

Separable Organic Evaluation: Waste Feed Delivery Impacts – 17563

Bryce Eaton, Washington River Protection Solutions

ABSTRACT

The potential for separable organic materials to separate out from Hanford tank waste requires consideration for future Waste Feed Delivery operations. Separable organic materials are organic compounds of very limited solubility in bulk waste that can form a separate phase or layer. If the organic materials bound to waste separates during mixing and transfer operations, the feed batch would be disqualified under the Hanford Tank Waste Treatment and Immobilization Plant (WTP) waste acceptance criteria for “no visible immiscible layer.”

Sample data and process history were used to identify tanks with the potential to contain separable organic materials. Centrifuge testing was performed on available archived tank samples and on waste simulants developed to mimic characteristics of the archived tank samples. A separable layer formed during centrifuge testing of archived samples 241-C-204, 241-SY-102, and for all developed simulants tested.

Due to the formation of a separable organic layer during the centrifugation studies, an impact assessment was performed. This impact assessment identified forty-four potential tanks of concern regarding the release of organic material bound to solids during waste disturbing activities. A Hanford Tank Waste Operations Simulator model run was modified to trace the origin of each batch to the WTP. The outputs of the model run indicated that a separable organic layer would form during High Level Waste Feed Delivery operations and would cascade to all tanks containing or receiving significant amounts of organic solvents/diluents. Hence, there is a potential for a ripple effect across the feed batches.

INTRODUCTION

Tank Mixing and Waste Feed Delivery (WFD) operations may separate organic materials that are presently bound to Hanford tank waste sludge solids. If these organics were to separate out during WFD operations, an immiscible layer may form thereby creating a batch that would be disqualified under the Hanford Tank Waste Treatment and Immobilization Plant waste acceptance criteria specified in [1] for “no visible immiscible layer.”

An evaluation was conducted that culminated historical process and chemical constituent information, and testing results from laboratory studies of actual tank waste. The evaluation identified potential tanks of interest (TOI) containing waste that may release organic material bound to sludge during waste disturbing activities. An impact assessment was performed on batch contamination by organic materials, using tanks identified as TOI.

BACKGROUND

Separable organics are likely to be present in various Hanford tanks as a result of the waste generated from Hanford Site process operations. Waste streams, often containing organics, were transferred to Single-Shelled Tanks (SSTs) and Double-Shelled Tanks (DSTs). Several organic waste streams from historical Hanford process operations are known to have been disposed of in the waste tanks:

- Diluents and solvents used to extract plutonium, uranium, and other products;
- Chelating agents to separate out strontium and cesium products;
- Reagents used for recovery, washing, and purification steps in Hanford process operations; and
- Laboratory testing and decontamination wash fluids (in minor quantities).

Of the organic constituents utilized in process operations, diluents and solvents are expected to be the largest contributors to the formation of separable layers in tank waste.

Diluents and Solvents

Separable organic contributions to the tank waste stemmed from solvent extraction processes: U Plant Recovery Process, Reduction Oxidation Processes, B Plant Waste Fractionation Process, Plutonium Finishing Plant Operations, and Plutonium/Uranium Extraction (PUREX) Process. Of these, the PUREX Process was the largest contributor of organic solvents into the waste.

PUREX was an advanced extraction process that operated from 1955 to 1972 and 1983 to 1990. Given the extent of operation, the PUREX process consumed the highest volume of solvents of any Hanford processing plant. Consequently, these solvents are the most extensively studied as documented in the topical report [2]. The single solvent used was tributyl phosphate (TBP), along with various diluents, Shell E-2342 (1955-1961), Soltrol- 170 (1961-1966), and from 19 the normal paraffin hydrocarbon (NPH) (from 1966 onwards). The diluents were changed to decrease its reactivity to nitric acid. [2]. Organic wash waste (OWW), which contained entrained and small amounts of soluble TBP and NPH, was discharged to SSTs and DSTs [3].

Organic Wash Waste

The PUREX Process was the largest contributor of organic solvents into the tank waste; making it the primary focus of this evaluation on separable organics. It is estimated that 5,260 kL (1390 kgal) of organic solvent were consumed at the PUREX Plant [2].

Of this 5,260 kL consumed at PUREX:

- about 2,480 kL (655 kgal) were estimated to have been discharged in the OWW sent to tank farms (see Fig. 1);
- 1,560 kL (412 kgal) were estimated to be in process condensate;
- 620 kL (164 kgal) were estimated to be in stack gaseous effluent;
- 220 kL (59 kgal) were disposed to the 216-A-2 Crib;
- 370 kL (98 kgal) were disposed to the 216-A-2 and 216-A-31 Crib;
- 7 kL (2 kgal) were HLW sent to tank farms [2].

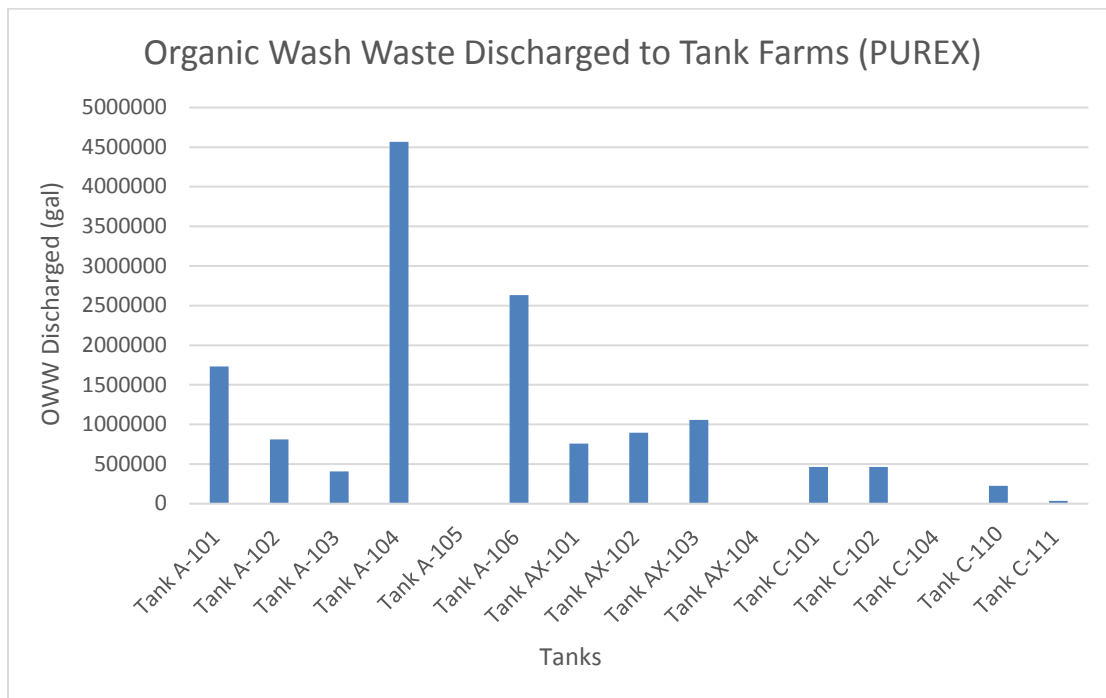


Fig. 1. Total Organic Wash Waste Discharged to Tank Farms

Present Status of Separable Organic Materials

It is assumed that the majority of separable organics exist in tank waste as organics coating sludge solids. Results from laboratory studies [4] support the mechanism of adsorption and subsequent separation of organic material from sludge solids. Tanks identified as containing floating organic layers (e.g., 241-C-103, 241-C-204, 241-C-104, and 241-C-102) were interim-stabilized in 2003 by saltwell pumping. Liquid was transferred out during this process and it is assumed that the floating organic either adhered to the sludge solids surface due to surface interaction or became trapped in the pores and interstitial spaces in the sludge layers of the waste [5].

Release of Separable Organic Materials

Aggressive and intrusive tank and transport operations –in a similar vein to centrifugation– have the potential to release organic compounds entrained in solids. Sluicing, one of the most aggressive operations performed at the Hanford Site, has historically dispersed solids and released volatile organic compounds from solids containing organics. This phenomenon was exhibited in 1998 during sluicing operations supporting retrieval of tank 241-C-106, when volatile organic compounds were released [6]. As described in the document on the origin of volatile organics [7], “The initiation of sluicing led to increases in the concentrations of the organic and inorganic compounds in the ventilation stack.” Sluicing operations increased the concentrations of water-soluble and water insoluble organic compounds in the ventilation stack. More importantly, the volatile organic compounds –distributed among the phases of the sludge– were released simultaneously.

Centrifugation of waste samples resulted in the separation of bound organics from solids. An oily layer separated out during centrifugation of C-106 sludge samples, but was not seen during retrieval of 241-C-106 to 241-AY-102 [5]. Separation may also occur without centrifugation in unsaturated samples of tank waste. Archived tank samples from C-204 and SY-102 tanks exhibited separation without centrifugation when a simulated supernatant based on the composition of tank 241-AN-106 waste was added [4].

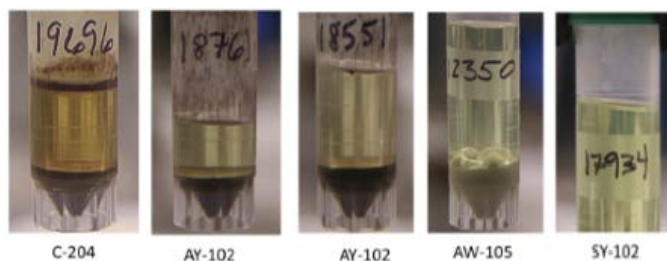


Fig. 2. Centrifugation of Archived Tank Waste (RPP-RPT-58822)

The addition of the electrolytic simulated supernatant caused the organic phase to “salt out” or alter the organic’s solvation chemical bonding properties that had originally caused the organic to be retained in the interstitial pockets of the archived sludge solids. Historically, tanks 241-C-103 and 241-C-204 have produced a separable phase without centrifuge [8]. Tanks other than 241-C-103 and 241-C-204 have shown a separable phase by severe shear forces through centrifugation and changes in solvation properties. Lab centrifugation data showed distinct separable organic layer for tanks 241-C-102, 241-C-104, 241-C-106, 241-AW-101, 241-AW-106, 241-AZ-101, and 241-SY-102 [8].

Study Supporting Evaluation of Separable Organic Materials

Testing was conducted on solids with varying particle sizes to determine if surface area affects adsorption of organics onto the solids [4]. Simulant solids representing tank wastes were developed with two different particle sizes of gibbsite (61% aluminum hydroxide Almatis C31C or C33) that was mixed with 39% of either ferric oxide (F) or goethite (G). The simulant solids were mixed with the simulated supernate used in testing of archive tank samples and were allowed to settle before being centrifuged [4].

Smaller particle sized solids (C33) appeared to retain slightly more separable organics across all solvents tested. C33 solids for Mineral Oil retained 3.18% more solvent for C33-F solids and 6.44% more solvent for C33-G solids (Fig. 3).

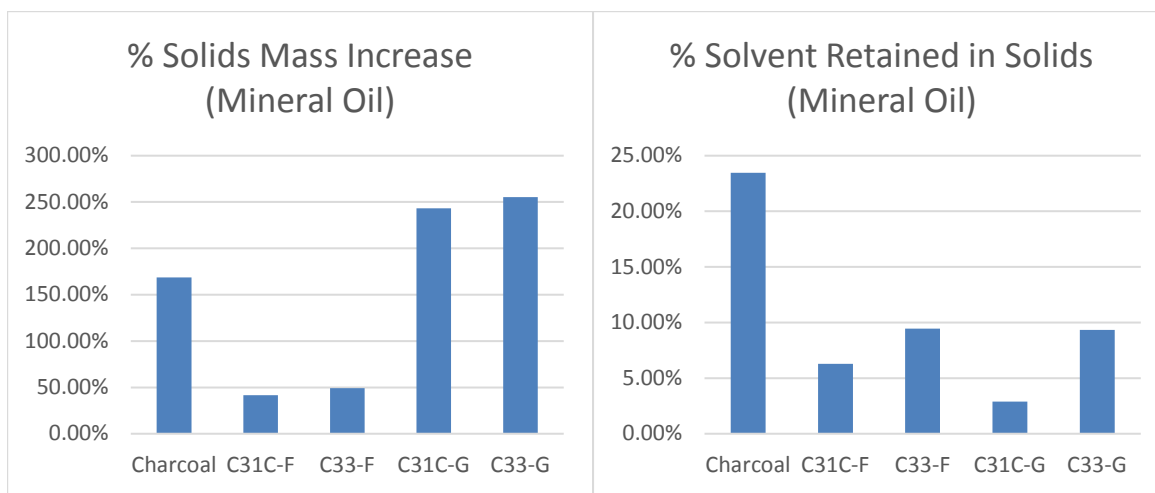


Fig. 3. Solids Mass Increase (%) and Solvent Retained in Solids (%) for Mineral Oil

In addition, samples with goethite solids appeared to retain slightly more supernatant and solvent. Solids consisting of goethite consistently displayed a larger percent increase in solids mass when compared to solids composed of ferric oxide. For Mineral Oil, the solids mass increased by 250% from an initial sample size of 8.96 g to 31.83 g (Fig. 3). For the mixture of 90% TBP and 10% hydraulic fluid, the solids mass increased by 266% with only 38% of the supernatant collected (Fig. 4).

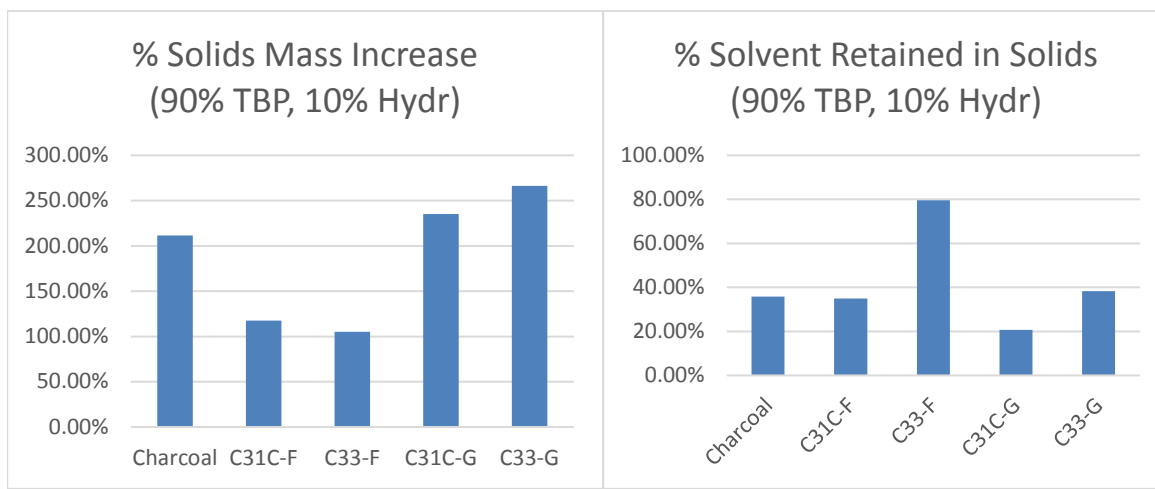


Fig. 4. Solids Mass Increase (%) and Solvent Retained in Solids (%) for Mixture of 90% TBP and 10% Hydraulic Fluid

EVALUATION OF WASTE FEED DELIVERY BATCH IMPACTS

Given that a separate organic layer formed during centrifugation tests, an evaluation was conducted on the impact this phenomenon would have for Waste Feed Delivery. If a separate organic layer is observed in samples taken for waste feed qualification, the feed will be disqualified until further mitigation steps are taken. Feed delivered to the WTP must not have a visible immiscible layer. If separable organics coating HLW is transferred or retrieved into a tank, it can be assumed that this tank now holds organic materials with the potential for future release of separable organics during additional WFD actions.

Tanks of Interest

One hundred and thirty-nine (139) tanks are known or suspected to contain TBP, NPH, or other paraffinic residues from the estimated 1.4 million gallons of solvent/diluents, chelating agents and other organics used in the PUREX process [9]. Other estimates place the number of tanks suspected to contain these components at closer to 116. This estimate is based on original distributions of organic waste from PUREX and the series of documented and undocumented inter-tank transfers that occurred over the duration of operations [10]. Lack of adequate historical records for inter-tank transfers has led to a discrepancy in the suspected separable organic inventories.

An effort was made to focus on tanks with waste consisting of mostly sludge and avoid tanks with waste consisting of mostly salt cake. The nitrate salts in the salt cake are generally believed to consist of large particles and would not provide a significant area for adsorption [11]. Emphasis was placed on tanks in consideration for HLW feed delivery, as these tanks consist of mostly sludge-like waste material.

In addition to the above considerations, SST retrieval histories were factored in. Eligible C-Farm tanks were excluded from the evaluation as they were consolidated into either AN-101, AN-106, AY-102 (which itself was retrieved into AP-102 and AW-105), and SY-102. Further exclusions were made for tanks identified as containing contact handled transuranic waste (CH-TRU). CH-TRU mixed waste is not slated for treatment by the WTP and is expected to be retrieved directly to the Supplemental Treatment Facility without affecting the DST system [12].

The priority set of TOI is represented by TABLE I. These twenty-three (23) tanks hold the greatest potential for spreading separable organics throughout the Hanford Tank Farms. An additional twenty-one (21) tanks were identified and queried based on the review of sampling data vulnerabilities. Per the vulnerability assessment [13], the tanks identified in TABLE II are those that have never been sampled. Where sampling data was unavailable, values were estimated from the Best Basis Inventory, BBI.

TABLE I. Tanks Identified with Potential for Separable Organic Layer, Priority Set

Tanks of Interest, Priority Set			
A-101	AW-104	B-111	SY-102
A-104	AW-105	BX-103	S-104
A-105	AW-106	BX-104	T-107
AN-101	AZ-101	BX-107	TY-103
AN-106	AZ-102	BY-107	TY-104
AP-102	B-103	BY-108	

TABLE II. Tanks Identified with Potential for Separable Organic Layer, Secondary Set

Tanks of Interest, Secondary Set			
B-105	SX-112	TX-106	TX-114
BX-102	SX-114	TX-108	TX-115
SX-107	TX-101	TX-109	TX-117
SX-109	TX-102	TX-110	
SX-110	TX-103	TX-111	
SX-111	TX-105	TX-112	

HTWOS Model Run Modifications and Assumptions

Hanford Tank Waste Operations Simulator (HTWOS) model run MMR-50057 [14] was modified for this evaluation to trace specific constituents. Total organic carbon concentrations were used to trace the origin of each batch to the Waste Treatment and Immobilization Plant.

HTWOS is a modeling tool that simulates the entirety of the River Protection Project (RPP) Mission, given certain constraints and assumptions, and projects the feed batches to be delivered to WTP. MMR-50057 reflects the updated stream data for the RPP flowsheet [15]. MMR-50057 includes proposed processing options such as utilization of the Low Activity Waste Pretreatment System and Tank Waste Characterization and Staging facilities; which are crucial when planning WFD options.

Tank inventories in HTWOS used in the planning and modeling of WFD are provided from the BBI. Additional model considerations are given for wash factors, leach factors, historical waste transfers, and near-term waste transfer plans [11]. HTWOS tracks total organic carbon (TOC) and oxalate in both liquids and solids (among many other constituents), and provides estimates of the concentrations for the feed to be delivered to WTP.

The TOC concentration estimates were used to trace the multitude of transfers for the identified tanks of interest (TOI) in this evaluation. A data package for TOC estimates was also created to support this evaluation [16].

DISCUSSION: THE RIPPLE EFFECT

The priority and secondary set of TOI were evaluated through tracking of TOC contributions in specific batches to be delivered to WTP.

When assuming an “all or nothing” approach for the distribution of potentially separable organics within Hanford tank wastes, a ripple effect occurs. The “all or nothing” approach assumes that if a tank was suspected of containing organics, that tank routed those organics to subsequent tanks when retrieved or transferred. This assumption quickly cascades.

Waste retrieval, transfers, and blending cause the ripple effect. The first feed batch of HLW (batch 195¹) contains waste from one TOI, AP-102. In the case of batch 237, the waste source is from seven TOI: A-101, AN-101, AN-106, AP-102, AW-105, AZ-101 and B-105. Two of these tanks (AN-101 and AN-106) contain waste from the retrieval of C-Farm tanks, which indicates contribution from sixteen (16) additional tanks to batch 237. For batch 476, the number of tanks contributing has risen to twenty (20), reaching the peak number of tanks per batch at thirty (30) in

¹ Feed batches to WTP are identified in transfer lists for HTWOS, MMR-50057.

batch 785. It is important to note that this is a subset of data. The makeup of batch wastes is not all-inclusive to the tanks in impact analysis and each batch may contain waste from more tanks than is covered by this evaluation.

While the number of tanks contributing waste per batch increases throughout the course of planned WFD to the WTP, this is not a constant rate of increase. Outliers are explained by waste feed designation; LAW feed instead of HLW feed. This criterion explains the discrepancy in batches 249, 263, 276, 304, 346, etc. This distribution pattern is demonstrated in Fig. 5. Of the nearly 70% of identified tanks contributing to batch 785, 53% have no sampling information [13].

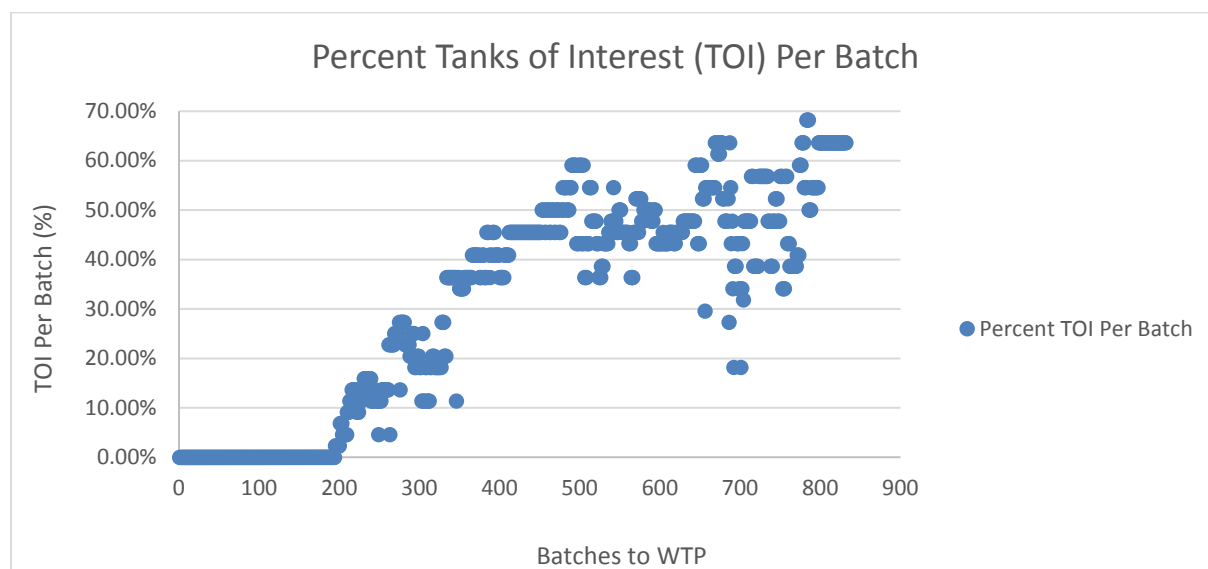


Fig. 5. Identified Tanks of Interest: Batches Delivered to WTP (%)

DISCUSSION: IMPACT ON DELIVERY OF HLW FEED

Separable organics (TBP and NPH) are present in tank waste liquids and bound to solids. The full extent of their presence is undetermined due to undocumented inter-tank transfers and insufficient sampling data. Regardless of the confirmation of their presence, these materials exist in tank waste and will be transferred to subsequent tanks. Evaluation of propagation of separable organic material for WFD batches posts complications arising from "Blind" blending of feed in the Staging Tank. Waste contributions to feed batches construe nearly 70% of tanks identified (Fig. 5).

HLW batches will be mixed during sampling and before any batch transfer would occur to another DST or the TWCS facility. It is unknown what type of mixing will be applied. It is possible a separable organic layer may form during WFD operations as indicated by separation of organic materials during laboratory studies. Also, a separable layer formed in archived tank samples during centrifuge testing

and without the use of a centrifuge was noted in the studies [4]. The addition of aqueous simulated supernatant to an archived subsample of Tank C-204 also resulted in the formation of a separable organic layer. Thus, confirming the potential for such a layer to form from waste disturbing activities. It was also confirmed that a solids simulant based on the chemistry of tank AN-106's supernatant was able to both separate out retained organic solvent/diluents when centrifuged and without the use of a centrifuge [4].

Despite positive separation tests, the extent of the organic materials separation remains unknown and highly dependent on the nature of the waste being examined. It is unknown the quantity of organic solvent that dissolved into the simulated supernatant and the amount of supernatant that adsorbed to the simulated solids. Organic material remained in the simulant solids post-separation but it would appear that most of the solids mass increase is attributed to adsorption of the simulated supernatant. Nearly 10% of solvent (mineral oil) was retained in the small particle (C33) goethite solids, but the solids mass saw an increase of 250% from an initial sample size of 8.96 g to 31.83 g. For the mixture of 90% TBP and 10% hydraulic fluid, the solids mass increased by 266% with only 38% of the supernatant collected. The solids are not only composed of organic solvent but also are saturated with supernatant. It is difficult to conclude whether all of the organic material was bound to solids, located within the interstitial spaces of the tank waste solids, dissolved in the simulated supernatant, or some combination thereof. Furthermore, it is difficult to then predict if the organic material will then separate out simultaneously or in phases when mixed, given that organics remained in solids post-separation.

CONCLUSIONS

Due to the ability of a separable organic layer forming during the study of small scale archived tank waste and simulant sample studies, an impact assessment was performed. This assessment assumed a separable organic layer would form during HLW WFD operations and could be cascaded to all HLW tanks containing or receiving significant amounts of organic solvents/diluents. It was confirmed that there is a potential for a ripple effect when tank wastes containing organic materials are retrieved, blended, and staged in preparation for transfer to a treatment facility. Waste contributions to feed batches incorporate nearly 70% of tanks as identified during the assessment. It is unknown at what point in the WFD operations that the organic materials would separate.

The separation of organic materials appears to be dependent on concentration. Due to their larger surface areas, smaller particle sized solids promote higher retention of separable organic materials. However, the full extent of separation remains unknown and may be highly dependent on the nature of the waste being examined. Furthermore, it is difficult to predict if the organic materials will separate out simultaneously or in phases when mixed.

Thus, the risks associated with the potential for separable organic materials to separate out from Hanford tank waste solids require consideration to meet the WTP waste acceptance criteria. Future mitigation of these risks may include resolution of tank waste sampling vulnerabilities, actual tank waste mixer pump testing, development of feed strategies, and/or addition of a tank waste characterization and staging ability to assist in removal of organic layers. Addition of a tank waste characterization and staging ability would also support the staging, sampling, mixing, characterization, and preconditioning of tank waste to meet the waste acceptance criteria as described in the WTP interface document.

REFERENCES

1. Taki, B. D. (2014). 24590-WTP-ICD-MG-01-019, *ICD-19 – Interface Control Document for Waste Feed*, Rev. 7, Bechtel National, Inc., Richland, Washington.
2. Cowley, W. L. and Meacham, J. E. (2000). HNF-4240, *Organic Solvent Topical Report*, Rev. 1, CH2M HILL Hanford Group, Inc., Richland, Washington.
3. Agnew, S. F. (1997). LA-UR-96-3860, *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*, Los Alamos National Laboratory, Los Alamos, New Mexico.
4. Meznarich, H. K., Pappas, A. D., and Page, J. S. (2016). RPP-RPT-58822, *Final Report for Investigation of Separable Organics in Solids*, Rev. 0, Washington River Protection Solutions LLC., Richland, Washington.
5. Smalley, C. S. and Nguyen, V. C. (2013). RPP-RPT-55646, *One System Evaluation of Separable Organics in the Tank Waste*, Rev. 0, Washington River Protection Solutions, LLC., Richland, Washington.
6. Meacham, J. E. (2004). RPP-21854, *Occurrence and Chemistry of Organic Compounds in Hanford Site Waste Tanks*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.
7. Stauffer, L. A. (1999). HNF-4261, *Origins of Volatile Organic Cmpds Emerging from Tank 241-C-106*, Rev. 1, Lockheed Martin Hanford, Corp., Richland, Washington.
8. Allen, D. I. (2001). [CHG-0103952 R1 (CCN 024433)], "Contract Number DE-AC-99RL14047; Separable Organics in Tanks and Impacts on Operational Waste Volume Projections," (letter from D. I. Allen to D. C. Bryson, U. S. Department of Energy, Office of River Protection, September 10), CH2M HILL Hanford Group, Inc., Richland, Washington.

9. Klem, M. J. (1996). Memo 73510-96-029, "Preliminary Estimate of Projected Process Organic Volume in Waste Tanks," (internal letter from M. J. Klem to D. J. Washenfelder, September 18), Westinghouse Hanford Company, Richland, Washington.
10. Dukelow, G. T. and Klem, M. J. (1996). WHC-SD-WM-ES-384, *Systems Engineering Study: Tank 241-C-103 Organic Skimming, Storage, Treatment, and Disposal Options*, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
11. Gerber, M. A., et al. (1992). PNL-8339, *Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
12. Fleming, J. T., et al. (2015). RPP-17152, *Hanford Tank Waste Operations Simulator (HTWOS) Version 8.1 Model Design Document*, Rev.12, Washington River Protection Solutions LLC., Richland, Washington.
13. Smalley, C. S. (2014). RPP-RPT-54509, *One System- Hanford Tank Waste Characterization Vulnerability Assessment*, Rev. 1, Washington River Protection Solutions, LLC., Richland, Washington.
14. Bergman, L. M. (2015). MMR-50057, "TWDIF Updated Stream Data" Rev. 0, Washington River Protection Solutions LLC., Richland, Washington.
15. Cree, L. H. (2015). RPP-RPT-57991, *One System RPP Integrated Flowsheet*, Rev. 1, Washington River Protection Solutions LLC., Richland, Washington.
16. Schubick, A. J. (2016). RPP-RPT-59633, *Hanford Tank Waste Operations Simulator (HTWOS) Model Data Package for TOC Traceback for MMR-50057: Updated TWDIF Stream Data*, Rev. 0, LLC., Richland, Washington.