Acid Evaporation of Ultima Gold™ AB Liquid Scintillation Cocktail Residue

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Characterization of the Organic Content
of H-Canyon Tank 10.5 Solution

SUMMARY

Prior analyses of samples from the F/H Lab solutions showed the presence of diisopropylnapthalene (DIN), a major component of Ultima Gold™ AB liquid scintillation cocktail (LSC). These solutions are processed through H-Canyon Tank 10.5 and ultimately through the 17.8E evaporator. Similar solutions originated in SRNL streams sent to the same H Canyon tanks. This study examined whether the presence of these organics poses a process-significant hazard for the evaporator.

Evaporation and calorimetry testing of surrogate samples containing 2000 ppm of Ultima Gold™ AB LSC in 8 M nitric acid have been completed. These experiments showed that although reactions between nitric acid and the organic components do occur, they do not appear to pose a significant hazard for runaway reactions or generation of energetic compounds in canyon evaporators. The amount of off-gas generated was relatively modest and appeared to be well within the venting capacity of the H-Canyon evaporators. A significant fraction of the organic components likely survives the evaporation process primarily as non-volatile components that are not expected to represent any new process concerns during downstream operations such as neutralization. Laboratory Waste solutions containing minor amounts of DIN can be safely received, stored, transferred, and processed through the canyon waste evaporator.

BACKGROUND

H-Canyon Tank 10.5 receives solutions from F/H Laboratory and SRNL High Activity Drain (HAD) systems which collect radioactive liquid material from the 772-F and 772-1F laboratories and the 773-A laboratories, respectively. After receipt into Tank 10.5, organic in the solution is removed by the 13.6-1S box decanter prior to being combined with other streams and evaporated in the 17.8E evaporator as shown in Figure 1. The use of this decanter is credited by the Documented Safety Analysis (DSA) for removal of a minimum of 90% of the organic from the solution[1] for explosion prevention from a TBP-nitric acid reaction. (Actual removal is believed to be above 98% for the typical acidic-TBP solutions used in H-Canyon processes.) After the solution is decanted the evaporator is initially filled with solution and the evaporator is heated with steam. After sufficient volume reduction, additional feed is added until the targeted specific gravity reading for the evaporator contents is obtained. If the decanter failed to remove organic in the solution, high boiling-point organics would tend to accumulate (along with nitric acid and salts) in the evaporator bottoms. Excessive accumulation of an organic phase in the evaporator could result in a runaway reaction with nitric acid; thus there are multiple levels of controls (including the before-mentioned decanter) to prevent such an accident. Volatile organic components, water and nitric acid are condensed into the overhead condensate stream and are transferred to the Acid Recovery Unit (or the General Purpose Evaporator) where there is opportunity for volatile organics to either vent to the ventilation system, or be sent into the HM process via the recycled acid stream. Prevention of the introduction of significant quantities of organics to the evaporator prevents these issues.

Previous studies[2,3] identified diisopropylnapthalene (DIN), a major component of Ultima Gold™ AB liquid scintillation cocktail (LSC) – see components reported in the MSDS[4] shown in Table 1 – used
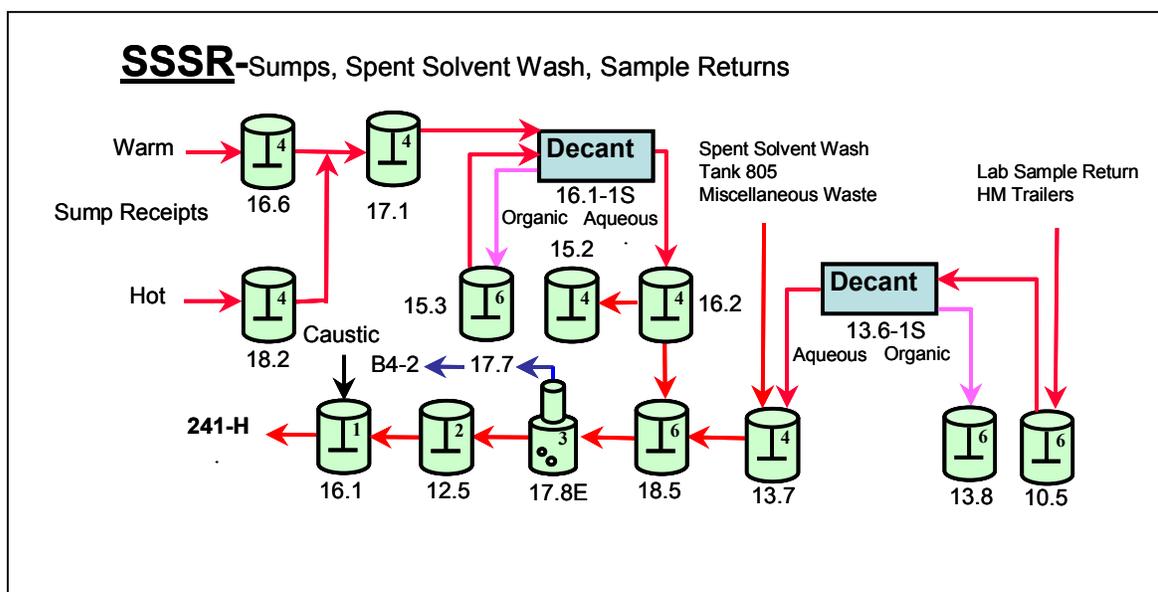
Figure 1. Sumps, Spent Solvent Wash, Sample Return Tankage in H-Canyon.

[1] Savannah River Site H-Canyon & Outside Facilities, H-Area, S-DSA-H-00001, Rev. 3, July 2011, Section 4.4.19, Table D.1 (H-Canyon Control Set), and Attachment B - Structure, System, and Component and Specific Administrative Control Functional Requirements Matrix.

[2] E. A. Kyser, F. F. Fondeur, and S. D. Fink, "Potential Impact of Tank F Flush Solution on H-Canyon Evaporator Operation", SRNL-STI-2010-00550, Savannah River National Laboratory, September, 2010.

[3] E. A. Kyser, F. F. Fondeur, J. H. Gray, "Characterization of the Organic Content of H-Canyon Tank 10.5 Solution", SRNL-TR-2010-00361, Savannah River National Laboratory, December, 2010.

[4] PerkinElmer, "Material Safety Data Sheet for Ultima Gold™ AB", January, 2009.

Table 1. Composition of Ultima Gold™ AB[4].

Name	CAS	wt %	comments
Polymer based on alkylphenolethoxylate		20-40	polymer of surfactant
2-(2-butoxyethoxy)ethanol	112-34.5	10-20	emulsifier
Polymer based on nonylphenolethoxylate		2.5-10	polymer of surfactant
nonylphenyl (branched) polyoxyethylene ether phosphate	68412-53-3	≤2.5	emulsifier
Diisopropyl naphthalene isomers	38640-62-9	40-60	solvent
2,5-Diphenyloxazole (PPO)	92-71-7	≤2.5	scintillator
1,4-Bis-(2-methylstyryl)-benzene (MSB)	13280-61-0	≤2.5	scintillator

in both F/H Laboratory and SRNL, as a source of cloudiness in samples from Tank 10.5 and related tanks. Since a cloudy emulsion probably does not allow complete phase separation by the box de-canter, the presence of liquid scintillation cocktail (LSC) in laboratory recycle streams likely intro-duces a quantity of organic to the 17.8E evaporator. H-Canyon requested[5] that SRNL perform a study to investigate the presence of expected quantities of LSC in the lab returns streams on the evap-oration of these solutions in the 17.8E evaporator.

EXPERIMENTAL
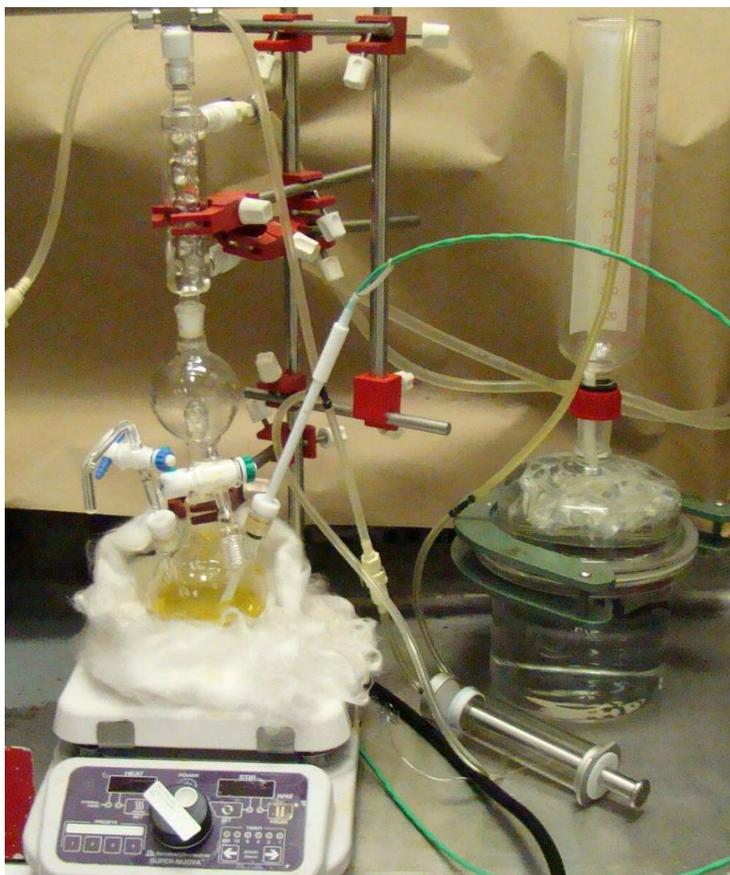
Figure 2. Evaporator Test Apparatus.

The experimental program for this task involved two parts: 1) an acid evaporation test to observe the effects of a bounding concen-tration of LSC under realistic pro-cess conditions, and 2) a solution self-heating investigation using Accelerating Rate Calorimetery (ARC) with a bounding concen-tration of LSC in 8 M nitric acid.

The evaporator test used a glass-ware laboratory evaporator appa-ratus similar to that used in previ-ous evaporation -denitration tests and a photo is included as Figure 2. A 100 mL sample of 8 M ni-tric acid with ~2000 ppm of LSC was placed in a 250 mL boiling flask with magnetic stirring. The temperature was increased to the boiling point of the solution. Glass wool was wrapped around the flask to reduce heat transfer losses and to reduce condensation on the upper surfaces of the flask. The evaporator model was oper-ated in a near total reflux mode for an extended period of time

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[5] W. Herrin, "DIN Analysis", NMMD-2010-3158, Technical Task Request, Savannah River Nuclear Solutions, Aiken, SC, January 24, 2011.

with the condensate collected and then returned to the evaporator pot. Recycle of the condensate allowed the experiment to operate for an extended period of time without the introduction of additional feed. Non-condensable gases were collected and measured using water displacement. A gas syringe connected to the gas collection system was used to remove or inject gas from the system to prevent pressure buildup (which could allow small unknown amounts of leakage from the system). The system was operated until the off-gas collection rate dropped significantly. A sketch of this experimental system is shown as Figure 3. A sample of condensate was collected after ~5 hours of total reflux under boiling conditions. After the system cooled to ambient temperature a sample of the evaporator bottoms was also collected. Samples of the untreated feed, condensate and bottoms were analyzed by gas chromatography – mass spectrometry (GC/MS).
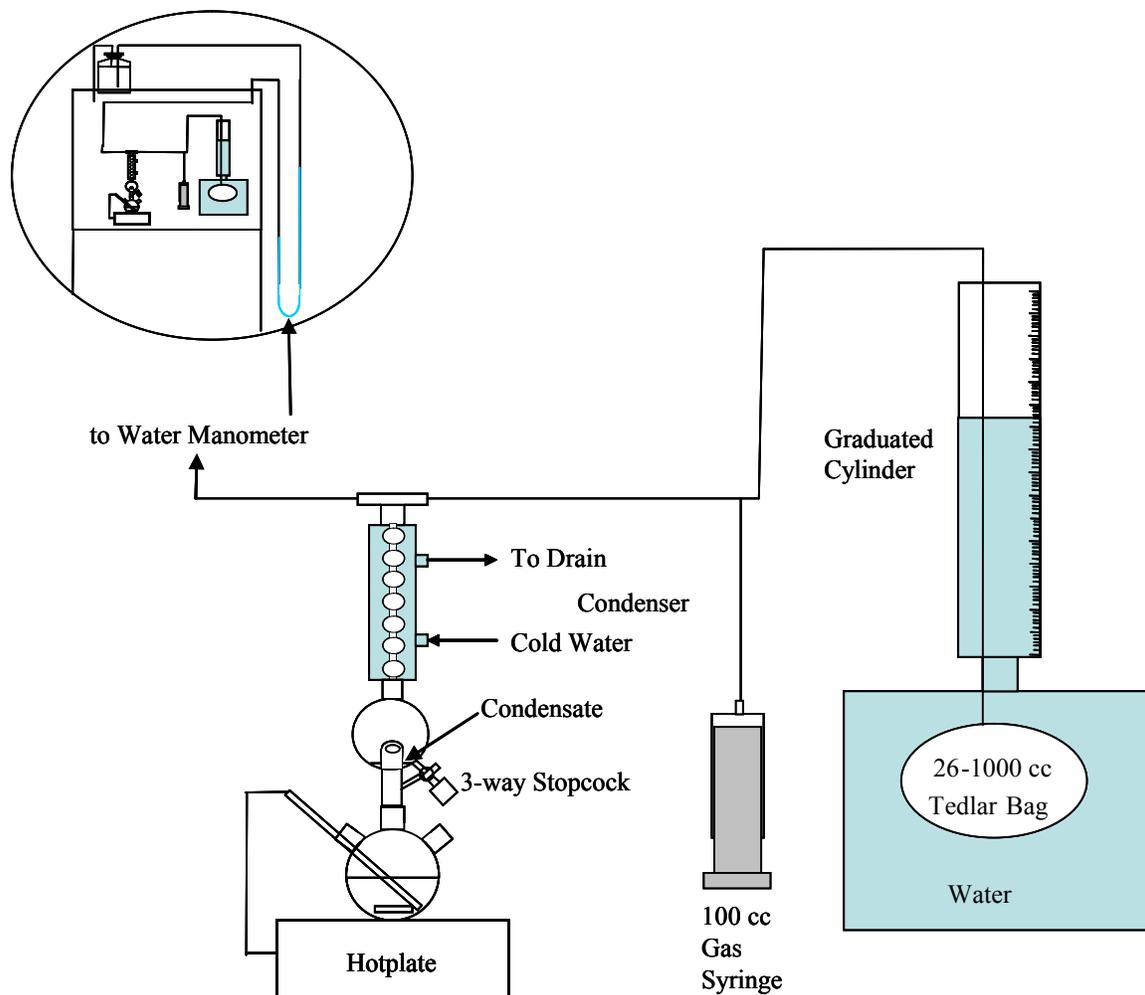
Figure 3. Experimental Setup for Evaporation Test.

The calorimetry test scanned for exothermic reactions (self-heating) up to at least 300 °C utilizing a standard "heat-wait-search" mode and measured both the energy released from any reaction and the amount of gas generated. This test used an ARC2000 instrument manufactured by TIAX as shown in Figure 4. Approximately 5 grams of 8 M nitric acid solution was initially placed in a 10 mL bomb vessel made of 316 stainless steel (with 2 mL volume in the overhead tubing) with an approximate

Figure 4. Accelerating Rate Calorimeter.

phi factor[6] of 2.13. Ultima Gold™ AB was added to the vessel within 5 min prior to the start of the test. The sample is not mechanically mixed after it is placed in the ARC. Nitrogen gas was used to put an initial 3 to 5 atm pressure on the vessel for leak check purposes and to suppress evaporation . The sample was heated in heat, wait and search mode. In this mode the sample container is heated in small increments (10 °C). The instrument waits a specified time to ensure the sample, the bomb, and the calorimeter are at the same temperature and then searches for signs of exothermic activity in the sample. If an exotherm is detected, then the calorimeter shifts into adiabatic mode and tracks the sample temperature as the sample "self-heats". Unless self-heating is detected the instrument will continue the heat-wait-search cycle until the upper limit temperature is reached (i.e., 300 °C in this case). This sample was heated at 2 °C /min to the starting temperature of 50 °C and the exotherm threshold for the sample temperature was set at 0.02 °C.

Qualitative analysis was performed on solid residue via Fourier Transform Infrared Spectroscopy (FTIR). For this technique ~20 mg of residue was placed on a single bounce (45 degrees) diamond crystal. The crystal was then placed on a Nicolet NEXUS 6700 spectrometer. More than 150 scans at 0.4 cm^{-1} wavenumber resolution were collected to generate a signal to noise ratio of ~350:1 in the 1600 cm^{-1} region. The background signal was collected without sample on the diamond crystal. The absorbance of the sample is then calculated relative to the background. The collected spectrum was compared with the reference spectra from the Aldrich FTIR database. Peak shape, position and peak height were used for qualitative identification of the molecule that gave the vibrational peak.

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[6] Phi Factor- in adiabatic calorimetry the phi factor is the ratio of the thermal mass of the sample holder to the thermal mass of the sample alone.

Solution samples were analyzed by semivolatile organic compound (SVOC) analysis using extraction into methylene chloride (dichloromethane) followed by analysis using GC/MS. Mass spectral identification used the NIST08 NIST/EPA/NIH Mass spectral Library of 220,460 electron impact mass spectra. Both a computer library and a manual review were used to identify the compounds with the mass spectroscopy results as the computer match did not provide an accurate identification for many of the large organic molecules found in this system.

RESULTS

Evaporation Test:

The preparation of the ~2000 ppm sample of Ultima Gold™ AB in 8 M nitric acid initially resulted in a white, cloudy solution (Figure 5a). The solution started to change color by the time it had been heated to 50 °C (Figure 5b) and by the time the temperature had reached 72 °C, the solution appeared noticeably yellow (Figure 5c). By the time the solution temperature reached 95 °C, its appearance was orange-yellow (Figure 5d), possibly from oxidation of components of the LSC organic and the initial appearance of NO_x gases in the vapor space. The cloudy appearance of the solution dissipated as the solution was heated above 75 °C and, when the stirring was stopped, floating droplets of organic were observed. At ~104 °C, the condenser vapor space had a visible yellow-brown appearance from NO_x gases indicative of nitric acid oxidation of organic components. As the solution continued to be heated, the yellow-brown appearance of NO_x gases became more evident. As the apparatus was
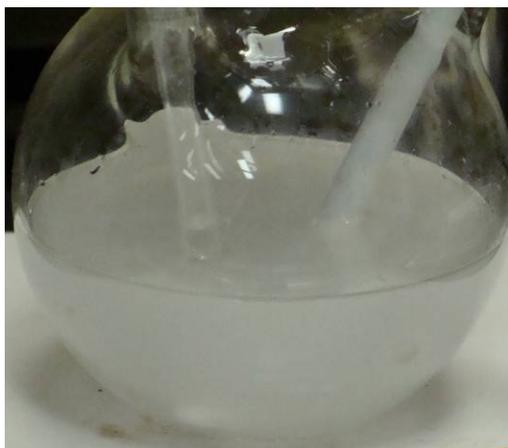
a) Initial Sol'n 8 M HNO3 2299 ppm LSC

b) Solution heated to ~50 °C

c) Solution heated ~72 °C
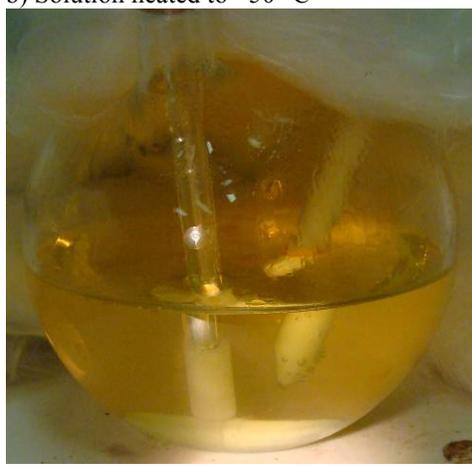
d) Solution heated to ~95 °C.

Figure 5. Solution appearance change during initial heating phase.

heated, water vapor displaced the initial air in the condenser. In addition, NO_x and CO_2 gases are assumed to have evolved. Approximately 100 cc of the 320 cc of total gas appeared to be due to water vapor displacement of air in the boiling flask. This volume is consistent with the available vapor space in the boiling flask. The net volume of ~220 cc of gas generated would amount to 9 mmol of gas (25 °C, 1 atm, ideal gas) compared with the potential of no more than 24 mmol of total carbon (assuming the organic to be 100% carbon). It is presumed that some CO_2 could be generated along

Table 2. Results from 2299 ppm Ultima Gold™ AB Evaporation Test in 8 M Nitric Acid.

T, min	V, cc	T, °C	Observations
0	0	18.3	white cloudy
10	6	49.9	white cloudy
11	6	55.2	pale yellow
12	10	65.6	
14	18	74.5	pale yellow, not cloudy
17	33	85.2	deeper yellow, took pictures, oily drops floating
21	65	100	NO$_x$ visible in condenser
24	83	107	
25	98	109	
26	108	111	
27	126	111	floating org visible
29	134	111	
30	136	111	
31	168	112	
34	156	112	offgas rate slow
37	138	111	
40	125	112	
45	135	112	
50	155	112	
108	225	114	
175	245	111	
230	260	112	organic color less
300	320	114	very little oil
305	280	114	drain condensate, collect fresh sample

with the visible NO$_x$ gases that were generated from the oxidation reactions during evaporation. Details on the temperature-time-gas evolution profile are shown in Table 2. The gas evolution rate peaked as the solution started boiling but then the rate declined.

The solution appeared less cloudy after the solution was heated for a short time and the solution color changed from white to orange and back to a light yellow (see Figure 5a, 5b, 5c, 5d, 6a, 6b, 6c, 6d). This change appeared to be partially due to the separation of oil droplets which floated on the surface of the solutions. After a heating cycle of five hours at boiling temperatures (111-114 °C), the amount of off-gas generated decreased and the oil droplets dispersed. When the solution cooled back to ambient temperature, neither the cloudiness nor the floating oil droplets re-formed. Foaming of the solution in the boiling flask was not observed. When the apparatus was disassembled, a drop or so of yellow-orange "grease-like" residue was found on the Teflon™ thermocouple. A sample of this residue was collected on a Petri dish for analysis and the total mass of residue was estimated at about three times the amount collected as a sample. FTIR analysis of this "grease" sample showed oxidation to benzylaldehyde and di-substituted aromatic compounds (Figure 7). The FTIR spectra showed no indication of nitrated organic species[7]. The GC/MS analysis of this "grease" sample will be discussed later in this report.

Unused "feed" solution (2299 ppm LSC in 8 M nitric acid) was left in a glass bottle. After a time (1 to 2 weeks) this solution was observed to have undergone some similar changes. The bottle appeared to have a small positive pressure and the solution had turned yellow. At some point during storage, some organic components separated into floating droplets and the solution was much less cloudy. These observations are consistent with previous observations[8] that Ultima Gold™ AB would react with nitric acid and release some offgas. Previously Kyser[2] reported that the emulsion observed in samples from the F/H HAD tanks could be broken by acidifying the solution.

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[7] D. L. Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules," Academic Press, NY, 1991.
[8] D. Diprete, "Experience Handling Spent Liquid Scintillation Cocktail", personal communication, Savannah River National Laboratory, December 1, 2010.

a) Boiling solution (10:57 AM)

b) NOx gas sample during evaporation

c) Boiling solution, note floating organic (12:17PM)
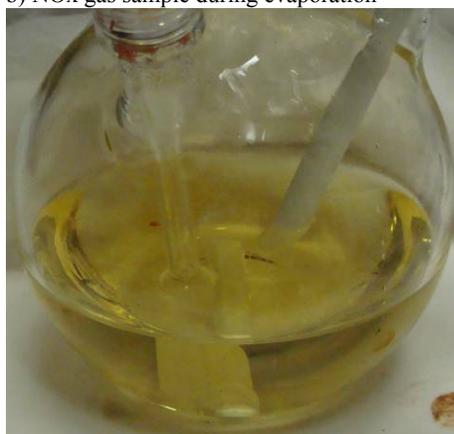
d) Post evaporation bottoms, no floating organic apparent, solution clear

Figure 6. Solution and Offgas changes during extended heating.
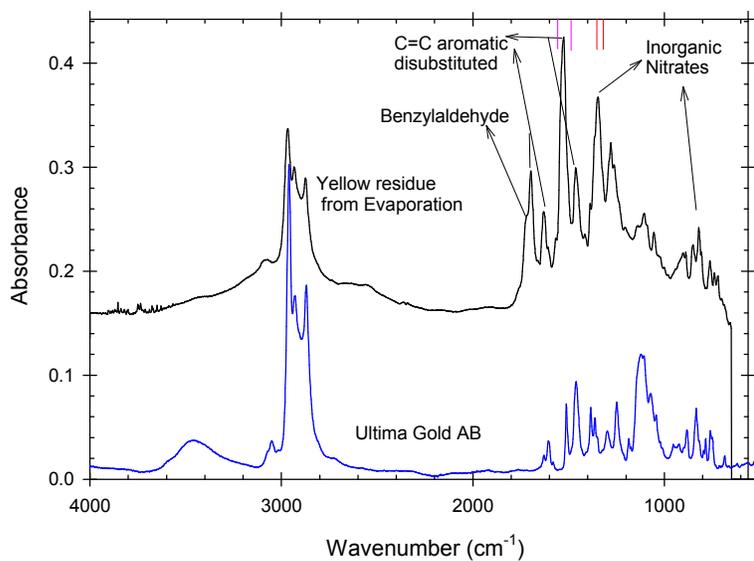
Note:
A nitrated aromatic has an asymmetric NO_2 peak at 1555-1487 cm^{-1} (very strong) and symmetric NO_2 peak at 1357-1318 cm^{-1} (strong).

Figure 7. FTIR Spectra of the Yellow Residue from Acid Evaporation of Ultima Gold^{TM} AB.

Accelerating Rate Calorimetery (ARC) Testing:

Duplicate tests were performed in the TIAX ARC2000 instrument with an ~2000 ppm solution of Ultima Gold™ AB in 8 M nitric acid. Temperature, pressure, rate of temperature rise, and rate of pressure rise were measured or calculated by the instrument. The Pressure/Temperature (P/T, K) ratio was also calculated as it represents a useful estimate for the change in the total number of moles in the sealed test cell (i.e., moles = P/T * V/R). Pressure, temperature and P/T versus time are shown in Figures 8a and 8b. Several inflection points are visible likely indicating a change in the reactions. The rate of pressure and temperature rise versus time and temperature are shown in Figures 9a and 9b. The initial portion of each test has a higher heating rate while the instrument heated the sample to
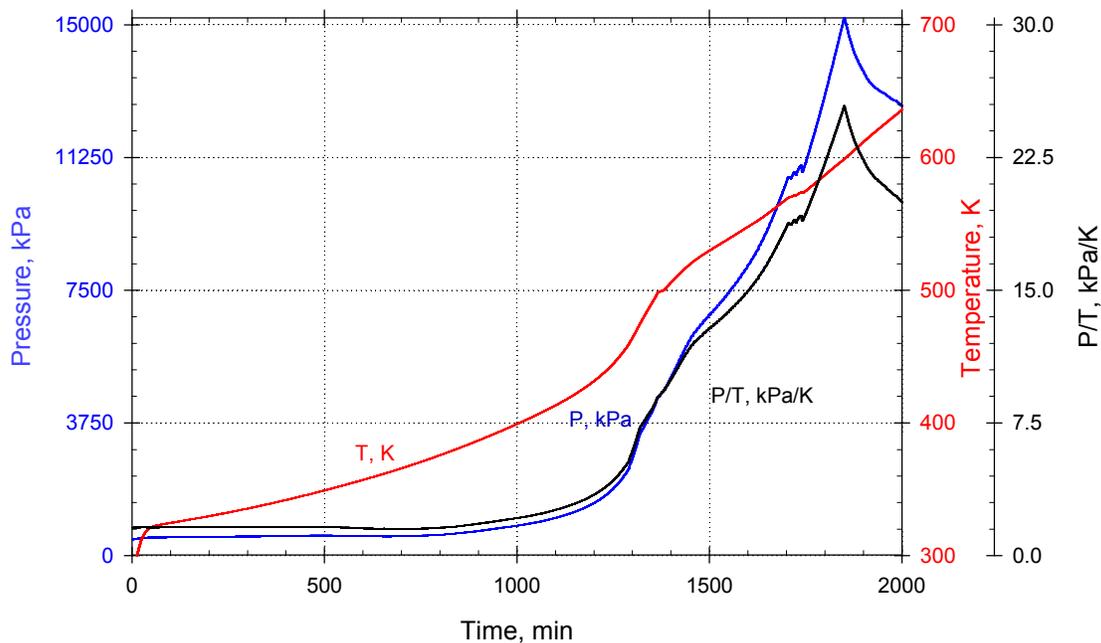

**Figure 8a. Pressure, Temperature and P/T ratio for 2000 ppm LSC in 8 M Nitric Acid A.**
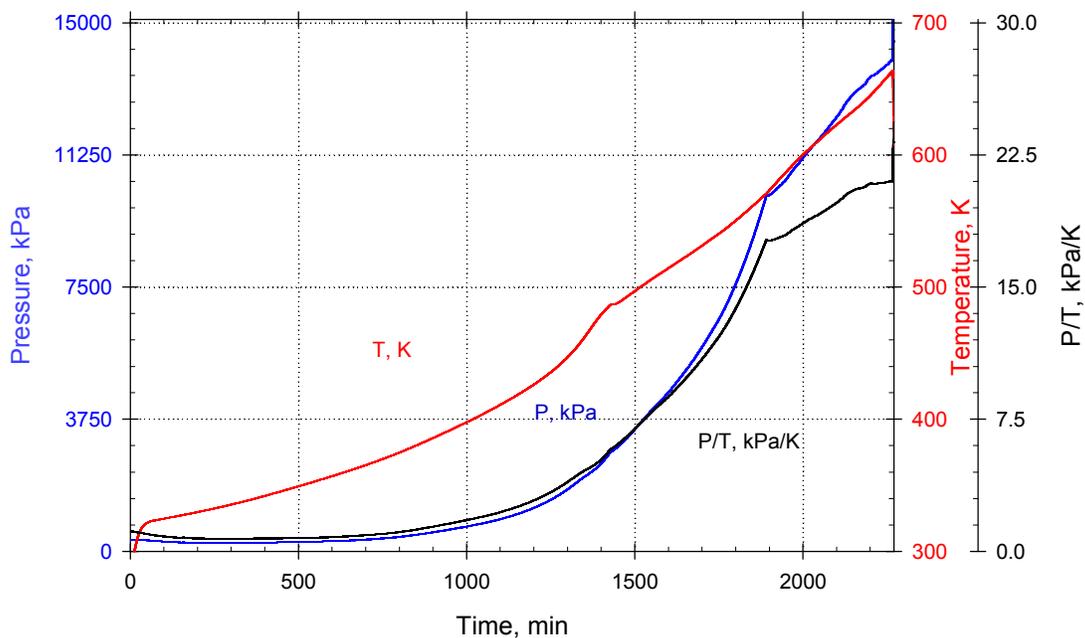
Figure 8b. Pressure, Temperature and P/T ratio for 2000 ppm LSC in 8 M Nitric Acid B.

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323 K (50 °C) prior to the start of the exotherm search cycle (heat-wait-search). Pressure rise rates of up to 45 kPa/min (~7 psi/min) and temperature rise rates of up to 0.6 K/min were observed in these tests in the 470-600 K temperature range. By comparison for the tributyl phosphate – nitric acid system, Epstein[9] has reported pressure rise rates (dP/dt) of 7200 kPa/min and temperature rise rates (dT/dt) of 180 K/min at 443 K. Bodman[10] classifies materials having dP/dt$_{max}$ < 1,700,000 kPa/min as not having deflagrating properties during heating under confinement. The reaction of up to 2000 ppm of Ultima Gold™ AB in 8 M nitric acid in a vented evaporator does not appear to be a significant process hazard.

The P/T ratio as a function of temperature provides a measurement for the increase in the number of moles of gas in the closed vessel (assuming no leakage). Figure 10a and 10b are plots of the pressure and P/T ratios versus temperature for the two ARC tests. By comparing the P/T ratios from the end of the test to the beginning of the test (with assumptions about the vapor volume in the test cell), the total number of mmoles of gas generated during the test can be calculated. The ARC experiment A generated 3.2 mmoles of gas while the ARC experiment B generated 7.5 mmoles of gas compared to the 9 mmoles of gas calculated from the evaporator test.

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[9] M. Epstein, M; H. K. Fauske, C. F. Askonas, M. A.Vial, P. Paviet-Hartmann, "Thermal stability and safe venting of the tri-n-butyl phosphate-nitric acid-water ("red oil") system-II: Experimental data on reaction self-heat rates and gas production and their correlation", Nuclear Technology, Vol: 163, No. 2, 294-306, August 2008.

[10] G. T. Bodman, S. Chervin, "Use of ARC in Screening for Explosive Properties", Journal of Hazardous Materials, Vol. 115, 101-5, 2004.
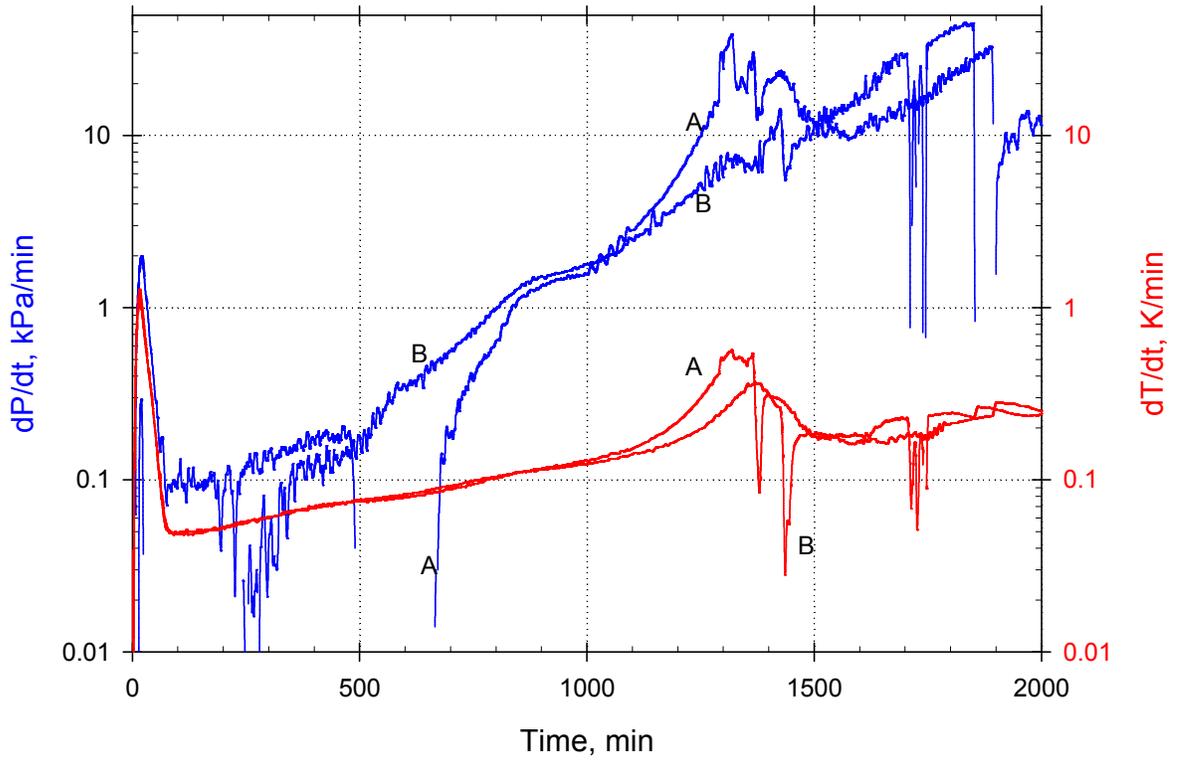
**Figure 9a.Rate of Pressure and Temperature Rise versus time- ARC Tests A and B combined.**
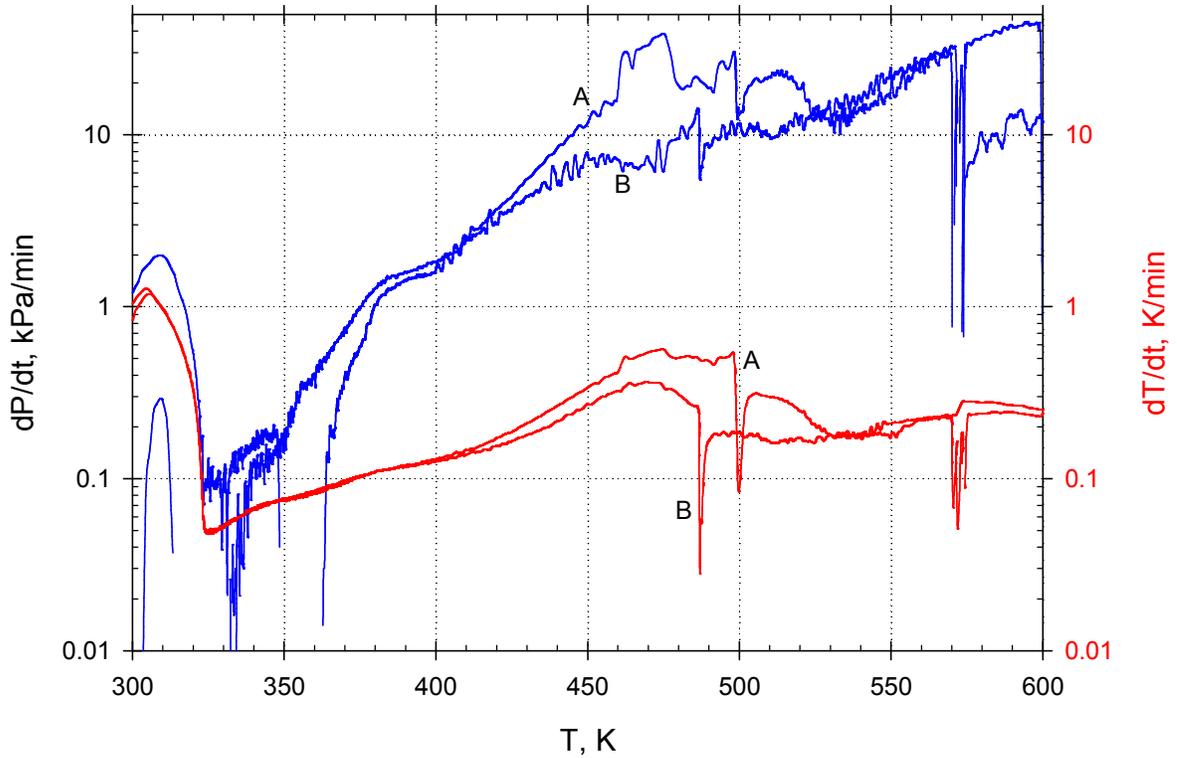
**Figure 9b. Rate of Pressure and Temperature Rise versus Temperature ARC Tests A and B combined.**

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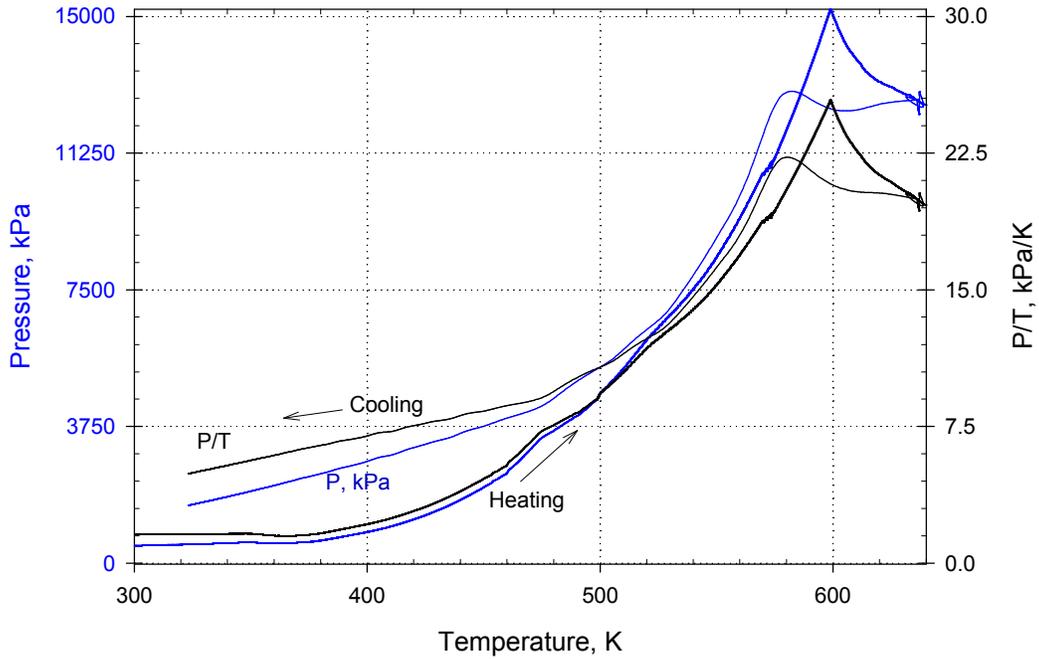
**Figure 10a. Pressure and P/T Ratio versus Temperature - ARC Test A.**
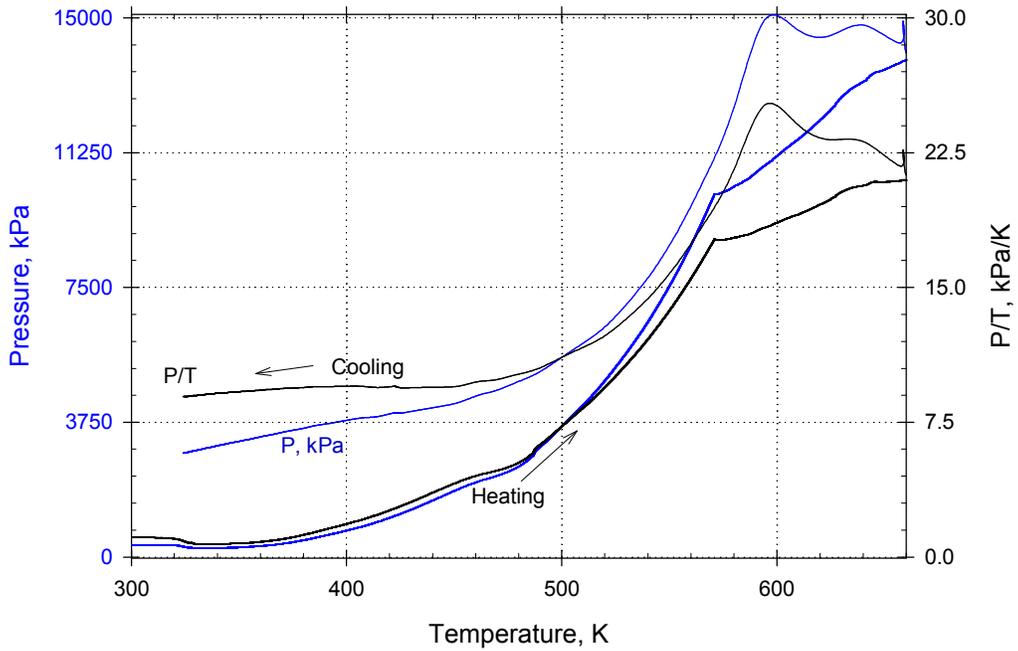
Figure 10b. Pressure and P/T Ratio versus Temperature - ARC Test B.

Chemical Composition by SVOC:
As previously stated, samples of feed, bottoms, and condensate from the evaporation test were analyzed by GC/MS in an attempt to identify the reaction products from Ultima Gold™ AB and nitric acid in an evaporator and in which streams those reaction products are expected to be present.

Analysis of the feed solution found a number of the compounds reported on the MSDS (Table 1); however, some compounds were not identified (Table 3) and the overall amount of organic was significantly less than the amount originally prepared (only ~3.5% of the 2299 ppm prepared). Based on observations of the unused feed solution, it is believed that the feed solution sample reacted at ambient temperature and a significant amount of the originally soluble organic probably separated after the experiment was performed but prior to the analysis. Although the sample would have been mixed prior to analysis, the phases probably separated quickly and the aliquot of sample that was analyzed

Table 3. GC/MS Results on Evaporator Feed Sample (#300286852).

Ret. Time min	Area %[1]	Analyte	Source	Conc ug/mL
14.429	13.45	Ethanol, 2-(2-butoxyethoxy)-	Emulsifier	43
13.602	5.15		Emulsifier related A?	17
19.174	4.69		Emulsifier related B?	15
27.936	1.91	Diisooctyl adipate	Plasticizer	6.1
24.775	1.01		DIN Derivatives	3.2
24.041	2.69			8.6
25.753	0.64			2.1
24.961	0.57			1.8
25.491	0.55	1,8-(2-Oxotetramethylene)naphthalene	DIN related ?	1.8
17.072	0.47	Ethanol, 2-butoxy-	Emulsifier related	1.5
9.655	0.4	2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl acetate	Emulsifier related	1.3
23.715	0.34			1.1
				102

[1] Area % does not total to 100% due to inclusion of internal standards.

did not contain a representative amount of the organic species. Although DIN is the majority component in Ultima Gold™ AB, it appears to be underreported in the feed sample analysis. The breakdown of the emulsion is likely responsible for this underreporting but the cause of the phase separation in not fully understood. It might be explained by the DIN's lack of solubility in the aqueous phase after reaction of the emulsifier agents with nitric acid however these agents are very dilute.

Analysis of the condensate (#300286851) sampled from the end of the evaporation (after five hours of reflux) did not detect any organics other than 8 ug/ mL diisoctyl adipate (a plasticizer used in a variety of plastics). This plasticizer was found in small amounts in most of the samples and may have been introduced by the plastics in the sample vial caps.

Analysis of the evaporator bottoms at the end of the evaporation (after five hours of reflux) detected a surprisingly small amount of organic species (32 ppm total, Table 4). Besides the plasticizer previously seen, several different compounds that appear to be derivatives of the emulsifiers were detected. DIN related compounds were not detected in this sample. With the small amount of organic involved in this experiment, it is thought that the poorly soluble DIN related species were preferentially separated from the aqueous phase and were not readily observed.

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Table 4. GC/MS Results on Evaporator Bottoms Sample (#300286850).

Ret. Time	Area%[1]	Analyte	Source	Conc
min				ug/mL
13.603	6.49		Emulsifier related A?	16
27.942	3	Diisooctyl adipate	Plasticizer	7.5
19.169	2.79		Emulsifier related B?	6.9
9.655	0.67			1.7
				32

[1] Area % does not total to 100% due to inclusion of internal standards.

Analysis of a sample of the drop of the yellow grease-like residue that was found on the thermocouple when the apparatus was disassembled found it to be primarily composed of DIN and derivatives of DIN (Table 5). The total mass of this residue was estimated at ~120 mg total (or ~26% of the original added organic). Other components of Ultima Gold™ AB such as the emulsifiers and scintillators were not detected. The portion of the grease sample that was analyzed amounted to the equivalent of ~167 ug/mL of total organic. Depending on the fraction of the total amount of grease that was sampled, the analysis could explain what happened to a significant fraction of the DIN originally introduced to the evaporator in the feed. The mechanism for the separation of the naphthalene derivatives is more difficult to understand. It was suggested that the partial oxidation of the emulsifiers and surfactants could have contributed to the separation of the naphthalene derivatives but these emulsifiers relatively dilute (~200 ppm) and it is not certain the effect that they have at this concentration. Whatever the mechanism for the breakdown of the emulsion, once it is broken and the species of limited solubility form a separate phase, the samples taken after that point are not representative and explain the lack of DIN and DIN derivatives in both the feed and bottoms samples.

Table 5. GC/MS Results on Grease Sample (#300286848, 37.3 mg).

Ret. Time	Area%[1]	Analyte	Source	Concentration		
min				ug/g	ug/mL [2]	ug/mL [3]
25.888	13.12		DIN related A	74000	28	83
24.13	11.84		DIN related B	67000	25	75
24.875	10.41		DIN related C	59000	22	66
24.374	9.6		DIN related D	54000	20	61
25.591	8.6		DIN acid product E	49000	18	54
25.05	6.6		DIN acid product F	37000	14	42
n/a-	6.37	Cumulative Diisopropylnaphthalenes	DIN isomers	36000	13	40
23.082	5.2		DIN product G ?	29000	11	33
23.769	5.08		DIN related D'	29000	11	32
25.923	4.31	2-Propenoic acid, 2-cyano-3-(4-methylphenyl)-, ethyl ester	DIN acid product I	24000	9	27
24.764	3.11	(1,1'-Biphenyl)-3-carboxylic acid	DIN acid Product J	18000	7	20
25.149	2.54	1,8-(2-Oxotetramethylene)naphthalene	DIN acid Product K	14000	5	16
25.964	2.42	5,11-Dihydro-8-methylthio-6H-pyrido[2,3-b][1,4]benzodiazepine-6-one	DIN acid Product L	14000	5	15
25.364	2.13			12000	4	13
n/a	7.83	19 Unidentified compounds		44380	16	40
				560380	209	626

[1] Area % does not total to 100% due to inclusion of internal standards

[2] Calculated assuming 100 mL solution volume.

[3] Assume that total organic present was three times the amount sampled.

DISCUSSION AND APPLICATION

Experimental measurements and observations did not observe any reactivity hazards for the evaporation of ~2000 ppm Ultima Gold™ AB in 8 M nitric acid. Ultima Gold™ AB has a low volatility and no evidence was observed of significant vapor carryover to the condensate. Although the evaporation test was performed over a five hour period of time, the condensate sample that was analyzed was collected over only a few minutes. Therefore high boiling compounds like diisopropylnaphthalene (DIN, boiling point 279 °C) might not be collected in significant concentrations in the sample. This experiment does not provide any indication as to how much evaporation might be required to "stream-strip" DIN-related compounds but DIN and TBP have similar boiling points (DIN- 279 °C vs TBP 289 °C) and the steam-stripping behavior of TBP is relatively well understood[11]. Heating solutions containing both Ultima Gold™ AB and 8 M nitric acid appeared to quickly break the initial cloudy emulsion and allow the DIN-related compounds to separate into a separate floating phase. In actual process operations this emulsion would likely remain until mixed with other more acidic solutions and heated in the canyon evaporator. In this experiment, these floating organic phases disappeared over time but a significant fraction of naphthalene derivatives accumulated on the Teflon™ thermocouple as a yellow grease-like material (~26% of total organic used in the experiment). In the canyon evaporator, these organics could cause minor operational problems if residues collected in the evaporator instead of being removed via stream-stripping or bottoms stream transfers. Note however, that significant quantities of Ultima Gold™ AB have been present in the SRNL sample returns for many years and processed in H-Canyon without reported problems.

Significant foaming did not occur while this solution was boiled and non-condensable gas generation appeared to be relatively modest. Previous work with the destruction of ammonia[12] with nitrite and solution denitration produced multiple liters of gas from a similar sized experiment[13], while in this test only a few 100 cubic centimeters of total gas was produced. The designs of the various canyon evaporators (9.1, 9.2 and 17.8) are all similar and the non-condensable vapor flow capacities are estimated to be at least 100 scfm (60 moles/min)[12]. Gas generation during the calorimetry experiments was <6 moles/min (below 135 °C) when scaled to a 6000 L evaporator batch size. The amount of non-condensable off-gas from the evaporation of solution containing large concentrations of Ultima Gold™ AB appears modest compared to the amounts considered for denitration or ammonia destruction and will not challenge the off-gas capacity of the equipment.

Calorimetry experiments (using the ARC2000), show that the exothermic reactions between the organics components of Ultima Gold™ AB and nitric acid are not particularly energetic for the conditions tested. Because the feed solution contains a large amount of water compared with the quantity of organic available, the system is highly tempered. The rates of pressure and temperature rise were found to be small compared with the "red-oil" type reactions involving much larger quantities of tri-n-butyl phosphate and nitric acid.

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[11] R. A. Pierce, M. C. Thompson, "Behavior of TBP and DBP during the Evaporation of Enriched Uranium Solutions", WSRC-TR-99-00040, Westinghouse Savannah River Co., Savannah River Technology Center, Aiken, SC, January 1999.

[12] E. A. Kyser, "Effects of Addition Rate and Acid Matrix on the Destruction of Ammonium by the Semicontinuous Addition of Sodium Nitrite during Evaporation", SRNL-STI-2007-00435, Savannah River National Laboratory, August, 2007.

[13] E. A. Kyser, "Denitration of Acidic Aqueous Waste Solutions to Eliminate Ammonium Content and Minimize Waste Volume from Processing Nuclear Fuel", SRNL-STI-2009-00232, Savannah River National Laboratory, August, 2010.

This study did not specifically include the neutralization of acid waste products from evaporation but the residues of these experiments were neutralized to pH >2 with sodium hydroxide. No unexpected behavior was noted during that neutralization and the residues from these experiments were discarded without incident.

CONCLUSIONS

Evaporation and calorimetry testing of surrogate samples containing ~2000 ppm of Ultima Gold™ AB LSC in 8 M nitric acid have been completed. These experiments showed that although reactions between nitric acid and the organic components do occur, they do not appear to pose a significant hazard for runaway reactions or generation of energetic compounds in canyon evaporators. The amount of off-gas generated was relatively modest and appeared to be well within the venting capacity of the H-Canyon evaporators. A significant fraction of the organic components likely survives the evaporation process primarily as non-volatile components that are not expected to represent any new process concerns during downstream operations such as neutralization. Laboratory Waste solutions containing minor amounts of DIN can be safely received, stored, transferred, and processed through the canyon waste evaporator.

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