Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.



Sample Results from Tank 48H Samples HTF-48-14-158, -159, -169, and -170

T. B. Peters

T. Hang

April 2015

SRNL-STI-2015-00141



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2. representation that such use or results of such use would not infringe privately owned rights; or
- 3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for U.S. Department of Energy

Keywords: *Macrobatch 8, MST solids, ISDP, Tank 21H*

Retention: Permanent

Sample Results from Tank 48H Samples HTF-48-14-158, -159, -169, and -170

T. B. Peters T. Hang

April 2015



Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

T. B. Peters, Advanced Characterization and Processing	Date
T. Hang, Advanced Characterization and Processing, Co-author	Date
TECHNICAL REVIEW: (Reviewed per E7 2.60)	
C. A. Nash, Advanced Characterization and Processing	Date
APPROVAL:	
F. M. Pennebaker, Manager Advanced Characterization and Processing	Date
S. L. Marra, Manager Environmental & Chemical Process Technology Research Programs	Date
R. T. McNew, Manager SRR Flowsheet Development and Facility Integration	Date

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 48H in support of determining the cause for the unusually high dose rates at the sampling points for this tank. A set of two samples was taken from the quiescent tank, and two additional samples were taken after the contents of the tank were mixed. The results of the analyses of all the samples show that the contents of the tank have changed very little since the analysis of the previous sample in 2012. The solids are almost exclusively composed of tetraphenylborate (TPB) salts, and there is no indication of acceleration in the TPB decomposition. The filtrate composition shows a moderate increase in salt concentration and density, which is attributable to the addition of NaOH for the purposes of corrosion control.

An older modeling simulation of the TPB degradation was updated, and the supernate results from a 2012 sample were run in the model. This result was compared to the results from the 2014 recent sample results reported in this document. The model indicates there is no change in the TPB degradation from 2012 to 2014.

SRNL measured the buoyancy of the TPB solids in Tank 48H simulant solutions. It was determined that a solution of density 1.279 g/mL (~6.5M sodium) was capable of indefinitely suspending the TPB solids evenly throughout the solution. A solution of density 1.296 g/mL (~7M sodium) caused a significant fraction of the solids to float on the solution surface. As the experiments could not include the effect of additional buoyancy elements such as benzene or hydrogen generation, the buoyancy measurements provide an *upper bound* estimate of the density in Tank 48H required to float the solids.

TABLE OF CONTENTS

LIST OF TABLESvii
LIST OF FIGURES
LIST OF ABBREVIATIONSviii
1.0 Introduction
2.0 Experimental Procedure
2.1 Analysis of the First Set of Tank 48H Samples (HTF-48-14-158, -159)2
2.2 Analysis of the Second Set of Tank 48H Samples (HTF-48-14-169, -170)
2.3 Preparation of Salt Solutions for Buoyancy Measurements
2.4 Quality Assurance
3.0 Results
3.1 Filtrate Results
3.2 Solids Results
3.3 Modeling of the TPB Decomposition in Tank 48H11
3.4 Buoyancy and Floatation Measurements
4.0 Conclusions14
5.0 References

LIST OF TABLES

Table 1.	Composition of Salt Solutions	5
Table 2.	Filtrate Results	6
Table 3.	Results from the HPLC Analysis of the Sample Solids	9

LIST OF FIGURES

Figure 1.	Solids on the Surface of Tank 48H1	
Figure 2.	Visual Appearance of the First Tank 48H Samples	;
Figure 3.	Surface of Tank 48H After Mixing4	ŀ
Figure 4.	Visual Appearance of the Second Set of Tank 48H Samples4	ŀ
Figure 5.	Potassium in Filtrate Data from 1999	,
Figure 6.	Potassium Data from Two Recent Points vs. Historical Trend9)
Figure 7.	FTIR Analysis of the Acetonitrile Solutions of the Second Samples)
Figure 8.	TPB Slurry in Salt Solutions After 4 Hours)
Figure 9.	TPB Slurry in Salt Solutions After 21 Hours	;
Figure 10.	. TPB Slurry in Salt Solutions After 117 Hours13	;

LIST OF ABBREVIATIONS

1PB	Phenylboronic acid
2PB	Diphenylborinic acid
3PB	triphenylboron
ACM	Aspen Custom Modeler
AD	Analytical Development
CsTPB	Cesium tetraphenylborate
DWPF	Defense Waste Processing Facility
FTIR	Fourier Transform Infrared spectroscopy
HPLC	High Performance Liquid Chromatography
IC-A	Ion Chromatography-Anions
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ITP	In-Tank Precipitation
KTPB	Potassium tetraphenylborate
LFL	Lower Flammability Limit
NMR	nuclear magnetic resonance
%RSD	% Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TPB	tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

At the Savannah River Site (SRS), Tank 48H currently holds approximately 255,000 gallons of slurry which contains potassium and cesium tetraphenylborate (KTPB and CsTPB). Original plans called for processing this tetraphenylborate (TPB) slurry in the In-Tank Precipitation (ITP) Facility, the Late Wash Facility, and the Defense Waste Processing Facility (DWPF) Salt Cell. That process scheme included concentrating the TPB, washing the non-radioactive salts to reduce the nitrite concentration, decomposing the TPB to benzene, and separating the benzene from the aqueous waste. However, these facilities ceased operation due to high benzene generation during startup of the ITP Facility.

Since that time, the contents of the tank have remained largely undisturbed, except for evaporative losses, addition of sodium hydroxide solution (for corrosion control), periodic slurry pump runs (and leaking pump seal water), and occasional additions of drain transfers (rainwater). Except for a month long period during September-October 2014, the tank has been actively ventilated.

On December 2, while preparing to remove a sample from the tank for corrosion control, a survey found that the whole body dose was higher than previous measurements. The work was stopped and consideration was given to the cause. On December 4, two corrosion control samples were pulled (HTF-48-14-158, -159) and sent to the Savannah River National Laboratory (SRNL) for analysis. A Task Technical Request (TTR)¹ was written to analyze the samples, and SRNL prepared a Task Technical and Quality Assurance Plan (TTQAP).² On December 4, a picture from inside of the tank was taken (Figure 1) which showed solids on the Tank surface. On December 18, the contents of Tank 48H were mixed, and two subsurface samples were pulled (HTF-48-14-169, -170) and sent to the SRNL for analysis.





2.0 Experimental Procedure

On December 4, two, 200 mL slurry samples were delivered to SNRL for the purposes of corrosion control; HFT-48-14-158, and -159. The samples were pulled from the surface of the tank, and due to the unknown degree of solids accumulation at the surface, are not expected to be representative of the tank as a whole.

Samples of the filtrate were sent forward for duplicate analysis by High Performance Liquid Chromatography (HPLC), Inductively Coupled Plasma Emission Spectroscopy (ICPES), Ion Chromatography-Anions (IC-A), Free Hydroxide, gamma scan, Total Inorganic Carbon/Total Organic Carbon (TIC/TOC), pH, and density. A small quantity of filtered solids was sent forward for duplicate analysis by HPLC.

Following mixing in the tank on December 18, two 200-mL slurry samples were delivered to SNRL; HFT-48-14-169, and -170. The samples were pulled 48" from the bottom of the tank. The samples were kept separate. A portion of each sample was filtered and the filtrate retained for use. Samples of each filtrate were sent forward for analysis by IC-A, Free Hydroxide, gamma scan, TIC/TOC, pH, and density. A small quantity of filtered solids from each sample was sent forward for analysis by HPLC and Fourier Transform Infra-Red (FTIR) spectroscopy.

Some of the results of these analyses have been previously reported.^{3,4} This report documents the results on all of the Tank 48H samples taken in December 2014. Details for the work are contained in a controlled laboratory notebook.⁵

2.1 Analysis of the First Set of Tank 48H Samples (HTF-48-14-158, -159)

As received, both dip bottles contained ~200 mL of sample material. The bottles were thoroughly agitated, and the contents poured into plastic cups for visual observation (Figure 2). In both cases, the material was an off-white slurry. In addition, at the bottom of each dip bottle, residual solids were present. From visual observations, sample HTF-48-14-159 had more solids, and in that sample the solids had a semi-crystalline appearance, suggesting inorganic solids, although these were not analyzed.

Both samples were composited into a single bottle, and the contents of the bottle thoroughly agitated before further work was performed. A sample of this composite was filtered through a 0.45 mm filter cup, to split the solids from the filtrate. The filtrate was noted to have a pale red-brown color.



Figure 2. Visual Appearance of the First Tank 48H Samples

A small sample of the composite solids was sent to Analytical Development (AD). At AD, the solids were prepared (dissolved) and analyzed in duplicate by HPLC.

2.2 Analysis of the Second Set of Tank 48H Samples (HTF-48-14-169, -170)

After the contents of Tank 48H were mixed (Figure 3), two samples were sent to SRNL. As received, each of the dip bottles contained ~200 mL of slurry. The bottles were thoroughly agitated, and the contents poured into plastic cups for visual observation (Figure 4). In both cases, the material was off-white slurry, similar in appearance and amounts to the first sample set.

Unlike the previous sample set, these two samples were kept as discrete samples. The contents of each sample bottle were thoroughly agitated before further work was performed.

A well-mixed sample from each bottle was filtered through a 0.45 mm filter cup, to split the solids from the filtrate. The filtrate was noted to have a pale red-brown color. For the analysis of the filtrates, single samples were analyzed for each filtrate. A small weighed sample of solids from each bottle was dissolved in acetonitrile and sent forward for HPLC and FTIR analyses.



Figure 3. Surface of Tank 48H After Mixing

Figure 4. Visual Appearance of the Second Set of Tank 48H Samples



2.3 <u>Preparation of Salt Solutions for Buoyancy Measurements</u>

In order to measure the buoyancy of the TPB solids, SRNL prepared 6 different salt solutions, using NaOH, NaAlO₂, NaNO₃, NaNO₂, Na₂CO₃•H₂O, and NaCl. The salts were dissolved into the proper amount of deionized water, giving compositions listed in Table 1. The composition of each solution mimics that of Tank 48H solution, but scaled up in salt concentrations to reach the higher density solutions. The sodium content ranges from 4.6 to 7.1 M, and resulted in solution densities of 1.197 to 1.296 g/mL (Table 1). SRNL prepared 200 mL of each solution. A literature reference on the density of KTPB and CsTPB indicates that the density range of the prepared solutions is appropriate.⁶

Compound	Μ	Μ	Μ	Μ	Μ	Μ
Target Na	4.5	5.0	5.5	6.0	6.5	7.0
Na	4.60	5.11	5.62	6.13	6.64	7.15
Free OH	1.66	1.84	2.02	2.21	2.39	2.58
Al	0.096	0.106	0.117	0.128	0.138	0.149
Nitrate	0.182	0.202	0.222	0.243	0.263	0.283
Nitrite	0.594	0.660	0.726	0.791	0.857	0.923
Carbonate	1.02	1.14	1.25	1.37	1.48	1.59
Cl	0.0191	0.0213	0.0234	0.0255	0.0277	0.0298
Density (mg/L)	1.197	1.229	1.237	1.256	1.279	1.296

Table 1. Composition of Salt Solutions

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results

3.1 Filtrate Results

The filtrate composition variance between the individual samples was quite small, as evidenced by the small relative standard deviation (%RSD) values (Table 2). Changes in the filtrate composition will only occur over longer periods of time, either due to addition of corrosion control chemicals, or due to the slow uptake of carbon dioxide, and the slow degradation of the TPB slurry. The average results from all four samples are reported in

A]	Average of all Samples	HTF-48-12-20/24		
Analyte	(2014)	(2012 sample)		
Al	2740 (7.0%) mg/L	2050 (7.5%) mg/L		
В	563 (4.2%) mg/L	463 (24%) mg/L		
Cr	53.8 (4.3%) mg/L	42.1 (15.4%) mg/L		
K	448 (8.5%) mg/L	286 (8.0%) mg/L		
Na	106000 (2.7%) mg/L	85800 (8.9%) mg/L		
F	<100 mg/L	<204 mg/L		
Formate	283 (10%) mg/L	296 (1.7%) mg/L		
Cl	703 (3.7%) mg/L	187 (9.0%) mg/L		
Nitrite	28500 (1.6%)	24500 (3.6%) mg/L		
nitrate	11500 (9.6%) mg/L	11000 (13%) mg/L		
Phosphate	594 (15%) mg/L	465 (16%) mg/L		
Sulfate	218 (2.0%) mg/L $^{\Sigma}$	209 (22%) mg/L		
oxalate	1660 (2.6%)	1590 (0.3%) mg/L		
Total Carbon	15300 (9.5%) mg/L	18500 (0.09%) µg C/mL		
Total Inorganic Carbon	12800 (12%) mg/L	16600 (2.1%) µg C/mL		
Total Organic Carbon	2450 (5.5%) mg/L	1890 (19%) µg C/mL		
Free Hydroxide	1.73 (1.1%) M	1.02 (2.0%) M		
¹³⁷ Cs	2.38E+07 (13%) dpm/mL	2.57E+07 (1.0%) dpm/mL		
TPB	<5 mg/L	< 10 mg/L f		
Triphenylboron (3PB)	<10 mg/L	<10 mg/L		
Diphenylboronic acid (2PB)	<10 mg/L	<10 mg/L		
Phenylborinic acid (1PB)	26 mg/L (10%)	NA		
phenol	275 (8.50%) [▽]	NA		
Density	1.225 g/mL $^{\Sigma}$	1.198 g/mL		

Table 2. Filtrate Results

Table 2.^{\oplus} Values in parentheses are the %RSD. For comparison purposes, results from a previous sample (HTF-48-12-20/24⁷) are also listed in Table 2. The tank contents level at the time of sampling in December 2014 was ~255,000 gallons, and the tank level at the 2012 sample time was ~245,000 gallons.

 $^{^{\}Sigma}$ This value is from samples HTF-48-14-158, and -159 only.

^{*f*} The TPB, 3PB and 2PB results are actually from D. P. Lambert, T. B. Peters, M. E. Stallings, S. D. Fink, "Analysis of Tank 48H Samples", WSRC-TR-2003-00270, rev.0, January 20, 2004. These three analytes were not measured in the filtrates from HTF-48-12-20/24.

 $^{^{\}nabla}$ This value is from samples HTF-48-14-169, and -170 only. The HTF-48-14-158/159 composite sample returned less than detectable results (<500 mg/L).

 $^{^{\}oplus}$ The individual sample results are retained in the ELN.

The analytical uncertainty for each sample is 10%, except for gamma scan, which is 5%; and for density it is 3%. The low %RSD of the average of all four 2014 samples is an indication that there was little change in the filtrate composition before and after the tank was mixed, which was as expected.

The results of the filtrate from the 2014 samples are similar as expected when compared to the 2012 samples. In some cases the analytes from the recent samples are slightly higher than the older samples, and in some cases the results are slightly lower. However, given past comparisons between different Tank 48H samples,⁷ this variation is neither unexpected nor alarming.

One general concern with the Tank 48 contents is that the TPB solids in the tank are decomposing, and releasing flammable gasses and liquids. One key piece of evidence for TPB degradation is the ¹³⁷Cs activity. Any degradation of the TPB solids should release ¹³⁷Cs into the filtrate. However, the ¹³⁷Cs activity in the filtrate is actually slightly lower in the December 2014 sample. Another piece of evidence pointing to the lack of any degradation are the HPLC results. If TPB is degrading, it follows a degradation chain of TPB \rightarrow 3PB \rightarrow 2PB \rightarrow 1PB \rightarrow benzene and phenol. HPLC results to date find no detectable levels of 3PB or 2PB.

The 1PB result is from sample HTF-48-14-169 only. The results from samples HTF-48-14-170, and the HTF-48-14-158/159 composite were less than detectable.

There are several results that need to be further considered. First, the sodium and hydroxide levels have notably increased. This is from the addition of 50 wt% NaOH which is used for corrosion control. Given the history of caustic additions that occurred between the current sample and previous sample, the increase of sodium by ~15000 mg/L is predicted. Second, the chloride results in the current sample are notably higher than the previous sample. However, these differences could be indicating a large variability in sample results over time. For example, a previous sample (HTF-E-05-21) was analyzed to have a chloride concentration of 854 (7.7%) mg/L.

The potassium results merit special attention. The potassium results for the current sample are ~60% higher than the previous sample. More potassium in solution could be taken as a sign of degradation of KTPB. From this data set and previous Tank 48H filtrate samples, the potassium data can be plotted over time to look for any indication of an acceleration of potassium ingrowth, which in turn implies an acceleration of KTPB degradation. All available potassium filtrate data was located from 1999 to the present and normalized to the current tank volume of 255,000 gallons. This was plotted against sample date and is shown in Figure 5.



Figure 5. Potassium in Filtrate Data from 1999

Once fitted to a line, the data shows a reasonable linear trend ($R^2 = 0.8637$). A recent acceleration in the rate of benzene generation would show an increase in potassium concentration and provide a poorer line fitting.

A previous document examined the potassium trends from 1999 to 2004.⁸ In this document, the potassium data over this period was found have a very linear increase over time (line fit $R^2 = 0.993$). If this line is plotted on a graph, with the two (2012, 2014) data points superimposed, an interesting trend is noted (Figure 6). The line from the early data is predicting a higher potassium concentration in solution than the two most recent data points. In fact, the largest deviation from the prediction is the 2012 data point. It is then realized that comparing the 2014 results *vs* the 2012 result does not indicate a notable increase in potassium levels – rather the 2012 data point is unusually low. More importantly, the recent data points indicates that since 2004, something has happened in the tank that appears to be suppressing the degradation of TPB, and has consequently decreased the rate of potassium coming into solution, when compared to the 1999 to 2004 data.

It is possible that continued addition of NaOH has increased the ionic strength in solution such that it is hindering the degradation of the TPB salts.



Figure 6. Potassium Data from Two Recent Points vs. Historical Trend

3.2 Solids Results

For the first set of samples (HTF-48-14-158/159), a small amount of the composite filtered solids was analyzed in duplicate by HPLC. The solids were slurried out of a subsample, so direct comparisons to previous solids samples from 2012 (HTF-48-12-20/24) would need to look at ratios, especially given that the 2012 solids were taken as a slurry from a well-mixed sample. The results are listed in Table 3. For the second set of samples (HTF-48-14-169, -170), individual small amount of solids were removed and dissolved into acetonitrile and sent for HPLC. The results are listed in Table 3. The results for the HTF-48-14-169, and -170 are reported in wt% units as the preparation method was different.

Sample	TPB	3PB	2PB	1PB	Phenol
HTF-48-12-20/24	19000 (0.0%)	100 mg/L	200 mg/L	NA	NA
HTF-48-14-158/159	15700 (3.2%)	<500 mg/L	<500 mg/L	<500 mg/L	<500 mg/L
HTF-48-14-169	30.7 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%	<1.5 wt%
HTF-48-14-170	39.7 wt%	<0.86 wt%	<0.86 wt%	<0.86 wt%	<0.86 wt%

The solids samples results cannot necessarily be compared against the 2012 slurry sample. However, the ratio of TPB to 3PB and 2PB should be the same across all samples if TPB decomposition is slow and approximately the same between over the time period.

As expected, the organic content is contained as TPB, which is the most stable of all the phenylborates. While TPB decomposition is slow, once started, progresses quickly. This explains the lack of 3PB and 2PB in the results.

Some of the acetonitrile solution from the second set of samples (HTF-48-14-169/170) was analyzed for organic content by FTIR. This method provided a qualitative assessment of the sample, demonstrating that the sample was mostly TPB (Figure 7), with evidence of some phenol and functionalized aromatic compounds. The TPB is expected, and the presence of phenol and other aromatic compounds has been noted in the past.

The acetonitrile samples were also analyzed by ¹³C nuclear magnetic resonance (NMR). This analytical method examines the chemical environment around each carbon atom and provides qualitative information. For these samples, the NMR method corroborated the FTIR results, and also indicated the possible presence of biphenyl (another aromatic compound noted in previous Tank 48H samples).



Figure 7. FTIR Analysis of the Acetonitrile Solutions of the Second Samples

3.3 Modeling of the TPB Decomposition in Tank 48H

The main concern for the Tank 48 contents is that the degradation of the TPB had dramatically increased, which would release benzene. While the results from the 2014 samples indicates TPB degradation is not increased, it is of use to model the decomposition of the TPB slurry using the latest set of data. Earlier models ^{9,10,11} that examined the TPB decomposition (benzene generation) have been revised and the recent sample results have been incorporated.

To estimate benzene emissions for the ITP process, a VAX FORTRAN dynamic computer model was first developed by Roger Franks (DuPont ESD) in the late 1980s. The original version modeled the precipitation process in Tank 48H only, but was later extended to include the operation of the stripping columns, the filtrate hold tanks, Tank 22, Tank 50, and Tank 49. In the early 1990s, with new test data on process chemistry,⁹ the model was updated and rewritten in FORTRAN 77. A user-friendly interface was added to allow execution on a PC.¹² In 1996, the model was converted into SpeedUp, and revised to include catalytic reactions for benzene formation due to copper and radiolytic hydrogen generation.¹¹

The current Tank 48 model is an Aspen Custom Modeler (ACM) version extracted from the ITP /SpeedUp model. Tank 48 ACM model provides the following features:

- 1. <u>Precipitation:</u> The model accounts for reactions of soluble nitrate salts with NaTPB, the dissolution of the TPB solids based on their solubilities.
- 2. <u>Benzene formation by radiolysis:</u> Formation rates for free and trapped benzene, and the rate of benzene release due to the dissolution of TPB solids are provided.
- 3. <u>Catalytic formation of benzene:</u> In presence of copper acting as catalyst, benzene is generated due to the decomposition of NaTPB. Catalytic reactions are implemented in the model.
- 4. <u>Equilibria:</u> The model includes the equilibria to account for benzene adsorption, and benzene evaporation.
- 5. <u>Hydrogen generation by radiolysis:</u> Radiolysis of cesium generates hydrogen. The hydrogen generation rate is provided.
- 6. <u>Tank vapor space</u>: The model derives a dynamic component mass balance on the tank vapor space. The composite Lower Flammability Limit (LFL) (benzene + H₂) is calculated.

Using this model, the supernate composition for the 2012 sample was entered and from this the benzene generation rate was modeled. Next, the supernate concentration from the current samples was entered, and the benzene generation rate was modeled. The two results were virtually identical; the model predicts that the changes in the supernate concentration do not affect a change in the TPB degradation/benzene generation.

3.4 Buoyancy and Floatation Measurements

Given the results from the recent samples, SRNL has concluded that the increased dose at the point of sampling was due to the floatation of some fraction of the TPB solids. The TPB solids contain the bulk of the cesium, and therefore, any floating TPB solids will not be shielded by the ~6' of salt solution in the tank. The buoyancy of some fraction of the TPB slurries is likely due to a temporary buildup of gas or organic liquid from normal, slow hydrolysis and TPB degradation. The buoyancy of the slurries can be increased by the increasing solution density, resulting from the addition of 50 wt% NaOH for the purposes of corrosion control. At some point in time, it may be that the continued addition of NaOH will increase the solution density such that a larger portion of the solids, if not all of the solids, will float to the surface. This would generate a radiation field that might completely prohibit activity at the top of the tank.

After discussion with the customer, a revision to the TTR ¹³ was generated that allowed SRNL to measure the buoyancy of the TPB solids.

From the most recent Tank 48H samples, a single composite of all 4 samples was created, and all of the solids were filtered from the Tank 48H composite and retained for use. 80 mL each of the salt solutions (see Table 1) were placed in suitable wide-diameter glass jars. Into each jar, SRNL then placed ~4g of filtered solids (avoiding the use of the large crystalline looking solids). The contents of each vessel were agitated to disperse the solids and allowed to settle (or float). The jars were capped and allowed to sit for 5 days. Over that period, pictures were taken to examine whether or not the solids floated.

The first picture was taken 4 hours after the addition of solids (Figure 8).



Figure 8. TPB Slurry in Salt Solutions After 4 Hours

Although slightly hard to see, the 4.5, 5, 5.5, and 6M bottles are showing signs of solids settling while the 6.5 and 7M bottles are not. The second picture was taken 21 hours after the addition of solids (Figure 9).



Figure 9. TPB Slurry in Salt Solutions After 21 Hours

By twenty-one hours after solids addition, the solids in the 7M solution were mostly floating. The solids in 6.5 M solution were still somewhat dispersed, and the solids in the other bottles were all settling. The third picture was taken 117 hours after the addition of solids (Figure 10).



Figure 10. TPB Slurry in Salt Solutions After 117 Hours

By 117 hours, the 4.5 through 6M solutions have appreciably clarified, while the 6.5 M solution has retained the dispersed solids. The 7M solution still has most of the solids floating.

While the floating or settling was not particularly rapid, it is quite clear that even without the buoyancy provided by the gas generation and retention, the solids will largely float on the surface of a 7.0M sodium solution of density 1.296 g/mL. The solids will remain somewhat dispersed in a 6.5M solution of density 1.279 g/mL (without the additional buoyancy of gas generation). Solutions of lower density will not float the solids to any extent, unless additional buoyancy is provided from gas generation. Compare this to the current sodium concentration of the Tank 48H filtrate of 4.60 M and a density of 1.225 g/mL, upon which the solids floated until being mixed.

4.0 Conclusions

Given the results from the current Tank 48H sample, characterization does not demonstrate accelerated TPB degradation. The high concentration of free hydroxide inhibits the normal pathways for TPB decomposition.

An older modeling simulation of the TPB degradation was updated, and the supernate results from a 2012 sample were run in the model. This result was compared to the results from the recent December 2014 sample results reported in this document. The model indicates there is no change in the TPB degradation from 2012 to 2014.

SRNL has concluded that the increased dose at the point of sampling was due to the floatation of some fraction of the TPB solids. The TPB solids contain the bulk of the cesium, and therefore, any floating TPB solids will not be shielded by the ~6' of salt solution in the tank. The buoyancy of some fraction of the TPB slurries is likely due to a temporary buildup of hydrogen and benzene from normal, slow hydrolysis and TPB degradation. The buoyancy of the slurries is likely increased by the increasing solution density, which in turn is caused by the continual addition of 50 wt% NaOH for the purposes of corrosion control.

SRNL measured the buoyancy of the TPB solids in Tank 48H simulant solutions. It was determined that a solution of density 1.279 g/mL (~6.5M sodium) was capable of indefinitely suspending the TPB solids evenly throughout the solution. A solution of density 1.296 g/mL (~7M sodium) caused a significant fraction of the solids to float on the solution surface. As the experiments could not include the effect of additional buoyancy elements such as benzene or hydrogen generation, the buoyancy measurements provide an *upper bound* estimate of the density in Tank 48H required to float the solids.

5.0 References

¹ H. J. Meraw, "Analysis of Tank 48H Corrosion and Flammability Samples", U-TTR-H-00031, rev. 0, December 4, 2014.

² T. B. Peters, "Task Technical and Quality Assurance Plan for Tank 48H Samples", SRNL-RP-2014-01208, December 9, 2014.

³ T. B. Peters, "SAMPLE RESULTS FROM SAMPLES HTF-48-14-158 AND -159", SRNL-L3100-2014-00280, December 19, 2014.

⁴ T. B. Peters, "PARTIAL SAMPLE RESULTS FROM SAMPLES HTF-48-14-169 AND -170", SRNL-L3100-2015-00022, February 10, 2015.

⁵ ELN A4571-00084-16.

⁶ U. Behrens, F. Hoffmann, F. Olbrich, "Solid-State Structures of Base-Free Lithium and Sodium Tetraphenylborates at Room and Low Temperature: Comparison with the Higher Homologues MB(C6H5)4 (M = K, Rb, Cs)", *Organometallics*, 2012, pg.905-913

⁷ C. A. Nash, T. B. Peters, "Analysis of HTF-48-12-20/24 (February, 2012) and Archived HTF-E-021 Tank 48H Slurry Samples", WSRC-STI-2012-00420, rev.0, August 2, 2012.

⁸ D. P. Lambert, T. B. Peters, M. J. Barnes, S. D. Fink, "Analysis of Tank 48H Samples HTF-E-04-049 and HTF-E-04-050", WSRC-TR-2004-00514, Novemver 2004.

⁹ D. D. Walker, T. Hang, "In-Tank Precipitation Process Dynamic Benzene Material Balance Computer Model Part 1: Process Chemistry Basis", WSRC-RP-93-299, February 10, 1993.

¹⁰ T. Hang, "ITP Stream Compositions", SRT-WHM-94-054, September 14, 1994.

¹¹ T. Hang, "Revision of the ITP / Speedup TM Model", SRT-WHM-96-070, November 4, 1996.

¹² Hang, T., and D.D. Walker. "In-Tank Precipitation Process Dynamic Benzene Material Balance Computer Model. Part 2: Model Development (U)," WSRC-RP-93-595, April 21, 1993.

¹³ H. J. Meraw, "Analysis of Tank 48H Corrosion and Flammability Samples", U-TTR-H-00031, rev. 1, February 9, 2015.

Distribution:

S. L. Marra, 773-A T. B. Brown, 773-A D. H. McGuire, 999-W S. D. Fink, 773-A C. C. Herman, 773-A E. N. Hoffman, 999-W F. M. Pennebaker, 773-42A W. R. Wilmarth, 773-A Records Administration (EDWS) A. Samadi-Dezfouli, 704-27S C. J. Scherman, 241-152H R. T. McNew, 241-152H J. K. Fortenberry, 766-H T. A. Le, 766-H S. A. Utlak, 704-27S M. C. Clark, 704-25S R. E. Edwards, 766-H M. A. Rios-Armstrong, 766-H J. M. Bricker, 704-S J. S. Contardi, 704-56H T. L. Fellinger, 766-H E. J. Freed, 704-S J. M. Gillam, 766-H J. F. Iaukea, 704-27S J. W. Ray, 704-27S H. B. Shah, 766-H C. B. Sudduth, 707-7E V. Jain, 766-H J. N. Leita, 704-56H T. E. Smith, 241-152H E. A. Brass, 241-121H C. K. Chiu, 704-30S A. G. Garrison, 241-121H D. L. McWhorter, 241-120H B. A. Gifford, 704-56H A. R. Shafer, 766-H P. R. Jackson, DOE-SR, 703-46A J. A. Crenshaw, 703-46A D. J. Martin, 766-H J. R Vitali, 704-30S K. N. Fleming, 241-153H M. A. Broome, 704-29S P. J. Rowan, 704-S R. D. Thames, 241-152H