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LABORATORY DEVELOPMENT OF THE ACID THOREX PROCESS FOR RECOVERY OF CONSOLIDATED EDISON THORIUM REACTOR FUEL

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL DEVELOPMENT SECTION B

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ABSTRACT

The acid Thorex process, in which nitric acid is the "salting" agent in the solvent extraction of thorium and uranium from an acid deficient feed with TBP in Amsco, was demonstrated in laboratory equipment for the recovery of synthetic Consolidated Edison Thorium Reactor fuel containing tracer fission products. The acid was removed from solution of the declad fuel pellets to produce an acid deficient feed by steam stripping, and the adjusted feed was treated with bisulfite to decrease the extractability of fission products. The thorium and uranium were extracted with 30% TBP in Amsco, and pregnant organic was scrubbed with dilute nitric acid to improve decontamination. Additional acid was added to the extraction section to increase the distribution coefficient of the thorium. The thorium and uranium could then be stripped either simultaneously or separately. No difficulties were found with either excessive reflux of acid or thorium, or with the formation of a second organic phase.

Decontamination factors from ruthenium γ, zirconium-niobium γ, protactinium γ, and rare earth β were about 1000, 5000, 1000, and 10^5, respectively, and uranium and thorium losses to the aqueous phase were <0.01 and $<0.3\%$. The concentrated aqueous waste was about 0.2 liter per kilogram of thorium processed, about 1/10 of that from the aluminum nitrate-salted process.

Engineering studies showed that the stage height in the extraction column with the acid Thorex process was 2.1 ft compared with 4 ft with the aluminum-salted Thorex process.

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1.0 INTRODUCTION

The development of the acid Thorex solvent extraction process with synthetic Consolidated Edison Thorium Reactor fuel solutions in laboratory equipment is summarized. The flowsheet conditions most extensively investigated were those that might be used in the ORNL Pilot Plant, but operating parameters were investigated sufficiently to adapt the process to the recovery of other fuels in other facilities. The principal advantage of this process over the original Thorex process is that the use of nitric acid as a "salting" agent in the extraction step results in an aqueous waste volume about 1/10 that from the aluminum-salted flowsheet.

The original Thorex flowsheet (1) was developed for the recovery of aluminum-clad thorium metal that had been irradiated to about 600 g of U-233 per metric ton of thorium, and used the dissolved aluminum from the clad as the salting agent in the feed and additional aluminum nitrate in the scrub. Decontamination was maximum when the feed and scrub were both acid deficient. However, nonvolatile aluminum nitrate in the concentrated aqueous waste solution resulted in much higher waste volume than in the nitric acid—salted Purex process for the recovery of uranium. In attempts to develop a flowsheet with aluminum and acid in the feed and acid in the scrub, a second organic phase formed or decontamination factors were lower (2). A flowsheet with acidified solvent was developed for recovery of unirradiated thorium (3), but in experiments at ORNL with irradiated thorium decontamination from fission products was low.

The elimination of aluminum as a cladding material for power reactor fuels and the removal of the cladding prior to the processing of the irradiated thorium added new impetus to the development of a solvent extraction flowsheet that does not require aluminum salting. The use of Decalin instead of Amsco as diluent for the tributyl phosphate (4,5) increases the solubility of the thorium-TBP complex in the presence of nitric acid and therefore decreases the difficulty with the formation of a second organic phase. However, decontamination factors are not so high as in the acid deficient process and the height of a theoretical stage in a pulsed column is greater. The acid Thorex process described in this report eliminates the necessity of aluminum as a salting agent without decreasing decontamination from fission products or increasing losses to the aqueous phase.

The greater difficulty in decontaminating thorium than uranium and the greater extraction of nitric acid in the presence of thorium than with uranium are apparent from the approximate extraction constants,

$$\begin{array}{lcll}
H^{+}_{(a)} + NO_3{}^{-}_{(a)} + TBP_{(o)} & \rightleftharpoons & HNO_3 \cdot TBP_{(o)} & K_H = 0.145 \\
Zr_{(a)} + NO_3{}^{-}_{(a)} + 2TBP_{(o)} & \rightleftharpoons & Zr(NO_3)_4 \cdot 2TBP_{(o)} & K_{Zr} = 0.0032 \\
UO_{2(a)} + 2NO_3{}^{-}_{(a)} + 2TBP_{(o)} & \rightleftharpoons & UO_2(NO_3)_2 \cdot 2TBP_{(o)} & K_{UO_2} = 5.5 \\
Th_{(a)} + 4NO_3{}^{-}_{(a)} + 2TBP_{(o)} & \rightleftharpoons & Th(NO_3)_4 \cdot 2TBP_{(o)} & K_{Th} = 0.85
\end{array}$$

which show that the separation factors of zirconium or nitric acid from uranium will be about 6.5 times as great as their separation from thorium.

The authors wish to thank the groups with G. R. Wilson and E. I. Wyatt for analytical services and P. F. Thomason and S. A. Reynolds for assistance in interpretation of analytical data, all members of the ORNL Analytical Chemistry Division.

2.0 ACID THOREX PROCESS FLOWSHEET

The fuel elements for the Consolidated Edison Thorium Reactor are stainless steel-clad 95% ThO_2 fuel pellets. The clad will be dissolved from the irradiated elements by sulfuric acid (Sulfex process) or dilute aqua regia (Darex process) (6). The declad pellets will be dissolved in 13 M HNO_3 containing fluoride to catalyze thorium dissolution and aluminum to decrease corrosion by the fluoride. The amount of nitric acid, fluoride, and aluminum used will depend on the type of pellet and possibly on the irradiation history of the fuel. The feed will be made acid deficient by evaporating to a boiling point of 135°C and steam stripping, and prior to the solvent extraction step will be heated at 55°C with 0.02 M bisulfite to convert the ruthenium to a nonextractable species.

The feed will be extracted with 30% tributyl phosphate (TBP) and scrubbed with 1 M HNO_3, followed by a scrub with water containing phosphate and ferrous sulfamate (Fig. 1). In the laboratory experiments, the single extraction step resulted in typical decontamination factors of 1000, 5000, 1000, and 10^5 from ruthenium, zirconium-niobium, protactinium and rare earth elements. Uranium and thorium losses were 0.01% and 0.3% or less. The extracted thorium and uranium may be selectively stripped or co-stripped as desired, and additional solvent extraction cycles may be used to increase decontamination.

The acid Thorex flowsheet is very flexible and may be varied to give maximum decontamination of feeds with various fission product ratios or adapted to available process equipment.

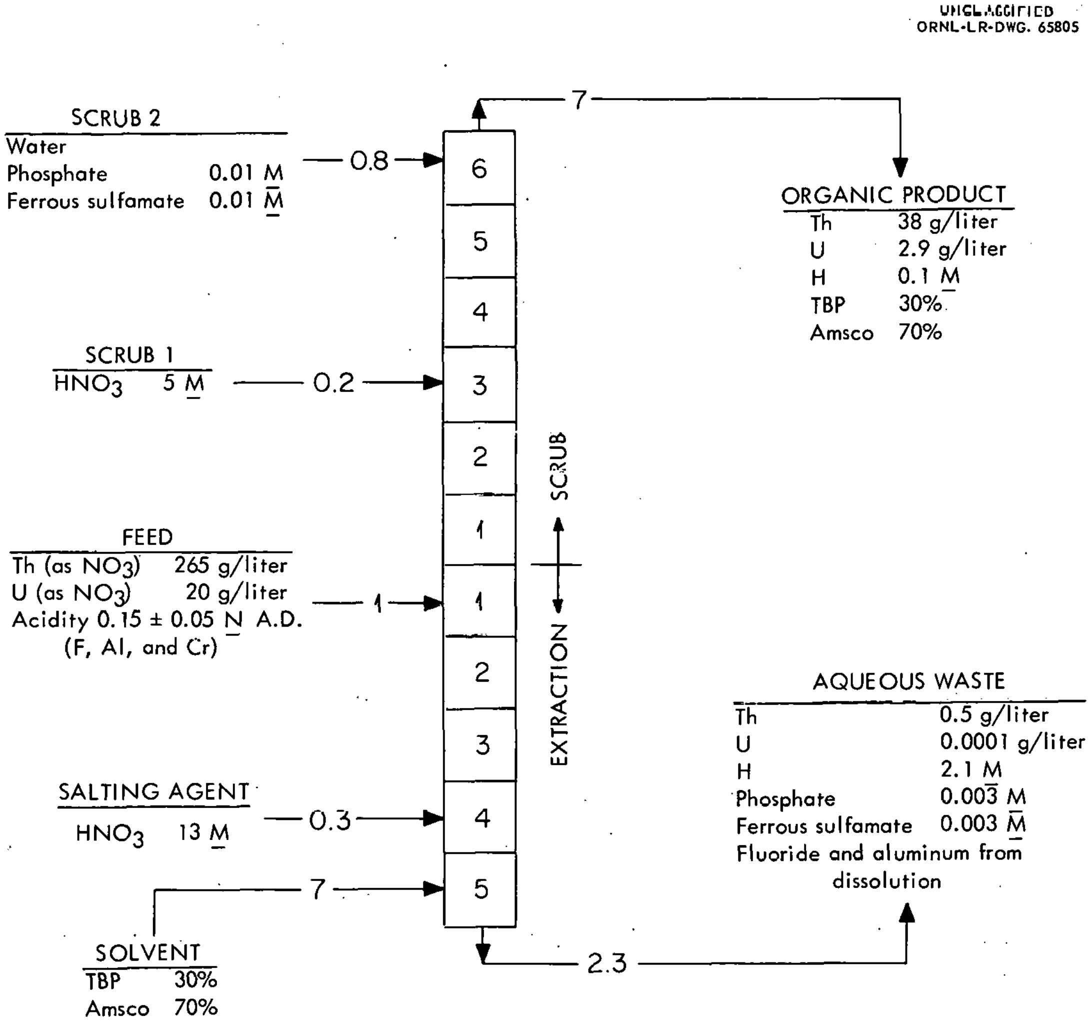

Fig. 1. Acid Thorex flowsheet for extraction of thorium from acid deficient feed by 30% TBP.

3.0 FEED ADJUSTMENT

The dissolver product contains ~1 M Th, ~0.06 M U, and ~9 M HNO_3. The best method found, in laboratory tests, for converting this solution to acid deficient conditions was to evaporate to a boiling point of 135°C to remove the bulk of the acid and then to steam strip to remove the remainder. The conversion of the solution to acid deficient conditions converts the zirconium-niobium, protactinium, and ruthenium to much less extractable species. Subsequent additions of 0.02 M $NaHSO_3$ and heating to 55°C for 1 hr further decreases the extractability of the ruthenium (5). The alternative feed adjustment method investigated consisted of evaporating to a boiling point of 165°C. This method does not require the steam stripping step but is not recommended due to increased corrosion at the higher temperature.

In the aluminum-salted Thorex flowsheet, heating the feed to 150°C to make it acid deficient results in low ruthenium and zirconium-niobium extraction (1). However, when this procedure was used with highly irradiated, short-decayed thorium, ruthenium extraction was high, apparently because of radiolytic conversion of nitrate to nitrite, which in turn reconverted the ruthenium to an extractable species. Treatment of this irradiation feed with bisulfite resulted in decontamination factors even greater than the factor for unirradiated and untreated feed (5).

Evaporation Studies. Evaporation of thorium nitrate—nitric acid solutions of the concentration range expected from the dissolution of thorium (25-200 g/liter Th and 2-9 M HNO_3) to a boiling point of >160°C removed all excess acid. The nitric acid concentration in the evaporator increased to a maximum as water was boiled off and then decreased, approaching zero as the thorium concentration increased to ~1300 g/liter (Fig. 2). The slopes of the boildown curves approach a common line for any initial solution composition. This line is nearly linear and can be extrapolated to azeotropic nitric acid at zero thorium concentration. Between 100 and 122°C the boiling points of the mixture of thorium nitrate and nitric acid lie on approximately straight lines connecting the nitric acid and thorium nitrate axes. The line connecting mixtures that boil above 122°C terminates

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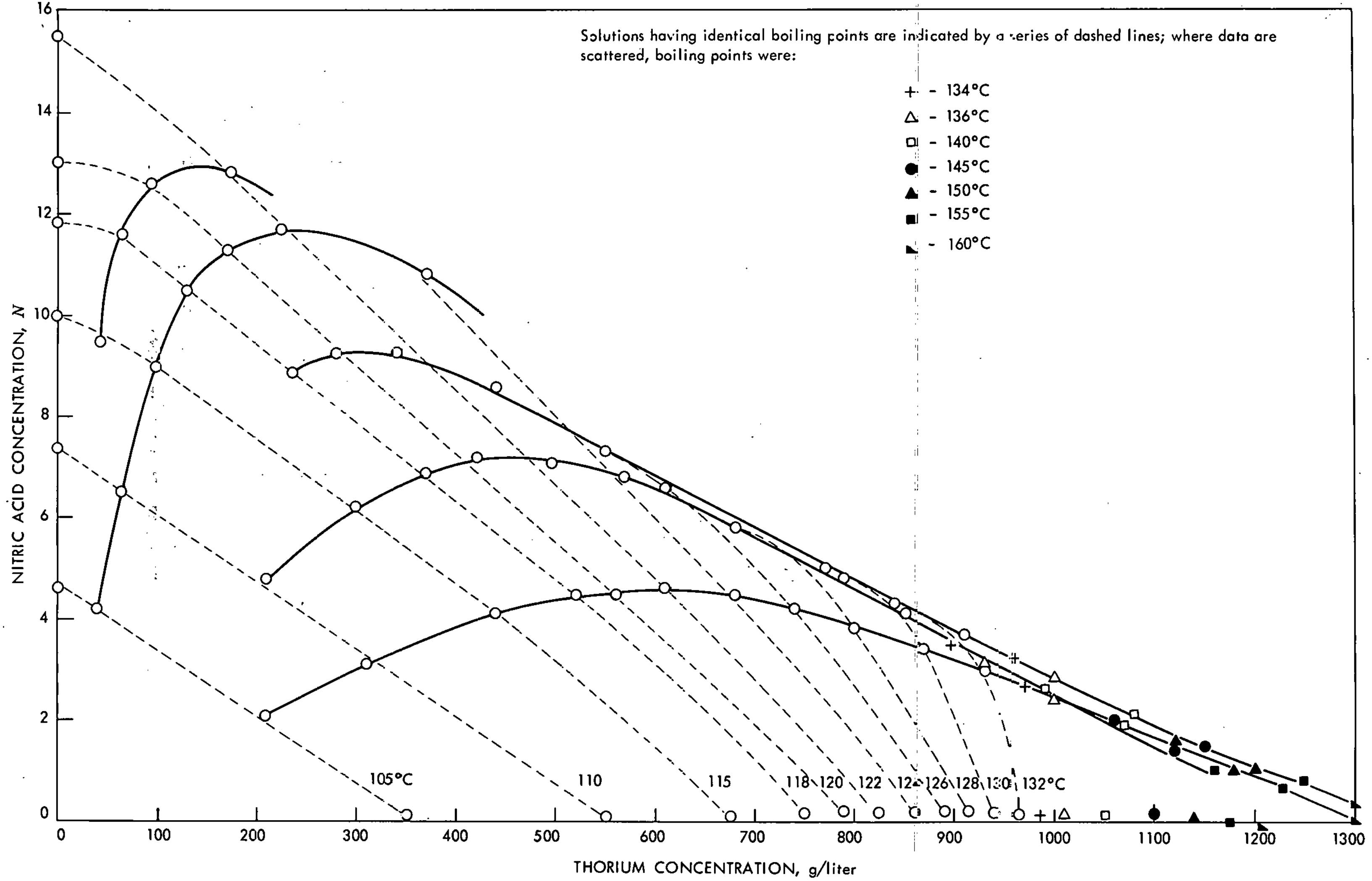

Fig. 2. Evaporation curves of thorium nitrate—nitric acid solutions.

at the line connecting 15.5 M HNO_3 and 1300 g/liter Th. The composition of the pot was determined by material balance, and errors were therefore large at high concentrations. However, solutions that were evaporated to a boiling point $>160^{\circ}C$ were acid deficient.

The evaporation curves of actual dissolver solutions deviated slightly from the data given above because of other ions. In a typical boildown curve for a dissolver solution containing 240 g of thorium and 9.5 g of uranium per liter, 8.78 M HNO_3, and 0.1 M boron (added to study compatibility in homogeneous neutron control) (7), all acid was removed when the boiling point reached $137^{\circ}C$ (Fig. 3), at which point the solution composition was then 930 g of thorium and 38 g of uranium per liter and 0.4 M in boron. In order to obtain a solution which upon dilution will result in a solvent extraction feed containing 265 g of thorium per liter, 0.15 M acid deficient, a solution of this composition must be concentrated to a boiling point of $\sim155^{\circ}C$.

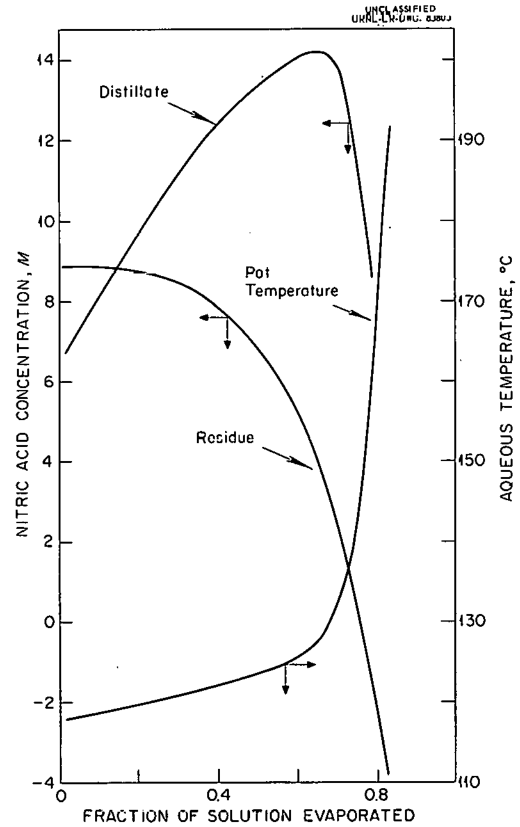

Fig. 3. Evaporation of simulated Consolidated Edison fuel solution.

Steam Stripping Studies. A similar synthetic core solution was made acid deficient by evaporating to a boiling point of 135°C (30% of original volume) and then steam-stripped (Fig. 4). During steam stripping, water was added slowly while the boiling temperature was kept constant. The condensate was 9 M HNO_3 and in a production plant would be recycled. There was no noticable difference in the decontamination from fission products between feed solutions that were adjusted by steam stripping and by the high-temperature boildown.

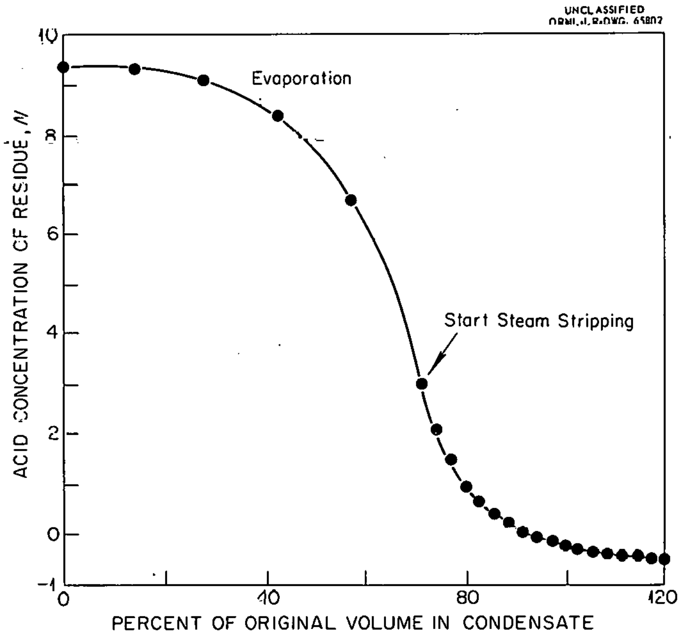

Fig. 4. Steam stripping of simulated Consolidated Edison fuel solution.

4.0 EXTRACTION-SCRUB COLUMN

The effect of a range of extraction and scrub conditions was investigated but no attempt was made to evaluate all the many possible combinations. As extractant, 30% TBP was selected since original plans (subsequently canceled) were to demonstrate the flowsheet in the ORNL pilot plant which would be using this concentration of solvent in other processes. Five extraction and six scrub stages were used because this is the number of stages obtainable in the existing extraction-scrub pulsed column. Other initial conditions were set by existing equipment (evaporators, etc.) or equipment that was being considered for addition to the plant.

In the initial flowsheet conditions (used as a control) the 0.15 M acid deficient synthetic feed contained 260 g of thorium and 20 g of uranium per liter, 1.14 M fluoride, 0.1 M aluminum, and radioactive tracer solution. It was heated 1 hr at 55°C with 0.02 M $NaHSO_3$. The dissolver composition corresponds to that obtained by dissolving Consolidated Edison fuel pellets in 200% excess dissolvent. Thorium and uranium were extracted with 7 vol of 30% TBP in Amsco and the pregnant solvent was scrubbed with 1 vol of 2 M HNO_3 containing 0.01 M H_3PO_4 and 0.1 M $Fe(NH_2SO_3)_2$. One volume of 13 M HNO_3 was added to the fourth extraction stage to increase thorium extraction.

The 2 M HNO_3 scrub was chosen as a result of preliminary data which indicated that a scrub of this composition would give maximum decontamination of a solution containing equal amounts of radioactive ruthenium and zirconium-niobium. Phosphoric acid was added to decrease extraction of zirconium-niobium and protactinium, and ferrous sulfamate was added to prevent extraction of chromium that might be present as a result of corrosion of the stainless steel vessels (8). A concentration of 13 M was selected for the acid to be added to the extraction section because this is the strength of the concentrated nitric acid routinely used in the pilot plant. The radioactive tracer solutions used were determined by availability. The maximum activity that could be safely processed in the laboratory equipment was 2×10^7 gross γ c/min.ml, and ruthenium and zirconium-niobium activities in the feed were usually 1 to 5×10^6 and 2 to 8×10^6, respectively. Therefore when the respective decontamination factors were 10^3 and 10^4 and the activity was diluted by extracting 1 vol of feed with 7 vol of organic, the product activity counted was a fraction of background and the reproducibility of decontamination factors was probably not better than a factor of 2. In order to obtain conditions for most favorable comparison, the same feed solution was used for each run in a comparative series.

4.1 Feed Composition

Bisulfite. Heating the feed at 50°C for 20 min in the presence of 0.02 and 0.05 M $NaHSO_3$ increased the decontamination from ruthenium to 700 and 3800, respectively. With no bisulfite treatment, decontamination was only

130. Decontamination from zirconium-niobium was increased from ~5000 to 7000 with 0.1 M bisulfite, and decontamination from protactinium was erratic:

$NaHSO_3$, M	D.F. from Ru	D.F. from Zr-Nb	D.F. from Pa
0	130	4700	750
0.02	700	3000	500
0.05	3800	--	800
0.10	2000	7000	100

Acidity. In duplicate experiments with feeds 0.14 M acid deficient and 0.01 M acid, decontamination factors from ruthenium were 700 and 30, and from zirconium-niobium were 3000 and 600, respectively. Increasing the acid deficiency to 0.34 M increased the decontamination from zirconium-niobium to 5000 but did not improve decontamination from ruthenium. Decontamination from protactinium decreased with increasing acidity:

Feed Acidity, N	D.F. from Ru	D.F. from Zr-Nb	D.F. from Pa
- 0.34 (a.d.)	800	5000	1000
- 0.14 (a.d.)	700	3000	500
0.01	30	600	-
0.07	30	600	-
0.45	13	2200	200
1.6	18	2200	100

Aluminum and Fluoride. The presence of aluminum and/or fluoride did not affect the decontamination.

4.2 Scrub Variables

Acidity. When the feed solution was maintained about 0.1 N acid deficient, the decontamination factor from zirconium-niobium decreased from 20,000 to 700 as the acidity of the scrub was increased from 0 to 4 N HNO_3. The scatter of data for ruthenium prevents evaluation of the effect of the acid between 0 and 3 N, but with 4 N acid ruthenium was no longer detectable in the product stream. The best decontamination factor from protactinium was 1200 with 1 N HNO_3 in the scrub, with a decrease to

55 with 4 N HNO_3 and about 200 at 0 acidity:

Acidity, N	Decontamination Factor			Acidity, N
Scrub	Ru	Zr-Nb	Pa	Product
0	1,000	17,000	190	0.02
0.5	1,000	22,000	160	0.08
1	570	10,000	1,200	0.11
2	700	3,000	500	0.24
3	1,500	1,000	60	0.35
4	>1,500	700	55	0.45

The concentration of acid in the organic product increased from 0.11 N with a 1 N acid scrub to 0.45 N with a 4 N acid scrub. Acid in the organic product adversely affects partitioning or co-stripping of the products from the organic phase. Since nitric acid is less extractable than either thorium or uranium, it readily moves to the aqueous phase in the strip column where it acts as a salting agent to increase extraction of the metal ions. In order to counteract this salting effect in the partitioning or stripping column, either the number of stages or the volume of the aqueous solution must be increased.

Split Scrub. The use of a divided scrub was investigated in which 80% of the volume of the scrub containing 0.01 M H_3PO_4 and 0.01 M $Fe(NH_2SO_3)_2$ was added at the sixth scrub stage, and the other 20%, 5 N HNO_3 (to give a composite scrub 1 N HNO_3), was added at the second scrub stage. This dual scrub resulted in decontamination factors from ruthenium, zirconium-niobium, and protactinium of 2300, 29,000 and 1000, respectively, and in an organic product containing 0.07 N acid. When the scrub stream was 2.5 HNO_3 (13 N acid in the second scrub) instead of 1 N HNO_3, the corresponding decontamination factors were 5000, 2000, and 100, respectively, and the organic stream contained 0.14 N acid.

4.3 "Salting" Acid

Volume. The volume of "salting" acid added to the column and the location of the addition also markedly affected the thorium and uranium losses. A thorium loss of <0.5 % and a uranium loss of <0.01% were ensured by adding 0.3 vol acid to the fourth extraction stage. Variations in the volume of acid did not markedly change the decontamination from fission products:

Relative Vol	Decontamination Factor Ru	Decontamination Factor Zr-Nb	Decontamination Factor Pa	Thorium Loss, %
None*	--	-	--	23
0.3**	1,000	3,000	~800	0.2
0.5	550	-	1,700	0.3
1	700	3,000	500	0.03
2	1,000	5,600	600	0.03

*Not at equilibrium

**0.2 vol of 5 N HNO_3 added at second scrub stage and 0.8 vol of water added at sixth scrub stage.

When acid was not added to the extraction section the thorium loss was at least 23%. The concentration of the acid added to the column was 13 N to maintain minimum aqueous volume in the extraction section.

Location of Addition Point. The location at which the acid was added modified the acid and thorium profiles of the column and therefore the decontamination from the various fission products. Decontamination factors from ruthenium decreased from about 1000 to 600 and from zirconium-niobium increased from 3000 to 10,000 as the point of addition of the acid moved from the first to the fourth stage. This variation is at the limit of the reliability of the experiments and may not be significant. The Ru and Zr-Nb factors were 120 and 100, respectively, when acid was added to the last stage. Thorium losses to the aqueous phase were:

Extraction Stage	Decontamination Factor Ru	Decontamination Factor Zr-Nb	Thorium Loss, %
1	1,000	3,000	0.27
2	800	-	0.30
3	500	5,000	0.29
4	600	10,000	0.63
5	120	1,500	2.0

For these experiments 0.3 vol of 13 N HNO_3 was added at the extraction stage indicated, 0.2 vol of 5 N HNO_3 was added at the second scrub stage, and 0.8 vol of water was added at the sixth scrub stage. The acid concentration at the feed plate decreased continously from 0.34 to 0.10 N in the organic phase and from 3.5 to 0.68 N in the aqueous phase as the acid addition point was moved from the first to the fifth extraction stage. Likewise, the acid in the organic product stream decreased from 0.17 N when the acid was added at the feed stage to about 0.08 N when added at any of the other stages.

The feed for each of these experiments contained 1 x 10^6 c/m·ml Ru and 5 x 10^6 c/m·ml Zr-Nb, and, except when acid was added at the feed plate, ruthenium was the limiting activity in the product. In an experiment in which the scrub acidity was increased from 1 to 2 N and 0.22 instead of 0.30 vol of 13 N HNO_3 was added at the fourth extraction stage, the acid in the aqueous phase of the extraction section being unchanged, the decontamination factor from ruthenium increased from 600 to 1200 but that from zirconium-niobium decreased from 10,000 to 3400. The resulting product contained about equal quantities of ruthenium and zirconium-niobium with an increase in gross γ decontamination from 4000 to 6000. Similar adjustments may be made to obtain maximum gross γ decontamination when the feed contains other ratios of ruthenium to zirconium-niobium.

Additional experiments made in an attempt to develop a process in which acid could be added at the feed plate were unsuccessful. When the acid was added to the system simultaneously with an acid deficient feed, zirconium-niobium decontamination decreased by a factor of about 10 from that when it was added at the fourth extraction stage. When the acid was added to the feed prior to treatment with bisulfite, ruthenium decontamination also decreased by a factor of 10. In some of the experiments in which acid was added at the feed plate, a second organic phase formed. The second organic phase did not occur in any experiment in which acid was added below the feed plate.

4.4 TBP Concentration

In a series of experiments (Table 1) to determine the range of TBP concentrations that may be used with the acid Thorex flowsheet, thorium losses with 10 and 20% TBP were 78 and 7.6%, respectively. Since the extraction factor at the feed plate with 10% TBP was 0.4, it does not seem likely that a practicable acid-salted flowsheet can be designed with this TBP concentration. However, the extraction factor with 20% TBP was 0.96 and a flowsheet with a larger volume of acid or lower solvent saturation may be satisfactory. With 40% TBP the thorium loss was only 0.005% and the extraction factor at the feed plate was 5.5. Decreasing this extraction factor to 2.7 by decreasing the acid from 1 to 0.25 vol and decreasing the solvent from 7 to 6 vol resulted in decontamination factors from ruthenium, zirconium-niobium, and protactinium of 150, 4000, and 12,000 respectively. It therefore seems possible to adapt the Acid Thorex flowsheet for at least the TBP concentration range 20-40%.

Table 1. Effect of Varying the TBP Concentration in the Acid Thorex Flowsheet

	Feed			Organic Product			Feed Plate				Decontamination Factor				Th	Balance	
TBP, %	Th, g/l	U, g/l	Acid, N a.d.	Th, g/l	U, g/l	H^+, N	Th in Org., g/l	Sat'n, %	D.C. (o/a)	E.F. (o/a)	Gr γ	Ru γ	Zr-Nb γ	Pa γ	Loss, %	Th, %	U, %
10	95	5.7	0.1	2.5	0.74	0.15	7.9	18	0.11	0.39	590	3600	1600	50	77	94	91
20	196	11.2	0.13	19.4	1.6	0.2	37	42	0.28	0.96	1100	2700	3180	140	7.6	79	102
30	278	16.2	0.16	40	2.03	0.24	50	38	0.50	1.7	660	600	900	100	0.08	101	88
40	363	21.5	0.1	55	2.6	0.4	58	33	1.58	5.5	940	342	900	220	0.005	107	86

In these experiments the concentration of thorium in the feed was varied directly as the TBP concentration, all other conditions remaining constant. Conditions in the experiment with 40% TBP were:

Feed:	360 g/l Th, 21.5 g/l U, 0.1 N a.d., 0.02 M $NaHSO_3$, 1.1 x 10^7 Gr γ c/m·ml, 5.0 x 10^5 Ru γ c/m·ml, 9 x 10^6 Zr-Nb γ c/m·ml, 5 x 10^5 Pa γ c/m·ml, 1 vol
Scrub:	2 N HNO_3, 0.01 M $Fe(SO_3NH_2)_2$, 0.01 M H_3PO_4, 1 vol, 6th scrub stage
Acid:	13 N HNO_3, 1 vol, 4th extraction stage
Solvent:	40% TBP-Amsco, 7 vol, 5th extraction stage

In the original Thorex process 42.5% TBP was used. In experiments with this TBP concentration, made in order to obtain direct comparison, decontamination factors from ruthenium, zirconium-niobium, and rare earths were about 2500, 4400, and 23,000 and the thorium loss was 0.06% with the acid Thorex flowsheet. Typical decontamination factors with the aluminum-salted Thorex process are 600, 3000, and 2×10^5, respectively, with a thorium loss of about 0.5%. The acid Thorex conditions were:

Feed: 312 g/l Th, 22.4 g/l U, 0.18 N a.d., 1 vol
Scrub No. 1: H_2O, 1 vol, 6th scrub stage
Solvent: 42.5% TBP in Amsco, 6 vol, 5th extraction stage
Acid: 13 N HNO_3, 0.3 vol, 4th extraction stage

4.5 Feed Irradiation

Irradiation of the feed for the acid Thorex process to 5 and 10 whr/liter prior to bisulfite treatment decreased the decontamination from zirconium-niobium, but further irradiation to 40 and 160 whr/liter increased the decontamination from both ruthenium and zirconium-niobium (Table 2). However, the series required ~3 weeks to complete and there was some uncertainty as to whether the improvement in decontamination was the result of irradiation or the effect of aging of the feed.

In a second series of experiments with similar conditions except that a different radioactive feed was used, duplicate experiments were conducted a week apart in which the aqueous feeds were irradiated to 166 whr/liter and compared with control runs made the following day. Since the Zr-Nb tracer concentration was only 5×10^4, the decontamination factors from these fission products are not reliable. Most of the feed activity was cesium and cerium. The decontamination factors from both gross γ and ruthenium γ were about 5 times as large for the irradiated feed as for the control. The gross γ decontamination factors for both the irradiated feed and for the control decreased about a factor of 2 with feed that had been aged for a week.

No explanation has been found for the apparent increase in decontamination on irradiation of the feed.

Table 2. Effect of Irradiation of Feed on Acid Thorex

Decontamination Factors

Feed: 275 g/l Th, 16 g/l U, 0.18 N a.d., treated 1 hr with 0.02 M $NaHSO_3$ at 50°C, 1 vol, stage 1E; in series 1, 1.7 x 10^7 Gr γ c/m·ml, 1.2 x 10^6 Ru γ c/m·ml, 1.3 x 10^7 Zr-Nb γ c/m·ml, in series 2, 1.2 x 10^7 Gr γ c/m·ml, 9.5 x 10^5 Ru γ c/m·ml, 5 x 10^4 Zr-Nb γ c/m·ml

Scrub No. 1: 0.01 M PO_4, 0.01 M $Fe(SO_3NH_2)_2$, 0.8 vol, stage 6S

Scrub No. 2: 5.0 M HNO_3, 0.2 vol, stage 2S

Acid: 13 M HNO_3, 0.5 vol, stage 4E

Solvent: 30% TBP-Amsco, 7 vol, stage 5E

Irradiation, whr/liter	Decontamination Factor			Th Loss, %	Th Balance, %	Feed Age, days
	Gross γ	Ru γ	Zr-Nb γ			
			Series 1			
Control	2,500	370	3,300	0.11	105	2
5.1	1,900	1,200	1,900	0.10	107	1
10.3	1,500	350	1,400	0.07	105	6
41	6,530	970	7,000	0.10	107	7
41	5,700	1,300	4,640	0.05	104	9
165	16,000	1,800	18,000	0.07	106	20
			Series 2			
Control	5,800	356	150	0.45	101	4
165	31,000	1,400	310	0.46	106	3
Control	2,400	470	130	0.43	100	11
167	14,000	2,000	290	0.41	100	10

4.6 Variations in Decontamination in Duplicate Experiments

Average decontamination factors in 10 essentially duplicate laboratory countercurrent batch extraction experiments, performed over a 9-month period with many different tracer solutions, were 1000, 5000, 1000, and 10^5 for ruthenium, zirconium-niobium, protactinium, and rare earths, respectively (Table 3). Uranium and thorium losses were about 0.01 and 0.3%.

Table 3. Decontamination Factors Obtained in Nearly Identical Countercurrent Batch Extraction Experiments

Run No.	Decontamination Factors				Remarks
	Gr γ	Ru γ	Zr-Nb γ	Pa γ	
903	5,800	2,300	29,000	960	
913	1,130	180	5,300	330	
914	1,830	1,700	5,300	360	1.5 g Fe in Feed
912	5,150	827	8,050	1,290	0.3 vol of acid at 4th extraction stage
920	2,300	180	3,800	1,200	Scrub acid at 1st scrub stage
954	4,300	1,210	4,440	1,610	
955	-	2,420	5,100	2,120	1 g/l Fe in feed
956	2,240	1,180	3,640	1,510	Duplicate of run 955 72 hr later
959	2,460	369	3,270	1,150	
1035	4,020	615	10,200	384	0.3 vol of acid at 4th extraction stage

4.7 Engineering Data*

Engineering data showed that the acid Thorex extraction column has almost the same operating characteristics as the Purex extraction column. The flooding rate was 1030 gal/ft^2·hr and the stage height about 2.1 ft. The experimental pulsed column contained sieve plates with 1/8-in. holes, 23% free area, spaced 2 in. apart, and was operated with top interface, aqueous continuous, 50 pulses per minute with 1 in. amplitude. Similar experiments with the aluminum nitrate Thorex process demonstrated stage heights of about 4 ft.

5.0 CO-STRIPPING OR PARTITIONING COLUMN

Uranium and thorium in the organic phase from the extraction-scrub column may be either co-stripped or selectively stripped. A partitioning flowsheet was designed which requires only 10 theoretical stages (10) instead of the 18 stages used in the partitioning column of the original Thorex flowsheet (8):

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* From A. D. Ryon's group, Unit Operations Section, Chemical Technology Division (9).

Feed: 42 g/l Th, 2.65 g/l U, 0.11 N HNO_3, 30% TBP in Amsco, 1 vol
Strip: 0.008 M $Al(NO_3)_3$, 0.6 vol
Scrub: 30% TBP in Amsco, 0.2 vol
Stages: 5 strip, 5 scrub

After 6 volume changes in a laboratory countercurrent batch extraction, the thorium and uranium material balances were 100%; 0.3% of the thorium remained in the organic phase with the uranium and 0.05% of the uranium was stripped with the thorium. The thorium and uranium in each stage are shown in Table 4. The aqueous phase in equilibrium with the organic stream containing the uranium product had 74 times the concentration of thorium found in the organic. Similarly, the organic phase in equilibrium with the aqueous thorium product stream contained 7 times the concentration of uranium found in the aqueous. De-entrainment of the second phase from these streams will therefore be vital to satisfactory partitioning when this minimum number of stages is used. An additional stage at each end of the column would give much more flexibility for plant operation.

Table 4. Partitioning of Uranium and Thorium with 0.008 M $Al(NO_3)_3$
Feed: 42 g/l Th, 2.05 g/l U, 0.11 N HNO_3 in 30% TBP-Amsco
Strip: 0.008 M $Al(NO_3)_3$
Scrub: 30% TBP-Amsco
F/St/Sc volume ratio: 1/0.6/0.2

	Thorium				Uranium			
Stage	Org(g/l)	Aq(g/l)	DC^a_o	EF^a_o	Org(g/l)	Aq(g/l)	DC^o_a	EF^o_a
5	0.105	7.43	7.08	3.54	2.25	3.44	0.65	1.30
4	3.79	30.1	7.94	3.97	4.17	1.32	3.16	6.32
3	14.9	51.8	3.48	1.74	2.78	0.50	5.56	11.12
2	25.4	69.6	2.74	1.37	2.25	0.35	6.43	12.86
1	34.9	81.9	2.35	1.18	2.25	0.30	7.50	15.0
1	36.8	82.2	2.23	6.69	0.97	0.11	8.82	2.94
2	35.8	81.3	2.27	6.81	0.38	0.050	7.60	2.53
3	35.7	80.3	2.25	6.75	0.14	0.021	6.67	2.22
4	34.5	79.5	2.30	6.90	0.050	0.007	7.14	2.35
5	34.4	70.5	2.05	6.15	0.015	0.002	7.50	2.50

In experiments with the above flowsheet conditions except that 4 stripping stages were used, 1.9% of the thorium remained with the uranium. Similarly, when 4 stripping stages were used and 0.1 N HNO_3 was used instead of 0.008 M $Al(NO_3)_3$, 6.4% of the thorium remained with the uranium.

The thorium and uranium were successfully separated with a stripping solution of 0.05 M dibasic aluminum nitrate. The thorium product contained 70 g/l Th, which was 0.04 N acid deficient and may be concentrated directly to give an acid deficient second cycle feed solution. The uranium stripping efficiency would also be improved by removing the acid from the organic phase (11).

The co-stripping of thorium and uranium is very sensitive to the acid in the organic feed. As previously shown (Sec. 4.2), the acid in the organic phase from the extraction column may be varied from about 0.02 N to about 0.2 N by varying the flowsheet conditions. A series of experiments was performed in which synthetic extraction column organic product containing about 42 g/l Th, 2.4 g/l U, and 0.001 N to 0.22 N HNO_3 in 30% TBP-Amsco was stripped with 1, 1.2, or 1.5 vol of 0.008 M $Al(NO_3)_3$ in 7 strip stages. When the organic feed containing 0.005 N HNO_3 was stripped with an equal volume of 0.008 M $Al(NO_3)_3$, 6 stages were required to decrease the uranium loss to less than 0.1%; when the feed contained 0.1 or 0.2 N HNO_3, 7 stages were required (Table 5). Increasing the volume of the aqueous stripping solution decreased the number of stages required to ensure $<$0.1% uranium loss. When the organic feed contained 0.003 N HNO_3, 6 stages were required when 1.2 vol was used and only 4 stages when 1.5 vol of stripping agent was used.

6.0 AQUEOUS WASTE

The volume of the concentrated aqueous waste that would result from processing of thorium fuel by the acid Thorex flowsheet would be 1/10 that from the aluminum nitrate—salted flowsheet (Table 6). Even less waste would be obtained from the acid Thorex process if the TBP concentration was increased to 42.5% with a corresponding increase in feed concentration as used in the aluminum-salted flowsheet.

Table 5. Effect of Acidity on Co-stripping of Thorium and Uranium

Stage	a/o = 1/1						a/o = 1.2/1						a/o = 1.5/1			
	0.005 $\underline{N}$ H^+		0.11 $\underline{N}$ H^+		0.22 $\underline{N}$ H^+		0.003 $\underline{N}$ H^+		0.13 $\underline{N}$ H^+		0.200 $\underline{N}$ H^+		0.001 $\underline{N}$ H^+		0.21 $\underline{N}$ H^+	
	Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org
	40.2 g/l Th Feed		42.7 g/l Th Feed		43.1 g/l Th Feed		46.2 g/l Th Feed		45.5 g/l Th Feed		48.0 g/l Th Feed		46.1 g/l Th Feed		43.0 g/l Th Feed	
	Thorium in Organic, g/liter															
1	44.2	8.45	40.9	10.7	43.8	13.0	38.6	6.14	35.7	8.04	33.1	23.4	29.9	3.31	27.0	4.89
2	9.12	0.275	11.5	0.55	12.6	0.725	4.82	0.082	7.19	0.190	3.63	0.107	2.10	0.034	3.31	0.085
3	0.468	0.016	0.748	0.015	0.918	0.024	0.119	<0.005	0.169	0.007	0.217	< .005	0.023	0.012	0.040	0.037
4	0.110	<0.005	0.031	0.007	0.110	0.006	0.024	<0.005	0.005	<0.005	0.006	0.006	<0.005	0.009	<0.005	0.014
5	0.015	<0.005	0.006	<0.005	0.008	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	0.014
6	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
7	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
	2.4 g/l U Feed		2.56 g/l U Feed		2.28 g/l U Feed		2.23 g/l U Feed		2.61 g/l U Feed		2.23 g/l U Feed		2.74 g/l U Feed		2.19 g/l U Feed	
	Uranium in Organic, g/liter															
1	2.47	9.96	2.28	10.2	1.98	10.7	2.46	8.49	2.41	9.96	2.36	10.2	1.75	4.32	1.49	5.15
2	10.7	9.29	10.5	12.7	10.4	15.0	7.34	3.94	8.22	6.71	2.38	7.55	2.95	0.430	3.49	1.24
3	9.96	3.33	12.4	5.68	14.5	8.05	3.04	0.333	5.24	0.915	5.24	1.09	0.404	0.031	0.781	0.068
4	3.07	0.25	5.38	0.91	7.46	1.62	0.214	0.082	0.760	0.120	0.917	0.099	0.023	0.004	0.050	0.018
5	0.280	0.055	0.81	0.094	1.64	0.11	0.045	0.040	0.055	0.046	0.081	0.027	0.002	<0.005	0.012	<0.005
6	0.084	0.002	0.094	0.046	0.044	0.115	0.021	0.005	0.023	0.008	0.030	0.005	<0.005	<0.005	<0.005	<0.005
7	0.023	0.001	0.038	0.008	0.040	0.005	0.004	<0.005	0.004	0.001	0.003	<0.005	<0.005	<0.005	<0.005	<0.005

Aqueous: 0.008 $\underline{M}$ $Al(NO_3)_3$

Organic: 30% TBP in Amsco

Table 6. Calculated Composition of Aqueous Waste from HNO_3-- and $Al(NO_3)_3$--salted Thorex Flowsheets

	Acid Salted		Aluminum Salted	
Composition, M	Unconcentrated	Concentrated	Unconcentrated	Concentrated
Al^{3+}	0.016	0.8	0.70	2.0
H^+	3.00	-	-	-
Na^+	0.008	0.4	0.01	0.03
NO_3^-	3.00	2.4	2.00	6.0
F^-	0.016	0.8	0.02	0.06
PO_4^{3-}	0.004	0.2	0.003	0.01
HSO_4^-	0.008	0.4	0.01	0.03
Vol liter/kg Th	10	0.2	5.7	2.0
Relative vol[a]	50	1	28.5	10

[a] Based on volume of concentrated acid Thorex waste.

In experiments to determine the volume of concentrated waste that might result from the processing of Consolidated Edison fuel by the acid Thorex process, synthetic aqueous waste, without fission products, was concentrated to 1.3% of its original volume to remove the free nitric acid, and then rediluted to 5% of its original volume with water until only a trace of solids remained undissolved at room temperature. Concentration of the original aqueous waste to 11% of its volume increased the acid from about 3 M to about 8 M. Further concentration to 1.3% of its original volume decreased the acidity to about 4 M. The boiling point of the concentrated solution was 119°C. From time to time during the evaporation step and after each water addition during the dilution step, the solutions were cooled to determine the temperature at which precipitation would occur (Fig. 5).

The following flowsheet conditions were assumed:

Feed: 265 g/l Th, 0.1 M H_3BO_3, 0.1 M $NaHSO_3$, 0.04 M NaF, 0.1 M $Al(NO_3)_3$, 1 vol

Scrub: 2.1 M HNO_3, 0.01 M H_3PO_4, 0.01 M $Fe(NH_2SO_3)_2$, 1 vol

Acid: 13 M HNO_3, 0.3 vol

Unconcentrated aqueous waste: 2.6 M HNO_3, 0.043 M $Al(NO_3)_3$, 0.043 M H_3BO_3, 0.043 M $NaHSO_3$, 0.017 M NaF, 0.0043 M H_3PO_4, 0.0043 M $Fe(NH_2SO_3)_2$, 2.3 vol

These conditions were chosen to result in the maximum concentration of nonradioactive solids likely to be encountered in the aqueous waste. The boric acid may or may not be added to the feed as a homogeneous criticality control. Experiments indicated that 0.02 $\underline{M}$ $NaHSO_3$ will be sufficient to adjust fission products to nonextractable species. The 0.1 $\underline{M}$ $Al(NO_3)_3$ will probably be required to decrease corrosion if the Sulfex head-end step is used, but only 0.04 $\underline{M}$ $Al(NO_3)_3$ will be required if Darex is used (12). The pilot plant used only 0.003 $\underline{M}$ PO_4^{3-} in the scrub, and the ferrous sulfamate may not be required to suppress chromium extraction when materials other than stainless steel are used in the fabrication of the dissolver and feed adjustment equipment. This solution did not contain fission product elements, however, which may contribute significantly to the volume of the waste from highly irradiated fuel.

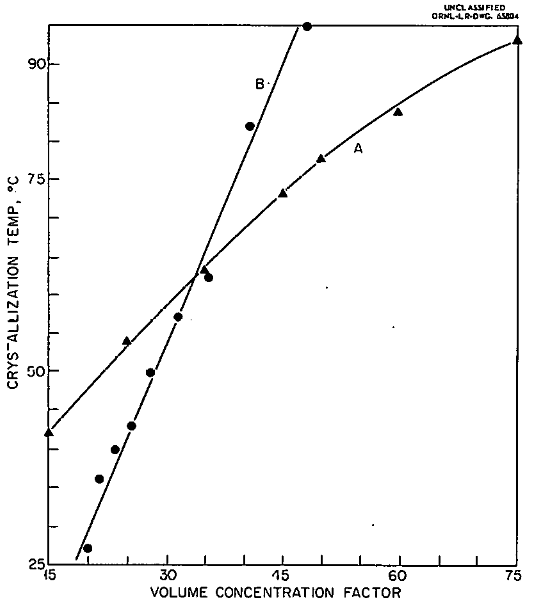

Fig. 5. Crystallization temperature of aqueous waste solutions. (A) Concentration curve. (B) Dilution curve.

7.0 THOREX FLOWSHEET WITH ALUMINUM NITRATE ADDED BELOW THE FEED PLATE

A brief investigation was made of the effect of the addition of acid deficient aluminum nitrate instead of nitric acid below the feed plate. Operation was satisfactory in countercurrent batch extraction. The flowsheet investigated was:

Feed: 433 g/l Th, 0.22 N a.d., treated with 0.02 M $NaHSO_3$ at 55°C for 1 hr, 1 vol, 1E stage
Scrub: 0.7 M Al, 0.2 N a.d., 0.003 M $Na(PO_4)_3$, 1 vol, 6S stage
Salt: 1.4 M Al, 0.2 N a.d., 1 vol, 3E stage
Solvent: 42.5% TBP-Amsco, 5 vol, 5E stage
Stages: 5 extraction 6 scrub

Decontamination factors from ruthenium, zirconium-niobium, and protactinium were >3500, 7900, and 2700, respectively. These decontamination factors are at least twice as high as those with the standard aluminum-salted Thorex flowsheet. The thorium loss was 0.7%.

8.0 ACID DEFICIENT FLOWSHEET FOR RECOVERY OF URANIUM

A few experiments were made to compare the decontamination of uranium in the present acidic Purex flowsheet and a flowsheet using an acid deficient feed with acid added to the extraction section. The decontamination factors with the acid deficient feed were about 4000 and 7000 for ruthenium and zirconium-niobium, and the corresponding values with the acid feed were 300 and 2000 (Table 7). The uranium loss was less than 0.01% in all experiments.

Table 7. Decontamination of Uranium from Acid and Acid Deficient Feed Solutions

Type of Flowsheet	Decontamination Factor				Feed Plate
	Gr γ	Ru	Zr-Nb	TRE	DC_a^o
Acid	1580	367	1310	<58,800	0.504
	1700	300	2500	117,000	0.511
Average	1640	333	1910		
Acid deficient	5250	1550	2580	-	0.461
	9470	6440	10800	230,000	0.455
Average	7360	4000	6690		

The acid deficient flowsheet cannot be used in its present form to process solutions for plutonium recovery but is applicable for processing unirradiated uranium or for uranium cycles after the plutonium has been removed.

The experiments with the acid deficient feed were made with the following flowsheet conditions:

Feed:	360 g/l U, 0.1 N a.d., treated with 0.02 N $NaHSO_3$ at $50^\circ C$ for 1 hr
Scrub:	2 N HNO_3, 1 vol, 5S stage
Acid:	13 N HNO_3, 0.3 vol, 4E stage
Extractant:	30% TBP in Amsco, 3.5 vol, 6E stage

Flowsheet conditions for the acid feeds were the same except the feed contained 1 N HNO_3, it was not treated with bisulfite, and no extra acid was added to the extraction section.

Decontamination from tracer quantities of plutonium is increased by the addition of 0.01 M $Na_2Cr_2O_6$ to the feed and 0.01 M $NH_2OH \cdot HCl$ to the scrub. With an acid deficient flowsheet containing these additives, decontamination factors were > 600, 23,000, and 4000, respectively, from plutonium, ruthenium, and zirconium-niobium.

9.0 DAREX-THOREX FLOWSHEET

Uranium and thorium may be recovered from Darex clad solution by adding the chloride—free solution to the acid Thorex solvent extraction column as a salting material. An alternative process involving total dissolution of the fuel element resulted in much decreased decontamination from fission products.

Early Darex decladding studies on unirradiated fuel pins indicated that the uranium loss to the clad solution would be less than 0.1%, and uranium recovery would therefore not be required. Additional data, however, indicated that uranium and thorium losses to the clad solution increased with an increased irradiation level and were so much as 3% with 25,000-Mwd/ton fuel (9). Recovery of uranium from this solution will therefore be necessary. Separate recovery would require additional equipment or alternative recovery in the equipment designed for recovery of the fuel pellets. Either process would increase considerably the cost of fuel processing; therefore methods of simultaneous recovery of the core and clad solutions were investigated.

After dissolution of the stainless steel clad in aqua regia the chloride will be removed and the solution concentrated to about 2 M stainless steel nitrate. This solution may be used as a salting agent in the recovery of thorium as follows:

Feed: 250 g/l Th, 20 g/l U, 0.1 N a.d., 0.05 M F, 0.1 M Al, 0.03 M B,
0.1 M $NaHSO_3$, 1 vol, 1E stage
Scrub No. 1: 5 M HNO_3, 0.2 vol, 4S stage
Scrub No. 2: 0.003 M PO_4, 0.01 M $Fe(NH_2SO_3)_2$, 0.8 vol, 6S stage
Darex clad Soln: 1 g/l Th, 1 g/l U, 2 M stainless steel, 0.8 M H,
0.2 M B, 0.8 vol, 3E stage
Extractant: 30% TBP in Amsco, 6 vol, 5E stage

In laboratory countercurrent batch extraction of synthetic solutions, decontamination factors from ruthenium, zirconium-niobium, and rare earths were 560, 9000, and 2.5×10^5, respectively. Uranium and thorium losses were $<0.001\%$ and 0.4%.

The dilute aqua regia used in the decladding can be used to dissolve the entire Consolidated Edison fuel element by adding 0.04 M fluoride as a catalyst. Steam stripping techniques previously described (Sect. 3.0) were successfully adapted for removal of excess acid to give a feed containing ~300 g/l Th, 20 g/l U, 2 M stainless steel, and 0.25 N HNO_3. Solvent extraction of this solution with 42.5% TBP, however, resulted in decontamination factors of only 20 and 500 from ruthenium and zirconium-niobium. The thorium loss was $<0.1\%$.

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