662966

DP-1361

PARTITIONING OF LIGHT LANTHANIDES FROM ACTINIDES BY SOLVENT EXTRACTION WITH TBP

J. M. McKIBBEN, H. P. HOLCOMB,
D. A. ORTH, W. E. PROUT, AND W. C. SCOTTEN

DU PONT
REG. U. S. PAT. OFF.

Savannah River Laboratory

Aiken, South Carolina

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $1.45

662966

DP-1361
UC-10

PARTITIONING OF LIGHT LANTHANIDES FROM ACTINIDES BY SOLVENT EXTRACTION WITH TBP

by

J. M. McKibben, H. P. Holcomb,
D. A. Orth, W. E. Prout, and W. C. Scotten

Approved by

R. Maher, Superintendent
Separations Technology Section

and

J. A. Porter, Research Manager
Separations Chemistry Division

Publication Date: August 1974

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, S. C. 29801

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(07-2)-1

ABSTRACT

A solvent extraction process was developed for removing the light lanthanides (La, Ce, Pr, Nd) from americium-curium produced by neutron irradiation of ^{239}Pu. The light lanthanides are extracted into 30% TBP in normal paraffin hydrocarbon diluent from a lithium-nitrate-salted system containing diethylenetriaminepentaacetic acid (DTPA) to complex the actinides and render them less extractable. The actinides and any residual lanthanides remain in the aqueous raffinate. Maleic acid is used to control the acidity in extraction. The aqueous raffinate containing the actinides and residual lanthanides is further processed by solvent extraction with 30% TBP to remove interfering salts before the actinides are purified by chromatographic ion exchange. In pilot tests in miniature mixer-settlers, at least 98% of the lanthanum and 88% of the neodymium were rejected from irradiated plutonium. Recovery efficiency for americium and curium was >99%.

CONTENTS

INTRODUCTION

The higher actinides ^{242}Pu, ^{243}Am, ^{242}Cm, and ^{244}Cm are produced at Savannah River by neutron irradiation of ^{239}Pu.[1] A large quantity of fission products, including substantial amounts of lanthanides, is associated with the products. Irradiated targets are dissolved and processed to separate the products from the principal bulk contaminants, which are fission products and aluminum from the target sheathing and matrix. The final separation of lathanides and individual actinides is made by rapid ion exchange (RIX).[2]

Figure 1 shows schematically the present processing scheme. A typical Purex process is used to isolate plutonium by extraction. The trivalent actinides, lanthanides, and aluminum remain in the aqueous stream, which is processed through a second solvent extraction cycle, where the actinides and lanthanides are extracted from aluminum and other salts. However, the product solution from this cycle contains approximately 20 moles of lanthanides per mole of americium-curium. This lanthanide bulk would limit the actinide batch size and production rate during the final purification of the americium and curium by RIX. Therefore, a third solvent extraction step would be advantageous if it could reject lanthanides while quantitatively recovering actinides.

The relative amounts of individual lanthanide elements produced in the first plutonium burner campaign* material are shown in Table I. Eight lanthanides are included, lanthanum through gadolinium, and 85% of the total lanthanide contribution is by the first four, lanthanum through neodymium.

A new solvent extraction flowsheet described in this report was developed to provide a method for lanthanide-actinide partitioning prior to RIX, to gain the following advantages: 1) greater actinide loading per RIX cycle and thus improved production rates; 2) potentially purer product as a result of purer RIX feed; and 3) reduced thermal and radiolytic effects from ^{144}Ce-^{144}Pr. Development included cold testing, tracer testing with americium and curium, and successful pilot demonstrations with Am-Cm from plutonium burner and Curium-I** feeds.

---

*The term "plutonium burner" signifies those campaigns at Savannah River in which ^{239}Pu is highly irradiated to produce ^{252}Cf precursors, primarily ^{242}Pu, ^{243}Am, and ^{244}Cm.[3]

**"Curium-I" and "Curium-II" as used in this report denote the initial two-stage irradiation campaigns at Savannah River to produce multi-kilogram quantities of ^{244}Cm.[4]

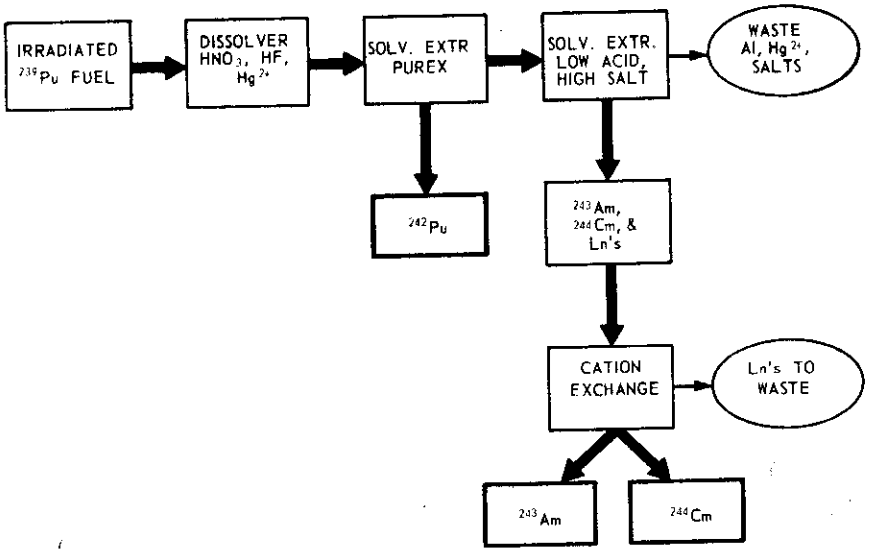

FIGURE 1. Processing Scheme for Irradiated Plutonium Burner Fuel

TABLE I

Concentration of Lanthanides in Irradiated Plutonium Burner Solution

Element	*mol %*
La	8
Ce	18
Pr	9
Nd	50
Pm	2
Sm	8
Eu	4
Gd	2

BASES FOR SEPARATION

Although the lanthanides are chemically similar, there are small differences from element to element due to the decrease in ionic size with increasing atomic number. Chemical evidence of this effect is shown in Table II by the stability constants of the lanthanide-DPTA complexes, which increase with increasing atomic number with a break between neodymium and samarium. The break between neodymium and samarium gives rise to a "light" and a "heavy" lanthanide group. The heavier group exhibits greater consistency in their respective stability constants.

TABLE II

Ionic Radii And DTPA Stability Constants For Lanthanides

Ion	*Ionic Radius, A*	*DTPA Stability Constant, log K (at 25°C)*[a]
La	1.061	19.48
Ce	1.034	20.40
Pr	1.013	21.07
Nd	0.995	21.60
Pm	0.979	*b*
Sm	0.964	22.34
Eu	0.950	22.52
Gd	0.938	22.45
Tb	0.923	22.70
Dy	0.908	22.76

---

a. R. M. Wallace and J. F. Hinton, Savannah River Laboratory, Aiken, S. C., to be published

b. Not determined.

Peppard[5] has shown that in the tributyl phosphate (TBP)-nitric acid system, the distribution coefficients of individual lanthanides increase with increasing atomic number. During Curium-II processing when solvent extraction with TBP was used to prepare RIX feed, lanthanide separation was observed in that decontamination factors for ^{144}Ce-^{144}Pr were greater than those for ^{154}Eu.

From a salted system, such as aqueous aluminum nitrate, 30% TBP extracts both the actinides and lanthanides with distribution coefficients increasing with increasing atomic number, but with overlap between the lighter lanthanides and the actinides (Figure 2). Such a system could not separate these two groups.

If diethylenetriaminepentaacetic acid (DTPA) is added to the system, an ordering of the distribution coefficients occurs and makes separation feasible (Figure 3). As demonstrated previously, the stability constants of the DTPA-lanthanide complexes increase with increasing atomic number. The stability constants of the DTPA complexes of actinides heavier than plutonium are numerically larger than those of any lanthanide. So, when DTPA is added to the aqueous phase, the lighter lanthanides, having weaker DTPA complexes than the actinides, are more readily extracted into TBP. However, at a pH of about 2.5 or below, the extractability factors of the lanthanides merge and reverse, so that they behave as if no DTPA were present, i. e., the order of increasing extractability is from lighter to heavier lanthanide. This results from protonation of DTPA, which destroys its complexing ability. The actinides form more-stable DTPA complexes and can compete with H^+ to much lower lower pH values.

The distribution coefficients for DTPA complexes of actinides and lanthanides, and therefore their separation factors, are quite pH dependent. Thus, the pH in the extraction must be closely controlled for a workable separations process. This is difficult in a TBP extraction system because TBP extracts nitric acid from the aqueous phase. Because of this sensitivity of the process to pH changes, buffering of the aqueous phase was necessary.

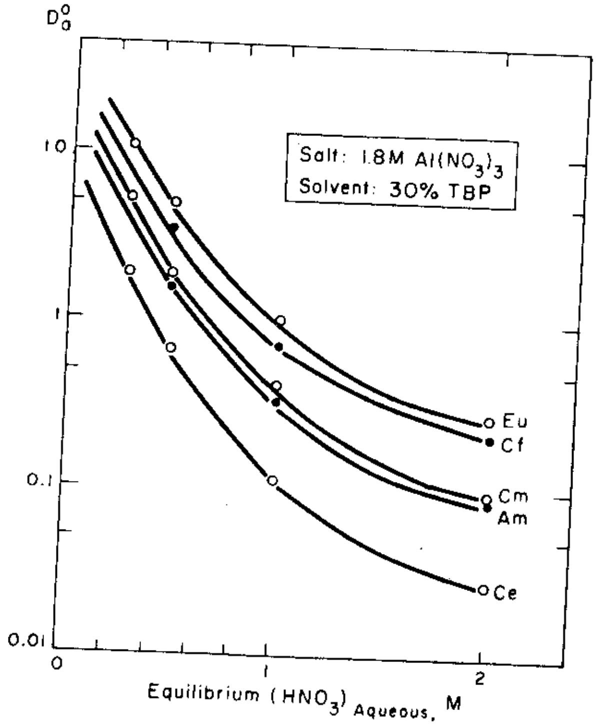

FIGURE 2. Distribution Coefficients as a Function of Acidity

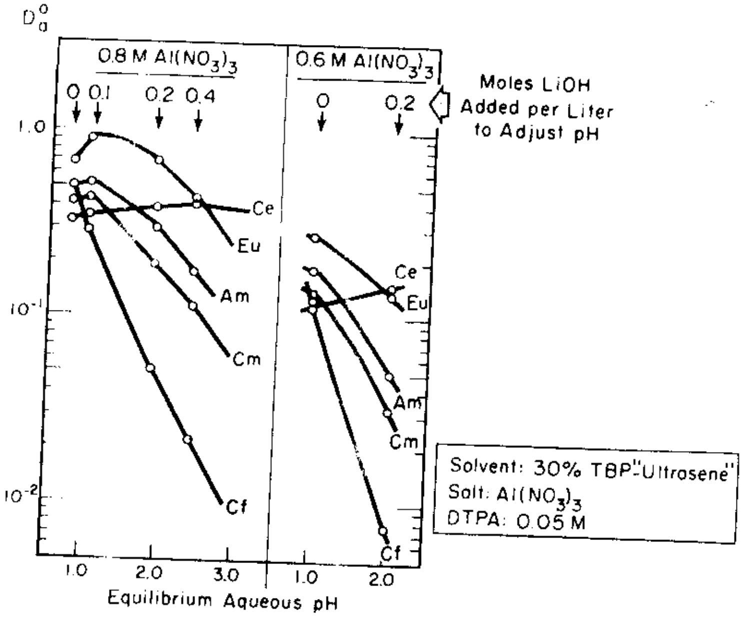

FIGURE 3. Distribution Coefficients as a Function of Acidity With DTPA Present.

LANTHANIDE REJECTION FLOWSHEET

GENERAL DESCRIPTION

Figure 4 outlines the lanthanide rejection flowsheet. One mixer-settler, designated the "A-bank," is operated as the extraction bank. The adjusted aqueous feed (1AF) containing the lanthanides and actinides is fed to the mixing section of Stage 9 of the A-bank; the organic extractant (1AX) enters the bank at Stage 16; and the aqueous scrub (1AS) enters at Stage 1. The combined aqueous stream moves from Stage 9 toward Stage 16, equilibrating at each stage with organic phase that extracts the light lanthanides. At Stage 15 (mixing section), an acid side stream (1AN) is introduced for acidity control. The aqueous stream exits at Stage 16 as the aqueous raffinate (1AW) containing the unextracted heavy lanthanides and actinides. The extractant (1AX) containing the light lanthanides, is washed by the 1AS scrub in Stages 8 through 1 and exits from Stage 1 as the 1AP.

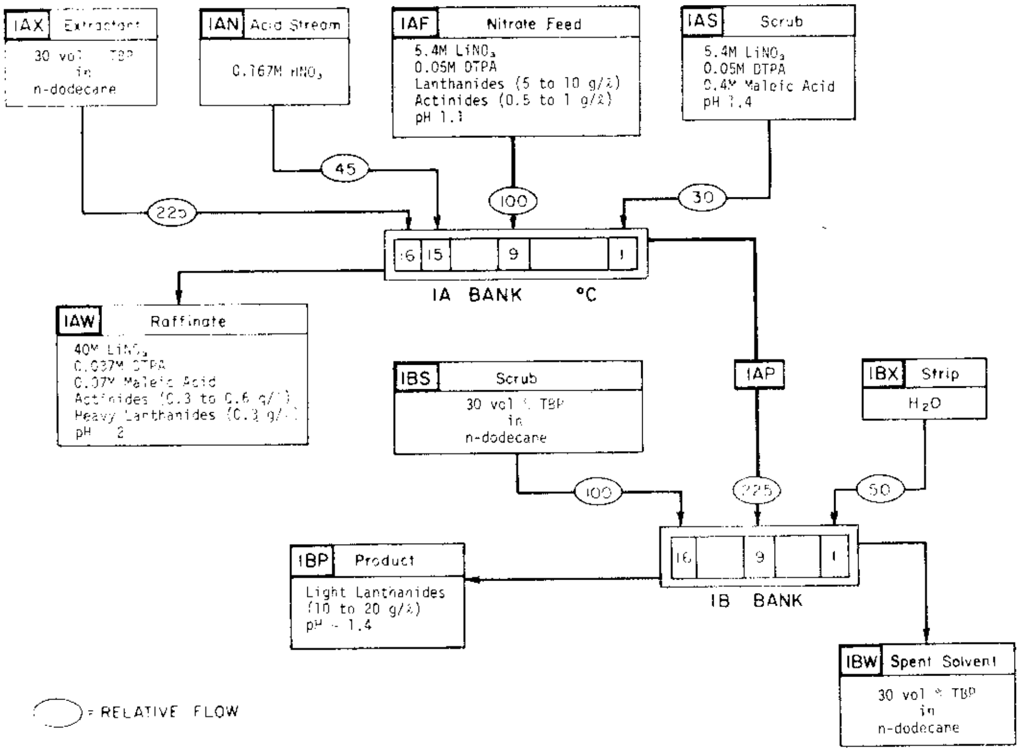

FIGURE 4. Lanthanide Rejection Flowsheet

The second mixer-settler, the B-bank, strips the light lanthanides from the organic phase. The organic from the A-bank (1AP) enters the B-bank at the mixing section of Stage 9; the aqueous strip (1BX) enters the bank at Stage 1; and the organic scrub (1BS) enters at Stage 16. As the organic phase moves from Stage 9 toward Stage 1, the light lanthanides are stripped into the aqueous phase in Stages 1 through 9. The aqueous stream, containing the light lanthanides, exits the bank at Stage 16 as the 1BP product stream.

MALEIC ACID AS BUFFER

Maleic acid (1,2-ethylenedicarboxylic acid) is added to the 1A bank through the scrub stream (1AS) to buffer the aqueous phase in the extraction bank and thereby to decrease the sensitivity of the process to changes in aqueous acidity. Maleic acid was selected for two reasons. First, maleic acid is an innocuous additive that can be decomposed by boiling in solutions of high nitrate concentration. Second, the initial ionization constant of maleic acid ($10^{-1.4}$) buffers in the desired pH range. Its buffering action is illustrated in Figure 5, where the effect of added acid or base on the distribution coefficient of californium is shown. For comparison, if a change in feed acidity that produces a 0.01M change in the aqueous phase occurs when operating at a pH of 1.1, the californium distribution coefficient would change by a factor of 2 without maleic acid buffering, but only by 10% with maleic acid buffering.

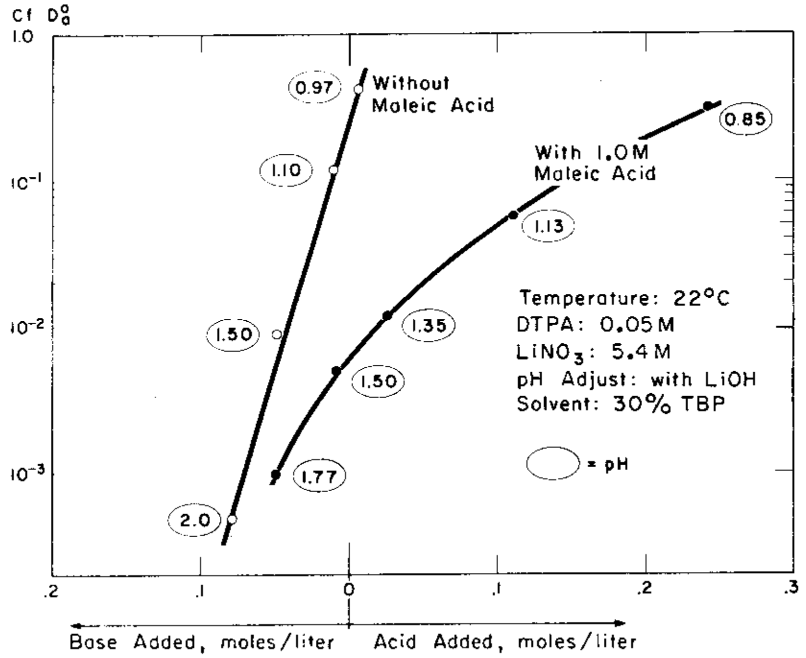

FIGURE 5. Buffering Action of Maleic Acid

SALTING AGENT

The choice of cation for the nitrate salting agent is important because of salting strength effects. Lithium nitrate was chosen because its salting ability is high,[4] it is monovalent, and, unlike trivalent aluminum it does not cause kinetic problems resulting from complex formation with DTPA. Distribution coefficients as a function of pH in the lithium nitrate-DTPA-maleic acid system are shown in Figure 6. High salting is necessary to raise to operable levels the distribution coefficients that have been depressed by the addition of DTPA.

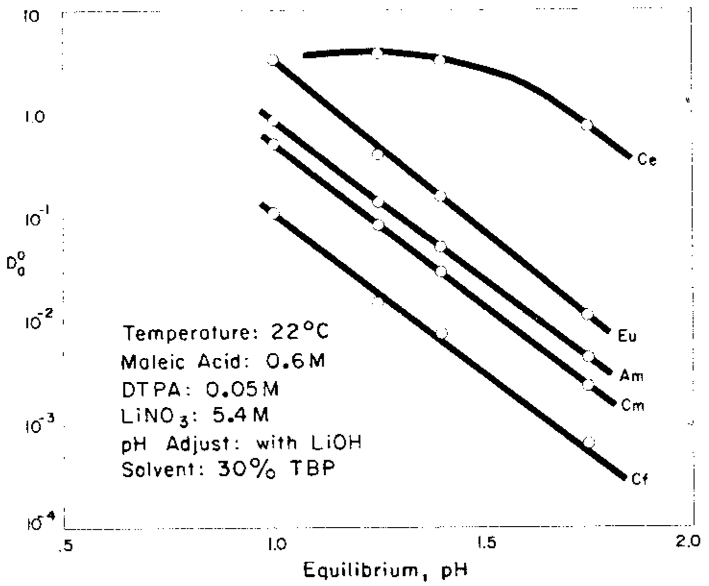

FIGURE 6. Distribution Coefficients of Actinides as a Function of pH

FLOWSHEET OPTIMIZATION AND TESTING

EQUIPMENT

Two 16-stage, countercurrent flow, miniature mixer-settlers described previously[6] were used for flowsheet development. In cold tests, Pr^{3+} or Nd^{3+} was used to represent the light lanthanides, and Eu^{3+} or Dy^{3+} was used to represent the actinides and heavy lanthanides. Process solutions from the plant were used to test flowsheet performance at full levels of radioactivity.

CONTROL OF pH IN EXTRACTION

The initial lanthanide rejection flowsheet shown in Table III was tested with nonradioactive Nd^{3+} and Eu^{3+}. Performance was satisfactory although even better decontamination factors from Nd^{3+} could have been obtained, as evidenced by the pH profile of the A bank given in Table IV. The pH of the scrub section is almost constant, but the pH increases rapidly in the extraction section due to extraction of nitric acid by TBP. Therefore, any Nd^{3+} or other light lanthanide that remains in the aqueous phase past the first two or three extraction stages will appear in the 1AW along with the actinides because distribution coefficients decrease with increasing pH. Because of this, a side stream of nitric acid (1AN) was introduced into the mixing section of Stage 15 to increase the acidity in the lower portion of the extraction section and to act as a barrier to light lanthanides.

The lanthanide rejection flowsheet with acid side stream for pH control was tested (Table V). The Nd^{3+} decontamination factor was improved, although an unexplained 3% loss of Dy^{3+} occurred. Table VI gives the pH profile. The 1AN stream controlled pH within a small range and provided improved lanthanide decontamination.

The effect of 1AN flow rate on performance was investigated. As Table VII indicates, acid excesses up to 167% of nominal do not cause adverse effects. In the absence of the 1AN stream or at low flows, the light lanthanides tend to leak to the 1AW. Decontamination from Nd^{3+} at the higher 1AN flows is probably beter than the data indicate because of limitations of the analytical method.

TABLE III

Initial Lanthanide Rejection Flowsheet

A-Bank

Aqueous feed to Stage 9: flow 100 (relative)

0.004M Eu; 0.016M Nd; 0.05M DTPA; 5.4M $LiNO_3$

0.6M maleic acid; pH 1.0 adjusted with LiOH

Solvent feed to Stage 16: flow 225

30 vol % TBP in n-dodecane

Scrub feed to Stage 1: flow 30

0.5M DTPA; 5.4M $LiNO_3$; 0.6M maleic acid

pH 1.5 adjusted with LiOH

B-Bank

Organic extract from A-Bank to Stage 9: flow 225

Aqueous back-extractant (H_2O) to Stage 1: flow 50

Organic scrub feed (30% TBP) to Stage 16: flow 100

	% in Stream at Steady State	
Element	*AW*	*BP*
Nd	6.2	93.8
Eu	73.9	26.1

TABLE IV

pH Profile of A-Bank in Initial Flowsheet

Stream in	*Stage*	*pH*	*Stream out*
1AS →	1	1.145	→ 1AP
	2	1.40	
	3	1.40	
	4	1.40	
	5	1.40	
	6	1.40	
	7	1.40	
	8	1.40	
1AF →	9	1.38	
	10	1.40	
	11	1.61	
	12	1.78	
	13	1.85	
	14	2.10	
	15	2.26	
1AX →	16	2.54	→ 1AW

TABLE V

Lanthanide Rejection Flowsheet Incorporating Acid Side Stream To Control pH

A-Bank

Aqueous feed to Stage 9: flow 100 (relative)

0.004M Eu; 0.016M Nd; 0.008M Dy

0.05M DTPA; 5.4M $LiNO_3$; 0.6M maleic acid

pH 1.0 adjusted with LiOH

Solvent feed to Stage 16: flow 225

30 vol % TBP in n-dodecane

Scrub feed to Stage 1: flow 30

0.005M DTPA; 5.4M $LiNO_3$; 0.6M maleic acid

pH 1.5 adjusted with LiOH

Acidification to Stage 15: flow 30

0.5M HNO_3

B-Bank

Organic extract from A-Bank to Stage 9: flow 225

Aqueous back-extractant (H_2O) to Stage 1: flow 50

Organic scrub feed (30% TBP) to Stage 16: flow 100

	% in Stream at Steady State	
Element	*AW*	*BP*
Nd	<0.2	>99.8
Eu	51.7	48.3
Dy	97.2	2.8

TABLE VI

pH Profile Of A-Bank With Acid Side Stream

Stream in	*Stage*	*pH*	*Stream out*
1AS →	1	1.78	→ 1AP
	2	1.80	
	3	1.80	
	4	1.80	
	5	1.80	
	6	1.80	
	7	1.76	
	8	1.76	
1AF →	9	1.74	
	10	1.72	
	11	1.68	
	12	1.60	
	13	1.58	
	14	1.50	
1AN →	15	1.34	
1AX →	16	1.55	→ 1AW

TABLE VII

Effect of Acid Sidestream (1AN) on Process Performance

Relative Flow of 1AN	*% of Element in Stream at Steady State*					
	AW			*BP*		
	Nd	*Eu*	*Dy*	*Nd*	*Eu*	*Dy*
0	30	99	>99	70	1	<1
15	25	99	>99	75	1	<1
30	<12	98	>99	>88	2	<1
45*a*	<14	98	>99	>86	2	<1
60	<19	98	>99	>81	2	<1
75	<16	97	>99	>84	3	<1

---

a. Nominal flow at $[H^+] = 0.167M$

LITHIUM NITRATE CONCENTRATION IN THE 1AS

Miniature mixer-settler tests with neodymium and dysprosium demonstrated that a variation of lithium nitrate concentrations in the 1A bank scrub stream of ±4% from the nominal 5.4M has no adverse effect. Recovery of dysprosium, the actinide stand-in, was 98% at the lower nitrate concentration and 99% at the higher; neodymium rejection was greater than 90% throughout the lithium nitrate concentration range.

MALEIC ACID EFFECTS

Maleic acid buffer was shown to be unnecessary in the feed stream where it would be susceptible to radiolytic degradation. With 0.6M maleic acid in the aqueous scrub (1AS), 95% of the neodymium was rejected and 99% of the dysprosium was recovered. When only 0.2M maleic acid was added to the scrub, 85 to 90% of the neodymium was still rejected and more than 99% of the dysprosium was recovered. In the nominal range pH 1.45 to 1.90 in the scrub, 90% or more of the neodymium was rejected. Below pH 1.6, however, loss of dysprosium to the 1BP increased as the result of increased distribution coefficients.

Performance was also tested with 0.2M maleic acid in the 1AS and none in the 1AF. Light lanthanide rejection and actinide recovery were not as effective at the lower maleic acid concentration. It was also found that the concentration of maleic acid must be maintained at less than 0.6M to avoid formation of a third phase, thought to be a TBP-lanthanide-maleic acid adduct, at temperatures less than 25°C. Multistage contactors are not normally operated at such reduced temperatures, but if they were, hydraulic upset would certainly result from the presence of the third phase.

Tests were conducted to optimize the maleic acid concentration with other flowsheet variables the same as in Table V. Based on these results (Table VIII), 0.4M maleic acid was chosen as the nominal concentration in the 1AS because of the excellent actinide recovery and good rejection of light lanthanides. The pH profiles of the scrub section in these runs revealed that as the concentration of the maleic acid in the 1AS increased, the overall pH of the scrub section also increased, promoting improved actinide recovery with little effect on light lanthanide rejection. An identical effect was observed when the acid input of the 1AN was decreased by about 20% which, in turn, increased the pH in the scrub section to a level similar to that found when 0.4M maleic acid was used.

TABLE VIII

Effect of Maleic Acid Concentration 1AS

	% of Element in Stream at Steady State							
Maleic Acid	^{242}Cm		^{241}Am		^{243}Am		^{142}Pr	
in 1AS, M	*AW*	*BP*	*AW*	*BP*	*AW*	*BP*	*AW*	*BP*
0.2	99.0	1.0	92.4	7.6	91.4	8.6	<15	>85
0.4	>99	<1	99.8	0.2	99.8	0.2	<15	>85
0.6	99.9	0.1	99.7	0.3	94.2	5.8	<10	>90

DESTRUCTION OF MALEIC ACID

Data in Table IX indicate that maleic acid in process solutions can be destroyed by boiling for two hours when the lithium nitrate concentration is 5.4M. At 3M lithium nitrate, only 25% of the initial maleic acid was destroyed in the same interval. However, it was not found necessary to destroy maleic acid before the second solvent extraction cycle described in the following section. Actually, some maleic acid is destroyed during feed adjustment; that remaining causes no adverse effects.

TABLE IX

Maleic Acid Destruction

Boiling Time, hr	*Maleic Acid, M*	
	5.4M $LiNO_3$	*3.0M $LiNO_3$*
0 (cold)	0.40	0.40
0.5	0.32	0.34
1.0	0.18	0.33
1.5	0.077	0.32
2.0	<0.005	0.29

SALT REMOVAL CYCLE

Following the lanthanide rejection cycle, the actinides and residual lanthanides are in solution with lithium nitrate, DTPA, and maleic acid. Another cycle of solvent extraction is necessary to remove the lithium nitrate and DTPA, which would interfere in the rapid ion exchange purification of the actinides. A cleanup cycle that had been demonstrated with residual Curium-I solution, containing relatively high phosphate concentration (∿0.3M) and sodium and aluminum salting, was adapted for use with lithium salting. Flowsheet parameters are outlined in Table X. A feed acidity of 1M permits quantitative actinide extraction into 30% TBP leaving the completely protonated DTPA, lithium salt, and residual maleic acid in the raffinate. The actinides and lanthanides in the organic phase are stripped by weak acid in the B-bank. A study was made of feed acidity versus actinide recovery. Using Dy^{3+} as the stand-in for actinides, losses to the raffinate were 4% and 8%, respectively, at feed acidities of 0.75 and 0.5M. Losses of Eu^{3+} in the same tests were less than 4%, indicating that complexing by DTPA was very slight at the lower acidities.

TABLE X

Salt Removal Cycle Flowsheet

A-Bank

Aqueous feed to Stage 9: flow 100 (relative)
$5.4M\ LiNO_3$; ∿0.05M DTPA; <0.1M maleic acid
∿0.5 g/l actinides; ∿1 g/l lanthanides

Solvent feed to Stage 16; flow 300
30 vol % TBP in n-dodecane

Scrub feed to Stage 1; flow 35
$6.0M\ NaNO_3$

B-Bank

Organic extract from A-Bank to Stage 9; flow 300

Acidic back-extractant ($0.5M\ HNO_3$) to Stage 1; flow 50
Organic scrub feed (30% TBP) to Stage 16; flow 100

FLOWSHEET DEMONSTRATION

TEST WITH PLUTONIUM BURNER SOLUTION

A full-level test of the flowsheet used plutonium burner solution from the first plutonium burner campaign in the plant. Irradiated Pu targets were dissolved, treated in head end, and processed through two cycles of solvent extraction, one to remove residual plutonium and a second to isolate the transplutonium actinides (and lanthanides) in a crude form as feed for RIX. The solution as received for the test contained $3.5M\ HNO_3$. The acidity was adjusted to about 0.1M with 5M lithium hydroxide. DTPA was added as the lithium salt. The solution was made 5.4M with respect to lithium nitrate, and the pH was adjusted to 1.1. Analysis of the adjusted feed is given in Table XI, and operating conditions are given in Table XII.

The test results in Table XIII show quantitative curium recovery with better than 90% americium recovery. Although some discrepancy exists between the two americium results, the value for ^{241}Am should be more accurate since it is based on a higher count rate. Spark source mass spectrometric analysis of two aqueous raffinate (1AW) samples, as compared with that of the feed, showed light lanthanide rejection to be accomplished with a break between the light lanthanide group ending with neodymium and the heavy lanthanide group starting with promethium.

TABLE XI

Composition of Plutonium Burner Solution Adjusted for Feed

	dis/(min-ml)		*mmol/liter*
Gross alpha	1.3×10^{10}	La	0.2
^{241}Am	1.1×10^{8}	Ce	0.2
^{243}Am	7.7×10^{7}	Pr	0.2
^{242}Cm	6.0×10^{9}	Nd	0.7
^{244}Cm	6.8×10^{9}	Pm	0.06
^{106}Ru	6.5×10^{10}	Eu	0.07
^{144}Ce	7.7×10^{10}	Mass 243	0.2
^{154}Eu	3.8×10^{9}		

TABLE XII

Lanthanide Rejection Flowsheet For Plutonium Burner Solution

A-Bank

Aqueous feed to Stage 9: flow 100 (relative)
5.4M $LiNO_3$; 0.05M DTPA; pH 1.1
Also see Table X

Solvent feed to Stage 16: flow 225
30 vol % TBP in n-dodecane

Scrub feed to Stage 1: flow 30
5.4M $LiNO_3$; 0.05M DTPA; 0.4M maleic acid; pH 1.4

Acidification to Stage 15: flow 45
0.167M HNO_3

B-Bank

Organic extract from A-Bank to Stage 9: flow 225
Aqueous back-extractant (H_2O) to Stage 1: flow 50
Organic scrub feed (30% TBP) to Stage 16: flow 100

TABLE XIII

Results of Lanthanide Rejection Test with Irradiated Plutonium Burner Solution

Actinide Distribution, %

^{244}Cm		^{242}Cm		^{241}Am		^{243}Am	
AW	*BP*	*AW*	*BP*	*AW*	*BP*	*AW*	*BP*
>99.9	<0.1	>99.9	>0.1	99	1	92	8

Lathanide Distribution, 10^{-3} *M*

	La	*Ce*	*Pr*	*Nd*	*Pm*	*Eu*
AF	0.2	0.2	0.2	0.7	0.06	0.07
AW						
Sample 1	<0.003	<0.08	<0.003	0.2	0.06	0.07
Sample 2	<0.003	<0.05	<0.003	0.2	0.08	0.07

TEST WITH CURIUM-I SOLUTION

^{241}Am, ^{243}Am, and ^{244}Cm were successfully recovered from a sample of Curium-I solution* by three cycles of solvent extraction with 30% TBP in the miniature mixer-settlers. The first cycle extracted the actinides and lanthanides from ions such as phosphate, iron, sodium, aluminum, mercury, ruthenium, nickel, and chromium. The second cycle removed the bulk of the light lanthanides that comprised most of solutes in the feed. The third cycle separated the actinides and remaining lanthanides from lithium salt and DTPA used in the second cycle. Because of a small loss (5 to 7%) of actinides in the third cycle to the 3AW, the aqueous end-streams were combined for feed to repeat the third cycle with slightly increased feed acidity to permit quantitative actinide recovery.

The composition of the Curium-I solution used in this test is given in Table XIV. Extraneous ions were removed with 30% TBP in a cycle (similar to that used for salt removal) that employed aluminum to complex the phosphate in the feed. The lanthanide rejection flowsheet was applied to remove the bulk of the light lanthanides. The conditions for this cycle were similar to those for the plutonium burner solution (Table XII). The relative flow of the solvent (1AX) was increased 33% (to 300), and that of the acidification stream (1AN) was increased 110% (to 100) to permit more-efficient extraction of the light lanthanides, including cold neodymium introduced into the feed during first cycle preliminary bank operation and flushing. Greater than 99% of the americium and curium were recovered in the 2AW. Spark source mass spectrometric analysis of the 2AW and 2BP composites and the separation factors obtained are listed in Table XV. The light lanthanides were extensively removed. As with the plutonium burner solution, a break occurred between neodymium and promethium, with the heavier but much less abundant lanthanides remaining with the actinides.

Third cycle extraction (salt removal) removed the actinides and residual lanthanides from the lithium salt and DTPA and produced a composite that could have been fed directly to rapid ion exchange for final purification and separation of the americium and curium.

---

* While recovering plutonium by TBP extraction of the Curium I solutions stable emulsion formation caused a small portion of the solution to become intractable to further processing. This solution had been stored for eight years during which time phosphate had formed from TBP degradation.

TABLE XIV

Composition of Curium-I Solution

Total Pu	42 g/ℓ	Al^{3+}	0.42M
^{241}Am	291 g/ℓ	Fe^{3+}	0.05M
^{243}Am	525 g/ℓ	NO_3^-	6.01M
^{244}Cm	70 g/ℓ	PO_4^{3-}	0.36M
HNO_3	1.1M	SO_4^{2-}	0.04M
Na^+	3.61M	Lanthanides	∿0.2M
Gross alpha	1.6×10^9 dis/(min-ml)		
Gross gamma	7.8×10^9 dis/(min-ml)		

TABLE XV

Results of Lanthanide Rejection Test with Cm-I Solution

(2AW = Actinide Product; 2BP = Lanthanide Extract)

	μg/ml		*Separation Factor*
Element	*2BP*	*2AW*	*(2BP/2AW)*
^{243}Am	<0.4	7	-----
Eu	<0.3	6	<0.05
Pm	3	9	0.3
Nd	4000	500	8
Pr	3000	100	30
Ce	70	<6	>10
La	60	<1	>60

REFERENCES

1. H. J. Groh, R. T. Huntoon, C. S. Schlea, J. A. Smith, and F. H. Springer. "^{244}Cm Production and Separation - Status of the Pilot Production Program at Savannah River." *Nucl. Appl. 1*, 327 (1965).

2. J. T. Lowe, W. H. Hale, and D. F. Hallman. "Development of a Pressurized Cation-Exchange Chromatographic Process for Separation of Transplutonium Actinides." *Ind. Eng. Chem. Process Des. Develop. 10*, 131 (1971).

3. J. A. Kelley. *Ion Exchange Process for Separating Americium and Curium from Irradiated Plutonium.* USAEC Report DP-1308, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1972).

4. D. A. Orth, J. M. McKibben, W. E. Prout, and W. C. Scotten. "Isolation of Transplutonium Elements." *International Solvent Ext. Conf., The Hague, Apr. 19,-23, 1971*, Vol. I. Published by Society of Chemical Industry, London (1971).

5. D. F. Peppard, J. P. Faris, P. R. Gray, and G. W. Mason. "Studies of the Solvent Extraction Behavior of the Transition Elements." *J. Phys. Chem. 57*, 294 (1953).

6. M. R. Caverly, E. C. Horni, H. E. Henry, and W. J. Jenkins. *A Miniature Pilot Plant for Processing Irradiated Nuclear Fuel.* USAEC Report DP-757, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

22 (Rev. 9 3)

SAVANNAH RIVER LABORATORY PUBLICATION APPROVAL SHEET

SHADED AREAS FOR TIS USE ONLY

TID-[illegible]-R61

DOCUMENT NO. DP-1361

TYPE OF PUBLICATION (Check one)

DP REPORT ☒ PAPER ☐

DP CATEGORY UC-10 Chemical [illegible]

AUTHOR(S) J. M. McKibben, H. P. Holcomb, D. A. Orth, W. E. Prout, W. C. Scotten

TITLE PARTITIONING OF LIGHT LANTHANIDES FROM ACTINIDES BY SOLVENT EXTRACTION WITH TBP

DIVISION Works Technical, SRP, Separations Chemistry, SRL

MANUSCRIPT APPROVAL

Route in turn to:

	Initials	Date
1. AUTHOR	HPH	3/5/74
2. SUPERVISOR	CMA	5/3/74
3. DIVISION HEAD		
4. TIS EDITOR	JK	6/12/74
5. DIVISION HEAD	JAP	7/1/74
6. SECTION DIRECTOR		7/4/74
7. ~~DIRECTOR OF ES~~ (if applicable)		
8. ASS'T. LAB. DIRECTOR		7-8-74
9. TIS		8-8

REPRODUCTION COPY APPROVAL

Route in turn to:

	Initials	Date
1. AUTHOR		
2. SUPERVISOR		
3. DIVISION HEAD		
4. TIS EDITOR		

CLASSIFICATION

Circle one for each

				CLASSIFICATION GUIDE TOPICS
OVERALL	S	C	[✓ U]	[illegible]
ABSTRACT	S	C	[✓ U]	151.2.1.9
TITLE	S	C	[✓ U]	151.5.1
TRANSMITTAL LETTER	S	C	U	151.5.2
				151.5.10
				207.13

APPROVAL: JAP Division Head; TIS

PATENT CONSIDERATIONS

POSSIBLE NOVEL FEATURES None

CLOSEST PRIOR ART

APPROVAL: Author; TIS

FILL IN FOR PAPERS ONLY

PAPER FOR: PRESENTATION ONLY ☐ PUBLICATION ONLY ☐ PRESENTATION AND PUBLICATION ☐

MEETING

Give complete official title and attach copy of instructions to contributors.

CITY

DATES

DEADLINE FOR SUBMISSION

CHAIRMAN

ABSTRACT NO. COPIES

ADDRESS

PAPER NO. COPIES

FOR ORAL PRESENTATION, THE AUTHOR MUST SIGN THE FOLLOWING STATEMENT AFTER THE CLASSIFICATION REVIEW IS COMPLETE:

I UNDERSTAND THE SIGNIFICANCE OF, AND THE LIMITATIONS IMPOSED BY, THE PERTINENT SROO CLASSIFICATION GUIDE TOPICS COVERING CLASSIFIED INFORMATION RELATED TO THE SUBJECT OF THIS PAPER. THE PERTINENT TOPICS INCLUDE:

Author

JOURNAL

CC: A. F. Westerdahl, SRCO
L. C. Evans - J. W. Crouch -
A. A. Johnson, Wilm.
S. A. McNeight
S. W. O'Rear - TIS File

August 9, 1974

TO: S. W. O'REAR

FROM: H. S. HILBORN

DOCUMENT REVIEW

Document: DP-1361

Title: Partitioning of Light Lanthanides from Actinides by Solvent Extraction with TBP

Author(s): J. M. McKibben, H. P. Holcomb, D. A. Orth, W. E. Prout, and W. C. Scotten

Contractual Origin: AT(07-2)-1

Present Classification: Unclassified DP

References:

No items were noted that, in my opinion, should be called to the attention of the AEC for patent consideration.

OSR 24-A116
(REV 1-72)

DU PONT

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
ATOMIC ENERGY DIVISION
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801
(TWX: 810-771-2670, TEL: 803-824-6331, WU: AUGUSTA, GA.)

CC: L. C. Evans - J. W. Croach -
A. A. Johnson, Wilm.
S. A. McNeight
S. W. O'Rear - TIS File

August 9, 1974

Mr. A. F. Westerdahl, Chief
Patent Branch
Savannah River Operations Office
U. S. Atomic Energy Commission
Aiken, South Carolina 29801

Dear Mr. Westerdahl:

REQUEST FOR PATENT REVIEW

Please review for patent matter:

DP-1361, "Partitioning of Light Lanthanides from Actinides by Solvent Extraction with TBP" by J. M. McKibben, H. P. Holcomb, D. A. Orth, W. E. Prout, and W. C. Scotten.

If any technical clarification is needed please call H. S. Hilborn, whose Document Review is attached.

Please telephone your comments to the TIS office (ext. 3598) and notify me by signing and returning to TIS the original of this letter. A copy is provided for your file.

If you decide to pursue a patent on any development covered, I shall be happy to supply additional information required such as appropriate references and the names of persons responsible for the development.

Very truly yours,

J. W. Croach, Director
Technical Division

By: ______________
H. S. Hilborn

The above item is approved for release.

Albert F Westerdahl 9/9/74
A. F. Westerdahl Date
Chief, Patent Branch
SROO, USAEC

EXTERNAL RELEASE OF TECHNICAL INFORMATION

Description of Material No. DP-1361 Date 8/9/74

Title: Partitioning of Light Lanthanides from Actinides by Solvent Extraction with TBP

Author(s): J. M. McKibben, H. P. Holcomb, D. A. Orth, W. E. Prout, and W. C. Scotten

Type of Material

[ ] Classified DP Report

[x] Unclassified DP Report

[ ] Classified Letter

[ ] Unclassified Letter

[ ] Classified Paper

[ ] Unclassified Paper

[ ] Classified Abstract or Summary

[ ] Unclassified Abstract or Summary

Technical Content

Approved by JAPorter Date 8/10/74
J. A. Porter

Classification

Approved by JAPorter Date 8/10/74
J. A. Porter

Approved by Date 8/9/74

Authority

Topic 5.1.1 Classification Guide - UF-2

Topics ~~151.2.1.9, 151.5.1, 151.5.8, 151.5.10, 250.7.13~~ 150.3.2, 150.3.8, 150.4.2, 150.4.9
SR Classification Guide

Category if DP Report

Approved by Date 8/9/74
Supervisor, TIS

Final Du Pont Release

Approved by Date 8/14/74
Coordinating Organization Director

Released by:

A. F. Westerdahl: 9/9/74

Form AEC 426
(6-73)
AECM 3201

U.S. ATOMIC ENERGY COMMISSION

MAJOR CONTRACTOR'S RECOMMENDATION FOR DISPOSITION OF SCIENTIFIC AND TECHNICAL DOCUMENT

*See Instructions on Reverse

1. AEC Report No. DP-1361

2. Subject Category No. UC-10

3. Title Partitioning of Light Lanthanides from Actinides by Solvent Extraction with TBP

4. Type of Document ("X" one)
   - ☒ a. Scientific and Technical Report
   - ☐ b. Conference Paper
     Title of conference ______
     Date of conference ______
     Exact location of conference ______
   - ☐ c. Journal article. Submitted to ______
   - ☐ d. Other *(Specify, Thesis, Translation, etc.)** ______

5. Copies Transmitted ("X" one or more)
   - ☒ a. Copies being transmitted for standard distribution by AEC-TIC.
   - ☐ b. Copies being transmitted for special distribution per attached complete address list.*
   - ☐ c. Two completely legible, reproducible copies being transmitted to AEC-TIC.

6. Recommended Distribution ("X" one)
   - ☒ a. Copies being transmitted for standard distribution by AEC-TIC.
   - ☐ b. Make available only to U.S. Government agencies and their contractors.
   - ☐ c. Make available only within AEC and to AEC contractors.
   - ☐ d. Make available only within AEC.
   - ☐ e. Make available only to those listed in item 12 below.
   - ☐ f. Other *(Specify)** ______

7. Recommended Announcement ("X" one)
   - ☒ a. Normal procedure may be followed.*
   - ☐ b. Recommend following announcement limitations: ______

8. Reason for Restrictions Recommended in 6 or 7 above.
   - ☐ a. Preliminary information.
   - ☐ b. Prepared primarily for internal use.
   - ☐ c. Other *(Explain)* ______

9. Patent Clearance ("X" one)
   - ☒ a. AEC patent clearance has been granted by responsible AEC patent group.
   - ☐ b. Document has been sent to responsible AEC patent group for clearance.

10. National Security Information *(For classified document only; "X" one)*
    - ☐ a. Document does contain national security information other than restricted data.
    - ☐ b. Document does not contain national security information other than restricted data.

11. Copy Reproduction and Distribution
    a. Total number of copies reproduced 168
    b. Number of copies distributed outside originating organization 0

12. Additional Information or Remarks *(Continue on separate sheet, if necessary)*

13. Submitted by *(Name and Position) (Please print or type)** F. H. Springer

14. Organization Savannah River Laboratory

15. Signature F. H. Springer Jr

16. Date 9/30/74

INTERNAL DISTRIBUTION

Copy No.	
1-3.	T. B. Niland, SR
4.	J. D. Ellett, Wilm
5.	S. A. McNeight
6.	F. E. Kruesi - J. F. Proctor
7.	L. C. Evans - J. W. Croach - A. A. Johnson
8.	W. File
9.	L. F. Shafranek, Eng Dept
10.	J. K. Lower - A. H. Peters, SRP
11.	W. P. Bebbington
12.	R. Maher
13.	D. A. Orth
14.	W. C. Scotten
15.	J. M. McKibben
16.	C. H. Ice - L. H. Meyer, SRL
17.	J. O. Morrison
18.	H. J. Groh
19.	J. A. Porter
20.	A. S. Jennings
21.	W. E. Prout
22.	M. L. Hyder
23.	H. P. Holcomb
24.	TIS Record Copy