ROUGH DRAFT

HW-32103 RE

[REDACTED]

July 20, 1961

GENERAL ELECTRIC **DECLASSIFIED**

HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

RESTRICTED DALLAS

THIS DOCUMENT CONTAINS UNCLASSIFIED DATA AS
DEFINED IN THE ATOMIC ENERGY ACT OF 1954.
ITS TRANSMISSION OR DISCLOSURE OF ITS
CONTENTS IN ANY MANNER TO ANY UNAUTHORIZED
PERSON IS PROHIBITED.

TITLE

LABORATORY STUDIES ON THE USE OF
URANIUM(IV) AS A PLUTONIUM REDUCTANT
IN A PUREX PROCESS

OTHER OFFICIAL CLASSIFIED INFORMATION

THIS MATERIAL CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECS. 793 AND 794, THE TRANSMISSION OR REVELATION OF WHICH IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

AUTHOR

J. E. Mendel

ISSUING FILE

THIS DOCUMENT IS NOT TO BE LEFT UNATTENDED OR MADE AVAILABLE TO UNAUTHORIZED PERSONS WHO HAVE ACCESS TO IT. WHEN NOT IN USE, IT MUST BE STORED IN A PROVED LOCKED REPOSITORY WITHIN AN APPROVED GUARDED AREA. WHILE IT IS IN YOUR POSSESSION, AND UNTIL YOU HAVE SIGNED A SIGNED RECEIPT FOR IT, IT IS YOUR RESPONSIBILITY TO KEEP IT AND ITS CONTENTS WITHIN THE LIMITS OF YOUR PROJECT AND FROM ANY UNAUTHORIZED PERSON. ITS TRANSMITTAL TO, AND STORAGE AT, YOUR PLACE OF RESIDENCE IS PROHIBITED. IT IS NOT TO BE DUPLICATED. IF ADDITIONAL COPIES ARE REQUIRED, OBTAIN THEM FROM THE ISSUING FILE. ALL PERSONS READING THIS DOCUMENT ARE REQUESTED TO SIGN IN THE SPACE PROVIDED BELOW.

ROUTE TO:

PAYROLL NO.

LOCATION

FILE	ROUTE	DATE
100-443888-100	100-443888-100	100-443888-100

SIGNATURE AND DATE

300 Files

REFERENCE COPY
RECEIVED 300 AREA

~~SEP 23 1964~~

RETURN TO

TECHNICAL INFORMATION FILES

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

54-3000-052 (7-59)

A.E.C.-G.E.-RICHLAND, WASH.

(CLASSIFICATION)

DECLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DECLASSIFIED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This document contains information defined in the Atomic Energy Act of 1946, its transmittal in any manner to an unauthorized person is prohibited.

- 1-3 D30R
- 4. Patent Branch, Washington
- 5. Chicago Patent Branch
- 6. 1300 Files
- 7 - 642
- 8 - 642
- 9 - 642

- 1. O. E. Beaulieu
- 2. E. E. Burns
- 3. J. E. Isacson
- 4. J. E. Isacson
- 5. J. E. Isacson
- 6. J. E. Isacson
- 7. J. E. Isacson
- 8. J. E. Isacson
- 9. J. E. Isacson
- 10. J. E. Isacson
- 11. J. E. Isacson
- 12. J. E. Isacson

Distribution:

DECLASSIFIED
Classification Cancelled (Change)
JULY 30, 1964
By Authority of [Signature]
J. E. Isacson

JULY 30, 1964

J. E. Isacson

by

DECLASSIFIED
Classification Cancelled and Changed To
By Authority of J. E. Isacson
CG-R-2, 4-14-94
By J. E. Isacson 4-19-94
Verified By [Signature] 4-19-94

LABORATORY STUDIES ON THE USE OF URANIUM (IV) AS A PHOTOGRAPHIC
REPRODUCING IN A PULVERIZED STATE

This document consists of

19

ROUGH DRAFT

DECLASSIFIED

I. INTRODUCTION

This report describes laboratory-scale studies made to evaluate the feasibility of using uranium(IV)-hydrazine instead of ferrous sulfamate-sulfamic acid as the partitioning agent in the Hanford Atomic Products Operation Purex separations plant. Iron(II), in combination with sulfamic acid as a holding reductant, has been used very successfully for many years as a plutonium reductant in solvent extraction separation processes for irradiated nuclear fuels. However, the iron remains in the radioactive wastes produced in the separation processes. Its presence in these wastes accelerates corrosion of waste concentration equipment, complicates treatment of the waste for by-product recovery and adds to the total quantity of contaminated salts which must be stored.

Much effort has gone into searches for plutonium reductants which would not have the disadvantages associated with iron(II). Uranium(IV) has been proposed since, having acted as reductant, it is extracted along with uranium from the irradiated fuels and does not remain in the waste. Previous studies on the use of uranium(IV) in solvent extraction separations processes have involved mixer-settler contactors.^(1,2) The HAPU Purex plant has pulsed-column contactors. This difference, plus certain problems due to the particular flowsheet conditions used, required that additional laboratory studies be made to determine the feasibility of using uranium(IV) in the HAPU Purex plant. These are described in the succeeding sections.

II. CONCLUSIONS

The studies indicate that uranium(IV) can be used satisfactorily as plutonium reductant in the Purex plant partitioning

DECLASSIFIED

column (LBX-LBS concatenated columns). A flowsheet was developed and proposed for use in a plant production test. The major innovation in this flowsheet is the introduction of the uranium(IV) in a solvent stream instead of as an aqueous stream.

III. FLOWSHEET CONSIDERATIONS

The Hanford Atomic Products Operation Purex LB column is, in reality, two concatenated columns locally designated the LBX column and the LBS column. For purposes of discussion, the two columns can be considered a single compound LB column in which the Purex LBX column functions as the extraction section and the LBS column functions as the scrub section. Figure 1 shows the present LB or partition column flowsheet in solid lines. Present Purex nomenclature for the various entering and leaving streams is used.

The feed stream to the LB column (LBF) is Hanford Purex process solvent (30 v/o TBP in Soltrol) containing uranium, plutonium, and trace amounts of impurities. The extractant or partitioning agent (a ferrous sulfamate-sulfamic acid solution) enters the top of the LBX column as the LBX stream. The LBXP-HNO₃ stream is not necessary for operation of the LB column. It is a plant stream containing a small amount of uranium; recovery of the uranium by adding the stream to the LBS column is convenient.

Modifications to the flowsheet, by HAPO Purex Process Engineering personnel, proposed to accommodate uranium(IV)-hydrazine instead of ferrous sulfamate-sulfamic acid as partitioning agent, are shown in dotted lines. Addition of the uranium(IV) as an aqueous stream above the LBX feed point is not possible in the existing

DECLASSIFIED

equipment; there is no feed point available. Addition of uranium(IV) as an aqueous stream at the existing feed point was considered not operable because uranium(IV) which followed the aqueous phase into the LBS column would be extracted into the solvent and not returned to the column until after a long residence time in the feed tank. The alternate chosen was, as indicated, to introduce the uranium(IV) in a combined aqueous and solvent stream with most of the uranium(IV) in the solvent.

Since the LBXF stream contains a small amount of nitrite and since nitrite oxidizes uranium(IV) rapidly, the modified flowsheet includes addition of hydrazine to the feed tank to destroy the nitrite. In the modified flowsheet, the solvent stream from the LBS column is added to the LBX feed tank instead of being routed back to the coextraction cycle.

The following sections describe laboratory studies made to evaluate the feasibility of the modified flowsheet.

IV. EXPERIMENTAL PROCEDURES AND DISCUSSION OF RESULTS

A. Uranium(IV)

1. Preparation

Uranium(IV) used in these studies was prepared from uranyl nitrate solution obtained from the HAPO Redox plant. In most cases, reduction of uranium(VI) to uranium(IV) was done with aluminum metal dust. In some cases, reduction was by sodium formaldehyde sulfoxalate⁽³⁾ or by formic acid catalyzed by platinum dispersed on alundum⁽⁴⁾. The method of preparing uranium(IV) has process significance

DECLASSIFIED

because, in the flowsheet proposed, the aqueous phase in which uranium(IV) is produced enters the extraction column.

2. Analysis

Uranium(IV) was determined by two procedures: (1) a direct spectrophotometric method⁽⁵⁾ and (2) a method in which uranium(IV) reduces iron(III) to iron(II) which is then measured⁽⁶⁾. The former procedure has a limit of detection of about 0.001M and requires correction for nitric acid concentration. The latter has a lower limit of less than 5×10^{-6} M and does not require correction for nitric acid. Both procedures were also used for analysis of uranium(IV) in 30% TBP-Soltrol solutions.

B. Liquid-liquid Contacting

1. Batch Contacting

Kinetic considerations were of primary importance in these studies and it was important to duplicate column conditions as closely as possible. Therefore, for the batch contacts, the phases were dispersed with a reciprocating plunger equipped with sieve-plates and operating at 60 cycles per minute. The apparatus was jacketed and controlled temperature was water-circulated through the jacket.

2. Continuous Counter Current Contacts

A miniature pulse column of the type devised by Koski⁽⁷⁾ was used to simulate the LBX column. A few runs were made, but were discontinued when it became apparent, as described later, that the organic phase residence time was too short to properly duplicate plant conditions.

DECLASSIFIED

C. Stability of Uranium(IV) in Solvent

One concern about the proposed flowsheet was the stability of uranium(IV) when extracted into solvent, since the solvent will have a finite residence time in the make-up tank (Tank J-2).

Tests were conducted to determine the rate of oxidation of uranium(IV) under conditions which will prevail in Tank J-2.

These data, presented in Table I, show that the residence time in Tank J-2 can be at least seven hours and considerably longer if good quality solvent is used. Other conclusions which may be drawn from these data are as follows:

1. About 30 per cent of the uranium(IV) was oxidized almost immediately on contact with solvent.
2. Oxidation of uranium(IV) was less rapid when it had been prepared by the de Leone process than when it had been prepared with aluminum as the reductant. Residual reducing capacity in the aqueous phase probably accounts for the difference noted.
3. Oxidation of uranium(IV) was less rapid when the solvent used had been washed recently with carbonate solution.
4. Blanketing the mixture with nitrogen did not decrease the rate of oxidation of uranium(IV) as compared to an air blanket. Removing the aqueous phase after the uranium(IV) was extracted into the solvent did not reduce the uranium(IV) oxidation rate.

D. Reduction of Plutonium in the LBX Column

The reduction of plutonium(IV) to plutonium(III) by uranium(IV) is rapid and only a small excess of uranium(IV) is normally required to attain complete reduction of plutonium. ()

DECLASSIFIED

The following batch contact experiments were performed to compare the effectiveness of uranium(IV) and ferrous sulfate (FS) as partitioning agents under LBX column operating conditions. Equal volumes of synthetic LBX column feed solution ($0.21M$ HNO_3 - $0.32M$ $UO_2(NO_3)_2$ - plutonium(IV) in 30% TBP-Soltrol) and LBX extractant solution were contacted in the reciprocating contactor. Plutonium distribution ratios were determined after two and ten minutes contact time. All contacts were made at a temperature of $45^\circ C$ which is considered to be the average plant operating temperature. Data obtained are shown in Table II.

That uranium(IV) was at least as effective as iron(II) as a plutonium reductant is apparent from the low plutonium distribution ratios obtained. When iron(II) and uranium(IV) were present at the same concentration, lower plutonium distribution ratios were obtained with uranium(IV) as reductant. In the proposed flowsheet for use in the Purex plant, initial uranium(IV) concentration in the LBX column solvent is $0.0013M$. In the experiments summarized in Table II, the lowest initial uranium(IV) concentration in the solvent was 0.0012 (assuming a $U(IV)$ E° of 1.4). At this concentration the plutonium distribution ratio was comparable to that obtained with ferrous sulfate and low enough to ensure adequate separation of plutonium from uranium. It should be noted that the tests shown in Table II were made under conditions expected in the bottom of the LBX column where salting strength in the aqueous phase due to

DECLASSIFIED

uranyl nitrate and nitric acid is relatively high. Higher in the column, the aqueous phase contains less nitric acid and uranyl nitrate. Plutonium (either (III) or (IV)) extraction should be even less there.

E. Stability of Uranium(IV) in the LBX Column

Residence time of the organic phase in the LBX column is estimated as about 15 minutes. The data given in Table II and Table (IV) indicate that, in the absence of oxidants other than plutonium(IV) in the organic phase, uranium(IV) is adequately stable under LBX conditions to insure its presence throughout the LBX column. In the current Purex process flowsheet, the LBXF contains a small concentration of nitrous acid (see Figure 1). Nitrous acid will oxidize uranium(IV) rapidly. For this reason, it is recommended that sufficient hydrazine be added to the LBXF feed tank to assure the feed is free of nitrous acid.

F. Plutonium Reflux in the LBS Column

In the present Purex plant flowsheet, plutonium is maintained in the trivalent state in the LBS column by ferrous ion in the aqueous phase. Concentration of ferrous ion is about $0.015M$. In the proposed uranium(IV) flowsheet, the concentration of reductant (U(IV)) will be much lower -- about $0.001M$ at the top and as low as $10^{-5}M$ at the bottom. If plutonium is re-oxidized and re-extracted under these conditions, reflux will occur. Excessive reflux could overload the reducing capacity in the LBX column and allow plutonium to go overhead in the uranium

DECLASSIFIED

stream. Batch contact experiments were made to determine the rate of re-oxidation of plutonium under LBS column conditions. These are summarized in Table IV. They show that, even in the absence of any uranium(IV), oxidation and re-extraction of plutonium is relatively slow. Residence time of the aqueous phase in the LBS column is estimated at 20 minutes. These experiments were made at plutonium concentrations less than anticipated under process conditions. However, the data indicate that the rate at which plutonium(III) is oxidized in the two-phase system has a less than first order dependency on the plutonium concentration in the aqueous phase. Hence, even lower plutonium distribution ratios would be expected under actual operating conditions. It is estimated that, with plutonium E_a^0 values of 0.1 or less, plutonium reflux in the LBS column will not be significantly greater than that which occurs in the present process (ca 10 per cent) with ferrous sulfamate as reducing and holding agent.

G. Uranium contamination in Product Plutonium

Under the proposed flowsheet, the aqueous stream entering the top of the LBS column should contain about 0.001M uranium(IV). To permit estimation of the amount of uranium which could leave the LBS column in the product plutonium stream, distribution ratios for uranium(IV) under LBS column conditions were determined. These are shown in Table V. Uranium(IV) distribution ratios remained essentially constant over an equilibrium aqueous phase concentration range of from 0.0003 to 0.015M. Oxidation of uranium(IV) to uranium(VI) is relatively slow, less than 50 per cent in two

DECLASSIFIED

hours. Since the LBS column conditions do not change appreciably after most of the uranium(VI) is removed in the top stages, the uranium(IV) distribution ratios shown in Table V can be considered to apply over most of the LBS column. If there are four theoretical stages in the column, the maximum uranium concentration expected in the product plutonium stream is about $5 \times 10^{-5}M$ when the nitric acid concentration is $4M$. If addition of the LBXP- HNO_3 stream was discontinued and the LBS aqueous stream was, consequently, two molar in nitric acid, the maximum uranium concentration in the product plutonium stream would be about $1.5 \times 10^{-4}M$. These values are approximations only and neglect the more complete extraction of any uranium oxidized to uranium(VI).

H. Continuous Counter Current Contacts

The results of several experiments in which simulation of the extraction section of the LB column (LBX) with a miniature pulsed column was attempted are given in Table III. In three runs, uranium(IV)-hydrazine was used as partitioning agent and in three others, ferrous sulfamate-sulfamic acid was used. High plutonium losses (about 10 per cent) occurred in all runs. The losses were about the same in all cases except Run 3. Emulsion formation caused unstable column performance in this run. Since the losses were independent of such variables as LBX flow, mole ratio of plutonium to reducing agent and the reducing agent, it was concluded that the rate of transfer of plutonium to the organic phase was limiting. Residence time of the organic phase in the dispersed portion of the column was only 10-15 seconds. To increase the organic

DECLASSIFIED

residence time appreciably would have required an impractical lengthening of the column. Consequently no further work was done with the miniature pulsed column.

IV. SUMMARY

A flowsheet for a plant production test of uranium(IV)-hydrazine instead of ferrous sulfamate-sulfamic acid as partitioning agent in the HAPU Purex partition column is proposed. An aqueous stream containing uranium(IV) is contacted with Purex solvent and both phases are introduced into the LBX column at the feed point. Hydrazine is added to the LBX column feed accumulation tank to destroy nitrite present in the organic feed stream. A hydrazine-nitric acid stream is introduced at the top of the LBX column instead of the usual ferrous sulfamate-sulfamic acid stream. The solvent phase leaving the LBS column is routed to the LBX feed tank instead of to the codecontamination cycle. Otherwise, the stream compositions and flows remain as at present.

The laboratory studies reported herein indicate that satisfactory operation of the LB column should be obtained with the proposed flow sheet. Uranium(IV) was shown to be adequately stable in Purex solvent to allow reasonable hold-up time in the vessel in which the feed stream is made up. Plutonium reduction is sufficiently rapid and complete under LBX extraction conditions to assure adequate separation of plutonium from the product uranium stream. Although some re-oxidation and re-extraction of plutonium in the LBS column (scrub section) is anticipated, the results indicate that the plutonium reflux will be no greater than occurs with the present flowsheet. Extraction of uranium(IV) in the LBS column should be adequate to insure acceptably

DECLASSIFIED

[REDACTED]

low uranium in the product plutonium stream, particularly if high acidity (HNO_3) is maintained through addition of the LBMP- HNO_3 stream.

DECLASSIFIED
[REDACTED]

TABLE I

URANIUM(IV) STABILITY IN 30% TBP-SOLVENT OF (3) AT 25°C

Run	Method of U(IV) Preparation	Per Cent theo. Approx. 5 min.	U(IV) Remaining (1)			
			1 Hours	2 Hours	5 Hours	24 Hours
1	Organic separated from Initial Aqueous, Air sparged (2)	62.5	69.1	73.1	65.5	57.4 12.1
5	" " " "	75.2	--	56.3	61.6	-- 28.7
9	" " " "	56.2	--	35.8	33.3	-- 11.1
2	Organic in contact with Initial Aqueous, Air sparged	73.4	74.5	75.7	83.0	81.8 5.3
6	" " " "	64.2	--	44.9	36.5	-- 0.0
10	" " " "	82.1	--	84.4	84.8	-- 103.4
3	Organic Separated from Initial Aqueous, N ₂ sparged (2)	80.1	68.9	68.4	66.4	61.5 20.0
7	" " " "	65.5	--	46.6	20.9	-- 0.0
11	" " " "	79.5	--	85.1	82.5	-- 84.8
4	Organic in contact with Initial Aqueous, N ₂ Sparged	69.8	--	60.6	67.2	-- 0.0
8	" " " "	56.3	--	59.8	25.9	-- 0.0
12	" " " "	79.3	--	85.5	94.5	-- 108.6
13	Organic in contact with Initial Aqueous, Air sparged	67.3	--	76.7	68.6	-- 61.5
14	" " " "	106.4	--	88.6	103.2	-- 0.7
15	" " " "	72.3	--	49.0	35.2	-- 0.6

(1) Theoretical initial concentrations were 0.023, 0.026, and 0.025M, for runs with DeLeone, Al-reduced, and Discolite, prepared U(IV), respectively.

(2) Spurge rate = 200 ml/min.

(3) 30% 30% TBP-Solvent was laboratory carbonate-washed and allowed to stand about 2 months, Run 1 through 9; laboratory carbonate - washed and used immediately, Runs 10 through 14, and Puron R-7 (aged 2 months), Run 15.

DECLASSIFIED

TABLE IV

LBK COLUMN BATCH CONTACTS

<u>HNO₃</u>	<u>Initial Aqueous Phase</u>			<u>Platinum</u>	
	<u>UNH</u>	<u>Reducing Agent</u>	<u>Holding Reductant</u>	<u>2 min.</u>	<u>10 min.</u>
2.0M	0.12M	None	None	1.91	1.56
"	"	0.02M FS	0.03M SA	0.016	0.010
"	"	0.02M FS	"	0.025	0.095
"	"	0.02M U(IV) ⁽¹⁾	0.02M N ₂ H ₄	0.009	0.009
"	"	0.003M U(IV)	"	0.003	0.012
"	"	0.002M U(IV)	"	0.023	0.014

(1) Uranium(IV) prepared by reduction of UNH with aluminum powder.

DECLASSIFIED

TABLE III

LBX COLUMN DEMONSTRATION RUNS IN MINIATURE PULSE COLUMN

	Run 1 ⁽¹⁾	Run 2	Run 3	Run 4	Run 5	Run 6
Flows, ml/min.						
LBKF	1.27	1.0	1.0	2.02	1.55	1.58
LBK	0.052	0.060	0.039	0.137	0.474	0.388
U(IV)	0.076	--	0.058	--	--	0.574
LBKF Composition, M						
Pu	2.62-4	2.42-4	3.14-5	3.22-4	1.97-4	1.97-4
U	0.336	0.347	0.32	0.311	0.328	0.32
HNO ₃	0.25	0.331	0.337	0.097	0.22	0.161
LBK Composition, M						
Fe(NH ₂ SO ₃) ₂	--	00.03	--	0.03	0.03	--
N ₂ H ₄	0.02	--	0.05	--	--	0.05
HNO ₃	0.30	0.50	0.30	0.50	1.0	1.0
U(IV) Composition, M (in 30% TBP-Soltrol)						
U(IV)	0.023	--	0.031	--	--	0.029
Total U	0.068	--	0.078	--	--	0.076
Mole Ratio, Reductant/Plutonium	4.6	7.4	55.4	6.3	46.5	53.6
Plutonium Material Balance, Per Cent ⁽²⁾	28.7	93.2	170	90	99.4	103
Plutonium Loss to LEU, Per Cent	8.4	9.5	23.2 ⁽³⁾	10.7	9.4	9.1

(1) Runs 1, 2, and 3 made in 0.23 in. dia. column, Runs 4, 5, and 6 in 0.268 in. dia. column.

(2) Poor material balance in Run 1 due to plutonium loss to aqueous in pulse leg, in Run 3 due to back-transfer of plutonium out of aqueous in pulse leg.

(3) Column very severely emulsified, even when pulse amplitude increased, and pulse frequency lowered.

DECLASSIFIED

TABLE IV

1BS COLUMN BATCH CONTACTS

Procedure: Equal volumes, contacted at 45 C, using reciprocating sieve plate agitation (40 strokes/min.). Phases re equilibrated (without plutonium) and preheated before adding plutonium(III). (Stock plutonium(III) prepared by reduction with Al metal, contacted with 0.2M D2EHPA-Solntrol prior to each use to remove any Pu(IV) present).

Results:

<u>Initial Aqueous Phase Composition</u>			<u>Total Pu, Distribution Ratio</u>		
<u>HNO₃</u>	<u>N₂H₄</u>	<u>Pu(III)</u>	<u>10 min.</u>	<u>30 min.</u>	<u>90 min.</u>
2.0 M	0.02M	7.65x10 ⁸ c/m/gal	0.40	Insuf. Spl.	1.6
"	"	3.61 x 10 ⁹	0.11	0.58	
"	"	7.87 x 10 ⁹	0.068	0.19	0.36
"	"	2.38 x 10 ¹⁰	0.038	0.10	0.22
"	"	3.27 x 10 ¹⁰	0.062	0.11	0.21
1.0M	0.02M	3.85 ⁹	0.33	1.15	6.25

DECLASSIFIED

TABLE V

URANIUM(IV) DISTRIBUTION RATIOS AT 45 C

<u>HNO₃ in</u> <u>Aqueous Phase</u>	<u>Contact</u> <u>Time</u>	<u>Uranium(IV) (1)M</u>		<u>U(IV)</u> <u>E₀</u>	<u>% Initial</u> <u>U(IV) Remaining</u>
<u>Aqueous</u>	<u>Phase</u>	<u>Aqueous</u>	<u>Organic</u>		
2.0M	10 min.	0.0162	0.0224	1.38	91.5
"	40	0.0148	0.0202	1.36	82.5
"	120	0.0097	0.0140	1.44	56.2
4.0	10	0.015	0.039	2.60	102.2
"	10	0.0056	0.016	2.86	102.2
"	10	0.001	0.003	3.00	94.7
"	10	0.0003	0.0006	2.00	85.7

DECLASSIFIED

V. REFERENCES

- (1) DP-308, "Uranium(IV) Nitrate as a Reducing Agent for Plutonium(IV) in the Purex Process," C. S. Schlea, M. R. Caverly, H. E. Henry, W. J. Kenkins, April, 1963.
- (2) AERE R-4381, "Mixer-Settler Runs to Study Uranium(IV) as a Reductant in Uranium/Plutonium Separation." H. A. C. McKay, R. J. W. Streeton, A. G. Main,
- (3) NP 12121, The Possibility of Using "Rongalit" as Reducing Agent for Preparing U(IV) Nitrate and Reducing Pu(IV) to Pu(III) in the Reprocessing Plant, T. Erben, 2-17-61.
- (4) Studies of Uranium(IV) Nitrate, R. DeLeone, G. Cogliate, L. Lowenzine, and R. Lanz, Presented at Third Nuclear Chemistry Conference, Gatlinberg, Tennessee, October 11, 1962.
- (5) DP-578, "Colorimetric Determination of Uranium(IV)," R. S. Dorsett, May 1961.
- (6) AERE-R-3938, "The Preparation, Stabilization and Analysis of Uranium(IV) Nitrate Solutions." R. J. W. Streeton and E. H. Jenkins. February, 1962.
- (7) HW-39938, "Invention Description: Devices for Improving the Efficiency of Separation in Pulsed Liquid-Liquid Extraction Columns," O. H. Koski, 11-15-55.
- (8) Rydberg, J., "The Reduction of Plutonium by Tetravalent Uranium," J. Inorg. Nucl. Chem. 5, 79-86 (1957).

DECLASSIFIED

1000000000

1000000000
1000000000
1000000000
1000000000

1000000000
1000000000
1000000000
1000000000

1000000000

1000000000
1000000000
1000000000
1000000000

1000000000
1000000000
1000000000
1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

1000000000

FIGURE 1
PARTITION CYCLE FLOW SHEET

DECLASSIFIED