

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

37

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-84

**TRI-N-BUTYL PHOSPHATE EXTRACTION OF URANYL
NITRATE FROM AN ION EXCHANGE MILL ELUATE FOR THE
PRODUCTION OF HIGH PURITY URANIUM DIOXIDE**

by

A. J. GILMORE, V. M. McNAMARA & R. SIMARD

EXTRACTION METALLURGY DIVISION

**NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE
REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE
USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.**

COPY NO. 4

AUGUST 11, 1960

Mines Branch Investigation Report IR 60-84

TRI-N-BUTYL PHOSPHATE EXTRACTION OF URANYL
NITRATE FROM AN ION EXCHANGE MILL ELUATE FOR THE
PRODUCTION OF HIGH PURITY URANIUM DIOXIDE

by

A. J. Gilmore^{*}, V. M. McNamara^{*} and R. Simard^{**}

SUMMARY OF RESULTS

Batch and continuous extraction tests were done on a leach plant ion exchange nitrate eluate with 25 to 30% TBP in kerosene. Uranium distribution data for the extraction and stripping were determined at varying nitrate and sulphate levels. The results show that a barren effluent containing less than 0.1 g U_3O_8/l can be obtained from an eluate feed containing 20 g U_3O_8/l in four countercurrent stages. Minimum nitrate concentration used was 3N total NO_3 and 1N HNO_3 . Improved results were obtained by lowering the sulphate concentration from 1.3N to 0.5N. The organic extract, containing 40-70 g U_3O_8/l was stripped with water in three stages, to yield a strip solution containing 25-30 g U_3O_8/l . Continuous precipitation of this solution with ammonia gas at pH 7.0 - 7.5 gave a filterable product of nuclear grade purity except for its thorium content. High density sintered UO_2 pellets were produced from this precipitate.

^{*}Scientific Officers, and ^{**}Head, Solution Metallurgy Section, Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Summary of Results	i
Introduction	1
Equipment and Procedure	3
Results	6
Feed Solution	6
Batch Equilibrium Tests	7
Continuous Extraction and Stripping ...	11
Precipitation	15
Discussion	15
Conclusion	19
References	19
Appendix	20

INTRODUCTION

In existing acid leach plants where uranium is recovered by ion exchange and the resin eluted by nitrate-nitric acid solutions, the eluate is normally treated in two stages to recover a uranium concentrate, these stages being: 1) lime addition to pH 3.5 to remove sulphate as gypsum and precipitate the bulk of the ferric iron and thorium, the combined gypsum-iron cake being recycled to leaching, and 2) further neutralization of the filtrate to pH 7.0 with ammonia gas to precipitate the uranium as a hydroxide-diuranate cake. The product from the second stage is upgraded to nuclear purity in a custom refinery by a solvent extraction process using tri-butyl phosphate (TBP), and the filtrate is recycled to ion exchange after acidification to 0.3 to 0.4 N HNO_3 .

Previous work reported in IR 59-4⁽¹⁾ has shown that uranium can be recovered effectively by treating acidified nitrate eluate directly with 30% TBP in kerosene followed by a water strip of the extract. A near-nuclear-grade UO_3 product is produced by evaporation of the water strip. This circumvents the second stage precipitation.

In order to complete this investigation, it was necessary to determine what recovery and purity of product were possible in a truly continuous extraction system that could be adapted to a typical plant flowsheet. Also it was felt that a minimum nitric acid

concentration should be used in accordance with efficient operation and available acid-resistant equipment.

A 1000-litre batch of ion exchange eluate from the Stanleigh Uranium Corporation Ltd. leach plant, Elliot Lake, Ontario, was obtained to carry out this work and other proposed studies. The eluate from this plant was chosen because ammonia was being used in the uranium precipitation step while in several other plants, caustic soda or magnesia were the adopted precipitants. The presence of sodium or magnesium in solution could affect the purity sought in the product and also the uranium distribution in the extraction stage.

Existing solvent extraction mixer-settler equipment was used for this work (2). In practice pulse columns are also used for uranyl nitrate - TBP systems (3); but in view of the low uranium concentration in the feed which dictates a higher aqueous/organic flow ratio, mixer-settlers are more suitable since internal organic recycle can then be used to reduce the ratio and avoid "aqueous continuous" mixed phases, and resulting emulsions.

EQUIPMENT AND PROCEDURE

Batch Extraction

Preliminary batch cross-current extraction and stripping tests were done in 250-ml separatory funnels with acidified (3N HNO₃) Stanleigh eluate and 30% TBP in Shell kerosene (flash point 140° F). The tri-n-butyl phosphate was supplied by Electric Reduction Co., Buckingham, Que. The solvent was first equilibrated with 3N HNO₃ before use and then contacted with successive fractions of eluate to determine the distribution of uranium at varying degrees of saturation. A similar procedure using uranium-saturated solvent, was used to determine stripping coefficients with distilled water. Samples of the aqueous phases, final extract and stripped solvent were analysed for uranium. The two latter samples were analysed as described in the appendix.

Continous Extraction and Stripping

A four-stage mixer-settler unit with an operating volume of 800 ml per mixing stage and 2400 ml per settling stage was used as the extractor. Details of construction and operation have been reported previously (2). A smaller three-stage unit with volumes of 400 and 1200 ml for the respective mixing and settling stage was used for water stripping. A simplified flowsheet shown in Figure 1, illustrates the main control features.

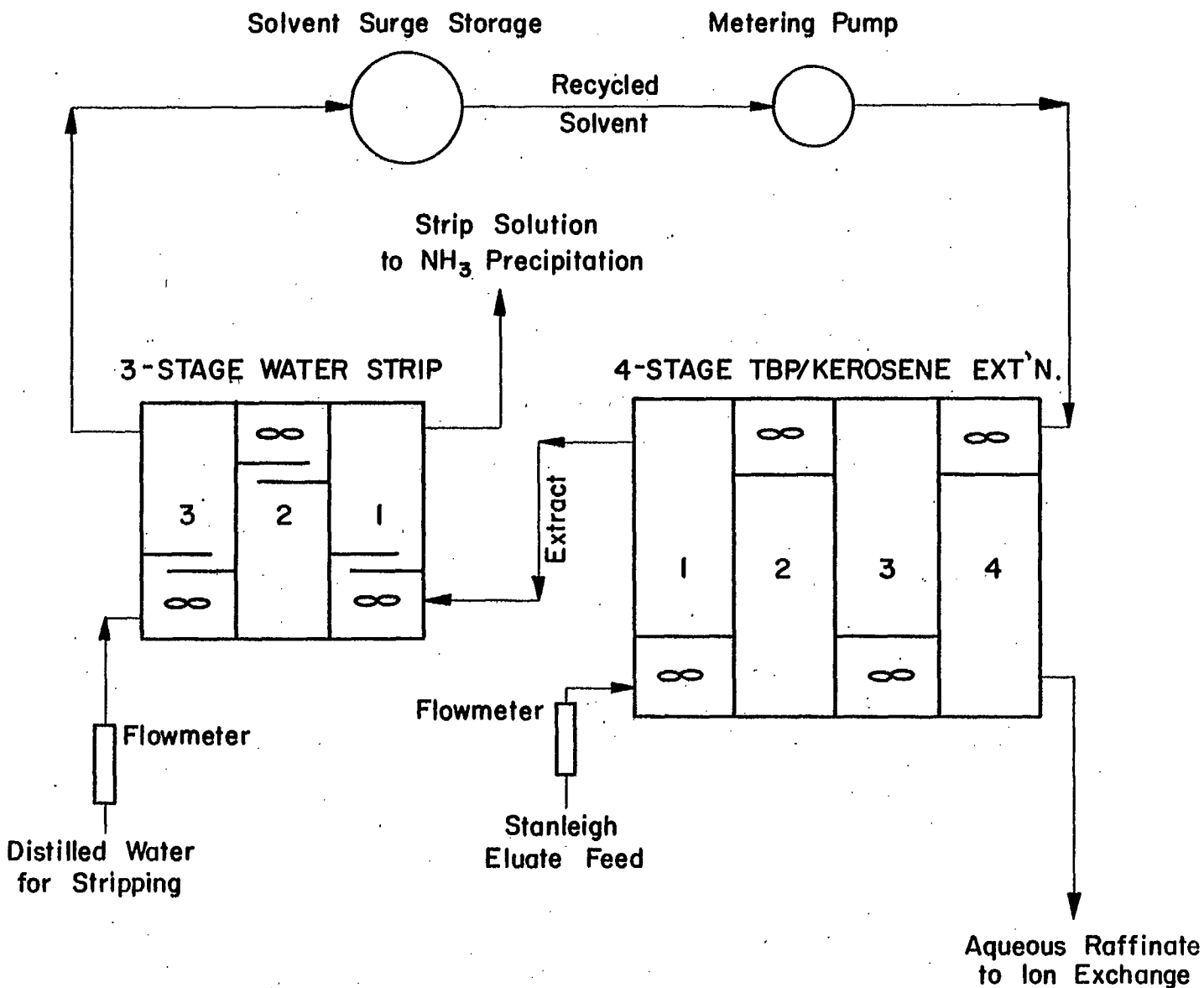


FIGURE I
FLOWSHEET OF EXTRACTION CIRCUIT

For each run, at least one solvent cycle (20 litres) was completed to attain equilibrium, before sampling the aqueous underflow from each settler and the loaded extract and recycle solvent. During operation an organic/aqueous mixing ratio of approximately 2/1 was maintained by internal recycle and an adjustment of the final stage aqueous underflow leg. Flowrates were held constant throughout each run.

Where it was necessary to reduce the sulphate concentration of the eluate feed to study the effect of lower sulphate levels, lime was added as required to a batch of feed solution after acidification with the nitric acid. The resultant gypsum product was then filtered from the eluate on a stationary filter and the filtrate pumped to the head tank.

Precipitation

The water strip, collected from each run, was precipitated continuously in four 1500-ml beakers connected in series. The solution was fed to the first beaker at the rate of 100 ml/min and ammonia gas was metered to maintain a pH of 7.0 - 7.5. Temperature was maintained at 40° to 45°C. On the fourth stage, a Separan-glue mixture (1 part of 0.1% Separan; 4 parts of 1% glue) was added at the rate of 1% of the feed volume with slow stirring. The overflow, which settled readily, was decanted and the thickened slurry was filtered and washed with 2 to 3

displacements of water. The precipitate, dried at 110°C, was analysed chemically for U, Th, NO₃, and NH₃ and a quantitative spectrographic analysis was done on the more representative samples. Three samples were also submitted to the Eldorado Mining and Refining Ltd. Research and Development Laboratory for hydrogen reduction and sintering tests.

RESULTS

Feed Solution

The nitrate eluate, as received, was analysed for the more important constituents and results are given in Table 1.

TABLE 1

Analysis of Stanleigh Nitrate Eluate

Ref. no. 5/59 - 8

	<u>g/l</u>	<u>Normality</u>
U ₃ O ₈	21.96	
Total nitrate as NO ₃	65.9	1.06
Free acid as HNO ₃	22.0	0.35
SO ₄	63.3	1.30
Cl	1.6	
Fe	2.2	
CaO	1.13	
ThO ₂	0.47	

The above analysis represents the composition of the solution before any lime addition, which would lower the sulphate concentration by an amount equivalent to the free acid concentration, or from 1.30 to 0.95 N SO_4 . This would still represent a higher than normal sulphate concentration for Elliot Lake area eluates which normally contain 0.5 N SO_4 after the liming step. For this reason, some further reduction of the sulphate concentration was carried out in the last two runs by acidifying the eluate to 2 N HNO_3 before the liming step. This allowed more lime to be added to neutralize to 1.2 N HNO_3 thus lowering the sulphate concentration to 0.5 N SO_4 .

The thorium content in the eluate is also higher than normal for Elliot Lake plants which report 0.1 to 0.4 g ThO_2 /l. This can usually be reduced to 0.1 g/l by lime addition to pH 3.5.

Batch Equilibrium Tests

Results of extraction and stripping tests in separatory funnels are shown in Tables 2 and 3. These results, plotted on log-log paper in Figure 2, indicate that four stages of extraction and three to four stages of stripping would give satisfactory uranium recoveries when operating at a feed/organic flow ratio of 2.5/l and at a strip/organic flow ratio of 1.5/l. Operating ratios are usually set by the uranium content of the recycle eluate which must be less than 0.1 g U_3O_8 /l for efficient elution, and by the uranium content of the recycle solvent which should be less than the 1.0 g U_3O_8 /l for efficient extraction.

TABLE 2

Extraction Equilibrium Data from Batch Tests

Eluate: 3 N HNO₃
 19.6 g U₃O₈/l
 Solvent: 30% TBP in kerosene
 conditioned with 3 N HNO₃

Stage No.	g U ₃ O ₈ /l		Stage No.	g U ₃ O ₈ /l	
	Eluate	Solvent		Eluate	Solvent
1.	0.60	7.60	14.	13.79	72.77
2.	1.00	15.04	15.	14.72	74.72
3.	2.00	22.08	16.	15.44	76.38
4.	2.85	28.78	17.	16.12	77.77
5.	3.62	35.17	18.	16.82	78.88
6.	4.43	41.24	19.	17.01	78.92
7.	5.86	46.74	20.	17.80	81.36
8.	6.79	51.86	21.	18.41	82.31
9.	8.35	56.36	22.	18.83	82.93
10.	8.53	60.79	23.	18.86	84.11
11.	10.55	64.41	24.	18.89	85.25
12.	11.45	67.67	25.	19.31	85.71
13.	12.66	70.45	26.	19.40	86.03

TABLE 3

Stripping Equilibrium Data from Batch TestsExtract: 81.7 g U_3O_8 /l in 30% TBP

Strip Solution: distilled water

Stage No.	g U_3O_8 /l		Uranium Distribution Strip/Solvent
	Water Strip	Solvent	
1.	33.97	68.04	0.59
2.	45.52	49.84	0.91
3.	40.17	33.77	1.21
4.	31.55	21.17	1.49
5.	23.85	11.63	2.05
6.	15.96	5.25	3.04
7.	8.79	1.73	5.00
8.	2.98	0.54	5.52
9.	0.70	0.26	2.70
10.	0.31	0.14	2.21
11.	0.16	0.076	2.11
12.	0.11	0.032	3.44

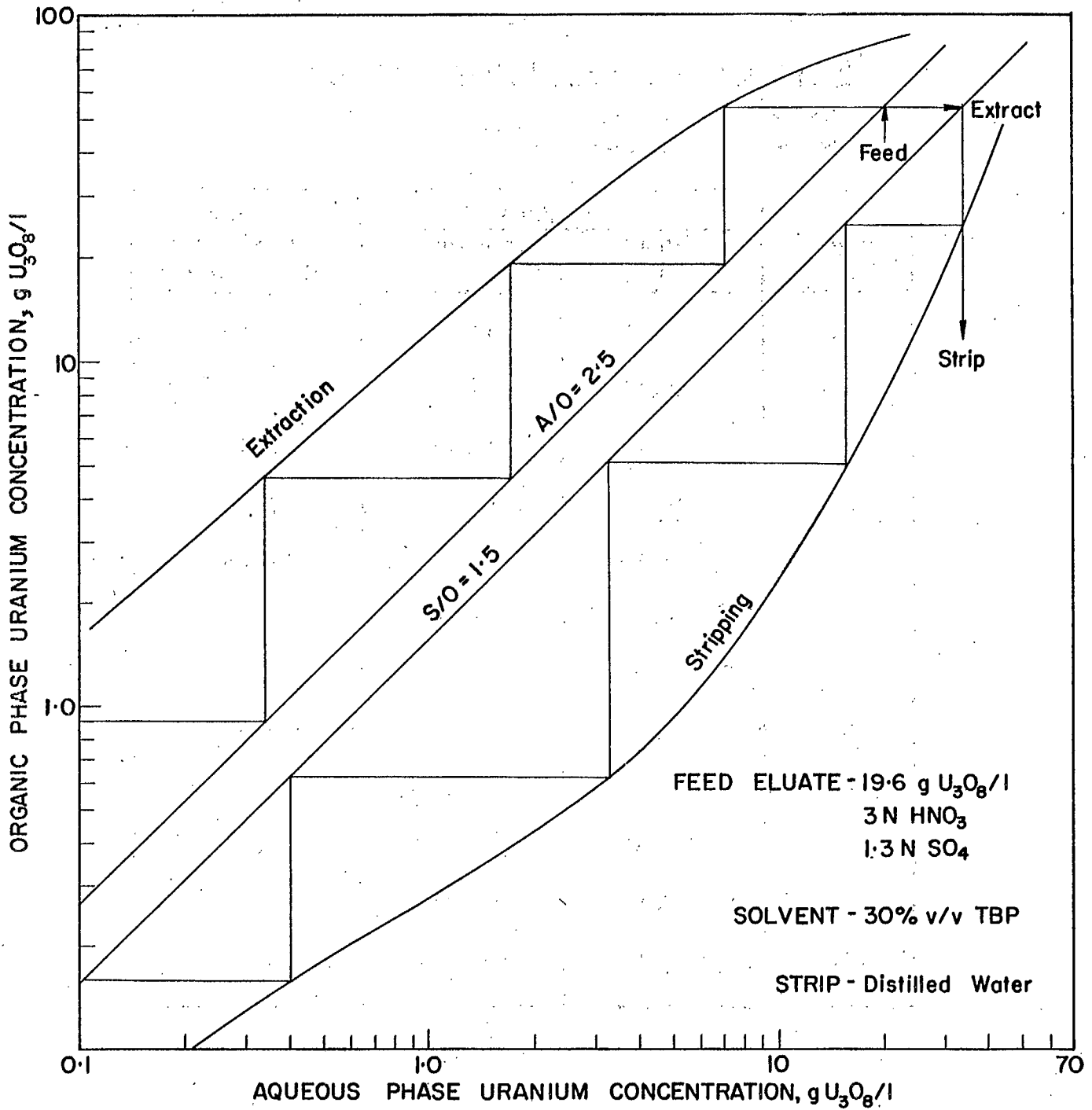


FIGURE 2
GRAPHICAL CALCULATION OF EXTRACTION
AND STRIPPING STAGES FROM BATCH EQUILIBRIA

Stripping equilibria for the first stage shows a much lower uranium distribution coefficient than that of subsequent stages. This is attributed to the presence of free nitric acid in the loaded extract and the subsequent higher acidity of the first strip fraction.

Continuous Extraction and Stripping

Following the batch equilibrium tests, seven continuous runs in the mixer-settler circuit were completed on the same sample of eluate at various nitric acid nitrate and sulphate levels. Solvent flowrates were held constant at approximately 100 ml/min while the eluate feed flowrate was varied from run to run to obtain different degrees of saturation. Water strip flowrates were also kept constant. Results are summarized in Table 4 and reproduced graphically in Figure 3. Extraction equilibria from Figure 2 are included for comparison.

As shown by Table 4, equivalent extraction was obtained from feed solutions containing 3.3 N and 1.2 N to HNO_3 by lowering the sulphate concentration of the feed solution from 1.2 N to 0.5 N SO_4 respectively. The data indicate that, for efficient extraction in four stages, maximum extract loadings should be limited to 37 to 40 g $\text{U}_3\text{O}_8/\text{l}$. Good stripping efficiencies were possible with strip loadings of 35 to 40 g $\text{U}_3\text{O}_8/\text{l}$.

TABLE 4
Continuous Extraction and Stripping Tests
Conditions and Results

Run No.		1	2	3	4	5	6	7
Feed Eluate Analysis								
U ₃ O ₈ g/l		19.4	20.7	20.4	19.1	19.4	20.5	21.3
HNO ₃ Normality		3.3	3.3	1.7	1.0	1.0	1.2	1.2
Tot. NO ₃ "		4.0	4.1	2.8	3.4	3.1	3.1	3.1
SO ₄ "		1.2	1.2	1.2	1.1	1.2	0.5	0.5
Operating Time hr.		4 1/2	5 1/2	5	5	6	5	4
Flowrates ml/min								
Feed Eluate		275	370	300	275	185	170	270
Solvent (25% TBP)		100	95	90	100	100	110	110
Water		135	140	135	130	145	135	175
Analysis U ₃ O ₈ g/l								
Extraction Stage 1	O*	57.8	59.1	55.2	46.4	38.9	37.2	76.0
"	A*	11.8	17.2	20.0	16.8	13.5	4.6	16.4
"	2 O	38.0	60.4	50.5	38.4	24.9	9.7	56.6
"	A	5.4	12.8	17.2	12.8	8.0	0.9	8.9
"	3 O	17.0	43.1	40.6	27.1	14.9	3.6	18.2
"	A	1.9	6.7	12.0	8.1	4.4	0.4	2.1
"	4 O	5.4	19.3	24.2	12.8	5.6	0.8	3.5
"	A	0.5	2.0	5.1	4.3	2.1	0.07	0.3
Stripping Stage 1	O	42.1	44.1	24.4	28.6	16.2	20.7	5.4
"	A	42.4	40.1	32.0	34.0	24.9	26.3	15.6
"	2 O	15.1	11.7	2.7	7.3	1.8	2.9	0.5
"	A	32.1	24.9	13.9	20.7	11.3	15.3	3.4
"	3 O	1.4	0.6	0.3	0.7	0.1	0.2	0.02
"	A	11.7	6.6	1.6	5.1	1.1	2.3	0.30
Final Strip Solution								
Volume litres		30	50	44	40	52	41	34
Analysis U ₃ O ₈ g/l		34.8	39.7	33.1	32.6	25.4	26.5	27.9

* O = organic phase
A = aqueous phase

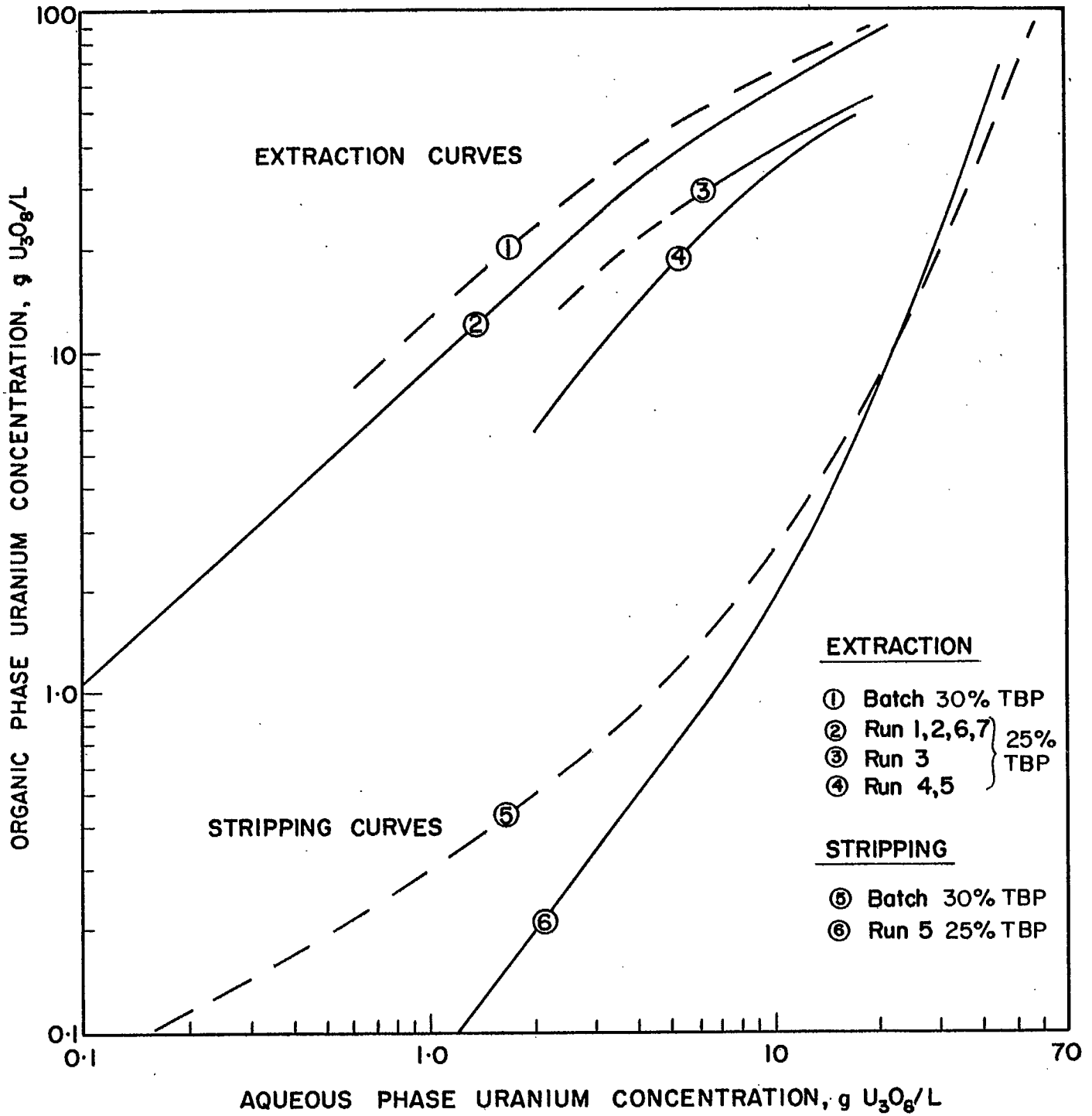


FIGURE 3

EXTRACTION AND STRIPPING
MIXER-SETTLER EQUILIBRIUM DATA

TABLE 5
Continuous Ammonia Precipitation
Conditions and Results

Run No.	1*	2	3	4	5	6	7
Strip Solution							
pH	0.8	0.8	1.2	1.2	1.0	0.8	0.9
Volume litres	52	50	44	40	52	41	34
Analysis	g/l						
U ₃ O ₈	30.57	39.74	33.14	32.60	25.36	26.46	27.88
HNO ₃	11.5	11.8	6.6	6.6	7.8	13.1	8.7
Tot. NO ₃	29.0	31.2	23.5	21.8	22.8	21.4	21.9
Tot. U ₃ O ₈ g	1590	1987	1458	1304	1319	1085	948
Barren Solution							
pH	7.2	7.1	7.3	7.4	7.4	7.5	7.3
Analysis	g/l						
U ₃ O ₈	0.006	< 0.001	< 0.001	0.003	0.001	< 0.001	< 0.001
Tot. NO ₃	28.8	30.5	22.0	21.5	22.4	21.9	--
NH ₃	8.05	8.64	6.24	6.12	4.77	6.07	5.82
Precipitate							
Dry Wt. g	1960	2460	1815	1445	1545	1240	1135
Analysis	%						
U ₃ O ₈	84.96	86.35	86.10	86.08	87.95	84.67	89.72
NO ₃	0.03	0.05	0.034	0.040	0.20	0.28	0.054
NH ₃	2.12	2.18	2.26	2.04	1.80	2.11	1.66
ThO ₂	0.05	0.03	0.01	0.01	0.01	0.09	0.085
H ₂ O	5.55	5.27	4.95	5.97	3.67	4.95	3.86
Tot. U ₃ O ₈ g	1665	2124	1563	1244	1359	1050	1018

*Included in this run were 22 litres of strip solution which were produced from the start-up operation of the extractor-stripper unit, and which were not included in Table 4 results.

Precipitation

Table 5 summarizes the results of continuous precipitation tests carried out on the strip solution collected from the circuit. A quantitative spectrographic analysis of two precipitates is shown in Table 6.

TABLE 6

Quantitative Spectrographic Analysis of Precipitate

Run No.	ppm, U-basis						
	100	50	50-10	10-5	5-2	2-0.5	< 0.5
5	Zn	V	As, Co, Fe, Pb	Bi, Mn, Mo	B, Cr, In, Sn	Ni	Be, Ge
7	Th, Zn	Fe, Pb	Bi, Co V	Mn, Mo	B, As, Cr, Sn	In, Ni	Be, Ge

Samples from runs 1, 5 and 7 were submitted to the Eldorado Mining and Refining Ltd. Research and Development Laboratory for hydrogen reduction at 600°C and subsequent pelletizing at 40,000 psi followed by sintering at 1650°C in hydrogen. Sound pellets of densities of 10.66, 10.56 and 10.49 were produced.

DISCUSSION

Uranium Recovery

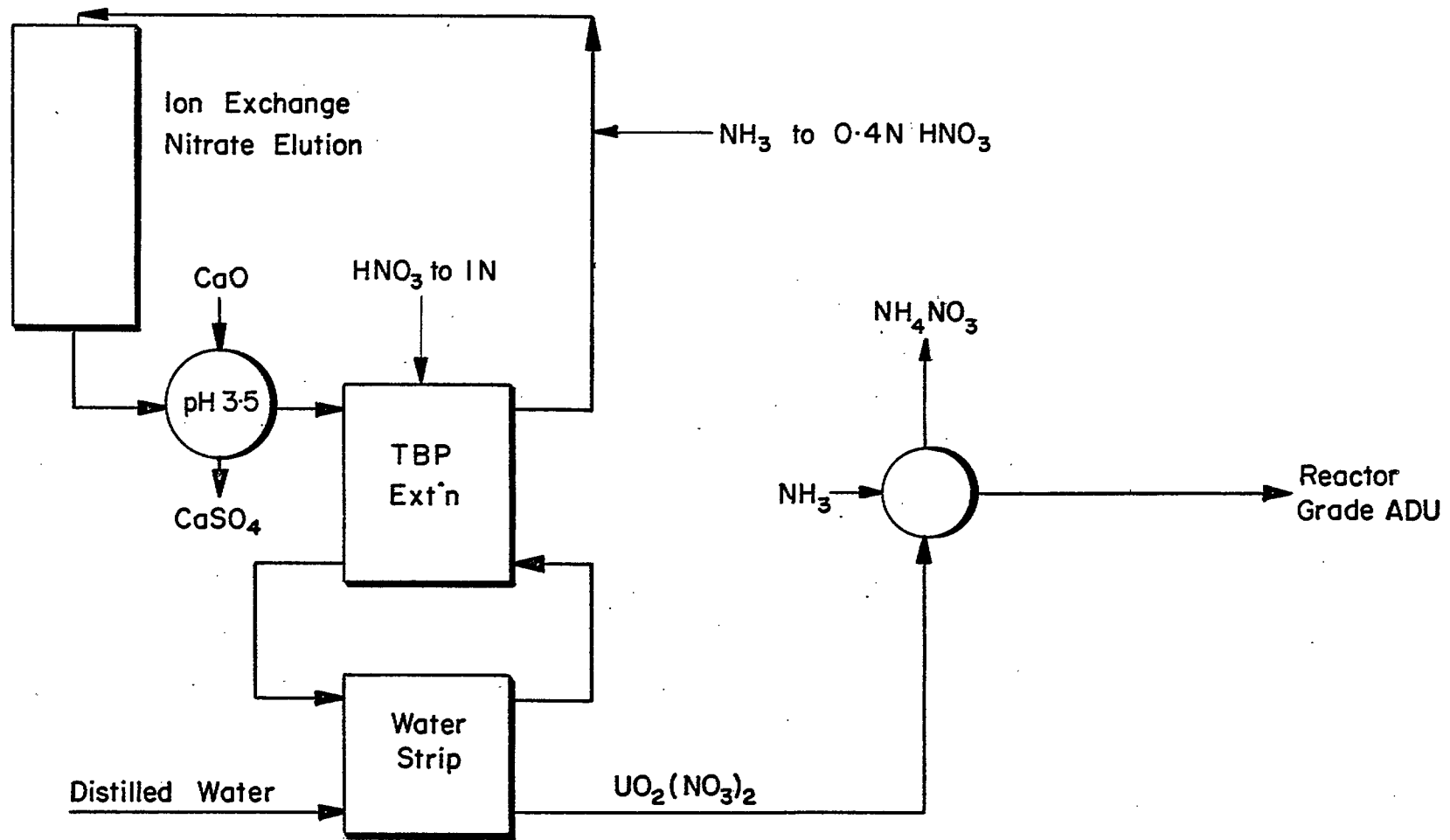
Continuous operation in countercurrent mixer-settlers has shown that barren eluates containing less than 0.1 g U₃O₈/l can be obtained from ion exchange eluates. These barren solutions may subsequently be recycled to the ion exchange circuit.

An acidity of 1.2 N HNO_3 and a total nitrate content of 3.1 N in the eluate feed solution appear to be the minimum allowable for efficient extraction. Results could be improved by increasing the number of extraction stages to five or six, to take advantage of the total uranium capacity of the solvent. In such a case, from the known equilibrium data of Figures 2 and 3, an operating loading of 60 g U_3O_8 /l extract is possible. This would materially improve uranium purity.

The stripping operation was relatively trouble-free. Since the water strip is to be precipitated directly, a higher uranium concentration at this point is of no great advantage and three to four stages of stripping are adequate. The nitrate concentration will follow that of the uranium at approximately 30 g NO_3 /l. If this is to be evaporated to reclaim the nitrate salt as proposed in the flowsheet of Figure 4, evaporation cost would have to be balanced against the price of nitric acid as an alternate source of nitrate make up.

Grade of Precipitate

The main concern in the refining of uranium is with the high neutron absorbers such as boron, cadmium and certain rare earths. Also with the TBP refining process, thorium is not as readily separated as other impurities.



- 17 -

FIGURE 4
 PROPOSED FLOWSHEET FOR PRODUCTION
 OF REACTOR GRADE ADU FROM NITRATE ELUATES

The thorium concentration in the present feed solution is relatively high (0.47 g/l) and the quantity in the final product is above the specification limit of 10 ppm. In the proposed flowsheet of Figure 4, the lime-addition step would reduce the concentration of thorium in the feed to 0.1 g ThO₂/l or less, as has been in plant practice. The addition of phosphate to complex thorium in the extraction circuit was not investigated but has proven successful in the refining of Stanleigh concentrate⁽⁴⁾.

The boron content is also above specification (0.2 ppm) but subsequent work by the present authors in the refining of uranium solutions with other solvents, has shown that the contamination is largely due to the use of borosilicate glassware in bench-scale precipitation work, and is not of a serious nature in larger scale equipment.

Rare earths in the product were not determined.

Reagent Consumption

One limitation of this flowsheet is in the necessity of using higher nitric acid and nitrate concentrations than are normally used in the uranium ion exchange circuit. Nitric acid consumption will be increased from the present 1.6 - 1.7 lb/lb U₃O₈ to 5 lb/lb when using 1 N HNO₃ in the solvent extraction circuit. Subsequent ammonia consumption will increase from 0.3 to approximately 0.5 lb/lb U₃O₈.

CONCLUSION

Although this investigation was of a preliminary nature, the results point out the limitations of TBP refining of uranium at the leach plant. A nuclear grade product was not obtained but it is felt that by including the lime-addition step before extraction, thorium in the precipitate could be reduced to near nuclear grade specification. Further study would be required to confirm this. The proposed flowsheet of Figure 4 also would mean an increased consumption of nitric acid and ammonia.

Current work is now directed to the study of other selective solvents, tertiary amines and dialkyl alkyl phosphonates, as other possible extractants of uranium from sulphate and nitrate eluates.

REFERENCES

1. A. J. Gilmore. Testwork on Solvent Extraction of Nitrate Eluates for the Production of Uranium Trioxide, -- Progress Report -- Mines Branch Investigation Report IR 59-4 -- Department of Mines and Technical Surveys, Ottawa, Canada. January 1959.
2. R. Simard. Solvent Extraction Studies. Special Report SR 416/56. Mines Branch, Department of Mines and Technical Surveys,

Ottawa, Canada. April 1956.

3. J. C. Burger and J. McN. Jardine. Canadian Refining Practice in the Production of Uranium Trioxide by Solvent Extraction with Tributyl Phosphate. Second U.N. International Conference on the Peaceful Uses of Atomic Energy, Paper 228, September 1958.
4. N. R. Leist, C. T. Hicks and J. R. Nelli. Laboratory and Pilot Plant Evaluation of Stanleigh Uranium Concentrate. U.S.A.E.C. Report NLCO-777. March 1959.

APPENDIX

Preparation of Organic Solvents for Uranium Analysis

1. A 25 ml aliquot of organic sample is transferred to a 100 ml separatory funnel.
2. The organic phase is contacted for 3 to 5 minutes with successive 25 ml fractions of distilled water until a nilspot is obtained with 0.5 M potassium ferrocyanide.
3. The total strip volume is recorded and the aqueous solution is analysed for uranium by the ammonium thiocyanate method.
4. The organic solution is returned to the extraction circuit.

AJG:VMMcN:RS:im