Dibutyl Phosphoric Acid Solubility in High-Acid, Uranium-Bearing Solutions at SRS

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WESTINGHOUSE SAVANNAH RIVER COMPANY
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ABSTRACT

The Savannah River Site has enriched uranium (EU) solution which has been stored for almost 10 years since being purified in the second uranium cycle of the H area solvent extraction process. The concentrations in solution are ~6 g/L U and about 0.1 M nitric acid. Residual tributylphosphate in the solutions has slowly hydrolyzed to form dibutyl phosphoric acid (HDBP) at concentrations averaging 50 mg/L. Uranium is known to form compounds with the dibutylphosphate ion (DBP) which have limited solubility. The potential to form uranium-DBP solids raises a nuclear criticality safety issue.

Prior SRTC tests (WSRC-TR-98-00188) showed that U-DBP solids precipitate at concentrations potentially attainable during the storage of enriched uranium solutions. Furthermore, evaporation of the existing EUS solution without additional acidification could result in the precipitation of U-DBP solids if the DBP concentration in the resulting solution exceeds 110 mg/L at ambient temperature. The same potential exists for evaporation of unwashed 1CU solutions. As a follow-up to the earlier studies, SRTC studied the solubility limits for solutions containing acid concentrations above 0.5M HNO_3.

The data obtained in these tests reveals a shift to higher levels of DBP solubility above 0.5M HNO_3 for both 6 g/L and 12 g/L uranium solutions. Analysis of U-DBP solids from the tests identified a mixture of different molecular structures for the solids created. The analysis distinguished $UO_2(DBP)_2$ as the dominant compound present at low acid concentrations. As the acid concentration increases, the crystalline $UO_2(DBP)_2$ shows molecular substitutions and an increase in amorphous content. Further analysis by methods not available at SRS will be needed to better identify the specific compounds present. This data indicates that acidification prior to evaporation can be used to increase the margin of safety for the storage of the EUS solutions.

Subsequent experimentation evaluated options for absorbing HDBP from solution using either activated carbon or anion exchange resin. The activated carbon outperformed the anion exchange resin. Activated carbon absorbs DBP rapidly and has demonstrated the capability of absorbing 15 mg of DBP per gram of activated carbon. Analytical results also show that activated carbon absorbs uranium up to 17 mg per gram of carbon. It is speculated that the uranium absorbed is part of a soluble U-DBP complex that has been absorbed. Additional testing must still be performed to 1) establish absorption limits for uranium for anion exchange resin, 2) evaluate desorption characteristics of uranium and DBP, and 3) study the possibility of re-using the absorbent.

INTRODUCTION

The Savannah River Site has enriched uranium (EU) solution which has been stored for almost 10 years since being purified in the second uranium cycle of the H area solvent extraction process. The concentrations in solution are ~6 g/L U and about 0.1 M nitric acid. After reprocessing, the solution contained an estimated 200 μg of dissolved tributyl phosphate (TBP) per gram of solution and a thin film of 7.5 vol.% TBP in n-paraffin diluent floating on top of the solution. The dissolved TBP has slowly hydrolyzed to dibutyl phosphoric acid (DBP) giving an average concentration of DBP in solution of 50 mg/L. The uncertainty associated with DBP data has been reduced from 25-30% uncertainty to 10-15%.

The hydrolysis reaction is slow at ambient temperature and low acid concentration so that all the TBP has not yet hydrolyzed. Uranium is known to form compounds with DBP which have limited solubility.[1-9] The solubility of $UO_2(DBP)_2$ has been reported to be 5.6×10^{-4} in 0.2 M HNO_3 and a solubility product constant was calculated to be 6.1×10^{-11}.[5,7] Previous unpublished studies at SRTC have shown that at ambient temperature U does not precipitate from 6 g/L U solutions with 100 mg DBP/L solution, but does precipitate when the concentration reaches 125 mg DBP/L solution.[9] If all the dissolved TBP were converted to DBP, the solution could reach 158 mg DBP/L solution. Precipitation of U by DBP will occur at DBP concentrations below 158 mg/L. However, DBP is also hydrolyzed slowly to MBP to reduce the maximum attainable concentration. The present concentration is 50-60 mg/L based on analyses of past samples of the solution with high uncertainty. Possible precipitation represents a nuclear criticality concern. A better understanding and measurement of the solubility limits for the U-HNO_3-DBP system are needed to establish safety and operating limits for storage and operations.

An earlier study in SRTC (WSRC-TR-98-00188) established a solubility limit for solutions containing 0.1-0.5M HNO_3. It was expected that higher acid concentrations would yield a correspondingly higher DBP solubility. Data relating elevated DBP solubility for higher acid concentrations could be used to support higher safety margins for EUS storage. If successful, Separations would be able to acidify the EUS before concentrating it via evaporation.

An additional need exists for a way to remove HDBP from solution by absorption in a column. It was proposed that testing be done to examine the absorption characteristics of HDBP on activated carbon and an anion exchange resin. Preliminary work looked at DBP absorption rates, DBP absorption capacity, and U absorption.

EXPERIMENTAL

Solutions were prepared with reagent grade HNO_3 and uranyl nitrate hexahydrate (UNH) and with 98% pure DBP solution obtained from Aldrich. Stock solutions of UNH and DBP were prepared in glass volumetric flasks with 0.5M HNO_3 prepared from 15.7M acid. The UNH solution containing 150 g/L U was prepared by dissolving 79.20 g of UNH solids in a 250 mL volumetric flask using 0.5M HNO_3 and diluting to the mark.

Two separate DBP solutions were made. The first was made by dissolving 0.2804 g of DBP in a 100 mL volumetric flask using 0.5M HNO_3 and diluting to the mark. The nominal DBP concentration based on 98% purity is 2750 mg/L. The second DBP solution was prepared by dissolving 0.8946 g of DBP in a 200 mL glass volumetric flask using 0.4M HNO_3 and diluting to the mark. The nominal concentration of DBP based on 98% purity is 4380 mg/L. The stock solutions were then used to prepare test solutions. Solubility in the $UO_2(NO_3)_2$-HNO_3-H_2O system was approached by way of precipitation.

Separate experiments used DBP and uranium stock liquids to prepare starting solutions for DBP absorption on columns of absorbent. Activated carbon absorbent was taken from Supelco ORBO 32L gas absorption tubes. Ionac A-641 anion exchange resin was also used to compare against activated carbon. Where appropriate, solutions were circulated at 3.5 mL/min using a Cole-Parmer peristaltic pump.

Precipitation Tests

Precipitation tests were done at ambient temperature (22-23°C) and at 0°C. Three sets of samples were made containing 0.1M, 0.5M, 1.0M, 2.0M, and 4.0M HNO_3. The three sets included 1) 12 g/L U at 0°C, 2) 12 g/L U at 23°C, and 3) 6 g/L U at 23°C. Tests were carried out by intentionally preparing solutions that would precipitate, and by allowing the solutions to sit in a hood at ambient temperature or in a constant temperature bath at 0°C. The samples were made with high DBP concentrations to cause rapid precipitation; the solutions precipitated within four hours and were allowed to equilibrate. Samples were taken periodically to analyze the DBP concentration remaining in solution and determine if equilibrium has been established. The quantity of solids precipitated was small so that the concentrations of U and acid should not be significantly affected.

The solutions were prepared in glass vials with Teflon liners in the caps to prevent adsorption of DBP by the plastic. The total solution volume in the vials was 12.5 mL in all cases. Table 1 shows preparation of the samples. The samples were stored at the appropriate temperatures and sampled for DBP analyses after 4 days, 11 days, and 35 days to determine if equilibrium has been established.

Table 1. Solution Preparation for High Acid Solubility Tests

STOCK SOLUTIONS					FINAL CONCENTRATIONS		
Stock HNO3 (M)	mL Stock HNO3	mL of 150 g/L U	mL of 2750 mg/L DBP	mL DI Water	HNO3 (M)	DBP (mg/L)	U (g/L)
0.1	5.00	0.50	1.00	6.00	0.1	220	6
0.5	10.50	0.50	1.50	0.00	0.5	330	6
8.0	1.41	0.50	2.00	8.59	1.0	440	6
8.0	2.91	0.50	3.00	6.09	2.0	660	6
8.0	5.88	0.50	5.50	0.63	4.0	1210	6
0.1	2.50	1.00	1.00	8.00	0.1	220	12
0.5	10.00	1.00	1.50	0.00	0.5	330	12
8.0	1.38	1.00	2.00	8.13	1.0	440	12
8.0	2.88	1.00	3.00	5.63	2.0	660	12
8.0	5.84	1.00	5.50	0.16	4.0	1210	12

In a separate experiment, solids were precipitated from 0.13M, 1.0M, and 4.0M HNO_3 to observe their crystalline structures using x-ray diffraction (XRD). Sample bottles containing 100 mL of sample were prepared using the amounts listed in Table 2. After 16 hours, the resulting solids were filtered and mounted on slides for XRD analysis. The remaining solids have been retained for future analyses, as needed.

Table 2. Solution Preparation for XRD Analysis of Solids

STOCK SOLUTIONS					FINAL CONCENTRATIONS		
Stock HNO3 (M)	mL Stock HNO3	mL of 150 g/L U	mL of 4380 mg/L DBP	ML DI Water	HNO3 (M)	DBP (mg/L)	U (g/L)
15.7	0.00	8.00	23.0	69.0	0.13	1008	12
15.7	5.53	8.00	23.0	63.5	1.0	1008	12
15.7	24.16	8.00	41.8	26.0	4.0	1833	12

Absorption Tests

Several scouting experiments were conducted to gain preliminary information. The four tests evaluated the following: 1) DBP absorption using activated carbon, 2) DBP absorption using anion exchange, 3) absorption of uranium by activated carbon, and 4) DBP absorption capacity of activated carbon. In Tests 1-3, 100 mL of 0.1M HNO_3 solution was prepared with 75-85 mg/L of DBP; Test 3 also contained about 6 g/L uranium. Test 4 used 100 mL of 0.1M HNO_3 with approximately 250 mg/L of DBP.

In Test 1, 1.20 g of activated carbon was placed in a 9.5 mm column (bed height = 38 mm) and attached to a peristaltic pump. The solution with 75-85 mg/L of DBP in 0.1M HNO_3 was placed in a beaker and stirred using a magnetic stirrer. The solution was continuously recirculated through the column at 3.5 mL/min (residence time approximately 30 minutes) and samples were withdrawn for DBP analysis at 0, 4, 8, and 12 column passes. Test 2 was similar to Test 1 except 3.3 g of Ionac A-641 resin was placed in the 9.5 mm column (bed height = 70 mm) and samples were withdrawn for DBP analysis at 0, 2, 8, and 14 column passes.

Test 3 used 2.35 g of activated carbon in a 9.5 mm column. The starting solution contained 6 g/L U and 75 mg/L DBP in 0.1M HNO_3. The solution was gravity fed through the column four times; each pass lasted 3.5-5.0 minutes. A sample for DBP analysis was collected after each pass, and a sample for uranium analysis was withdrawn after the 2^{nd} and 4^{th} passes. After the last pass through the column, the column was rinsed three times with a single 20 mL aliquot of 0.1M HNO_3; a sample of the rinse was withdrawn for U analysis. Last, the column was scrubbed three times with a single 20 mL aliquot of 10M HNO_3; a sample of the scrub was pulled for U analysis. The residual activated carbon was submitted for α/β analysis.

In Test 4, 1.20 g of activated carbon was placed in a 9.5 mm column similar to Test 1 and 2. In this experiment, the starting solution was continuously recirculated through the column at 15 mL/min. Samples were pulled from the liquid after 3 and 5 hours for DBP analysis. Following recirculation, the column was scrubbed three times with a single aliquot of 15.7M HNO_3; the scrub solution was sampled for DBP (sample diluted 10X prior to submission).

Analyses

Analysis for U in solution was done by the Chem Check instrument, which utilizes U phosphorescence. The crystal structures of U-DBP solids were analyzed using x-ray diffraction (XRD). The measurement of α/β radiation was performed using RadScreen. DBP analyses were done by ion chromatographic analysis (IC). Considerable effort was made to improve the DBP analysis method to obtain reproducible results with the lowest uncertainty.[13] Samples without U or high nitrate ion can be run without significant pretreatment. However, U and high nitrate can interfere with the analysis.

RESULTS AND DISCUSSION

Precipitation Tests

The solubility of U in HNO_3 solutions containing DBP is expected to be a function of acid concentration, and U concentration as can be seen from the reaction governing precipitation (equation 1).

$$UO_2^{2+} + 2\,HDBP \leftrightarrow UO_2(DBP)_{2\,solid} + 2\,H^+ \qquad (1)$$

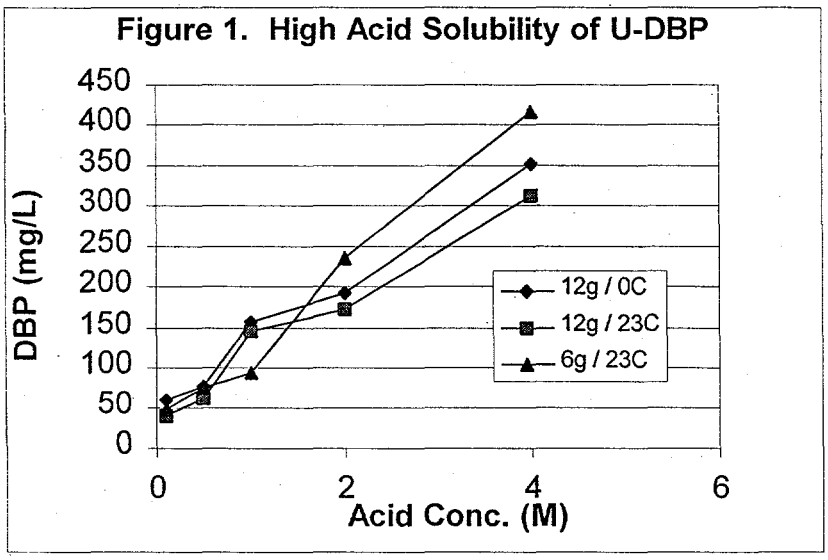
Temperature is also a variable since solubility generally increases with increasing temperature. The reaction given above is the overall reaction to yield a precipitate. There are actually several reactions and associated equilibrium constants involved. These have been discussed in an earlier report.[3,13]

Furthermore, the literature discusses the finding of different uranium compounds at low acid concentrations when compare to those forming at higher acid concentrations. The literature indicates that at 0.2M HNO_3, $UO_2(DBP)_2$ is formed upon precipitation. However, in 6M HNO_3 the precipitate is reported to be $UO_2(NO_3)(H[DBP]_2)$, $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$, or their mixture.[5,6] In light of Equation 1, it is not difficult to understand why NO_3^- becomes involved in the precipitation reaction when NO_3^- is a major component in solution. The literature does not present data or theory regarding compounds that exist between 0.2 and 6.0M HNO_3. The same references also discuss interconversion between the various compounds meaning that the high acid compound, if placed in water, will convert to $UO_2(DBP)_2$, and vice versa.

The final analyses for high acid solubility of U-DBP compounds (samples described in Table 1) are shown in Figure 1. An examination of the associated data shows that the data at 0°C for 0.1M and 0.5M HNO_3 is comparable to those reported earlier.[13] Some concerns exist regarding the accuracy of the data at room temperature because, unlike the 0°C samples, the room temperature samples were stored in the light. Photolysis of TBP is a known occurrence, and it is unclear whether there is a photolysis of DBP occurring in these samples.[14] This is emphasized by the fact that the room temperature curve for 12 g/L U is consistently below the curve for the samples at 0°C; U-DBP solubility should be higher at elevated temperatures. Also, the data as a function of time shows that the DBP data for low acid samples (0.1-0.5M) starts at the levels reported earlier and then decreases with the analyses showing changes on the order of 20-35%. In contrast, the high acid data (2.0-4.0M) remains essentially constant for duplicate and triplicate analyses with data variability on the order of 2-8%. This could be caused by slower kinetics in reaching equilibrium under low acid conditions or by the filtering of light in higher acid concentrations to prevent DBP degradation. More research needs to be performed to better understand and quantify the behavior of the system because it is possible that we have created a different system by intentionally spiking significant excesses of DBP into the system.

While the low acid data has an element of uncertainty, the high acid data shows a good degree of repeatability as a function of time. Furthermore, an examination of Figure 1 shows a clear shift in DBP solubility between 0.5M and 1.0M acid for 12 g/L U samples and between 1.0M and 2.0M for 6 g/L U samples. Additional analysis of the slopes of the lines before and after the shifts reveals that the slopes for the three lines before the shift are essentially the same; this is also observed for the lines following the shift. The difference in line slopes between 6 g/L and 12 g/L samples during the solubility shift can be attributed to the greater spacing between samples at the point of the solubility shift. The fact that the slopes of many of these lines are the same implies that the same general reactions and equilibria are occurring in the three sets of samples.

Figure 1. High Acid Solubility of U-DBP



The presence of the solubility shift is extremely interesting in light of the information in the literature regarding distinctly different compounds present at low acid (0.2M) versus high acid (6M). XRD analysis of the solids from 0.1M HNO_3 shows a close match to the crystalline pattern for $UO_2(DBP)_2$. Analyses of the compounds precipitated in 1.0M clearly indicate that some molecular substitutions have occurred. XRD of the solids from 4.0M HNO_3 show a decreasing presence of $UO_2(DBP)_2$ and an increase in amorphous content. The increasing amorphous character of these solids is consistent with the literature that describes solids created in 6M HNO_3 as "viscous liquids" which form vitreous masses when washed with water in air.[5] Analyses not available at SRS will be needed identify the specific compounds present.

In combining XRD data with DBP solubility data, the increased DBP solubility in high HNO_3 suggests the presence of compounds in equilibrium with $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$ in significant quantities because $UO_2(NO_3)(H[DBP]_2)(HDBP)_2$ contains four DBP molecules per UO_2 molecule versus the two DBP molecules associated with $UO_2(NO_3)(H[DBP]_2)$. Also, an analysis of the slopes of the solubility lines reveals that the slopes following the shift are approaching two times the slopes prior to the shift (80 mg/L per M vs. 47). However, with only limited data available it is difficult to draw firm conclusions about the nature of the compounds causing the DBP solubility shift.

Absorption Tests

While increasing DBP solubility is one way to resolve the EUS storage issue, another option is to remove the DBP from solution by contacting it with an absorbent. The data in Table 3 shows the effect of two absorbents, activated carbon and anion exchange resin, on DBP concentrations in dilute nitric acid solutions. Activated carbon is much more effective at removing DBP from solution than the anion exchange resin. It removes the DBP quickly and absorbs up to 15 mg of DBP per gram of activated compared to approximately 1 mg of DBP per gram of anion exchange resin. However, the activated carbon will also absorb approximately 17 mg of uranium per gram of absorbent; it is speculated that most of the uranium absorbed is bound to the absorbed DBP. In addition to absorbing uranium, the ability to remove the uranium from the activated carbon is questionable. Testing shows that approximately 35% of the uranium absorbed by activated carbon is not eluted even when eluting with 10M HNO_3; testing of DBP stripping from activated carbon using 15.7M HNO_3 yields an identical 35% retention. Neither uranium loading nor desorption of U and DBP have been measured for the anion exchange resin.

Table 3. DBP Absorption Results

Absorption onto Ionac A-641		Absorption onto Activated Carbon		Absorption onto Activated Carbon		Absorption onto Activated Carbon			
Column Passes	DBP (mg/L)	Column Passes	DBP (mg/L)	Column Passes	DBP (mg/L)	Column Passes	DBP (mg/L)	U Conc. (mg/L)	
0	82	0	86	0	218	0	72	6200	[100%]
2	67	4	18*	6	31	1	32	xx	
8	62	8	17*	10	35	2	22*	5800	[93.5%]
14	59	12	18*			3	21*	xx	
						4	19*	5800	
						Rinse	xx	980	[3.2%]
						Scrub	xx	300	[1.0%]

* Indicates a sample which looks like a blank (<20 mg/L)
xx Indicates where no sample was taken

The data depicts that activated carbon is more effective at absorbing DBP, but its absorption of uranium does place limitations upon its use due to criticality concerns. While the loading of DBP on an anion exchange resin may not appear attractive, it may be a very good option if the resin does not absorb uranium and can be regenerated through pH adjustment. Additional research and development is needed in this area before making conclusions and recommendations.

CONCLUSIONS

Previous work has shown that U-DBP solids will precipitate at concentrations potentially attainable during storage of enriched uranium solutions, and that DBP solubility increases with increasing acid concentration from 0.1 to 0.5M HNO_3. More recent tests in 1.0 to 4.0M HNO_3 indicate much higher DBP solubility regimes.

Furthermore, the data indicates an upward shift in DBP solubility attributable to a U-DBP precipitate that differs from those formed at lower acid concentrations. Analysis of the solids using x-ray diffraction shows that $UO_2(DBP)_2$ is the prominent compound in low acid and that molecular substitution is occurring as the acid concentration increases. This is consistent with observations previously reported in the literature. This is importance because it reveals that acidifying and evaporating the EUS solution may provide higher safety margins over storage alone.

The SRTC studies also show that activated carbon is very effective at removing DBP from solution and has an absorption capacity of approximately 15 mg DBP per gram of activated carbon. The Ionac A-641 anion exchange resin will also remove DBP, but it has a much lower absorption capacity. However, a concern does arise because activated carbon will remove some uranium along with the DBP. This presents a criticality safety concern. Most of the uranium can be stripped using more concentrated nitric acid. Additional work remains to be done to 1) assess the amount of U absorption by the anion exchange resin, 2) quantify the U and DBP absorption capacities of both absorbents, and 3) address the potential for in situ regeneration of the absorbents.

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