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IDAHO CHEMICAL PROCESSING PLANT
TRIBUTYL PHOSPHATE EXTRACTION OF URANIUM
FROM AMMONIUM NITRATE SOLUTIONS

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A B S T R A C T

The uranium distribution data required for the ammonium nitrate salted feed resulting from the ammonium fluoride dissolution-barium fluozirconate head-end flowsheet for STR-type fuel have been obtained with 5, 10, and 20 per cent tributyl phosphate. The results show that ammonium nitrate is an adequate salting agent. Nitric acid inhibits the extraction slightly, but small amounts of fluoride ion interfere seriously.

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IDAHO CHEMICAL PROCESSING PLANT

TRIBUTYL PHOSPHATE EXTRACTION OF URANIUM
FROM AMMONIUM NITRATE SOLUTIONS

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The extraction of uranium from ammonium nitrate-salted solutions may be required in chemical reprocessing for STR fuel flowsheets which use ammonium fluoride dissolution of zirconium-uranium fuels, followed by head-end precipitation of the zirconium and fluoride. Therefore, uranium distribution data were obtained for macro uranium concentrations between 0 and 9M ammonium nitrate and 5, 10, and 20 volume per cent tributyl phosphate in Amsco 125-90W. These data were readily correlated into a general expression for the distribution coefficient as a function of uncomplexed tributyl phosphate and ammonium nitrate molarity. The effect of added nitric acid on the distribution was similar to that experienced in mixed metal nitrate-nitric acid systems. With added hydrofluoric acid, the distribution was inversely proportional to the 1.7 power of the hydrogen fluoride molarity.

II. INTRODUCTION

Several tentative flowsheets which involve an ammonium fluoride dissolution followed by barium fluozirconate precipitation have been written for the high zirconium-uranium fuels, such as the naval reactor type. One such flowsheet is shown in Table I and a further description is given in IDO-14471(1). The specific flowsheet written here shows a solvent extraction feed of 7.3M ammonium nitrate, 1.2M nitric acid, and 0.1M fluoride ion. Anticipating that variations of this flowsheet might be of continuing interest, the distribution data for the tributyl phosphate extraction of uranium from pertinent compositions in this general system were obtained.

TABLE I
FLUOZIRCONATE PROCESS FLOWSHEET

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
FLOW l/b	FUEL	DISSOL. REAGENT	DISSOL. PRODUCT	DISSOL. RESIDUE	DISSOL. WASH	BARIIUM REAGENT	LOW LEVEL SOLID	SUPERNATE	CONCENTRATE	URANIUM DISSOLVENT	URANIUM SOLUTION	BLENDED IAF
U g/l	1.9 kg	1144	1144	1.8 kg	96	1392		2632	322	40	40	362
Zr M	93 kg		0.9		H ₂ O		1020 MOLES	0.038	0.30		47.5	5.25
Sn M	1.4 kg			1.4 kg			BaZrF ₆				0.29	0.032
Ba M						1.0	372 MOLES					
H M			0.1				BaF ₂	0.04	0.36	8	7.2	0.95
NH ₄ M		6	2.3					1.0	8.18			7.3
F ⁻ M		6	6					<0.01				<0.1
NO ₃ ⁻ M						2.0		1.06	8.65	8	7.6	8.5

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III. EXPERIMENTAL

Fifteen milliliter aqueous samples were prepared by aliquoting from concentrated analyzed stock solutions. These stock solutions were uranyl nitrate containing 55.5 grams of normal uranium per liter, 9.85M ammonium nitrate, 10.3M nitric acid, and 10.27M hydrofluoric acid.

Five, ten, and twenty per cent solutions of tributyl phosphate in Amsco 125-90W were prepared. The tributyl phosphate was washed with sodium sulfate solution and then with carbonate solution.

The aqueous solutions were contacted with fifteen milliliter solutions of tributyl phosphate in Amsco. Single contacts were made, the two phases being contacted by shaking for one minute at room temperature. The phases were separated and both the aqueous and organic layers were analyzed for uranium content.

Table 2 summarizes the compositions studied in the general system tributyl phosphate in Amsco-uranyl nitrate-ammonium nitrate-nitric acid and hydrofluoric acid. The uranium distribution data are given in Tables 3 through 10 and Figures 1 through 5.

TABLE 2

URANIUM DISTRIBUTION EXPERIMENTS

Table No.	TBP Conc. %	Ammonium Nitrate Concentration <u>M</u>	Nitric Acid Conc. <u>M</u>	Hydrofluoric Acid Con. <u>M</u>
3	5	0-6.6	---	---
4	10	0-8.9	---	---
5	20	0-7.9	---	---
6a	5	3.94	0.5-2.6	---
6b	5	6.89	0.5-2.6	---
7a	10	3.94	0.5-2.6	---
7b	10	6.89	0.5-2.6	---
8a	5	2.83	---	0.1-0.5
8b	5	5.91	---	0.1-0.5
9a	10	1.97	---	0.1-0.5
9b	10	5.91	---	0.1-0.5
10a	10	3.94	1.01	0.1-0.5
10b	10	3.94	3.03	0.1-0.4

IV. DISCUSSION

A. Salting Effect of Ammonium Nitrate

Tables 3, 4, and 5 give the distribution data for uranyl nitrate between 0 and 8M ammonium nitrate and 5, 10, and 20 per cent tributyl phosphate. Although formal solubility data suggest that it is possible to prepare about 10M ammonium nitrate solutions, solutions of concentration greater than 8.5M were found to be unstable. This factor placed a practical limit on the concentrations to be examined. Figure 1 shows all of these data plotted as a function of ammonium nitrate molarity with the free tributyl phosphate concentration normalized. As might be expected, the lower portion of this curve is linear and has a slope of two. The deviation from linearity at high salting strengths can be completely eliminated by use of ammonium nitrate molarity and the reapplication to the data of activity coefficients

TABLE 3

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH 5 PER CENT TBP

Initial Aqueous Uranium Conc. g/l	Ammonium Nitrate Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
4.97	0	0.003
2.34	0.68	0.18
3.00	1.37	0.6
2.42	1.37	0.68
3.30	2.06	1.08
2.66	2.0	1.22
2.60	2.74	2.17
3.60	2.74	2.10
2.64	3.42	3.50
3.76	4.7	6.83
3.40	6.6	27.3

TABLE 4

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH 10 PER CENT TBP

Initial Aqueous Uranium Conc. g/l	Ammonium Nitrate Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
4.73	0	0.01
2.54	0.68	0.68
2.44	1.37	1.98
6.44	1.97	4.85
2.35	2.00	4.88
2.53	2.74	9.54
2.58	3.42	16.2
2.72	3.42	17.1
6.62	3.94	27.8
6.36	5.91	108
6.58	7.88	252
6.54	8.87	407

TABLE 5

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH 20 PER CENT TBP

Initial Aqueous Uranium Conc. g/l	Ammonium Nitrate Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
4.82	0	0.04
6.88	0	0.06
2.40	0.68	2.58
3.35	1.37	12.95
3.20	2.0	28.1
2.51	2.74	44.7
2.23	3.42	60.8
6.49	3.94	97.4
6.57	5.91	455
6.29	7.88	2000

for uranyl nitrate derived from the collected data. This approach does not enhance the utility of these data, nor has it facilitated the interpretation of the more complex system where fluoride ion is present. Therefore, these correlations have not been presented here.

Although ammonium nitrate is not as effective a salting agent as aluminum nitrate when compared on the basis of equal nitrate ion concentrations, it would appear to be an adequate salting agent at practical concentrations. Thus, a 6M ammonium nitrate solution would yield a uranium distribution coefficient of 20 with 5.3 per cent free tributyl phosphate.

B. Effect of Added Nitric Acid

In solvent extraction systems in which a nitrate salt is the principal salting agent, a significant effect is noted when nitric acid is added. This phenomenon has been discussed by McKay⁽²⁾ and the aluminum nitrate-nitric acid system studied by S. J. Horn⁽³⁾. Anticipating use of the latter data as a guide for interpolation, only a few experiments were run in the ammonium nitrate system. These data are given in Tables 6 and 7 and Figures 2 and 3. The experiments at 3.9M ammonium nitrate effectively indicated the region wherein the uranium distribution coefficient is independent of small amounts of added nitric acid. The 1.0 to 1.1M aluminum nitrate solutions show a similar lack of sensitivity. With higher salting strengths the distribution decreases rapidly with added acid. With lower salting strengths the distribution coefficients increase with added acid. It is not anticipated that these latter compositions will represent useful systems.

TABLE 6a

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH NITRIC ACID-5 PER CENT TBP

3.94M Ammonium Nitrate - 5% Tributyl Phosphate in Amsco

<u>Initial Aqueous Uranium Conc. g/l</u>	<u>Nitric Acid Conc. Molarity</u>	<u>Distribution Ratio for Uranium (E⁰/A)</u>
6.49	0.517	4.85
6.64	1.035	4.82
6.50	1.55	4.55
6.61	2.07	3.65
6.16	2.59	3.16

TABLE 7a

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH NITRIC ACID-10 PER CENT TBP

3.94M Ammonium Nitrate - 10% Tributyl Phosphate in Amsco

<u>Initial Aqueous Uranium Conc. g/l</u>	<u>Nitric Acid Conc. Molarity</u>	<u>Distribution Ratio for Uranium (E⁰/A)</u>
7.34	0.517	22.6
4.39	1.035	22.1
6.43	1.55	21.1
7.06	2.07	19.7
6.34	2.59	15.2

TABLE 6b

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH NITRIC ACID-5 PER CENT TBP

6.89M Ammonium Nitrate - 5% Tributyl Phosphate in Amsco

<u>Initial Aqueous Uranium Conc. g/l</u>	<u>Nitric Acid Conc. Molarity</u>	<u>Distribution Ratio for Uranium (E⁰/A)</u>
7.13	0.517	11.2
7.81	1.035	7.81
7.92	1.55	4.44
7.24	2.07	2.83
6.39	2.59	2.97

TABLE 7b

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH NITRIC ACID-10 PER CENT TBP

6.89M Ammonium Nitrate - 10% Tributyl Phosphate in Amsco

<u>Initial Aqueous Uranium Conc. g/l</u>	<u>Nitric Acid Conc. Molarity</u>	<u>Distribution Ratio for Uranium (E⁰/A)</u>
6.68	0.517	34.1
6.17	1.035	35.2
4.43	1.55	33.0
7.04	2.07	17.0
3.57	2.59	7.5

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C. Effect of Hydrofluoric Acid

Since ammonium nitrate salting might be used in a system derived from ammonium fluoride dissolution, it would be anticipated that small amounts of fluoride ion might be present in the extraction feed. Since uranyl ion forms relatively stable fluoride complexes, which would presumably reduce the uranium distribution, a few measurements were made to determine the magnitude of this effect. These data are shown in Tables 8 and 9 and Figure 4. The uranium distribution coefficients are inversely proportional to the 1.9, 1.8, and 1.5 power of the fluoride ion for systems of Tables 9b, 8b, and 9a, respectively. At the lowest salting strength and tributyl phosphate concentration, Table 8a, the dependency is much weaker.

TABLE 8a

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION WITH HYDROFLUORIC ACID-5 PER CENT TBP

2.83M Ammonium Nitrate - 5% Tributyl Phosphate in Amsco

Initial Aqueous Uranium Conc. g/l	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
5.25	0.103	0.000495
5.06	0.205	0.000276
5.30	0.308	0.000226
5.06	0.41	0.000148
5.24*	0.513	0.000171

* 1.42M Ammonium Nitrate

TABLE 8b

AMMONIUM NITRATE SALTED URANIUM EXTRACTION WITH HYDROFLUORIC ACID-5 PER CENT TBP

5.91M Ammonium Nitrate - 5% Tributyl Phosphate in Amsco

Initial Aqueous Uranium Conc. g/l	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
5.41	0.103	0.091
5.29	0.205	0.025
5.46	0.308	0.013
5.36	0.41	0.006
5.37	0.513	0.005

TABLE 9a

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH HYDROFLUORIC ACID

1.97M Ammonium Nitrate - 10% Tributyl Phosphate in Amsco

Initial Aqueous Uranium Conc. g/l	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
5.21	0.103	0.027
5.22	0.205	0.009
5.47	0.308	0.005
5.16	0.41	0.0038
5.21	0.513	0.0026

TABLE 9b

AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH HYDROFLUORIC ACID

5.91M Ammonium Nitrate - 10% Tributyl Phosphate in Amsco

Initial Aqueous Uranium Conc. g/l	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E^0/A)
5.30	0.103	0.259
5.37	0.205	0.059
5.18	0.308	0.040
5.05	0.41	0.017
5.22	0.513	0.012

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A general expression for the uranium distribution coefficient in the presence of hydrofluoric acid could not be derived from the data. Interestingly, the data from systems 8b and 9b, 10 and 5 per cent tributyl phosphate, at constant 5.91M ammonium nitrate salting strength gave separate curves when normalized on the basis of the second power of the free tributyl phosphate.

For application, the variation in the uranium distribution coefficient behavior for the 5.91M ammonium nitrate-10 per cent tributyl phosphate may be typical. At 0, 0.01, 0.1, and 0.5M fluoride, the values for the distribution coefficient are 15, 8, 0.25, and 0.012, respectively.

D. Combined Effect of Nitric and Hydrofluoric Acids

In order to demonstrate a means of partially overcoming the effect of hydrofluoric acid, a few measurements were made in the presence of both nitric and hydrofluoric acids. (Figure 5 and Table 10.) An ammonium nitrate concentration of 3.9M was used since it had been shown earlier that this was the salt concentration at which the uranium distribution coefficient was independent of added nitric acid in a fluoride-free system. Therefore, the results could be interpreted directly in terms of the suppression of the hydrofluoric acid ionization. In the system 3.94M ammonium nitrate, 1M nitric acid, 10 per cent tributyl phosphate, the uranium distribution coefficient varied inversely as the 1.5 power of the hydrofluoric acid concentration. At 3.0M nitric acid, this dependency was reduced to about the -0.8 power. At this

TABLE 10a
AMMONIUM NITRATE-SALTED URANIUM EXTRACTION
WITH HYDROFLUORIC AND NITRIC ACIDS-10 PER CENT TBP

3.94M Ammonium Nitrate; 1.01M Nitric Acid; 10% Tributyl Phosphate		
Initial Uranium Conc. g/l	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E°/A)
5.33	0.103	5.83
5.35	0.205	2.05
5.35	0.308	1.14
5.12	0.41	0.78
5.30	0.513	0.536

TABLE 10b
AMMONIUM NITRATE SALTED URANIUM EXTRACTION
WITH HYDROFLUORIC AND NITRIC ACIDS-10 PER CENT TBP

3.94M Ammonium Nitrate; 3.03M Nitric Acid; 10% Tributyl Phosphate		
Initial Uranium Conc. g/l -	Hydrofluoric Acid Conc. Molarity	Distribution Ratio for Uranium (E°/A)
5.06	0.103	6.44
5.40	0.205	4.57
5.18	0.308	2.55
5.35	0.41	2.00

salting strength and zero molar nitric acid, the distribution coefficients would vary between about 0.1 and 0.01 for 10 per cent tributyl phosphate and 0.1 to 0.5M hydrofluoric acid.

In application, the system 3.9M ammonium nitrate-1M nitric acid-10 per cent tributyl phosphate would give uranium distribution coefficients of 28, 18, 5, and 0.5 at 0, 0.01, 0.1, and 0.5M hydrofluoric acid, respectively. These data should be adequate for preliminary designs of extraction flowsheets in these systems.

V. LITERATURE CITED

- (1) Stevenson, C. E., Technical Progress Report for January through March, 1959, Idaho Chemical Processing Plant, IDO-14471, p. 34.
- (2) McKay, H. A. C., "The Physical Chemistry of Uranyl Nitrate Solutions", Chemistry and Industry, 32-1549 (1954)
- (3) Stevenson, C. E., Technical Progress Report for Second Quarter, 1954, Technical Branch, Idaho Chemical Processing Plant, IDO-14324, p. 45.