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A Review of Recent ORNL Studies in Solvent Cleanup  
and Diluent Degradation\*

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## SUMMARY

The testing of solvent cleanup methods to replace the use of sodium carbonate in the Purex process has been ongoing for several years in the Consolidated Fuel Reprocessing Program. The incentive for such improved processes is to reduce the quantity of waste sodium nitrate generated and to improve phase separation behavior in the solvent scrubber. Alternate solvent cleanup methods which accomplish these goals include the use of packed columns of base-treated silica gel or solvent scrubbing with hydrazine oxalate. In related studies, the degradation of the diluent was shown to generate, among other products, long-chain organic acids. These acids appear to be the major culprits in the phase separation problems encountered in sodium carbonate scrubbers; reactions between sodium carbonate and the long-chain acids generate soaps. Solvent scrubbing with hydrazine oxalate avoids the formation of soaps and gives improved phase separations. Solvent cleanup in columns packed with base-treated silica gel avoids the phase separation problem since a dispersible aqueous phase is not present. Removals of TBP degradation products and metal-ion complexes by sodium carbonate, hydrazine salts, or by packed beds of base-treated silica gel are all satisfactory.

Solvent scrubbing by hydrazine oxalate solutions is the prime candidate for solvent cleanup in fuel reprocessing plants. A demonstration of the solvent cleanup system and disposal of spent cleanup solution in equipment which can be scaled up is necessary. Columns packed with base-treated silica gel are a viable option in small demonstration facilities.

## INTRODUCTION

Most existing and planned reactor fuel reprocessing plants use the Purex solvent extraction process for recovery of fissionable materials from spent fuel elements. The process consists in dissolution of the oxide fuel in nitric acid to yield a solution containing about 200 g of heavy metals per liter in 3 or 4  $M$   $HNO_3$ . This is then extracted using a 6 to 30 vol% solution of tri-n-butylphosphate (TBP) in a normal, saturated hydrocarbon, commonly referred to as normal paraffin hydrocarbon (NPH). The uranium and plutonium are preferentially extracted into the organic phase and are then separated from extractable fission products by combinations of various acid scrubbing, stripping, and re-extraction steps. The TBP and NPH used in these processes are degraded by radiation damage and by hydrolytic and nitrolytic reactions with nitric and nitrous acids to form many products including acidic degradation products from the TBP and carboxylic acids, esters, and many other compounds from the diluent. The degradation products tend to accumulate in the organic phase and degrade the performance of the process both by changing the interfacial tension of the aqueous-organic systems (leading to a greater tendency to form stable emulsions) and by forming complexes with actinides and fission products which degrade the separation performance of the process. An integral part of the Purex process is a solvent scrubbing step for removal of these degradation products. Most processes in use or proposed utilized an aqueous scrubbing system which is basic and which contains anions which will complex the cations stripped from the organic phase to prevent precipitation of hydroxides. Proposed aqueous scrubbing systems include sodium carbonate, hydrazine carbonate (1), and hydrazine oxalate (2). The basic nature of these scrubbing solutions allows removal of the short-chain organic acids which are formed by degradation of TBP, dibutylphosphoric acid (HDBP) and monobutylphosphoric acid ( $H_2MBP$ ), through formation of aqueous-soluble salts. Processes using solid sorbents have also been proposed including macroreticular resins (3,4), hydrous titanium dioxide (5), and lead dioxide on silica gel (1). A new "solid sorbent" developed at ORNL (6) is silica gel which

has been treated with a strong base and possesses a strongly basic adsorbed water layer. Except for the lead dioxide solid, all the solid sorbents mentioned act as bases to effect removal of the acidic degradation products and are thus similar, in principle, to the aqueous scrubbing systems. Longer-chain organic acids, such as those formed by degradation of the hydrocarbon diluent and those formed by secondary reactions between the TBP degradation products and the diluent degradation products such as butyllarylphosphoric acid (HBLP) (7,8) are not effectively removed by standard scrubbing systems due to the significant organic solubility of their sodium salts (9).

Wastes from the solvent scrubbing system may require special treatment, especially in the case of the hydrazine salts. Hydrazine reacts rapidly with an excess of nitrous acid to give innocuous gaseous products, but with lesser amounts of nitrous acid it forms hydrazoic acid. Hydrazoic acid is explosive, and it can react to form explosion-sensitive metal azides. Disposal requires either reaction with an excess of nitrous acid, as proposed by the CFRP, or electrolytic decomposition, as originally proposed by German workers (10).

Although past workers have recognized the possible contribution of secondary degradation products such as HBLP to the deterioration of the phase separation and separation behavior of the Purex system, little attention has been given to the significant degradation of these properties by the simple long-chain carboxylic acids. Since these compounds are primary degradation products of the diluent, they would be expected to be more prevalent than secondary degradation products such as HBLP. Our recent studies suggest that long-chain carboxylic acids may be responsible for a large fraction of the problems found in the Purex process which are not readily controlled by the standard solvent-scrubbing systems.

This paper summarizes the work conducted at ORNL in the areas of solvent cleanup and diluent degradation. Included is information on the use of hydrazine oxalate and base-treated silica gel for solvent cleanup, disposal of hydrazine oxalate by reaction with nitrous acid (disposal of hydrazine) followed by either reaction of nitric acid with the oxalate or

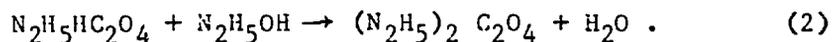
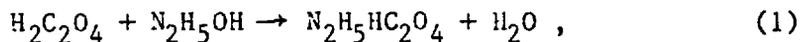
reaction with  $\text{HNO}_3\text{-H}_2\text{O}_2$ , disposal of hydrazine oxalate by electrolytic decomposition, and studies of acid degradation of the diluent and the effects of the diluent degradation products on solvent extraction operations. This discussion will not address economic evaluation of the process options or process engineering aspects.

### SOLVENT CLEANUP USING HYDRAZINE OXALATE

#### Preparation

Hydrazine oxalate,  $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$  solutions are prepared either by mixing aqueous solutions of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) and hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) or by dissolving solid oxalic acid in aqueous hydrazine hydrate solutions. The pH of the solutions ranged from 6.1 to 7.0 depending on concentration. A hydrazine hydrogen oxalate compound ( $\text{N}_2\text{H}_5 \cdot \text{HC}_2\text{O}_4$ ) of limited solubility can also be formed. However, formation of this compound is avoided where the hydrazine/oxalate mole ratio is  $\geq 2.0$ .

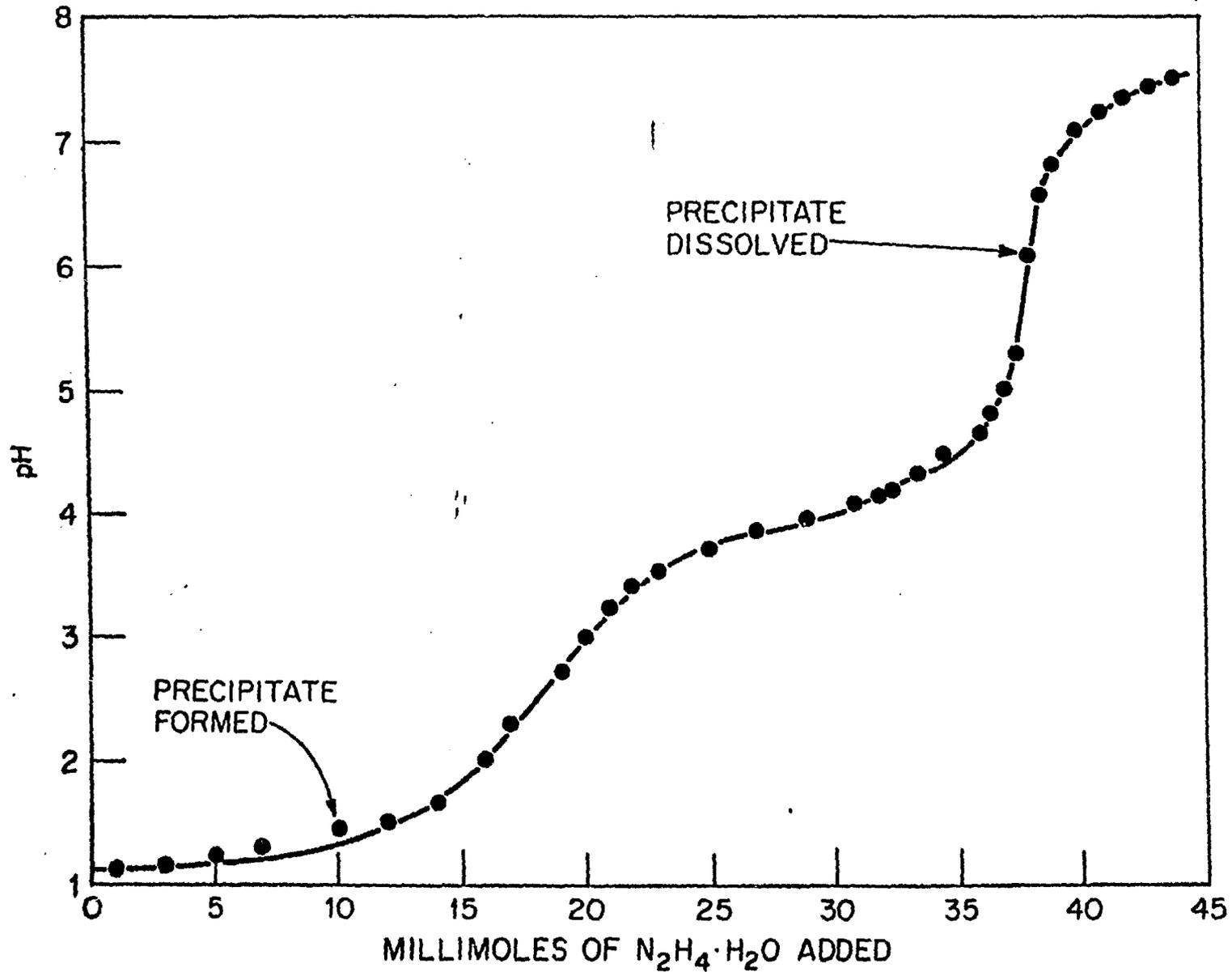
Hydrazine hydrogen oxalate and hydrazine oxalate are formed by acid-base type reactions as follows:



The formation of  $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$  (Eq. 1)) and  $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$  (Eq. (2)) is indicated by equivalence points at pH 3 and 6, respectively, on the titration curves shown in Fig. 1.

#### Solution Stability

No instability of hydrazine oxalate solutions was observed during the studies. The concentrations of hydrazine oxalate in solutions which had been allowed to stand for six months at room temperature remained



TITRATION OF 40 mL OF 0.475 M OXALIC ACID WITH 1.0 M HYDRAZINE HYDRATE SOLUTION AT 25 °C

unchanged. The pH of 2.0 M hydrazine oxalate solutions with a slight excess of hydrazine hydrate remained unchanged at 7.85 after the solution had been sealed in glass bottles and heated at 40°C for seven days, then cooled to room temperature. Hydrazine carbonate solutions are also under consideration for use as solvent cleanup washes, even though they are much less stable than hydrazine oxalate solutions. Under normal conditions, the carbonate solutions decompose significantly (11) in <24 h, producing carbon dioxide gas and oxidizing the hydrazine component, with a resultant change in the pH. The superior stability of hydrazine oxalate solutions appears to be an advantage in solvent cleanup processes.

#### Solvent Cleanup Tests

Hydrazine oxalate was found to have a distribution coefficient from 0.2 M hydrazine oxalate (pH of 6.8) to 30% TBP-NPH of only about 0.007. The small amount extracted was easily removed by a water scrub.

Solvent cleanup tests were conducted both with irradiated and with chemically degraded, unirradiated solvents. Chemically degraded solvents containing solvent degradation products complexed with uranyl and zirconium ions were prepared by refluxing 30% TBP-70% NPH with equal volumes of 3.0 M HNO<sub>3</sub>, 2 mg/mL UO<sub>2</sub><sup>2+</sup>, or 2 mg/mL Zr<sup>4+</sup> for 7 h at 100°C in glass flasks fitted with glass cooling condensers. After refluxing, the organic phases were separated and equilibrated five times with equal volumes of 0.01 M HNO<sub>3</sub> solutions to strip uranyl or zirconium ions complexed with TBP and leave ions complexed with DBP and MBP. Finally, the solvents were filtered through a fine glass frit, sampled, and analyzed for uranium or zirconium by x-ray fluorescence (12) and for DBP and MBP by liquid chromatography (13). The solvents were found to contain ~1.8 mg/mL uranium or ~0.1 mg/mL zirconium plus 4 mg/mL DPB.

Three sets of experimental conditions were used in tests of the chemically degraded solvents. Tests to compare the solvent cleanup effectiveness of hydrazine oxalate with that of sodium carbonate solutions were conducted by equilibrating 0.2 M solutions of the salts with

equal volumes of the standard degraded solvents for 30 min at room temperature. After equilibration, the separated phases were sampled and analyzed for  $\text{UO}_2^{2+}$  (or  $\text{Zr}^{4+}$ ), DBP, and MBP. Tests to determine the effect of hydrazine oxalate concentration were conducted under these same conditions except that various concentrations of hydrazine oxalate (0.246 to 0.008 M) and hydrazine hydrate (0.17 to 0.006 M) were used in the wash solution. Tests to determine the effect of wash solution pH were conducted using a 0.668 M hydrazine oxalate-0.176 M hydrazine hydrate stock solution. This solution was contacted with equal volumes of chemically degraded solvent in a consecutive series of 10-min equilibrations. Between equilibrations, samples of each phase were taken and 0.5 M  $\text{HNO}_3$  was titrated into the remaining aqueous phase to lower the pH, in increments of 0.5, from 8.0 to 3.0. The samples were analyzed for DBP, MBP, and uranium or zirconium.

Similar testing was done with an irradiated solvent that had been contacted with H. B. Robinson-2 dissolver solution in a mixer-settler at the ORNL Transuranium Processing Plant. The plutonium had been reductively stripped from the solvent with nitrous acid reductant (14), leaving significant quantities of uranium in the solvent. That solvent was sampled, filtered through a fine glass frit, resampled, stripped four times with equal volumes of 0.01 M  $\text{HNO}_3$ , and sampled a third time. The treatment removed any suspended material and the easily stripped uranium. Aliquots of the solvent were equilibrated for 20 m with two equal volumes of 0.2 M hydrazine oxalate, 0.25 M sodium carbonate, or 0.25 M hydrazine carbonate wash solution, after which both phases were sampled. These samples, along with samples of the initial solvent, were analyzed for uranium, gross alpha activity, and sometimes,  $\text{H}^+$  concentration. The samples were not directly analyzed for DBP and MBP; however, the plutonium retention properties (4) in the washed solvents were determined by tests in which 5-mL aliquots of each solvent were equilibrated with one drop of 0.25 M Pu -1.0 M  $\text{HNO}_3$  solution, washed twice with equal volumes of 0.01 M  $\text{HNO}_3$  solution, and sampled for gross alpha activity.

## Results and Discussion

The uranium concentration in chemically degraded solvent was decreased from 1.8 mg/mL to about 0.001 mg/mL when the solvents were contacted with equal volumes of either 0.2 M  $\text{Na}_2\text{CO}_3$  or 0.2 M hydrazine oxalate wash solutions. Similarly, the zirconium concentration in the solvents was decreased from 0.109 to about 0.01 mg/mL by each wash solution. Typically, the concentration of DBP in solvents containing either of the metal ions was decreased from about 20 to <0.5 micromol/mL. The concentrations of MPB in the washed solvents were less than the  $1 \times 10^{-5}$  micromol/mL limit of detection for the liquid chromatographic analytical method (13). These results indicate that hydrazine oxalate and sodium carbonate wash solutions are equally effective in removing degradation products and complexed metal ions.

It was observed that phase separations were about twice as fast with hydrazine oxalate as with sodium carbonate wash solutions. This is because the degradation of the diluent creates long-chain organic acids which react with the sodium carbonate to form soaps which, in turn, cause the observed phase separation difficulties. Diluent degradation will be discussed later. The hydrazine oxalate solutions do not form soaps and do not show any decline in phase separation behavior.

The cleanup effectiveness of hydrazine oxalate solutions increases with concentration as is shown in Table 1. The uranium concentrations in the washed solvent were changed only slightly by uranium retention tests (Table 1) indicating that the DBP was removed as effectively as the uranium.

The removal of uranium and DBP is, for practical purposes, quantitative over the pH range of 8.0 to 4.0 as is shown in Fig. 2. The apparent constant levels of unstripped uranium and DBP probably represent the analytical limits in this system; removals likely continue to improve at higher pH values. Even though the wash solution is effective to pH 4, the capacity of the solution to react with nitric acid at pH <6.5 is

Table 1. Effect of reagent concentration on uranium retention in washed solvent<sup>a</sup>

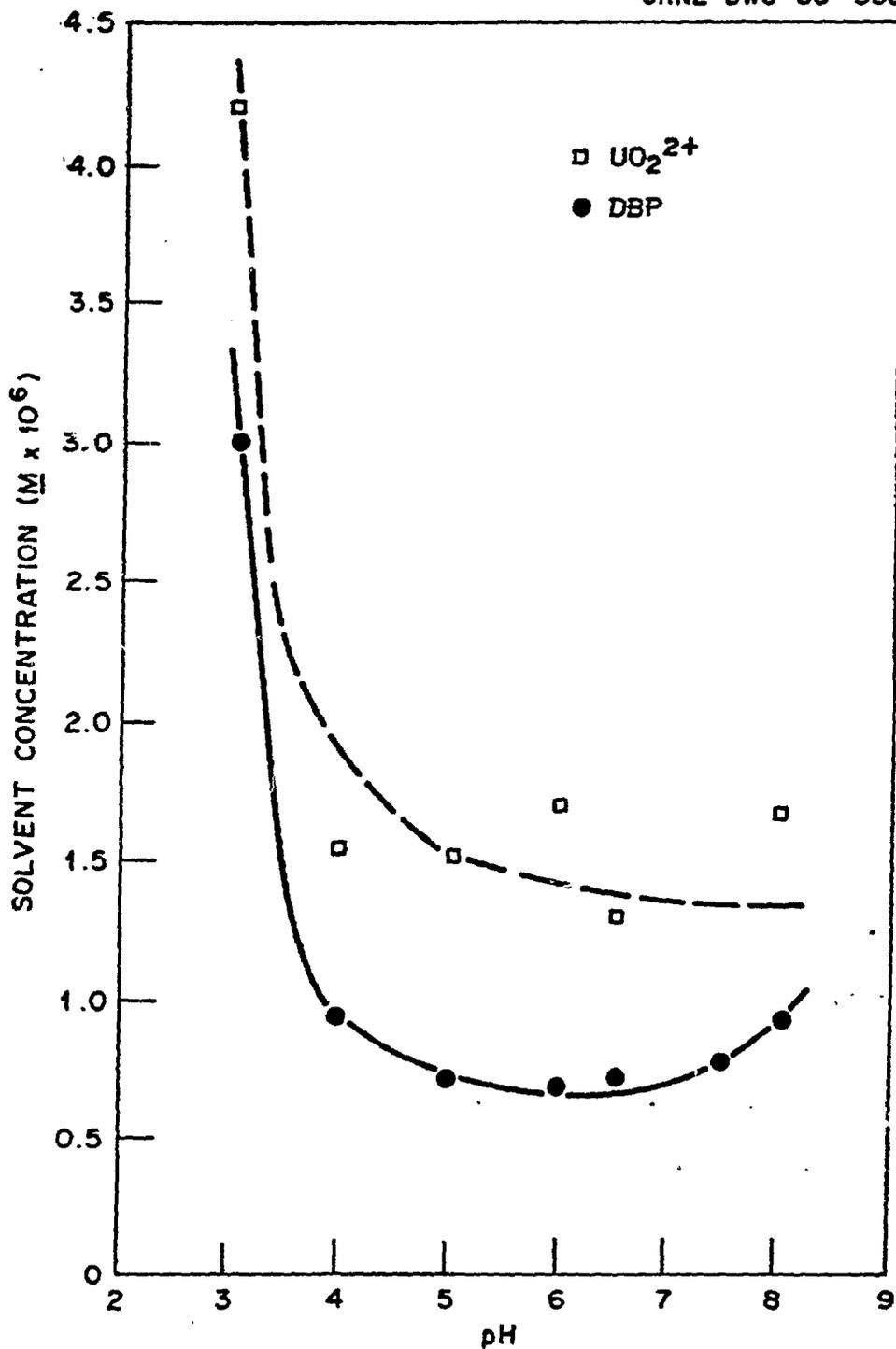
Wash reagent <sup>b</sup>		Uranium concentration	
(N <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> concentration (M)	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O concentration (M)	After washing <sup>c</sup> (mg/mL)	After retention test <sup>d</sup> (mg/mL)
0.041	0.029	0.520	0.441
0.065	0.058	0.096	0.119
0.162	0.116	0.010	0.010
0.246	0.176	<0.010	<0.001

<sup>a</sup>Feed solvent contained 30% TBP, ~70% NPH, <0.01 M H<sup>+</sup>, 1.8 mg/mL uranium, and ~4 mg/mL DBP.

<sup>b</sup>Wash solution pH varied from 6.8 to 8.0.

<sup>c</sup>Aqueous wash/organic solvent volume ratio = 1. Temperature was 25°C.

<sup>d</sup>Washed solvents were equilibrated with 2 mg/mL UO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> solution and rewashed three times with equal volumes of 0.001 M HNO<sub>3</sub> solution.



RETENTION OF  $\text{UO}_2^{2+}$  AND DBP IN STANDARD DEGRADED SOLVENT AFTER WASHING WITH  $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$  [0.16 TO 0.08 M] -  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  [0.11 TO 0.055 M] SOLUTION, pH VARIED BY  $\text{HNO}_3$  ADDITION, TEMPERATURE 25 °C

small as seen in Fig. 3 for titration of 150 mL of 0.16 M  $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4^-$  0.11 M  $\text{N}_2\text{H}_5 \cdot \text{H}_2\text{O}$  with 0.5 M  $\text{HNO}_3$ . The major factor is the presence of hydrazine hydrate which reacts with  $\text{pH} > 6.5$ .

In the tests with the irradiated solvent, any differences in the solvent cleanup effectiveness of the four wash solutions tested were small, as seen in Table 2. The sodium carbonate wash was slightly more effective in gamma activity removal (99% as opposed to 95% for the oxalate washes), while 97 to 98% of the gross alpha activity was removed in each test. The levels of gross gamma and gross alpha count in the solvent after washing were, in each instance,  $\sim 2 \times 10^3$  cpm/mL or less. The plutonium retention test, which has traditionally been regarded as a sensitive measure of the presence of dibutyl phosphoric acid (HDBP) or deleterious diluent degradation products (4), indicates  $\sim 4 \times 10^{-8}$  M equivalent HDBP in the solvent washed with hydrazine oxalate solution, if the plutonium was retained as the 1:1 complex. As with the chemically degraded solvent experiments, these results indicate that there are few significant differences in the solvent cleanup effectiveness of hydrazine oxalate, hydrazine carbonate, and sodium carbonate washes.

#### Solvent Scrubbing Kinetics

The solvent scrubbing kinetics of the uranium- and zirconium-dibutyl phosphate complexes were studied using sodium carbonate, hydrazine carbonate, and hydrazine oxalate solutions (15). The scrubbing transfer rates differed for the various species and solutions, but the zirconium-dibutyl phosphate complex, the most recalcitrant species, was scrubbed at approximately the same rate by all three solutions. This indicated that the kinetics would not be a significant factor in the choice of a solvent scrubbing solution.

#### Destruction of Hydrazine Oxalate in Spent Wash Solutions

The spent hydrazine oxalate wash solution must be disposed of in a safe manner. The major concern is to assure that hydrazoic acid or

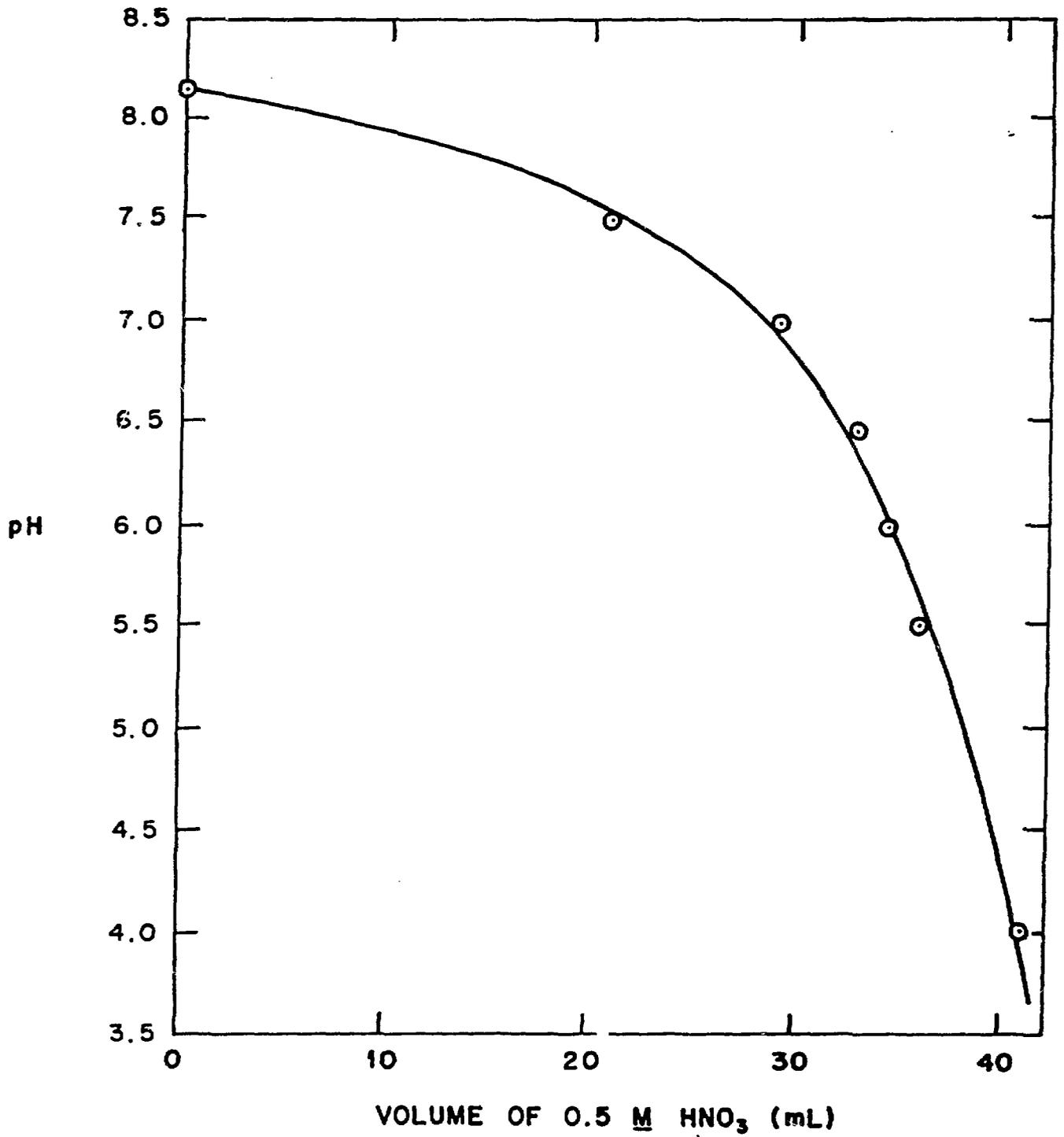


Table 2. Cleanup of irradiated solvent with hydrazine oxalate and other wash solutions

Wash solution <sup>b</sup>	Washed solvent <sup>a</sup>				Plutonium alpha retention (cpm/mL)
	Gross gamma (cpm/mL)	Removal (%)	Gross alpha (cpm/mL)	Removal (%)	
Hydrazine oxalate <sup>e</sup>	$1.7 \times 10^3$	95	$1.8 \times 10^3$	98	$1.3 \times 10^3$
Hydrazine oxalate <sup>e</sup>	$1.8 \times 10^3$	95	$2.3 \times 10^3$	98	$7.0 \times 10^2$
Sodium carbonate	$5.0 \times 10^2$	99	$3.0 \times 10^3$	97	Not determined
Hydrazine carbonate	$2.2 \times 10^3$	94	$1.7 \times 10^3$	98	Not determined

<sup>a</sup>Solvent contacted with H. B. Robinson-2 fuel solution, filtered, and stripped with 0.01 M HNO<sub>3</sub> solution, as described in Sect. 3.2.1.

<sup>b</sup>Solvents were washed with equal volumes of wash solution for 20 min at 25°C.

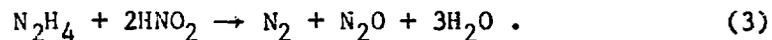
<sup>c</sup>Initial gross gamma =  $3.53 \times 10^4$  cpm/mL.

<sup>d</sup>Initial gross alpha =  $1.01 \times 10^5$  cpm/mL.

<sup>e</sup>Duplicate tests.

azides are not produced or allowed to accumulate in significant quantities. No problem is anticipated with destruction of oxalate which can be oxidized with nitric acid with or without catalysts (16,17). The two methods examined are the reaction of hydrazine with excess nitrous acid and the electrolytic destruction of hydrazine.

Destruction using nitrous acid was demonstrated by pumping simulated 1AW solution (0.25 M NaNO<sub>3</sub>-3.0 M HNO<sub>3</sub>) simultaneously with simulated spent wash solution (0.2 M hydrazine oxalate-0.1 M HNO<sub>3</sub>-0.01 M DBP-0.005 M UO<sub>2</sub><sup>2+</sup>-0.003 M Zr<sup>4+</sup>) into the bottom of a reaction column at a ratio of 29 mL of 1AW to 1 mL of spent wash solution. A 10-min plug-flow residence time was allowed in the reaction column, after which the mixed solutions were transferred from the top of the vessel into a vacuum flask. Samples of the mixed solution were withdrawn from the vacuum flask and analyzed for oxalic acid and hydrazine contents. The results showed that the hydrazine concentrations in the mixed spent wash and 1AW solutions were decreased to <=0.001 M, consistent with the occurrence of the following reaction:



A series of experiments was conducted at ORNL by D. W. Holladay examining the feasibility of destroying the hydrazine portion of the spent hydrazine oxalate wash solution by anodic oxidation as originally suggested by German workers (7, 8). These experiments will be reported fully in an ORNL/TM. In this technique the spent wash solution is first acidified using nitric acid to precipitate most of the metal ions as DBP and oxalate compounds. This acidification is also required to achieve the conductivity necessary for a practical electrolysis operation. The hydrazine is then oxidized at the anode.

The tests used a synthetic spent wash solution with a composition approximately 1.0 M N<sub>2</sub>H<sub>4</sub> (equivalent), 0.4 M C<sub>2</sub>O<sub>4</sub><sup>-</sup>, 0.05 M UO<sub>2</sub><sup>2+</sup>, 0.01 M Zr<sup>4+</sup>, 0.1 M NO<sub>3</sub><sup>-</sup>, and 0.01 M DBP. Electrode current densities were between 1 to 100 A/m<sup>2</sup>, stirring power inputs were 1400 to 11200 watts/m<sup>3</sup>,

and electrode surface areas ranged from 10 to 270 cm<sup>2</sup>. In most tests platinum electrodes were used, but in a limited number of tests a titanium cathode was used. Cell designs included cells with no separation of the electrodes, cells with a glass frit separator, and cells with a cationic exchange membrane. This latter type of cell prevented mixing of ammonium ion between the cell compartments in tests determining the source of ammonium ion.

The expected anode reactions were (1):



Under the conditions of the experiments the major product at the cathode was hydrogen with little nitrous acid produced (18). Thus, the destruction of hydrazine and formation of hydrazoic acid at the cathode should be minimal.

The current efficiency ranged from about 2 to about 3.5 faradays/mol of hydrazine destroyed; this is considerably different than the expected value of 4 (Eq. 4), and suggests that the expected reactions are not the actual mechanism. This in turn gives the possibility that hydrazoic acid may be one product. Unfortunately, the volatility of hydrazoic acid would have caused it to be lost from the warm electrolytic solutions due to the sparging action of the hydrogen and oxygen generated at the electrodes. Table 3 shows the data for the tests using separated electrode compartments. The tests using the cationic exchange membrane (Runs 27-29) show that the ammonium ion is primarily generated at the cathode and is likely not produced from hydrazine since the amount of ammonium ion produced is much greater than the small losses of hydrazine at the cathode. A single test (Run 30) indicates that the substitution

Table 3. Runs with Cation Exchange Membrane Separator

Run Number	27	29	30	31
$\text{HNO}_3$ , <u>M</u>				
Feed	3.05	3.05	3.1	7.0
Anolyte*	3.82	1.9	2.08	7.06
Catholyte*	1.06	1.29	1.34	5.7
$\text{H}_2\text{N}_4$ , <u>M</u>				
Feed	0.87	0.87	0.87	0.87
Anolyte*	0.35	0.32	0.15	0.42
Catholyte*	0.61	0.79	---	0.82
$\text{NH}_4^+$ , <u>M</u>				
Feed	0.008	0.009	0.009	0.009
Anolyte*	0.062	0.16	0.074	0.023
Catholyte*	0.588	0.386	0.138	0.21
$\text{NH}_4^+$ rate	0.0025	0.0028	0.00039	0.0063
(moles/amp.h)				
(at cathode)				

\*Concentrations at end of run.

of titanium for platinum in the cathode will reduce the formation of ammonium ion by 85% under comparable conditions. Another single test (Run 31) indicates that the formation of ammonium ion increases greatly with increasing nitric acid concentration.

#### Conclusions; Electrolytic Hydrazine Destruction

This series of electrolytic tests demonstrated that the anodic oxidation of hydrazine in spent hydrazine oxalate wash solutions is chemically feasible. From the brief examination of the effects of cathode material and acid concentration it appears that the formation of ammonium ion at the cathode could be minimized by proper choices of current density, acid concentration, and cathode material. Unanswered questions include the actual anode reactions and whether they generate hydrazoic acid. Additional studies to define the factors which control the formation of ammonium ion are needed if electrolytic destruction is to be considered. The use of nitrous acid or  $\text{NO}_x$  gas, however, appears to be straightforward and should be considered the first choice for hydrazine destruction.

#### Hydrazine Destruction by Catalyzed Reaction with Nitric Acid

Another disposal method recently tested at the Barnwell nuclear reprocessing facility (19) is to feed the spent hydrazine oxalate solution, perhaps along with a sucrose solution, into a refluxing nitric acid solution which contains either manganese or vanadium as an oxidation catalyst. In this system, the oxidizable species such as oxalate, sucrose, and part of the hydrazine are oxidized by nitric acid and generate nitrous acid. The nitrous acid will then assure that no hydrazoic acid remains after the reaction. This system has considerable merit, but needs to be examined closely to determine conditions which assure no hydrazoic acid formation and which minimize ammonium ion formation (20).

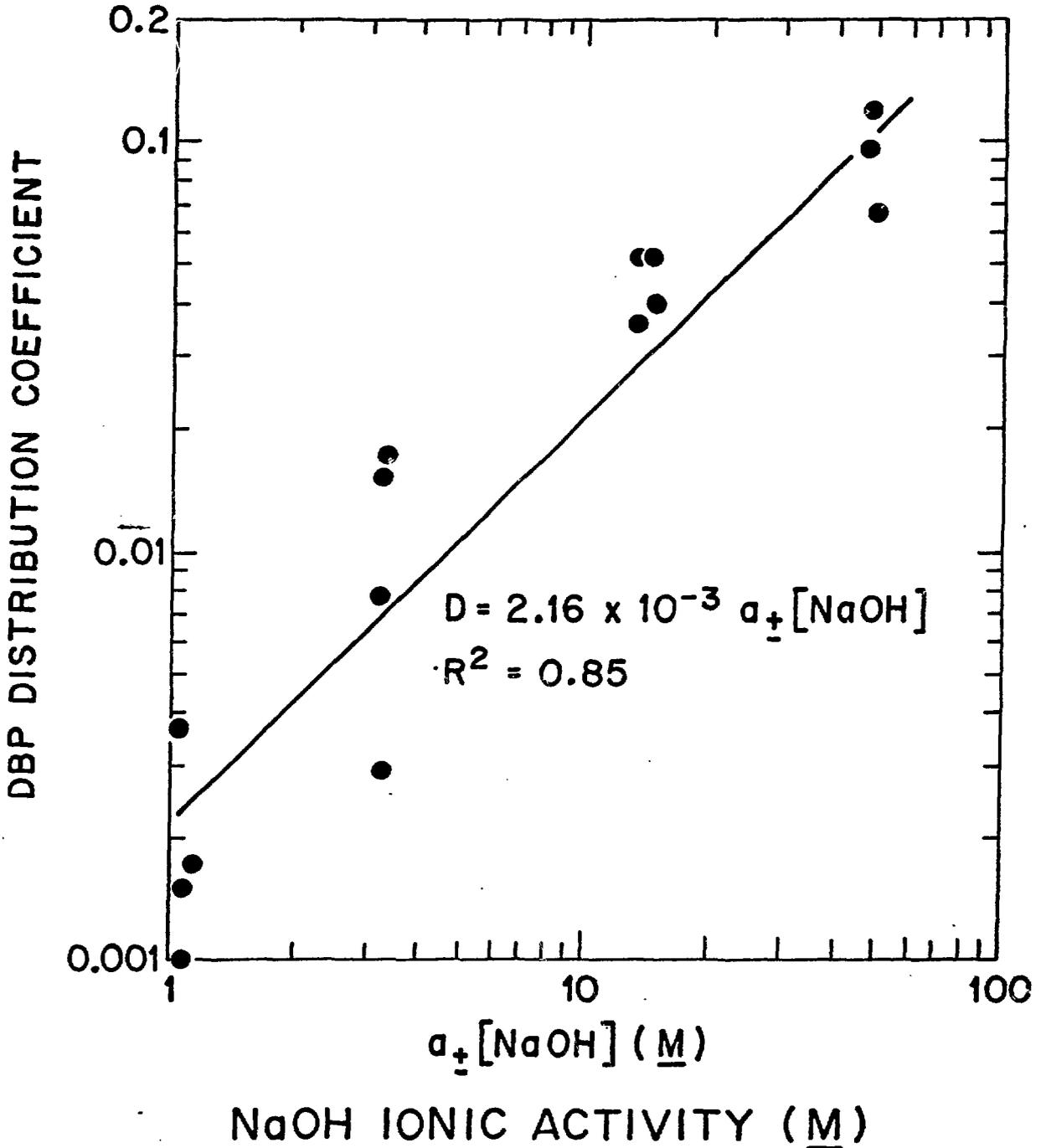
SOLVENT CLEANUP USING BASE TREATED SILICA GEL

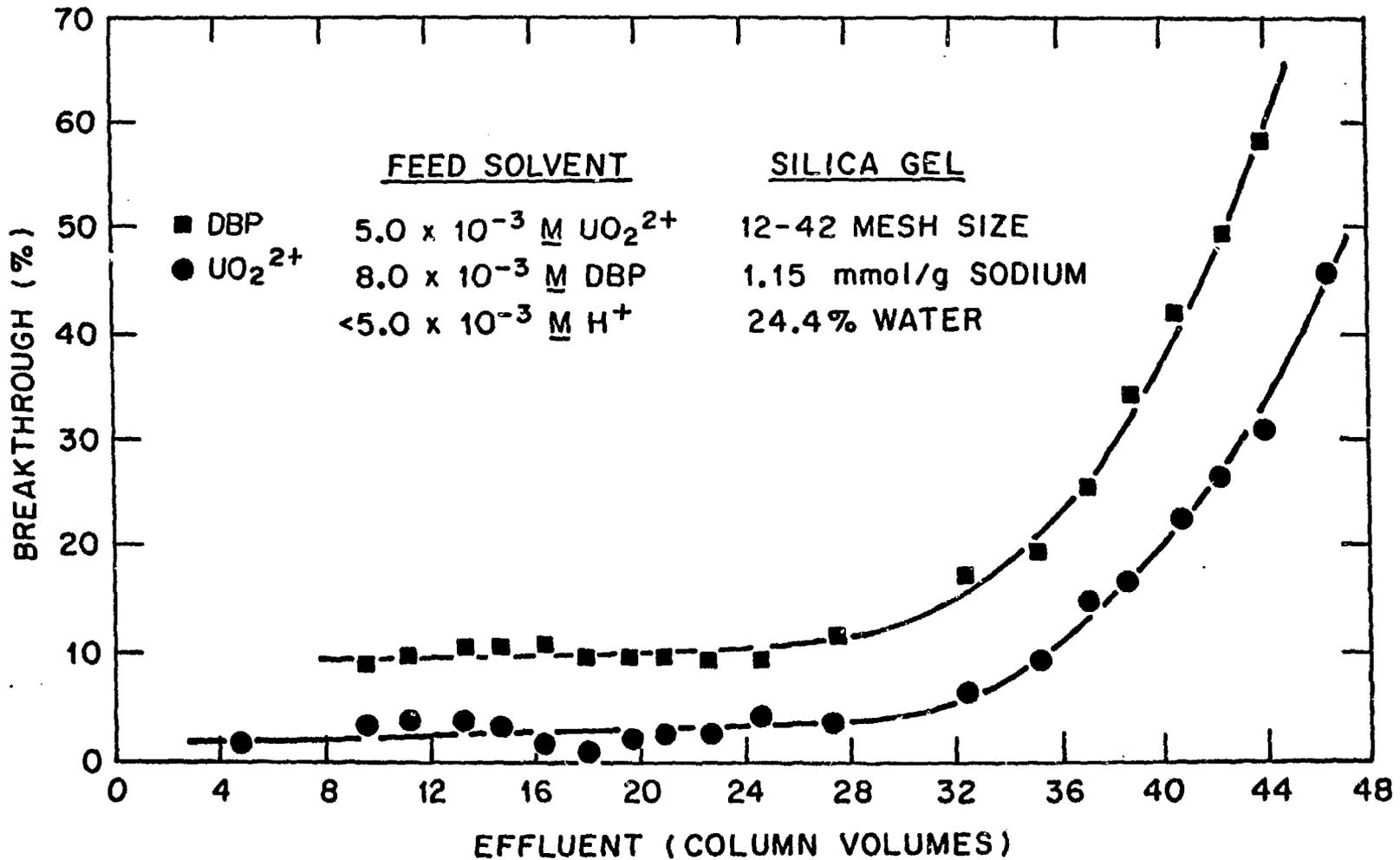
Solid sorbents have been considered in the past for use in solvent cleanup principally aiming at simplification of the solvent cleanup operations. Among the improvements cited is the lack of phase separation problems. Materials studied have included macroreticular resins (3,4), hydrous  $TiO_2$  (5), and  $PbO_2$  (1). O. K. Tallent has recently examined the use of base-treated silica gel for solvent cleanup (6). Solvent cleanup tests using treated silica gel included batch tests, small column tests using both synthetic irradiated solvent and solvent from SETF tests and larger column tests (2.5 and 7.5 cm diam) using synthetic irradiated solvent. Most of the tests were conducted at  $45^\circ C$ . The silica gel was treated with either NaOH or LiOH solutions to produce a basic layer on the surface of the silica gel and in the adsorbed water layer. In some ways this system is chemically similar to the standard base scrubbing technique of solvent cleanup, but it eliminates phase separation problems. Additionally, whereas the standard sodium carbonate scrubbing system requires replacement of the solution when approximately 50% of the sodium has been utilized, the treated silica gel method allows essentially complete use of all the sodium. This reduces the sodium requirements of the process by about 50%. The silica gel base has the advantages of being inert to all process solutions and, due to its high surface area, it has a high capacity. Although higher loadings were attainable, about 1 to 2 mmol/g sodium loading on 12-42 mesh silica gel was found to be optimum. Higher loadings gave gels which had a greater capacity for metal ion-DBP complexes but, in column tests, the higher loadings tended to fill the interstitial spaces between the gel grains with insoluble precipitate and led to unacceptable back pressure. The effect of temperature on the rate of loading of HDBP and the uranyl-DBP complex was small indicating that the loading rate was diffusion controlled. The capacity of the treated silica gel for nitric acid was consistent with a simple neutralization reaction to form nitric acid. The capacity for uranyl-DBP complex indicated a combination of neutralization to form sodium uranate, sodium-dibutylphosphate, and sodium

nitrate plus some surface adsorption. The reaction of HDBP with the treated gel was more complex including neutralization to form NaDBP, adsorption, and distribution of the NaDBP back to the organic phase. The distribution of NaDBP between aqueous solutions and TBP-NPH is not unique to the treated silica gel system, but it is not normally observed in the standard sodium carbonate scrubbing due to the much lower sodium activity. Figure 4 is a plot of the distribution coefficient of DBP as a function of NaOH activity (21). Here it is seen that in the standard sodium carbonate scrubbing system where the NaOH activity is less than 1 the amount of NaDBP extracted into the solvent will be negligible. The line shown in the figure has the equation:

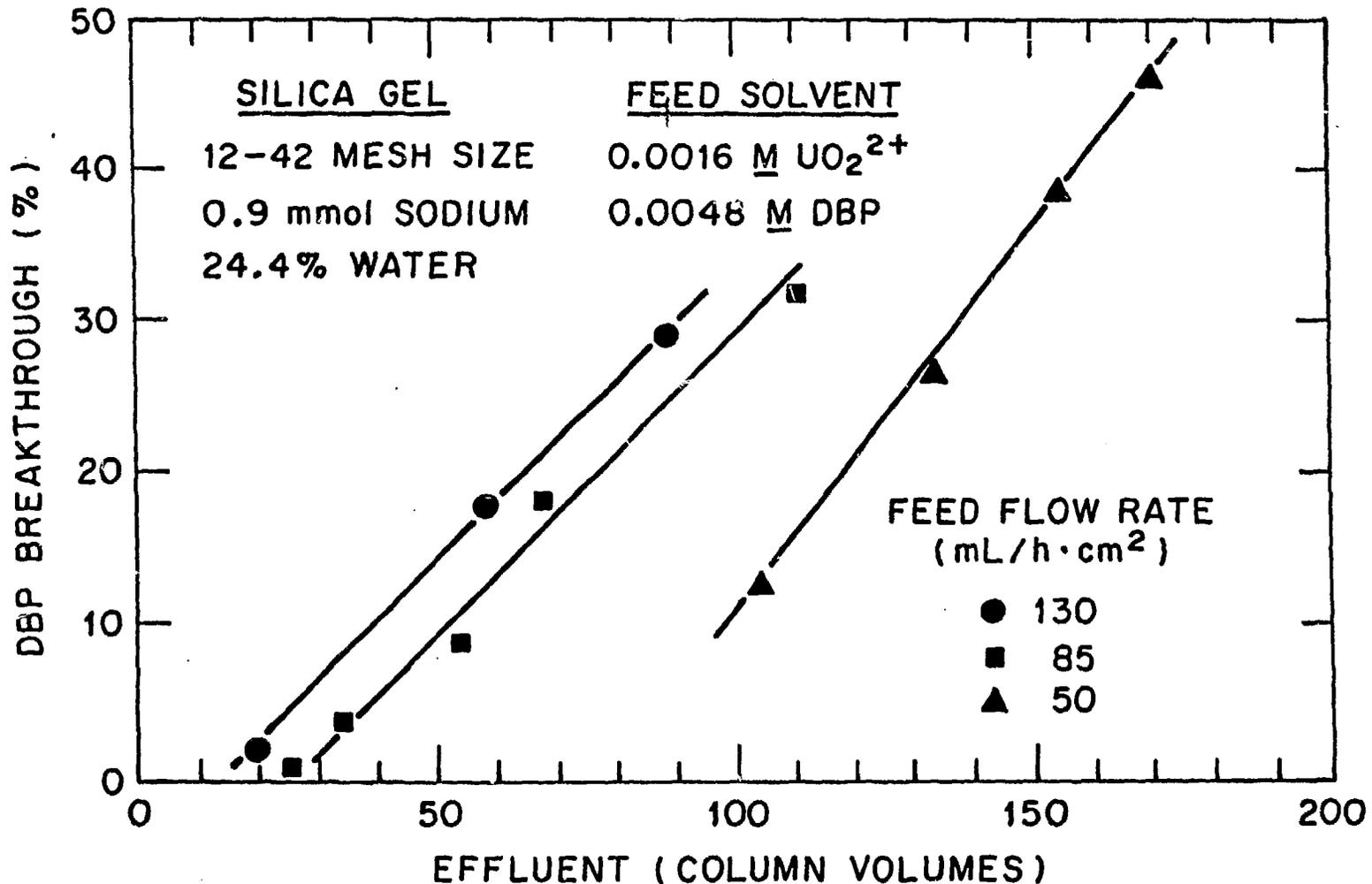
$$D = 2.157 \times 10^{-3} a \pm (\text{NaOH}) \quad (8)$$

with a correlation coefficient ( $R^2$ ) of 0.85. The distribution of NaDBP to the organic phase is observed in column tests where the NaDBP appears in the effluent organic before uranium. The normal method of detecting the NaDBP was to do a uranium retention test (extract excess uranium and strip the excess with water). Figure 5 shows the results of a typical column run removing uranyl-DBP complex. The NaDBP breakthrough occurred at about 28 column volumes whereas the breakthrough of uranyl did not occur until about 32 column volumes. The breakthrough of NaDBP depends on the organic flow rate as is shown in Fig. 6; breakthrough was delayed by operating at low flow rates. The low distribution coefficient of NaDBP between aqueous and organic solutions suggests simple methods for removal of the material. A simple water scrub readily removes NaDBP; however, this would introduce phase separation problems which the solid sorbent approach attempts to avoid. A simple, acceptable approach may be to follow the base-treated silica gel column with a damp silica gel column. Silica gel can adsorb up to 20 to 25% water by weight. Thus a damp silica gel column would contain a significant quantity of water. If the organic exiting the base-treated silica gel column contained 0.001 M NaDBP (probably much higher than the average effluent concentration),





SORPTION OF URANYL DIBUTYL PHOSPHATE FROM FEED SOLVENT  
AT 40°C. COLUMN LENGTH: 21 cm FLOW RATE 0.3 mL/min



BREAKTHROUGH OF DBP DURING LOADING OF URANYL  
DIBUTYL-PHOSPHATE ON 10-ml SILICA GEL COLUMNS  
AT 40°C

then the inlet portion of the damp silica gel column could contain about 1 M NaDBP in the aqueous phase on the silica gel. This should give a very high capacity. Regeneration of this column would require only washing with clean water and draining. This system is currently under test.

The silica gel column requirements for cleanup of the solvent from a one-half ton per day fuel recycle plant have been estimated. It is assumed that 13,500 liters of solvent containing a total of 13.5 moles each of  $\text{UO}_2^{2+}$ , DBP, and  $\text{HNO}_3$  will be processed each day. It is further assumed that the column will be operated between 25 and 40°C, that 12-42 mesh silica gel containing from 1 to 1.5 millimoles of adsorbed sodium per gram (wet weight) of gel will be used, and that the column will be loaded upflow. Tests have shown that silica gel columns of this description can be loaded at a rate of 75 mL/h per cm of column cross sectional area and that the silica gel can be loaded to a capacity of 0.15 millimoles of  $\text{UO}_2^{2+}$  per gram of gel. More conservative operating parameters of 50 mL/h/cm flow rate and 0.136 millimoles  $\text{UO}_2^{2+}$ /g gel capacity were used for the estimates listed in Table 4. It is estimated that a 1.2 m diam column 2.0 m in length containing 2000 Kg of silica gel would be sufficient to process the solvent from a one-half ton fuel recycle plant for 20 days. This estimate is based on operation of columns in series such that each column would be loaded to 100%  $\text{UO}_2^{2+}$  (or other cation equivalent) effluent breakthrough capacity with an auxiliary process step to strip out any NaDBP breakthrough from the solvent. It is important to note that the 2000 Kg of silica gel would not necessarily be discarded after the column is saturated. Various recycle options including acid elution followed by retreatment with base and thermal decomposition of nitrates and organics followed by rehumidification have been demonstrated. At the end of its useful life, which could include several recycles, the discarded gel might be incorporated into a glass wastefrom with the rest of the reprocessing waste where it could replace a portion of the normally-added silica.

Table 4. Estimates solvent cleanup operation requirements  
for one-half ton per day fuel recycle process

Solvent volume, $\ell$ /day	13,500
Moles/day DBP, etc.	13.5
Moles/day of metal ion $\text{UO}_2^{2+}$ , $\text{Pu}^{4+}$ , etc.	13.5
Moles/day of $\text{HNO}_3$	13.5
Flow rate, $\ell$ /h	526.5
Silica gel for 20 day column loading, kg	2,000
Column size, in m (diam x height)	1.2 x 2.0

The initial amount of sodium in the 2000 Kg column would be expected to vary from 46 to 69 Kg. It is conservatively estimated that the column would clean up solvent from reprocessing 10 metric tons of fuel, thus 4.6 to 6.9 Kg of sodium would be required per metric ton of fuel. Wash methods with sodium carbonate require from 3 to 5 times more sodium (as  $\text{Na}_2\text{CO}_3$ ) per ton of fuel reprocessed. The wash methods do not fully utilize the sodium present since any attempt to do so would result in precipitation of uranium or other metal ions. In the NaOH treated gel columns, precipitation is not a problem, and the sodium is almost completely utilized.

#### DILUENT DEGRADATION

The NPH used in the Purex process can be degraded by nitric acid to form numerous compounds. Such degradation has been studied (22,23) and found to be caused by  $\text{NO}_2$  monomer. A possible sequence of reactions is given below:

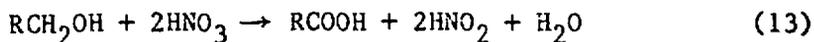
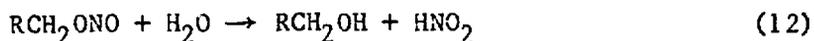
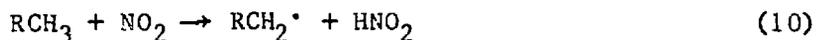
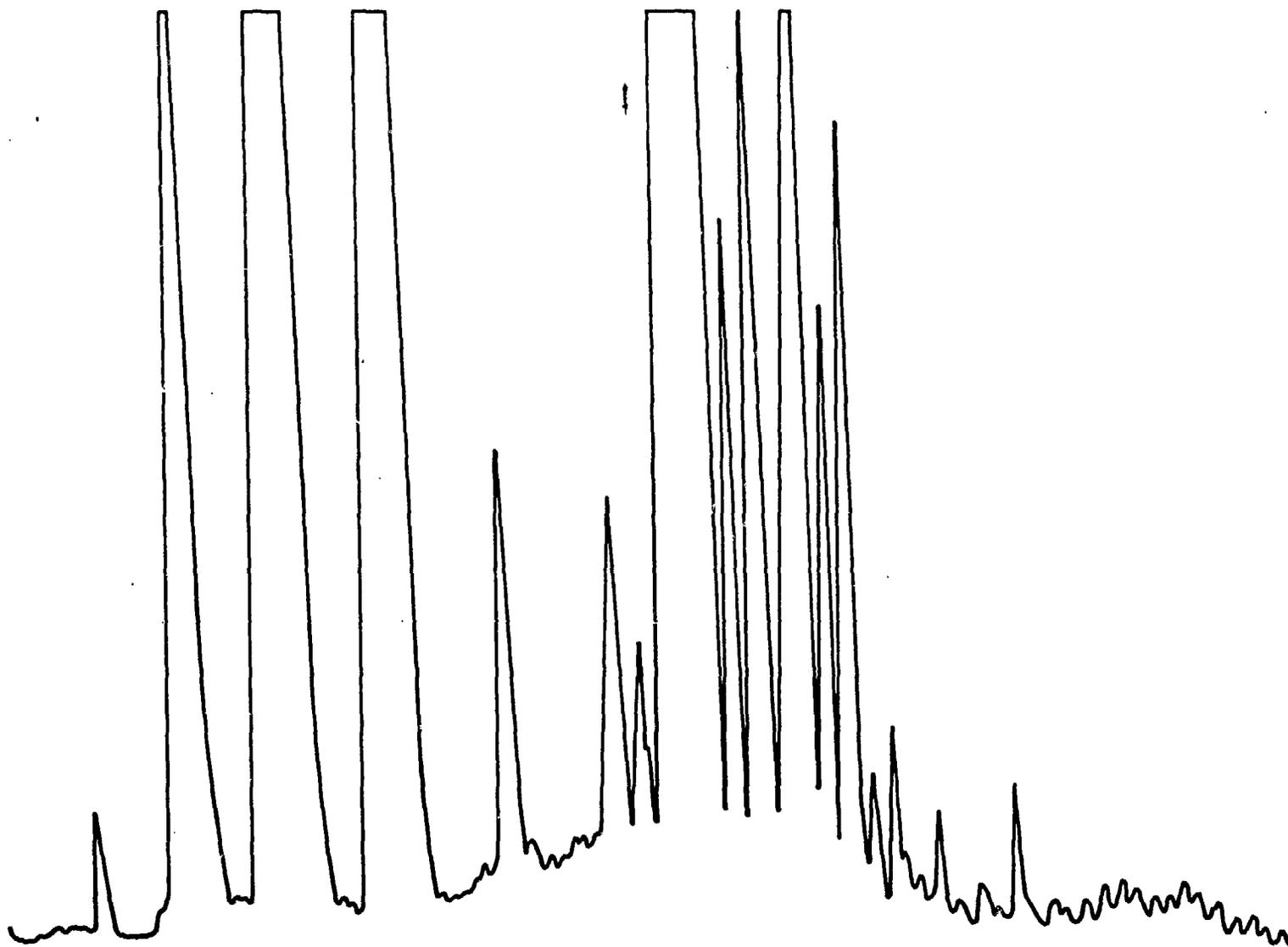


Figure 7 shows a gas chromatographic trace of a solvent which was degraded by heating with 8 M nitric acid for 24 h. Many new peaks were formed and a portion of these have been identified. Among the identified classes of new compounds are organic acids, esters, aldehydes, ketones, nitro compounds, and organic nitrates. Small amounts of compounds which

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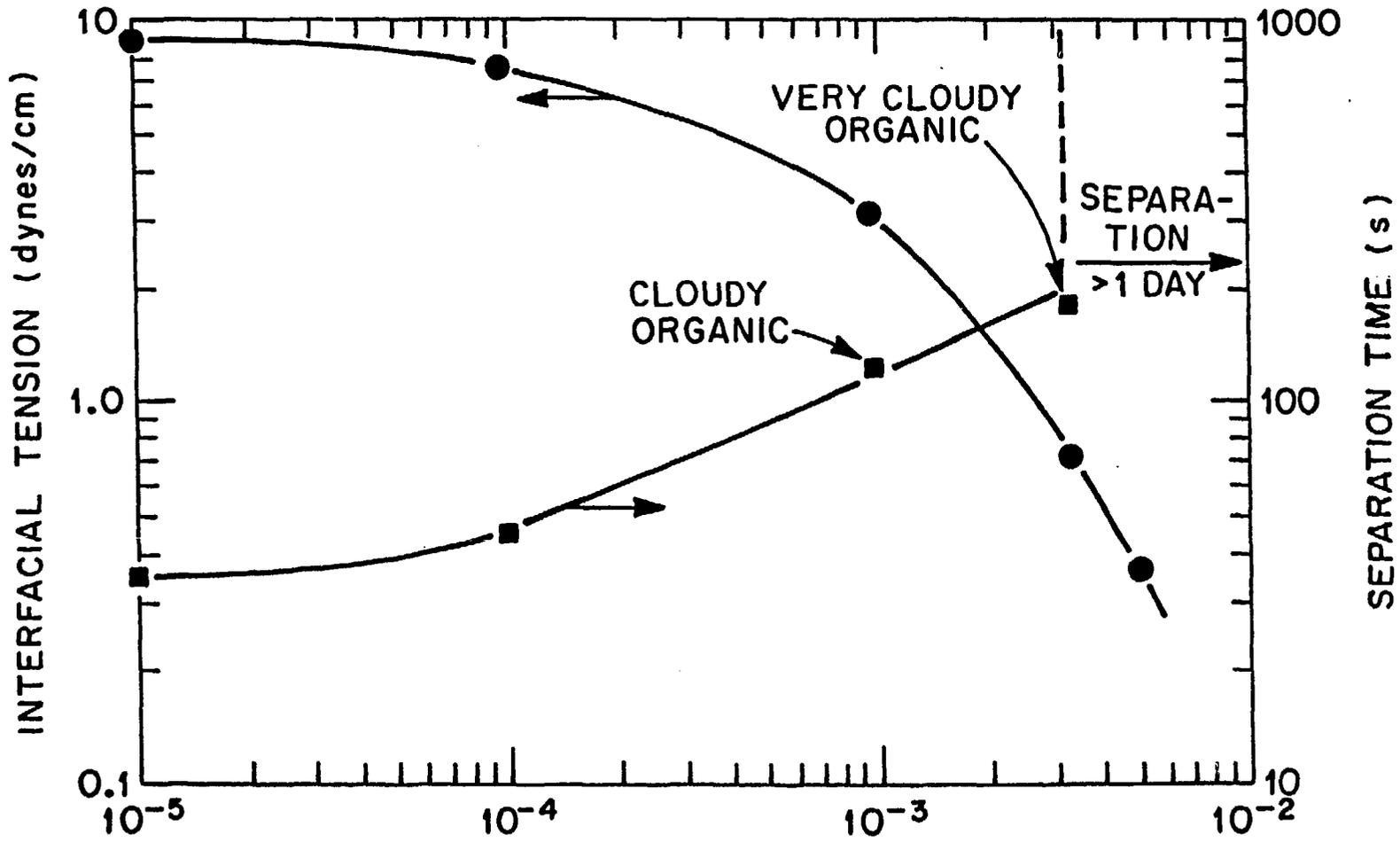


GAS CHROMATOGRAM 30% TBP ~70% NPH (DEGRADED)

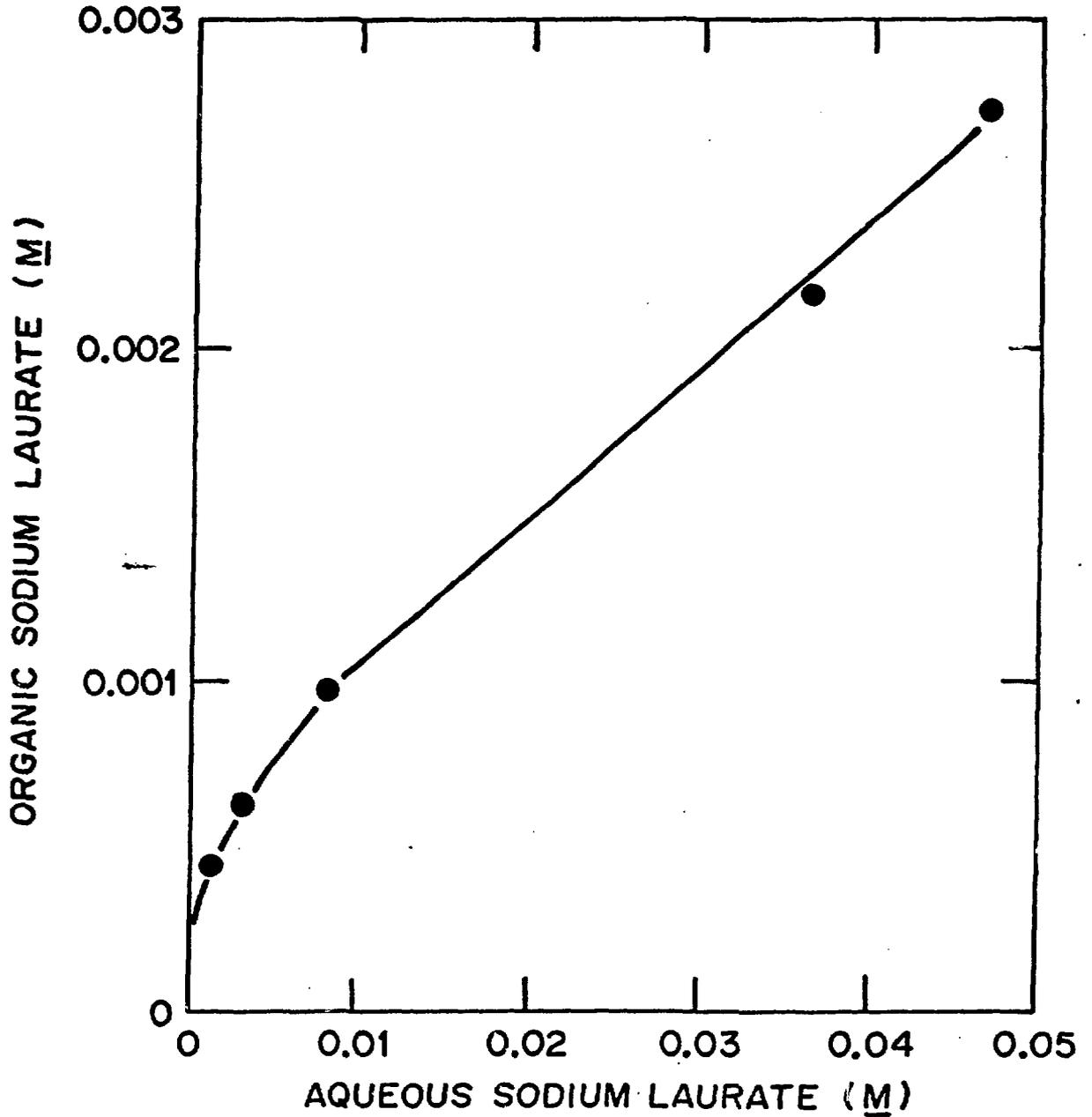
complex Pu, but which are not removed by standard sodium carbonate scrubbing are also formed. Since these compounds are formed in very small amounts it is not possible to identify them although they may be long-chain dialkyl phosphates as suggested by German workers (7,8). The diluent degradation increased with nitric acid concentration, temperature, the presence of nitrogen oxides, and time. Under normal circumstances in a fuel recycle plant the degradation will be much slower than in these tests which were designed to accelerate the degradation. However, in tests conducted in contact with 3 to 4 M nitric acid at 45°C, the degradation products appeared to be similar. Recycle solvent from the Savannah River Plant was also examined and showed some similarities but, also significant differences; these differences are attributed to degradation by radiation. The SRP solvent was found to contain 0.0014 M long-chain organic acids (acids which are not removed by treatment with sodium carbonate). When a heated nitric acid-solvent mixture was sparged with a 50-50 vol% mixture of NO<sub>x</sub> in air the degradation was increased by a factor of about 10. As expected, sparging the two-phase system with argon decreased the degradation by about a factor of 10 to 20 over the case where no sparging occurred. Eliminating nitrogen oxides by sparging with argon decreased both the overall degradation and the formation of the complexers which were not removed by sodium carbonate scrubbing.

Since the nitric acid degradation of the diluent appears to proceed partially by a free radical mechanism inclusion of a free-radical scavenger in the organic phase should decrease the overall degradation. Addition of butanol was examined since its inclusion would increase the concentration of a compound already present from TBP degradation. Inclusion of 10 vol% butanol was found to decrease the overall degradation of the diluent by nitric acid by about a factor of 10. Formation of the complexers which are not removed by sodium carbonate scrubbing was also reduced by a comparable amount.

Phase separation problems are reported in the sodium carbonate scrubber and especially in water scrubbers which have occasionally been placed after the sodium carbonate scrubber (24). The long-chain organic acids formed by degradation of the diluent are prime suspects in this problem since when contacted with sodium carbonate they form sodium salts (soaps). In simulated tests the interfacial tension of the organic in contact with 0.5 M sodium carbonate was noticeably decreased by as little as  $10^{-4}$  M sodium laurate (Fig. 8). Above about  $10^{-3}$  M the interfacial tension dropped precipitously. Also shown in the figure is the effect on the phase separation time in a mixer stirred by a 0.5 in. diam perforated mixer turning at 2400 rpm for 1 min. Note that starting at about  $10^{-3}$  M sodium laurate the organic phase did not completely clear even though a clear aqueous phase did separate. Above  $3.3 \times 10^{-3}$  M the phases did not separate in one day. The long-chain organic acid content of the SRP solvent is in the region where phase separation problems are imminent. However, SRP solvent shows better phase separation behavior than synthetic degraded solvent with the same long-chain organic acid content; this is probably due to beneficial effects of other degradation products present in SRP solvent. Figure 9 shows the distribution of sodium laurate between water and 30% TBP-NPH. At the sodium concentrations present in standard sodium carbonate scrubbers and with the 100:1 ratio of organic volume processed to scrub solution volume, most of the sodium laurate will remain with the organic and pass back into the solvent extraction system. It should be possible to continuously remove the sodium salts of the long-chain organic acids by following the sodium carbonate scrubber with an aqueous scrubber; this is not feasible with badly degraded organic since an unmanageable emulsion will form in the aqueous scrubber. The long-chain organic acids were initially suspected of contributing to metal-ion retention problems; tests have now shown that they do not cause significant retention of either uranium or plutonium. They do produce changes in extraction and stripping behavior but, in the concentrations expected in a progressing plant these effects will be negligible.



INTERFACIAL TENSION OF 0.5 M  $\text{Na}_2\text{CO}_3$  CONTAINING SODIUM LAURATE vs 30% TBP-NPH AT  $\sim 45^\circ\text{C}$



**EXTRACTION OF SODIUM LAURATE  
BY 30% TBP-NPH**

These diluent degradation studies suggest several precautions for operation of Purex plants. Nitric acid solution concentrations and operational temperatures should be minimized. The time during which the organic phase contains nitric acid should be minimized. The nitrous acid content of the acid and organic phases should be kept to a minimum, particularly if the organic is exposed to  $\geq 3 \text{ M HNO}_3$ . Fortunately, these precautions are met during standard operations. However, upset conditions could lead to diluent degradation problems. Significant reduction in the formation of diluent degradation products should be possible by sparging the nitrous acid out of either or both phases. This could be accomplished by sparging holding and feed tanks. The phase separation problem in the sodium carbonate scrubber can be alleviated by scrubbing with hydrazine oxalate which showed no phase separation problems even when scrubbing  $0.1 \text{ M}$  sodium laurate solutions in 30% TBP-NPH.

#### EVALUATION OF SOLVENT CLEANING OPTIONS

Solvent cleanup using conventional sodium carbonate scrubbing has the advantages of long experience in operating plants and the use of innocuous chemicals. Its disadvantages are that it generates large quantities of sodium nitrate waste, and it has some phase separation problems with degraded organics containing long-chain organic acids. A slow increase in retained ions with time has been observed in fuel reprocessing plants. Part of this increase may be due to the small distribution of NaDBP back to the organic from the sodium carbonate scrub solution observed in these studies. This possible problem and the ineffectiveness of the standard sodium carbonate scrubber for the removal of long-chain organic acids would be relieved by the use of a larger volume of more dilute sodium carbonate scrub solution. Then the sodium salts of both HDBP and the long-chain organic acids would distribute favorably to the scrub solution. The aqueous waste volume from the scrubber would be increased significantly, but the total amount of sodium nitrate would not be greatly increased.

The base-treated silica gel system has the advantage of simplicity, at least on the surface. Its use does not require mixers or separate pumps, phase separation problems are eliminated, and its space requirements are small. On the other hand, the spent silica gel may represent a fairly large waste mass unless it can be incorporated in place of silica in a glass wasteform. In addition, it will introduce solids handling into the solvent cleanup system, probably a disadvantage.

One advantage of the hydrazine oxalate scrubbing system is that it does not change the general operation of the scrubbing system as used in sodium carbonate scrubbing. Hydrazine oxalate will give better phase separations since it does not produce soaps from long-chain organic acids. Most important is the essential elimination of solid wastes generated by the solvent cleanup system. The major disadvantages of the hydrazine oxalate system reside in the disposal requirements. Although hydrazine can be easily disposed of by treating with excess nitrous acid or by catalyzed reaction with nitric acid, an integrated test of the complete system in realistic equipment including both continuous solvent scrubbing and disposal of the spent scrub solvent is necessary. The preferred method of disposal is to catalytically oxidize the spent scrub solution during the standard sugar denitration treatment of the aqueous waste which also oxidizes the oxalate to  $\text{CO}_2$  and water. This requires no changes in the standard processes except the addition of a small amount of manganese or vanadium catalyst to the waste solution. This appears to be much simpler than incorporation of an electrolytic destruction system.

The hydrazine oxalate system has such significant advantages over sodium carbonate that it should be considered the prime candidate for use in a full-scale reprocessing plant. However, before this can be done a demonstration of a realistic scrubbing and disposal system on a significant scale should be made. The base-treated silica gel option appears to be ideally suited for use in small-scale plants where the simplicity of operation and small space requirements should overcome the possible handling and disposal problems.

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