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PUREX 1A COLUMN STUDIES

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PUREX 1A COLUMN STUDIES

1.0 Introduction

The initial separation of uranium and plutonium from fission products is accomplished in the 1A column. Irradiated slugs, previously de-canned with a mixture of caustic and sodium nitrate, are dissolved in nitric acid, and the solution is adjusted to 1A column feed concentration (1.35 M U-2 M HNO_3). The feed is treated with nitrite to convert plutonium to the tetravalent state, since the TBP extractability of Pu (IV) is known to be a factor of two to three greater than Pu (VI) and a factor of 50-100 greater than Pu (III). The solvent extractant is 30% by volume TBP diluted with an inert carrier to enlarge the specific gravity difference of the contacting phases. Three molar nitric acid is employed as scrub. The extractant TBP complexes uranium and plutonium and moves upward through the scrub section where most of the fission products picked up at the feed plate are back extracted into the aqueous stream. The solvent stream is fed into the 1B column for uranium-plutonium partitioning, and the bulk of the fission products remain in the aqueous phase and are discharged from the bottom of column 1A.

The choice of 1A column operating conditions is dictated by the desire to attain the maximum product throughput compatible with efficient separation of fission products from plutonium and uranium. There are a number of chemical and physical variables which must be considered in order to define a flowsheet which meets these requirements.

Maximum uranium throughput per volume of "hot" waste is approached by increasing the TBP concentration in the diluent so that more uranium is complexed per volume of solvent mixture. There are limits to increasing the TBP content of the solvent mixture such as the specific gravity relationship between the aqueous and organic phases in the column, freezing point of the necessary aqueous feed and the uranium, plutonium, and fission product distribution between the phases; and the selection of 30% TBP as the most suitable solvent concentration was based largely on these considerations.

2.0 Experimental

2.1 Freezing Point of Uranium-Nitric Acid Solutions

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Freezing point data applicable to 1A column operation are shown in Figure 1a. For feed solutions having freezing points around zero degrees centigrade and containing 3 M, 2.5 M and 2 M nitric acid, the maximum permissible uranium concentrations were found to be 325, 355, and 380 grams per liter, respectively.

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2.2 Specific Gravity of Solvent Solutions Containing Uranium

A series of 1A aqueous solutions (feed plus scrub) were equilibrated with 30% TBP-70% Gulf "BT" for ten minutes using two volumes of organic to one of aqueous. Specific gravities were taken on the resulting solvent phases (Figure 1b).

A solution of 30% TBP in Gulf "BT" will complex a maximum of 125 grams of uranium per liter. If the 1A column is designed to operate at 85% uranium saturation at the feed plate, the specific gravity of the solvent phase would be 0.975. Since the specific gravity of the entering aqueous scrub is 1.096, it is felt that 30% TBP is about the maximum allowable concentration for stable 1A column operation, according to the conditions specified in Purex Flowsheets Numbers 1 and 3.

2.3 Distribution Coefficients of Uranium, Plutonium and Fission Products as a Function of Percent Uranium Saturation of the Solvent

Previous investigation of the 15% TBP system (ORNL-717) had shown that 70% uranium saturation at the feed plate was compatible with satisfactory Pu(IV) extraction, if the nitric acid concentration was held at 3 M or higher. Plutonium (IV) distribution data (Table I) was obtained by batch-contacting 15% TBP in "Varsol" with aqueous feeds of plutonium (IV), nitric acid, and varying uranium content to produce the desired range of uranium saturation. Comparison of these data with those obtained from a similar study of Pu(IV) extraction with 30% TBP (Table II) indicates that the 30% TBP system could be operated at about 85% uranium saturation and yet maintain a Pu(IV) extraction factor equivalent to that realized with 15% TBP at 70% uranium saturation. Thus, it is possible to increase the uranium throughput by a factor of 2.4 without loss of Pu(IV) extraction efficiency.

The distribution of individual fission products as a function of percent uranium saturation of the solvent (30% TBP) was determined to establish which of the principal fission products (total rare earth, ruthenium and zirconium) limited the beta decontamination. The results (Table II) show that while the distribution coefficients of the rare earth and ruthenium become quite small as the uranium saturation increases, the decrease in extractability of plutonium, uranium and zirconium is fairly uniform: ca. 8 fold from 28 to 87% uranium saturation.

As the percent uranium saturation of the solvent increases, the separation of the rare earth and ruthenium from the products increases; whereas, zirconium separation is not markedly affected. These trends are illustrated in Table III and Figures 2 and 3, where uranium-fission product and plutonium-fission product separation factors are plotted against percent uranium saturation of the solvent.

At higher uranium saturation values, zirconium limits the gross beta decontamination realized at the feed plate. It was found by laboratory column

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runs, however, that zirconium is readily back extracted from the solvent in the scrub section of column 1A by 3 M nitric acid.

2.4 Distribution Coefficients of Uranium, Plutonium and Fission Products as a Function of Aqueous Phase Nitric Acid Concentration

The effect of increased nitric acid concentration on uranium, plutonium and fission product distribution in the 30% TBP system was measured over a range of 50 to 80% uranium saturation by laboratory batch extraction (Table IV). Increase in feed plate acidity from 3 to 5 M HNO_3 resulted in increased extraction of uranium, plutonium, and fission products. At low uranium saturation values, the increase in plutonium and uranium distribution coefficients is quite pronounced. Although more efficient extraction of uranium and plutonium is obtained at the higher nitric acid concentrations, this is accompanied by greater transfer of fission products into the solvent phase which permits little or no gain in decontamination. These results coupled with the data on uranium saturation of the solvent suggest that optimum 1A column operating conditions should be as high a uranium saturation as can be tolerated and a nitric acid feed plate concentration as low as possible still permitting an acceptable plutonium distribution coefficient.

2.5 Initial Flowsheet Evaluation in Laboratory Batch Countercurrent Equipment

From the limiting conditions of specific gravity of the phases, freezing points of the feed solutions and distribution of uranium, plutonium and fission products, an approximate flowsheet was derived. Using a feed to scrub to solvent flow ratio of 3/2/10, it follows that a feed 1.35-1.43 M in uranium and 2-3 M in nitric acid should be optimum for a 30% TBP system. A laboratory countercurrent batch extraction using these conditions to simulate 1A column operation resulted in a beta decontamination factor with respect to uranium and plutonium of 5.3×10^3 , a uranium loss of 0.0016% and a plutonium loss of 0.4% (Table V).

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Table I

Effect of Percent Uranium Saturation of Solvent on the

Plutonium IV Distribution Coefficients

Conditions:

Aqueous feed - HNO_3 and uranium concentrations as indicated,
plutonium IV - $1.25 \times 10^{-5} \text{ M}$

Solvent - 15% TBP, 85% "Varsol"

One volume of feed equilibrated for five minutes, at room temperature,
with double volume of solvent.

HNO_3 Concentration of Feed (M)	Plutonium (IV) Distribution Coefficient (O/A)	Percent Uranium Saturation of Solvent
1.5	0.70	37
1.5	0.68	42
1.5	0.49	51
1.5	0.39	54
1.5	0.38	59
1.5	0.33	64
1.5	0.28	72
1.5	0.21	80
1.5	0.13	84
3.0	2.59	37
3.0	1.67	44
3.0	1.09	57
3.0	1.06	59
3.0	0.77	65
3.0	0.79	68
3.0	0.44	77
3.0	0.36	84
3.0	0.24	88
5.0	4.15	42
5.0	3.42	44
5.0	2.55	53
5.0	2.49	53
5.0	1.63	61
5.0	1.36	68
5.0	1.34	70
5.0	0.87	80
5.0	0.62	85
5.0	0.46	90

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Table II

Uranium, Plutonium and Fission Product Distribution Coefficients
as a Function of Percent Uranium Saturation of the Solvent

Aqueous: Variable uranium concentrations corresponding to feed plus scrub of column 1A, 3 M HNO₃, 1.6×10^6 c/m/ml Pu α , 1×10^7 c/m/ml gross β .

Solvent: 30% TBP in Gulf "BT"

Solvent to aqueous ratio: 2/1

Equilibration Time: 5 minutes

Percent Uranium Saturation of Solvent	Distribution Coefficient (o/A)					
	Uranium	Plutonium	Gross β	Total Rare Earth	Ruthenium	Zirconium
28.0	16.7	4.0	0.013	0.0096	0.067	0.041
37.0	13.7	3.7	0.011	0.0073	0.039	0.026
45.6	12.1	2.3	0.0065	0.0048	0.028	0.025
54.9	10.2	1.3	0.005	0.0032	0.016	0.025
61.7	7.9	1.6	0.0035	0.0021	0.0096	0.020
70.2	6.4	1.3	0.0025	0.0014	0.0060	0.014
72.0	5.4	1.1	0.0018	0.0011	0.0037	0.012
77.2	4.5	1.0	0.0015	0.0007	0.0027	0.013
82.4	3.6	0.79	0.0011	0.0004	0.0016	0.009
86.8	2.3	0.57	0.0007	0.0002	0.0007	0.007

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Table III

Separation of Uranium and Plutonium from Fission Products as a Function
of Percent Uranium Saturation of the Solvent

Percent Uranium Saturation of Solvent	*Separation Factor					
	U/TRE	U/Ru	U/Zr	Pu/TRE	Pu/Ru	Pu/Zr
28.0	1740	249	407	416	59	98
37.0	1870	351	527	507	95	142
45.6	2520	432	484	479	82	92
54.9	3190	638	407	406	81	52
61.7	3760	820	395	762	162	80
70.2	4570	1070	457	929	217	93
72.0	4910	1460	450	1000	297	92
77.2	6330	1670	346	1410	370	77
82.4	9000	2250	400	1970	494	88
86.8	14400	3330	315	3570	826	78

*Separation Factor = $\frac{\text{U(or Pu) Distribution Coefficient}}{\text{Fission Product Distribution Coefficient}}$

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Table IV
Uranium, Plutonium and Fission Product Distribution Coefficients
as a Function of Aqueous Phase Nitric Acid Concentration

Conditions:

Aqueous: Uranium concentration varied to effect a 50 to 80% uranium saturation of the solvent phase, HNO_3 as indicated,
 1×10^6 c/m/ml Pu α , 2×10^6 c/m/ml gross β

Solvent: 30% TBP in Gulf "BT"

Solvent to aqueous ratio: 2/1

Equilibration time: 5 minutes

Percent Uranium Saturation of Solvent	HNO_3 in Aqueous (M)	Distribution Coefficient (O/A)					
		U	Pu	Gross β	TRE	Ru	Zr
49	3.20	13.5	2.3	0.0088	0.0050	0.028	0.042
	4.20	17.1	4.5	0.0105	0.0045	0.013	0.100
	5.05	21.9	5.0	0.0121	0.0034	0.006	0.212
65	3.20	9.1	2.0	0.0047	0.0020	0.010	0.034
	4.20	10.3	2.6	0.0058	0.0016	0.004	0.070
	5.05	11.2	3.7	0.0066	0.0010	0.002	0.109
72	3.20	6.2	1.5	0.0036	0.0010	0.006	0.024
	4.20	7.2	2.2	0.0031	0.0007	0.002	0.037
	5.05	8.4	2.5	0.0051	0.0006	0.002	0.099
80	3.20	4.4	1.1	0.0033	0.0006	0.003	0.015
	4.20	5.5	1.5	0.0034	0.0005	0.002	0.037
	5.05	6.5	2.0	0.0036	0.0004	0.001	0.059

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Table V

Countercurrent Batch Extraction Simulating 1A Column

Conditions:

Stages: 6 extraction, 4 scrub

Flow Ratio: Feed/Scrub/Solvent = 3/2/10

Feed: 315 g/liter U, 2 M HNO₃, 1.39×10^6 c/m/ml Pu α ,
1.46 $\times 10^8$ c/m/ml gross β

Scrub: 3 M HNO₃

Solvent: 30% TBP - 70% Gulf "BT"

Equilibration Time: 3 minutes

Results

Percent U loss	0.0016
Percent Pu loss	0.41
Total U and Pu Decontamination Factor (beta)	5.28×10^3
Scrub U and Pu Decontamination Factor (beta)	26.5
Extraction U and Pu Decontamination Factor (beta)	199

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FREEZING POINT OF URANIUM
SOLUTIONS IN NITRIC ACID

Figure 1a

TEMPERATURE °C

(%) UNH	(M)
70	2.74
65	2.42
60	2.10
57.5	1.97
55	1.84
52.5	1.71
50	1.59
45	1.37
40	1.16
0	0
10	.23
20	.50
30	.81

Note: Data taken from HW-10309 C.5B, p. 16-4.

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Figure 1b

SPECIFIC GRAVITY OF URANIUM CONTAINING ORGANIC SOLUTIONS RESULTING FROM BATCH
EQUILIBRATION OF 30 PERCENT TBP-70 PERCENT GULF B.T. WITH PUREX AQUEOUS SOLUTIONS

Conditions:

Aqueous-Variable U, 3M HNO_3
Organic-30% TBP in Gulf "BT"

Volume Ratio O/A - 2/1

Equilibration Time - Ten Minutes

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Figure 2

URANIUM-FISSION PRODUCT SEPARATION FACTORS AS A FUNCTION
OF NITRIC ACID CONCENTRATION IN AQUEOUS PHASE

Conditions:

Aqueous: Variable U and HNO_3 , Pu(IV) -1×10^6 c/m/ml, Gross β -2×10^6 c/m/ml

Solvent: 30% TBP in Gulf "BT"

Solvent to Aqueous Ratio: 2/1

Uranium Saturation of Solvent: 80%

Equilibration Time: 5 Minutes

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Figure 3

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PLUTONIUM (IV) - FISSION PRODUCT SEPARATION FACTORS AS A
FUNCTION OF NITRIC ACID CONCENTRATION IN AQUEOUS PHASE

Conditions:

Aqueous: Variable U and HNO_3 , $\text{Pu(IV)} - 1 \times 10^6 \text{ c/m/ml}$, Gross $3-2 \times 10^5 \text{ c/m/ml}$
Solvent: 30% TBP in Gulf "BT" Solvent to Aqueous ratio: 2/1
Uranium Saturation of Solvent: 30% Equilibration time: 5 minutes

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