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OXIDATION OF URANIUM (IV) BY OXYGEN AND NITROUS ACID

by

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ABSTRACT

The oxidation of uranium(IV) by oxygen and nitrous acid was studied in both 30% TBP (tri-n-butyl phosphate) - "Ultrasene" and in aqueous solutions. Emphasis was placed on reactions between uranium(IV) and nitrous acid. Distribution coefficients were measured for uranium(IV) and uranium(VI) in the nitric acid - 30% TBP system. The use of uranium(IV) as a reductant for plutonium in the Purex process is discussed.

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INTRODUCTION

In the 1B bank of the Purex process⁽¹⁾, plutonium is separated from uranium by reducing the extractable Pu(IV) to the poorly extractable Pu(III). The most commonly used reducing agent is ferrous sulfamate, $Fe(SO_3NH_2)_2$, whose effectiveness in a nitric acid system depends upon the rapid reduction of Pu(IV) to Pu(III) by Fe(II), and the rapid destruction of the interfering nitrous acid by sulfamate ion. In the absence of nitrous acid, the rate of oxidation of Pu(III) and Fe(II) by nitric acid is extremely slow, and therefore the reduced valence states can be maintained for the time necessary to separate plutonium from uranium.

The major objection to the use of ferrous sulfamate as a reductant is that it introduces a nonvolatile constituent that eventually must be stored as waste. Jenkins and Streeton⁽²⁾ studied the use of uranous solutions as reductants for Pu in a Purex process in which 20% TBP was used as the solvent. Regnaut⁽³⁾ reported the use of uranous sulfate as a reductant in the process at the Fontenay-aux-Roses Pilot Plant; in this process 40% TBP was used as the solvent. Uranous nitrate is preferred to uranous sulfate as a reductant because both iron and sulfate are eliminated from the waste by use of the nitrate salt.

At the Savannah River Plant, the ferrous sulfamate produces about 100 pounds of solid waste per ton of uranium processed. This solid waste must be stored at a substantial cost. Becuase of this economic incentive, uranium(IV) nitrate, stabilized with hydrazine, was tested in miniature process equipment as a possible reductant for Pu in the 1B bank. The expected behavior of the 1B bank was that U(IV) would reduce Pu(IV) to Pu(III), and the excess U(IV) would be recovered with the uranium product. The actual behavior showed an adequate separation of Pu(IV) from uranium, but excessive amounts of U(IV) were apparently required to achieve this separation; smaller amounts of U(IV) did not reduce Pu(IV) effectively. These observations led to the assumption that U(IV) was being oxidized rapidly in the organic phase.

The objective of the work discussed in this report was to determine the cause of the apparent loss of U(IV); oxidation of U(IV) by O_2 and/or HNO_2 in the organic phase was suspected. An additional objective was to determine the extraction behavior of U(IV) under 1B bank conditions.

SUMMARY

A laboratory study of the oxidation of U(IV) by HNO_2 and O_2 showed that U(IV) has adequate stability for use as a reducing agent for plutonium in the Purex process. The halftime for oxidation of unstabilized U(IV) by 0.025M HNO_2 was 3 to 4 hours in either 30% TBP or nitric acid solution; oxidation by air in 30% TBP required about 15 hours before any appreciable loss of U(IV) occurred.

The extraction coefficients measured for U(IV) indicated that excess U(IV) would extract into the organic phase (30% TBP) in the 1B bank so that adequate separation of plutonium from uranium would be achieved. It is necessary to add an excess of U(IV) over that stoichiometrically needed to effect the rapid reduction of Pu(IV) to Pu(III); a part of this excess will be oxidized by nitrite in the 1B bank, but it is probable that an appreciable concentration of U(IV) will remain. Therefore, it is necessary that U(IV) extract with uranyl nitrate into the organic phase, to ensure adequate removal of uranium from the aqueous plutonium stream.

DISCUSSION

EXPERIMENTAL

PREPARATION OF REAGENTS

Uranium(IV) nitrate was prepared by electrolysis of 0.6 to 1.5M uranyl nitrate in the presence of 0.4 to 0.9M hydrazine and 1.5 to 2.0M nitric acid.

U(IV) sulfate was prepared by electrolysis of 0.4M uranyl sulfate in 0.8M sulfuric acid.

Platinum electrodes were used for the electrolysis. The anode and cathode chambers were separated by a medium-frit, porcelain disc. Fifty per cent conversion to U(IV) was achieved. No attempts were made to remove the remaining uranyl nitrate.

The TBP (tri-n-butyl phosphate) was purified by vacuum distillation, and diluted to 30% by volume with "Ultrasene" before use.

ANALYTICAL METHODS

U(IV) and nitrite ion were determined, together, by oxidation with an excess of ceric ion and back titration with Fe(II) and ferroin indicator.

The Fe(II) solution was analyzed each day before use by titration with standard ceric ammonium sulfate and ferroin indicator.

The total hydrogen ion concentration was determined in solutions containing uranium as uranyl ion only. The uranyl ion was complexed with excess sodium fluoride and the solution was titrated with standard sodium hydroxide; a Beckman pH meter was used to determine the endpoint.

U(IV) concentrations were determined by measuring the absorbance at 650 mμ; U(VI) was determined by measuring the absorbance of the thiocyanate complex at 405 mμ. The molar absorbance for U(IV) was 16.4 in 30% TBP and 38 in aqueous nitrate solutions.

RATE MEASUREMENT

The rate of oxidation of U(IV) was measured by determining the U(IV) absorbance at appropriate time intervals with a Model II Cary recording spectrophotometer. Initial concentrations were calculated from the known concentration and volumes of the stock solutions mixed at the beginning of the reaction; organic phase reactions were initiated by mixing together separate solutions of U(IV) nitrate, HNO_2, and HNO_3 in 30% TBP.

When reaction rates were measured in the aqueous phase, U(IV) sulfate solutions were added to the reaction mixture. U(IV) nitrate could not be used because it is not stable in the absence of a stabilizing agent such as hydrazine or sulfamic acid. Both stabilizing agents react very rapidly with nitrous acid, so the oxidation of U(IV) does not occur in their presence.

RESULTS

REACTION OF U(IV) WITH OXYGEN

Comparison of two solutions of U(IV) in 30% TBP, one sparged continuously with nitrogen and the other with air, showed that only 2 to 5% of the U(IV) was oxidized in 12 hours for both solutions. After this period the U(IV) in the solution sparged with nitrogen rapidly oxidized to U(VI); about 3 hours later, U(IV) in the solution sparged with air oxidized in the same fashion. After oxidation of the U(IV), the absorption spectrum of HNO_2 was observed in both solutions. The decrease of U(IV) with time after the long induction period is shown in Figure 1. The first-order rate curve shows an increasing reaction rate, a characteristic of an autocatalytic reaction.

The results of these tests can be explained by the following series of reactions.

$$U^{+4} + NO_3^{-} + H_2O \rightarrow UO_2^{++} + HNO_2 + H^{+} \qquad (1)$$

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

$$2NO + HNO_3 + H_2O \rightleftharpoons 3HNO_2 \qquad (3)$$

Reaction (1) occurs chiefly during the induction period; following this period reaction (2) becomes the major reaction because of the increasing concentration of HNO_2. The NO produced in reaction (2) reacts with nitric acid to produce 1.5 moles of HNO_2 for every mole of HNO_2 consumed in reaction (2), and thus the reaction becomes autocatalytic. The apparent stabilizing effect of the air sparge, compared to nitrogen, is the result of a contribution from the reaction, $2HNO_2 + O_2 \rightarrow 2HNO_3$. This reaction tends to decrease the accumulation of HNO_2 and delay the initiation of the autocatalytic oxidation.

REACTION OF U(IV) WITH NITROUS ACID

Organic Phase

The rate of oxidation of U(IV) by HNO_2 in 30% TBP was first order in U(IV) during the early stages of the reaction, but because the oxidation of U(IV) produced HNO_2, the rate accelerated beyond that of a first-order reaction (Figure 2).

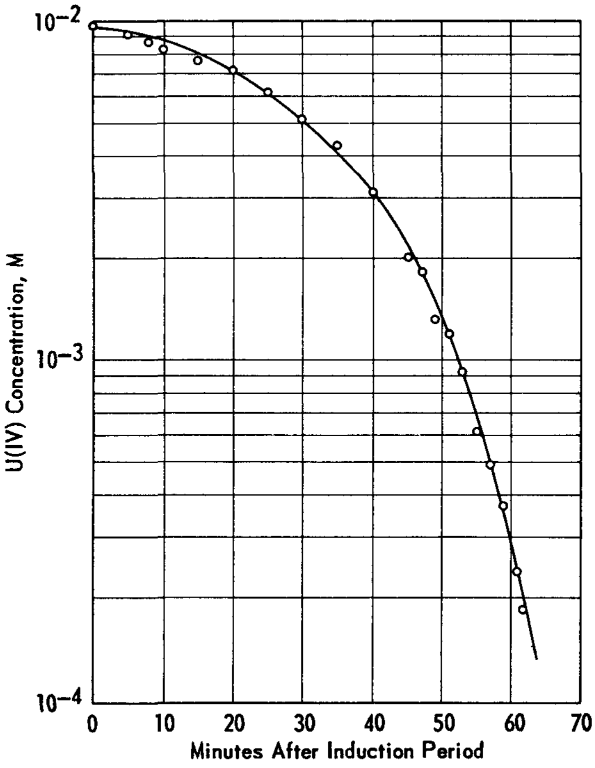

FIG. 1 OXIDATION OF U(IV) IN TBP - "ULTRASENE"

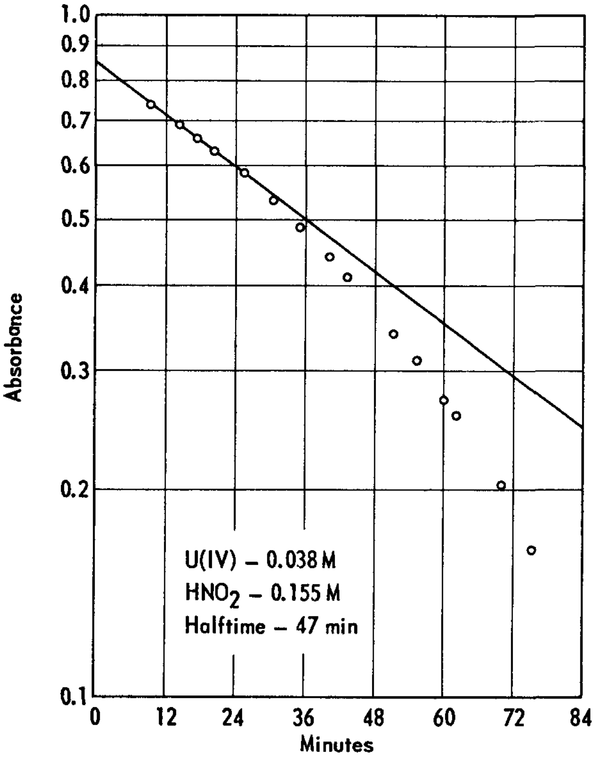

FIG. 2 OXIDATION OF U(IV) BY NITROUS ACID IN TBP - "ULTRASENE"

Attempts to avoid this effect by reacting a large excess of HNO_2 with U(IV) were not successful; some deviation from the first-order rate invariably occurred. The rate in the early stages of oxidation (0-25% of the reaction) showed no deviation from first-order kinetics. The effect of HNO_2 concentration on the initial reaction rate indicated that the oxidation rate was one-half order in HNO_2 when the organic phase was about 1M in HNO_3 (Figure 3 and Table I).

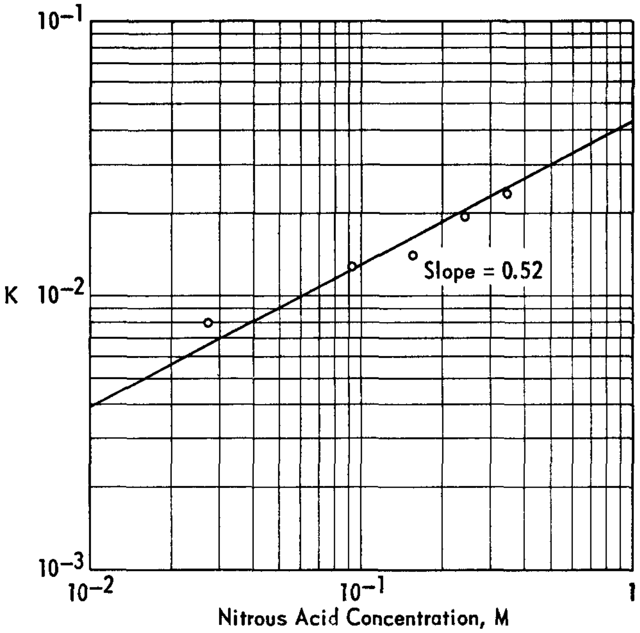

FIG. 3 EFFECT OF NITROUS ACID CONCENTRATION ON OXIDATION OF U(IV)

TABLE I

Oxidation of U(IV) by Nitrous Acid in TBP-"Ultrasene"

Solutions 1M in HNO_3

Initial U(IV), M	Initial HNO_2, M	Halftime, minutes	Rate Constant, K (min^{-1})
0.032	0.32	30	2.31×10^{-2}
0.033	0.093	54	1.28
0.041	0.027	86	0.80
0.038	0.16	48	1.40
0.030	0.24	36	1.91

Solutions Typical of Organic Phase in the 1B Bank of Purex Process

Initial U(IV), M	Initial HNO_2, M	HNO_3, M	Halftime, minutes	Rate Constant, K (min^{-1})
0.012	0.008	0.035	448	0.16×10^{-2}
0.032	0.032	0.09	184	0.38
0.028	0.023	0.10	216	0.32
0.028	0.024	0.33	245	0.28
0.014	0.034	0.34	337	0.21

Additional measurements in solutions typical of the organic phase in the Purex 1B bank showed that the oxidation was slow under these conditions; the expected reaction halftime would be 3 to 5 hours (Table II). Comparison of the data in Tables I and II indicates that the organic phase reaction probably depends upon the acidity of the organic phase. It is also probable that the concentration of water will affect the rate of the reaction (see equation 1). Extensive experimental work would be required to demonstrate the detailed reaction mechanism.

TABLE II

Oxidation of U(IV) by Nitrous Acid in Aqueous Solution

Initial U(IV), M	Initial HNO_2, M	Initial H^+, M	Initial Nitrate, M	Sulfate, M	Rate Constant, K (min^{-1})
0.059	0.10	1.57	1.24	0.30	0.26×10^{-2}
0.039	0.10	1.45	1.24	0.20	0.31
0.016	0.10	1.26	1.24	0.08	0.33
0.008	0.10	1.17	1.24	0.04	0.44
0.015	0.10	3.72	3.72	0.08	0.34
0.015	0.10	2.60	2.48	0.08	0.32
0.016	0.10	1.26	1.24	0.08	0.33
0.016	0.10	0.86	0.74	0.08	0.34
0.016	0.10	0.62	0.50	0.08	0.17
0.015	0.10	0.37	0.25	0.08	0.14
0.015	0.02	2.60	2.48	0.08	0.27
0.015	0.04	2.60	2.48	0.08	0.35
0.015	0.06	2.60	2.48	0.08	0.40
0.015	0.08	2.60	2.48	0.08	0.43
0.015	0.09	2.60	2.48	0.08	0.48

Aqueous Phase

The oxidation of U(IV) by HNO_2 in an aqueous nitric acid system was similar to that in the organic phase; the rate was first order in U(IV), and the dependence on nitrous acid was approximately half order. At acidities greater than 0.8M, the rate of oxidation was unaffected by the acid concentration.

The results of the aqueous phase oxidation are tabulated in Table III. Generally the reaction was slightly more rapid in the aqueous phase than in the organic phase; the reaction halftime with 0.01 to 0.02M U(IV) - 0.1M HNO_2 was about 3 hours.

EXTRACTION OF U(IV)

U(IV) extracts into 30% TBP, and measurement of extraction coefficients showed that essentially all the U(IV) would be recovered in the 1B bank with the U(VI). Data for the distribution coefficients of mixtures of U(IV) and U(VI) are presented in Table III.

TABLE III

Distribution Data for U(IV) and U(VI) in the Nitric Acid - 30% TBP System

Initial HNO_3 Conc. Aqueous, M	U(IV) Conc. Aqueous, M	U(IV) Conc. Organic, M	U(IV) E o/a	U(VI) Conc. Aqueous, M	U(VI) Conc. Organic, M	U(VI) E o/a
0.35	0.057	0.011	0.19	0.024	0.092	3.83
0.94	0.043	0.025	0.58	0.014	0.070	5.00
1.59	0.044	0.037	0.84	0.008	0.086	10.8
2.83	0.0342	0.0428	1.25	0.0058	0.1022	17.6
4.07	0.0297	0.0503	1.69	0.0022	0.0978	44.5
5.31	0.0268	0.0552	2.06	0.0024	0.0996	41.5
10.1	0.0124	0.0716	5.77	0.0049	0.0691	14.1

The extraction coefficient for U(IV) into 30% TBP was about 1.3 from 2.8M HNO_3, and about 0.2 from 0.35M HNO_3 - 0.11M $UO_2(NO_3)_2$. Combined with the organic/aqueous flow ratio of 7 to 10 in the 1B bank, these data predict that U(IV) would be extracted and leave the bank with the uranium stream. In the test in miniature process equipment, the U(IV) reductant was introduced into the 1B bank at stages 1 and 6. Due to the extraction of U(IV), it is apparent that large amounts of U(IV) must be introduced at stage 6 to maintain reducing conditions at stage 8, where the organic stream carrying Pu(IV) and U(VI) enters the contactor. Introduction of U(IV) in the region of stages 10 to 12 should require a smaller amount of U(IV), and result in a more efficient reduction of Pu(IV) in the organic phase.

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