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Savannah River Site Liquid Waste Tank Storage: Tank 48H History and Recent Waste Characterization Results – 23508

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ABSTRACT

The Savannah River Site (SRS) H and F Area Tank Farms (HTF and FTF) have 43 active underground waste tanks used to store and support processing of radioactive liquid waste. Tank 48H is a Type IIIA waste tank, which is the most recent style of tanks built between 1976 and 1981 with a storage capacity of approximately 4,900,000 L (1,300,000 gallons).

In 1983, Tank 48H was utilized for a demonstration of the In-Tank Precipitation (ITP) process to determine the effectiveness in separating radioactive constituents such as cesium-137 (Cs-137) and actinides for further processing at the Defense Waste Processing Facility (DWPF). As a part of this process, sodium tetraphenylborate (NaTPB) was added to the dissolved salt solution to produce a precipitation reaction with Cs-137. In contrast to the soluble NaTPB, when potassium (K) or Cs-137 combines with the TPB anion, an insoluble particle is formed (KTPB or CsTPB), which can be filtered from the supernatant liquid and sent to DWPF for further processing. Monosodium titanate (MST) was also added to adsorb strontium-90 (Sr-90) and actinides, such as uranium (U) and plutonium (Pu), for subsequent downstream separation from the supernatant liquid. The successful outcome of this demonstration resulted in the construction of the permanent ITP processing facility (Building 241-96H). The ITP process planned on using Tanks 48H, 49H, and 50H to process salt solution and send precipitate and decontaminated solution to DWPF and the Saltstone Production Facility (SPF or Saltstone), respectively.

In the Fall of 1995, ITP processing of the remaining Tank 48H material commenced with an addition of NaTPB and MST followed by slurry pump operation to complete the desired reactions. After a brief quiescent period, the slurry pumps were reenergized in December 1995, resulting in an immediate release of higher levels of benzene gas than anticipated (although remaining below the Lower Flammability Limit (LFL)). In the years that followed, occasional slurry pump runs were performed to allow for controlled releases of benzene from Tank 48H while laboratory testing was conducted to better understand benzene evolution from TPB. Under certain conditions, the TPB anion decomposes in solution and releases benzene, which is a highly volatile and flammable organic compound. The rate of decomposition was determined to be enhanced by a variety of factors. Flammability concerns associated with the use of NaTPB subsequently led to the abandonment of the ITP process in early 1998.

Since the abandonment of the ITP process, Tank 48H has undergone routine slurry pump operation to release any accumulated trapped gas in the waste (e.g., benzene, hydrogen). Testing has also been conducted on methods to destroy the residual TPB in Tank 48H, including Fluidized Bed Steam Reforming (FBSR), Wet Air Oxidation (WAO), and Copper Catalyzed Peroxide Oxidation (CCPO). Due to the downstream facility impacts, these methods were never implemented despite the effectiveness of TPB remediation that was shown in laboratory experiments.

Periodic sampling of Tank 48H contents has also been conducted since ITP abandonment to note the behavior of TPB degradation over time and to ensure that accurate characterization of the waste exists. Recent sample analysis indicates little to no TPB degradation over the past 10 years with no detectable benzene from the samples collected. Further, no TPB was detected in free supernate located above the

solids phase, which suggests that the compound exists only in the form of insoluble CsTPB and KTPB particles in the waste tank. Recent sampling efforts have also determined that the majority of the Cs-137 exists as solid CsTPB when comparing sludge slurry and filtered solids radioactivity measurements.

This paper will discuss the history of Tank 48H in relation to its use both during and after the ITP process and recent waste characterization discerned from sampling efforts.

INTRODUCTION

The Savannah River Site (SRS) has 51 underground waste storage tanks located in the H and F Area Tank Farms (HTF and FTF), which, along with other equipment, are known as the Concentration, Storage, and Transfer Facilities (CSTF). There are currently 43 active waste tanks remaining in the CSTF and eight of the original 51 tanks that are closed and filled with grout. The mission of the CSTF is the storage and processing of legacy radioactive waste in a manner that prevents releases to the environment and minimizes exposure to both on-site and off-site personnel [1]. Access into the waste tanks is limited by available waste tank openings or risers. The original waste tanks in the CSTF were built in the early 1950s to support the reactor and separations processes. Additional waste tanks were constructed in the decades that followed, with different styles of construction being utilized to produce more secure structures for waste storage. A total of five different tank types were used, those being Type I, II, III, IIIA, and IV [1]. Type IIIA tanks were the last group of waste tanks built at SRS between the years of 1976 and 1981 [2] and are regarded as the best and most robust of the tanks built due to improved materials of construction and cooling capabilities. Tank 48H is an HTF Type IIIA waste tank with a storage capacity of approximately 4,900,000 L (1,300,000 gallons) and has an inner diameter of 25.9 meters (85 feet). Tank 48H was built along with Tanks 49H, 50H, and 51H in a project that was authorized in 1978 and completed in the early 1980s [3].

DISCUSSION

In-Tank Precipitation (ITP) Process

A timeline of Tank 48H historical events is shown in Figure 1 below.

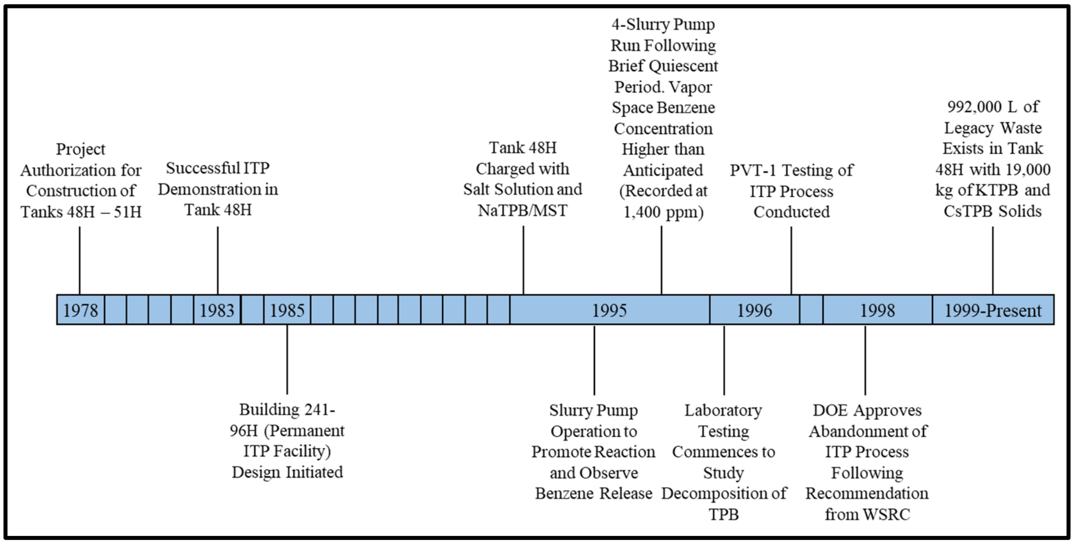

Fig. 1. Tank 48H Timeline.

Shortly after its construction, Tank 48H was utilized in 1983 for a demonstration of the In-Tank Precipitation (ITP) process to determine the effectiveness of the technology in separating radioactive constituents such as cesium-137 (Cs-137) and actinides for further processing at the Defense Waste Processing Facility (DWPF). The ITP process was a batch addition process during which two chemical reagents, those being sodium tetraphenylborate (NaTPB or STPB) and monosodium titanate (MST or ST), were added to the resident dissolved salt solution followed by mixing of the waste tank contents via slurry pumps to ensure the desired reactions were driven to completion. Specifically, NaTPB was added to the dissolved salt solution to initiate a precipitation reaction with resident Cs-137 inside the waste tank. The reaction mechanism with Cs-137 is shown in Equation 1. A similar mechanism occurs with resident potassium (K) in the waste tank, which is shown in Equation 2.

(Eq. 1) $NaTPB_{(aq)} + Cs^{+}_{(aq)} \rightleftharpoons CsTPB_{(s)} + Na^{+}_{(aq)}$

(Eq. 2) $NaTPB_{(aq)} + K^{+}_{(aq)} \rightleftharpoons KTPB_{(s)} + Na^{+}_{(aq)}$

As annotated in the two equations above, NaTPB readily dissolves in aqueous-based solutions. However, in contrast to the soluble NaTPB compound, when K or Cs-137 combines with the TPB anion, an insoluble particle is formed that is not easily disassociated back into ions. The bulk of the precipitate that is produced during this process is KTPB (i.e., 99 mol %) with a smaller amount of CsTPB precipitate being produced [4]. The creation of this insoluble particle allows for Cs-137 to be separated by filtration from the liquid waste and processed at DWPF. In addition to TPB related reactions with Cs-137, MST was added to the dissolved salt solution to adsorb strontium-90 (Sr-90) and actinides such as uranium (U) and plutonium (Pu). Specifically, the radioactive isotopes of interest adsorb onto the MST particles, which remain insoluble and can be separated by filtration in a similar manner to the TPB-based solids.

A process flow diagram of the ITP process in shown in Figure 2 below.

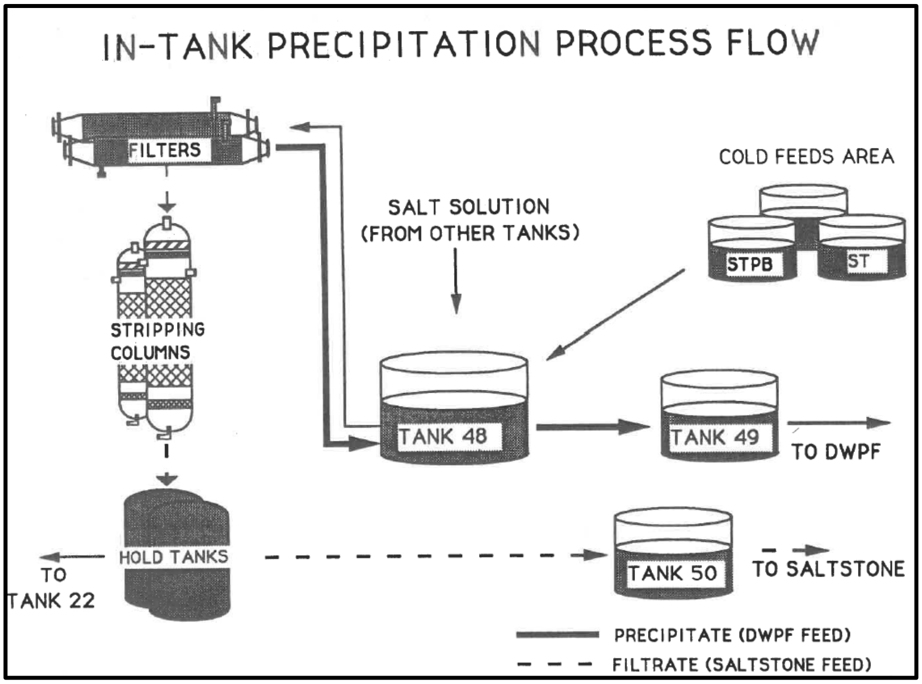

Fig. 2. ITP Process Flow Diagram.

As shown in the Figure 2, NaTPB and MST are first added to Tank 48H to drive the desired reactions to completion with the help of mechanical agitation via slurry pumps. The newly formed supernate/precipitate slurry is subsequently sent through crossflow filters to separate the precipitate from the filtrate and is then returned to Tank 48H. Filtrate from the separations process is then sent through stripping columns to remove residual benzene from solution and is stored in Hold Tanks until eventual transfer to the Saltstone Production Facility (SPF or Saltstone) via Tank 50H. After three supernate batches are precipitated, the residual slurry is then washed to remove excess TPB and soluble salts. This wash water is processed in a similar manner to the decontaminated filtrate but is sent to Tank 22H for future use in the ITP Process. The resulting washed precipitate is then transferred to Tank 49H for subsequent processing at DWPF.

The 1983 ITP demonstration in Tank 48H utilized approximately 1,900,000 L (500,000 gallons) of dissolved salt solution which produced 200,000 L (53,000 gallons) of precipitate [4]. The results of this demonstration indicated that the ITP Process was a promising method by which to separate radioactive constituents from salt solution. Thus, design work on the permanent ITP facility (Building 241-96H) began shortly thereafter in 1985 and construction was completed in the early 1990s. Building 241-96H was designed to house the crossflow filters used to separate precipitate from filtrate, the filtrate benzene stripping column, as well as the Hold Tanks used to send material to Tank 22H or Tank 50H that are shown in Figure 2. Supplemental equipment in support of these processes such as back-flushing components, stripping column off gas systems, and other items were also contained in the 241-96H facility. Despite the successful outcome of the demonstration, it was noticed that benzene evolved at higher rates from the dissolved salt solution during processing than what models suggested at the time. It was believed that concerns over benzene evolution were addressed in design features of the ITP processing facility.

One method to drive the reactions outlined in Equations 1 and 2 further to completion is to add excessive reactant to create an imbalance of the chemical equilibrium (i.e., Le Chatelier’s Principle). In September of 1995, ITP processing of “Batch 1” of Tank 48H material was initiated. Using the 241-96H facility, Batch 1 included the addition of 141,000 L (37,300 gallons) of NaTPB and 492,000 L (130,000 gallons) of dissolved salt solution to the resident washed slurry in Tank 48H from the 1983 demonstration. Three subsequent slurry pump runs were conducted during the months of October and November, with recorded vapor space benzene readings of 60, 160, and 320 parts per million (ppm) during the respective runs [4]. After a brief quiescent period, the slurry pumps were reenergized on December 1, 1995, which resulted in an immediate release of high levels of benzene with a recorded concentration of 1,400 ppm, which is approximately 10.5% of the Composite Lower Flammability Limit (CLFL) for Tank 48H. Due to the unexpected nature of the benzene releases, the ITP process was temporarily halted until further research was conducted to better understand benzene evolution via the use of NaTPB as a reagent. In the months that followed December 1995 operations, routine slurry pump runs were conducted with additional safety controls in place to allow for controlled releases of benzene from the Tank 48H resident material.

It was determined that the mechanism behind the benzene releases was due to the decomposition of the TPB anion in solution. The rate of TPB decomposition was determined to be enhanced by a variety of factors, including [5,6]:

1. Increasing solution temperature
2. Increasing NaTPB concentrations in solution
3. Decreasing hydroxide (OH^-) concentrations in solution
4. Presence of copper (Cu) and palladium (Pd) in solution that act as catalysts

In addition to the external environment conditions listed above that were determined to influence the rate of TPB decomposition, the nature of the TPB species itself, namely the associated cation that the anion was bonded to, was shown to have an influence on decomposition rate. This behavior is summarized in Equation 3 below [6].

(Eq. 3) $Rate_{NaTPB} = 24\ x\ Rate_{KTPB} = 73\ x\ Rate_{CsTPB}$

Considering Equation 3, the rate of decomposition of NaTPB is substantially greater than that of KTPB and CsTPB (24 times and 73 times, respectively). This can be explained by soluble nature of NaTPB in solution in contrast to the durable insoluble particle that is formed when the anion combines with K and Cs-137. The relative rate of reaction also explains the phenomena which occurred in December 1995, since an excess of NaTPB reagent was added to Tank 48H prior to ITP processing in September 1995. The quiescent period that followed the initial slurry pump runs provided time for most of the NaTPB to decompose and collect in solution and among the insoluble TPB particles [6]. The mechanical agitation facilitated by slurry pump operation then provided the means for the accumulated benzene to be released from solution. In addition to benzene, additional decomposition products identified included triphenylboron (3PB), diphenylborinic acid (2PB) and phenylborinic acid (1PB). The generation of benzene and other decomposition products was an undesired result associated with NaTPB usage due to flammability and occupational health concerns.

In parallel to the laboratory studies performed following the initial ITP operations in late 1995, Process Verification Testing (PVT) was conducted in Tank 48H to study multiple variables associated with the ITP process, one of which being benzene evolution from solution. A second phase of this testing (PVT-2) was planned which involved transferring a large volume of dissolved salt solution and addition of NaTPB to Tank 48H. However, questions remained surrounding the decomposition mechanism of TPB, indicating a potential risk associated with the nature of the benzene releases [6]. Subsequently, the ITP process was abandoned in early 1998 following recommendation by the Liquid Waste contractor and approval by the Department of Energy (DOE). In the years since abandonment of the ITP process, the contents of Tank 48H have remained relatively undisturbed except for the routine slurry pump operation to release any accumulated trapped gas in the waste and occasional corrosion inhibitor additions. Tank 48H contains approximately 992,000 L (262,000 gallons) of legacy waste from the ITP process with approximately 19,000 kg of insoluble TPB-based compounds (i.e., KTPB and CsTPB) that are not compatible with the current liquid waste system at SRS.

Post ITP Remediation Efforts

Since the abandonment of the ITP process in early 1998, Tank 48H has undergone routine slurry pump operation to release any accumulated trapped gas in the waste, which includes benzene associated with TPB decomposition and hydrogen generated from the radiolysis of water. Additionally, controls were put in place to manage Tank 48H, including but not limited to: prohibiting the addition of any new waste to Tank 48H, limiting the Tank 48H waste to a temperature no greater than 35 °C, and requiring the Tank 48H waste to have a free OH^- concentration of 1 M. Reference 4 presents Gas Chromatograph (GC) benzene readings that were conducted during slurry pump runs from 1996 until 2005. The results from the earliest and most recent slurry pump run analyzed by this reference are shown in Figures 3 and 4, respectively.

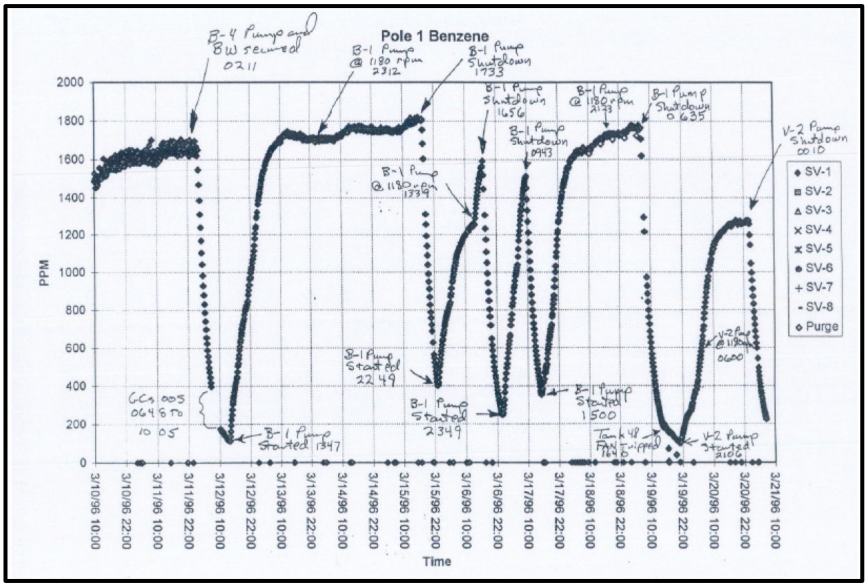

Fig. 3. Benzene Concentration Trend during March 1996 Slurry Pump Operation [4].

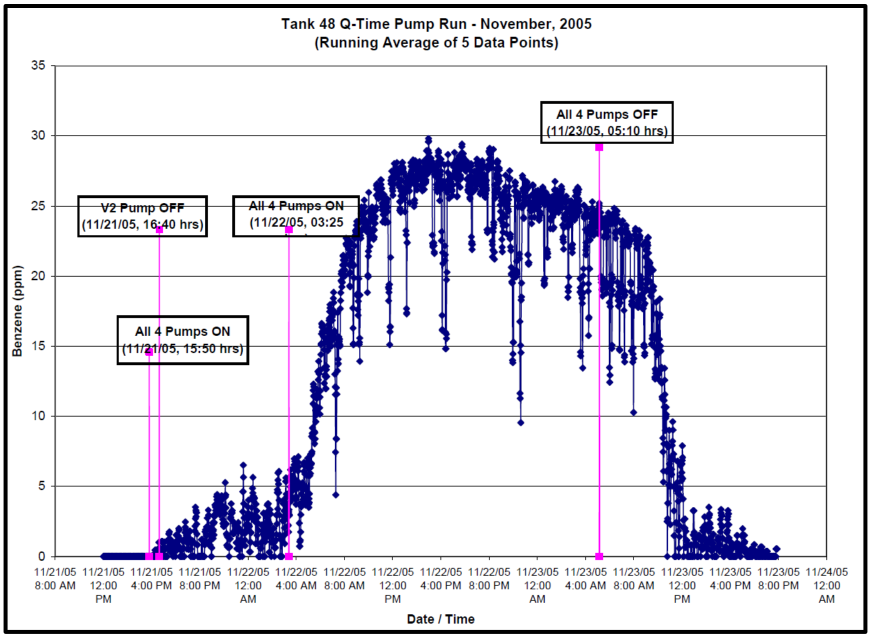

Fig. 4. Benzene Concentration Trend during November 2005 Slurry Pump Operation [4].

As annotated in the figures above, the maximum benzene concentration recorded from the 1996 slurry pump trend was ~1,800 ppm whereas the 2005 trend recorded a maximum concentration of ~30 ppm. Thus, when comparing the two trends above, the resulting vapor space benzene concentration during waste agitation activities has decreased substantially as time has progressed since the ITP process was abandoned. Also, the most recent benzene concentration reading from Tank 48H was performed in December of 2018 during a 4-slurry pump run, with the concentration being below the analytical limit of detection (LOD) of 2 ppm [7,8]. This behavior supports prior laboratory studies, which suggested relatively rapid decomposition of NaTPB in solution and that KTPB and CsTPB solids are much more resistant to decomposition. Thus, it can be discerned that the majority of the resident NaTPB has decomposed in Tank 48H.

Despite the presence of evidence that suggests that NaTPB has significantly decomposed in Tank 48H, the remaining KTPB and CsTPB solids remain incompatible with the liquid waste system. The intent of the ITP process was to send these solids to DWPF for vitrification. Due to the extreme conditions (e.g., high temperatures) experienced at DWPF, concerns related to TPB decomposition still existed. Thus, efforts were made to investigate methods that could be utilized to destroy the remaining TPB solids in Tank 48H and to process the resident waste in a different manner. In total, approximately 40 different options were investigated. The three most prominent of the methods included Fluidized Bed Stream Reforming (FBSR), Wet Air Oxidation (WAO), and Copper Catalyzed Peroxide Oxidation (CCPO) [9,10,11].

The first alternative method to discuss is the Fluidized Bed Stream Reforming (FBSR) process, which involved two major steps. First, the waste slurry was sent through a Denitration and Mineralization Reformer (DMR) via steam as a carrier fluid. This high temperature environment evaporates all the water in the waste and converts the organic material (i.e., TPB) into carbon and other small molecule gases (e.g., methane, carbon monoxide, and hydrogen). Radioactive constituents of the waste are entrapped carbonate or silicate-based solids in this step that could be sent to DWPF for processing. Off gases from the DMR were then oxidized to carbon dioxide via a carbon reduction reformer (CRR). This method showed promise due to TPB and all decomposition products being present below detection limits during laboratory analysis [9]. The solids generated during this process were also compatible with the melting requirements for glass feed at DWPF. However, the solids were not compatible with DWPF particle size requirements and would have required further manipulation (e.g., processing through rod mill grinders). This would have increased the complexity and associated capital cost of this remediation pathway.

The second alternative method is the Wet Air Oxidation (WAO) process. In contrast to producing a new solid waste form in the FBSR process, WAO involved using high pressure and temperature (i.e., 7 atm – 210 atm and 150 ℃ – 320 ℃) as well as copper sulfate as a catalyst to oxidize the organic material found in the waste. The outcome of the WAO process would return the radioactive constituents to a soluble state for future processing. Like FBSR, bench scale testing of this method with actual Tank 48H waste resulted in the complete destruction of TPB and most of its decomposition products [10]. Despite this success, this mechanism resulted in the formation of biphenyls, which are a reaction intermediate in the formation of hazardous polychlorinated biphenyls (PCBs).

The final alternative method to discuss is the Copper Catalyzed Peroxide Oxidation (CCPO). The CCPO was similar to WAO in that the goal of the process was to completely oxidize all organic material and to return radioactive constituents to a soluble form. This method also used copper sulfate as a catalyst but used hydrogen peroxide as an oxidizing agent. Two separate studies were conducted, one with the intent of using the process directly in Tank 48H and the other utilizing the stainless-steel strike tanks in the 241-96H Facility. Laboratory testing on simulant Tank 48H waste in both studies showed an inverse relationship between the rate of TPB oxidation and pH of solution, with an optimum pH of 9 being recommended [11,12]. Due to the primary containment of Tank 48H being constructed of carbon steel, the desired pH required usage of the stainless-steel strike tanks in the 241-96H Facility as reaction vessels. In contrast to FBSR and WAO, the reaction times associated with CCPO were much longer (i.e., on the order of days) to ensure completed destruction of TPB. Testing also suggested that decomposition products of TPB (i.e., 3PB, 2PB, 1PB) took much longer to oxidize to levels below detection limits. This longer reaction time coupled with corrosion concerns due to the pH dependence of the reaction rate made this remediation pathway unattractive.

Recent Waste Characterization Efforts

In addition to recording vapor space benzene readings and investigating potential remediation pathways, numerous samples have been taken from the resident Tank 48H material to accurately characterize the waste in relation to radionuclide composition and extent of TPB decomposition. Sampling in SRS waste tanks is conducted using available waste tank risers that are temporarily opened to allow for stainless-steel sample vials to be lowered into the liquid waste below. The sampling process is resource intensive involving multiple steps, including the following: fabrication of glove bags for safe acquisition (refer to Figures 5 and 6), pre-job briefings, actual acquisition of the sample (refer to Figure 7), and subsequent shipment to the Savannah River National Laboratory (SRNL) in casks for analysis by Shielded Cell Operations (SCO) (refer to Figure 8).

Figs. 5 & 6. Example of CSTF glove bag and detailed image of sample vial reel arrangement.

Figs. 7 & 8. Example of tank top sample extraction and SCO sample vial dismantling.

In August of 2021, six 200-mL samples were pulled from Tank 48H in support of a Systems Engineering Evaluation (SEE) that revisited potential remediation options for the waste tank [13,14]. Three of the six samples (HTF-48-21-74, HTF-48-21-75, and HTF-48-21-76) were pulled during a tank quiescent period at a depth of 2.54 cm (1 inch) under the liquid surface, corresponding to an elevation of 186.7 cm (73.5

inches) above the tank bottom, to accurately characterize the free liquid present above the solids. These three samples obtained at a depth of 2.54 cm (1 inch) under the liquid surface are commonly referred to as surface samples. The three remaining samples (HTF-48-21-81, HTF-48-21-82, and HTF-48-21-83) were pulled immediately following a three-slurry pump run at respective depths of 121.9 cm (48 inches), 63.5 cm (25 inches), and 25.4 cm (10 inches) from the bottom of the waste tank. These three samples obtained at depths greater than 2.54 cm (1 inch) below the liquid surface are commonly referred to as Variable Depth Samples (VDSs). Once the six samples were received at SRNL, the contents were transferred from the stainless-steel sample vials to individual clear glass containers. The six samples were then allowed to settle for approximately 1 month to understand the settling behavior of the solids obtained. Figure 9 shows images of all six samples from Tank 48H, organized in numerical order from left to right (starting with HTF-48-41-74 and ending with HTF-48-21-83). Each grouping of the six samples shown below also includes the settling time allowed within the glass container (i.e., 0 days, 4 days, 8 days, and 33 days).

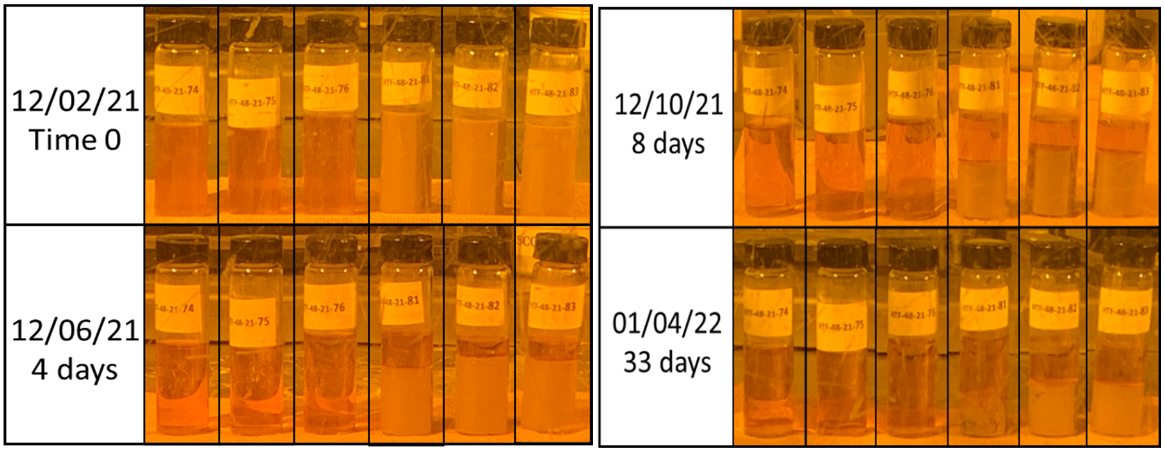

Fig. 9. 2021 Tank 48H samples following receipt at SRNL [13].

The three surface samples all retained the same appearance of a clear amber liquid throughout the duration of the solids settling progression, although it was noted that a slight haze was present inside the three sample vials at the onset of the settling period. In contrast, the three VDSs contained a significant amount of solids, which eventually settled out in the approximate 30-day progression. The solids from these samples were filtered and washed to determine the relative weight percentage (wt. %). Table I outlines the identification, sample depth above waste tank bottom, density, and measured insoluble solids from all six samples collected.

TABLE I. Tank 48H sample identification and physical properties [13]

Sample ID	Sample Depth (cm)	Density (g/mL)	Measured Insoluble Solids (wt. %)
HTF-48-21-74	186.7	1.262	< 0.01%
HTF-48-21-75	186.7	1.289	< 0.01%
HTF-48-21-76	186.7	1.275	< 0.01%
HTF-48-21-81	121.9	1.318	1.98%
HTF-48-21-82	63.5	1.245	2.30%
HTF-48-21-83	25.4	1.216	1.56%

In the case of the three surface samples, the densities were almost identical, and the concentration of insoluble solids was below the detection limit (i.e., 0.01 wt. %). In contrast, the VDSs appear to show an increasing trend of density as the sample elevation from tank bottom increases (i.e., VDS at 121.9 cm has the higher density than the VDS at 63.5 cm and 25.4 cm). However, all three VDSs have a comparable insoluble solids concentration, with an average of just under 2 wt. %.

High Performance Liquid Chromatography (HPLC) was used to determine the presence of TPB and the major decomposition products (i.e., 3PB, 2PB, 1PB, and phenol). The results of this analysis are presented in Table II.

TABLE II. HPLC analysis results for TBP and decomposition products [13]

Sample ID	TPB (mg/L)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	[a]Phenol (mg/L)
HTF-48-21-74	< 100	< 100	< 100	< 100	< 100
HTF-48-21-75	< 100	< 100	< 100	< 100	< 100
HTF-48-21-76	< 100	< 100	< 100	< 100	< 100
HTF-48-21-81	17,100	< 100	< 100	< 100	< 100
HTF-48-21-82	19,700	< 100	< 100	< 100	< 100
HTF-48-21-83	17,500	< 100	< 100	< 100	< 100

[a]Phenol was not detected via HPLC but was detected via Semi Volatile Organic Analysis (SVOA). Maximum readings from surface samples and VDSs are 43.8 mg/L and 40.8 mg/L, respectively.

The HPLC analysis of the three surface samples obtained resulted in concentrations below the LOD for TPB and the major decomposition products. In contrast, TPB was detected in the VDSs, with a maximum reading of 19,700 mg/L being recorded from the sample pulled at 63.5 cm (25 inches) from the tank bottom. Although TPB is present in all VDSs, the concentrations for all the major decomposition products were below the LOD. The results of this analysis are consistent with prior laboratory studies related to the decomposition of TPB following the 1995 operations period. Particularly, it can be discerned that the majority, if not all, of the NaTPB present in Tank 48H has decomposed and that any remaining TPB exists in the form of stable KTPB and CsTPB insoluble particles. A comparison of the results from the 2021 samples can be made to a 2012 slurry analysis, which determined a TPB anion concentration of 19,000 mg/L in the Tank 48H slurry [15]. This suggests that there has been little to no decomposition of the TPB solids over the past decade. Further, no benzene was detected in the 2021 samples in contrast to the 2012 study, which further substantiates that TPB decomposition has essentially ceased in Tank 48H.

Extensive radionuclide analysis was also performed on the six samples pulled in support of investigating remediation pathways. The maximum activity levels for various radionuclides of interest, along with the associated analytical method utilized, are summarized in Table III. Table III divides the six samples obtained from Tank 48H in 2021 into two distinct sets: (1) Surface Samples and (2) VDS.

TABLE III. Radionuclide Analysis of 2021 Tank 48H Samples [13]

Radionuclide	Analytical Method	Surface Samples	VDS
		Activity (Bq/mL) (pCi/mL)	Activity (Bq/mL) (pCi/mL)
Al-26	Gamma Scan (Cs removed)	< 1.86E+00 (< 5.04E+01)	< 1.42E+00 (< 3.85E+01)
Am-241	Am/Cm	1.32E+00 (3.57E+01)	3.77E+01 (1.02E+03)
Am-242m	Am/Cm	< 6.36E-02 (< 1.72E+00)	< 7.88E-01 (< 2.13E+01)

Radionuclide	Analytical Method	Surface Samples	VDS
		Activity (Bq/mL) (pCi/mL)	Activity (Bq/mL) (pCi/mL)
Am-243	Am/Cm	< 1.43E-01 (< 3.87E+00)	< 2.40E+00 (< 6.49E+01)
Sb-125	Gamma Scan (Cs removed)	< 8.99E+00 (< 2.43E+02)	< 1.01E+01 (< 2.73E+02)
Ba-137m	Secular Equilibrium w/ 94.6% of Cs-137	3.81E+05 (1.03E+07)	1.01E+07 (2.74E+08)
Ce-144	Gamma Scan (Cs removed)	< 1.70E+01 (< 4.59E+02)	< 1.66E+01 (< 4.48E+02)
Cs-134	Gamma Scan	< 3.00E+02 (< 8.11E+03)	NM[a]
Cs-135	Cs-135	2.76E+00 (7.45E+01)	8.66E+01 (2.34E+03)
Cs-137	Gamma Scan	4.03E+05 (1.09E+07)	1.17E+07 (3.17E+08)
Co-60	Gamma Scan (Cs removed)	< 3.20E+00 (< 8.64E+01)	< 1.88E+00 (< 5.09E+01)
Cm-242	Am/Cm	< 5.25E-02 (< 1.42E+00)	5.18E-01 (1.40E+01)
Cm-244	Am/Cm	< 5.25E-02 (< 1.42E+00)	6.11E-01 (1.65E+01)
Cm-245	Am/Cm	< 4.37E-01 (< 1.18E+01)	< 7.18E+00 (< 1.94E+02)
Eu-154	Gamma Scan (Cs removed)	< 4.66E+00 (< 1.26E+02)	< 4.37E+00 (< 1.18E+02)
Np-237	ICP-MS	1.12E+00 (3.04E+01)	2.49E+00 (6.74E+01)
Ni-63	Ni-59/63	< 2.83E+00 (< 7.66E+01)	< 5.51E+00 (< 1.49E+02)
Pu-238	Pu-238/241 Pu alpha PHA	9.47E+00 (2.56E+02)	5.70E+03 (1.54E+05)
Pu-239	ICP-MS	< 1.01E+01 (< 2.73E+02)	< 9.47E+00 (< 2.56E+02)
Pu-239/240	Pu-238/241 Pu alpha PHA	3.03E-01 (8.18E+00)	1.15E+01 (3.12E+02)
Pu-242	ICP-MS	< 6.22E-01 (< 1.68E+01)	< 5.81E-01 (< 1.57E+01)
Pu-244	ICP-MS	< 2.87E-03 (< 7.77E-02)	< 2.69E-03 (< 7.28E-02)
K-40	Gamma Scan (Cs removed)	< 4.48E+01 (< 1.21E+03)	< 2.75E+01 (< 7.42E+02)
Ra-228	Gamma Scan (Cs removed)	< 1.32E+01 (< 3.56E+02)	< 7.14E+00 (< 1.93E+02)
Rh-106	Secular Equilibrium w/ 100% of Ru-106	< 1.86E+01 (< 5.04E+02)	< 1.52E+01 (< 4.11E+02)
Ru-106	Gamma Scan (Cs removed)	< 1.86E+01 (< 5.04E+02)	< 1.52E+01 (< 4.11E+02)
Se-79	Se-79	< 4.40E+00	< 9.73E+00

Radionuclide	Analytical Method	Surface Samples Activity (Bq/mL) (pCi/mL)	VDS Activity (Bq/mL) (pCi/mL)
Se-79	Se-79	(< 1.19E+02)	(< 2.63E+02)
Sr-90	Sr-90 Liquid Scintillation	3.56E+01 (9.62E+02)	2.42E+03 (6.53E+04)
Te-125m	Secular Equilibrium w/ 100% of Sb-125	< 8.99E+00 (< 2.43E+02)	< 1.01E+01 (< 2.73E+02)
Th-232	ICP-MS	1.98E-05 (5.35E-04)	2.80E-05 (7.56E-04)
Sn-126	Gamma Scan (Cs removed)	7.03E+00 (1.90E+02)	< 3.32E+00 (< 8.98E+01)
Total Alpha	Liquid Scintillation (Cs removed)	< 1.99E+04 (< 5.39E+05)	< 6.44E+04 (< 1.74E+06)
U-232	U-232	4.59E-01 (1.24E+01)	6.81E+00 (1.84E+02)
U-233	ICP-MS	5.88E+00 (1.59E+02)	2.42E+01 (6.55E+02)
U-234	ICP-MS	2.24E+01 (6.06E+02)	8.14E+01 (2.20E+03)
U-236	ICP-MS	9.55E-02 (2.58E+00)	4.07E-01 (1.10E+01)
U-238	ICP-MS	1.36E-02 (3.68E-01)	5.88E-02 (1.59E+00)
Y-90	Secular Equilibrium w/ 100% of Sr-90	3.56E+01 (9.62E+02)	2.42E+03 (6.53E+04)
Zr-93	Zr-93	< 8.47E-01 (< 2.29E+01)	< 7.07E+00 (< 1.91E+02)

[a] Denotes that species was not measured

In the case of the surface samples, the majority of the radionuclides were present at activities lower than the LOD. A similar conclusion can also be made for the VDSs, but radionuclides that were detected were present at activities which were multiple orders of magnitude higher than the activities present in the surface samples. This suggests that the bulk of radioactivity resides in the TPB-based solids and that the free liquid in Tank 48H could be processed with little to no intervention once separated from the solids phase.

The SEE conducted in 2021 [14] was tasked to "Investigate, evaluate and recommend a preferred path forward for the disposition of Tank 48 legacy materials to support eventual Tank 48 closure". This resulted in a myriad of different processing options being investigated, with 20 options remaining after the preliminary screening process. Although multiple methods were highly ranked by the 2021 SEE as potential remediation pathways, no official path forward for Tank 48H has been agreed upon between the Integrated Mission Completion Contractor (IMCC), DOE, and other applicable regulatory bodies. Further work and research are required to determine the future disposition path for Tank 48H and the remaining by-product of the ITP process.

CONCLUSIONS

The use of Tank 48H in the ITP process in the 1980s and 1990s showed promise as demonstrations of the technology suggested effective separation of radionuclides such as Cs-137, Sr-90, U, and Pu from dissolved salt solution for subsequent processing at DWPF. During Batch 1 processing in late 1995, concerns associated with benzene evolution became evident and the ITP was temporarily suspended until research was conducted to better understand the benzene generation mechanism. Laboratory studies conducted in 1996 and afterwards concluded that benzene was generated due to the decomposition of TPB in solution. The rate of decomposition was determined to be enhanced by a variety of external factors and was substantially greater for NaTPB in comparison to KTPB and CsTPB. Despite an overall cause being determined, questions remained surrounding the decomposition mechanism of TPB, indicating a potential risk associated with the nature of the benzene releases. This resulted in the abandonment of the ITP process in early 1998. Since that time, Tank 48H retains approximately 992,000 L (262,000 gallons) of legacy waste from the process which contains 19,000 kg of insoluble TPB-based compounds (i.e., KTPB and CsTPB) that are not compatible with the current liquid waste system at SRS.

Benzene readings conducted during slurry pump operations in Tank 48H following ITP abandonment have shown a dramatic reduction in the amount of benzene released during mechanical agitation of the resident material. More recent vapor space readings suggest that the benzene released during slurry pump operation are negligible, with readings being present at concentrations less than the LOD. This supports previous laboratory experiment conclusions that NaTPB decomposes relatively quickly and the KTPB and CsTPB are mostly stable and remain intact as an insoluble particle. Although stable, these compounds remain incompatible with the SRS liquid waste system. Potential remediation options were investigated to eliminate the risks associated with TPB and change the impacted radionuclides into a form that could be easily processed. These investigation efforts included using FSBR, WAO, and CCPO as remediation options, but were not pursued due to downstream facility impacts and the capital costs required.

Sampling of the resident Tank 48H material was conducted in 2021 during both a quiescent period and after slurry pump operation to provide an updated characterization of the waste in support of a SEE. The surface samples pulled from the free liquid during a quiescent period were virtually identical and did not show the presence of any insoluble solids above the LOD. In contrast, VDSs pulled following slurry pump operation showed a significant amount of insoluble solids that settled over the course of a 30-day period. Chemical analysis of the surface samples showed that TPB and all associated decomposition products were present at concentrations less than the LOD. VDSs samples showed the presence of TPB at a maximum concentration of 19,700 mg/L, but all decomposition products were present below the LOD. The results of this analysis suggest that all TPB exists in the form of KTPB and CsTPB solids which are resistant to decomposition. This combined with the lack of benzene present suggests that decomposition of TPB in Tank 48H has essentially ceased due to the current facility controls in place. Radiological analysis of the samples show that many radionuclides are present at activities lower than the LOD for both surface samples and the VDSs. However, measurable activities from the VDSs were order of magnitudes larger than those present in the surface samples.

The results of this recent waste characterization sampling effort show promise that risk associated with residual TPB has reduced and that the Tank 48H material can be effectively remediated to support the mission of the CSTF. Multiple remediation options have been presented in the 2021 SEE, but no official path forward has been agreed upon between the IMCC, DOE, and other regulatory bodies.

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