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Potential Impact of Tank F Flush Solution on H-Canyon Evaporator Operation

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Potential Impact of Tank F Flush Solution on H-Canyon Evaporator Operation

SUMMARY

Previous chemical analysis of a sample from the liquid heel found in Tank F of the High Activity Drain (HAD) system in F/H laboratory revealed the presence of n-paraffin, tributyl phosphate (TBP), Modifier¹ from the Modular Caustic-Side Solvent Extraction Unit (MCU) process and a vinyl ester resin that is very similar to the protective lining on Tank F. Subsequent analyses detected the presence of a small amount of diisopropylnaphthalene (DIN) (major component of Ultima Gold™ AB liquid scintillation cocktail). Indications are that both vinyl ester resin and DIN are present in small amounts in the flush solution. The flush solution currently in the LR-56S trailer likely has an emulsion which is believed to contain a mixture of the reported organic species dominated by TBP. An acid treatment similar to that proposed to clear the HAD tank heel in F/H laboratory was found to allow separation of an organic phase from the cloudy sample tested by SRNL. Mixing of that clear sample did re-introduce some cloudiness that did not immediately clear but that cloudiness is attributed to the DIN in the matrix. An organic phase does quickly separate from the cloudy matrix allowing separation by a box decanter in H-Canyon prior to transfer to the evaporator feed tank. This separation should proceed normally as long as the emulsion is broken-up by acidification.

¹ Modifier is 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, also known as Cs-7SB, used in the Modular Caustic-Side Solvent Extraction Unit (MCU).

BACKGROUND

The High Activity Drain (HAD) System collects radioactive liquid material from the 772-F and 772-1F Laboratories and temporarily holds this material in the transfer tank (Tank F) for delivery to the 221-H Canyon for further processing.

The HAD Tank F is a lined stainless steel (304L) tank approximately six feet in outer diameter (OD). The tank is lined with Sherwin-Williams COR-COTE Ven FF, B88-25 Resin, approximately 40 mils thick. HAD Tank F is the replacement tank for HAD tank C which developed a leak that could not be repaired. Tank F has been in service for 1.5 years.

The HAD Tank F receives sample returns from the various F/H Laboratory Modules. The sample returns include the unused sample material, any material used to prepare the sample for analysis and small volumes of expired reagent along with flush water.

When volume in the HAD Tank F reaches a predetermined value the tank is removed from service to permit acid washing followed by a water rinse. Following the final rinse the tank is opened and any solids on the bottom of the tank are sampled and a new baseline fissile hold-up is calculated. This is the first baseline for this tank.

Following transfer of the third water rinse the tank was opened for observation. The remaining heel material was observed to have a milky white appearance with what appeared to be patches of black material floating on the surface as opposed to an expected clear appearance². Subsequent activities removed floating pipette tips and other plastic items and no additional dark-colored floating material was observed.

Previously SRNL personnel characterized the chemical behavior of the liquid heel. Acidification with 2 M nitric acid (to ~0.75 M) was recommended to “break” the emulsion and produce a clear solution to allow for inspection of the tank bottom³. The LR-56S trailer contains ~3900 pounds of flush water (second and third flushes) which must be periodically vented until it is unloaded in H-Canyon. This flush solution is planned to be transported to H-Canyon and unloaded. SRNL has been requested⁴ to evaluate the compatibility of this solution to the planned processing in H-Canyon.

EXPERIMENTAL

The HAD liquid heel from F/H laboratory was provided to SRNL on August 12, 2010. A picture of the sample (picture taken on August 20) sent to SRNL is shown in Figure 1. As seen in Figure 1, the sample has a white and hazy (turbid and opaque) appearance. Also, the top surface of the liquid sample near the glass edge has the appearance of suspended, spherical droplets (slightly yellow in color) approximately one millimeter in size. The liquid sample has maintained its suspension (liquid-insoluble structure) despite the long undisturbed time in the laboratory.

The measured density is 0.9940 ± 0.0002 g/mL (from duplicate measurements) which is slightly less than that of pure water. Using a pH paper (visual matching to a color scale), the sample measured a pH value of 2 (~0.01 M nitric acid). This value is reasonably consistent with the value of pH 1.2 and 0.05 M reported by F/H Laboratory personnel⁵.

Further analysis of the residues from the initial testing was performed. Where filtration was performed, a 0.2 or 0.45 micron nylon membrane syringe filter was used to filter an aliquot of the sample. Acid treatment of the sample was performed using incremental amounts of 2 M nitric acid until the sample aliquot was adjusted to ~0.75 M nitric acid. Qualitative analysis was performed via Fourier Transform Infrared Spectroscopy (FTIR).

² D. M. Nichols, “Path Forward for HAD Tank F, Baselineing”, SRNS-N3400-2010-00145, August 24, 2010.

³ F. F. Fondeur, S. D. Fink, “Initial Characterization of the Liquid Heel in the F/H Laboratory High Activity Drain Tank”, SRNL-L3100-2010-00185, Savannah River National Laboratory, Aiken, SC, September 2, 2010.

⁴ D. Nichols, “Characterization of High Activity Drain Tank (Tank F) Contents,” NMMD-2010-3159, August 12, 2010.

⁵ D. M. Nichols, “Acid Flushes of HAD Tank”, email to S. D. Fink and F. F. Fondeur dated 8/26/2010.



Note the small yellow droplets at the liquid surface in the magnified cropped picture.

Figure 1. As-received Tank F Sample (HAD in F/H Laboratory).

Both filtered and acid-treated samples were analyzed by semivolatiles organic compound (SVOC) analysis (using extraction into methylene chloride followed by analysis by GC/MS).

RESULTS

Filtration Treatment:

Approximately 1 mL of the sample was filtered through a 0.45 micron nylon filter. The filtrate still had a hazy and translucent appearance. The test was repeated by filtering the sample through a 0.2 micron nylon filter and the filtrate was transparent as shown in of Figure 2. Analysis of the filtrate by FTIR revealed that the bulk of the organic constituents were no longer in the solution. It is presumed that the nylon filter removed the organic components by filtration but it is possible that some may have been absorbed.

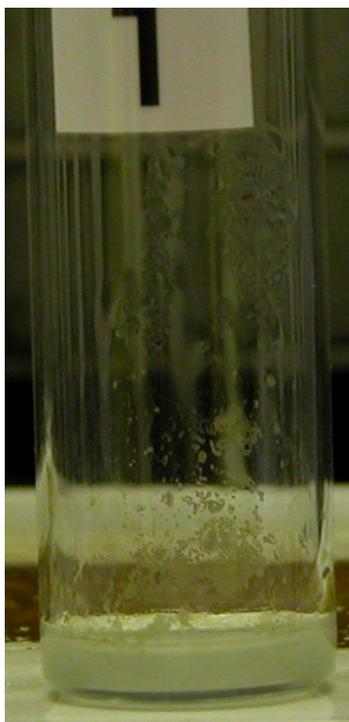


- 0.2 micron nylon filtered the liquid heel to clear transparency
- 0.45 micron did not filter the liquid heel to complete transparency

Figure 2. Results of Filtration Treatment of Tank F Sample.

Heat Treatment:

In another test, 1 mL of the liquid heel was placed on a heater plate and heated from 27 °C to 81 °C in 2.3 hours while allowing evaporation. A 26% volume reduction in the sample volume was performed (see Figure 3). At approximately 68 °C, personnel noticed the formation of brown colored skin (typically associated with oxidized organic) floating on the top surface of the heated liquid heel. H-Canyon is expected to evaporate this solution at a temperature in excess of 100 °C for a volume reduction of 95 to 99%. Organic residue that reaches the evaporator will likely be oxidized to a much greater extent than observed in this laboratory test. Volatile and semivolatile components and reaction by-products will be steam-stripped to the overheads. The overheads from the evaporator that processes laboratory residue returns are eventually fed to the Acid Recovery Unit (ARU), so volatile liquid components could be recycled into the HM process via the recycled acid stream. Evaporator bottoms will be neutralized and sent to the tank farm. Alternatively if the ARU is not operational the overheads from the evaporator may be transferred to the Effluent Treatment Facility (ETF).



- Heated the sample from room temperature to 27 °C to 81 °C in 2.3 hours.
- A brown film developed near 68 °C around the glass vial

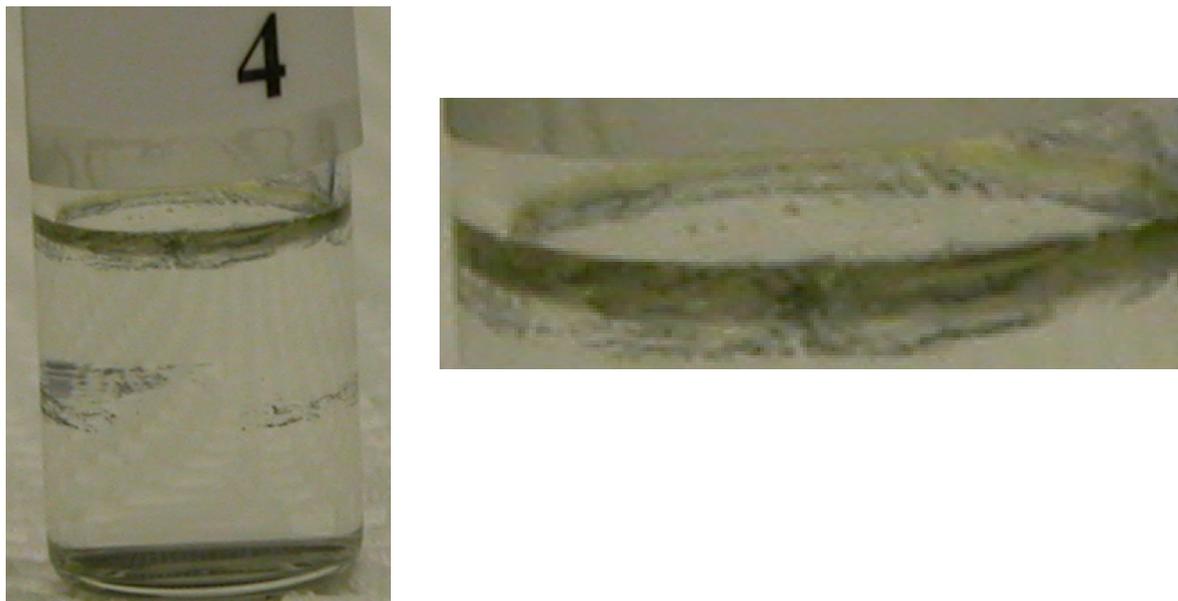
Figure 3. Results of Heat Treatment of Tank F Sample.

Acid Treatment:

In another series of tests, several 1 mL samples received sequential doses (i.e., small portion added, mix for one minute and observed after 5 minutes) of various inorganic salts, 2 M nitric acid and 2 M sodium hydroxide.

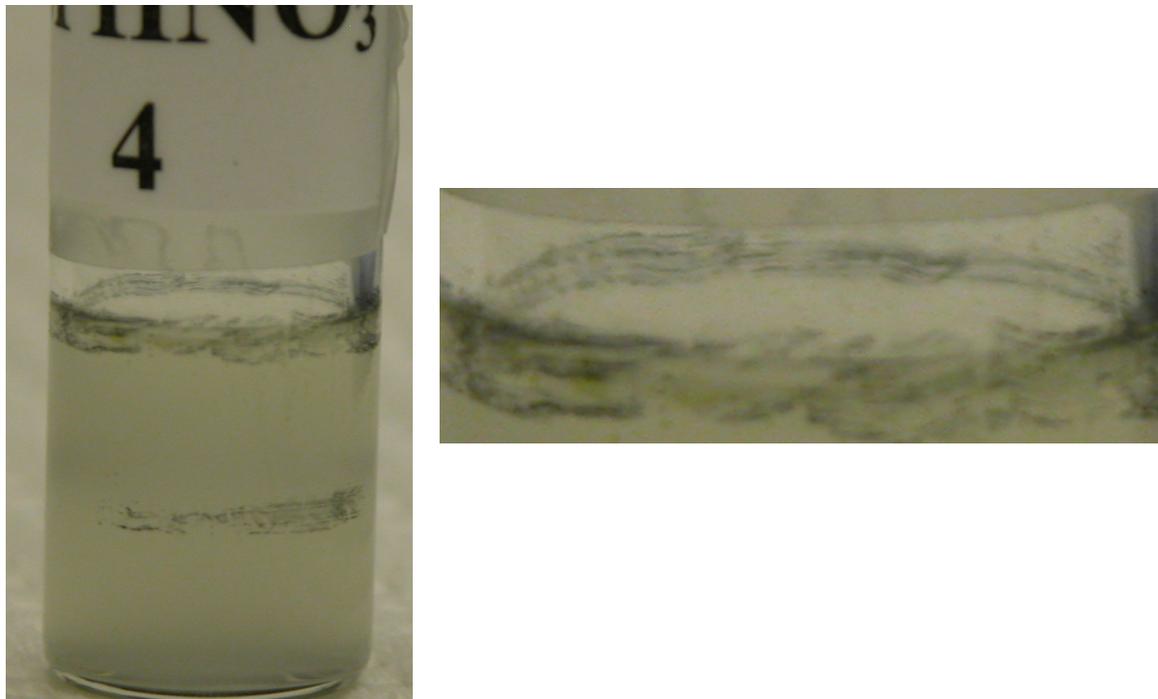
The recommended treatment (i.e. that produced the most transparent resulting sample) was the addition of 2 M nitric acid (yielding an nominal concentration of ~0.75 M nitric acid). Four hours after this treatment was performed, significant cloudiness was still apparent but after 16 hours, the solution had cleared and no solids were observed. A yellow floating organic phase had separated and was visible as a ring around the vial at the liquid surface (see Figure 4). A similar treatment may be performed in either the HAD Tank F (to allow inspection of the tank bottom) or in one of the H-Area tanks to allow for decanting of the solution. The cloudiness of the initial solution is presumed to be due to the nature of the colloidal micelles of organic-aqueous material. Preparation of surrogate solutions showed that DIN alone at very low concentrations (< 100 ppm) made the solution cloudy. The length of time to “break” the emulsion is likely due to surface tension effects and the limitations of gravity alone in aggregating these small structures into larger ones which can separate. Once the initial separation is complete, such small structures are more difficult to reform although it appears that DIN is easily dispersed into the solution and causes additional cloudiness (see Figure 5) which took some

time to clear. Figure 5 also shows the yellow droplets of separated organic phase which did not disperse when the sample was shaken.



Note that no settled solids were observed but yellow organic phase separated at surface. Black marks are volume marks placed on the outside of the vial.

Figure 4. Results of Acid Treatment of Tank F Sample (after 16 hours settling).



Note that after remixing the separated yellow phase immediately separated at the surface. Black marks are volume marks placed on the outside of the vial.

Figure 5. Results of Acid Treatment of Tank F Sample (immediately after remixing).

Chemical Composition:

Samples of filtered and acid-treated sample were analyzed by GC/MS analysis. The main organic compound identified was TBP. Smaller amounts of DIN and MCU modifier were identified but the corresponding solvent component, n-paraffin and Isopar™ L, were not found. The results from these analyses are shown as Table 1. One possible explanation is that significant n-paraffin and Isopar™ L solvent components were removed by evaporation due to the relatively high air-flow through the HAD tank in F-Area. Alternatively, the absence of these solvents may be due to their low solubility and the emulsion in the sample may have formed without incorporating these compounds. Also Isopar™ L is not quantitatively recovered in this analytical procedure (due to evaporation). Either way, assuming that the Tank F sample is representative of the entire contents of the HAD tank during the third water flush, the GC/MS results indicate that the total organic content of that third flush would only amount to ~10 g of TBP, Modifier and DIN total. If a floating organic layer is present in Tank F, then any such layer could involve more material than is present in the emulsified sample. However as long as any such material floats on the surface, it should be removed by the H-Canyon 13.6-1S box decanter. It is likely that higher concentrations of organic material were present in the second flush, but the same compounds should have been present and they should behave in a similar manner.

Table 1. Results from GC/MS Analysis of Acid-Treated and Filtered Samples.

	TBP ppm	DIN ppm	MCU Modifier ppm	n-paraffin ppm
0.75M HNO ₃ Sample ^a	7	<1	<1	nd
Filtered Sample (0.2 um)	1.8	nd	nd	nd

^aComposition of acidified sample corrected to original sample volume
nd – not detected, ~1 ppm quantification limit

A filtered sample and acid-treated sample were both analyzed by FTIR. The FTIR spectra (shown in Figure 6) suggest that the filtration removed the organic constituents below the detection limit of the method (upper spectra). After the acid-treated sample cleared, the only remaining FTIR organic signal (from the clear phase) was from a soluble carboxylic acid (lower spectra).

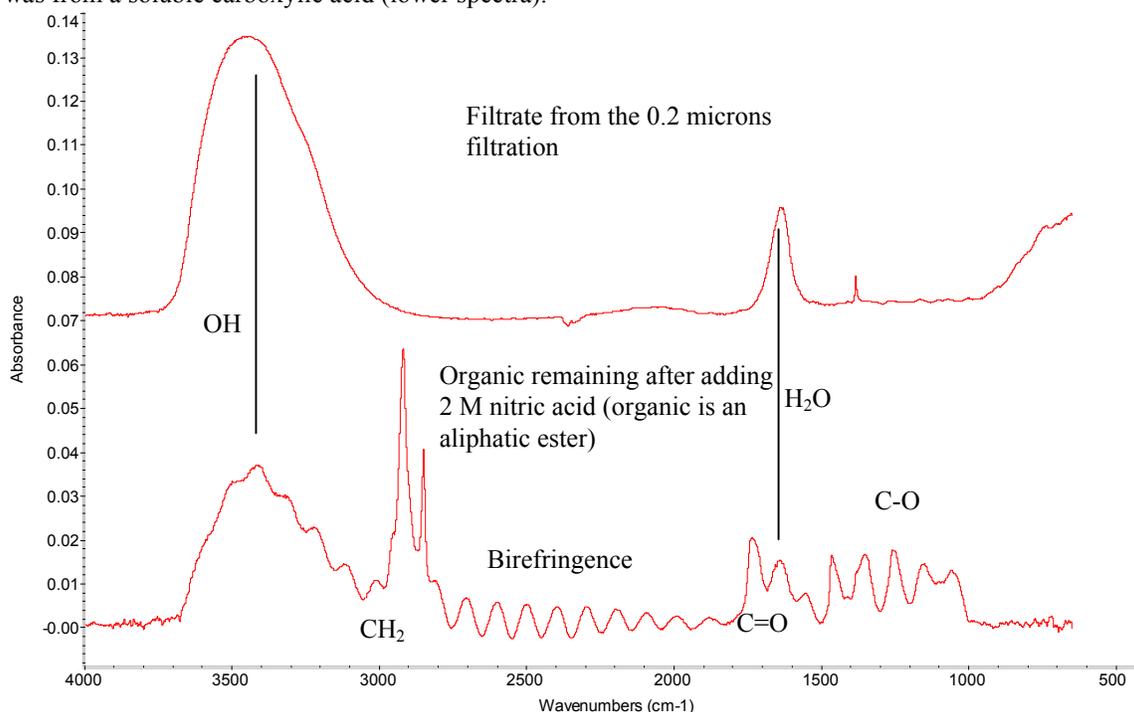


Figure 6. FTIR Spectra of the Filtered Sample Aliquot and the Acid Treated Aliquot.

FTIR analysis of a sample of DIN and comparison with the spectra from the original sample found many of the same features of the spectra that were initially attributed to the vinyl-ester compound from the tank lining. It is considered likely that both DIN and vinyl ester are present in small amounts in the flush solution.

DISCUSSION AND APPLICATION

Upon receipt by H-Canyon the laboratory waste solution must be transferred through a series of tanks and mixed with other streams (including sump flushes and solvent wash solution) prior to evaporation in the 17.8E batch evaporator. Prior to addition to the evaporator, organic in the solution is removed by the 13.6-1S box decanter. 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 solution⁶ (although actual removal is believed to be above 98% for the typical acidic-TBP solutions used in H-Canyon processes) for explosion prevention from a TBP-nitric acid reaction. 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, it 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 ARU 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 all of these issues.

With a solution that forms an emulsion that does not allow phase separation by the box decanter, an unknown quantity of organic could be introduced to the 17.8E evaporator. Although there is likely to be a higher concentration of organic in the LR-56S tanker for shipment to H-Canyon than in the flushed heel sample from Tank F, the total amount of organic is still expected to be relatively small. As long as the emulsion is “broken” prior to feeding, allowing the separated organic phase to be separated by the box decanter, no unusual amount of organic is expected in the evaporator feed and this solution should behave as normal laboratory waste solution. In the laboratory testing, there appeared to be a kinetic limitation to breaking of the emulsion, which appeared to require the solution to stand undisturbed overnight. The amount of DIN in the solution may make the solution still appear cloudy but that observation alone should not be considered a reliable indication of an emulsion of TBP. DIN is not a new component of the laboratory waste streams and it has been present in larger amounts in the past. The amounts present in the LR-56S tanker should be insignificant compared with the normal amounts in laboratory waste as the current solution is primarily flush water. The only new component that may be present is the vinyl ester that may be leaching into the solution in small but detectable amounts.

Although no particular study was performed on the downstream mixing of this solution with other canyon solutions, or poisoning and neutralization operations with this material, no problems are foreseen with these operations.

CONCLUSIONS

Acidification of the flush solution from the F/H laboratory HAD tank (to greater than 0.75 M nitric acid and settling without mixing for at least 16 hours) should allow the insoluble organic phase which likely contains TBP to separate into a independent phase which should be readily separated by the box decanter. Mixing will likely cause the aqueous phase to temporarily become cloudy, but the principal insoluble organic components should separate immediately. Once the emulsion has been broken, this solution is expected to behave as normal laboratory waste in downstream operations.

⁶ H-Canyon Documented Safety Analysis, WSRC-SA-2001-00008, Rev. 19, June 2010, Section 8.3.2.2.1.2.