URANIUM(IV) NITRATE AS A REDUCING AGENT
FOR PLUTONIUM(IV) IN THE PUREX PROCESS

by

Carl S. Schlea
Myron R. Caverly   Hugh E. Henry
William J. Jenkins

Approved by

C. H. Ice, Research Manager
Separations Chemistry Division

April 1963

DISCLAIMER

DISCLAIMER

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

ABSTRACT

Practical procedures were demonstrated for partitioning plutonium from uranium in the Purex process with hydrazine-stabilized uranium(IV) nitrate as the reducing reagent for plutonium. Typical partitioning results were 0.04-0.2% loss of plutonium to the uranium product and less than 1 wt % uranium in the plutonium product. With uranium(IV) nitrate as a replacement for ferrous sulfamate, most solids in wastes from the Purex process can be eliminated. No undue hazard is expected from the use of hydrazine as the stabilizing agent.

CONTENTS

LIST OF TABLES AND FIGURES

URANIUM(IV) NITRATE AS A REDUCING AGENT
FOR PLUTONIUM(IV) IN THE PUREX PROCESS

INTRODUCTION

The recovery and purification of plutonium from irradiated natural uranium by the Purex process involves first coextracting Pu(IV) and U(VI) from nitric acid into diluted tri-n-butyl phosphate (TBP) and then selectively partitioning plutonium into an aqueous stream by reducing the Pu(IV) to Pu(III). The most commonly used reductant is ferrous sulfamate, $Fe(SO_3NH_2)_2$, which is effective because Fe(II) rapidly reduces Pu(IV) to Pu(III), and because the sulfamate ion stabilizes Pu(III). Ferrous sulfamate has the disadvantage of introducing nonvolatile constituents, iron and sulfate, into the process wastes. These constituents increase the volume of radioactive wastes to be stored and may accelerate the corrosion of evaporators.

The disadvantages of ferrous sulfamate were recognized early in the development of the Purex process. Attempts to use U(IV) as the reductant began at Chalk River. Since then, uranium(IV) sulfate has been successfully used in the French adaptation of the Purex process[1], and the use of U(IV) has also been studied at Harwell[2,3]. The advantage of U(IV) is that it introduces no nonvolatile or corrosive constituents into the process.

Uranium nitrate can act as an effective reducing agent only if it is stabilized by a chemical, such as hydrazine, which will rapidly and completely destroy the nitrous acid that accompanies Pu(IV) in the organic product stream from the first coextraction contactor. If the nitrous acid is not completely destroyed, it will reoxidize Pu(III) to Pu(IV). Since both the hydrazine and the uranium(IV) are introduced simultaneously into the partitioning contactor, the destruction of nitrite must be very rapid to prevent excessive consumptions of U(IV). Hydrazine is particularly advantageous since the reaction products, N_2, N_2O, and H_2O, do not contribute to the volume of stored wastes.

SUMMARY

Procedures for partitioning plutonium from uranium in the Purex process with hydrazine-stabilized uranium(IV) nitrate as the reducing reagent for plutonium were developed, and practical applications of the procedures were demonstrated. Typical partition results were 0.04-0.2% Pu loss to the uranium product and less than 1 wt % U in the plutonium product.

The flowsheet for partitioning with uranium(IV) nitrate is a substitute for the original flowsheet with ferrous sulfamate as the reducing reagent. In the original Purex flowsheet ferrous sulfamate was converted to ferric sulfate, which is a solid in waste storage tanks. With the revised flowsheet U(IV) is converted to U(VI), which is extracted by the organic stream, and hydrazine is converted to gaseous products by reaction with nitrite normally present in the process. Hydrazine-stabilized uranium(IV) nitrate is added as a side stream near the center of the partitioning contactor. This stream also contains enough nitric acid to provide salting strength for the extraction of U(IV) by the organic stream, thereby preventing gross contamination of the plutonium product with unreacted U(IV). The U(IV) follows the route of the U(VI). Hydrazine is also added to the usual aqueous extractant stream to react with the nitrite in the system.

The minimum quantity of U(IV) that gave adequate partitioning in miniature mixer-settlers was three times the molecular equivalent of Pu(IV). The major variable affecting removal of plutonium from the uranium product was the degree of agitation in the contactors. The major variable affecting the amount of uranium in the plutonium product was the salting strength in the aqueous phase of the partitioning contactor. Partitioning in a centrifugal extractor,[4] in which residence times are lower by a factor of forty than in a conventional pump-mix mixer-settler, was similar to partitioning in a mixer-settler and indicates that the rate process is controlled by mass transfer.

Dilute solutions of hydrazoic acid, HN_3, are generated by the chemical reaction between hydrazine and nitrous acid. With the dilute solutions of hydrazine used (less than 0.2M N_2H_4), hydrazoic acid does not reach hazardous concentrations in the process.
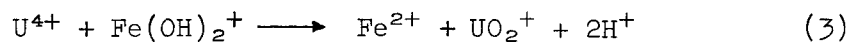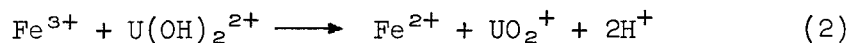
DISCUSSION

CHEMISTRY OF U(IV)

OXIDATION-REDUCTION

The U(IV)-U(V) and U(IV)-U(VI) oxidation potentials (E_f^o) are -0.58 v and -0.33 v, respectively. Neither of the electrodes is thermodynamically reversible, and the half-cell reaction

$$U^{4+} + 2H_2O \longrightarrow UO_2^{2+} + 4H^+ + 2e^- \qquad (1)$$
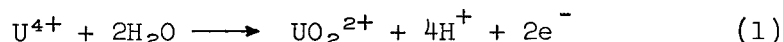
illustrates the stabilizing effect that hydrogen ion has for U(IV). Reduction of metal ions by U(IV) is believed to take place through hydrolyzed ions, which allow electron transfers in a single collision. An example is the reduction of Fe^{3+} by U(IV),[5] for which the following mechanisms were demonstrated:

$$Fe^{3+} + U(OH)_2^{2+} \longrightarrow Fe^{2+} + UO_2^+ + 2H^+ \qquad (2)$$

$$U^{4+} + Fe(OH)_2^+ \longrightarrow Fe^{2+} + UO_2^+ + 2H^+ \qquad (3)$$

The few U(IV) reductions studied and a study of U(IV)-U(V)-U(VI) exchange[6] infer that many reductions by U(IV) proceed through the $U(OH)^{3+}$ ion, and thus the reaction rates are faster at low acid concentrations. Depending on whether a one-electron or two-electron reaction is involved, the primary oxidized species may be either UO_2^+ or UO_2^{2+}; if UO_2^+ is produced, it disproportionates rapidly to U^{4+} and UO_2^{2+}.

The reaction of Pu(IV) with U(IV) has been investigated only slightly. Reduction of Pu(IV) by U(IV) is very fast in 1-2M acid solutions.[7]

The stability of U(IV) toward air oxidation has been investigated in both TBP[8] and aqueous solutions[9,10]. The reaction in TBP was found to be quite slow (a half-time of several days). Oxidation by oxygen in perchloric acid solutions follows the relation[9]:
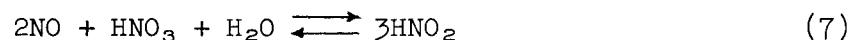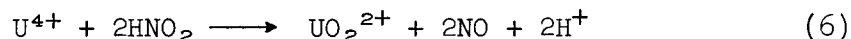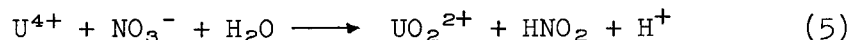
$$- \frac{d[U(IV)]}{dt} = \frac{k[U(IV)][O_2]}{[H^+]} \qquad (4)$$

where $k = 10^{-3}$ sec^{-1} in 1M HClO$_4$. In 1M HNO$_3$, the half-time is about 1 hour in an oxygen-sparged solution, and about one month in a static system with only diffusion to transfer oxygen through the solution. The stability toward air

oxidation varies with the acidity and degree of contact with air; increased stability is achieved with higher acid concentrations and with minimum exposure to air.

In nitrate solutions, $U(IV)$ is unstable toward HNO_2-catalyzed oxidation by HNO_3.[8] The reactions are

$$U^{4+} + NO_3^- + H_2O \longrightarrow UO_2^{2+} + HNO_2 + H^+ \qquad (5)$$

$$U^{4+} + 2HNO_2 \longrightarrow UO_2^{2+} + 2NO + 2H^+ \qquad (6)$$

$$2NO + HNO_3 + H_2O \underset{\longleftarrow}{\longrightarrow} 3HNO_2 \qquad (7)$$

Reaction 5, the net reaction for the oxidation, is chiefly important as a means of producing HNO_2. Once sufficient HNO_2 is produced, $U(IV)$ is oxidized via reaction 6, and the NO produced by reaction 6 produces more HNO_2 (reaction 7). Since 1.5 mols of HNO_2 are produced for each mol of HNO_2 consumed, the reaction proceeds faster as the HNO_2 concentration increases and is autocatalytic. The reaction rate is proportional to the first power of the $U(IV)$ concentration and to the square root of the HNO_2 concentration; the rate is independent of HNO_3 concentrations from 0.8 to 3.7M.[8,9] Oxidation in 30% TBP - "Ultrasene"*[8] is slower than in aqueous solutions.

Oxidation of $U(IV)$ in nitric acid solution can be decreased to a very low rate by adding a stabilizing agent. A stabilizing agent reacts with HNO_2 and prevents oxidation by the autocatalytic mechanism mentioned previously. Hydrazine, sulfamate ion, and urea have been used; of these reagents, hydrazine is most effective.[3] Ondrejcin[11] found the average oxidation of $U(IV)$ was about 0.5% a day from solutions that originally contained 0.1-0.2M $U(IV)$, 0.5-1M HNO_3, and 0.1-0.2M N_2H_4. The oxidation was linear over a 90-day period and more rapid on exposure to light. The decrease in hydrazine concentration was about 0.05M per month. Long-term storage of uranium(IV) nitrate solutions required periodic additions of hydrazine to maintain an effective concentration of stabilizer.

SOLVENT EXTRACTION

Like other quadrivalent actinides, uranium(IV) nitrate is extracted by TBP. The extraction reaction is

$$U^{4+}_{aq} + 4NO_3^-{}_{aq} + 2TBP_{org} \underset{\longleftarrow}{\longrightarrow} U(NO_3)_4(TBP)_2{}_{org} \qquad (8)$$

---
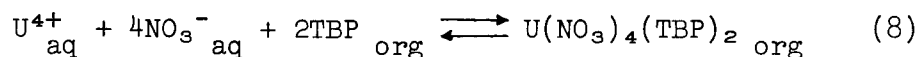
*A refined kerosene product of Atlantic Refining Co.

The increase in U(IV) extraction with increasing acidity is shown in Figure 1. U(IV) is about as extractable as Th(IV), is about one-fifth as extractable as Pu(IV), and one-tenth as extractable as U(VI). As a result of the lower degree of extraction of U(IV) relative to U(VI), the presence of large quantities of U(VI), such as in the partitioning contactor of the Purex process, would decrease the extraction of U(IV) considerably.
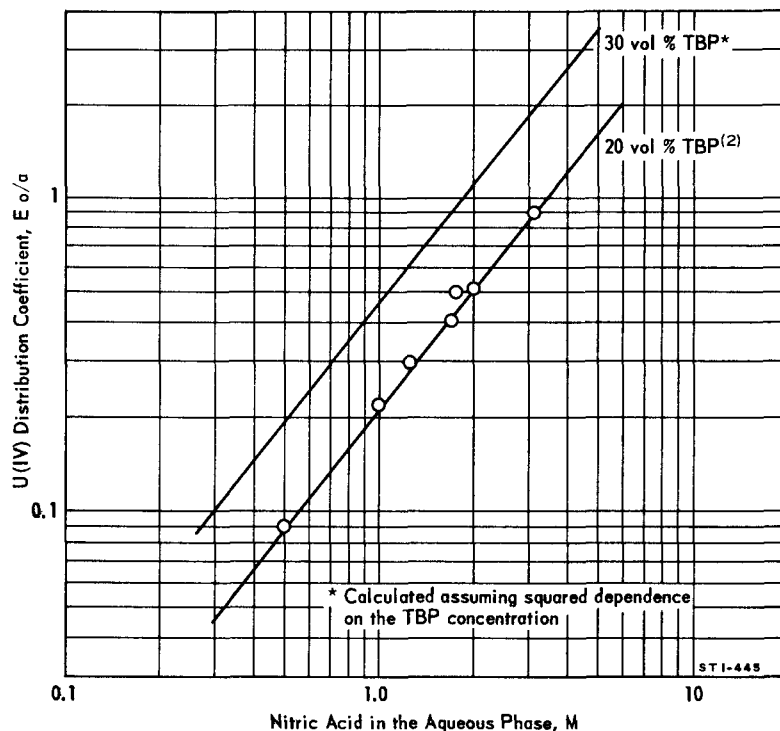
FIG. 1 EXTRACTION OF URANIUM (IV) NITRATE BY TBP

COMPLEXES AND HYDROLYSIS

Only limited investigations have been made of the complex ions formed by U(IV); in general, complexes would be expected with anions that are complexing agents for other quadrivalent actinides. Relatively strong complexes with sulfate, phosphate, oxalate, and fluoride are predicted and would decrease the extraction of uranium(IV) nitrate by TBP.

Studies of the hydrolysis of U(IV) have not been as extensive as studies of other quadrivalent ions, but they do indicate that the U^{4+} ion is predominant in noncomplexing acidic solutions. The hydrolysis behavior of U(IV) resembles that of Pu(IV); the equilibrium constant for the reaction

$$U^{4+} + H_2O \rightleftharpoons U(OH)^{3+} + H^+ \qquad (9)$$
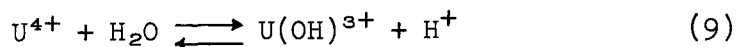
is about 0.21, and for the same reaction of Pu(IV), K = 0.18 (zero ionic strength).[12] U(IV) will probably polymerize in weakly acidic solutions in the same manner as Pu(IV).

DESCRIPTION OF THE PROCESS FLOWSHEET

The Purex solvent extraction flowsheet with uranium(IV) nitrate as the plutonium reductant is shown in Figure 2. There are four input streams and two output streams associated with the partitioning contactor (1B bank). The organic product (1AP) of the coextraction contactor (1A bank) is introduced near the center of the partitioning contactor. The aqueous extractant (1BX), which contains hydrazine, is introduced at the end of the extraction section and flows countercurrent to the organic stream. The organic scrub (1BS) is introduced at the end of the scrub section and removes uranium from the aqueous stream containing the plutonium product (1BP). Uranium(IV) nitrate is introduced in a side stream (1BX') near the center of the contactor, is extracted by the organic scrub, refluxes in the extraction section of the contactor where it reduces Pu(IV) to Pu(III), and finally accompanies the uranium product (1BU). Excess hydrazine in the plutonium product (1BP) is destroyed by nitrite, which is normally added to oxidize Pu(III) to Pu(IV) as a part of subsequent processing operations.
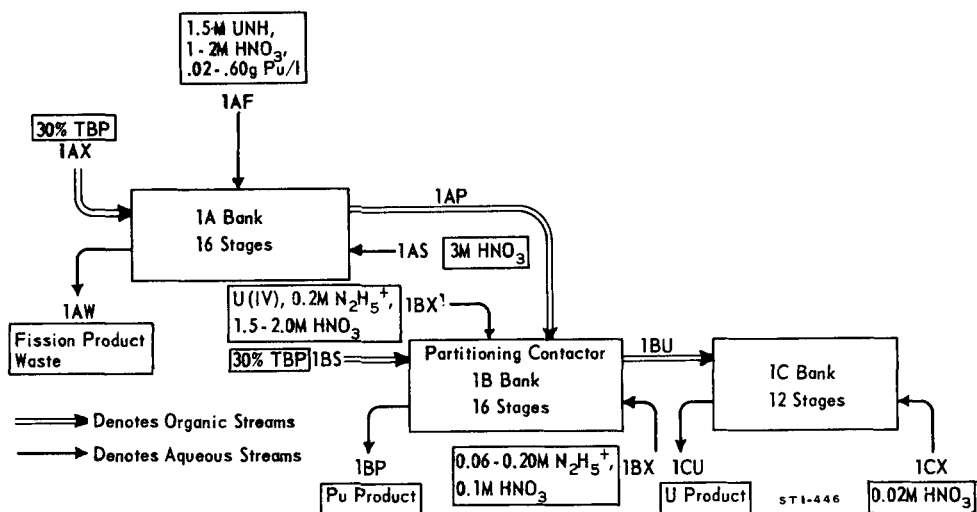

FIG. 2 SOLVENT EXTRACTION FLOWSHEET

The major change in the operation, as a result of substituting uranium(IV) nitrate for ferrous sulfamate, is the place of introducing the reducing reagent. In the original flowsheet the inextractable ferrous sulfamate is introduced in the 1BX stream at the end of the extraction section; excess ferrous

sulfamate, as well as ferric sulfate formed as a result of plutonium reduction and nitrate destruction, leaves the contactor in the plutonium product (1BP) stream. In the revised flowsheet hydrazine-stabilized U(IV) is introduced near the center of the contactor as a side stream; formation of ferric sulfate, which ultimately contributed to the solids in waste storage tanks, is eliminated.

The equivalents of U(IV) and hydrazine required for adequate partitioning are equal to the chemical equivalents of Fe^{2+} and $SO_3NH_2^-$ ions, respectively, that were required in the original flowsheet. One mol of U(IV) is equivalent to two mols of Fe^{2+}, and one mol of hydrazine is equivalent to two moles of $SO_3NH_2^-$. In practice, the consumption of U(IV) and hydrazine will vary with the irradiation level of the fuel that is processed and with the concentration of radiolytically generated HNO_2. A typical concentration in the 1BX stream is 0.04M $Fe(SO_3NH_2)_2$; the corresponding quantities are 0.04M N_2H_4 in the 1BX stream and a U(IV) concentration in the 1BX' stream of 0.02M times the 1BX/1BX' flow ratio.

Adequate extraction of U(IV) in the scrub section of the 1B bank is required to prevent excessive uranium in the plutonium product stream. The requisite extraction is obtained by (1) adding nitric acid in the 1BX' so that the distribution coefficient of U(IV) is high in the scrub section of the bank and (2) adjusting the organic-to-aqueous flow ratio. If nitric acid is not added to the 1BX', the nitric acid concentration in 1BP will be about 0.6M, which is too low for extraction of uranium from the plutonium product. However, when the 1BP acid concentration is increased to 1.2-1.5M by adding nitric acid in the 1BX', an insignificant amount of uranium remains with the plutonium.

Hydrazine in the 1BP stream must be destroyed before reoxidation of Pu(III) to Pu(IV) for second-cycle solvent extraction processing. The normal valence adjustment in the Purex process involves oxidation of Pu(III) and ferrous sulfamate with sodium nitrite; this treatment is also effective for oxidation of Pu(III) and hydrazine. The destruction of hydrazine by nitrous acid is a two-step reaction[13]:

$$N_2H_5^+ + HNO_2 \longrightarrow HN_3 + 2H_2O + H^+ \qquad (10)$$

$$HN_3 + HNO_2 \longrightarrow N_2O + N_2 + H_2O \qquad (11)$$
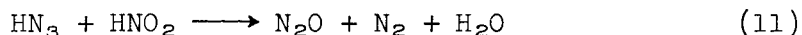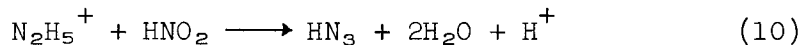
Both reactions are too fast for rate measurements, and total destruction of both $N_2H_5^+$ and HN_3 occurs before Pu(III) is completely oxidized.

TESTS OF THE PROCESS FLOWSHEET

Laboratory tests with miniature mixer-settlers[14] and miniature centrifugal extractors[15] showed that uranium(IV) nitrate stabilized by hydrazine is a satisfactory reductant. Typical results showed 0.04-0.2% Pu loss to the uranium product (1CU) and less than 1 wt % U in the plutonium product (10^{-5} to 10^{-7}M U in the 1BP). A major variable in the operation of the 1B bank was the amount of agitation in the two-phase system; inadequate agitation resulted in high plutonium concentrations in the 1CU. The residence time in the partitioning contactor was not important as shown by equivalent partitioning with centrifugal extractors in which the residence times of process solutions are lower than in mixer-settlers by a factor of forty.

Tests of U(IV) as a partitioning agent were made with miniature mixer-settlers[14] or miniature centrifugal extractors[15] connected as in the Purex first cycle (Figure 2). The flowsheet is given in Table I.

TABLE I

Purex Flowsheet

Stream	Relative Flow	Enters Process at Stage	Composition
1AF	100	A-8	1.5M UNH, 1-2M HNO_3, 0.02-0.60 g Pu/l
1AS	67	A-1	3M HNO_3
1AX	380-400	A-16	30% TBP[b]
1BX	50	B-1	0.06-0.20M $N_2H_5^+$, 0.1M HNO_3
1BX'	20	B-7 or B-9[a]	U(IV), 0.2M $N_2H_5^+$, 1.5-2.0M HNO_3
1BS	160	B-16	30% TBP[b]
1CX	610	C-1	0.02M HNO_3

(a) Concentration of U(IV) and point of introduction into the 1B bank were varied during tests.

(b) Both "Ultrasene" and "Adakane 12" diluents were used. "Adakane 12" is a product of Archer-Daniels-Midland Co.

Tests were made with feed solutions prepared by dissolving irradiated natural uranium fuel elements in nitric acid, clarifying the solution with either gelatin or MnO_2 precipitation, and adjusting the clarified solution to proper concentrations with water or nitric acid. Additional tests were made with simulated feed solutions prepared by mixing uranyl nitrate, nitric acid, plutonium, and water. The results of all tests are shown in Table II.

TABLE II

Tests with Uranium(IV) Nitrate as Reductant

Test	Pu in 1AF, g/l	U(IV) Feed Stage	U(IV) Consumption U(IV)/U(VI)	U(IV)/Pu	Pu to 1CU, %	U in 1BP, M
1	0.6	B-9	0.021	12.8	0.04[a]	6×10^{-7}
2	0.6	B-9	0.005	3.2	0.04[a]	9.5×10^{-6}
3	0.6	B-9	0.0018	1.1	10[a]	9.1×10^{-6}
4	0.24	B-9	0.016	23.9	9[b]	1.3×10^{-5}
5	0.02	B-9	0.0125	260	0.2	3.4×10^{-7}
6	0.02	B-9	0.0125	260	1.1[c]	
7	0.02	B-7	0.0125	260	0.17	4×10^{-7}
8	0.02	B-7	0.025	520	0.17	
9	0.6	B-1	0.007	4.5	20	
10[d]	0.55	B-9	0.006	3.7	0.02	

(a) The 1BX stream for these tests was 0.05M acid deficient.
(b) Mixing intensity was low (decreased impeller speeds).
(c) The 1BX stream for this test did not contain hydrazine.
(d) With miniature centrifugal extractors; all other tests with
    miniature mixer-settlers.

Partitioning was most effective when U(IV) was introduced
adjacent to the point of introduction of the organic product
stream (1AP) from the 1A bank, and when hydrazine was added
to the normal 1BX stream. Under these conditions, partitioning
was excellent with as little as 3 mols U(IV) per mol of Pu(IV)
(Tests 2 and 10). Only 0.04% of the total plutonium was lost
to the 1CU stream, and only 10^{-5}M U was present in the 1BP
stream, corresponding to 0.25 wt % U in the plutonium product.
The amount of U(IV) was equivalent to 0.5 to 2% of the total
uranium throughput.

Other tests demonstrated that hydrazine was necessary
in both the 1BX and 1BX', and that the U(IV) could be intro-
duced either in stage 7 or stage 9. U(IV) introduced in
the 1BX was ineffective, since extraction of the U(IV)
prevented partitioning in more than two or three stages.

U(IV) extracts well in the scrub section (stages 8-16) of
the 1B bank, but extracts less in the extraction section
(stages 1-7) because most of the TBP is complexed with U(VI)
and because the acid concentration is low. The estimated
extraction factors in stage 6 are 0.5 to 1.5; U(IV) color is
easily visible, and detection of the green-colored U(IV)
ion by its optical absorption is useful in control of the U(IV)

bank profile. Aqueous stage samples had the following U(IV) concentrations, which indicate a considerable reflux of U(IV) in the extraction section of the 1B bank.

Stage	U(IV) Concentration, M
2	0.04
3	0.07
4	0.09

A study of the reaction of Pu(IV) in 30% TBP with uranium(IV) nitrate demonstrated that the rate of removal of Pu(IV) from the organic phase depends almost entirely on the efficiency of mixing the organic and aqueous phases. This rate was pseudo-first order and was essentially unaffected by the concentrations of Pu(IV), U(IV), or aqueous acidity. The reaction was investigated by agitating a synthetic 1AP solution (10^6 Pu α d/(min)(ml), 0.4M $UO_2(NO_3)_2$, 30% TBP) with an aqueous phase containing uranium(IV) nitrate, nitric acid, and hydrazine. The reduction was followed by measuring the Pu(IV) concentration in the organic phase. The relative effects of mixing and chemical composition are shown in Table III.

TABLE III

Reduction of Pu(IV) by U(IV)

Mixing Intensity[a]	Initial Aqueous[b] Composition, M		Half-time for Reaction[c], sec
	U(IV)	HNO₃	
Low	0.02	0.5	40
Intermediate	0.02	0.5	7.5
High	0.02	0.5	3
Intermediate	0.05	0.5	6.8
Intermediate	0.02	0.5	7.5
Intermediate	0.005	0.5	9.5
Intermediate	0.02	1.0	8.2
Intermediate	0.02	0.5	7.5
Intermediate	0.02	0.2	9.4

(a) Mixing power inputs are in the approximate ratio 1:8: >15 for low, intermediate, and high intensity, respectively. The mixing intensity in these experiments was not measured quantitatively other than by measurement of agitator speed; thus, the effect of mixing intensity is qualitative. However, these data demonstrate that an effective reaction rate depends on proper mixing in a two-phase system.

(b) The aqueous phase also contained 0.2M N_2H_4.

(c) Half-time for the first-order decay of the Pu(IV) concentration in the organic phase.

Dilute hydrazoic acid solutions are generated in the 1B bank where nitrous acid reacts with hydrazine and in the second-cycle feed (2AF) adjustment vessel where excess hydrazine is destroyed by the addition of nitrite. Since the generated hydrazoic acid competes with hydrazine for the nitrous acid, the yield of hydrazoic acid is less than the initial equivalent concentration of hydrazine. The second-cycle feed adjustment was simulated by titrating 0.2-$0.4M$ N_2H_4 with sodium nitrite. Typical titration curves, given in Figure 3, show that the yield of hydrazoic acid was equivalent to 12% of the initial hydrazine. The transient concentration expected during the 2AF adjustment operation with $0.2M$ N_2H_4 (the maximum concentration if none was destroyed in the B-bank)

Initial Aqueous Acid: $1.26M$ HNO_3

Initial N_2H_4, M	Component	Symbol
0.19	N_2H_4	●
	HN_3	○
0.44	N_2H_4	▲
	HN_3	△

Concentration of N_2H_4 or HN_3, mols/liter

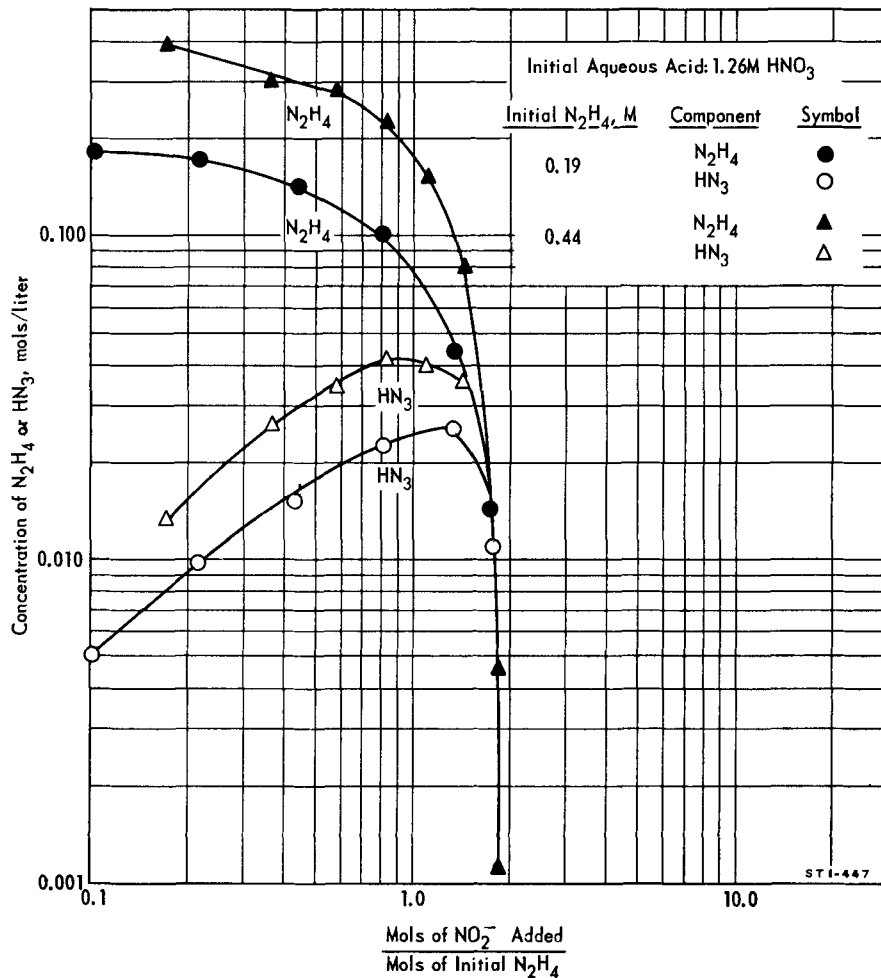$\dfrac{\text{Mols of } NO_2^- \text{ Added}}{\text{Mols of Initial } N_2H_4}$

STI-447

FIG. 3 DESTRUCTION OF NITRITE IN THE ABSENCE OF THE ORGANIC PHASE

is therefore less than 0.024M HN_3. Typical results of, similar tests to simulate the 1B bank, where the reaction occurs in presence of TBP, are shown in Figure 4. The maximum yield of hydrazoic acid was equivalent to 6% of the initial hydrazine; the lower yield results from preferential extraction of nitrous acid and hydrazoic acid into the organic phase with no extraction of hydrazine.

Initial Organic Composition:
29.1% TBP

Initial Aqueous Composition:
1.25M HNO_3, 0.22M N_2H_4

Temperature: 25°C

N_2H_4

Organic HN_3

Aqueous HN_3

STI-448

Concentration of N_2H_4 or HN_3, mols/liter

$$\frac{\text{Mols of } NO_2^- \text{ Added}}{\text{Mols of Initial } N_2H_4}$$
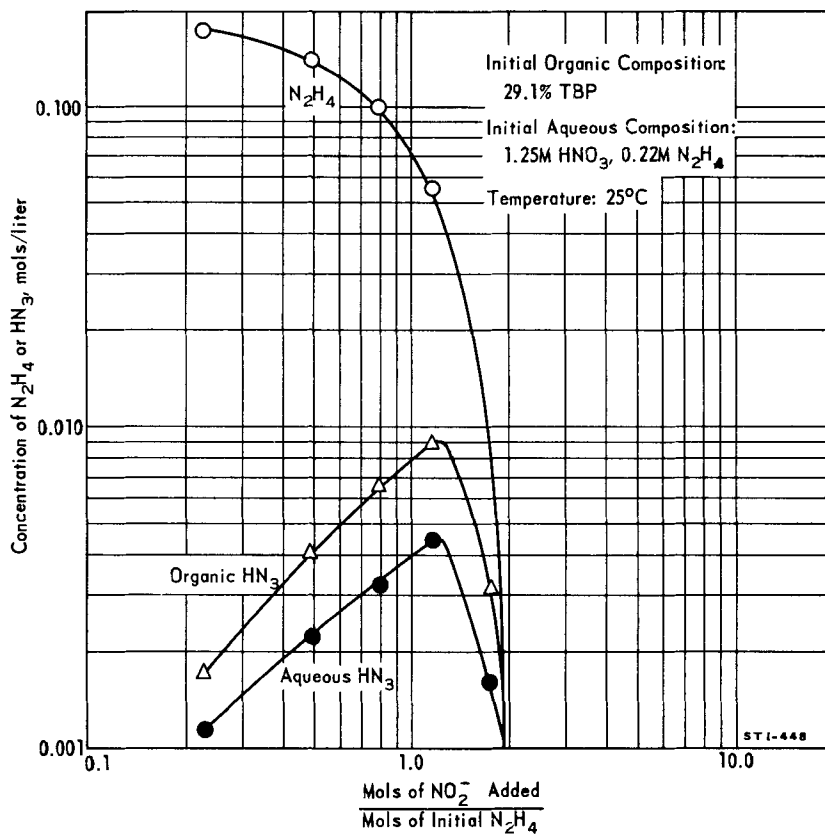
FIG. 4 DESTRUCTION OF NITRITE IN THE PRESENCE OF THE ORGANIC PHASE

Hydrazoic acid extraction was measured by batch equili-
brations that simulated various stages of the Purex process.
The distribution coefficients depended on the concentration of
TBP that was not complexed with uranyl nitrate, nitric acid, or
hydrazoic acid; this dependence is shown in Figure 5. Because
the concentration of uncomplexed TBP in the 1B and 1C banks is
greater than 0.3M, the distribution coefficient of hydrazoic
acid is greater than 2 throughout the process. As a consequence
of favorable organic-to-aqueous flow ratios, hydrazoic acid
will preferentially follow the solvent phase without refluxing.
About 20% will be stripped into the uranium product stream,
where it will normally be destroyed by nitrite generated in the
destruction of soluble organic materials during evaporation.

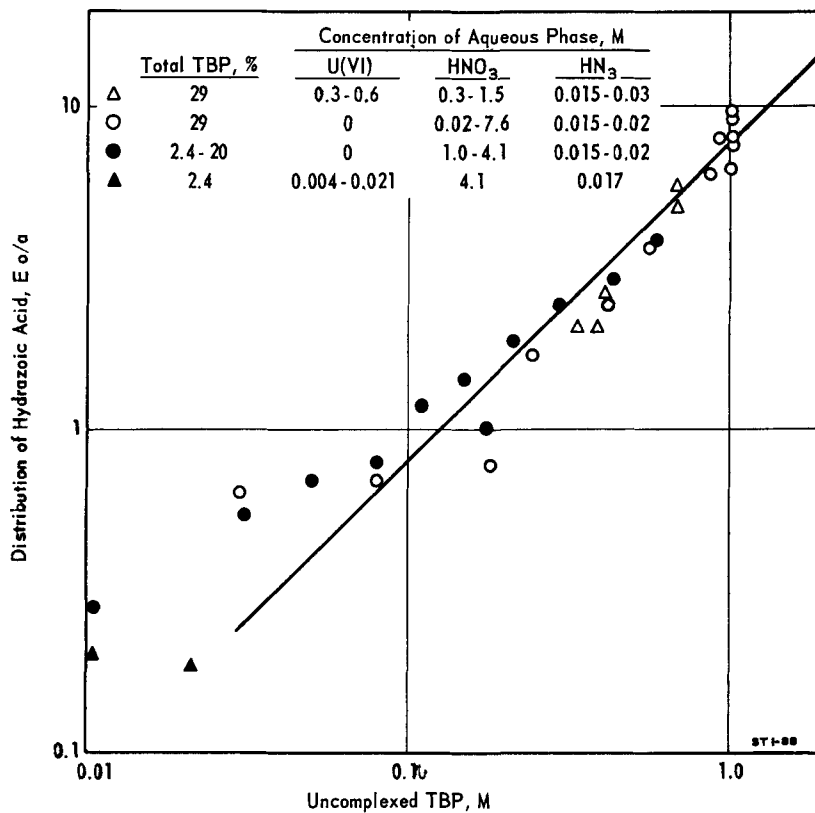|	Total TBP, %	U(VI)	HNO$_3$	HN$_3$
△	29	0.3-0.6	0.3-1.5	0.015-0.03
○	29	0	0.02-7.6	0.015-0.02
●	2.4-20	0	1.0-4.1	0.015-0.02
▲	2.4	0.004-0.021	4.1	0.017

FIG. 5 EXTRACTION OF HYDRAZOIC ACID

Hydrazoic acid extraction is negligible when the acid is below a pH of about 4; therefore, the basic solvent wash solution quantitatively strips the hydrazoic acid from the solvent and converts it to sodium azide. In the Purex process, all solutions that the solvent contacts prior to entering the basic washer contain high acid concentrations to maintain most of the hydrazoic acid in the organic phase. The highest concentration of hydrazoic acid in the solvent wash solution would be less than 0.045M based on a 6% yield from the original hydrazine added to the process and a solvent-to-wash ratio of 40:1.

Sodium azide in the alkaline solvent wash solution is not hazardous, but discharge of the azide into waste tanks is not recommended. The azide can be destroyed by adding 20% excess sodium nitrite to the solvent wash solution and then acidifying it. In laboratory tests with sodium azide in 0.5M Na_2CO_3, 95% of the azide was destroyed when the alkaline solution contained an equivalent concentration of sodium nitrite before acidification to 0.5M HNO_3. The 20% excess is sufficient to assure complete destruction of the azide.

The lower explosive limit for aqueous solutions of hydrazoic acid is 17% (4.7M). This concentration can be attained in the condensate while distilling at 20°C solutions that contain at least 0.05M HN_3. At normal process temperatures (40°C) or higher, more water is distilled so that solutions containing 0.05M HN_3 deposit condensate that is within the safe concentration range. With the dilute solutions of hydrazine used (less than 0.2M N_2H_4) hydrazoic acid is not accumulated to this potentially hazardous concentration.

A conservative value of the hazardous concentration of hydrazoic acid in the gas phase is the concentration which contains a potential heat of reaction sufficient to heat the gas to a temperature at which rapid decomposition occurs. The rate of decomposition becomes measurable at 290°C[13] and the calculated concentration of hydrogen azide that would have to be decomposed to heat air from 35 to 290°C is about 2.5 vol %. On the basis of vapor pressures of pure HN_3[13] and measured values of activity coefficients, the concentration of hydrazoic acid in aqueous solution that is in equilibrium with 2.5 vol % hydrogen azide in the gas phase is calculated to be about 0.2M HN_3 at 37°C, or greater than the safe limit established for hydrazoic acid in the liquid phase.

The potential of accumulating solid deposits of explosive heavy metal azides (Hg, Pb, Ag, Cu, Tl) is insignificant. None of these elements are normal components of the 1B bank, 1C bank, and the solvent washer. If one of the heavy elements were inadvertently added to the basic solvent wash solution, it would precipitate as a hydroxide rather than an azide.

BIBLIOGRAPHY

1. Regnaut, P., et al. "The Processing of Irradiated Uranium in the Fontenay-aux-Roses Pilot Plant". Proc. U. N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 17, 73-95 (1958).

2. Jenkins, E. N. and R. J. W. Streeton. The Use of Uranium IV as a Reagent in the Aqueous Processing of Irradiated Uranium. United Kingdom Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Berkshire, England. Research and Development Report AERE-R3158 (1959).

3. Streeton, R. J. W. and E. N. Jenkins. The Preparation, Stabilisation and Analysis of Uranium(IV) Nitrate Solutions. United Kingdom Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Berkshire, England. Research and Development Report AERE-R3938 (1962).

4. Webster, D. S., C. L. Williamson, and J. F. Ward. Hydraulic Performance of a 5-inch Centrifugal Contactor. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. USAEC Report DP-370 (1962).

5. Betts, R. H. "Kinetics of the Oxidation of Uranium(IV) by Iron(III) in Aqueous Solutions of Perchloric Acid". Can. J. Chem. 33, 1780-91 (1955).

6. Masters, B. J. and L. L. Schwartz. "An Isotopic Exchange Study of the U(IV)-U(V)-U(VI) Equilibrium in Aqueous Perchlorate Solutions". J. Am. Chem. Soc. 83, 2620-4 (1961).

7. Rydberg, J. "The Reduction of Plutonium by Tetravalent Uranium". J. Inorg. Nucl. Chem. 5, 79-86 (1957); Acta Chem. Scand. 11, 201-2 (1957).

8. Slade, A. L. Oxidation of Uranium(IV) by Oxygen and Nitrous Acid. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. USAEC Report DP-554 (1961).

9. Halpern, J. and J. G. Smith. "Kinetics of the Oxidation of Uranium(IV) by Molecular Oxygen In Aqueous Perchloric Acid Solution". Can. J. Chem. 34, 1419-27 (1956).

10. Jenkins, E. N. "The Effect of Dissolved Air on the Reduction of Tracer Level Plutonium-IV by Uranium-IV". J. Inorg. Nucl. Chem. 13, 323-5 (1960).

11. Ondrejcin, R. S. Preparation of Uranium(IV) Nitrate Solutions. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. USAEC Report DP-602 (1961).

12. Katz, J. J. and G. T. Seaborg. The Chemistry of the Actinide Elements. New York: Wiley Company (1957).

13. Yost, D. M. and H. Russell, Jr. Systematic Inorganic Chemistry of the Fifth- and Sixth-Group Nonmetallic Elements. New York: Prentice-Hall, Inc. (1946).

14. Schlea, C. S., et al. A Miniature Pilot Plant for Processing Irradiated Nuclear Fuel. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. USAEC Report DP-757 (1962).

15. Schlea, C. S., et al. Purex Process Performance with Short Residence Time Contactors. E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. USAEC Report DP-809 (to be issued).