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BATCH SOLVENT EXTRACTION OF PROTACTINIUM-233
FROM THORIA DISSOLVER SOLUTION

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ABSTRACT

Head-end removal of undecayed ^{233}Pa from irradiated thoria dissolver solution is desirable prior to Purex process recovery of ^{233}U and thorium to minimize radiolysis of the tributyl phosphate extractant. A batch solvent extraction process for this purpose is described; the extractant is diisobutyl carbinol (DIBC) diluted (20 vol% DIBC) with normal paraffin hydrocarbon (NPH). This process is specifically intended for operation in single-stage centrifugal contactors and was satisfactorily demonstrated in laboratory-scale centrifugal extraction equipment.

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BATCH SOLVENT EXTRACTION OF PROTACTINIUM-233 FROM THORIA DISSOLVER SOLUTION

INTRODUCTION

Protactinium-233 ($t_{1/2} = 27.4$ days) is produced as an intermediate when ^{232}Th is irradiated with neutrons to produce ^{233}U :

Cooling of the irradiated thoria or thorium fuel for about 250 days^[1] is sufficient to ensure insignificant ($\leq 0.1\%$) ^{233}U waste loss as its ^{233}Pa parent. However, cooling times up to two years^[1] are required before the amount of ^{233}Pa decays to a level where it cannot influence solvent radiolysis during fuel reprocessing.* To circumvent problems engendered by radiolysis of TBP while also avoiding long and expensive cooling times, procedures for removal of all or most of the undecayed ^{233}Pa from irradiated thoria dissolver solutions are desirable.

Scavenging and precipitation processes for removal of ^{233}Pa from thoria dissolver solutions have been described earlier.^[3-6] A batch solvent extraction process for removal of the ^{233}Pa is described in this report. This process employs diisobutyl carbinol (DIBC) diluted with normal

* Troublesome white solids identified as thorium dibutyl phosphate precipitated in the 1C Th-stripping column during processing of thoria containing about 3 to 6 grams ^{233}Pa per ton in the 1966 Hanford Thorium Campaign.^[2] Excessive concentrations of dibutylphosphoric acid were produced by (^{233}Pa) radiolysis of the TBP extractant.

paraffin hydrocarbon (NPH) as the extractant and is specifically designed for operation in short residence time centrifugal contactors. [Normal paraffin hydrocarbon is a mixture of C_{10} to C_{14} alkanes.] The scouting nature of the work reported here, which was conducted in connection with the 1970 Hanford Thorium Campaign, is emphasized. Although the initial results indicate process feasibility, available time and money did not permit detailed investigation of all facets of the extraction scheme.

Previous application of DIBC and also diisopropyl carbinol (both undiluted) for process and analytical solvent extraction of ^{233}Pa from various media have been described elsewhere. [1, 7-10]

SUMMARY AND CONCLUSIONS

A simple batch solvent extraction process for removal of undecayed ^{233}Pa from irradiated thoria dissolver solutions has been developed. In this head-end scheme the dissolver solution is contacted with an equal volume of 20 vol% DIBC in NPH to extract about 90% of the ^{233}Pa ; about 50% of the ^{95}Nb , and only 0.4% of the ^{233}U also extract. Subsequent contact of the DIBC extract with an equal volume of 0.25M HNO_3 -0.025M HF solution removes about 95% of the protactinium and 75% of the niobium. The stripped DIBC solvent is recycled to the extraction contact.

Protactinium transfers rapidly between aqueous and DIBC phases. The batch extraction-strip process is thus especially suited for operation in centrifugal contactors. In process tests in a miniature single-stage centrifugal contactor, ~88% of the ^{233}Pa extracted and ~95% stripped even at organic phase residence times as short as 20 to 30 seconds.

Operation of the batch process at such short organic phase residence periods is desirable to minimize radiolysis of the DIBC extractant. Further process testing in centrifugal contactors is required and recommended to establish degree and effects of DIBC radiolysis.

Stripping of plutonium and uranium from Purex process 25 to 30 vol% TBP-NPH solvents is not adversely affected by the presence of small concentrations (1 to 5 vol%) of DIBC. Under these conditions DIBC acts essentially as an inert diluent for the TBP. Incorporation of the batch ^{233}Pa extraction process into a Purex plant complex should not pose serious solvent compatibility problems.

CHEMICAL FLOWSHEET AND PROCESS DESCRIPTION

A chemical flowsheet for the batch DIBC protactinium extraction process is shown in Figure 1. In the extraction step the irradiated thorium dissolver solution is contacted with an equal volume of 20 vol% DIBC-NPH solvent to extract about 90% of the ^{233}Pa , 50% of the ^{95}Nb , and 0.4% of the ^{233}U . Subsequently, the pregnant organic phase is contacted with an equal volume of 0.25M HNO_3 -0.025M HF solution to strip 95% of the protactinium and about 75% of the niobium. The stripped organic phase containing small amounts of ^{233}Pa and ^{95}Nb is recycled to the extraction step.

To minimize radiolysis of the DIBC extractant, this batch extraction process is intended for operation in single-stage centrifugal contactors. Phase residence times as low as three seconds can be achieved in such contactors.^[11,12] A typical plant-scale unit (0.5-gallon mixing section and 4-gallon centrifuge bowl) was recently constructed at Hanford for possible use as a solvent washing device in one part of the Waste Management Program.^[13]

FIGURE 1
CHEMICAL FLOWSHEET FOR DIBC EXTRACTION
OF ²³³Pa FROM THORIA DISSOLVER SOLUTION

This size unit can accommodate a total throughput (sum of phases) of about 50 gal/min. For the flowsheet conditions shown in Figure 1, such a unit could process a 3000-gallon batch of thoria dissolver solution in about four hours. With some sacrifice in the amount of ^{233}Pa extracted, this time could be reduced to two or three hours.

Extraction of 0.4% of the ^{233}U from the thoria solution is a disadvantage of the Pa removal scheme. If loss of this much ^{233}U cannot be tolerated, the flowsheet can be modified to include scrubbing ^{233}U from the DIBC extract with a small volume of concentrated $\text{Al}(\text{NO}_3)_3$ solution as is done in the Thorex No. 1 process.^[1]

EXPERIMENTAL

MATERIALS

Aqueous feedstock for use in determining equilibrium ^{233}Pa extraction data was prepared by dissolution of irradiated thoria wafers.^[14] Typical composition of the solution produced in such dissolutions is listed in Table I (Solution No. 1). Synthetic dissolver solution (Solution No. 2, Table I) of approximately the same gross salt composition and spiked with $^{233}\text{UO}_2(\text{NO}_3)_2$ was used to determine DIBC extraction of uranium. Another synthetic dissolver solution (Solution No. 3), spiked with a small amount of actual dissolver solution, was used as feedstock in the single-stage centrifugal contactor experiments. Gross salt composition of Solution No. 3 was approximately that of dissolver solutions produced in the 1970 Hanford Thorium Campaign.

The protactinium extractant was prepared by diluting as-received DIBC (Pfaltz and Bauer Company) with NPH (South Hampton Company). Immediately prior to contact with thoria

TABLE I
COMPOSITION OF THORIA DISSOLVER SOLUTIONS

Component	Concentration		
	Solution No. 1 ^{a, b}	Solution No. 2 ^c	Solution No. 3 ^{d, b}
HNO ₃ , M	7.4	7.0	6.5
Th(NO ₃) ₄ , M	1.4	1.4	0.78
Al(NO ₃) ₃ , M	0.1	0.1	0.13
KF, M	0.05	0.05	0.04
²³³ U, g/liter	<i>e</i>	0.5 ^f	<i>e</i>
²³³ Pa, μCi/liter	4.8 x 10 ⁸	<i>g</i>	1.37 x 10 ³
⁹⁵ Zr- ⁹⁵ Nb, μCi/liter	4.9 x 10 ⁶	<i>g</i>	<i>e</i>
⁹⁵ Zr, μCi/liter	<i>e</i>	<i>g</i>	1.63 x 10 ³
⁹⁵ Nb, μCi/liter	<i>e</i>	<i>g</i>	3.06 x 10 ³

a From dissolution of irradiated thoria wafer.

b Dissolver solution also contained ¹⁴⁴Ce, ¹⁴⁴Pr, ¹⁰⁶Ru, ¹⁰⁶Rh, ¹³⁷Cs, and ¹³⁴Cs.

c Synthetic dissolver solution.

d Synthetic dissolver solution spiked with small amount of Solution No. 1.

e Concentration not measured.

f Added when appropriate.

g Not present.

dissolver solutions, DIBC-NPH extractants were contacted twice with equal volumes of 6 to 7M HNO₃.

Tributyl phosphate (TBP) was obtained from the Commercial Solvents Corporation. Solvents containing 25 to 30 vol% TBP and 0 to 5 vol% DIBC (in NPH) were prepared from as-received reagents and washed successively with 0.24M Na₂CO₃, 1M HNO₃, and water.

Extraction of uranium from synthetic thoria dissolver solution was followed with the aid of ²³³U tracer. This latter material was available as a purified ²³³UO₂(NO₃)₂ solution from Hanford Purex plant processing of irradiated thoria in the 1966 Thorium Campaign.^[15]

All other chemicals were of reagent grade quality.

PROCEDURES AND EQUIPMENT

DISTRIBUTION RATIO MEASUREMENTS

The distribution ratio (E_a^O) is defined as the ratio of the concentration of the element of interest in the organic phase to the concentration of the element in the aqueous phase after equilibration of the two essentially immiscible liquids.

A standard 10-minute contact period at 25 °C (mechanical stirring) was used to determine equilibrium $^{233}\text{Pa } E_a^O$ data in both extraction and stripping steps. Phases were separated by centrifugation. Equilibrium data for transfer of uranium and plutonium between TBP-DIBC-NPH solvents and various aqueous solutions were also determined by 10-minute mechanical mixing periods at 45 °C.

Extraction of HNO_3 into 20% DIBC-NPH was measured by contacting the DIBC extractant three times (10 minutes, 25 °C) with fresh, equal-volume portions of each particular aqueous HNO_3 solution. Aqueous and organic phases resulting from the third contact were analyzed for HNO_3 . Distribution of HNO_3 under process flowsheet conditions was determined with synthetic dissolver solution.

SINGLE STAGE CENTRIFUGAL CONTACTOR

A miniature single-stage centrifugal contactor was used to demonstrate and test the batch extraction process. An overall view of the contactor and associated experimental equipment is pictured in Figure 2. Component parts of the mixing chamber and centrifuge bowl are illustrated in Figure 3; these parts were constructed according to the basic design given originally by Jennings.^[12] Except for the glass-filled Teflon bearing used to support the

FIGURE 3
COMPONENT PARTS OF MINIATURE CENTRIFUGAL CONTACTOR
Top - Centrifuge Parts
Bottom - Mixing Chamber

centrifuge bowl, all parts, including the block, were made from 304-L stainless steel.

Individual motors (Indiana General Corporation Models P/N 1509-39 and P/N 1509-40) powered by separate DC sources (Electro Products Laboratories, Inc., Model PS 1000-32) were used to operate the mixer and centrifuge. In all tests the mixer and centrifuge were operated at 4500 and 5500 rpm, respectively. Aqueous and organic solutions were metered (Fluid Metering, Inc. pumps) to the contactor through glass surge tanks (Figure 2); the latter tanks permitted a steady flow of liquid to the mixing chamber.

Runs under both extraction and stripping conditions were both made at about 25 °C. In the extraction runs, aqueous feedstock (Solution No. 3, Table I) and 20% DIBC-NPH pre-equilibrated with 6.4M HNO₃ were metered to the contactor at the lowest desired flow rates for about 10 minutes to allow the system to come to steady state. Then, while flows of both aqueous and organic streams were maintained constant, triplicate samples of each effluent stream were taken over a 15-minute period. Flow rates of the influent streams were then increased to the next (predetermined) higher level and the sampling sequence repeated over a 15-minute period. This procedure was repeated until the highest desired flow rates were attained.

Suitably modified, the procedure just described was used to study kinetics of stripping of ²³³Pa and ⁹⁵Nb from 20% DIBC solvent into 0.25M HNO₃-0.025M HF solution. In this case the contactor was started up with nonradioactive 20% DIBC-NPH solvent (pre-equilibrated with 6.4M HNO₃) prior to introduction of the 20% DIBC extract containing ²³³Pa. The latter material was prepared by operating the centrifugal contactor under extraction contact conditions immediately

prior to the stripping experiments.

Calculation procedures devised by G. L. Richardson^[16] were used to estimate organic residence times in the centrifugal contactor. These procedures are described in the Appendix.

RESULTS AND DISCUSSION

DISTRIBUTION RATIOS--EXTRACTION AND STRIPPING CONTACTS

Distribution ratios for extraction of various components of thorium dissolver solution into DIBC-NPH solvents are listed in Table II; additional distribution ratio data for

TABLE II
DIBC EXTRACTION OF ^{233}Pa --
DISTRIBUTION RATIO DATA

Conditions: Thorium dissolver solution contacted with equal volume of indicated DIBC-NPH solvents. All DIBC solvents pre-equilibrated by contacting twice with equal volumes of 7M HNO_3 .

<u>DIBC</u> <u>Vol%</u>	E_a^0		Percent Extracted	
	$^{233}\text{Pa}^a$	$^{233}\text{U}^b$	^{233}Pa	^{233}U
100 ^c	52.3	0.134	98.1	11.8
70	<i>d</i>	0.0545	<i>d</i>	5.03
50	<i>d</i>	0.0279	<i>d</i>	2.69
30	14.7	0.0136	95.5	1.35
20 ^e	7.16	<i>d</i>	89.8	<i>d</i>
10	1.82	0.00108	65.3	0.104

a With Thorium Dissolver Solution No. 1, Table I.

b With Thorium Dissolver Solution No. 2, Table I.

c Thorium E_a^0 was 0.00069.

d Not determined.

e ^{95}Nb E_a^0 was 1.42 for a 30-minute contact.

undiluted DIBC are tabulated in Reference 1. In a single batch contact at equal phase volumes an extractant containing as little as 20 vol% DIBC extracts 85 to 90% of the ^{233}Pa . At this DIBC concentration about 60% of the ^{95}Nb , about 0.4% of the ^{233}U , and less than 0.1% of the Th extract. Save for ^{95}Nb , none of the fission products report to the 30 vol% DIBC phase.

In agreement with literature accounts,^[8] HNO_3 solutions containing small amounts of HF effectively remove protactinium from DIBC solutions (Table III). A strip composition

TABLE III
DISTRIBUTION RATIOS FOR STRIPPING OF ^{233}Pa
FROM 20% DIBC-NPH SOLVENT

Conditions: 20% DIBC-NPH, preequilibrated with 7M HNO_3 , contacted with an equal volume of Thoria Dissolver Solution No. 1, Table I. Portions of resulting organic phase contacted with equal volumes of indicated HNO_3 -HF solutions.

<u>Strip Composition</u>		^{233}Pa $\frac{E}{a}$
$\frac{\text{HNO}_3}{M}$	$\frac{\text{HF}}{M}$	
0.1	0.025	0.0130
0.25	0.025	0.0075
0.50	0.025	0.0032
1.0	0.025	0.0039
0.1	0.5	0.0051
0.25	0.05	0.0074
0.50	0.05	0.0037

of 0.25M HNO_3 -0.025M HF is specified for flowsheet purposes; at equal phase volumes this solution strips about 95% of the ^{233}Pa and, as results presented in the next section show, about 75% of the ^{95}Nb from the 20% DIBC phase.

Data for distribution of HNO_3 between 20% DIBC-NPH and

aqueous solutions are plotted in Figure 4.

MINIATURE CENTRIFUGAL CONTACTOR TESTS

Tests of the batch protactinium extraction process in a miniature centrifugal contactor were very successful. These experiments show that protactinium transfers rapidly between aqueous and DIBC phases. For example, under extraction conditions (Figure 5), about 88% of the ^{233}Pa in the thoria dissolver solution extracts into the DIBC solvent at an organic phase residence time as short as 0.3 minute. In comparison, only about 90% of the ^{233}Pa extracts even at prolonged organic phase residence times (30-minute batch contact). Stripping of the ^{233}Pa proceeds equally rapidly (Figure 6); at an organic phase residence time of 0.3 minute, about 93% of the ^{233}Pa transfers to the 0.25M HNO_3 -0.025M HF strip solution.

Results in Figures 5 and 6 show that ^{95}Nb strips about as fast as ^{233}Pa but extracts slightly more slowly. At equilibrium (30-minute batch contact), only about 60% of the ^{95}Nb extracts and of that extracted, the HNO_3 -HF solution strips only about 84%. At an organic phase residence time of 0.3 minute, 50% of the ^{95}Nb extracts and 72% strips.

COMPATABILITY OF DIBC WITH PUREX PROCESS

Incorporation of a DIBC extraction process in a Purex plant would convert it from the traditional one-solvent plant to a two-solvent one. The DIBC process is a low-volume batch operation which, as currently projected, would be performed in a section of the plant isolated from the mainline Purex process solvent. Loss of the entire inventory of 20% DIBC extractant to the TBP solvent would be improbable. However, even in such an unlikely event, the Purex process

FIGURE 4
DISTRIBUTION OF HNO_3 BETWEEN 20% DIBC-NPH
AND AQUEOUS HNO_3 SOLUTIONS

FIGURE 5
KINETICS OF EXTRACTION OF ^{233}Pa AND ^{95}Nb
INTO 20% DIBC EXTRACTANT

FIGURE 6
KINETICS OF STRIPPING ^{233}Pa AND ^{95}Nb
FROM 20% DIBC EXTRACT

solvent would contain only 1 to 5 vol% DIBC.

Batch contacts were made to determine the effects of DIBC on the equilibria and kinetics of stripping of uranium and plutonium from 30% TBP containing up to 5% DIBC solutions. Equilibrium distribution data shown in Tables IV and V and in Figure 7 indicate that small concentrations of DIBC act as an inert diluent for the TBP and have no deleterious effect on strippability of either plutonium or uranium. Kinetic data for stripping of plutonium and uranium from TBP-DIBC solutions are shown in Table VI. Following techniques developed by Mendel,^[17] these kinetic data were obtained with a dispersion-disengaging apparatus of a familiar type.^[18] The presence of 1 to 5 vol% DIBC in the TBP solvent does not appear to have any significant effect upon kinetics of transfer of plutonium and uranium between aqueous and organic phases.

TABLE IV
EFFECTS OF PRESENCE OF DIBC IN PUREX SOLVENT--
MULTIPLE BATCH CONTACTS

Contact Number ^a	Pu E _a ^o		
	Volume Percent DIBC ^{b, c}		
	0	1	5
1	0.198	0.143	0.142
2	0.0407	0.0071	0.0025
3	0.0031	-	0.0016
4	0.0024	0.0010	0.00057

^a Four successive contacts at 45 °C of each organic phase with one-third volume portions of 0.1M HNO₃-0.045M H₂SO₄-0.045M sulfamic acid.

^b All solvents were also 30 vol% TBP-NPH.

^c Initial organic in each case was about 0.18M HNO₃-0.015M Pu(NO₃)₄.

TABLE V
URANIUM DISTRIBUTION RATIOS FOR TBP-DIBC SOLVENTS

Conditions: Each of the indicated TBP-DIBC-NPH solutions was contacted twice with fresh portions of $2M$ $UO_2(NO_3)_2$ solution. Portions of the resulting organic phases were contacted at $45^\circ C$ with various volumes of $0.01M$ HNO_3 .

<u>DIBC</u> <u>Vol%</u>	<u>TBP</u> <u>Vol%</u>	<u>Equilibrium Uranium, M</u>		<u>U</u> <u>E_a^0</u>
		<u>Aqueous</u>	<u>Organic</u>	
0.0	30	0.0174	0.00106	0.061
		0.0654	0.0151	0.231
		0.128	0.0616	0.480
		0.211	0.152	0.719
		0.264	0.210	0.797
		0.314	0.248	0.792
		0.363	0.290	0.797
1.0	29	0.106	0.0109	0.103
		0.206	0.126	0.614
		0.270	0.178	0.660
		0.339	0.230	0.680
		0.381	0.263	0.691
2.0	28	0.107	0.00832	0.078
		0.220	0.125	0.567
		0.276	0.171	0.618
		0.294	0.190	0.647
		0.383	0.247	0.644
5.0	25	0.0996	0.0019	0.019
		0.210	0.0887	0.422
		0.266	0.127	0.479
		0.326	0.159	0.488
		0.396	0.190	0.480

FIGURE 7
EQUILIBRIUM URANIUM EXTRACTION DATA FOR TBP-DIBC-NPH SOLVENTS

TABLE VI
EFFECTS OF PRESENCE OF DIBC IN PUREX SOLVENT--
KINETIC MEASUREMENTS

No.	Solvent ^a		Contact Time min ^b	Pu, $E_a^{\circ c,d}$	U, $E_a^{\circ e,f}$
	DIBC	Vol%			
1	0		2	0.0159	0.0117
			5	-	0.0187
			10	0.0133	0.0205
2	1		2	0.00863	0.0206
			5	0.00796	0.0210
			10	0.00869	0.0212
3	5		2	0.0108	0.0167
			5	0.00879	0.0172
			10	0.00840	0.0168

^a All solvents were also 30% TBP-NPH.

^b Equal volume contacts at 45 °C.

^c Typical Hanford Purex plant 2B Column conditions.

^d Initial organic in each case was about 0.18M HNO₃-0.015M Pu(NO₃)₄ while initial aqueous in each case was 0.1M HNO₃-0.045M H₂SO₄-0.045M sulfamic acid.

^e Typical Hanford Purex plant 1C Column conditions.

^f Initial organic in each case was about 0.33M UO₂(NO₃)₂-0.088M HNO₃ while initial aqueous was 0.01M HNO₃.

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APPENDIX

CALCULATION OF ORGANIC PHASE
RESIDENCE TIMES

APPENDIX
CALCULATION OF ORGANIC PHASE
RESIDENCE TIMES

Multistage centrifugal contactors with stages of the same dimensions as used in our single-stage device have been constructed and operated recently by G. L. Richardson of the Westinghouse Hanford Company.^[16] For these dimensions Richardson estimates that the approximate total volume of a stage--mixer plus centrifuge plus underflow channel--is 6 to 7 ml and that the approximate volume of "emulsions" in mixer and centrifuge feed lines is 2.3 ml.

The organic phase residence time per stage is calculated according to the following steps:

1. Estimate volume fraction of organic in emulsion as

$$\frac{O}{O+A} = \frac{1}{1+A/O}.$$

2. Estimate volume of organic in emulsion as

$$(2.3)/(1 + A/O) \text{ ml.}$$

3. Use curves plotted in Figures A-1 and A-2 to estimate the volume of organic in the centrifuge bowl. Data points plotted in these figures were calculated from the formulae listed in USAEC Report DP-680 for a centrifuge bowl speed of 5500 rpm and for $r_o = 0.3607$ cm and $r_a = 0.4178$ cm.
4. Calculate the total organic volume as the sum of the volumes calculated in Steps 2 and 3.
5. Calculate the organic residence time by dividing the total organic volume (Step 4) by the organic flow rate.

FIGURE A-1
ESTIMATION OF VOLUME OF ORGANIC PHASE IN
CENTRIFUGE BOWL FOR AQUEOUS FLOW OF 1 ml/min

FIGURE A-2
ESTIMATION OF VOLUME OF ORGANIC PHASE IN CENTRIFUGE BOWL
FOR AQUEOUS FLOW OF 10 ml/min

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