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MINES BRANCH INVESTIGATION REPORT IR 59-4

TESTWORK ON SOLVENT EXTRACTION OF NITRATE
ELUATES FOR THE PRODUCTION OF URANIUM TRIOXIDE
PROGRESS REPORT

by

A. J. GILMORE

RADIOACTIVITY DIVISION

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SUMMARY OF RESULTS

A solvent extraction technique, employing tributyl phosphate (TBP) in kerosene as extractant followed by a water strip, has been used successfully for recovering high grade uranium products from uranium mill nitrate eluates containing 8 to 12 g U_3O_8 /l. Uranium recoveries ranging from 73.4% to 96.5%, depending on free acid concentrations of eluate, are possible. Calculated loadings of 64 g U_3O_8 /l organic were obtained. Evaporation and ignition of water strip liquors gave uranyl oxide products averaging 96.0% U_3O_8 . Details of test work at various concentrations of nitric acid and TBP are presented.

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(14 pages, 2 tables, 1 figure)

INTRODUCTION

This work was done to study the feasibility of producing a metal grade uranyl oxide (UO_3) from mill samples of uranium-bearing nitrate eluates (Samples 4/57-7B and 1/58-3) which were received from a uranium-producing property at Elliot Lake, Ontario. Such a process could (1) replace the existing processes in which the ion exchange nitrate eluates are neutralized with magnesia or lime and caustic, (2) decrease shipping costs by increasing the grade of the product by 10% to 30% or (3) be adapted for production of a metal-grade oxide at a central location when present uranium contracts are terminated.

LITERATURE SURVEY

A survey of some of the literature reveals that tributyl phosphate (TBP), $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ is a very stable compound, as evidenced by its thermal stability and resistance to oxidation.⁽¹⁾ Acid hydrolysis depends on the nature and concentration of the acid. Hydrolysis is catalyzed by both acids and bases, and the rate increases with a rise in temperature.

TBP, although selective, is not specific for uranium.⁽²⁾ Other elements in uranium slurries are extracted to some degree. Hexavalent elements, such as Mo^{6+} and Cr^{6+} are extracted in TBP, but those of an anionic nature, such as MoO_4^- and Cr_2O_7^- are most extractable.⁽³⁾ The tetravalent elements such as Pa^{4+} , Zr^{4+} , Ce^{4+} and Th^{4+} are next in order of selectivity. Trivalent elements are held more loosely and are readily replaced by either of the above series, but under special conditions may be readily extracted. Pentavalent ions that tend to

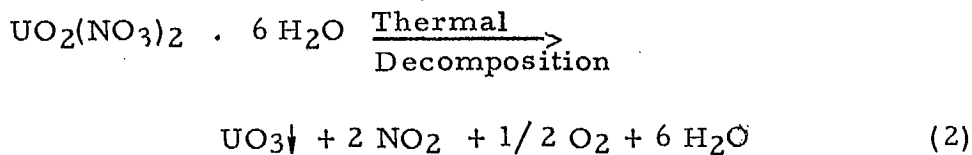
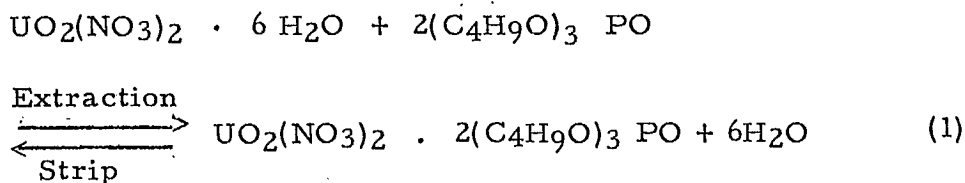
become anionic like Nb^{5+} and Pa^{5+} are held together loosely, resembling trivalent metals. Apparently, none of the divalent or monovalent cations extract. However, our work shows that Na and Mg are extracted or entrained by the TBP process from nitrate eluates and report in the uranyl oxide product as major impurities (See Table 1). Other possible contaminants in the extraction of uranium from slurries are B, Cd, Rare Earths, Li, As, S, C, V, Pb, Ru, Zn, Sn and Si.

As the uranium concentration of slurries decreases, impurity concentrations and the amount of HNO_3 -soluble material increases. Also, increasing difficulties in processing and meeting recovery and purity specifications are experienced. Impurities may be controlled by a high degree of uranium saturation of the organic phase.⁽⁴⁾ Saturation loadings may be controlled by density measurements. A hot water scrub of the organic phase is reported to give better purity.

Gypsum formation and the presence of insoluble silicates present scaling problems. Emulsion problems are caused more by the presence of soluble rather than insoluble silica. Fluorides and chlorides with HNO_3 result in corrosion problems. Sulphate and phosphate, in the form of anions, are not extracted by TBP. When the concentration of the sulphate and phosphate ions becomes too great, they preferentially associate with the uranyl ion. As a result, the efficiency of the extraction process tends to be reduced. The arsenate and vanadate ions also fall into this group. Considerable uranium could be lost in the raffinate stream due to the formation of uranium complexes with these

undesirable anions at high concentrations. To maintain a low solvent loss, the raffinate stream may be washed with kerosene to recover TBP.

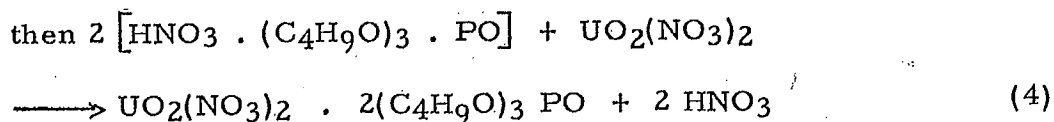
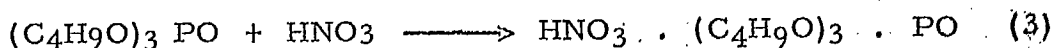
The following equations (1) and (2) give some conception of the chemistry of the TBP recovery process of uranium



GENERAL PROCEDURE

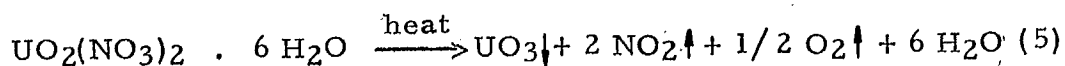
The conditions of the shake-out tests in separatory funnels described in this report were based on the process described in IR 226/56 (5) for UO_3 production by TBP/kerosene columnar extraction from uranium-bearing nitric acid slurries (250 to 275 g $\text{U}_3\text{O}_8/1$),

In the case of the tests with nitrate eluates (≈ 8 to 12 g $\text{U}_3\text{O}_8/1$), the aqueous phase was contacted for 3 to 5 minutes with the organic solvent at organic/aqueous ratios of 1/1 to 2.5/1. Nitrate concentrations were varied between 0.2N and 3N with HNO_3 or NaNO_3 . The organic, at concentrations of 1% and 24% TBP in a good commercial grade kerosene, was nitrate conditioned with HNO_3 and/or NaNO_3 solution prior to contact with the uranium-bearing eluate. (Equations 3 and 4).



A cation exchange of $[\text{UO}_2]^{++}$ for $[\text{H}]^+$ is suggested.

In our tests, the loaded solvent was stripped with distilled water at organic/aqueous ratios of 33/1 to 3/1. The water strip was evaporated in stainless steel containers to produce a concentrated uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) solution. This solution was then transferred to platinum dishes for pre-ignition, over a bunsen flame, to drive off nitrogen dioxide, followed by ignition in a muffle furnace at 400°C for about 5 hr (Equation 5).



RESULTS

Production of a UO_3 Product

In IR 243/57 (6), where a preliminary attempt was made to produce a UO_3 product, the major contaminants boron and silica were presumed to have been a result of using Pyrex glassware in the evaporation step.

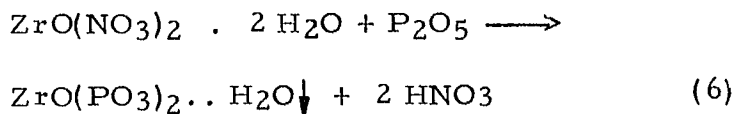
A similar test, reported here, was performed in an endeavour to minimize some of these undesired impurities. The nitrate eluate treated (Sample No. 4/57-7B), from a uranium mining property at Elliot Lake, Ontario, assayed as follows:

U ₃ O ₈	10.33 g/1
Cl	0.35 g/1
Total NO ₃	34.8 g/1 (0.56N)
Free HNO ₃	21.0 g/1 (0.33N)
P ₂ O ₅	0.16 g/1
ThO ₂	0.07 g/1
SO ₄	20.3 g/1

After the extraction and stripping steps, the strip solution was evaporated in stainless steel beakers, then the concentrated liquor was transferred to platinum dishes for final evaporation and ignition.

The results of the Port Hope refinery spectrographic analysis (See Test 1 of Table 1) indicated that the concentration of some of the contaminants had been minimized successfully. The comparable results from IR 243/57 (6) are presented in Table 1 for comparison purposes.

In an attempt to reduce possible phosphorous contamination of the UO₃ product, 77% of the P₂O₅ in the nitrate eluate was eliminated by pretreating the eluate with zirconyl nitrate to precipitate the phosphorous as a filterable zirconium phosphate (Equation 6).



Other means such as precipitation from hot strip solutions as calcium, iron or thorium phosphate may be more practical and economical.

TABLE 1
Comparison of Analyses of UO₃ Products

	Test No.			
	IR 243/57*	Test 1	Test 3(a)	Test 3 (b)
U	81.03%**	82.30%**	82.14%	82.11% **
UO ₃ (from U)	97.37%**	98.89%**	98.70%	98.66%**
U ₃ O ₈	95.55%	97.05%	96.87%**	96.83%
H ₂ O			0.43%	0.75%
NO ₃			0.41%	0.62%
Fe	28 ppm	25 ppm	131ppm	585 ppm
Th			81ppm	96 ppm
Mo			0.6 ppm	15 ppm
<u>Spectrographic Analysis (U-Basis) (ppm)</u>				
Ag	1	1.8	0.5	3.7
Al	5	<10	<10	<10
As	<5	<5	12	<5
B	1.25	0.5	0.12	0.3
Bi	<0.2	<0.2	2	>300
Cd	<0.1	<0.1		
Co	<1	<1	<1	<1
Cu	2	<1	2	2
Cr	<10			
Mg	5	20	150	10
Mn	<1	<1	20	5
Na			1500	>5000
Ni	2	<2	18	20
P	175	50	110	10
Pb	4	6	60	30
Si	80	<5	20	<5
Sn			5	25
Dy			0.009	
Gd			0.01	
Y			0.028	

* Brought forward from IR 243/57(6) for comparison.
** Calculated

Effect of Varying HNO₃ Concentrations in Eluate

Six shake-out tests were performed with 24% TBP in kerosene, using the same loading technique described in the general procedure, to study the effect of varying free HNO₃ concentration in the nitrate eluates. A distribution curve for each acid concentration was plotted (See Figure 1), to relate the uranium concentration in the aqueous phase to that in the organic phase after contact. The higher the free HNO₃ concentration, (Table 2), the higher was the initial distribution coefficient $E_{o/a}$ attained at equilibrium. Also, the higher the free HNO₃, the more saturated was the organic phase. Hence, fewer impurities would be expected in the uranium oxide, and the uranium concentration in the treated eluate (raffinate), recycling through an ion exchange circuit, would be lower.

TABLE 2

Effect of HNO₃ Concentration in Eluate on Loading of 24% TBP/Kerosene

Test No.	Solvent Extraction Feed		Loaded Organic Concentration Calculated (g U ₃ O ₈ /l)	Organic Saturation (%)	Initial Raffinate (g U ₃ O ₈ /l)	Initial Distribution Coeff. (E _{o/a})
	U ₃ O ₈ (g/l)	HNO ₃ (N)				
18AN-4	10.49	0.37	7.26	100.0	2.79	2.8
18AN-5	10.05	0.85	23.94	99.0	1.47	5.8
18AN-6	9.82	1.38	36.87	98.3	0.92	9.7
18AN-3	9.78	1.56	48.57	97.0	0.76	11.9
18AN-2	8.91	2.57	61.77	92.1	0.45	18.8
18AN-1	8.61	3.31	66.97	86.1	0.30	27.7

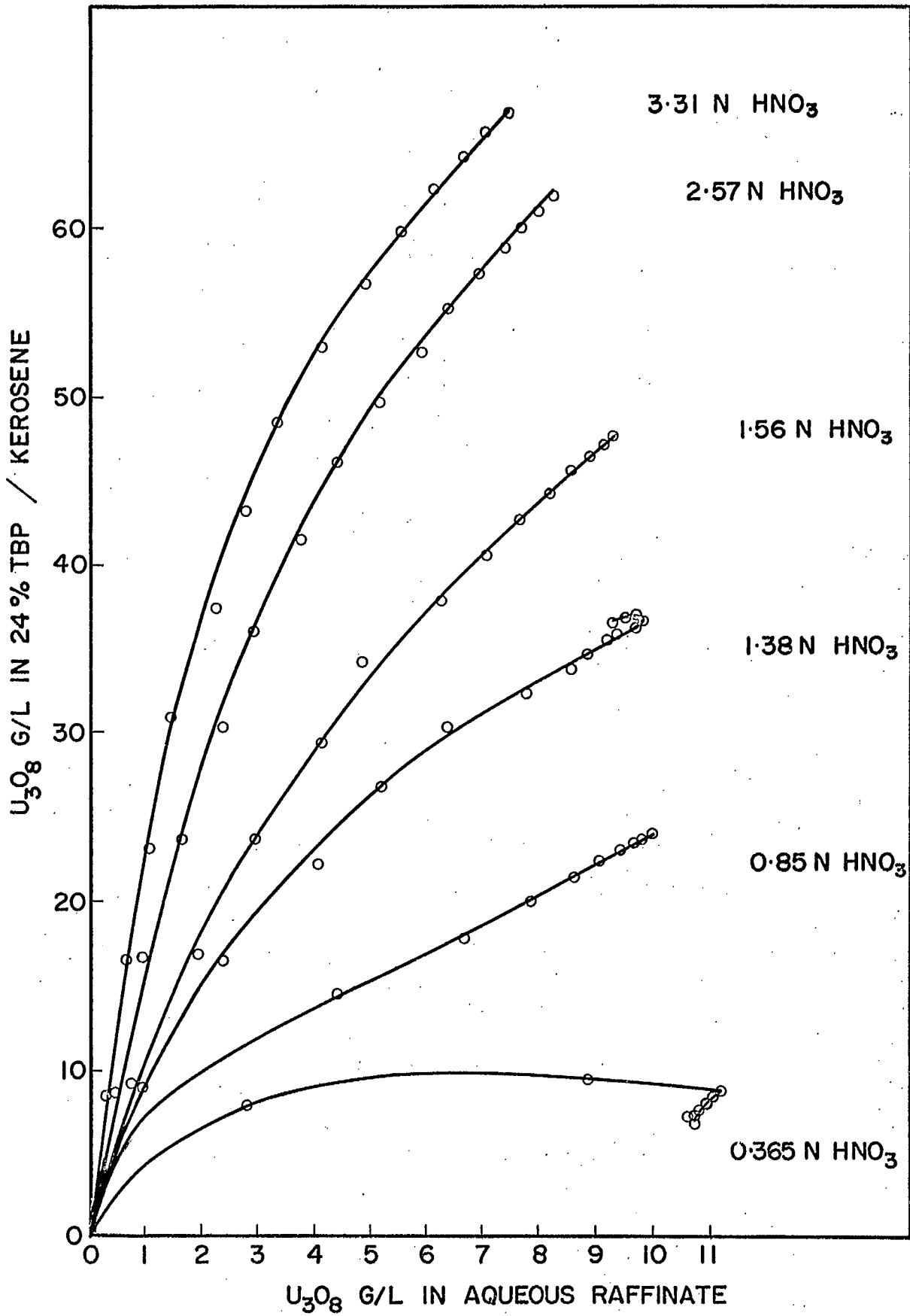


FIGURE I
DISTRIBUTION CURVES AT VARIOUS HNO_3 CONCENTRATIONS

Comparison of Batch UO₃ Products from Nitrate Eluates at 3N HNO₃
and 0.2N HNO₃

Two similar solvent extraction tests, one at 3N HNO₃ and the other at 0.2N HNO₃, were performed in a Patterson-Kelly Twin Shell Dry Blender (approx 5 litre capacity) to obtain 150 g batches of uranyl oxide for comparison of contaminants. A different batch of uranium-bearing nitrate eluate (Ref.No. 1/58-3) was treated in these tests. The assays for this eluate are given below.

U ₃ O ₈	11.97 g/l
Cl	1.09 g/l
Total NO ₃	50.4 g/l (0.8N)
Free HNO ₃	12.6 g/l (0.2N)
P ₂ O ₅	0.084 g/l
ThO ₂	0.06 g/l
SO ₄	36.1 g/l

(a) The above eluate, adjusted to 2.9N free HNO₃, was contacted with HNO₃-conditioned 24% TBP/kerosene v/v until the organic phase was 95.8% saturated with uranium. The uranium concentration of this phase was calculated at 69 g U₃O₈/l. The water strip was treated as described on page 5 to obtain the uranyl oxide. The refinery assay results are reported in Table 1 under Test 3(a).

(b) The technique of this test 3(b), with the eluate at 0.2N HNO₃ was similar to (a) above with the exception that a considerably greater number of loading and stripping operations was necessary as the average organic loading before stripping was 2.2 g U₃O₈/l due to the

low eluate acidity. This necessitated evaporating an excessive volume of water before the uranyl nitrate hexahydrate could be ignited to UO_3 ,

The assay results on the above 150 g batch products are reported in Table 1 for comparison purposes under Test 3(a) and Test 3(b). The uranium grade of both products is satisfactory. While both contain impurities above specification, the product from the 3N HNO_3 eluate is the closer to the purity specifications.

Uranium Loading on 1% TBP/Kerosene

Three tests were performed to determine the uranium loading of 1% TBP/kerosene v/v:

- (1) Using nitrate eluate as received (0.2N free HNO₃)
- (2) Using eluate made up to 3N free HNO₃
- (3) Using eluate made up to 3N total nitrate by NaNO₃ addition.

The nitrate conditioned organic was contacted with a nitrate adjusted eluate (averaging 10 g U₃O₈/l). The resulting uranium loadings were as follows:

<u>Eluate Concentrations</u>	<u>Organic Phase Loading</u> g U ₃ O ₈ /l
(1) "As received" Total NO ₃ = 0.8N Free HNO ₃ = 0.2N	0.017
(2) Total NO ₃ = 3.6N Free HNO ₃ = 3 N	0.91
(3) Total NO ₃ = 3.1N Free HNO ₃ = 0.2N	0.11

The best uranium loading was obtained from the high free-HNO₃ eluate. From the latter two tests, it would appear that a decrease in the extraction of uranium by TBP/kerosene is caused by the presence of dissolved NaNO₃.

DISCUSSION AND CONCLUSIONS

In the uranyl oxides produced in the laboratory, no great difficulty has been experienced in attaining the refinery specification of 96% U₃O₈. The problem has been to prepare a product relatively free

of impurities. It is suggested that the concentration of contaminants may be minimized by:

1. maintaining a free HNO_3 concentration of 1.5 to 3N in the solvent extraction feed,
2. loading the organic phase with uranium until as close to saturation as possible,
3. a hot water scrub of the organic phase before water stripping ($\text{O/A} = 12/1$). This scrub could be recycled to extraction feed,
4. chemical treatment of the water strip such as the addition of NH_3 to pH 2.1 to precipitate some impurities such as iron and zirconium.

In the existing plants, most of the Na and Mg ions present in the high grade eluate are introduced during the lime and caustic precipitation steps. If a process, such as outlined herein, were adopted, many of the impurities in the UO_3 product such as Na and Mg would be minimized due to the elimination of the neutralization procedures.

An expected problem is the sulphate build-up in recycled eluates that will occur without a bleed by the lime precipitation. The uranium may be expected to preferentially associate with the sulphate rather than the nitrate ion if other ions that bind sulphate are not present in high enough concentration.

The literature suggests that by using a hot water strip at 60°C , the volume of concentrated uranyl nitrate solution could be reduced by 25%.

There is the further possibility that an electrolytic reduction of the uranyl ion in these concentrated strip solutions may produce a reactor-grade UO_2 .

At this stage in the production of a UO_3 product from a nitrate eluate, some of the factors to be determined appear to be:

1. Free HNO_3 in eluate
2. Uranium concentration of recycled eluate (raffinate)
3. Uranium loading of organic
4. Purity of product
5. Sulphate concentration of eluates allowable at optimum conditions for satisfactory extraction.

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