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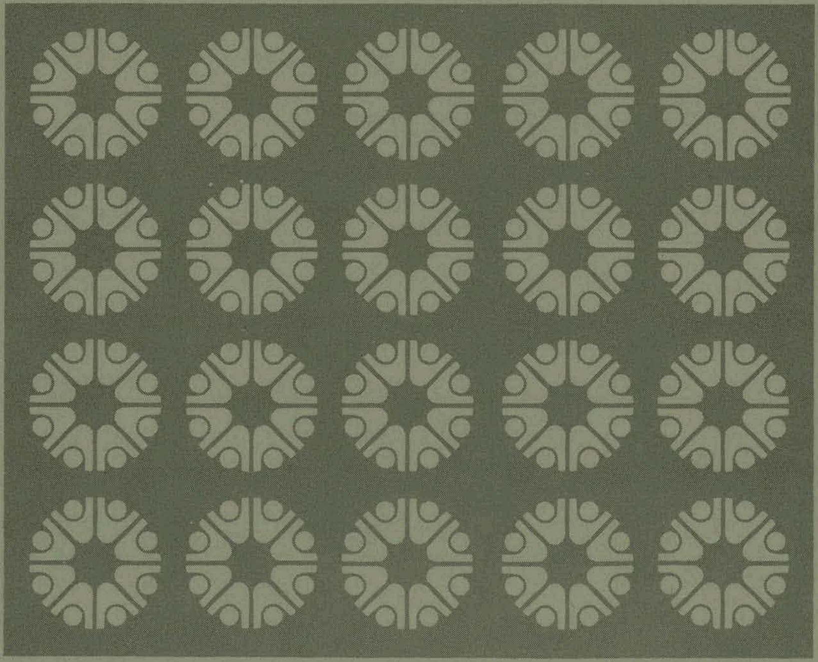
AUGUST 1971



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BNWL-B-121

DESTRUCTION OF NITROUS ACID AND HYDRAZOIC ACID IN PUREX SYSTEMS

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August 1971

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J. L. Swanson

INTRODUCTION

In the Purex process for the recovery and purification of uranium and plutonium, separation of the plutonium from the uranium is generally accomplished by reducing plutonium(IV) to plutonium(III), which is virtually inextractable. This reduction step is performed in the presence of a "holding reductant" which is added to react with nitrous acid and thus prevent reoxidation of the plutonium. Sulfamic acid has proven to be a very successful holding reductant but the fact that it is converted to sulfuric acid is detrimental. Because hydrazine also reacts rapidly with nitrous acid and does not form corrosive reaction products, it has seen increasing use as a holding reductant.

The reaction of hydrazine with nitrous acid is known to produce hydrazoic acid under certain conditions. Although hydrazoic acid can form explosive compounds or mixtures under appropriate conditions, the probability of this occurring in the Hanford plant as normally operated is extremely minute. However, means of minimizing its formation and/or safely destroying that which does form were desired as a precautionary measure. An additional goal was to accomplish this by methods suitable for use in existing equipment and which would add little or no salts to the waste stream.

SUMMARY

Most of the hydrazoic acid formed in the Purex process will be present in the organic phase until it is removed as azide ion by the carbonate wash in the organic recovery process. The destruction of the azide ion in the carbonate solution can be accomplished by platinum-

catalyzed hydrazine reduction. Azide destruction can be accomplished in several ways in acid solution; the most promising method for use at Hanford is the reaction with permanganate following acidification of the mixed permanganate-carbonate solvent wash solution.

Elimination of nitrous acid from the organic stream fed to the partition column (the 1BXF solution) would markedly reduce if not eliminate hydrazoic acid formation in the 1BX column. Several ways of accomplishing this were demonstrated; the most promising method for plant application is the reaction with hydroxylamine before the organic stream is fed to the column.

RESULTS AND DISCUSSION

Nitrous acid reacts with hydrazine to form hydrazoic acid

$$HNO_2 + N_2H_4 = HN_3 + 2H_2O. \qquad (1)$$

Nitrous acid also reacts with hydrazoic acid

$$HNO_2 + HN_3 = N_2O + N_2 + H_2O \qquad (2)$$

so that the overall reaction with an excess of nitrous acid is

$$2HNO_2 + N_2H_4 = N_2O + N_2 + 3H_2O. \qquad (3)$$

With a sufficient excess of hydrazine, however, reaction (2) is unimportant and essentially quantitative conversion of nitrous acid into hydrazoic acid occurs.(1) Quantitative conversion of nitrous acid into hydrazoic acid is also aided by the presence of a tributyl phosphate (TBP) phase, which extracts hydrazoic acid and thus decreases the possibility of reaction (2) occurring.

The use of hydrazine as a holding reductant in a Purex process partition column (1BX column) thus presents an ideal situation for quantitative conversion of nitrous acid into hydrazoic acid in that there is both an excess of hydrazine and an organic phase to extract the hydrazoic acid as it forms. A reduction in the amount of nitrous acid fed to the 1BX column would result in a corresponding reduction in the amount of hydrazoic acid formed in this column.

DESTRUCTION OF NITROUS ACID IN 1BXF SOLUTION

The organic feed solution to the 1BX column in the Hanford Purex plant contains not only the organic product from the first extraction column but also organic streams recycled from several other process steps. This solution, called 1BXF, contains nitrous acid from three sources; that present in the feed to the first extraction column (the HA column), that added to the HA column to improve neptunium recovery, and that added to the feed to the third plutonium cycle in excess of the amount required to react with the plutonium(III) and reductants present in the product of the second plutonium cycle. Destruction of the HNO_2 present in this solution before it is fed to the 1BX column would markedly reduce (if not eliminate) the formation of hydrazoic acid.

One way of destroying the nitrous acid present in the 1BXF before it is fed to the 1BX column is to contact the 1BXF with an aqueous phase containing a material which reacts with nitrous acid. With the present equipment, aqueous solutions added to the 1BXF tank accompany the organic solution into the 1BX column; the volume of aqueous phase must therefore be kept small.

With hydrazine as the reactant, rapid reaction occurred but hydrazoic acid was formed unless the quantity of hydrazine was limited to one-half mole per mole HNO_2 or less. With less than one-half mole hydrazine per mole HNO_2, complete reaction of the HNO_2 cannot be accomplished. Thus for complete reaction of the HNO_2 without hydrazoic acid formation, the precise stoichiometric amount of hydrazine must be used. Data showing yields of hydrazoic acid at various hydrazine to HNO_2 ratios are given in Table 1.

With hydroxylamine as the reactant, slower reaction of the HNO_2 was observed. In an experiment similar to those in Table 1, only 68% of the HNO_2 reacted in five minutes when an organic phase was contacted with 0.02 volumes of 0.2$\underline{M}$ hydroxylamine (giving a hydroxylamine to HNO_2 mole ratio of 3.5). Other evidence that hydroxylamine reacts more slowly with HNO_2 than does hydrazine was obtained by contacting simulated 1BXF with an aqueous phase containing equal concentrations of hydrazine and hydroxylamine. Nearly all of the HNO_2 was converted to HN_3, demonstrating that the HNO_2 reacted with the hydrazine in preference to the hydroxylamine. While the hydroxylamine reaction is considerably slower than the hydrazine reaction, it should still be sufficiently rapid to react with all the HNO_2 in the 1BXF (the temperature of the solution in the 1BXF tank is about 50 °C and the average residence time is about one hour).

TABLE I. Hydrazoic Acid Yields

Conditions: Simulated 1BXF solution contacted with aqueous phase for one minute at ∿23 °C

HNO_2 in organic initially, M	mole N_2H_4 / mole HNO_2	In organic after contact, M		Percentage of HNO_2 converted to HN_3
		HNO_2	HN_3	
0.0012	0.56	N.D.(1)	0.00009	7
0.00044	0.76	N.D.	0.00017	38
0.013	43	N.D.	0.013	100

(1) N.D. indicates none detected.

With urea as the reactant, much slower reaction of the HNO_2 was observed, as shown in Figure 1. These data were obtained in the absence of light in stainless steel equipment, with stirring just sufficiently vigorous to suspend droplets of the aqueous phase in the organic phase. The urea reaction appears to be too slow to be of much value.

Hydrogen peroxide rapidly oxidizes HNO_2 to nitric acid. The addition of H_2O_2 to 1BXF would necessitate strict control, however, since any excess would consume reductant in the 1BX column. Since H_2O_2 extracts appreciably into 30% TBP-NPH (normal paraffin hydrocarbon), the peroxide could be added to the 1BXF tank as an organic solution if desired. Peroxide distribution coefficients of about 0.1 were measured from dilute HNO_3 solutions.

Nitrous acid is unstable in acid solution, especially when gaseous products are removed to shift the equilibria in the desired direction.

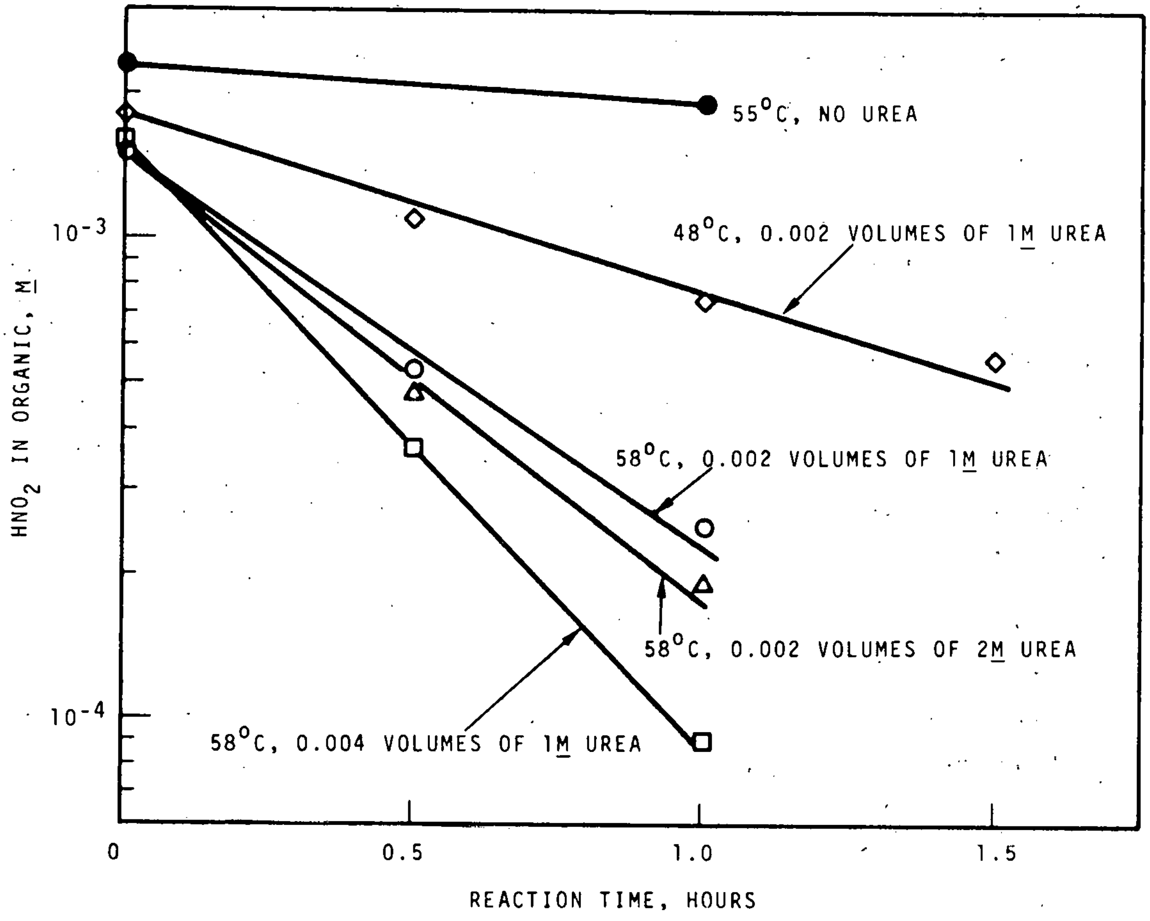

FIGURE 1. DESTRUCTION OF HNO_2 IN 1BXF WITH UREA

Two such reactions are

$$2HNO_2 = NO + NO_2 + H_2O \qquad \text{and}$$

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O.$$

The results of experiments in which air was bubbled into or swept over simulated 1BXF solutions are presented in Figure 2. The rate of HNO_2 decomposition increased with increasing air sparge rate but at a reasonable sparge rate decomposition was not very rapid. These data were obtained with the solution being stirred in a stainless steel beaker simulating the 1BXF tank; perhaps more rapid decomposition would occur if the gas-liquid contact were more efficient (as in a packed column).

Another possibility for reducing the concentration of HNO_2 in 1BXF is that of photochemical reduction of the HNO_2. Nitrous acid was observed to be much more stable in 1BXF in the absence of light than on exposure to the normal fluorescent lighting of the laboratory. A few scouting experiments were performed with ultraviolet lamps but no marked effect was observed. One possible complication is that HNO_2 can be formed by photochemical reduction of nitric acid as well as being destroyed by photochemical reduction.

The HNO_2 added to the 1BXF in the recycle organic stream from the third plutonium cycle (3BW) is normally only a small fraction of the total present. Destruction of the HNO_2 in the stream would, however, prevent significant increase in the HNO_2 content of 1BXF in the event of an exceptionally large addition of $NaNO_2$ to the solution fed to this cycle.

Data on the rate of removal of HNO_2 from simulated 3BW by contacting with aqueous phases containing various reactants are shown in Figure 3. Very rapid removal of HNO_2 occurred with hydrogen peroxide or hydrazine; very slow removal occurred with urea or hydroxylamine. Addition of nitric acid gave more rapid reaction with hydroxylamine or peroxide (the only two tested at higher acidities). As before, hydrazoic acid was formed when using hydrazine.

DESTRUCTION OF HYDRAZOIC ACID

Since hydrazoic acid is quite highly extractable,(2) most of that

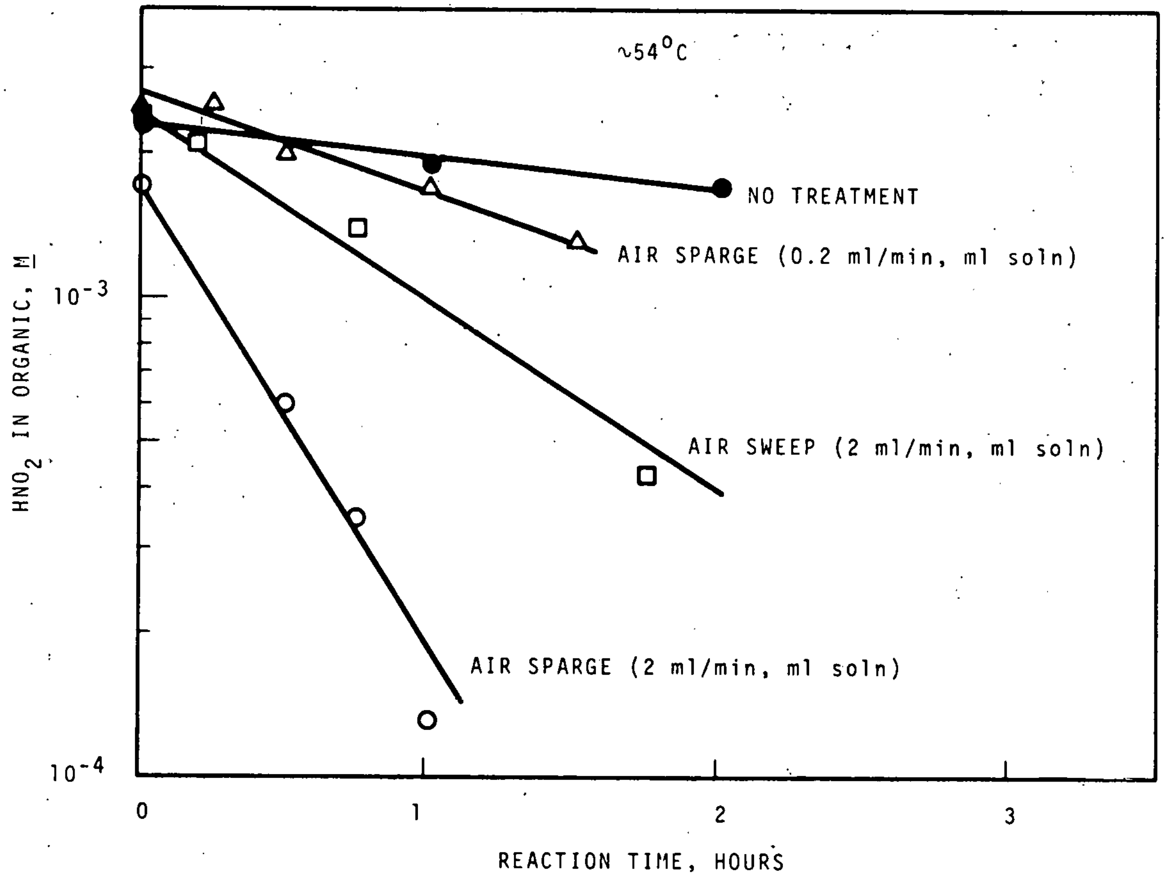

FIGURE 2. EFFECT OF AIR ON HNO_2 DECOMPOSITION

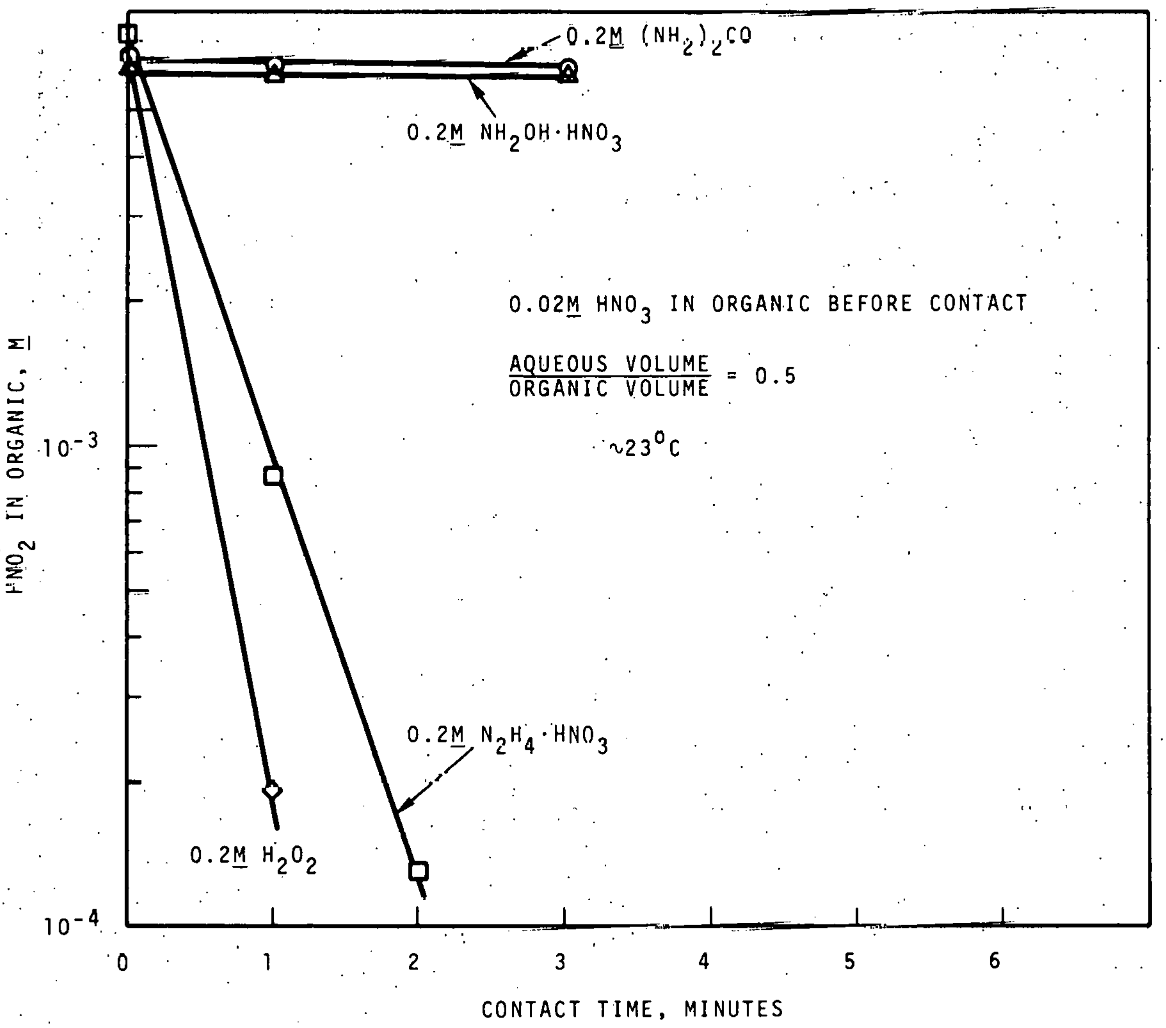

FIGURE 3. DESTRUCTION OF HNO_2 IN SIMULATED 3BW

formed in the 1BX column will leave the column in the organic phase and remain in the organic when the uranium is stripped out in the 1C column. The hydrazoic acid will be neutralized and stripped from the organic phase during the carbonate wash portion of the organic recovery process. Means of treating this solution to destroy the azide were investigated.

When the carbonate solution used to wash the solvent contains permanganate and manganese dioxide, as it does at Hanford, the azide can be destroyed by simply acidifying the solution. While reaction of permanganate or MnO_2 with azide ion occurs slowly if at all in carbonate solution, it occurs relatively rapidly in acid solution. No azide was found after one minute (at ∿23 °C) in a $0.1\underline{M}$ HNO_3 solution initially containing $0.015\underline{M}$ $KMnO_4$ and $0.04\underline{M}$ NaN_3. Reaction of hydrazoic acid with freshly prepared MnO_2 was found to be slower than the reaction with permanganate. When solutions initially $0.01\underline{M}$ in HN_3 were stirred with 0.75 mole MnO_2/mole HN_3 at ∿23 °C for five minutes, 60% of the HN_3 was destroyed when the HNO_3 concentration was $0.1\underline{M}$, 90% was destroyed in $0.3\underline{M}$ HNO_3, and 100% was destroyed in $1\underline{M}$ HNO_3.

When the solvent wash solution does not contain permanganate, destruction of the azide can be accomplished by adding sodium nitrite and then acidifying. The reaction

$$HN_3 + HNO_2 = N_2O + N_2 + H_2O$$

is very rapid in aqueous acid solution.

Other ways of destroying hydrazoic acid (in acid solution) and sodium azide (in sodium carbonate solution) were also studied. Hydrazoic acid is thermodynamically unstable with respect to its decomposition into nitrogen and ammonia

$$3HN_3 = 4N_2 + NH_3$$

and catalysis of the decomposition by platinum has been reported.$^{(3)}$ This catalysis was verified but the decomposition was still not very rapid; when 50 ml of $0.01\underline{M}$ HN_3 in $0.3\underline{M}$ HNO_3 was stirred in contact with 5 grams of 0.5% Pt on alumina pellets, the HN_3 disappeared with a half-time of about 20 minutes at ∿55 °C. Platinum-catalyzed decomposition of organic-phase hydrazoic acid was also observed but it also was not especially rapid.

The platinum-catalyzed hydrazine reduction of hydrazoic acid in nitric acid solution was found to be more rapid than the platinum-catalyzed decomposition of hydrazoic acid; with the conditions described above the addition of 0.02$\underline{M}$ $N_2H_5NO_3$ increased the rate of hydrazoic acid disappearance by a factor of about five, giving a half-time of about 4 minutes. Increasing the hydrazine concentration to 0.2M did not further increase the rate, however.

Platinum was also found to catalyze the hydrazine reduction of azide in sodium carbonate solution. The rate in 0.05$\underline{M}$ Na_2CO_3 was about the same as in 0.3$\underline{M}$ HNO_3 and was also independent of hydrazine concentration. This reaction provides a means of destroying azide ion without acidifying the solvent wash solution. Presumably the azide ion is reduced to ammonia in this reaction.

EXPERIMENTAL

Concentrations of hydrazoic acid were determined spectrophotometrically using the highly colored ferric azide complex.(4) Reactant mixtures often had to be treated before analysis to prevent reaction in the analytical solution. For example, organic phases containing both nitrous acid and hydrazoic acid were contacted with sulfamic acid to destroy the nitrous acid before the hydrazoic acid was stripped into carbonate solution and then acidified for analysis. Also, hydrazoic acid-permanganate mixtures were added to stirred mixtures of 30% TBP, HNO_3, and H_2O_2 to destroy the permanganate and extract the hydrazoic acid, which was then stripped from the organic and analyzed.

Nitrous acid concentrations were also determined spectrophotometrically. Uranium was stripped from the organic samples with 1:1 H_3PO_4 to avoid interference.

The simulated 1BXF used here was prepared by contacting three volumes of 30% TBP-NPH with one volume of 0.72<u>M</u> U in 4<u>M</u> HNO_3. The resultant organic phase contained about 0.24<u>M</u> U and 0.3<u>M</u> HNO_3.

ACKNOWLEDGEMENT

It is a pleasure to acknowledge the able assistance of Mrs. Doris M. Meier, who performed the bulk of the experimental work. Many helpful discussions with Mr. G. E. Benedict of the Atlantic Richfield Hanford Company are gratefully acknowledged.

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