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ORNL-TM-515

ISOTOPES DEVELOPMENT CENTER

PROGRESS REPORT

FISSION PRODUCTS

OCTOBER - NOVEMBER 1962

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FISSION PRODUCTS

October - November 1962

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1. TREATMENT OF PUREX WASTE

Extraction of Acid, Ce^{+++}, and Ruthenium by Alamine-336

Preliminary data have been reported[1] on the extraction of acid from Purex waste. Also reported were data indicating that the only significant extraction of fission products which occurred was that of ruthenium. Further data were required to define this extraction more fully, particularly from solutions at high pH and under conditions of differential extraction.

Two series of experiments, one using Ce^{+++} tracer and one using ruthenium tracer, were made on synthetic Purex waste from which the iron and Zr-Nb had been removed by successive batch extraction with D2EHPA. The distribution coefficients obtained are shown in Table 1.1.

Table 1.1. Extraction of Acid, Ce^{+++} and Ruthenium By Successive Contacting With Alamine-336

Starting Organic Phase: 25% Alamine-336, 15% 2-ethylhexanol, 60% Amsco
Starting Aqueous Phase: 2 M HNO_3, 1 M H_2SO_4, 0.25 M $NaNO_3$ and tracer
O/A = 1; 5 min contact time

Contact Number	Aqueous Phase Acid Normality	K_d Ce^{+++}	K_d Ru
1	3.36	0.0054	1.46
2	2.80	0.0046	0.28
3	2.30	0.0044	0.15
4	1.72	0.0036	0.13
5	1.00	- - -	- - -
6	0.35	0.0061	0.33
7	0.02	0.0067	0.81

A batch of feed (similar to that above) containing ruthenium tracer was extracted differentially to a pH of 6. The conditions of extraction were:

Aqueous Volume - 1 liter

Organic Volume - 3.5 liters

Organic Phase Composition - 50% Alamine-336, 15% 2-ethylhexanol, 35% Amsco

Organic Flow Rate - 2 liters/hr

Aqueous Recycle Rate - 28 liters/hr

[1] Isotopes Division Quarterly Report, April - June 1961, ORNL-TM-76.

During this extraction, 81% of the ruthenium activity was removed from the aqueous phase. This value confirmed data indicating that the only significant extraction of fission products from Purex waste was that of ruthenium.

Differential Extraction of Ce^{+++}, Aluminum, and Strontium Using D2EHPA

The synthetic waste from the ruthenium extraction described above was spiked with a Ce^{+++} tracer and the acidity adjusted to 0.5 normal. The cerium was then extracted differentially with 1 M D2EHPA. The conditions of the extraction were:

Aqueous Volume - 1 liter

Organic Volume - 3.5 liters

Organic Flow Rate - 1 liter/hr

Aqueous Recycle Rate - 28 liters/hr

During the extraction, 88% of the cerium was removed. Under these conditions, promethium and europium would have been extracted quantitatively.

To extract the aluminum, the aqueous phase from the cerium extraction was adjusted to pH 1 and strontium tracer added. This aqueous phase was contacted with 3600 ml of 1 M D2EHPA under conditions the same as the cerium extraction. During this extraction ~80% of the aluminum was extracted. Only 1.2% of the strontium was extracted, and therefore the removal of strontium during the cerium extraction was extremely small.

The aqueous phase from the aluminum extraction was adjusted to pH 2.5 and extracted with 2 liters of 1 M D2EHPA under the same flow conditions as the cerium and aluminum extractions. Eighty-eight percent of the strontium was extracted along with the remaining aluminum. The amount of strontium extracted can be increased by contacting with an additional quantity of organic. The strontium in the organic phase from the above extraction was readily stripped (97%) by 1/4 volume of 0.2 M HNO_3. No aluminum was detected in the strontium product.

The Effect of Phosphate on Extraction With D2EHPA

Iron

The effect of phosphate ion in stripping iron from D2EHPA extracting solutions has been previously reported.[2] Since the phosphate ion reduces the distribution coefficient of iron, its presence should be considered in any flowsheet which requires that iron be extracted from Purex waste containing appreciable phosphate ion.

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[2] Ibid.

Data on the extraction of iron from synthetic Purex waste which contained varying amounts of phosphate are shown in Table 1.2. These data indicate that phosphate ion lowers the distribution coefficient of iron but shortens the time required to reach equilibrium.

Table 1.2. Extraction of Iron With 1 M D2EHPA From Solutions Containing Phosphate Ion

Aqueous Phase: 4 M HNO_3, 0.1 M Al^{+++}, 0.5 M Fe^{+++}, 1 M SO_4^{--}, 0.5 M Na^+, PO_4^{---}

Organic Phase: 1 M D2EHPA

O/A = 0.5

Forward Extraction

Contact Time (min)	Distribution Coefficient			
	0.0 PO_4^{---}	0.1 M PO_4^{---}	0.2 M PO_4^{---}	0.5 M PO_4^{---}
15	---	2.00	1.69	1.26
30	4.9	2.07	1.75	1.32
60	5.1	2.07	1.64	0.98

The effect of phosphate ion in reducing the time for equilibrium is shown in Tables 1.2 and 1.3. The time required to reach equilibrium when back extracting with 4 M HNO_3 is >30 min (Table 1.3), but with a concentration of as little as 0.1 M PO_4^{---} the equilibrium time is <15 min.

Table 1.3. Back Extraction of Iron From D2EHPA With Phosphate Ion

Aqueous Phase: 4 M HNO_3 + phosphate

Organic Phase: 1 M D2EHPA, 20 g/liter Fe

O/A = 1

Contact Time (min)	Distribution Coefficient		
	0.1 M PO_4^{---}	0.2 M PO_4^{---}	0.5 M PO_4^{---}
15	10.51	5.19	1.87
30	10.28	5.09	1.87

The difference between the final values of distribution coefficients in the forward and backward extraction in Tables 1.2 and 1.3 may be explained by the presence of sulphate ion during the forward extractions which would tend to complex the iron.

Aluminum

The distribution coefficient of aluminum ion between aqueous HNO_3 solutions and 1 M D2EHPA is very high (K_d = 5 in 0.325 N HNO_3).[3] The equilibrium value, however, is approached only after 10-12 hr of contacting. The back extraction of aluminum is slow even in 5 M HNO_3 (1 hr is required to reach approximate equilibrium).

Several experiments using aqueous phases of different compositions were run in an attempt to find a system which would reach equilibrium more rapidly and yet have sufficiently high distribution coefficients to make the extraction useful in the removal of aluminum from Purex waste following the rare earth extraction. These data are shown in Tables 1.4 and 1.5. The temperature of the extraction was also varied as shown in the tables.

As in the case of iron, phosphate ion lowered the distribution coefficients and decreased the time required to reach equilibrium. An increase in temperature also reduced the time required to approach equilibrium.

Table 1.4. Back Extraction of Aluminum From 1 M D2EHPA By Several Acids

O/A = 1

Contact Time (min)	1 M HNO_3	1 M H_3PO_4	2 M H_3PO_4	1 M PO_4^{---} (pH = 2.5)	2 M HNO_3 0.5 M H_3PO_4
5	--	1.7	--	~0	--
10	--	1.7	0.19	~0	0.065
20	229	1.6	--	~0	--
30	32	1.6	--	~0	0.057
40	--	--	--	--	--
50	--	--	--	--	--
60	12	1.7	0.19	--	--

[3] R. G. Deshpande and R. E. McHenry, Extraction of Aluminum With D2EHPA (unpublished).

Table 1.5. Forward Extraction of Aluminum by 1 M D2EHPA From Several Solutions

O/A = 1

Contact Time (min)	Aqueous Phase								
	Temperature = 23°C							Temperature = 65°C	
	HNO_3 (pH = 1)	0.1 M CH_3COOH (pH = 1)	0.1 M HCOOH (pH = 1)	HNO_3 (pH = 2.5)	0.5 M H_3PO_4 (pH = 1)	1 M HNO_3	1 M H_3PO_4	0.1 M HCOOH (pH = 1)	HNO_3 (pH = 1)
5	0.38	--	--	--	--	0.057	0.34	--	--
10	--	0.35	0.32	--	0.42	--	--	0.96	2.6
15	0.58	--	--	--	--	0.035	0.36	--	--
20	--	0.53	0.50	--	--	--	--	22.6	8.5
30	0.72	0.63	0.63	--	0.38	0.14	0.47	304.	75.
40	--	--	--	--	--	--	--	182.	152.
50	--	--	--	14.	--	--	--	1170.	229.
60	--	0.91	0.95	--	--	--	--	768.	305.

2. EXTRACTION OF RUTHENIUM FROM 15.7 M HNO_3 BY TBP

The extraction behavior of ruthenium from nitrate solution up to 7 molar has been reported by Fletcher.[4] He reports that, at higher nitric acid concentrations, the fraction of the more extractable complexes increased but that the net effect of increased acid concentration is a gradual decrease in the overall distribution coefficient of ruthenium.

Data on the extraction of ruthenium by TBP at acid concentration of 15.7 molar were required so that the separation between ruthenium and the rare earth as well as the actinide elements americium and curium could be calculated. These data shown in Table 2.1 are compatible with the conclusions of Fletcher -- that there are at least two species of ruthenium in the aqueous phase (in this case predominatly the trinitrato with a small amount of tetra or penta-nitrato), one of which is more extractable (tetra or penta-nitrato). The conversion of the less extractable to the more extractable complex proceeds very slowly in the aqueous phase (Table 2.1, Exp. No. 1-3). According to Fletcher, some of the less extractable complex is converted to the more extractable complex in the organic phase. When the organic phase is scrubbed with fresh aqueous phase, the conversion to the less extractable form takes place with a half-time of ~2 min (Table 2.1, Exp. No. 5-7).

Table 2.1. Distribution of Ruthenium Between 100% TBP-15.7 M HNO_3

Exp. No.	Extraction	O/A	Contact Time	K_d
1	Forward	1	2 min	0.012
2	Forward	1	17 min	0.013
3	Forward	1	92 min	0.020
4	Forward[a]	1	2 min	0.012
5	Back[b]	1	2 min	1.37
6	Back[b]	1	4 min	0.54
7	Back[b]	1	6 min	0.45

[a]Aqueous phase from Exp. No. 3 contacted with fresh organic phase.

[b]Organic phase from Exp. No. 3 contacted with fresh aqueous phase.

[4]F. R. Bruce, J. M. Fletcher, H. H. Hyman and J. J. Katz, Process Chemistry, Series III, p. 135, Pergamon Press, New York, 1956.

3. HOT CELL CALORIMETER

One of the Cs^{137} calorimeters (Gamma 2) previously described[5] was calibrated and its general performance characteristics investigated. The principal difference in the Gamma 2 calorimeter and the Gamma 1 (ref 6) was the reduction in thickness of the uranium shield cup walls from 1-1/16 to 3/8 in. This change greatly reduced the heat capacity of the cup and allowed it to heat more rapidly to the steady state temperature. Since the thinner shield cup would absorb less of the heat producing gamma rays, a precise evaluation of this factor was required.

The efficiency of gamma-ray absorption was determined in two ways. First, a small Cs^{137} source was placed in the cup. Measurements of the gamma ray intensity were made at five different points on the outer surface of the cup and at the same points with the shielding cup removed. The average value of the ratios of shielded to unshielded radiation measurements at the five points (0.08) is the fraction of the gamma energy not absorbed in the shield.

The second and more precise determination of the efficiency of absorption was made by measuring the total rate of absorption of the heat from a 2200-curie Cs^{137} source in both the Gamma 1 and Gamma 2 calorimeter. The temperature drop per unit heat input in both calorimeters had previously been determined using an electrical heater in the cup instead of the radioactive source. The results are given in Table 3.1.

Table 3.1. Comparison of Total Energy Absorption in Calorimeters When Tested With the Same Cesium-137 Source

Gamma 1 Watts Absorbed	Gamma 2 Watts Absorbed
10.169	9.656
10.193	9.658
10.181 average	9.657 average

The ratio of the averages, which is the efficiency of total energy absorption, is 0.9487. The corresponding value, calculated from the gamma absorption efficiency of 0.92 with allowance for the contribution of beta radiation to the total energy, is 0.95.

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[5] R. E. McHenry, Fission Products, July-September 1962, ORNL-TM-451.

[6] J. C. Posey, T. A. Butler, and P. S. Baker, "Hot Cell Calorimeter for the Routine Determination of Thermal Power Generated by Kilocurie Sources," Proceedings of the Tenth Conference on Hot Laboratories and Equipment, pp 263-8, American Nuclear Society, Inc., 86 E. Randolph, Chicago, Illinois, 1962.

The Gamma 2 calorimeter approached steady state much more rapidly than Gamma 1. The rate of approach of the shaft temperature difference (ΔT) to the steady state value is illustrated by Table 3.2.

Table 3.2. Approach of Gamma 2 Calorimeter to Steady State[a]

Time (min)	$\Delta T/(\Delta T$ steady state)
10	.60
40	.90
120	.99
200	.999

[a]7-8 hr required to approach .999 steady state by Gamma 1.

4. IODINE-131 ADSORPTION FROM AQUEOUS SOLUTIONS

Investigation of the use of activated charcoal to adsorb I^{131} from gas streams has proved that the iodine is highly adsorbed by the charcoal. In the clean-up system for hot off-gases, the activated charcoal traps do not accomplish the predicted degree of iodine removal.

There are several possible factors which could account for this behavior, one of which is that the iodine may exist in several forms such as compounds and iodine adsorbed on particulate matter. Another possible difference in the behavior of the iodine in the laboratory and in the hot off-gas system may be due to the saturation (or actual wetting) of the activated charcoal by water vapor when the charcoal has been used over a long period of time. Several different activated charcoals were tested for their ability to adsorb I^{131} from aqueous solutions.

A 0.2-g amount of 200-mesh charcoal and 10 ml of water containing I^{131} as I_2 were contacted. Several charcoals adsorbed 90+% of iodine in 1 hr while others required 1 week to adsorb 90+% (Table 4.1).

Table 4.1. Fraction of I_2 Adsorbing on Charcoal

Carbon	Structure	Fraction Adsorbed		
		1 hr	1 day	1 week
Coconut (Norite)	Crystalline	.12	.83	.995
Graphite (Reactor Grade)	Crystalline	.64	.72	.880
RC (Pittsburg Coke & Carbon)	Crystalline	.77	.90	.950
RB (Pittsburg Coke & Carbon)	Crystalline	.67	.97	.986
OL (Pittsburg Coke & Carbon)	Microcrystalline	.93	.94	.999
BL (Pittsburg Coke & Carbon)	Microcrystalline	.94	.999	.999
C (Pittsburg Coke & Carbon)	Microcrystalline	.95	.98	.993
GW (Pittsburg Coke & Carbon)	Microcrystalline	.98	.993	.999
BPL (Pittsburg Coke & Carbon)	Amorphous	.48	.83	.992
SGL (Pittsburg Coke & Carbon)	Amorphous	.61	.87	.992
CAL (Pittsburg Coke & Carbon)	Amorphous	.59	.90	.999

These experiments suggest that tests should be made comparing the microcrystalline structure charcoals with the presently used activated coconut charcoal.

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