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REMOVAL OF FISSION PRODUCTS FROM REACTOR WASTES

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REMOVAL OF FISSION PRODUCTS FROM REACTOR WASTES: Laboratory Studies of Liquid-Liquid Extraction from an Acid Aluminum Nitrate Solution

Herman L. Krieger, Bernd Kahn, and Conrad P. Straub+

DATE ISSUED

MAY 3 1957

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ABSTRACT

Liquid-liquid extraction of the major long-lived fission products was evaluated as a method for decontaminating an acid aluminum nitrate waste. Tributyl phosphate, di-2-ethylhexyl phosphoric acid, tridecyl phosphine oxide, tri-n-octyl amine and thenoyl trifluoroacetone were found to be effective in extracting one or more of the cerium, yttrium, zirconium, niobium, and ruthenium tracers used in this study. After converting ruthenium and niobium to an extractable form, more than 99% of the tracers was extracted into undiluted tributyl phosphate. Cesium was not extracted, and strontium very slightly extracted. The extracted radionuclides were stripped from tributyl phosphate with water, dilute hydrofluoric acid and nitric acid, permitting reuse of the organic phase.

INTRODUCTION

The separation of the major radioactive fission products from a reactor waste solution by means of solvent extraction has been studied. This particular waste solution, one of several resulting from the dissolving of reactor fuel elements and the recovery of fissionable material, contained nitric acid and aluminum nitrate, and was typical in that non-radioactive salts greatly exceeded the concentration of fission products.[1,2] The study was one of several undertaken to develop waste treatment methods other than the tank storage of liquids, an expensive procedure whose cost varies from $0.35 per gallon for neutralized wastes stored in concrete tanks to $2.00 per gallon for high level acid wastes in water-cooled stainless steel tanks.[1]

Storage of fission products in solid rather than liquid form may be preferable both for increased safety and for reduced waste volume. Solidification has been attained by drying, coprecipitation, and absorption on soil and ion exchange resins,[3-23] frequently after separating the fission products from non-radioactive ions by distillation, crystallization, and electrical means.[3,5, 6, 24-26] The radioactive solids may then be processed for use or fused at high temperatures for permanent storage. The large residual volume of wastes may be stored under less stringent conditions, discharged to the environment, or processed for the recovery of non-radioactive ions, depending on the effectiveness of the fission product separation.

Solvent extraction of the fission products was considered as a means of separating them from the waste solution because of the successful application of this technique in the recovery of uranium and other fissionable material

from the same reactor fuel solution. In this process, an organic liquid immiscible in the fuel solution is placed in contact with the aqueous phase until most of the uranium has been transferred to the organic phase. Uranium is extracted because it is more soluble in the organic than in the aqueous phase, while purification is achieved because all other ions are less soluble. The organic phase is washed for additional uranium purification, and the uranium is stripped into an aqueous phase in which uranium is more soluble than in the organic. The uranium is then converted to a solid without interference from the other ions which originally accompanied it, and the organic extractant is reused. An analogous process was proposed for the fission products.

This study was undertaken because the direct extraction of the major fission products from a particular reactor waste solution has been reported only in isolated instances.[27] A number of organic substances have been reported to form readily extractable complex molecules with some fission products. Among these are tributyl phosphate, thenoyl trifluoroacetone, and organic phosphine oxides with zirconium, niobium, yttrium, and the lanthanum rare earths.[28-42] The reactions occurring between zirconium and either thenoyl trifluoroacetone (TTA) or tributyl phosphate (TBP), and which are typical of such complexing reactions, have been written, respectively,

$$Zr^{+4}_{(A)} + 4\ H(TTA)_{(O)} \rightleftharpoons Zr(TTA)_{4(O)} + 4\ H^{+}_{(A)} \qquad (1)$$

and[31]

$$Zr^{+4}_{(A)} + 4\ NO_3^{-}{}_{(A)} + 3\ (TBP)_{(O)} \rightleftharpoons Zr(NO_3)_4(TBP)_{3(O)} \qquad (2)$$

where the subscripts (A) and (O) refer to the aqueous and organic phases. The ratio of zirconium in the organic phase to that in the aqueous, called the distribution coefficient (D.C.) or ratio (D.R.), is, from equation (1) for TTA

$$D.C. = K_{eq}\left[H(TTA)\right]^4_{(O)} / \left[H^+\right]^4_{(A)} \qquad (3)$$

and from equation (2) for TBP

$$D.C. = K_{eq} \left[NO_3^-\right]^4_{(A)} \cdot \left[TBP\right]^3_{(O)} \qquad (4)$$

K_{eq} being the equilibrium constants of equations (1) and (2). Equations (3) and (4) indicate that the extraction efficiency is a function of the concentration of the complexing agent and varies inversely with the acidity in the first case and directly with the nitrate concentration in the second. Thus, ideally, extraction is independent of the extractable ion concentration and could be performed with identical effect repeatedly on the same solution, were it not for the presence of competing ions and other complexing agents.

Solvent extraction recommends itself for large-scale fission product separation because it can readily be made a continuous process. It would be preferrable to several other methods if

1) the distribution coefficient for a number of major fission products were large, so that the organic volume may be small,

2) the distribution coefficient remained constant for successive extractions, so that the fraction of fission products extracted could be controlled,

3) the extractant could be reused. Losses by solution in the aqueous phase and radiation damage must be small, and stripping of the fission products effective.

PROCEDURE

General A synthetic waste solution was prepared, consisting of 1.6M aluminum nitrate, 0. 16M nitric acid, 0.02M sulfuric acid, and the non-radioactive fission product ions listed in Table I. Individual radioactive tracers were added, and 50 ml. of this solution was shaken for at least 5 minutes in separatory funnels with 5 ml. of the organic extractant. The phases were separated, a fresh volume of extractant added to the synthetic waste, and the extraction repeated, in duplicate, four consecutive times. Aliquots of the aqueous phase were taken before and after each extraction and counted with a sodium iodide gamma scintillation counter or a Geiger - Müller beta counter. The per cent extracted, listed in Tables IV to XIV, was calculated from the difference in the count rate of the aqueous phase before and after extraction, divided by the count rate before extraction. Distribution coefficients (D.C.) were obtained from the difference of the activities in the aqueous phase before and after extraction, divided by the activity after extraction, and multiplied by the aqueous/organic volume ratio. The coefficients were listed whenever they were found to be constant for successive extractions, otherwise only the per cents extracted were given.

After extraction, the four organic volumes were combined and counted. The organic solution was then shaken either with fresh acid aluminum nitrate solution to determine the reversibility of extraction; or with other aqueous solutions to strip the fission products from the extractant to permit its reuse.

In addition, the effects of extraction time, temperature, aqueous to organic ratio, and concentration of solvent, carrier, acid, and aluminum nitrate were studied.

TABLE I

Fission Products Studied

Tracer	Mode of Counting	Carrier	Carrier Concentration mg/liter
Cs^{137}-Ba^{137}	$Ba^{137}\gamma$ at equilibrium	Cs	21.6
Sr^{89}	$Sr^{89}{}_{\beta}$	Sr	9.4
Y^{91}	$Y^{91}{}_{\beta}$	Y	4.4
Ce^{144}-Pr^{144}	Ce^{144} and $Pr^{144}\gamma$ at equilibrium	Ce	23.6
Ru^{106}-Rh^{106}	$Rh^{106}\gamma$ at equilbrium	Ru	11.2
Zr^{95} -Nb^{95}	Zr^{95} and $Nb^{95}\gamma$ not at equilibrium (~50% of each)	Zr	25.6
Nb^{95}	$Nb^{95}{}_{\gamma}$	Nb	1.2
		Others Added (Ba, La, Pr, Mo)	62.2
		Others in a fission product solution, but not added (Tc, Rh, Pd, Xe, and Kr)	40.8
		Total	200.0

Critical Fission Products The tracer radionuclides, the mode of counting, and the carrier concentrations are given in Table I. The tracers were obtained from the Operations Division, ORNL. Radioactive contamination was reported to be less than 2%, and was found to be generally less the 0.5%. The carrier concentration is based on calculations for a power reactor waste stored 30 days after separation from uranium which had been in a reactor for 30 days. The carriers were added as nitrates.

Extractants Extraction of the major fission products was first attempted with the readily available organic solvents listed in Table III. Upon observing their ineffectiveness, the complexing agents given in Table II were tested. Tributyl phosphate, tridecyl phosphine oxide, and thenoyl trifluoroacetone were considered because they extracted several fission products from a variety of solutions,[27-41] and "Primene-JMT" (a primary amine), tri-n-octyl amine (a tertiary amine), and di-2-ethylhexyl phosphoric acid because their effectiveness for uranium[41, 43-45] indicated the possibility of fission product extraction. Because of the increase in distribution coefficient with concentration, the complexing agents were tested in the highest concentration possible: tributyl phosphate undiluted, and the concentration of the others limited only by the formation of a solid phase on contact with the waste solution. To prevent the extraction of aluminum nitrate or acids from the waste, the organic phase was saturated before use by repeated contact with a 1.6M aluminum nitrate, 0.16M nitric acid, and 0.02M sulfuric acid solution.

Tributyl phosphate [46,47] was found to be the most effective extractant, and was therefore studied in greatest detail.

TABLE II

Organic Extractants for Fission Products

Name	Formula	Molecular Weight	Concentration
2-thenoyl trifluoroacetone (TTA)	$(C_4H_3S)(C_3H_2O_2)CF_3$	222	0.5M in Benzene
Tributyl Phosphate (TBP)	$(C_4H_9)_3PO_4$	267	3.6M (100%)
"Primene - JMT"	$[R(CH_3)_2\ CNH_2]$ R is 15-21 carbon alkyl group	-	Diluted 1:2 in Benzene
Tri-n-Octyl Amine	$[CH_3(CH_2)_7]_3N$	353	1.3M in Benzene
Tridecyl Phosphine Oxide	$(C_{10}H_{21})_3\ PO$	471	0.9M in Benzene
Di-2-ethylhexyl Phosphoric Acid	$(C_8H_{17}O)_2\ PO_2H$	322	1.3M in Benzene

+ Suggested and supplied by K. B. Brown (Chemical Technology Division)

++ Suggested and supplied by W. H. Baldwin (Chemistry Division)

TABLE III

Organic Extractants Found Ineffective

Solvent	Fission Product:	Percent Extracted into Organic Phase			
		Ru^{106}	Zr^{95}- Nb^{95}	Sr^{89}	Cs^{137}
"Amsco"		0	0	-	-
Diisopropyl carbinol		10	0	-	0
Methyl isopropyl ketone		10	0	0	0
Amyl acetate		0	0	0	0
Hexane		0	0	-	-
2-ethyl n-hexanol		20	0	-	-
Chloroform		0	0	0	0
Ether		0	0	0	0
8-hydroxyquinoline in Benzene		-	0	0	0
0.5M TTA in Chloroform		0	-	-	-
0.5M TTA in Methyl isobutyl ketone		-	-	0	0
Isopropyl ether		0	-	0	0
Dibutoxytetraethylene glycol (Penta ether)		0	-	0	0
Dibutyl phosphate		Aluminum Precipitates			
Pyridine		} Soluble in $Al(NO_3)_3$ Solution			
2-4-6 Collidine					

RESULTS

Cesium: No cesium was removed from the aluminum nitrate solution with any of the organic solvents and complexing agents.

Strontium: Strontium has been extracted into thenoyl trifluoroacetone, 0.05M in benzene or hexone, from aqueous solution at pH values above 5.5,[48] but was not extracted from the 0.16M nitric acid solution. A small but significant distribution coefficient was obtained with tributyl phosphate, hence extraction from a number of salt solutions in the various concentrations listed in Table IV was studied to determine maximum strontium extraction. Strontium was extracted appreciably only from aluminum nitrate, the distribution coefficient increasing with the aluminum nitrate concentration. A low distribution coefficient with molten aluminum nitrate (4M) at 100°C was obtained presumably because of the adverse effect of higher temperatures indicated in Table IV.

No other extractant removed strontium from the aluminum nitrate solution.

Yttrium and the Rare Earths: The relatively long lived fission products include the light rare earths cerium, promethium, samarium, and europium, and heavy-rare-earth-like yttrium. Because of the chemical similarity of these elements only tracer cerium (III) and yttrium, representing the extremes of behavior, were studied. Cerium (unlike the other rare earths) also has a valence of +4 and is presumably more readily extracted in this state, hence $NaBrO_3$ was added as an oxidizing agent to extractants for which cerium (III) had a low distribution coefficient.

Distribution coefficients for cerium and yttrium are listed in Table V. While the acidity is too great to permit extraction into TTA, extraction into TBP was enhanced by the high nitrate concentration.[31] High distribution coefficients were obtained for both cerium and yttrium with tridecyl phosphine

TABLE IV

Strontium Extraction into 100% TBP

Aqueous Phase	Distribution Coefficients
A) Effect of $Al(NO_3)_3$ Concentration	
1.0 M	0.06 ± 0.05
1.6 M	0.16 ± 0.03
2.5 M	0.27 ± 0.03
3.0 M	0.35 ± 0.04
B) Effect of other Nitrates	
15 M HNO_3	0
9 M NH_4NO_3	0.05
1.6 M $Fe(NO_3)_3$	0
3.5 M $Ca(NO_3)_2$	0.05
3.0 M $Mg(NO_3)_2$	0.06
C) Effect of other Anions	
1.6 M $Al_2(SO_4)_3$	0
3 M $Al(OH)_2NO_3$	0.07
D) Effect of Strontium Carrier [2.5 M $Al(NO_3)_3$]	
0.01 mg/ml	0.27 ± 0.03
1.0 mg/ml	0.27 ± 0.02
10.0 mg/ml	0.30 ± 0.03
E) Effect of Temperature [2.5 M $Al(NO_3)_3$]	
74° F	0.23 ± 0.04
190° F	0.12 ± 0.02

oxide, for yttrium only with di-2-ethylhexyl phosphoric acid, and for cerium (IV) only with tri-n-octylamine.

The cerium distribution coefficient varied strongly with TBP concentration (which is expected from equation (4)), and also with organic to aqueous volume ratio (which is puzzling). The distribution coefficients for 100% TBP listed in Table V remain constant, within the deviations given, for three consecutive extractions. That the fraction extracted into 100% TBP in the fourth pass was generally lower (see Tables XIII and XIV) may be attributable to the presence of a small radioactive impurity becoming significant when 99.9% of the cerium or yttrium had been extracted.

The effectiveness of extracting cerium (III) and yttrium differs for all complexing agents. Some values of their extraction into tri-n-octylamine are listed in Table VI. As predicted,[8] the percent extracted varies uniformly with atomic number.

Ruthenium: The fraction of ruthenium extracted into TBP depended on the length of time the ruthenium had been in solution and varied irregularly with the aqueous to organic ratio as shown in Table VII. These effects may be attributed to the existence in the solution of one or more inextractable ruthenium complexes[49-53] in partial equilibrium with extractable nitrosylruthenium trinitrate, and to the increase of the latter if the solution is stored, boiled, or heated with reducing metals. Assuming that after long storage 94% of the ruthenium will be in the extractable species, a distribution coefficient of 18 ± 2 was calculated for the nitrosylruthenium trinitrate.

TABLE V

Rare Earth Extraction

Solvent	Distribution Coefficient Ce III	Ce IV	Y
100% TBP			
5:1 ratio aqueous to organic	142 ± 30	-	-
10:1 ratio aqueous to organic	104 ± 6	-	75 ± 8
20:1 ratio aqueous to organic	42 ± 12	-	-
50% TBP by wt. with "Amsco"			
10:1 ratio aqueous to organic	14 ± 4	-	-
25% TBP by wt. with "Amsco"			
10:1 ratio aqueous to organic	2.4 ± 0.5	-	-
0.5 M TTA in Benzene	0	0	0
1.3 M Di-2-ethylhexyl Phosphoric Acid	2	1	104
0.9 M Tridecyl Phosphine Oxide	115	-	190
0.2 M Tridecyl Phosphine Oxide	5	-	-
1.3 M Tri-n-octylamine	3.6 ± 0.6	61	0.2 ± 0.2
"Primene - JMT"	0.5	0	0

TABLE VI

Extraction of Rare Earths with 1.3 M Tri-n-Octylamine

Tracer	Pass No.:	Percent Activity Removed Per Pass 1	2	3	4
La^{140}		23.8	29.5	35.2	36.1
Ce^{144}		21.0	28.5	25.7	30.9
Pm^{147}		3.2	6.8	20.4	22.7
Eu^{155}		2.9	4.4	13.2	15.1
Y^{91}		0.7	5.1	1.4	0.4

TABLE VII

Ruthenium Extraction Into TBP

Aqueous Phase	Cumulative Percent Ru^{106} Extracted Pass No.: 1	2	3	4
A) Effect of Age of Ru^{106} in $Al(NO_3)_3$				
(10:1 ratio of Aqueous:Organic)				
Fresh	3	15	23	27
2 Weeks	61	70	73	--
4 Months	62	80.1	89.3	94.7
9 Months	61	82.4	89.8	92.4
B) Effect of Aqueous:Organic Ratio				
(9 months old)				
10:1	61	82.4	89.8	92.4
5:1	91.0	95.0	96.2	----
2:1	91.0	96.0	----	----
1:1	94.0	96.8	----	----
C) Effect of Temperature				
(Fresh solution 5:1 ratio)				
30° F	35.2	58.2	68.4	74.1
70° F	24.1	54.2	65.5	71.8
190° F	32.7	61.7	72.0	75.9
D) Effect of TBP Concentration				
Fresh Ru^{106} 100%	----	15		
50%	----	7		
Old Ru^{106} 100%	----	82.4		
50%	----	30.8		

While ruthenium extraction remained almost constant between 30° and 190° F, boiling the solution resulted in the conversion of ruthenium to the more extractable form as shown in Table VIII. More effective extraction was obtained by dissolving a small amount of the metals listed in that table in the boiling solution.

Of the complexing agents listed in Table IX, only TBP and tri-n-octylamine extracted an appreciable fraction of even old ruthenium.

Zirconium and Niobium: Tracers for these elements were available as combined Zr^{95} - Nb^{95} and as Nb^{95}, hence the behavior of the zirconium was obtained by subtracting niobium values from the values of the combined radioactive tracers, and examining the radiations of the extracted radionuclides. Zirconium extractions into 100% TBP, determined by these means, appear to be at least as effective as cerium extraction. Niobium exists in at least two phases, only one of which is extractable as indicated by the rapid decrease in removals with successive TBP passes (Table X). The non-extractable form is probably the result of hydrolysis, which occurs even in 0.16M nitric acid, but its existence is unimportant since niobium in this form has been observed to be removed readily by adsorption on surfaces. Little of the niobium extracted into TBP remains dissolved in that phase. The fraction of unextractable niobium can be slightly decreased by heating (see Table XI), and can be almost eliminated by complexing with cupferron as shown in Table XII.

Di-2-ethylhexyl phosphoric acid, tridecyl phosphine oxide and TTA in benzene all extracted combined zirconium - niobium more effectively than tributyl phosphate, as shown in Table X.

TABLE VIII

Ruthenium Extraction into 100% TBP

Effect of Heating Solution with Metals+

Metal Concentration	Percent Extracted After 4 Consecutive Passes			
	Magnesium	Iron	Zinc	Control
Fresh $Al(NO_3)_3$ Solution				
1) 100 mg/50 ml	97.5	96.2	97.8	79.4
2) 50 mg/50 ml	95.6	96.7	96.4	----
3) 15 mg/50 ml	97.2	97.7	97.3	----
4) 15 mg/50 ml (added in 1st and 3rd passes)	99.2	99.1	99.2	90.3
9-Month Old $Al(NO_3)_3$ Solution				
1) 15 mg/50 ml (added in 1st and 3rd passes)	98.9	98.8	98.9	98.5

+ Metal added slowly; solution cooled to room temperature before extraction.

TABLE IX

Ruthenium Extraction

Extractant	Length of Time of Ru^{106} in $Al(NO_3)_3$	Cumulative Percent Ru^{106} Extracted Pass No.: 1	2	3	4
100 % TBP	Fresh	3.1	13.3	23.1	27.3
100 % TBP	9 Months	60.8	82.4	89.8	92.4
1.3 M Tri-n-octylamine	Fresh	----	14.0	----	----
1.3 M Tri-n-octylamine	9 Months	----	53.1	----	----
1.3 M Di-2-ethylhexyl Phosphoric Acid	9 Months	----	6.3	----	----
0.9 M Tridecyl Phosphine Oxide	9 Months	----	14.0	----	----
0.5 M TTA in Benzene	9 Months	0	0	0	0
"Primene JMT"	9 Months	----	11	----	----

TABLE X

Extraction of Zirconium and Niobium

Extractant	Pass No.: 1	2	3	4
	Cumulative Percent Zr^{95} - Nb^{95} Extracted			
100 % TBP	72.4	87.2	88.7	88.7
10 % TBP in "Amsco"	----	----	----	51.0
1.3 M Tri-n-octylamine	----	22.0	----	----
1.3 M Di-2-ethylhexyl Phosphoric Acid	97.6	99.4	----	----
0.9 M Tridecyl Phosphine Oxide	95.7	96.5	----	----
0.5 M TTA in Benzene	91.1	93.9	95.1	95.9
"Primene - JMT"	----	29	----	----
	Cumulative Percent Nb^{95} Extracted			
100 % TBP	26.6	36.7	41.9	44.0
1.3 M Tri-n-octylamine	----	34.0	----	----
"Primene - JMT"	----	21	----	----

TABLE XI

Zirconium-Niobium Extraction into 100% TBP

Aqueous Phase	Cumulative Percent Zr^{95} - Nb^{95} Extracted Pass No.: 1	2	3	4
A) Effect of HNO_3 added to 1.6 M $Al(NO_3)_3$ (5:1 ratio of Aqueous:Organic)				
0.16 M	68.7	72.4	86.8	87.2
0.3 M	71.0	84.2	86.1	88.0
1.0 M	73.6	84.5	86.3	87.6
B) Effect of Aqueous:Organic Ratio				
10:1	72.4	87.2	88.7	88.7
5:1	89.0	90.0	89.8	89.8
2:1	71.0	----	----	----
1:1	52.0	----	----	----
C) Effect of Temperature (10:1 ratio)				
30° F	61.5	82.1	84.2	
70° F	72.4	87.2	88.7	
190° F	90.5	91.8	91.8	
D) Effect of Shaking Time at Room Temperature				
1 min.	46.0	61.1	68.0	68.1
5 min.	57.0	74.7	79.7	80.0
10 min.	68.7	78.3	81.4	82.0
E) Effect of the Ru^{106} treatment with metal addition				
Control	83.3	86.0	90.1	91.3
15 mg Mg/50 ml (in 1st and 3rd passes)	81.5	86.7	86.8	86.9

TABLE XII

Zirconium and Niobium Extraction into 100% TBP

Effect of Added Cupferron

ml of 6 % Cupferron Added	Percent Activity Extracted After 4 Passes Zr^{95} - Nb^{95}	Nb^{95}
0	88.2	44.0
0.1 + 0.1+	96.2	88.3
0.2	91.9	----
0.1 + 0.1 + 0.1 + 0.1++	99.1	96.6
0.5	98.0	----
0.5	99.3	----
1.0	99.5	99.2
2.0	99.7	----

+ added in 1st and 2nd passes

++ added consecutively in each of the 4 passes

Combined extraction of the fission products into 100% TBP To permit comparison of the efficiency with which the fission products are extracted into 100% TBP, their per cent removal from the acid aluminum nitrate solution for four consecutive extractions is listed in Table XIII. Of the other extractants studied, only di-2-ethylhexyl phosphoric acid and tridecyl phosphine oxide yielded values of the same magnitude. The major fission products appear to be grouped into poorly extractable elements (cesium and strontium), readily extractable elements (zirconium, the rare earths, and yttrium), and partially extractable elements (ruthenium and niobium). In order to make more extractable the elements of the latter group, the following procedure was used with all the fission products:

1. Shake 50 ml of acid aluminum nitrate solution containing the fission products with 5 ml 100% TBP plus 0.1 ml 6% cupferron for five minutes. Separate phases.

2. Repeat step 1.

3. Boil the aqueous phase with 10 mg iron, zinc, or magnesium to dissolve the metals. Cool, shake with 5 ml 100% TBP, and separate phases.

4. Shake aqueous phase with 5 ml 100% TBP and separate phases.

5. Repeat step 3.

6. Repeat step 4.

The sequence of the procedure was dictated by the destruction of cupferron upon heating. (In nitric acid, cupferron begins to decompose even at room temperatures.) A shaking time of 5 minutes was found to be sufficient for the attainment of equilibrium conditions. The results, listed in Table XIV, indicate an increase in ruthenium and niobium extraction and no change in the extraction of the other fission products.

TABLE XIII

Extraction of Major Long-Lived Fission Products into 100% TBP

Fission Product	Cumulative Percent Removal of Activity Pass No.: 1	2	3	4
Ce^{144}	86.3	99.0	99.9	99.93
Y^{91}	91.2	99.2	99.8	99.96
Old Ru^{106}	60.8	82.4	89.8	92.4
Fresh Ru^{106}	3.1	13.3	23.1	27.3
Zr^{95} - Nb^{95}	72.4	87.2	88.7	88.7
Nb^{95}	26.6	36.7	41.9	44.0
Sr^{89}	5.1	7.7	9.3	10.1
Cs^{137}	0	0	0	0

TABLE XIV

Extraction of Major Long-Lived Fission Products into 100% TBP

(Cupferron and Metals Added)

Fission Product	Pass No.:	Cumulative Percent Removal of Activity 1	2	3	4	5	6
Ce^{144}		84.3	99.0	99.8	99.9	99.92	99.93
Y^{91}		90.0	99.2	99.7	99.8	99.90	99.93
Old Ru^{106}		63.7	83.3	95.8	97.1	97.8	98.1
Fresh Ru^{106}		11.7	27.5	90.8	96.5	98.8	99.4
Zr^{95} - Nb^{95}		91.7	94.5	95.9	96.2	96.2	96.2
Nb^{95}		68.7	88.3	88.3	88.3	----	-----
Sr^{89}		6.1	7.2	7.7	8.2	8.4	8.5
Cs^{137}		0	0	0	0	0	0

Fission product stripping from 100% TBP To determine the reversibility of the reaction by which the fission products are extracted into 100% TBP, organic phases into which the tracer radionuclides had been extracted were repeatedly shaken for 15 mintues with non-radioactive acid aluminum nitrate solution. The re-extraction distribution coefficients given in Table XV for cerium, yttrium, and ruthenium differ from those obtained by extraction, indicating a degree of irreversibility. The fraction of ruthenium which was re-extracted decreased with successive extractions; apparently a small fraction of the ruthenium cannot be re-extracted except possibly by a method opposite to that used to extract it. Little of the extracted niobium remained soluble in the TBP.

The fission products were effectively stripped from TBP by the solutions listed in Table XVI. Greater stripping by use of more passes appeared possible except for ruthenium, 2% of which was unextractable. However, repeated ruthenium extraction and decontamination of one portion of TBP caused little decrease in extraction efficiency. For decontaminating TBP of mixed fission products, a combination of two stripping solutions, such as concentrated nitric acid followed or preceded by 0.1M hydrofluoric-nitric acid, appears to be necessary. A degree of fission product separation may be achieved by consecutive stripping with different aqueous phases; greater separation than that given in Table XVII should be possible by controlling acid concentration and volume ratios.

TABLE XV

Back Extraction of Fission Products From 100% TBP

Into Acid Aluminum Nitrate Solution

Tracer	Aqueous/Organic Volume Ratio	Distribution Coefficients o/o or o/a ?
Zr^{95} - Nb^{95}	10	62 ± 6
Ce^{144}	5	27 ± 5
Ru^{106}	10	39 ± 8
Y^{91}	10	48 ± 9

TABLE XVI

Stripping of Fission Products from 100% TBP

Organic:Aqueous Volume Ratio = 1.0

Aqueous Phase	Fission Product:	Percent Activity Recovered After Four Passes			
		Ce^{144}	Ru^{106}	Zr^{95}-Nb^{95}	Y^{91}
Distilled Water		99.98	38.2	0	-
0.1 M HNO_3		99.98	39.1	0	99.7
Conc. HNO_3		97.1	97.4	-	39.0
0.1 M NaOH		99.2	17.3	73.7	----
0.5 M HF		99.92	40.5	98.9	----
0.1 M HF - 0.1 M HNO_3		-----	----	98.2	----

TABLE XVII

Consecutive Stripping of Fission Products from 100% TBP Into 4 Aqueous Phases

Organic:Aqueous Volume Ratio = 1.0

Fission Product	Conc. HNO_3	0.1 N HNO_3	0.1 M HF-0.1 M HNO_3	Distilled Water	TOTAL
Ce^{144}	79.9	17.0	2.3	0.7	99.9
Y^{91}	21.1	57.5	17.1	4.2	99.9
Ru^{106}	94.2	0.5	0.4	0	95.1
Zr^{95}- Nb^{95}	18.9	20.9	54.5	4.9	99.2
Nb^{95}	17.6	8.8	65.3	6.3	98.0

CONCLUSION

A number of organophosphorus compounds and amines, and thenoyl trifluoroacetone, were found effective for extracting one or more of the long-lived fission products. Undiluted tributyl phosphate, the most extensively studied reagent, extracted more than 99% of the cerium, yttrium, zirconium, niobium, and ruthenium, though prior treatment was needed to convert the latter two elements to more extractable states. Strontium was extracted to a small degree, and cesium not at all. Among incidental observations, not pertinent to this study, were (1) the relatively large differences in distribution coefficient between cerium and yttrium in di-2-ethylhexyl phosphoric acid, tridecyl phosphine oxide, and tri-n-octylamine, potentially useful in separating the rare earths; and (2) the small but significant extraction of strontium into TBP.

Liquid-liquid extraction appears to be feasible for removing zirconium, the rare earths, and yttrium from the acid aluminum nitrate solution, especially since greater removals than those obtained here can be predicted because of the constancy of the distribution coefficient for these elements in successive extractions. The extraction for ruthenium and niobium depends upon their chemical state -- a function of prior treatment and storage -- and cannot be readily predicted. The advantages of solvent extraction, compared to other methods of waste treatment, are (1) the high decontamination factors potentially attainable for some of the fission products, and (2) the fact that the waste solution is relatively unchanged in composition after extraction, permitting the application of other treatment methods.

For future work it is suggested that

1) Liquid-liquid extraction with 100% TBP be studied as a large-volume continuous operation, to determine decontamination values, and observe the effect of radiation and the formation of undesirable solids;[8]

2) A number of other organic complexing agents, especially organophosphorus compounds, be studied in greater detail;

3) Other decontamination methods, such as volatilization and ion exchange, be studied; and

4) Liquid-liquid extraction be combined with other methods, such as precipitation[18] for decontamination of the waste solution from fission products which remain after extraction.

The authors gratefully acknowledge the suggestions and criticisms of S. J. Rimshaw, ORNL, and A. S. Goldin, USPHS.

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