are shown in Table A-2. The electrical conductivity of the organic phase dropped below the detectable limit of the instrument at low thorium concentrations.

The properties of the two phases of the C-column are listed in Table A-3.

Properties of the Organic Phase. Because the countercurrent extraction in the laboratory did not conform strictly to the flowsheet conditions, it was necessary to calculate the properties from the analysis of a previous run, using the physical data obtained in the present study. The calculated data for the A column are listed in Table A-4. Figure A-1 is a plot of the electrical conductivity of the extract as a function of the thorium concentration on a linear scale. Figure A-2 shows the same data on a semi-log scale. The plots indicate that the conductivity of the organic phase may be used as a measure of the thorium content. (This can be used with reliability only if the free nitric acid concentration in the extract is so low that it does not contribute to the electrical conductivity. The nitric acid concentration is not high enough to contribute to the conductivity in the present case.)

Figure A-3 is a plot of the viscosity of the extract as a function of the thorium concentration. The viscosity increases with an increasing rate as the thorium concentration approaches and exceeds 90 mg/ml, the point at which the TBP/Th mole ratio is 4.

Table A-2

Physical Properties of Phases in B-Column

Sample	Density	Viscosity (centipoises)	Conductivity ($ohms^{-1}$ cm^{-1})	pH	Concentration		
					H^+ (M)	U (g/liter)	Th (g/liter)
Aqueous Phase							
8St-A	1.0011	0.8874	0.0775	0.78	0.195	0.090	0.044
6St-A	1.0025	0.8887	0.0846	0.71	---	0.068	0.716
4St-A	1.0298	0.9364	0.1048	0.63	---	0.018	14.7
2St-A	1.0795	1.0474	0.110	0.55	---	0.0047	43.2
1S-A	1.1169	1.1319	0.104	0.60	---	0.0038	65.2
3S-A	1.1257	1.523	0.106	0.57	---	0.00066	71.2
5S-A	1.1038	1.0934	0.098	0.55	---	0.00002	59.3
Aq. comp.	1.1010	1.0934	0.0956	0.60	---	0.00007	57.6
Strip	0.9973	0.8917	0.0754	0.85	0.19	---	---
Organic Phase							
8St-O	0.8453	1.990	---	---	0.035	0.070	0.047
6St-O	0.8452	1.995	---	---	---	0.098	0.116
4St-O	0.8521	2.084	---	---	---	0.078	4.05
2St-O	0.8868	2.576	---	---	---	0.046	25.2
1S-O	0.9140	3.031	4.5×10^{-6}	---	---	0.046	43.0
3S-O	0.9186	3.151	7.34×10^{-6}	---	---	0.0066	46.4
5S-O	0.9004	2.754	4.89×10^{-6}	---	---	0.00062	36.3
Org. Comp.	0.8451	1.994	---	---	0.038	0.035	0.32

Table A-3

Physical Properties of Phases of C-Column

Sample	Density	Viscosity (centipoises)	Conductivity ($ohms^{-1}$ cm^{-1})	pH	Concentration		
					H^+ (M)	U (g/liter)	Th (g/liter)
Aqueous Phase							
5St-A	0.9944	0.884	4.0×10^{-3}	2.0	0.008	0.00086	0.002
3St-A	0.9944	0.883	4.59×10^{-3}	1.9	0.008	0.025	0.0003
1St-A	0.9971	0.885	3.14×10^{-2}	1.15	0.075	0.170	0.0125
Aq. comp.	0.9966	0.885	3.2×10^{-2}	1.03	0.078	0.170	0.0133
CX	0.9916	0.889	4.04×10^{-3}	2.04	0.008	---	---
Organic Phase							
5St-O	0.8451	1.988	---	---	0.005	0.00018	0.008
3St-O	0.8453	1.984	---	---	---	0.0020	0.018
1St-O	0.8447	1.984	---	---	---	0.046	0.018
Org. comp.	0.8449	1.987	---	---	0.01	0.00085	0.012

[redacted]

[redacted]

Table A-4

Typical Profile of Properties of A-Column

Feed: Th, 346.4 mg/ml; U, 0.34 mg/ml; HNO_3, 0.44 N; Al, 0.6 M

Scrub: Al, 0.6 M; $PO_4^{\equiv}$, 0.002 M; 0.7 M HNO_3 deficient

Organic: 41% TBP in Amsco 125-90W

Stage	Th Conc. (mg/ml)		Calcd. Viscosity (centipoises)		Calcd. Conductivity ($ohms^{-1}$ cm^{-1})		Calcd. Density	
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
8Sc	57.2	70.0	1.405	4.13	0.085	1.65×10^{-4}	1.158	0.953
6Sc	78.0	85.0	1.525	5.32	0.092	2.12×10^{-4}	1.185	0.976
4Sc	96.0	87.0	1.645	5.55	0.0966	2.21×10^{-4}	1.208	0.978
2Sc	102.2	87.0	1.695	5.55	0.098	2.21×10^{-4}	1.218	0.978
1E	64.2	89.5	1.750	5.85	0.104	2.33×10^{-4}	1.192	0.982
3E	0.086	0.738	1.35	4.39	0.092	1.68×10^{-4}	1.093	0.958
5E	0.086	0.025	1.35	1.95	0.092	---	1.093	0.845
Composite	0.086	61.3	1.35	3.65	0.092	1.25×10^{-4}	1.093	0.938

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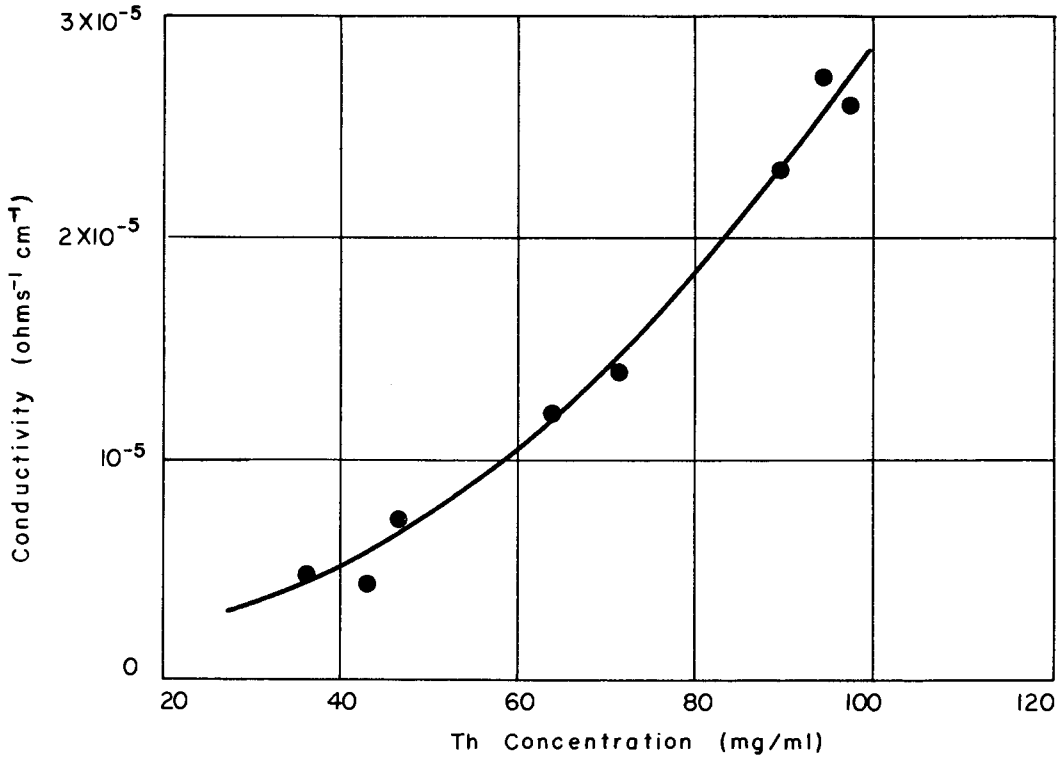

Solvent: 42.2 % TBP in Amsco 125-90W

Fig. A-1 ELECTRICAL CONDUCTIVITY OF A-COLUMN EXTRACT AS A FUNCTION OF THE THORIUM CONCENTRATION (Linear Scale).

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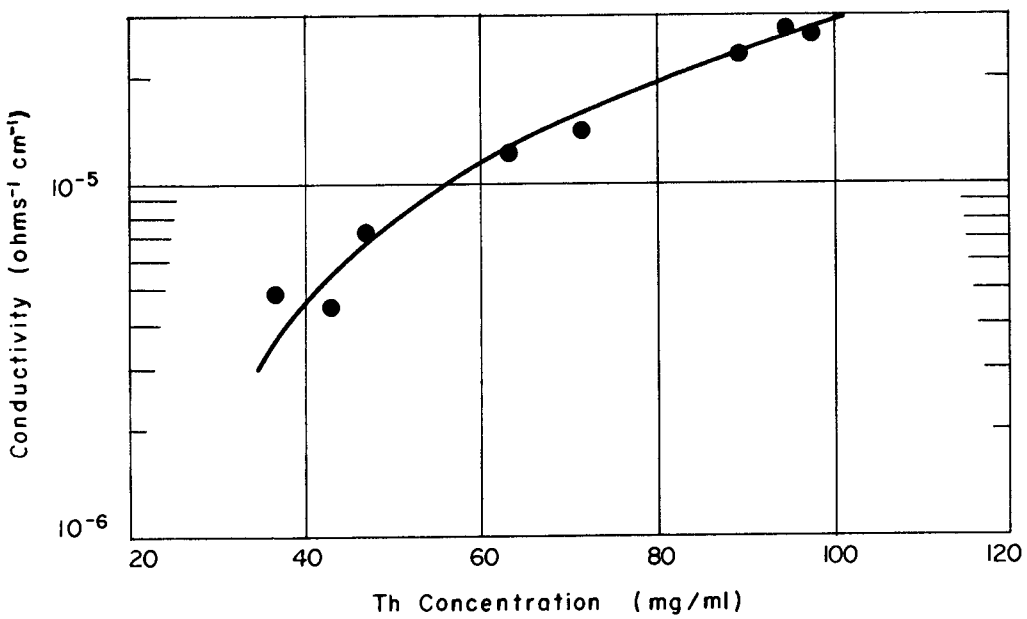

Solvent: 42.2 % TBP in Amsco 125-90W

Fig. A-2. ELECTRICAL CONDUCTIVITY OF A-COLUMN EXTRACT AS A FUNCTION OF THE THORIUM CONCENTRATION (Semi-log Scale).

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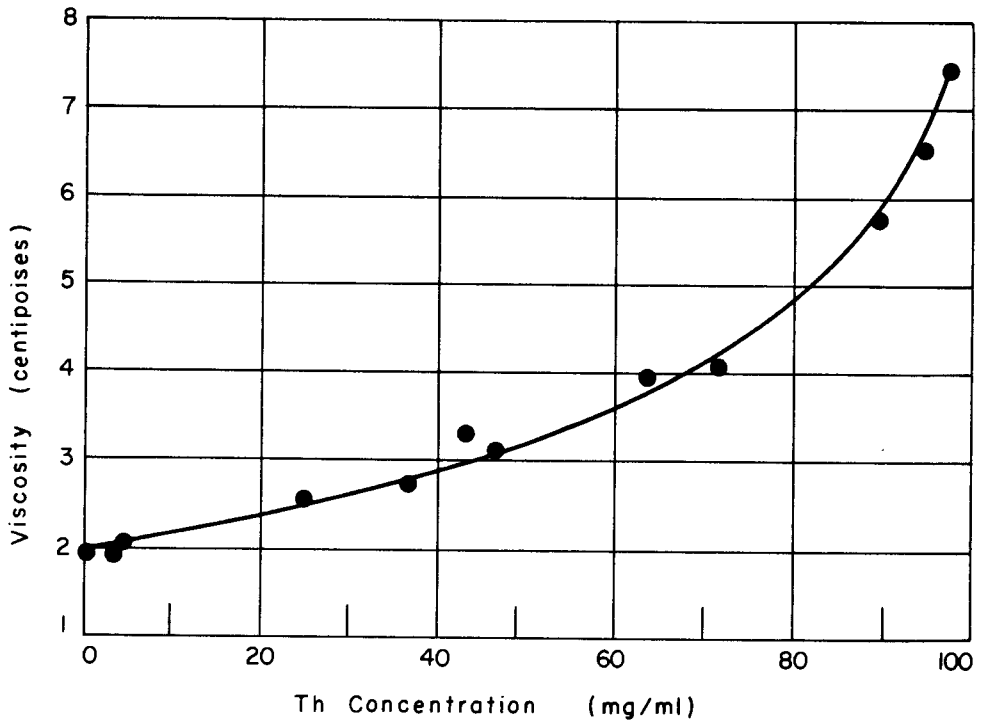

Solvent: 42.4 % TBP in Amsco 125-90W

Fig. A-3 VISCOSITY OF A-COLUMN EXTRACT AS A FUNCTION OF THE THORIUM CONCENTRATION.

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The density of the extract is plotted as a function of the thorium concentration in Fig. A-4. A measure of the viscosity or the density may be used to indicate the thorium content of the extract. However, the sampling difficulties in obtaining a measurement of either of these properties of the organic phase within the column may restrict the use to monitoring the terminal streams of the column, or to critical points within the column.

Properties of the Aqueous Phases. The conductivities of the A-column aqueous solutions are plotted in Fig. A-5 as a function of the thorium concentration. The conductivity of the aqueous phase in the scrub section of the column shows a leveling off of the conductivity at concentrations above 120 mg/ml. Similar behavior is expected in the extraction section. The higher conductivity of the aqueous phase in the extraction section compared to that of the scrub section is attributed to the lower acid deficiency. If this acid deficiency varies in the extraction section, it will be reflected in the conductivity and will make this measurement unreliable for indicating thorium concentration. In the scrub section, conductivity may be used as a measure of the thorium concentration below 100 mg/ml.

The conductivities of the aqueous phase of the B-column are plotted in Fig. A-6 as a function of the thorium concentration. The plot shows that the conductivity is dependent on the position within the column as well as the thorium concentration. This behavior is probably caused by changes in the nitric acid concentration along the column. The mobility of the hydrogen ion, which is present because of the free acid, is greater than that of the other ions in these solutions and would therefore have a large effect on the conductivity.

Figure A-7 shows the effect of thorium concentration on the viscosity of the aqueous phase in the A- and B-columns. The slopes of the curves indicate that the value of the viscosity may be used to indicate the thorium concentration.

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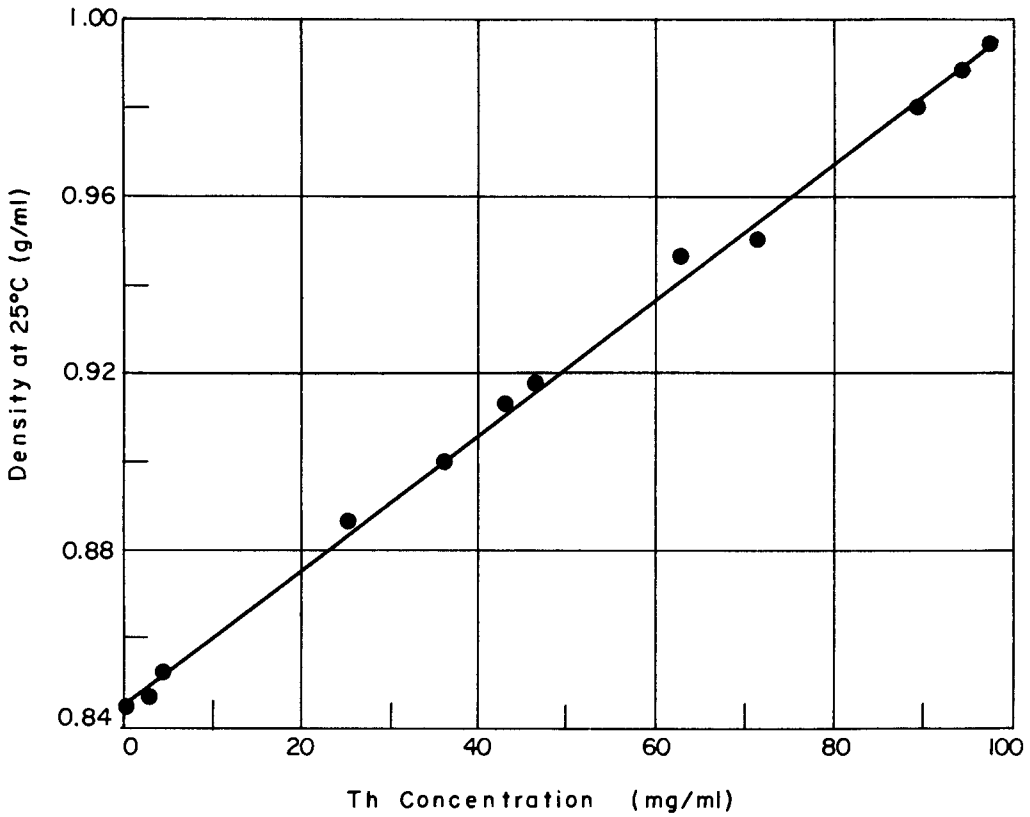

Solvent: 42.2 % TBP in Amsco 125-90 W

Fig. A-4 DENSITY OF A-COLUMN EXTRACT AS A FUNCTION OF THE THORIUM CONCENTRATION.

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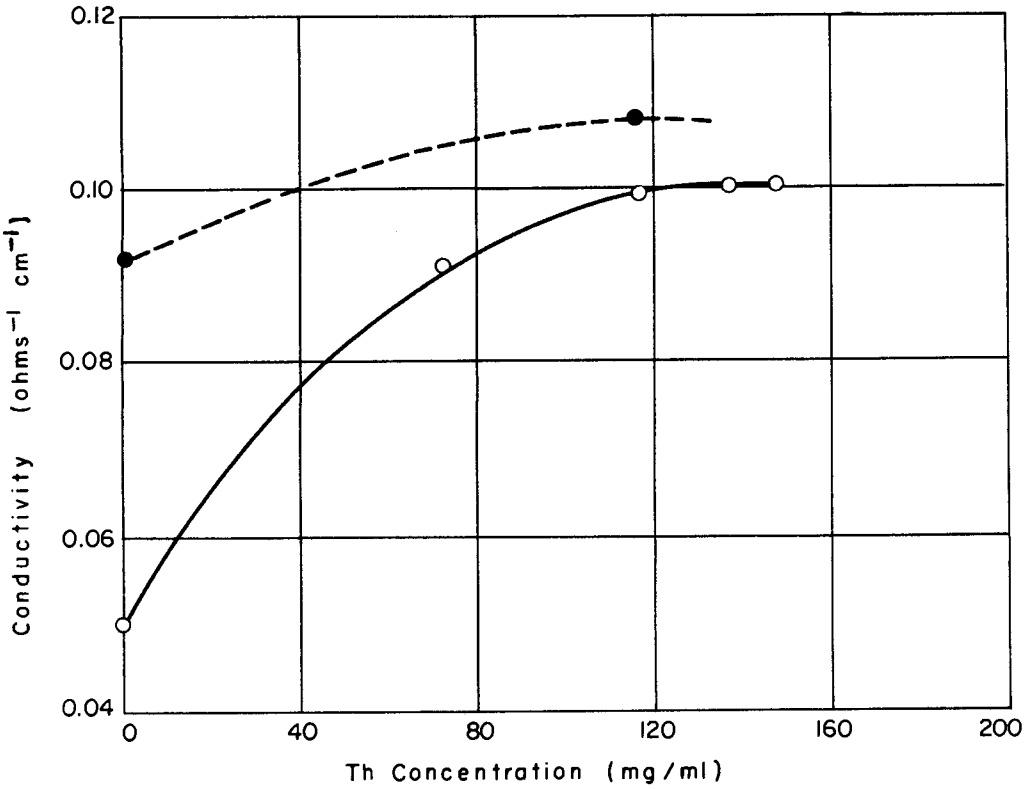

——— Extraction section

——— Scrub section

Fig. A-5 CONDUCTIVITIES OF A-COLUMN AQUEOUS SOLUTIONS AS A FUNCTION OF THE THORIUM CONCENTRATION

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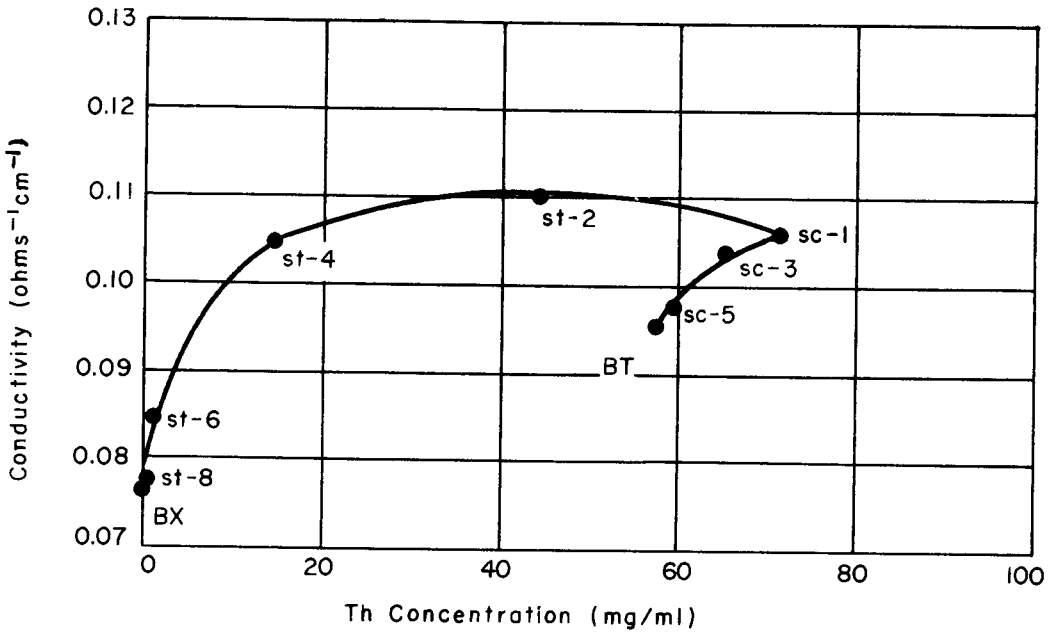

St = Stage number in strip section.

Sc = Stage number in scrub section.

Fig. A-6 CONDUCTIVITY OF B-COLUMN AQUEOUS SOLUTIONS AS A FUNCTION OF THE THORIUM CONCENTRATION.

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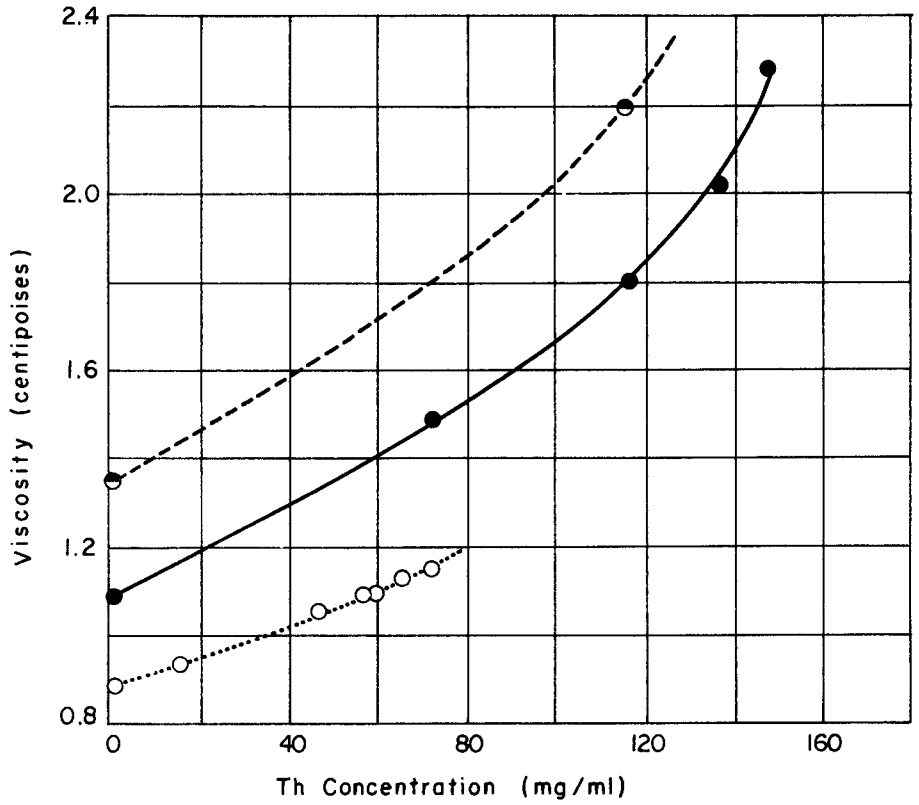
Dwg No 18970



A-Column Extraction Section, 0.5 *M* Al, 0.2 *M* acid deficient.

A-Column Scrub Section, 0.5 *M* Al, 0.7 to 0.8 *N* acid deficient.

B-Column, 0.19 *M* HNO_3.

Fig. A-7. EFFECT OF THORIUM CONCENTRATION ON VISCOSITY OF THE AQUEOUS PHASES IN THE A- AND B-COLUMNS. DATA TAKEN FROM TABLES A-1 – A-3.

JF

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[redacted]

The influence of the uranium on the physical properties of the solutions in the A- and B-columns was not noticeable because of its low concentration relative to the other ionic constituents. The conductivity of the aqueous phase of the C-column shows a decided change with the uranium concentration. The changes in the other properties of the solutions in this column are negligible, as can be seen in Table A-3.

The profile plots of concentration, viscosity, conductivity, and density of the aqueous and organic phases in the A- and B-columns are shown in Figs. 4-2 and 4-5.

A-2 Proposed Reactions in the HNO_3-Hg^{++} Dissolution of Aluminum Metal

When aluminum metal is dissolved in nitric acid containing mercury catalyst, aluminum nitrate is the initial reaction product:

$$Al + 3.75\ HNO_3 \xrightarrow{Hg^{++}} Al(NO_3)_3 + 0.225\ NO\uparrow + 0.15\ N_2O\uparrow + 0.1125\ N_2\uparrow + 1.875\ H_2O.$$

However, in the presence of excess metal, the reaction will proceed to form "acid-deficient" aluminum nitrate, presumably by virtue of "free" nitric acid formed by hydrolysis of the nitrate salt:

$$Al + 0.875\ Al(NO_3)_3 + 1.875\ H_2O \xrightarrow{Hg^{++}} 1.875\ Al(OH)_2NO_3 + 0.225\ NO\uparrow + 0.15\ N_2O\uparrow + 0.1125\ N_2\uparrow$$

To define and describe the nitric acid consumption in the preparation of HNO_3-deficient aluminum nitrate and/or dibasic aluminum nitrate by the HNO_3-Hg-Al reaction, the series of reactions below are postulated. Whole numbers are used to permit direct comparison of acid consumption.

(1) $36\ Al + 136\ HNO_3 \xrightarrow{Hg^{++}} 6\ Al_6(NO_3)_{18} + 10\ NO + 6\ N_2O + 3\ N_2 + 68\ H_2O$

(2) $36\ Al + 130\ HNO_3 \xrightarrow{Hg^{++}} 6\ Al_6(OH)(NO_3)_{17} + 10\ NO + 6\ N_2O + 3\ N_2 + 62\ H_2O$

(3) $36\ Al + 124\ HNO_3 \xrightarrow{Hg^{++}} 6\ Al_6(OH)_2(NO_3)_{16} + 10\ NO + 6\ N_2O + 3\ N_2 + 56\ H_2O$

(7) $36\ Al + 100\ HNO_3 \xrightarrow{Hg^{++}} 6\ Al_6(OH)_6(NO_3)_{12} + 10\ NO + 6\ N_2O + 3\ N_2 + 32\ H_2O$

(12) $36\ Al + 70\ HNO_3 \xrightarrow{Hg^{++}} 6\ Al_6(OH)_{11}(NO_3)_7 + 10\ NO + 6\ N_2O + 3\ N_2 + 2\ H_2O$

(13) $36\ Al + 64\ HNO_3 + 4\ H_2O \xrightarrow{Hg^{++}} 6\ Al_6(OH)_{12}(NO_3)_6 + 10\ NO + 6\ N_2O + 3\ N_2$

(14) $36\ Al + 58\ HNO_3 + 10\ H_2O \xrightarrow{Hg^{++}} 6\ Al_6(OH)_{13}(NO_3)_5 + 10\ NO + 6\ N_2O + 3\ N_2$

[redacted]

Note that Eq. (1) represents the formation of aluminum nitrate, $Al(NO_3)_3$; Eq. (7), that of monobasic aluminum nitrate, $Al(OH)(NO_3)_2$; and Eq. (13), that of dibasic aluminum nitrate or "Diban," $Al(OH)_2NO_3$. Equation (14) conforms with the composition postulated for the solid Diban produced in the laboratory by the precipitation method described in Sec. 5.3.

Reaction rates obviously decrease as the dissolving solution becomes more acid-deficient, and significant quantities of heat must be supplied to sustain the reaction. However, it can be observed that raw material costs for production of Diban are less than those for aluminum nitrate. Diban production appears peculiarly adaptable to the vertical continuous dissolver developed[8] by the Unit Operations Section.

A-3 The pH and Specific Gravity of Acid-Deficient Aluminum Nitrate Solutions as Functions of Hydroxyl Ion Concentration

(R. P. Wischow)

The pH and specific gravity of 4 M basic aluminum nitrate solutions vary as the mole ratio of hydroxyl ion to nitrate ion changes (see Table A-5).

Table A-5

Variation of pH and Specific Gravity with Variation in OH/NO_3 Ratio

Conditions: 4 M Al^{3+}, measured at 21.5°C

OH^- (M)	NO_3^- (M)	pH	Specific Gravity
2.0	10.0	1.0	1.3797
4.0	8.0	1.25	1.3675
5.0	7.0	1.4	1.3595
6.0	6.0	1.6	1.3528
7.0	5.0	1.8	1.3425
8.0	4.0	2.0	1.3327

A-4 Scintillation Spectrography for Identification of Pa^{233}, Th^{234} Fission Products, and Thorium Daughters

Scintillation spectrograms have been obtained* to supplement radiochemical analyses, especially under conditions limited by low activity levels. Figures A-8 through A-10 are presented to illustrate the nature of these spectrograms.

A-5 Properties of Diisobutyl Carbinol**

Diisobutyl carbinol, nonyl alcohol, is a nine-carbon secondary alcohol having a relatively high boiling point. It is only slightly soluble in water, but is miscible with most organic liquids. Diisobutyl carbinol and water form a heterogeneous constant-boiling mixture, which contains 29.6% by weight of the alcohol and boils at 98.5°C.

Diisobutyl carbinol has a pronounced and persistent defoaming action on aqueous systems when present in minute quantities. Usually, the amount needed is near the solubility of diisobutyl carbinol in the aqueous system involved. Physical properties of DIBC are shown in Table A-6.

Table A-6

Physical Properties of Diisobutyl Carbinol

Nomenclature	2,6-Dimethylheptanol-4, or nonyl alcohol
Formula	$(CH_3)_2CHCH_2CHOHCH_2CH(CH_3)_2$
Molecular weight	144.25
Specific gravity at 20/20°C	0.8121
Boiling point at 760 mm	173.3°C
Vapor pressure at 20°C	0.3 mm Hg
Freezing point	-65°C
Solubility in water at 20°C	0.06% by wt.
Solubility of water in DIBC at 20°C	0.99% by wt.
Absolute viscosity at 0°C	56.0 centipoises
Absolute viscosity at 20°C	14.3 centipoises
Average weight at 20°C	6.75 lb/gal

*In cooperation with S. A. Reynolds of the Analytical Chemistry Division.

**Information taken from C and CCC Form No. F-7001 (October, 1948).

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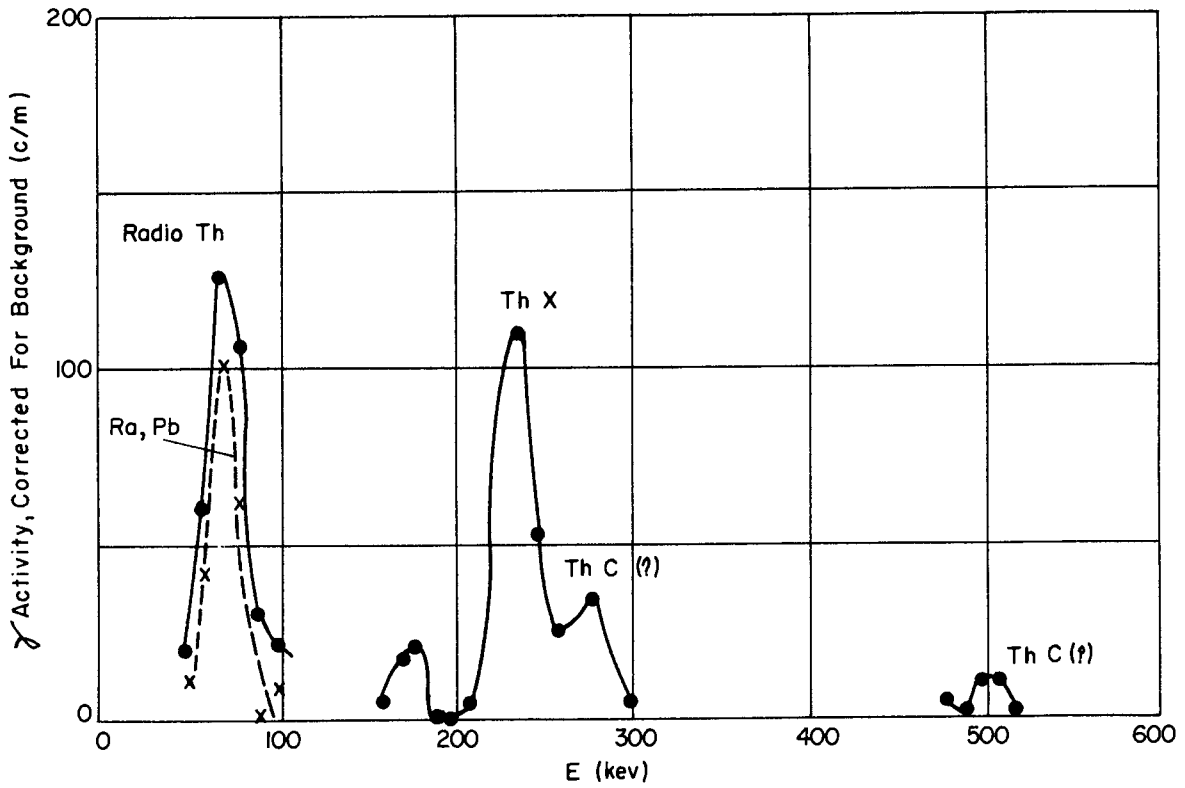

● Natural Thorium feed solution (dissolver solution)

x Barium sulfate precipitate

Fig. A-8. SCINTILLATION SPECTROGRAM OF THORIUM DAUGHTERS, AT 70, 240, AND 180 kev; CONFIRMED BY BARIUM SULFATE PRECIPITATION.

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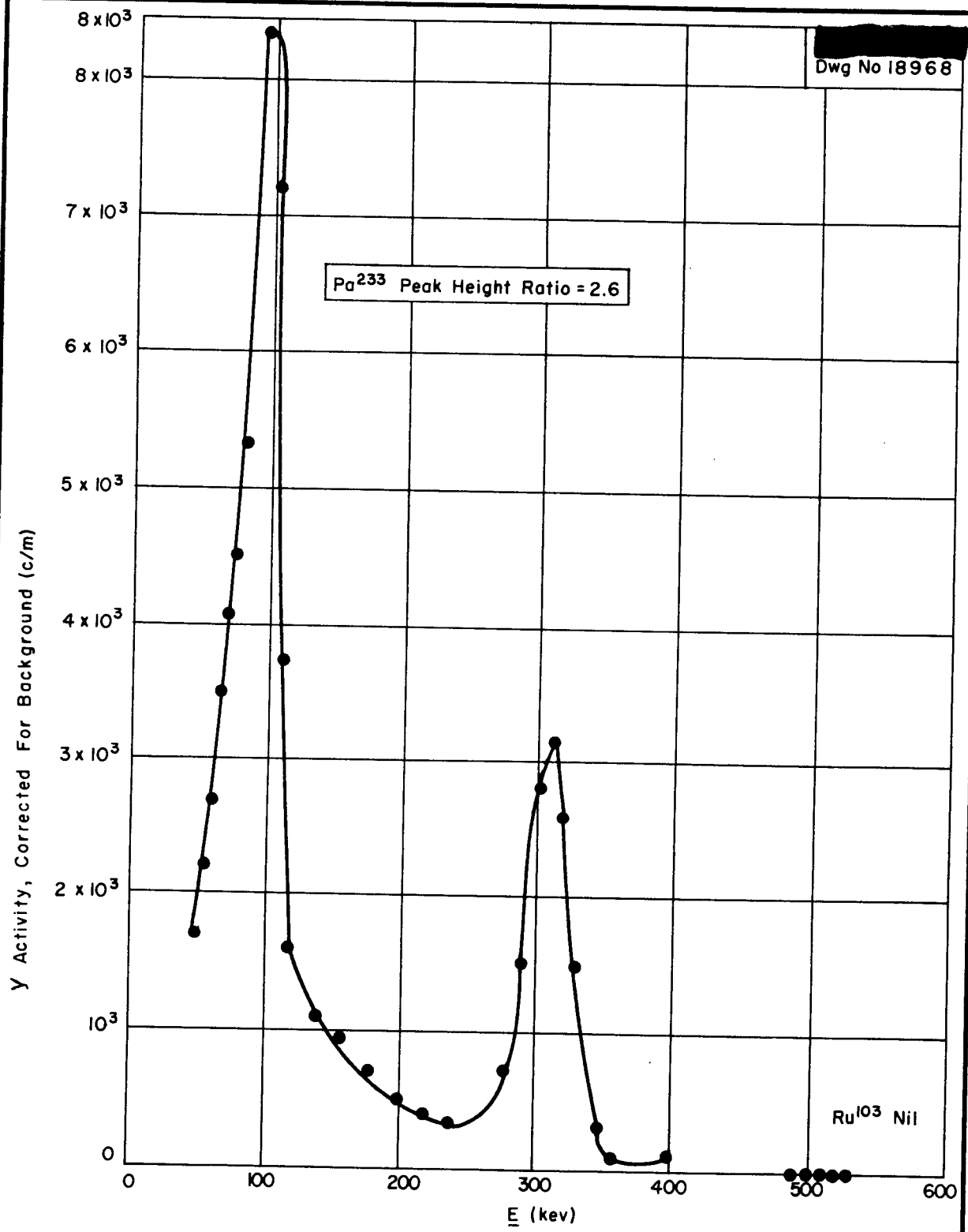

Fig. A-9. SCINTILLATION SPECTROGRAM OF Pa^{233}; MADE FROM THORIUM FEED SOLUTION SPIKED WITH INTERIM-23 DISSOLVER SOLUTION. (RUN X-119)

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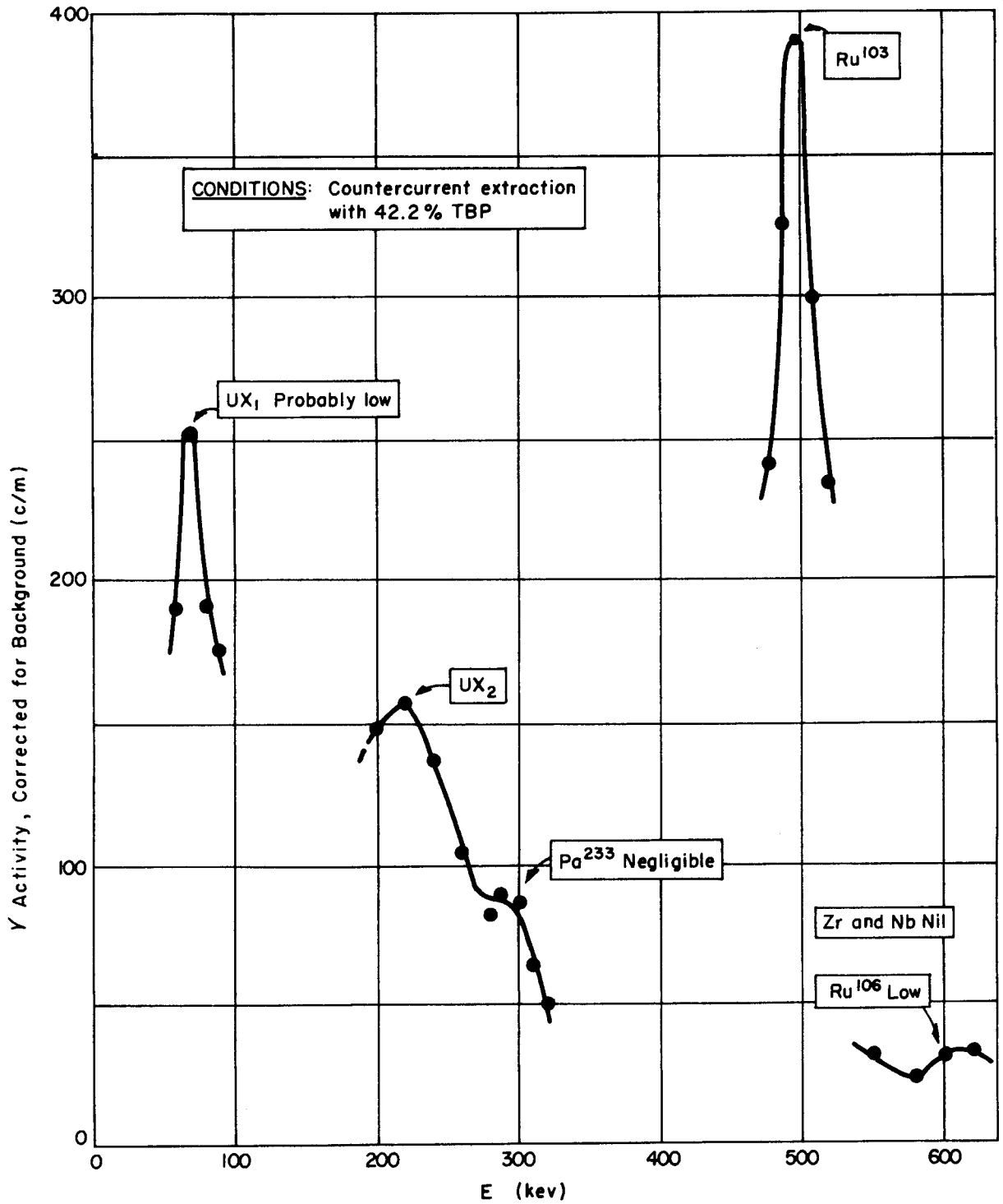

Fig. A-10 SCINTILLATION SPECTROGRAM OF THOREX BT STREAM COMPONENTS, 8th SCRUB STAGE ORGANIC PHASE, THE AF SPIKED WITH INTERIM-23 FEED (Run X-119).

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A-6 The Distribution of Nitric Acid in an $Al(NO_3)_3$-DIBC System

(J. E. Savolainen)

The distribution of nitric acid between DIBC and a 1.9 M $Al(NO_3)_3$ solution containing nitric acid was determined. The results (plotted in Fig. A-11) show the distribution coefficient as a function of the nitric acid concentration in the aqueous phase. At saturation the DIBC/HNO_3 ratio appears to be about 3.33.

A-7 Regeneration of Silica Gel Used in Diluent Preconditioning

(W. T. McDuffee)

The material adsorbed on the silica gel may be removed by passing 2 volumes of methanol through the bed at 25 to 30°C and then displacing the methanol with previously treated diluent at a temperature of 70 to 80°C. It was necessary to remove practically all the methanol from the silica gel in order to restore its adsorption ability. The hot diluent serves to displace and distill the methanol from the bed. About 1.5 volumes of diluent are required to remove the methanol thoroughly.

Because of the mixing of the diluent and the methanol during the elution, some means must be provided for separating these from each other and from the eluted impurities. A distillation step appears to be indicated. Methanol will dissolve ~10% by volume of the diluent. Excess diluent remains as a separate phase. This makes for somewhat easier separation and handling of the eluting and displacing volumes.

The regenerated silica gel apparently is not completely restored to its original capacity by this method, but the useful life of the adsorbent is effectively lengthened. It will probably be more convenient to use the silica gel only once than to regenerate it, since the capital outlay for the methanol recovery equipment would not justify its installation. The figures in Table A-7 are presented to show the approximate cost of the silica gel, which would be added to the cost of the diluent if the silica gel is used only once. It may be seen that the materials cost, assuming 97% recovery of the diluent, would be $0.192 per liter, or $0.736

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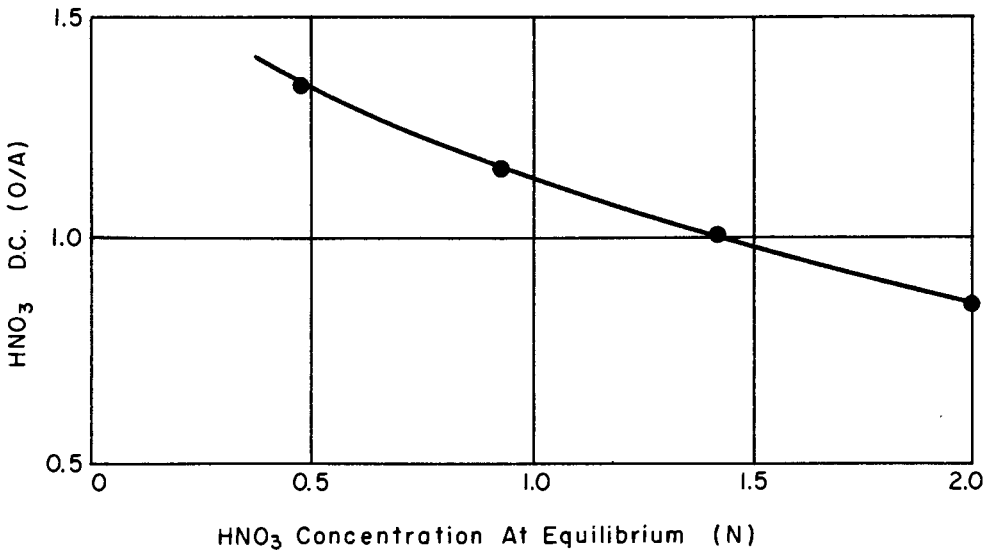

Fig. A-II DISTRIBUTION COEFFICIENTS OF NITRIC ACID BETWEEN DIBC AND 1.9 *M* $Al(NO_3)_3$ SOLUTION CONTAINING NITRIC ACID.

JF

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per gallon. Silica gel, on this basis, would impose an additional cost of only $0.078 per gallon of Amsco 125-90W, and the reuse of silica gel does not appear essential.

Table A-7

Cost of Materials Used in Diluent Preconditioning

Basis	
Diluent, per gallon	$0.43
Silica Gel, Davidson's refrigeration grade	0.50
Nitric acid, c.p., 70%, per pound	0.15
Calcium hydroxide, c.p., per pound	0.50
Requirements	
Diluent, 25 liters	$2.85
Nitric acid, 10 N, 60% consumed, 2.5 liters	0.152
Calcium hydroxide, 100% consumed, 500 g	0.552
Silica gel, 100% consumed, 1 liter	1.110
Total	$4.654

A-8 Hazards Involved in the Use of Silica Gel Columns with Volatile Solvents

(W. T. McDuffee)

An incident has been reported[9] in which sufficient static charge was built up by packing silica gel into a glass column (2 in. diameter, 4 ft. long) to generate a spark and ignite vapors of isooctane (b.p. 117.2°C at 760 mm Hg) being poured on the bed.

Subsequent testing revealed that a charge, generated during loading of the column through a ceramic-coated metal funnel, had collected on both the funnel and the silica gel. When the funnel, which was chipped in spots to expose the metal, was brought close to the lead of a grounded voltmeter, a visible spark jumped the gap. It was also found that when a column

equipped with a grounded wire braid around the outside and extending over into the silica gel bed was packed, a potential of 25 volts existed between the braid and a probe-lead inside the bed. The potential was proportional to the area of the gel in contact with the grounded wire braid. The use of a grounded metal funnel resulted in no charge being built up on the funnel or the apparatus even though the apparatus itself was not grounded.

The following recommendations are made for use with silica gel columns processing volatile solvents:

1. Ground all metal apparatus.
2. Use grounded metal funnels for loading.
3. If possible, use metal columns rather than glass.
4. Check for static charges before introducing volatile solvent into the bed.
5. Use a closed system.
6. Flush the system with an inert gas prior to introduction of the volatile solvent.

Hydrocarbon diluents absorb very little moisture and, when pumped or moved through nongrounded systems such as ceramic filters or rubber hose, or even when allowed to drop free in electrically insulated tanks, will create an appreciable electrical charge. Therefore, all such equipment as drum loaders, tanks, dollies, and pipes should have some <u>positive</u> ground connection. Automatic grounding devices should be provided to permit the safe handling of volatile solvents.