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OXIDATION OF NEPTUNIUM(V)
IN NITRIC ACID SOLUTION -
LABORATORY STUDY
OF
RATE ACCELERATING MATERIALS (RAM)

April 1969

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IN NITRIC ACID SOLUTION -
LABORATORY STUDY
OF
RATE ACCELERATING MATERIALS (RAM)

By

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Chemistry and Metallurgy Division

April 1969

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ABSTRACT

Oxidation of neptunium(V) to neptunium(VI) can be accelerated by the addition of "Rate Accelerating Materials" (RAM). These materials that accelerate oxidation of neptunium(V) in HNO_3 - HNO_2 solutions are obtained by reacting the aci-form of 1-nitropropane with HNO_3 in the presence of nitrite. The preparation of this material and its effect on the oxidation rate were studied in detail. The data indicate that addition of a low concentration of RAM could increase the rate of neptunium(V) oxidation by several orders of magnitude. The extractability and stability to radiation of RAM appear to be adequate for plant use, and tests indicate that it has no effect on the solvent extraction behavior of plutonium or fission products or on phase disengaging times.

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OXIDATION OF NEPTUNIUM(V) IN NITRIC ACID SOLUTION -
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INTRODUCTION

The process used at the Hanford Purex Plant for the recovery of neptunium involves the extraction of neptunium(VI) in the HA column.* Since the neptunium is present mainly as the virtually inextractable neptunium(V) in the feed solution, oxidation of neptunium(V) to (VI) must be accomplished in the column. In 1960, Benedict, McKenzie, and Richardson⁽¹⁾ developed a process to accomplish this based on the HNO_2 catalyzed oxidation of neptunium(V) by HNO_3 , first reported by Siddall and Dukes.⁽²⁾ Recent interest in reducing the loss of neptunium from the plant prompted a re-examination of the kinetics of this reaction.

The initial results showed that, in pure HNO_2 - HNO_3 systems, the rate of oxidation was slower than what it must be in the plant for the recovery to be as good as it is. It was then found that products of the reaction of uranium carbide (which is present in the metallic uranium fuel elements) with HNO_3 and of the reaction of the plant solvent with HNO_3 accelerated the rate of neptunium(V) oxidation, thus providing an explanation for the level of recovery obtained in the plant.

Subsequent work showed that materials that accelerate the oxidation of neptunium(V) could be prepared more simply by reacting the aci-form of 1-nitropropane with HNO_3 in the presence of nitrite. Such material has been termed "RAM," the acronym for "Rate Accelerating Material." The status of this work is the subject of this report.

* HA is the designation used at Hanford for the first column in the process.

SUMMARY

Material that accelerates the oxidation of neptunium(V) in HNO_3 - HNO_2 solutions (termed "RAM" for Rate Accelerating Material) is obtained by reacting the aci-form of 1-nitropropane with HNO_3 in the presence of nitrite. The preparation of this material and its effect on the oxidation rate were studied in detail.

The data indicate that addition of a low concentration of RAM to the HA column could increase the rate of neptunium(V) oxidation by several orders of magnitude. The extractability and stability to radiation of RAM appear to be adequate for plant use, and tests indicate that it has no effect on the solvent extraction behavior of plutonium or fission products or on phase disengaging times.

OXIDATION RATE STUDIES

EXPERIMENTAL METHOD

In HNO_2 - HNO_3 solutions, the amount of neptunium(V) that can be oxidized under a given set of conditions is governed by the equilibrium reaction

In this research, the rate of attainment of the equilibrium position and the equilibrium position itself were obtained from spectrophotometric measurements of the concentration of neptunium(V) at various times.

The experiments were performed with HNO_2 and HNO_3 concentrations high enough that the observed order of the reaction was with respect to neptunium concentration. The reaction rate was found to be first order with respect to the difference between the concentration of neptunium(V) at a given time and the concentration at equilibrium:

$$-dC_5/dt = k(C_5 - C_{5,eq}) \quad (2)$$

This result is the result expected for a reversible reaction which is first order in both directions; the approach to equilibrium is a first-order process with effective rate constant being the sum of the constants for the forward and reverse directions. The fact that the process is first order means that the results obtained in the laboratory at neptunium concentrations of about $5 \times 10^{-4}M$ (high enough for spectrophotometric measurement) should hold equally well at the lower concentrations that exist in the plant.

The ratio of neptunium(VI) to (V) at equilibrium was calculated from the total neptunium concentration and the concentration of neptunium(V) at equilibrium:

$$C_6/C_5 = (C_T - C_5)/C_5 \quad (3)$$

In some cases (where the reaction was slow) the total neptunium concentration was determined from the concentration of neptunium(V) at zero time and the composition of the neptunium stock solution added [96% Np(V) and 4% Np(VI)]. In other cases, the solution was made $0.05M$ in $NaNO_2$ to reduce nearly all the neptunium(VI) to neptunium(V) and its concentration then determined.

The solutions were prepared by dilution of HNO_3 and $NaNO_2$ solutions of known composition. The concentration of nitrite at equilibrium was taken as that added plus one-half the concentration of neptunium(V) oxidized. While nitrite is known to decompose in acid solutions, little error is introduced by ignoring its decomposition, since the time required for decomposition of a significant fraction was found to be long compared to the time required for completion of the neptunium reaction.

Most of the experiments were performed at room temperature (about $24^\circ C$). In the few experiments done at elevated

temperatures, the solution temperature was controlled (to within about 1 °C) by controlling the temperature of a special furnace that held the cell which contained the solution. In the elevated temperature experiments, the solution (except for neptunium or nitrite) was brought to temperature, and the missing reactant was then injected (in a small volume) into the solution to initiate the reaction with little change in temperature.

RESULTS IN ABSENCE OF RAM

Results of kinetic experiments performed at different concentrations of HNO_2 and HNO_3 are presented in Figure 1, where reaction half-times are plotted against the concentration of HNO_2 added (the changes in HNO_2 concentration as the reaction proceeded were generally minor). The half-times were obtained from plots of $\log (C_5 - C_{5,\text{eq}})$ against time.

The rate of approach to equilibrium is seen to be first order in HNO_2 concentration and independent of HNO_3 concentration above about two molar. Thus, at HNO_3 concentrations prevalent in the Purex HA column, the rate of oxidation of neptunium(V) in the absence of RAM follows the equation:

$$-dC_5/dt = k_1[\text{HNO}_2](C_5 - C_{5,\text{eq}}) \quad (4)$$

where, as before, C_5 and $C_{5,\text{eq}}$ denote the concentration of neptunium(V) at the given time and at equilibrium. At 24 °C, k_1 was found to be about 46 (M, min)⁻¹. At 46 °C, k_1 was found to be about 250 (M, min)⁻¹, giving an activation energy of about 15 kcal/mole.

It should be mentioned that these results are not at all in agreement with those of Siddall and Dukes,⁽²⁾ who used a solvent extraction technique to follow the reaction. Those investigators found the neptunium(V) oxidation rate to be independent of HNO_2 concentration at these concentrations and to increase with the fourth power of HNO_3 concentration. The

FIGURE 1. Rate of Reaction in HNO_2 - HNO_3 Solutions

reason for these differences is not known, but it is considered probable that it is at least partially due to the formation of a RAM by solvent degradation during the course of their experiments.

Data on the equilibrium ratio of neptunium(VI) to (V) are presented in Figure 2. The equilibrium ratio is seen to decrease with increasing HNO_2 concentration (negative one-half power dependence) and to increase with increasing HNO_3 concentration, as expected from Equation (1). Increased temperature also produces an increase in the equilibrium ratio.

The equilibrium data can be correlated equally well on the basis that the equilibrium neptunium(VI) to (V) ratio (at a given HNO_2 concentration) increases with the HNO_3 concentration to the third power or with the HNO_3 activity to the second power. The former correlation is the simpler to use while the latter is more aesthetically gratifying since it is the dependence expected for Reaction (1). These results are shown in Table 1.

TABLE 1. Equilibrium Quotient for the Reaction

Temperature $\sim 24^\circ \text{C}$

HNO_3 Molarity, $[\text{HNO}_3]$	HNO_3 Activity, ^(a) $m\gamma$	$\frac{[\text{Np(VI)}][\text{HNO}_2]^{1/2}}{[\text{Np(V)}][\text{HNO}_3]^3}$	$\frac{[\text{Np(VI)}][\text{HNO}_2]^{1/2}}{[\text{Np(V)}](m\gamma)^2}$
2.0	1.7	2.7×10^{-4}	7.4×10^{-4}
3.1	3.2	2.4×10^{-4}	7.0×10^{-4}
4.4	5.5	2.5×10^{-4}	6.9×10^{-4}
4.7	6.3	3.2×10^{-4}	8.4×10^{-4}

a. Interpolated from the data of Landolt-Bornstein⁽³⁾.

FIGURE 2. Ratio of Np(VI) to Np(V) at Equilibrium

Because of the strong dependence of the equilibrium ratio of neptunium(VI) to (V) on HNO_3 concentration, a much greater fraction of neptunium(V) is oxidized in a given period of time (at a given HNO_2 concentration and temperature) in 4.7M HNO_3 than in 2M HNO_3 even though the rate constant is the same at the two acidities. Data illustrating this effect are shown in Figure 3, along with data to illustrate the effect of having an organic phase present to extract the neptunium(VI) as it is formed.

RESULTS IN PRESENCE OF RAM

In 3.1M HNO_3 solutions containing RAM, the rate of oxidation of neptunium(V) is described by the equation

$$-dC_5/dt = (k_1[\text{HNO}_2] + k_2[\text{RAM}][\text{HNO}_2]^{0.3}) (C_5 - C_{5,\text{eq}}) \quad (5)$$

This equation was found to apply with dilutions of several different RAM preparations even though it is likely that different RAM's were present in the different preparations. The presence of RAM did not affect the equilibrium neptunium(VI) to (V) ratio.

Since there was no way of knowing the concentration of RAM in these experiments, the value of k_2 could not be determined. However, from the rate measured in the presence of RAM, the nitrite concentration, and the previously determined value of k_1 , the quantity $k_2[\text{RAM}]$ could be calculated. For a given RAM, variations in this quantity measure variations in the RAM concentration; for different RAM's, variations can indicate variations in the value of k_2 as well as in RAM concentration. Regardless of which of these two possibilities is being measured, the quantity $k_2[\text{RAM}]$ is a measure of the desired property - that of making neptunium(V) oxidize more rapidly.

To compare the effectiveness of various preparations of RAM, the term $k_2[\text{RAM}]/[\text{RNO}_2]$ was employed, where $[\text{RNO}_2]$

At $\sim 24^{\circ}\text{C}$ with $5 \times 10^{-4}\text{M NaNO}_2$ in Aqueous Phase

Aqueous Only

○ 2.0M HNO_3

□ 4.7M HNO_3

Aqueous in Equilibrium with Equal Volume 30% TBP

● 2.0M HNO_3

■ 4.7M HNO_3

FIGURE 3. *Effects of HNO_3 Concentration and of Organic Phase on Amount Neptunium(V) Remaining*

denotes the concentration of nitropropane that would have been present had it not been consumed in the formation of RAM. As will be seen in the following section, values of $k_2[\text{RAM}]/[\text{RNO}_2]$ typically ranged from 0.1×10^4 to 1.0×10^4 ; the data in Table 2 and Figure 4 illustrate the effect on the neptunium(V) oxidation rate of the presence of various amounts of RAM, as calculated from Equation (5).

TABLE 2. *Illustration of Effect of RAM on Neptunium(V) Oxidation Rate*

Conditions: $3.1\text{M HNO}_3 + 5 \times 10^{-4}\text{M NaNO}_2$ at $\sim 24^\circ\text{C}$

$$t_{1/2} = \frac{0.693}{k_1[\text{HNO}_2] + k_2[\text{RAM}][\text{HNO}_2]^{0.3}}$$

$[\text{RNO}_2]$	$k_2[\text{RAM}]/[\text{RNO}_2]$	$k_2[\text{RAM}]$	$t_{1/2}, \text{ min}$
-	-	-	30
0.001	0.1×10^4	1	7
0.001	1.0×10^4	10	0.8
0.01	0.1×10^4	10	0.8
0.01	1.0×10^4	100	0.09

As a basis of comparison, for the Purex Plant to recover 85% of the neptunium the half-time of neptunium(V) oxidation in the HA column currently must be of the order of a minute (at approximately 50°C). If a reasonable value for the activation energy is assumed, chemical conditions giving a half-time of the order of 10 min in these experiments (at approximately 24°C) should provide rates at approximately 50°C comparable to those currently in the HA column. In a plausible example listed in Table 2, a rate a hundredfold greater is seen to be obtained by the addition of RAM.

The necessity of having HNO_2 present for RAM to be effective, as indicated in Equation (5), was emphasized in an

FIGURE 4. Effect of Different Amounts of RAM

experiment involving the addition of sulfamic acid (to assure the absence of HNO_2) to a RAM solution. No oxidation of neptunium(V) was observed until the sulfamate was destroyed with HNO_2 . Rapid oxidation then occurred, demonstrating that the RAM itself had not been destroyed.

The effect of HNO_3 concentration on the effect of RAM was examined only briefly. In 4.7M HNO_3 the oxidation rate was found to be independent of nitrite concentration (at concentrations greater than 0.0005M at least), as opposed to the approximately one-third power dependence observed in 3.1M HNO_3 . At nitrite concentrations below about 0.001M , the effect of the RAM was greater in 4.7M HNO_3 than in 3.1M HNO_3 .

One experiment was performed to demonstrate that RAM is as effective in a solvent extraction type experiment with a low neptunium concentration as in the usual experiments involving a higher neptunium concentration and only an aqueous phase. With 10^{-5}M Np in the two-phase experiment, the measured half-time agreed very well with that obtained when using $5 \times 10^{-4}\text{M}$ Np in an aqueous phase only.

PREPARATION OF RAM

EXPERIMENTAL METHOD

The detailed study of the production of RAM was carried out in backmix flow reactors, as represented schematically in Figure 5. In the bulk of the work, a glass reactor having a diameter of 3.6 cm and a solution depth of 3.2 cm (giving a hold-up volume of about 30 ml) was employed. A stainless steel reactor of approximately the same dimensions gave the same result as the glass reactor. Glass reactors giving solution dimensions of 5.8 cm diameter by 2 cm depth and 3.6 cm diameter by 8 cm depth were also employed satisfactorily. In all of the runs a stirrer having a paddle diameter of 2.5 cm was used. The same results were obtained when air was swept

FIGURE 5. Preparation of RAM

over the surface of the solution in the reactor as when access of air was restricted by a lid which covered 95% of the top of the reactor.

Temperatures were measured with a thermometer immersed in the solution. The thermometer used was checked against a precision thermometer. Temperature control was accomplished in most cases by controlling the flow of water through a cooling coil immersed in the reactor solution. In the few cases where a temperature higher than that resulting from the mixing of the solutions was desired, a rheostat-controlled heater was used.

Practical grade 1-nitropropane from several sources (Commercial Solvents, Eastman, and Baker) was used. The concentration of the as-received material was taken to be 10M (pure 1-nitropropane would be 11M). The nitropropane was mixed with a NaOH solution to give the required aci-form and NaNO_2 was added to the desired concentration. While the solubility of normal 1-nitropropane in water is only about 0.15M, the solubility of the aci-form is much greater; concentrations as high as 2M were used. The amount of NaOH used was little more than that required to convert the nitropropane to the aci-form.

The solutions were fed to the reactor through rotameters that had been calibrated with solutions of the compositions used. The product solution was diluted a known factor (with water) to quench the reaction. The rate of neptunium(V) oxidation was then determined in a solution containing a spike of the diluted product.

RESULTS

As mentioned in an earlier section, the term $k_2[\text{RAM}]/[\text{RNO}_2]$ was employed to compare the effectiveness of various preparations of RAM. It will be remembered that the value of $k_2[\text{RAM}]$ was obtained from the neptunium(V) oxidation rate in the

presence of RAM, the nitrite concentration, and the known oxidation rate in the absence of RAM. The term $[RNO_2]$ is used to denote the concentration of nitropropane that would have been present had none been consumed in the formation of RAM. Thus, the value of $k_2[RAM]/[RNO_2]$ is proportional to the ratio of the concentration of the desired material to the concentration of starting material added and thereby provides a means of comparing the relative yields of RAM obtained under different conditions.

Variables of importance to the formation of RAM in the backmix reactor are temperature, residence time, nitric acid concentration in the reactor solution, nitrite-to-nitropropane ratio in the solution fed to the reactor, and the degree of agitation of the reactor solution. Data illustrating the effects of these variables are presented in Figures 6 through 9.

The yield of RAM varies markedly with the nitrite-to-nitropropane ratio in the solution fed to the reactor, as illustrated by the data in Figure 6. At a nitrite-to-nitropropane ratio of 0.6, there is seen to be only a gradual change of yield with temperature but the yields are relatively low. At lower nitrite-to-nitropropane ratios, the effect of temperature on the yield of RAM is seen to be more pronounced and higher yields can be achieved.

The very abrupt increase in RAM yield as the temperature is increased at the lower nitrite-to-nitropropane ratios is felt to be due to the initiation of a reaction to produce a different, especially effective RAM, rather than to the production of a greater amount of the same RAM. The production of this especially effective RAM appears to occur via an autocatalytic type reaction. Once the production commences, it goes well and in a reproducible manner but the commencement of the reaction at a lower temperature is not so reproducible.

Residence Time ~ 2 min

Stir Speed = 70 rpm

FIGURE 6. Effect of Nitrite to Nitropropane Mole Ratio

It was found to be best to let the temperature be high initially to get the reaction started and then cool to the desired temperature. It is seen that the temperature to which the reactor solution can be cooled and still allow the desired reaction to proceed at a self-sustaining rate is about 5 °C lower at a nitrite-to-nitropropane ratio of 0.4 than at a ratio of 0.3. The degree of sensitivity of yield to temperature is about the same at these two ratios.

The effect of HNO_3 concentration on the yield of RAM is illustrated in Figure 7. There is less sensitivity of the yield of RAM to temperature at a lower HNO_3 concentration, but this arises from a reduction in the maximum attainable yield rather than from a broadening of the range giving a high yield, as would be desirable.

In Figure 8 are presented data obtained at different nitropropane concentrations at a nitrite-to-nitropropane ratio of 0.4 and a HNO_3 concentration of 7M. In the range 0.1 to 0.6M there is seen to be no effect of nitropropane concentration on the relative yield of RAM. Below 0.1M nitropropane the yield peak was not as high, possibly due to the lack of a sufficient concentration of some material required for the production of the especially effective RAM.

Also presented in Figure 8 are data obtained at two different residence times. It is seen that an increase in residence time appears to simply result in a decrease in the temperature which gives the best yield. This effect would appear to provide a simple means of varying the output of a plant reactor at constant solution composition and yield of RAM; when the flow rates are changed (thereby changing the residence time of the solution in a reactor of a given holdup volume) the temperature can also be changed to keep the desired yield of RAM.

Residence Time ~ 2 min

Stir Speed = 70 rpm

FIGURE 7. Effect of HNO_3 Concentration

FIGURE 8. *Effects of Nitropropane Concentration and Residence Time*

When the degree of agitation of the reactor solution was increased above a certain value, the maximum attainable yield of RAM decreased, as shown in Figure 9. Good mixing of the solution was obtained even at the lower stir speeds with the size of stirrer and reactor used. At the higher stir speed there appeared to be greater gas evolution, suggesting that the effect may be due to the expulsion from solution of a gaseous intermediate required for the formation of the especially effective RAM before the gas has time to participate in the desired reaction.

OTHER ASPECTS OF RAM

STABILITY OF RAM IN PRODUCT SOLUTIONS

In the product solutions from the backmix reactor, reactions involving RAM continued to occur. Depending on the conditions of operation of the reactor, the concentration of RAM in the product solution decreased with time or increased at first and then decreased. Data illustrating this are presented in Figure 10.

Changes with time were slowed by diluting the product solutions. Even with this, however, reactions occurred fast enough to make long-term storage of RAM solutions unattractive, as shown in Figure 11. The fact that RAM disappeared more rapidly in the presence of nitrite complicated the study of RAM stability since the product solutions likely contained differing amounts of nitrite depending on the conditions of reactor operation. When used in the Purex Plant it would appear to be best to feed the product solution to the HA column with as little delay as possible.

The reactions leading to the formation and destruction of RAM are exothermic. In the runs at the higher nitropropane concentration (0.6M), the temperature of the product solution increased on standing, even though the initial temperature was

0.15M RNO_2 7M HNO_3

0.4 Nitrite/Nitropropane

Residence Time ~ 2 Min

□ 30 rpm

● 70 rpm

△ 140 rpm

FIGURE 9. Effect of Stir Speed

Reactor Solution:

0.15M RNO_2

7M HNO_3

0.4 Nitrite/Nitropropane

Cooled to $\sim 25^\circ\text{C}$ on Leaving Reactor

○ Reactor Solution $T \sim 30^\circ\text{C}$

△ Reactor Solution $T \sim 35^\circ\text{C}$

□ Reactor Solution $T \sim 47^\circ\text{C}$

FIGURE 10. Changes in Product Solution with Time

FIGURE 11. Changes in Diluted Product Solutions with Time

greater than the ambient temperature. Provision for this effect may be required in the Plant, depending on the method of operation.

EFFECT OF RADIATION ON RAM STABILITY

Irradiation of RAM-HNO₃ solutions to a dose of 10⁵ R (several times the dose to the aqueous phase in the extraction section of the HA column) resulted in decreases in RAM concentration. As seen in Table 3, the effect appears to be such that a concentration of RAM obtained from about 0.005M added nitropropane is sufficient to assure the presence of RAM throughout the extraction section of the column.

TABLE 3. *Decrease in RAM Concentration on Irradiation*

Dose: $\sim 10^5$ R (⁶⁰Co)
3.1M HNO₃ at ~ 24 °C

<u>Conditions of RAM Preparation</u>			<u>In Solution Irradiated</u>		<u>Percent Decrease in RAM</u>
<u>[RNO₂]</u>	<u>[HNO₃]</u>	<u>Nitrite Nitropropane</u>	$\frac{k_2[\text{RAM}]}{[\text{RNO}_2]}$	<u>[RNO₂]</u>	
0.32	3.1	0.5	0.16	0.014	18
0.33	3.2	0.5	0.15	0.0070	39
0.33	3.2	0.5	0.14	0.0070	45
0.16	7.2	0.4	0.67	0.0013	100
0.16	7.2	0.4	0.67	0.0082	32

SOLVENT EXTRACTION BEHAVIOR OF RAM

For the proposed use of RAM, low extractability into 30% TBP-NPH is desired so that RAM will stay in the aqueous phase in the extraction section of the HA column. The extractability of RAM was found to vary with the conditions of preparation demonstrating that different RAM's were obtained under different conditions. Fortunately, the RAM prepared under the conditions that give high $k_2[\text{RAM}]/[\text{RNO}_2]$ values exhibited low extractability.

With RAM solutions prepared in the backmix reactor at 3M HNO_3 , the RAM extractability was sufficiently high that extraction coefficients could be calculated from the difference in concentration of RAM found in the aqueous phase before and after extraction. Values ranged from 0.3 to 0.8, much higher than desired. With RAM solutions prepared at 7M HNO_3 , the extractability was too low to be measured by difference in the aqueous phase before and after extraction. Instead, it was necessary to use the amount of RAM found in subsequent scrub and strip solutions as a measure of the amount of extracted RAM. In such an experiment, RAM distribution coefficients of 0.02, 0.2, and 0.6 were obtained for an extraction and two scrub contacts (all with 3M HNO_3 in the aqueous phase), if all of the RAM that did extract was removed in the scrub contacts and three subsequent water strips.

EFFECT OF RAM ON OTHER ASPECTS OF PUREX PROCESS

Solutions containing RAM were used in solvent extraction tests to measure phase disengaging times, plutonium extraction and stripping behavior, and fission product extraction and scrubbing behavior. In no case was any effect of RAM observed.

In the plutonium experiment, pre-equilibrated organic phases containing 10^{-2} and 10^{-4} g/l plutonium(IV) were contacted with 3.2M HNO_3 containing 0.05M RNO_2 (from a preparation that gave $k_2[\text{RAM}]/[\text{RNO}_2] = 0.2 \times 10^4$). In each case the plutonium extraction coefficient was 18, essentially identical with that reported for pure solutions. The 10^{-2} g/l organic was then stripped three times with equal volumes of water, resulting in the removal of 99.99% of the plutonium. The RAM preparation used in this experiment exhibited abnormally high RAM extractability; a RAM extraction coefficient of 0.8 was measured in an equal volume contact in a parallel experiment.

In the fission product extraction and scrubbing experiment, plant solutions were carried through an extraction

and four equal volume scrub contacts in the absence of RAM and with RAM present ($0.015M$ RNO_2 from a preparation that gave $k_2[RAM]/[RNO_2] = 0.6 \times 10^4$). To exaggerate any effect that might occur, RAM was added to the scrub solutions as well as to the aqueous phase before extraction. Nominal phase compositions were $0.015M$ $U + 3.1M$ HNO_3 in the aqueous and $0.23M$ U in the organic. With RAM present, decontamination factors of 24,000 for ZrNb and 6,500 for Ru were obtained, essentially the same as in the absence of RAM. The RAM preparation used in this experiment exhibited low extractability; a RAM extraction coefficient of about 0.02 was measured in a parallel experiment.

COMMENTS ON IDENTITY OF RAM

Conversion of 1-nitropropane to the aci-form before reaction with HNO_3 was found to be required for the formation of RAM; simple addition of 1-nitropropane itself to an HNO_3 - HNO_2 solution of neptunium(V) had no effect on the oxidation rate. Since RAM was not obtained from the aci-form of 2-nitropropane or 2-nitrobutane, it appears that the preparation of RAM occurs only with primary nitroalkanes.

Reactions known to occur when a solution containing the aci-form of a primary nitroalkane is acidified are as follows:

Reaction (a), conversion to the true nitroalkane, is favored at low acidity and low temperatures⁽⁴⁾ and is thus not likely to occur to any great extent under the conditions of RAM preparation. Stronger acid and higher temperature favor reaction (b), the Nef reaction, giving an aldehyde and nitrous oxide. The mechanism of this reaction is apparently quite complex and poorly understood,⁽⁴⁾ even in the absence of nitrite. In the presence of nitrite, the reaction is probably even more complex though nitrolic acids are known to be obtained at low temperatures.⁽⁵⁾

The reaction products shown here are, with the exception of the nitrolic acid, only those of relatively high stability. Based on the observed sensitivity of RAM formation to the preparative conditions, it is felt that RAM is an intermediate in, or a by-product of, one or more of these reactions.

Several qualitative observations regarding RAM may be of interest. When RAM was obtained in good yield, the reactor solution invariably was blue or purple in color; attempts to correlate the intensity of the color with the concentration of RAM were, however, unsuccessful. Another point of possible interest is that neutralization of a RAM solution to a pH of ten resulted in its destruction. Also, RAM was not extracted into chloroform and, as mentioned earlier, was not destroyed by sulfamic acid. In addition, RAM was apparently not consumed by reaction with the neptunium(V).

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