AEC RESEARCH and DEVELOPMENT REPORT

BNWL-57

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RECOVERY OF PLUTONIUM AND URANIUM FROM REACTOR FUEL METALLURGICAL SCRAP

JUNE, 1965

PROJECT NO.	REV.	DATE	BY
Extra City of Portland, Jr.	60000	717	MAY 10 1965
CPD	70000	2710	MAY 10 1965
RA Harty	30857	325	JUN 5 1965

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for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

BNWL-57
UC-10, Chemical
Separations Processes
for Plutonium and Uranium

RECOVERY OF PLUTONIUM AND URANIUM
FROM REACTOR FUEL METALLURGICAL SCRAP

By

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June, 1965

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in USA. Price \$2.00. Available from the
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards
U. S. Department of Commerce
Springfield, Virginia

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RECOVERY OF PLUTONIUM AND URANIUM FROM REACTOR FUEL METALLURGICAL SCRAP

INTRODUCTION

Expansion of the United States nuclear power industry has intensified interest in plutonium-uranium, plutonium-thorium, and plutonium-uranium-thorium fuels. Metallurgical scrap containing these materials has been and will be generated. Facilities in the Hanford 234-5 Building are being considered for separation and recovery of plutonium and, if present, U^{235} or U^{233} from this scrap.

Chemical flowsheets for dissolution of the various kinds of scrap and subsequent solvent extraction separations were drawn up initially by L. Bruns.^(1, 2) Studies reported here were confined primarily to testing of proposed, and development of new or modified, solvent extraction flowsheets for separating plutonium from uranium and thorium. Limited testing of the flowsheet proposed for separation of uranium from thorium was done and results are summarized.

SUMMARY AND CONCLUSIONS

Two flowsheets for the solvent extraction separation of plutonium from uranium and thorium are presented and discussed. In both, uranium and thorium are coextracted (partition column) into a $TBP-CCl_4$ solvent from an aqueous feed solution derived from various kinds of metallurgical scrap. Plutonium is rejected to the aqueous phase as plutonium(III) in both flowsheets. Finally, in both flowsheets, uranium and thorium are stripped from the organic phase into dilute HNO_3 . However, in one flowsheet, a modified version of one proposed earlier by Bruns,⁽²⁾ a small volume of HNO_3 is used to concentrate the uranium and thorium; the bulk of this concentrate is recycled to the partition column as a reflux stream. Uranium and thorium are stripped into a larger volume of HNO_3 in the other flowsheet and concentration and reflux features are not involved.

The reflux flowsheet was tested extensively in mixer-settler runs as well as on a batch scale. Satisfactorily low losses of thorium and

uranium to the aqueous phase in the partition column were achieved at the expense of extraction of 0.1 to 0.2% of the plutonium. The nonreflux flowsheet appears capable of giving a cleaner separation of plutonium from uranium and thorium but involves handling large volumes of solution.

The possibility of using a static bed of 30% DBBP- CCl_4 to separate plutonium(III) and thorium (after prior extraction of uranium into a TBP- CCl_4 solution) was scouted briefly. This approach does not appear feasible.

Finally, extraction of thorium by mixed TBP-DBBP extractants was studied under the condition that the total concentration of both extractants was held constant at 20 vol%. In one set of experiments an unexpected and unexplained, but apparently real, minimum thorium distribution ratio occurred at about 19.5% TBP-0.5% DBBP.

FLOWSHEET CONCEPTS

Dissolution and Leaching

According to Bruns⁽¹⁾ reactor fuel metallurgical scrap may require some type of treatment before it can be dissolved or leached. For example, a blend of plutonium, thorium, and graphite may require crushing and grinding before leaching. After such pretreatment, if necessary, the scrap is dissolved or leached in a HF-HNO_3 mixture. Figure 1 is the preparation flowsheet specified by Bruns. This process step was not studied.

Solvent Extraction Flowsheets

Partitioning of Plutonium from Uranium

The bulk of the scrap presently available and predicted for the future contains only plutonium and uranium. The purification flowsheet recommended by Bruns is given in Reference (2). Abundant technology for this separation exists; detailed studies were not made in this investigation.

Partitioning of Plutonium from Uranium and Thorium

Reflux flowsheets - Figure 2 is the reflux flowsheet currently favored. In the reflux flowsheet concept, uranium and thorium are

- (a) Miscellaneous includes glass, carbides, magnesium, cobalt, iron, manganese, etc.
 (b) Variable depending on solvent extraction flowsheet.
 (c) FS is ferrous sulfamate.

FIGURE 1
 Scrap Feed Preparation Flowsheet

coextracted into a 30% TBP- CCl_4 solution while plutonium is rejected to the aqueous raffinate as plutonium(III). The organic phase is diluted to 15 vol% TBP by adding CCl_4 ; uranium and thorium are costripped from it into a small volume of dilute HNO_3 . The bulk of this strip solution is recycled to the partition (CB) column. The concentrated U-Th solution, eventually obtained from the strip column, is either neutralized and discarded to waste or, if the uranium is worth recovering (U^{235} or U^{233} present), stored for later partitioning. Plutonium in the aqueous raffinate from the partition column is subsequently recovered and further purified in the Hanford 234-5 Building 880 facility. ⁽³⁾

According to current specifications, amounts of uranium or thorium in excess of 10,000 parts per million parts of plutonium are not tolerable in feeds to the 880 facility. A further specification is that the plutonium concentration in the U-Th product must be less than 0.02 g/liter to permit disposal of this solution to cribs. The flowsheet shown in Figure 2 is designed to meet, in a single cycle of solvent extraction, all these specifications.

The flowsheet shown as Figure 2 resembles very closely that recently recommended by Bruns. ⁽²⁾ Important modifications include:

- The CBF stream aluminum concentration is decreased from 1.0M to 0.6M.
- The CBS stream acidity and flow are changed from 3.0M and 125 liter flows to 0.05M HNO_3 and 250 liter flows.
- Prior to stripping of uranium and thorium, CCl_4 is added to the organic stream from the partition column to dilute the TBP concentration from 30 to 15 vol%.
- It is specified that the U-Th aqueous product from the stripping column can contain as much as 0.02 g/liter plutonium instead of limiting this stream to 10 or less parts plutonium per billion parts of uranium.

The first two modifications are straight-forward and were made to decrease the amount of plutonium coextracted with uranium and thorium. The latter two modifications require additional comment.

FIGURE 2

Reflux Flowsheet for Partitioning of Plutonium from Uranium and Thorium

Concentration of uranium and thorium is achieved in this flowsheet by limiting the aqueous flow in the strip column to one-fourth the organic flow. Mixer-settler data (Table V, p. 19) and distribution ratio data obtained by Bruns⁽⁴⁾ indicate uranium cannot be adequately stripped from 30% TBP at this flow ratio. The distribution ratio data do indicate, however, that satisfactory stripping of uranium can be achieved at this flow ratio if the TBP concentration is 15 vol%. Therefore, to obtain the desired concentration of uranium and thorium, CCl_4 is added to the organic stream before the strip column operation. Because of its volatility, CCl_4 is easily removed from the organic waste from the strip column to reconstitute solvent for the partition column.

With respect to the plutonium specification in the strip column U-Th product, it is true that the low plutonium specification (≤ 10 ppb) must be met for purified U^{233} or U^{235} . In many cases, however, the uranium involved may not be worth recovering and can be discarded along with thorium and 0.02 g/liter plutonium after only one cycle of solvent extraction. When required, the lower plutonium specification can be met by one or more additional solvent extraction cycles of the uranium.

It must be emphasized that accepting a plutonium concentration in the U-Th product of 0.01 to 0.02 g/liter is equivalent to losing 0.1 to 0.2% of the feed plutonium. Losses of this magnitude may be prohibitively high. If so, it may be necessary to recycle the U-Th product through the partition column with cold CBF (no plutonium) until plutonium losses are acceptably low.

Nonreflux Flowsheet. Flowsheets proposed heretofore for partitioning plutonium from uranium and thorium have all provided for reflux and concentration of the uranium and thorium. Such concentration and reflux have been considered desirable to reduce solution volumes and to achieve better purification of the uranium and thorium from plutonium and other metallic impurities. Actually, these flowsheets features make it more, not less, difficult to separate plutonium from uranium and thorium. Difficulties encountered in stripping uranium and thorium in a reflux

flowsheet have been mentioned. Although such difficulties can be overcome (e. g., by adding CCl_4 to dilute the TBP concentration), they are an objectionable feature of a reflux flowsheet.

Figure 3 shows a flowsheet in which the reflux and concentration features have been eliminated. Uranium and thorium are simply coextracted into a TBP- CCl_4 solution and then costripped, without concentration, into a dilute HNO_3 solution. As in the reflux flowsheet, plutonium is maintained in the aqueous phase as plutonium(III) in the partition column. Stream compositions and flows shown in Figure 3 represent extrapolations and interpolations of data obtained in this and other studies. Even though not actually demonstrated under countercurrent conditions, this flowsheet is believed to be workable and to offer certain advantages over one of the reflux type.

For example, this flowsheet specifies 20% TBP rather than 30% TBP as the extractant. This change is desirable because 20% TBP- CCl_4 is normally used in the Hanford 234-5 Building 880 facility. Also, with the elimination of the reflux and concentration features, the salting strength of the partition column feed can be decreased substantially. This change should provide for much better retention of plutonium in the aqueous raffinate from the column. Finally, the large flow of dilute HNO_3 in the strip column facilitates stripping uranium and thorium. Potentially cumbersome addition and boil-off of CCl_4 are eliminated.

The aqueous stream from the strip column can be discarded to waste without concentration. Alternatively, this stream can be concentrated by boiling for either subsequent disposal or partitioning of uranium from thorium.

Other Flowsheet Approaches. Still another way of partitioning plutonium from thorium and uranium proposed by Bruns⁽³⁾ was briefly scouted. This approach also involves extraction of the uranium into a TBP- CCl_4 solution. But, in this flowsheet concept, both plutonium and thorium are routed to the aqueous phase in the partition column. On subsequent passage of the aqueous phase through a static bed of 30% DBBP- CCl_4 thorium is preferentially extracted while plutonium remains in the aqueous

FIGURE 3

Nonreflux Flowsheet for Partitioning of Plutonium from Uranium and Thorium

phase as plutonium(III). As before, plutonium is then recovered and purified in the 880 facility.

An attractive feature of this flowsheet concept is that it offers the promise of not only partitioning plutonium from thorium and uranium but also of partitioning of uranium from thorium. The key step is the degree to which plutonium and thorium can be separated by the static bed of 30% DBBP- CCl_4 . Extraction of small amounts of plutonium(IV) from 880-facility extraction column aqueous raffinate into a static DBBP- CCl_4 bed has proven to be a satisfactory technique. ^(5, 6) Our results (p.) indicated, however, extensive development effort would be required to define satisfactory flowsheet conditions for the separation of plutonium(III) from thorium by this technique. Accordingly, this flowsheet concept was not explored further.

Partitioning of Uranium from Thorium

The flowsheet recommended by Bruns for separation of uranium from thorium is given as Figure 4. This flowsheet also involves a partition-strip cycle with flows adjusted to provide for reflux and concentration of uranium. Partition column conditions are adjusted to extract only uranium. Ferrous sulfamate is added to the feed and the partition column scrub stream to provide required (<10 ppb) decontamination from plutonium. The aqueous waste from the partition column, containing thorium and no more than 0.02 g/liter plutonium, is neutralized and discarded.

Studies of this separation scheme were limited to a few mixer-settler runs (Table IX, p. 24). As in the studies of the Pu-Th-U reflux flowsheet, uranium could not be properly stripped at the low aqueous to organic flow ratio specified for this flowsheet. Also, under partition column conditions, where adequate uranium extraction was realized, about 8% of the thorium also extracted. Current specifications call for 1000 ppm (or less) thorium in the uranium product.

FIGURE 4
Flowsheet for Partition of Uranium from Thorium

EXPERIMENTAL

Tributyl phosphate and DBBP, as received, were diluted with CCl_4 to prepare extractants unless otherwise specified. All extractants were washed twice with one-fifth volume portions of 5% Na_2CO_3 and once with one-fifth volume of 5% HNO_3 before use unless otherwise specified.

Th^{234} was milked from natural uranium. Uranium trioxide was dissolved in 12M HCl to yield a 6M-2.0M UO_2Cl_2 solution. This solution was passed through a bed of cation exchange resin (AG 50W-x8, 100 to 200 mesh). The adsorbed thorium was eluted with saturated oxalic acid. Oxalic acid was destroyed by reaction with boiling, concentrated HNO_3 .

Stock 3.25M ferrous sulfamate (FS) solution and standardized $\text{Pu}(\text{NO}_3)_4$ solution (259 g plutonium per liter, 4.3M HNO_3) were obtained. All other chemicals used to prepare aqueous solutions were of reagent grade quality or better.

A standard 10 min contact (mechanical stirring) at 25 °C was used to determine distribution ratios (E_a^0).

Twelve and 16-stage mixer-settlers were used to test chemical flow-sheets under countercurrent conditions. These units were modified versions of a type developed at the Knolls Atomic Power Laboratory by Coplan and others.⁽⁷⁾ Mixer-settlers were operated with the aqueous or organic feed, scrub, and organic extractant or aqueous strip solutions required until a steady-state in the effluent stream was reached. Flow rates were maintained either with metering pumps or by a syringe-drive feed system. Samples of the effluent streams were taken hourly and analyzed to determine when steady-state was reached. Waste losses were computed from analyses of steady-state effluent streams.

Uranium and macro amounts of thorium in aqueous solutions were determined by X-ray fluorescence spectrometry.⁽⁸⁾ Organic samples were batch stripped with water, Na_2CO_3 , and HNO_3 to provide aqueous solutions for analysis of uranium and thorium. Plutonium in both aqueous and organic solutions was determined by simple alpha counting of aliquots. Th^{234} in aqueous and organic phases was determined by gamma energy pulse-height analysis.

RESULTS AND DISCUSSION

Flowsheet for Separation of Plutonium from Thorium and Uranium

Extraction of Uranium and Thorium into TBP-CCl₄ Solutions

Uranium and thorium distribution ratios as a function of aqueous and organic phase volume ratios, extractant concentration, and salting strength are given in Tables I and II. In agreement with the results of other investigators these results demonstrate uranium is far more extractable into TBP solutions than is thorium. Nevertheless, counter-current extraction conditions can be found either to coextract both elements (Figures 2 and 3) or to extract uranium selectively (Figure 4).

TABLE I
U-Th DISTRIBUTION INTO TBP-CCl₄ SOLUTIONS

A. Conditions

1. CBF Composition: 0.00462M UNH 0.05M Fe(NO₃)₃
0.00473M Th(NO₃)₄ 0.04M Mn(NO₃)₃
2.97 M HNO₃ 0.04M Mg(NO₃)₂
0.045 M FS 0.03M HF
2. CBIS Composition: 3.0M HNO₃, 0.1 or 0.23M UO₂(NO₃)₂, and Th(NO₃)₄ as indicated.
3. CBS Composition: 3.0M HNO₃, 0.05M FS.
4. CBX Composition: 20, 25, and 30% TBP-CCl₄.
5. Contacts: Mix 450 volumes CBF, 110 volumes CBIS, and 50 volumes CBS. Contact with CBX solutions at indicated aqueous/organic flow ratios.

CBF Al(NO ₃) ₃ , M	CBIS UO ₂ (NO ₃) ₂ , M	CBIS Th(NO ₃) ₄ , M	CBX TBP, vol%	U E _a ^o			Th E _a ^o		
				Aqueous/Organic			Aqueous/Organic		
				1	2	3	1	2	3
1.0	0.23	0.23	20	129	71	37	1.22	0.90	0.51
1.0	0.23	0.23	25	161	89	61	1.87	1.41	1.14
1.0	0.23	0.23	30	1000	179	109	3.20	2.47	1.96
1.5	0.23	0.23	20	1000	103	80	2.60	1.60	1.22
1.5	0.23	0.23	25	415	147	117	4.31	2.76	2.08
1.5	0.23	0.23	30	1000	383	271	8.39	5.15	3.45
0.50	0.23	0.23	20	74	51	41	1.25	0.86	0.62
0.50	0.23	0.23	25	1000	79	68	1.92	1.35	1.27
0.50	0.23	0.23	30	380	109	84	3.35	2.57	1.99
1.50	0.23	0.23	20	1000	79	70	2.20	1.45	1.08
1.50	0.23	0.23	25	685	187	106	3.49	2.44	1.96
1.50	0.23	0.23	30	387	197	132	6.25	4.09	3.05
0.50	0.10	0.10	20	5000	243	69	1.99	1.79	1.54
0.50	0.10	0.10	25	277	754	944	2.87	2.87	3.02
0.50	0.10	0.10	30	48	366	---	4.09	4.28	4.64

TABLE II

U-Th DISTRIBUTION INTO TBP-CCl₄ SOLUTIONS

Conditions: CBF, CBIS, and CBS (2.0M HNO₃, 0.05M FS) solutions of indicated compositions mixed in proportions of 450 CBF : : 110 CBIS : : 50 CBS. Resulting aqueous phase contacted 10 min at 25 °C with either 15 or 20% TBP-CCl₄ at flow ratio indicated.

CBF(a)		CBIS(b)		Extractant vol% TBP	Flow Ratio Aq/Org	E _a ^o	
HNO ₃ M	Al(NO ₃) ₃ M	HNO ₃ M				Th	U
2.79	0.56	3.0	20	3.05	0.70	33.5	
2.79	0.56	3.0	20	3.50	0.75	28.6	
2.79	0.56	3.0	20	4.00	0.58	27.1	
2.79	0.56	3.0	20	5.00	0.47	22.2	
2.79	0.56	3.0	15	3.05	0.34	15.4	
2.79	0.56	3.0	15	3.50	0.31	15.9	
2.79	0.56	3.0	15	4.00	0.29	13.4	
2.79	0.56	3.0	15	5.00	0.31	11.6	
2.79	0.56	2.0	20	3.05	0.48	30.2	
2.79	0.56	2.0	20	3.50	0.61	24.8	
2.79	0.56	2.0	20	4.00	0.49	21.2	
1.79	0.56	2.0	20	5.00	0.42	17.5	
1.79	0.56	2.0	15	3.05	0.28	14.1	
1.79	0.56	2.0	15	3.50	0.25	12.9	
1.79	0.56	2.0	15	4.00	0.27	12.4	
1.79	0.56	2.0	15	5.00	0.21	9.8	
1.79	0.25	2.0	20	3.05	0.28	15.2	
1.79	0.25	2.0	20	3.50	0.30	15.3	
1.79	0.25	2.0	20	4.00	0.29	13.9	
1.79	0.25	2.0	20	5.00	0.25	12.9	
1.79	0.25	2.0	15	3.05	0.20	9.5	
1.79	0.25	2.0	15	3.50	0.20	9.1	
1.79	0.25	2.0	15	4.00	0.20	8.2	
1.79	0.25	2.0	15	5.00	0.20	8.0	

(a) All CBF solutions also were 0.00462M UO₂(NO₃)₂, 0.00473M Th(NO₃)₄, 0.09M FS, 0.03M HF, 0.09M H₂SO₄, 0.05M Fe(NO₃)₃, 0.04M Mg(NO₃)₂, 0.04M Mn(NO₃)₂, and 10⁹ counts/min/gal plutonium.

(b) All CBIS solutions also were 0.23M UO₂(NO₃)₂.

TBP Extraction of Plutonium from Plutonium(III) Solutions

Plutonium(III) is ordinarily regarded as being only slightly extracted by TBP-diluent solutions. Indeed, under the conditions we are most accustomed to, it is, as witness the routine successful operation of the Hanford Purex plant 1-B column.

Nevertheless, under certain conditions (Table III) TBP solutions extract appreciable plutonium from HNO₃ solutions containing plutonium(III). Extraction of plutonium from such solutions is particularly high when the

nitrate ion concentration is increased by addition of $\text{Al}(\text{NO}_3)_3$. On the other hand, satisfactory extraction of thorium under the flowsheet conditions shown in Figure 2 requires a fairly high $\text{Al}(\text{NO}_3)_3$ concentration. Successful partition of plutonium(III) from thorium thus requires careful control of salting strength.

TABLE III
TBP-EXTRACTION OF PLUTONIUM FROM VARIOUS
PLUTONIUM(III) SOLUTIONS

Conditions: Aqueous solutions of composition indicated contacted
10 min at 25 °C with an equal volume of 30% TBP- CCl_4 .

Experiment	Composition								Plutonium, g/liter	Plutonium, E_a°
	HNO_3 , <u>M</u>	$(\text{NO}_3)_3$ <u>M</u>	FS, <u>M</u>	$\text{Fe}(\text{NO}_3)_3$, <u>M</u>	HF, <u>M</u>	$\text{Mg}(\text{NO}_3)_2$, <u>M</u>	$\text{Mn}(\text{NO}_3)_2$, <u>M</u>			
1	3.0	----	0.045	----	----	----	----	0.5	0.0240	
2	3.0	0.50	0.045	----	----	----	----	0.5	0.0781	
3	3.0	1.0	0.045	----	----	----	----	0.5	0.446	
4	3.0	----	0.045	0.025	----	----	----	0.5	0.0384	
5	3.0	----	0.045	0.050	----	----	----	0.5	0.0536	
6	3.0	1.0	0.045	0.025	----	----	----	0.5	0.845	
7	3.0	1.0	0.045	0.025	----	----	----	4.0	2.63	
8	3.0	0.5	0.045	0.025	----	----	----	4.0	0.384	
9	3.0	0.33	0.034	----	0.02	0.026	0.026	0.33	0.0347	
10	3.0	0.33	0.034	0.016	0.02	0.026	0.026	0.33	0.0548	
11	3.0	0.33	0.034	0.033	0.02	0.026	0.026	0.33	0.0986	
12(a)	3.0	0.33	0.034	----	0.02	0.026	0.026	0.33	0.0360	
13(a)	3.0	0.33	0.034	0.016	0.02	0.026	0.026	0.33	0.0758	
14(a)	3.0	0.33	0.034	0.033	0.02	0.026	0.026	0.33	0.116	
15(a)	3.0	0.67	0.034	0.016	0.02	0.026	0.026	0.33	0.198	
16(a, b)	3.0	0.67	0.034	0.016	0.02	0.026	0.026	0.33	0.168	
17(a, c)	3.0	0.67	0.034	0.016	0.02	0.026	0.026	0.33	0.202	

(a) These solutions were also 0.021M in $\text{UO}_2(\text{NO}_3)_2$ and 0.021M in $\text{Th}(\text{NO}_3)_4$.

(b) This solution was also 0.2M hydrazine.

(c) This solution was also 0.1M in sulfamic acid.

British workers^(9, 10) have studied the TBP extraction of various inorganic nitrates, including plutonium(III), yttrium, and the lower lanthanide (La-Gd) nitrates. They find extraction of these elements from HNO_3 solutions generally increases with acidity. For yttrium and the

lanthanide elements, increase in nitrate concentration (added, for example, as NaNO_3) resulted in increased extraction.

The British work makes it tempting to believe that the increased extraction we observed when $\text{Al}(\text{NO}_3)_3$ was added to HNO_3 -plutonium(III) solutions was simply a "salting in" of plutonium(III) to the organic phase. Other explanations of the increased extraction also appear possible, however. For example, oxidation of plutonium(III) to plutonium(IV) by HNO_2 in the organic phase may occur more readily when the nitrate concentration of the aqueous phase is increased. This change in oxidation state would require more extraction of plutonium(III) to maintain the extraction equilibrium.

Note, also the dependence of the plutonium E_a^0 on the ratio of iron(II) to iron(III) concentration in the aqueous phase (e. g., results of Experiments 1, 4, and 5). Increased extraction at the lower ratios is in agreement with predictions to be made from the Nernst Equation.

Reflux Flowsheet Demonstration: Mixer-Settler Runs

Table IV summarizes results of various mixer-settler runs made to study the effect of flowsheet variables on the partitioning of plutonium from thorium and uranium. Runs 8 and 9, Table IV, were performed under essentially the conditions of the reflux flowsheet shown in Figure 2. The uranium concentration in the aqueous raffinate was within stated specifications ($\leq 10,000$ ppm plutonium) under these conditions while the thorium concentration was four to seven times above this specification.

The flowsheets shown in Figure 2 specifies a plutonium concentration in the CCU stream of 0.01 to 0.02 g/liter. To meet this specification under the strip column flows shown in Figure 2, the organic feed plutonium concentration should be in the range 0.0046 to 0.0092 g/liter before dilution with CCl_4 . The plutonium concentration of the steady-state organic product obtained under recommended partition column conditions (Runs 8 and 9, Table IV) was within the specified range.

TABLE IV
MIXER-SETTLER DEMONSTRATION OF REFLUX FLOWSHEET FOR SEPARATION OF PLUTONIUM
FROM URANIUM AND THORIUM: PARTITION COLUMN RUNS

Conditions: Flows and Stream Compositions. Those shown in Figure 2 except for
modifications indicated.
Stages. Extraction: 10 Scrub: 1 CBIS, variable CBS.

Run ^(a)	CBF				CBS			Aqueous Waste						Organic Product	
	Al(NO ₃) ₃	FS,	Fe(NO ₃) ₃	FS,	HNO ₃ ,	Flows	Stages	Uranium		Thorium		Plutonium	Plutonium		
	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>			g/liter	%	g/liter	%	g/liter	g/liter	%	
1	1.0	0.045	0.05	0.05	3.0	125	5	<0.005	<0.1	0.008	0.15	0.12	0.31	75	
2	0.6	0.045	0.025	0.0	0.0	0.0	0	<0.005	0.08	0.013	0.27	0.31	0.081	22	
3	0.6	0.045	0.025	0.05	3.0	125	5	0.004	<0.1	0.004	0.08	0.36	0.074	17	
4	0.6	0.045	0.025	0.05	3.0	125	8	<0.005	<0.1	---	---	0.34	0.071	16	
5	0.6	0.045	0.025	0.05	3.0	250	5	<0.005	<0.1	0.10	0.19	0.27	0.051	16	
6	0.6	0.045	0.025	0.05	3.0	250	8	<0.005	<0.1	0.008	0.15	0.29	0.027	8.1	
7	0.7	0.045	0.025	0.05	0.05	250	8	<0.005	<0.1	0.048	0.92	0.34	0.018	6.8	
8	0.6	0.045	0.025	0.05	0.1	250	8	<0.005	<0.1	0.012	0.23	0.30	0.0075	2.3	
9	0.6	0.045	0.025	0.05	0.05	250	8	<0.005	<0.1	0.022	0.42	0.38	0.0095	2.7	
10	0.5	0.045	0.025	0.05	3.0	125	5	0.007	0.14	0.22	4.5	0.30	0.041	12	

(a) In all runs CBIS was 3.0M HNO_3 , 0.084M $\text{UO}_2(\text{NO}_3)_2$, 0.084M $\text{Th}(\text{NO}_3)_4$.

As pointed out earlier, successful partitioning of plutonium from thorium requires careful control of salting strength. Data in Table IV offer ample confirmation for this statement.

Flowsheets for stripping uranium and thorium from the TBP-CCl₄ phase obtained in the partition column were also tested in mixer-settler runs (Table V). The organic feed in these runs was 30% TBP. At this TBP concentration uranium losses to the organic phase were very high when the aqueous flow was only one-half that of the organic flow. Much better stripping was obtained at equal phase volumes.

TABLE V
MIXER-SETTLER DEMONSTRATION OF FLOWSHEET FOR SEPARATION
OF PLUTONIUM FROM URANIUM AND THORIUM:
STRIP COLUMN RUNS

Conditions: As stated. CCX was 0.01M HNO₃ in all cases and
organic was 30% TBP in all cases.

Run	Flowsheet ^(a)	Flows		Mixer-Settler Stages	Percent Not Stripped	
		CCX	Feed		Uranium	Thorium
1 ^(b)	1	100	200	8	66	21
2 ^(c)	2	100	200	10	54	0.30
3 ^(c)	2	100	100	10	0.38	0.10

(a) Flowsheet 1 is listed as Figure 2 and Flowsheet 2 as Figure 3.

(b) Organic feed was organic product collected at steady-state in Run 1, Table IV.

(c) Organic feed was organic product collected at steady-state in Run 11, Table IV.

As mentioned earlier, the reflux flowsheet currently favored calls for dilution of the TBP concentration to 15 vol% before stripping. At this TBP concentration, it is believed uranium and thorium can be stripped successfully even at low aqueous flows. This was not tested in our studies.

DBBP Extraction of Thorium and Plutonium(III)

Following the early work of Baldwin⁽¹¹⁾ at ORNL and Burger⁽¹²⁾ at Hanford, Siddal⁽¹³⁾ at Savannah River made extensive studies of the extraction of uranium and other actinides from HNO₃ by DBBP-diluent solutions. He found distribution coefficients for hexavalent actinides with DBBP are about 10 times as large as with TBP while distribution coefficients for tetravalent actinides are as much as 50 times greater with DBBP.

These observations, together with the work of Kingsley, Crocker, and Creighton at Hanford already cited, ^(5, 6) suggested the possibility of using a static column of DBBP-CCl₄ to separate thorium from plutonium(III). Initial results (Table VI) indicated that, although thorium did indeed extract very well into 30% DBBP-CCl₄, appreciable extraction of plutonium from a plutonium(III) solution also occurred. This latter result might have been anticipated in view of the appreciable TBP extraction of plutonium from such solutions mentioned earlier.

TABLE VI
EXTRACTION OF THORIUM AND PLUTONIUM(III)
INTO 30% DBBP-CCl₄

Conditions: Aqueous HNO₃-Al(NO₃)₃ solutions [all 0.025M Fe(NO₃)₃, 0.1M FS, 0.00473M Th(NO₃)₄, 0.03 g/liter Plutonium(III)] contacted with 1/9 volume of 30% DBBP-CCl₄.

HNO ₃ , <u>M</u>	Al(NO ₃) ₃ , <u>M</u>	Plutonium ^(a) <u>E_a^o</u>	Thorium <u>E_a^o</u>
1.0	0.0	0.40	41
2.0	0.0	0.44	68
3.0	0.0	0.56	83
4.0	0.0	0.99	90
1.0	0.5	1.20	--
2.0	0.5	1.90	--
3.0	0.5	3.10	--

(a) Solutions allowed to stand 30 min at 25 °C after adding Pu(NO₃)₄ and FS to insure reduction to plutonium(III).

One further experiment was performed (Table VII) to study DBBP extraction of thorium and plutonium from plutonium(III) solutions. Equilibrium thorium and plutonium loading was apparently obtained after five contacts. At this point the organic phase was about 0.35M thorium and about 0.025M plutonium. A 30% DBBP-solution is 1.09M DBBP. ⁽¹²⁾ Thus, the total concentration of plutonium and thorium in the loaded organic phase agrees well with that expected if the extraction reactions were:

and

TABLE VII
MULTIPLE BATCH EXTRACTION OF THORIUM AND PLUTONIUM(III)
INTO 30% DBBP-CCl₄

Conditions: One portion of 30% DBBP-CCl₄ contacted 10 times
with fresh nine-volume portions of feed. (a)

Contact No.	Thorium			Plutonium		
	Aqueous, g/liter	Organic g/liter	E _a ^o	Aqueous, g/liter	Organic, g/liter	E _a ^o
1	0.06	14.9	248	0.545	7.96	14.6
2	0.17	30.8	181	0.832	15.6	18.8
3	0.30	47.9	160	1.10	15.2	13.8
4	0.46	55.1	120	1.22	14.4	11.8
5	0.62	82.8	134	1.17	6.19	5.3
6	0.73	65.5	89.7	1.27	6.57	5.2
7	0.77	81.9	106	1.08	8.61	8.0
8	0.89	78.8	88.4	1.19	4.03	3.4
9	0.92	78.9	85.7	1.18	4.80	4.1
10	0.99	84.2	85.3	1.18	6.19	5.3

(a) Feed was: 2.67M HNO₃ 0.02M Mn(NO₃)₂
 0.78M Al(NO₃)₃ 0.015M HF
 0.086M FS 0.00473M Th(NO₃)₄
 0.025M Fe(NO₃)₃ 1.13 g/liter plutonium
 0.02M Mg(NO₃)₂

Madigan and Cattrall⁽¹⁴⁾ have previously found that, at least at low organic phase loading, DBBP extraction of thorium can be correlated satisfactorily by Equation (1).

Plutonium extracted in Contacts 1 and 2 in this latter experiment was only partially displaced by thorium on subsequent contacts. Furthermore, the aqueous phase from the very first contact had a higher Pu/Th ratio than tolerable in feeds to the 800 facility. These discouraging results prompted abandonment of this flowsheet approach in favor of those shown in Figures 2 and 3.

Mixed TBP-DBBP Extractants

An unexpected minimum thorium distribution ratio was observed (Table VIII and Figure 5) when mixed TBP-DBBP extractants were used to extract uranium and thorium from a synthetic CBF solution. In these studies the sum of the TBP and DBBP concentrations in the initial extractants was maintained constant at 20 vol%. This condition, because of the

TABLE VIII

EXTRACTION OF THORIUM AND URANIUM FROM CBF SOLUTION BY
MIXED TBP-DBBP EXTRACTANTS

Conditions: CBF solution of composition indicated contacted (10 min
at 25 °C) with one-third volume of each of organic
solutions indicated.

Extractant Composition(a, b)				Uranium E _a ^o	Thorium E _a ^o	
DBBP		TBP			X-Ray Data ^(c)	Th ²³⁴ Data ^(d)
vol%	<u>M</u>	vol%	<u>M</u>			
0.00	0.00	20.0	0.730	29.5	0.659	0.647
0.50	0.019	19.5	0.712	29.7	0.535	0.516
1.00	0.038	19.0	0.694	32.3	0.622	0.586
2.50	0.095	17.5	0.639	36.9	0.811	0.827
5.00	0.190	15.0	0.548	46.8	1.06	1.15
10.0	0.380	10.0	0.365	68.8	1.75	1.72
15.0	0.570	5.0	0.183	---	2.87	3.06
20.0	0.760	0.0	0.00	---	3.99	4.84

(a) Diluent was CCl_4

(b) CBF composition was:

0.045M	$\text{UO}_2(\text{NO}_3)_2$	0.022M	HF
0.045M	$\text{Th}(\text{NO}_3)_4$	0.066M	H_2SO_4
0.036M	FS	0.037M	$\text{Fe}(\text{NO}_3)_3$
2.85M	HNO_3	0.03M	$\text{Mn}(\text{NO}_3)_2$
0.41M	$\text{Al}(\text{NO}_3)_3$	0.03M	$\text{Mg}(\text{NO}_3)_2$

(c) Average of duplicate experiments.

(d) TBP and DBBP used in these experiments were specially purified by gas chromatography procedures.

FIGURE 5

Extraction of Thorium by Mixed TBP-DBBP Extractants

similarity in density and molecular weight of TBP and DBBP, is essentially equivalent to maintenance of a constant extractant molarity.

These experiments were motivated by a desire to take advantage of the greater affinity of DBBP over TBP for thorium and uranium. Initially, therefore, it was anticipated that substitution of DBBP for an equal concentration of TBP in the system delineated in Table VIII would result always in increased extraction of both elements. That this expectation was not realized for thorium is clearly evident from Figure 5.

Occurrence of an unexpected minimum distribution ratio for thorium in the system delineated in Table VIII appears to be well established. Thorium distribution ratios calculated from X-ray fluorescence analyses are in excellent agreement with those obtained from independent experiments employing Th^{234} tracer. These latter data were obtained by a separate observer using specially purified TBP and DBBP.

A completely satisfactory explanation cannot be given for the occurrence of a minimum thorium distribution ratio. Results obtained in these experiments have, however, prompted a more detailed consideration of mixed-extractant systems where the total concentration of the extractants is kept constant. Progress to date is outlined in the Appendix.

Flowsheet for Separation of Uranium from Thorium

Results of mixer-settler runs to test proposed flowsheet conditions for the separation of uranium from thorium are listed in Table IX. The significance of these results has already been discussed (see p. 13)

ACKNOWLEDGEMENT

The author is indebted to L. L. Burger and J. E. Mendel of Battelle-Northwest for many helpful discussions concerning solvent extraction by mixed extractants. Special thanks are also due L. E. Bruns for permission to reproduce certain of his chemical flowsheets in this report.

TABLE IX
FLWSHEET FOR SEPARATION OF URANIUM FROM THORIUM:
MIXER-SETTLER RUNS

Conditions: Flows and Stream Composition - Except for modifications indicated, those given in Figure 4 were used.

<u>Run</u>	<u>Column Type</u>	<u>CBX Flow(a)</u>	<u>CCX Flow(b)</u>	<u>Stages: Partition Column</u>		<u>Strip Column</u>		<u>Thorium in Uranium</u>	
				Extraction-10 Scrub-1 CBIS -6 CBS		Strip-10		ppm (x 10 ⁻⁴)	
				<u>Percent Extracted</u>		<u>Percent Not Stripped</u>		<u>CDF</u>	<u>CCU</u>
				<u>Thorium</u>	<u>Uranium</u>	<u>Thorium</u>	<u>Uranium</u>		
10	Partition	275	---	8.3	99.5	---	---	3.24	---
10-B	Partition	195	---	2.4	92.4	---	---	0.85	---
11	Strip	---	550	---	---	4.3	3.8	---	1.89
11-B	Strip	---	1100	---	---	<0.01	0.12	---	2.98

(a) CBF Flow = 500

(b) Organic (CDF) Flow = 500

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APPENDIX

SOLVENT EXTRACTION OF A METAL SPECIES BY MIXTURES OF TWO EXTRACTANTS

Consider a liquid-liquid solvent extraction system in which the organic phase contains two extractants diluted with a carrier solvent if necessary or desired. Suppose each of these extractants reacts with a metal species in an aqueous phase to form an organic-phase-soluble complex. Impose the following restrictions:

- The extractants are so mixed that the sum of their molar concentrations remains constant.
- The metal exists in the aqueous phase in only one form.
- Each extractant reacts independently with the metal species, i. e., formation of mixed extractant-metal complexes is excluded.
- Formation of 1:1 metal-extractant adducts by both extractants is excluded.

This section shows that in such a system some particular mixture of the two extractants will extract less metal than either of the extractants by itself.

Denote by M the metal species in the aqueous phase (charges are omitted for simplicity) and by S and P the two extractants. Reaction of S and P with M to form organic-phase-soluble complexes can be represented as

and

where the subscripts aq and org denote aqueous and organic phases.

Using concentration in place of activities, expressions for the overall formation constants for Reactions (1) and (2) can be written as

$$K_s = [M \cdot mS]_{org} / [M]_{aq} [S]_{org}^m \quad (3)$$

and

$$K_p = [M \cdot nP]_{org} / [M]_{aq} [P]_{org}^n \quad (4)$$

From Equations (3) and (4) we can write, omitting the subscripts,

$$[M \cdot mS] = K_s [M] [S]^m \quad (5)$$

and

$$[M \cdot nP] = K_p [M] [P]^n \quad (6)$$

Denote by D the equilibrium distribution ratio of the metal. The defining equation for D is

$$D = \frac{\text{total concentration of metal in organic phase}}{\text{total concentration of metal in aqueous phase}} \quad (7)$$

From the second and third restrictions imposed earlier, Equation (7) can be written as

$$D = \frac{[M \cdot mS]_{org} + [M \cdot nP]_{org}}{[M]_{aq}} \quad (8)$$

From Equations (5) and (6) we can write

$$D = \frac{K_s [M] [S]^m + K_p [M] [P]^n}{M} = K_s [S]^m + K_p [P]^n \quad (9)$$

At sufficiently low loading of the metal into the organic phase we have essentially

$$[S] + [P] = \text{a constant} = C \quad (10)$$

This condition follows from the first restriction imposed above. Equation (9) can be rewritten as

$$D = K_s [C - P]^m + K_p [P]^n \quad (11)$$

Elementary calculus can be used to determine critical points of Equation (11). The first derivative is

$$\frac{dD}{d[P]} = -mK_s [C - P]^{m-1} + nK_p [P]^{n-1} \quad (12)$$

and the second derivative is

$$\frac{d^2D}{d[P^2]} = m(m-1)K_s [C - P]^{m-2} + n(n-1)K_p [P]^{n-2} \quad (13)$$

Critical points are obtained by setting Equation (12) equal to zero and substituting various integers for m and n. Some typical values are

<u>m</u>	<u>n</u>	<u>Critical Point</u>
1	2	$[P] = K_s / 2K_p$
2	1	$[P] = \frac{2K_s C - K_p}{2K_s}$
2	2	$[P] = \frac{K_s C}{K_s + K_p}$
2	3	$[P] = \frac{-K_s + \sqrt{K_s^2 + 6K_s K_p C}}{3K_p}$
		and
		$[P] = \frac{-K_s - \sqrt{K_s^2 + 6K_s K_p C}}{3K_p}$

A positive value results when the first four tabulated critical points are substituted in Equation (13). By the usual criterion, these values represent points where the distribution ratio is a minimum. The fifth listed critical point is a maximum point, but this point has mathematical significance only, i. e., $[P]$ cannot be negative.

Experimental demonstration of the occurrence of a minimum distribution ratio in a system obeying rigorously all the imposed restriction is required to substantiate the validity of this treatment. Such experimental evidence has not been obtained by the author.

Of interest, however, are the data shown in Table A-1 for the extraction of thorium by mixed TBP-DBBP extractants. Contrary to the experience discussed earlier (Table VIII and Figure 5) the thorium distribution ratio increased regularly with increasing DBBP concentration. Failure to find a minimum thorium distribution at some particular mixture of DBBP-TBP in the system delineated in Table A-1 makes the results presented in Figure 5 all the more perplexing.

TABLE A-1

EXTRACTION OF THORIUM BY MIXED TBP-DBBP EXTRACTANTS

Conditions: Portions of a 0.0107M $\text{Th}(\text{NO}_3)_4$ - 1.957M KNO_3 solution were contacted 1 hr at 25 °C with equal volume portions of each of the indicated organic solutions.

Extractant ^(a, b)		Thorium $E_a^{(c, d)}$
DBBP, vol%	TBP, vol %	
0.00	20.0	0.602
0.50	19.5	0.701
1.00	19.0	0.876
2.50	17.5	1.02
5.00	15.0	1.19
10.0	10.0	6.61
15.0	5.0	54.2
20.0	0.00	74.0

(a) Diluent was spectral grade isooctane.

(b) TBP and DBBP were purified by gas chromatography.

(c) Average of duplicate determinations.

(d) Thorium determined by X-ray fluorescence analyses.

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