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**Analyses of HTF-48-12-20/24 (February, 2012) and  
Archived HTF-E-05-021 Tank 48H Slurry Samples**

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## EXECUTIVE SUMMARY

Personnel characterized a Savannah River National Laboratory (SRNL) archived sample of Tank 48H slurry (HTF-E-05-021) in addition to the composite of samples HTF-48-12-20 and HTF-48-12-24, which were both retrieved in February 2012. The combined February 2012 sample is referred to as HTF-48-12-20/24 in this report. The results from these analyses are compared with Tank 48H samples analyzed in 2003<sup>1</sup>, 2004<sup>2</sup>, and 2005.<sup>3</sup> This work supports the effort to demonstrate copper-catalyzed peroxide oxidation (CCPO) of organic content in this material. The principal findings with respect to the chemical and physical characteristics of the most recent sample follow.

- The measured potassium tetrphenylborate (KTPB) solid concentration is 1.76 wt %.
- Titanium was in line with 2004 and 2005 slurry measurements at 897 mg/L. It represents  $0.1535 \pm 0.0012$  wt % monosodium titanate (MST).
- The measured insoluble solids content was 1.467 wt %.
- The free hydroxide concentration in the Tank 48H filtrate sample ( $1.02 \pm 0.02$  M) is close to the Tank 48H limit (1.0 M).
- Carbonate reported by total inorganic carbon (TIC,  $1.39 \pm 0.03$  M) is more than double the concentrations measured in past (2003-2005) samples.
- The soluble potassium content (measured at  $286 \pm 23$  mg/L) in the filtrate is in line with all past measurements.
- The measured  $^{137}\text{Cs}$  concentration is  $7.81\text{E}+08 \pm 3.9\text{E}+07$  dpm/mL of slurry ( $1.33 \pm 5\%$  Ci/gallon or  $3.18\text{E}+05 \pm 5\%$  curies of  $^{137}\text{Cs}$  in the tank) in the slurry which is in agreement with the 2005 report of  $3.14\text{E}+05 \pm 1.5\%$  curies of  $^{137}\text{Cs}$  in the tank<sup>3</sup>. The filtrate  $^{137}\text{Cs}$  concentration is  $2.57\text{E}+07 \pm 2.6\text{E}+05$  dpm/mL. This result is consistent with previous results. Significant analytical data are summarized in Table 1.

**Table 1. Summary of Significant Tank 48H Composite Sample Results (HTF-48-12-20/24)**

Analyte	Slurry	Supernate	Source
Density, g/mL	1.219±0.011	1.198 ± 0.01	Density
Total Solids, wt %	23.23 ± 0.06	22.08 ± 0.4	Solids
Total Insolubles, wt %	1.467 ± 0.873	NA	Calculation
KTPB, wt %	1.76	NA	HPLC
MST solids, wt %	0.1535 ± 0.0012	<0.5 mg/L	ICP-ES
<b><u>Metals</u></b>			
Sodium, M	NM	3.73 ± 0.33	ICP-ES
Potassium, M	0.0826 ± 0.0056	0.0073 ± 0.0006	ICP-ES
<b><u>Anions</u></b>			
Free Hydroxide, M	0.652 ± 0.229*	1.02	Titration
Nitrite, M	NM	0.534 ± 0.0158	Anion
Nitrate, M	NM	0.177 ± 0.0232	Anion
<b><u>RadChem</u></b>			
$^{137}\text{Cs}$ , dpm/mL	$7.81\text{E}+08 \pm 3.9\text{E}+07$	$2.57\text{E}+07 \pm 2.6\text{E}+05$	Gamma scan

\*possible solids interference    NA = not applicable    NM = not measured

## LIST OF ABBREVIATIONS

1PB – phenylborinic acid  
2PB – diphenylboronic acid  
3PB – triphenylboron  
AD – Analytical Development  
CCPO – Copper-catalyzed peroxide oxidation  
DI – Deionized (water)  
DS – Dissolved Solids  
F/H ALS – F/H Area Laboratory Services  
HPLC – High Performance Liquid Chromatography  
IC – Ion Chromatography  
ICP-ES – Inductively Coupled Plasma – Emission Spectrometry  
ICP-MS – Inductively Coupled Plasma - Mass Spectroscopy  
KTPB – Potassium tetrphenylborate –  $K[B(C_6H_5)_4]$   
LOD – Limit of Detection  
MST – Monosodium titanate  
NA – Not applicable  
NM – Not measured  
NR – Not reported  
RAD – Radioactive (analytical method)  
RSD - Relative Standard Deviation  
SCO – Shielded Cells Operations, Savannah River National Laboratory  
SRNL – Savannah River National Laboratory  
SRR – Savannah River Remediation  
SVOA – Semivolatile Organic Analysis  
TPB – tetrphenylborate -  $[B(C_6H_5)_4]^-$   
TTQAP – Task Technical and Quality Assurance Plan  
TTR – Technical Task Request  
TIC/TOC – Total inorganic carbon/total organic carbon analysis  
Std Dev – Standard deviation (of replicated measurements)

## LIST OF UNITS

dpm/mL – Decays per minute per milliliter  
mg – milligrams  
mg/L – Milligrams per liter  
mL – milliliters  
L – liters  
wt % – Weight percent (dissolved, insoluble, or total solids)



## 1.0 Introduction

Tank 48H samples HTF-48-12-20 and HTF-48-12-24 were sent to SRNL for characterization. The first sample (2.75 liters) was retrieved on February 8, 2012 and the second sample (3.25 liters) was retrieved on February 28, 2012. Shielded Cells Operations (SCO) personnel received each sample in the same day it was retrieved. In addition Savannah River Remediation (SRR) requested selected analyses of filtrate from a past tank farm archived sample (HTF-E-05-021). SRNL had received sample HTF-E-05-021 on March 6, 2005. The results from the analyses are presented in this document, and the combined sample is referred to as HTF-48-12-20/24. The work supports the effort to demonstrate the destruction of organic material contained in the Tank 48 waste, most notably tetraphenylborate (TPB), by a CCPO process.

Characterization of these samples was specified in a Technical Task Request (TTR) and in a Task Technical Quality and Assurance Plan (TTQAP) approved by the customer.<sup>4,5</sup> The TTR for the copper-catalyzed reaction work was also provided by the customer.<sup>6</sup> The TTR and TTQAP directed blending of the 2012 Tank 48H samples for characterization and processing.<sup>4,5</sup> An unexpected high volume of pump bearing water flowed into the tank between the samplings as discussed below. Results of the current work are compared to three past characterizations per customer request. The three characterizations were reported for samples retrieved in 2003 (HTF-E-03-073 and HTF-E-03-127)<sup>1</sup>, 2004 (HTF-E-04-049 and HTF-E-04-050)<sup>2</sup>, and 2005 (HTF-E-05-021)<sup>3</sup>. Sample HTF-48-12-24 filtrate results from F/H Area Laboratories are compared where available.<sup>7</sup> A summary of findings is that free hydroxide is just at or above 1 M, carbonate is higher than seen before (1.39 M by TIC), and both slurry and filtrate densities (~1.2 g/mL) are measurably higher than 2003-2005 historical values.

At the time of the February 8, 2012 sampling (HTF-48-12-20) the Tank 48H volume was approximately 240,084 gallons (waste level 68.4 inches from the bottom of the tank). On February 28 sample HTF-48-12-24 was retrieved. The tank level was 71.8 inches and the volume was 252,018 gallons. Both samples were collected as soon as possible after mixing pump shutdown (approximately 2 minutes afterwards). The sampler was operated about 15 inches below the liquid level. The volume increase between samplings was due to pump bearing water addition into Tank 48H. Sample HTF-48-12-24 was thus 5% more dilute than sample HTF-48-12-20. The volume weighted dilution caused the composite HTF-48-12-20/24 to be 2.56% more dilute than HTF-48-12-20.

## 2.0 Experimental Work

Tank 48H samples HTF-48-12-20 and HTF-48-12-24 were mixed together in an 8-liter carboy in SRNL A-Block cell 3. The first step was to recover filtrate for density and analytical samples. Some settling of solids was allowed and duplicate 50 mL subsamples of mostly filtrate were removed from the carboy. The sub-samples were filtered using 150-mL Nalgene cup filters with 0.45 micron pore size. Density measurements were taken by filling 2 mL density tubes and recording masses. The bulk of the filtrate samples were then diluted 1:1 with deionized water. Six 2 mL subsamples and a 10-mL sample were sent to Analytical Development (AD) in shielded plastic bottles. On March 21, 2012 the carboy was thoroughly agitated with a circulating pump and rotating propeller stirrer, and four ~1 mL slurry samples were taken and placed in shielded plastic bottles. Each sample was bagged separately because of the higher radiation dose associated with unfiltered slurry. Slurry samples were also sent to AD. Blank bottles were sent to AD to check level of contamination in cells processing and analysis.

The slurry samples were analyzed in duplicate (See Table 2). Each approximately 1-gram slurry aliquot was dried and was then fused with sodium peroxide at 675 °C. Each resulting fused mass was digested with stock nitric acid and then diluted to 100 mL with deionized water. This method oxidizes all of the organics in the sample. This same procedure was used in the 2005 slurry sample digestion.<sup>3</sup> The customer requested analyses of filtrate but not digested slurry for sample HTF-E-05-021.

**Table 2. Analysis of Tank 48H Slurry Samples**

Analysis	Samples	Sample Volume, (each), mL	Dilution Volume, mL	Diluent
GAMMA SCAN (Cs-137)	2	0.1	2 samples and a blank digested in Cells, then split into sub-samples for analysis	
RAD ICP-ES (Na, K, Ti, B, Si, Cu, Fe, RCRA metals)	2	1		
RAD ICP-MS (fission products, actinides, noble metals)	2	1		
GROSS ALPHA	2	0.5		
<sup>90</sup> Sr, <sup>99</sup> Tc	2	0.1		
<sup>238/241</sup> Pu	2	0.1		
VOA (Benzene)	2	0.1	0	None
SVOA (TPB decomposition products)	2	0.1	0	None
TOTAL SOLIDS	3	3	0	None
DENSITY	3	2 or 8.5	0	None
HPLC	2	2	0	None

Table 3 provides the list of methods requested for the filtrate of the composite HTF-48-12-20/24. In addition the filtrate of the SRNL archived sample of HTF-E-05-21 was analyzed by IC anions, ICP-ES, ICP-MS, and gamma scan.

**Table 3. Analysis of Tank 48H Filtrate**

Analysis	Samples	Sample Volume (each), mL	Diluent
GAMMA SCAN	2	0.1	DI Water
TITRATION BASE/OH/OTHER BASE (EXCLUDING CO <sub>3</sub> )	2	1	DI Water
IC ANIONS [F <sup>-</sup> , Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> <sup>-</sup> , (SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup> , (NO <sub>3</sub> ) <sup>-</sup> , (NO <sub>2</sub> ) <sup>-</sup> ]	2	1	DI Water
RAD ICP-ES (Na, K, Ti, B, Si)	2	2	DI Water
RAD ICP-MS (actinides)	2	2	DI Water
DISSOLVED SOLIDS	2	1	None
DENSITY	2	5	None
GROSS ALPHA	2	0.5	DI Water
<sup>90</sup> Sr, <sup>99</sup> Tc	2	0.1	DI Water
<sup>238/241</sup> Pu	2	0.1	DI Water

Personnel filtered approximately 50 mL of slurry in duplicate using 0.45  $\mu\text{m}$  supported acrylic copolymer disc cup filters. Each filtration provided approximately 24 mL of liquid. Density was measured at this point with 2-mL density tubes and an analytical balance. Filtrate was added to a 60 mL plastic bottle with a pre-measured 25 mL of deionized (DI) water (yielding slightly more than 2:1 dilution). The contents of the plastic bottle were well mixed by vigorously shaking and checked for solids. The liquid was then distributed into shielded plastic bottles for transfer to AD. Physical properties were measured in a shielded cell. The TTQAP cites the relevant AD procedures for this work.<sup>5</sup>

### 3.0 Results and Discussion

The HTF-48-12-20/24 slurry results are reported in units of mg/L of slurry and the filtrate results in units of mg/L filtrate. Radiochemical results are reported in dpm/mL of slurry or filtrate. Historical results are referred to by sample number and 2003, 2004, and 2005 report as cited. No analyses of the archived HTF-E-05-21 slurry were requested or performed. Section 3.2 includes analyses of archived HTF-E-05-21 filtrate.

#### 3.1 Slurry Sample Results for the HTF-48-12-20/24 Composite

##### 3.1.1 Radionuclide Composition in Slurry

Gamma scan was used to determine the  $^{137}\text{Cs}$  content of slurry after peroxide fusion digestion and nitric acid uptake. Separation and beta counting results for  $^{99}\text{Tc}$  and  $^{90}\text{Sr}$  are also reported here and compared to previous characterizations. Results are provided in Table 4. Duplicate results for  $^{99}\text{Tc}$ ,  $^{90}\text{Sr}$ , and gross alpha were  $<4.58\text{E}+04$ ,  $<4.26\text{E}+05$ , and  $<2.90\text{E}+05$  dpm/mL upper limits, respectively, because interference or other problems prevented quantification. The current work quantified  $^{238}\text{Pu}$  and that concentration (activity) should be used for gross alpha as well.

**Table 4. Slurry Radionuclide Composition Data, dpm/mL**

Radionuclide, dpm/mL	HTF-48-12- 20/24	HTF-E-05-21 <sup>3</sup>	HTF-E-04-049 and HTF-E-04- 050 <sup>2</sup>	HTF-E-03-127 <sup>1</sup>
$^{137}\text{Cs}$	$7.81\text{E}+08 \pm$ $3.9\text{E}+07$	$7.53\text{E}+08 \pm$ $2.5\text{E}+07$	$9.05\text{E}+08 \pm$ $1.1\text{E}+07$	$1.01\text{E}+09 \pm$ $5.0\text{E}+06$
$^{99}\text{Tc}$	$4.65\text{E}+04^*$	NM	NM	NM
$^{90}\text{Sr}$	$1.37\text{E}+05^*$	NM	NM	$1.63\text{E}+05 \pm$ $1.4\text{E}+04$
$^{238}\text{Pu}$	$3.13\text{E}+05 \pm$ $1.6\text{E}+04$	NM	NM	NM
$^{239/240}\text{Pu}$	$<6.74\text{E}+02$	NM	NM	NM
$^{241}\text{Pu}$	$<1.66\text{E}+04$	NM	NM	NM
Gross Alpha	$<2.88\text{E}+05^*$	NM	$1.01\text{E}+04 \pm$ $7.0\text{E}+02$	$2.80\text{E}+05 \pm$ $4.0\text{E}+03$

\* Second measurements were upper limit values, see text

NM = not measured

Americium, curium, and californium measurements are provided in Table 5 below. Characterization of samples in the past have always found these isotopes to be less than detectable, so no comparisons are available. In contrast this current characterization of sample HTF-48-12-20/24 was able to detect and report  $^{241}\text{Am}$  content. The analytical procedure provides unique LOD values from each measurement as shown in the table.

**Table 5. Americium, Curium, and Californium in HTF-48-12-20/24 Slurry**

Analyte	First Slurry Sample dpm/mL slurry	Second Slurry Sample dpm/mL slurry	Average and Std Dev dpm/mL slurry
$^{241}\text{Am}$	6.08E+03	4.91E+03	$5.50 \pm 0.830\text{E}+03$
$^{243}\text{Am}$	<2.44E+03	<2.29E+02	NA
$^{242\text{m}}\text{Am}$	<3.56E+02	<3.81E+01	NA
$^{243}\text{Cm}$	<8.44E+02	<8.37E+02	NA
$^{245}\text{Cm}$	<6.91E+03	<6.86E+02	NA
$^{247}\text{Cm}$	<4.68E+03	<2.03E+03	NA
$^{249}\text{Cf}$	<5.25E+03	<2.03E+03	NA
$^{251}\text{Cf}$	<4.76E+03	<2.20E+03	NA
$^{242}\text{Cm}$	<2.96E+02	<3.16E+01	NA
$^{244}\text{Cm}$	<1.14E+03	<2.36E+03	NA

NA = not applicable because LODs are not averaged

### 3.1.2 Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) for Digested Slurry

Table 6 presents the elemental composition (in mg/L of slurry) of the digested slurry by ICP-ES. The digestion method (sodium peroxide fusion in a zirconium crucible) masked the true concentration of sodium and zirconium in the slurry. Calcium, iron, magnesium, and strontium were found at significant levels in the duplicate sample blanks as shown in Table 7. The blank results indicate that concentrations of these four elements in Table 6 are likely from sample preparation rather than sample content.

AD personnel used about 100 mL of dilute nitric acid per gram of slurry for digestion and dilution. This dilution tends to raise LODs. LOD values for the current work are the lower of the duplicate LOD results, and this convention is used where needed in the rest of this report.

The major constituents in the slurry include Na, K, Al, Ti, Cr, and B. Titanium represents  $0.1535 \pm 0.0012$  wt % monosodium titanate (MST). This value is in agreement with the 2005 report ( $0.15 \pm 0.01$  wt % MST) and 2004 report ( $0.15 \pm 0.015$  wt % MST).<sup>2,3</sup> The 2003 report provided a slightly lower MST concentration of  $0.14 \pm 0.0025$  wt %.<sup>1</sup>

Boron concentrations were in line with measurements of past samples. Aluminum and potassium were measurably higher than concentrations found in previous samples. Chromium, which tends to be present as chromate in most waste supernate, was lower and was below detection in contrast to concentrations found in past samples. However, the current filtrate chromium concentration shown in Table 18 is 42 mg/L, indicating that soluble chromium is in line with expectations. Filtrate chromium is thus considered representative.

**Table 6. Comparison of ICP-ES Data for Slurry Samples**

Component	HTF-48-12-20/24 mg/L of slurry	HTF-E-05-21 mg/L of slurry <sup>3</sup>	HTF-E-04-049 and HTF-E-04-050 mg/L of slurry <sup>2</sup>	HTF-E-03-127 mg/L of slurry <sup>1</sup>
Ag	<225	<0.01	NR	NR
Al	3110 ± 387	2014	2240	2030
B	1070 ± 49	867	1030	987
Ba	<20	< 0.008	2.52	3.47
Be	<5	NM	NR	NR
Ca	606 ± 121*	43	21.4	19.7
Cd	<28	< 0.017	NR	NR
Ce	<166	5	7	NR
Cr	74 ± 3	70	51	46.6
Cu	<13	4	3	1.97
Fe	159*	169	43	53.9
Gd	<41	< 0.01	NR	NR
K	3230 ± 220	2658	2380	2570
La	<24	< 0.032	NR	NR
Li	<32	< 0.026	NR	0.99
Mg	27 ± 5*	19	18.5	20.2
Mn	10.6 ± 0.1	6	6.38	7.82
Mo	<235	< 0.053	13.3	9.19
Na	NA	NM	74900	64600
Ni	<86.2	< 0.015	NR	NR
P	<482	129	207	192
Pb	<373	< 0.283	NR	NR
S	<1130	378	245	259
Sb	<763	< 0.042	11.5	8.45
Si	<452	125	106	89.9
Sn	<310	< 0.11	22.1	NR
Sr	5.27 ± 0.59*	9	5.29	5.64
Ti	897 ± 7	826	840	776
U	<1230	7	17.6	NR
V	<11	< 0.007	NR	NR
Zn	<28	5	12	7.91
Zr	NA	1.47	NR	NR

\*Sample blanks showed significant concentrations of these elements. NR = Not reported

**Table 7. Results from Peroxide Fusion Blanks for ICP-ES**

Component	Blank 3-297687	Blank 3-298993
Ca	2000	1870
Fe	<158	336
Mg	11.2	47.2
Sr	17.6	16.8

### 3.1.3 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Table 8 presents analyses of Tank 48H (HTF-48-12-20/24) slurry for some heavy elements. Uranium and neptunium concentrations are in line with past measurements. The mass data for  $^{99}\text{Tc}$  translates to  $7.5\text{E}+04$  dpm/mL which is 50% higher than the radiochemical measurements for the slurry (Table 4) and filtrate (Table 17). Radiochemical measurements for technetium are considered more reliable. Mercury was not reported because the digestion process reached at least  $670^\circ\text{C}$ . At this temperature, we expect mercury to volatilize.

**Table 8. ICP-MS Data for Slurry**

Mass and Isotope	HTF-48-12-20/24 (mg/L slurry)	2005 HTF-E-05-21 (mg/L slurry) <sup>3</sup>	HTF-E-04-049 and HTF-E-04-050 (mg/L slurry) <sup>2</sup>	HTF-E-03-073 and HTF-E-03-127 (mg/L slurry) <sup>1</sup>
$^{99}\text{Tc}$	$2.0 \pm 0.73$	$1.23 \pm 0.08$	NR	NM
$^{133}\text{Cs}$	$15.0 \pm 1.62$	NR	NR	NR
$^{233}\text{U}$	<0.118*	<0.09	$0.0613 \pm 0.00739$	$0.0696 \pm 0.00131$
$^{234}\text{U}$	0.31*	$0.267 \pm 0.012$	$0.325 \pm 0.0194$	NR
$^{235}\text{U}$	0.73*	$0.564 \pm 0.050$	$0.653 \pm 0.0443$	$0.653 \pm 0.0201$
$^{236}\text{U}$	0.19*	$0.125 \pm 0.006$	$0.144 \pm 0.00485$	NR
$^{237}\text{Np}$	0.33*	$0.173 \pm 0.040$	$0.222 \pm 0.0081$	$0.229 \pm 0.00369$
$^{238}\text{U}$	$5.32 \pm 1.60$	$3.32 \pm 0.359$	$4.12 \pm 0.224$	$4.04 \pm 0.0595$

\* Second measurements were <2.07 mg/L NR = Not reported

### 3.1.4 Volatile and Semivolatile Organic Analyses for Slurry

Semivolatile organic analysis (SVOA) and volatile organic analysis (VOA) are used to detect aromatic compounds including breakdown products from TPB. The SVOA and VOA results from the slurry sample for the HTF-48-12-20/24 sample are shown in Table 9. Also shown in Table 9 are the results of similar compounds in the 2005 HTF-E-05-021 sample. The 2004 report for HTF-E-04-049 and HTF-E-04-050 samples did not run VOA or SVOA on slurry.<sup>2</sup> The 2003 characterization is not in Table 9 because it reported no significant SVOA analytes, and VOA at the time measured benzene at  $56 \pm 12$  mg/L.<sup>1</sup>

Slurry samples for SVOA are first extracted with hexane. The organic extract is analyzed with a gas chromatograph and mass spectrometer. The VOA preparation in contrast uses a purge and

trap system where the aqueous sample (slurry) has an inert gas bubbled through it. The gas is likewise analyzed with a gas chromatograph and mass spectrometer.

The analysis results indicate the presence of nitro-aromatic compounds and other condensed ring compounds. If no standard deviation value is given then the compound was detected in only one of the two analyzed samples. Although nitro-aromatic compounds are energetic, their low concentrations observed here will not result in a significant temperature rise or gas generation upon decomposition.

The diisooctyl adapate is not an aromatic species and is not expected. This compound assignment may be an artifact of the SVOA compound identification method or additives from contact with plastic. Volatile analysis indicates the presence of benzene in the slurry. Benzene is a by-product from the decomposition of TPB and its degradation products. The wide error band is due to the tendency of benzene to vaporize from aqueous material.

**Table 9. VOA and SVOA Analyses for Slurry**

Component	HTF-48-12-20/24 mg/L	HTF-E-05-021 (mg/L slurry) <sup>3</sup>
Biphenyl	925 ± 106	414.6 ± 106
Nitrobenzene	100*	180.6 ± 104
2-Nitrophenol	130*	ND
4-Nitrophenol	120*	ND
m-Terphenyl	25 ± 17	ND
p-Terphenyl	30.5 ± 3.54	182.0
Diisooctyl Adapate	170*	ND
1-Ethyldisopropyl Benzene	<1	64.3 ± 32.7
Nitrosobenzene	170*	25.3 ± 5.4
Benzene**	49.2 ± 66.3	17.9 ± 1.0
*Only one measurement provided a concentration for this compound		
**Values of 96 and 2.3 mg/L were measured for the current sample		

### 3.1.5 High Performance Liquid Chromatography (HPLC)

Personnel measured the concentration of tetraphenylborate and its degradation products in the HTF-48-12-20/24 slurry sample by HPLC. Table 10 lists the HPLC results for the slurry. The analytical method is considered more sensitive to organic anion measurement than the SVOA method. TPB, KTPB, and phenol concentrations, as shown in Table 10, are consistent with previous measurements.

HPLC provides the four phenylboron compounds found in Tank 48H slurry. The duplicate tetraphenylborate measurements provided the same value as indicated by the zero standard deviation. KTPB is calculated by multiplying the TPB anion value by the ratio of the KTPB/TPB molecular weights. No error is given because the anion duplicates were in agreement. The detection limits for the duplicate measurements for phenol, triphenylboron (3PB), diphenylboronic acid (2PB), and phenylborinic acid (1PB) were above the measured values shown, so no standard deviation is given.

**Table 10. HPLC Data for Slurry**

Analyte	HTF-48-12-20/24 mg/L	HTF-E-05-21 mg/L <sup>3</sup>	HTF-E-04-049 and HTF-E-04-050 mg/L <sup>2</sup>	HTF-E-03-073 and HTF-E-03-127 mg/L <sup>1</sup>
TPB Anion	19000 ± 0	21000 ± 970	20100 ± 235	18800 ± 1120
Calculated KTPB	21300	23796	22600 ± 263	21100 ± 1250
Phenol	609*	771 ± 22	735 ± 24	973 ± 165
3PB	100*	74 ± 16.5	162 ± 35	<50
2PB	200*	142 ± 19	123 ± 6.1	<50
1PB	180*	151 ± 7.6	120 ± 5.6	<50

\* Second measurements were below detection (<5000 mg/L)

### 3.1.6 Total Base, Organic and Inorganic Carbon

Table 11 contains the total base, free hydroxide, and other base data for the February 2012 slurry. There are no historical results using this analysis method on slurry that is available for comparison. The current results have a very high variation and this may be caused by the presence of the slurry solids interfering with the titration method.

**Table 11. Total, Free and Other Base Content of Slurry**

Analyte	HTF-48-12-20/24
	M
Total Base	1.85 ± 0.849
Free OH-	0.652 ± 0.229
Other Base	0.1 ± 0.117

### 3.2 HTF-48-12-20/24 Composite Filtrate Sample Results

AD personnel analyzed duplicate Tank 48H HTF-48-12-20/24 filtrate samples. Personnel removed samples of the Tank 48H filtrate from the Shielded Cells after approximately 2:1 dilution with DI water. The analytical data is reported together with the one standard deviation (1σ) uncertainty. To compare the slurry results with the filtrate results, the filtrate result would be multiplied by a factor of 1.0026 to convert to a slurry basis. This factor is the ratio of filtrate mass (mg/L) to slurry mass (mg/L). It is calculated by the following formula:

$$\begin{aligned} \text{filtrate correction factor} &= \text{slurry density} * (1 - \text{insoluble solids}) / \text{density filtrate} \\ &= 1.219 * (1 - 0.01467) / 1.198 = 1.0026 \end{aligned}$$

Given that the factor is so close to unity it was not applied to adjust any results.



### 3.2.1 IC Anions, Total Base, and Organic and Inorganic Carbon

AD personnel analyzed the HTF-48-12-20/24 filtrate samples using titration methods and density measurements. The HTF-48-12-20/24 total base concentration is  $2.56 \pm 0.02$  M and the free hydroxide is  $1.02 \pm 0.02$  M. The concentration of other bases is  $0.1 \pm 0.09$  M and carbonate concentration is 16646 mg/L carbon ( $1.385 \pm 0.01$  M carbonate). Historical results from 2003, 2004, and 2005 included carbonate (not TIC) measurement.<sup>1, 2, 3</sup> These are converted to a carbon basis and are shown for comparison in the TIC row of Table 12. The 2003 report also did include TIC and this is provided in Table 12 as well.<sup>1</sup> All historical data show that carbonate is now more than twice the past measured concentrations. A combination of carbon dioxide adsorbed from the air in Tank 48H and organic degradation over the years may explain this. Table 12 lists the IC anions results for the archived HTF-E-05-021 sample, but no titration or TIC/TOC work had been requested or performed for that sample.

The free hydroxide concentration (at 1.34 M) had increased since the September 2003 sampling (0.790 M) due to the addition of sodium hydroxide in October 2003 and December 2004. The current free hydroxide concentration shows a decline with time after 2005. The increase in carbonate suggests that breakdown of organic chemicals may have converted free hydroxide to carbonate.

**Table 12. Anion, Base and Carbon Content of Filtrate**

Analyte	HTF-48-12-20/24 mg/L	Cells Archived HTF-E-05-21 mg/L	2005 HTF-E-05-21 <sup>3</sup> mg/L	HTF-E-04-049 and HTF-E-04-050 <sup>2</sup> mg/L	HTF-E-03-127 <sup>1</sup> mg/L
F <sup>-</sup>	<204	<200	$14 \pm 0$	<20	<18
Cl <sup>-</sup>	$187 \pm 16$	$854 \pm 66$	$172 \pm 23$	$370 \pm 183$	$125 \pm 5.7$
HCOO <sup>-</sup>	$296 \pm 5$	$386 \pm 5$	$502 \pm 10$	$680 \pm 428$	$432 \pm 27$
NO <sub>2</sub> <sup>-</sup>	$24500 \pm 894$	$26000 \pm 1202$	$23750 \pm 350$	$30400 \pm 1800$	$21400 \pm 1380$
NO <sub>3</sub> <sup>-</sup>	$11100 \pm 1439$	$13100 \pm 1063$	$14250 \pm 150$	$18750 \pm 926$	$13400 \pm 893$
PO <sub>4</sub> <sup>2-</sup>	$465 \pm 75$	$682 \pm 11$	$428 \pm 9$	$916 \pm 222$	$515 \pm 23.5$
SO <sub>4</sub> <sup>2-</sup>	$209 \pm 45$	$214 \pm 4$	$323 \pm 1$	$528 \pm 210$	$273 \pm 11.4$
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	$1585 \pm 5$	$1755 \pm 148$	$1440 \pm 10$	$1613 \pm 116$	$1080 \pm 45.5$
	Molarity		Molarity	Molarity	Molarity
Total Base	$2.56 \pm 0.02$	NM	$2.485 \pm 0.05$	$2.04 \pm 0.071$	$1.755 \pm 0.035$
Free OH-	$1.02 \pm 0.02$	NM	$1.34 \pm 0.014$	$1.155 \pm 0.007$	$0.790 \pm 0.008$
Other Base	$0.1 \pm 0.09$	NM	$0.172 \pm 0.023$	$0.185 \pm 0.004$	$0.267 \pm 0.038$
	mg/L as C		mg/L as C	mg/L as C	mg/L as C
Total Inorganic Carbon (TIC)	$16646 \pm 347$	NM	4630 from carbonate	5900 from carbonate	$7840 \pm 212^{**}$
Total Organic Carbon (TOC)	$1887 \pm 358$	NM	NM	NM	$3010 \pm 283$
Total Carbon	$18512 \pm 16$	NM	NM	NM	$10850 \pm 71$

\*The duplicate result is below the LOD for that analysis

\*\*Carbonate on this sample was reported as  $5600 \pm 17$  mg/L C (as carbon only)

F/H Area Laboratory Services (F/H ALS) had performed IC anions, total gamma, free hydroxide, and density of solids-free liquid from sample HTF-48-12-24 separately from the HTF-48-12-20/24 composite.<sup>7</sup> Free hydroxide was reported to be 1.0061 M, in good agreement with the current work, and also very close to the tank corrosion limit of 1 M. Table 13 below shows that IC anions results agree except that sulfate, a minor component, shows more than 10% variance.

**Table 13. Comparison of IC Anions Results with Those of F/H Lab**

Analyte	HTF-48-12-20/24 mg/L (SRNL)	HTF-48-12-24 mg/L (F/H ALS)
Cl <sup>-</sup>	187 ± 16	199
NO <sub>2</sub> <sup>-</sup>	24500 ± 894	26460
NO <sub>3</sub> <sup>-</sup>	11100 ± 1439	11560
SO <sub>4</sub> <sup>2-</sup>	209 ± 45	298

### 3.2.2 Filtrate Mercury by Cold Vapor Atomic Absorption

Total mercury in duplicate filtrate samples was found to be below detection. The detection limit for mercury is 0.2 mg/L. Mercury was not measured for filtrate in the HTF-E-04-049, HTF-E-04-050, and HTF-E-05-21 samples.

### 3.2.3 Inductively Coupled Plasma Mass Spectroscopy of Filtrate

Table 14 provides isotope data determined by ICP-MS of filtrate. While the measurement of <sup>99</sup>Tc by radiochemistry is preferred (Section 3.2.4), the conversion of the radiochemical value provides 1.334 mg/L, which is within experimental error of the radiochemistry value.

**Table 14. ICP-MS Data for HTF-48-12-20/24 Filtrate**

Analyte	First Filtrate Sample mg/L	Second Filtrate Sample mg/L	Average mg/L
<sup>99</sup> Tc	1.52E+00	1.51E+00	1.51 ± 0.0234E+00
<sup>133</sup> Cs	4.326E-01	4.264E-01	4.29E-01 ± 4.41E-03
<sup>233</sup> U	1.201E-02	1.614E-02	1.41E-02 ± 2.92E-03
<sup>234</sup> U	7.107E-02	8.262E-02	7.68E-02 ± 8.17E-03
<sup>235</sup> U	1.306E-01	1.530E-01	1.42E-01 ± 1.58E-02
<sup>236</sup> U	3.296E-02	3.876E-02	3.59E-02 ± 4.10E-03
<sup>237</sup> Np	2.946E-02	3.284E-02	3.12E-02 ± 2.39E-03
<sup>238</sup> U	7.498E-01	8.180E-01	7.84E-01 ± 4.82E-02

Tables 15 and 16 provide comparisons of the current ICP-MS results with the 2005 archived sample HTF-E-05-21 and other historical measurements. The current uranium measurements are consistent with the archived, 2005, and 2003 work. Uranium concentration reported in the 2004 samples is consistently higher than the other analyses including the current ones.

**Table 15. Comparison of Current Filtrate ICP-MS Data with the 2005 Sample**

Analyte	HTF-48-12-20/24 mg/L	Cells Archived HTF-E-05-21 mg/L	2005 HTF-E-05-21 <sup>3</sup> mg/L
<sup>133</sup> Cs	4.29E-01 ± 4.41E-03	6.23E-01 ± 3.75E-02	Not Reported
<sup>233</sup> U	1.41E-02 ± 2.92E-03	1.51E-02 ± 1.63E-03	1.022E-02 ± 0.18E-03
<sup>234</sup> U	7.68E-02 ± 8.17E-03	6.56E-02 ± 7.42E-03	7.128E-02 ± 2.4E-03
<sup>235</sup> U	1.42E-01 ± 1.58E-02	1.24E-01 ± 2.83E-03	1.431E-01 ± 2.8E-03
<sup>236</sup> U	3.59E-02 ± 4.10E-03	3.11E-02 ± 3.61E-03	3.100E-02 ± 0.7E-03
<sup>237</sup> Np	3.12E-02 ± 2.39E-03	2.46E-02 ± 7.07E-04	1.856E-02 ± 0.1E-03
<sup>238</sup> U	7.84E-01 ± 4.82E-02	7.69E-01 ± 4.24E-03	8.253E-01 ± 2.8E-02

**Table 16. Comparison of Current Filtrate ICP-MS Data with the 2003/2004 Samples**

Analyte	HTF-48-12-20/24 mg/L	HTF-E-04-049 and HTF-E-04-050 <sup>2</sup> mg/L	HTF-E-03-127 <sup>1</sup> mg/L
<sup>133</sup> Cs	4.29E-01 ± 4.41E-03	Not Reported	Not Reported
<sup>233</sup> U	1.41E-02 ± 2.92E-03	6.13E-02 ± 7.39E-03	8.22E-03 ± 5.11E-04
<sup>234</sup> U	7.68E-02 ± 8.17E-03	3.25E-01 ± 1.94E-02	Not Reported
<sup>235</sup> U	1.42E-01 ± 1.58E-02	6.53E-01 ± 4.43E-02	8.94E-02 ± 2.20E-03
<sup>236</sup> U	3.59E-02 ± 4.10E-03	1.44E-01 ± 4.85E-03	Not Reported
<sup>237</sup> Np	3.12E-02 ± 2.39E-03	2.22E-01 ± 8.09E-03	1.81E-02 ± 1.29E-03
<sup>238</sup> U	7.84E-01 ± 4.82E-02	4.12E+00 ± 2.24E-01	5.88E-01 ± 1.69E-02

### 3.2.4 Radionuclide Composition of Filtrate

AD personnel analyzed the filtered sample using radiochemical methods. Cesium (<sup>137</sup>Cs) is the major radioactive analyte in the filtrate at a concentration of  $2.57 \pm 0.026 \text{ E7 dpm/mL}$ . F/H Area Laboratory Services reported a total gamma value of  $2.52\text{E}+07 \text{ dpm/mL}$  for HTF-48-12-24 filtrate, in close agreement with the result in Table 17.

Many comparisons with past samples are not possible because previous samples had no measurement. The current filtrate sample appears to have at least one order of magnitude less soluble plutonium than the 2003 samples.

**Table 17. Comparison of Filtrate Radiochemistry Data**

Radio Isotope	HTF-48-12-20/24 dpm/mL	2005 HTF-E-05-21 <sup>3</sup> dpm/mL	HTF-E-04-049 and HTF-E-04-050 <sup>2</sup> dpm/mL	HTF-E-03-127 <sup>1</sup> dpm/mL
<sup>244</sup> Cm	<1.51E+01*	NM	NM	NM
<sup>137</sup> Cs	2.57 ± 0.026E+07	3.0 ± 0.4E+07	2.57 ± 0.006 E+07	2.76 ± 0.057E+07
<sup>238</sup> Pu	2.89 ± 0.183E+02	NM	NM	1.69 ± 0.195E+03
<sup>239/240</sup> Pu	<23.1**	NM	NM	250. ± 0.812
<sup>90</sup> Sr	4.09 ± 3.6E+03	NM	NM	2.16 ± 0.625E+03
<sup>99</sup> Tc	5.02 ± 0.806E+04	NM	NM	8.51 ± 1.23E+04
<sup>241</sup> Pu	<7.34E+02**	NM	NM	NM
Gross Alpha	<1.93E+03**	NM	2.00 ± 0.389E+03	<1.33E+04

\*The lowest LOD is provided when both duplicates provide LOD values.

\*\* Upper limit values where interference prevents quantification

### 3.2.5 Inductively Coupled Plasma Emission Spectroscopy of Filtrate

AD determined the elemental composition of the filtrate by the ICP-ES method. The major constituents found in the filtrate included Na, Al, and B, as shown in Table 18. The element sodium is present in the highest concentration at 3.74 M. Elements measured below instrument detection limits include Ag, Ba, Cd, Ce, Fe, Gd, La, Li, Mg, Mn, Ni, Pb, Sn, Ti, U, and Zr (LOD values for these elements are listed in Table 18). The comparisons of measured elements with those of historical filtrate samples show no significant differences.

**Table 18. Comparison of Filtrate ICP-ES Data**

Component	HTF-48-12-20/24	HTF-E-05-21 archived	HTF-E-05-21 <sup>3</sup>	HTF-E-04-049 and HTF-E-04-050 <sup>2</sup>	HTF-E-03-073 and HTF-E-03-127 <sup>1</sup>
Ag	<3.0	<1.46	<3	NR	NR
Al	2050 ± 154	2370	2309	NR	2180
B	463 ± 110	485	460	412	443
Ba	<1.3	<0.52	<6	NR	NR
Be	<0.1	<0.08	NR	NR	NR
Ca	<1.2	<0.56	NR	NR	0.642
Cd	<0.6	<0.7	<1	NR	NR
Ce	<14.6	<6.03	<35	NR	NR
Cr	42.1 ± 6.5	48.	NR	NR	47.5
Cu	<1.3	<0.63	<3	1.01	0.617
Fe	<2.0	<0.33	<3	NR	NR
Gd	<1.6	<0.78	<4	NR	NR
K	286 ± 23	335	266.7	373	248
La	<1.1	<0.54	<13	NR	NR
Li	<3.0	<1.46	<12	NR	NR
Mg	<0.3	<0.15	<1	NR	NR
Mn	<0.4	<0.21	<1	NR	0.036
Mo	<12.7	<6.26	NR	NR	9.94
Na	85800 ± 7670	86700	87899	68800	69300
Ni	<3.3	<1.6	<10	NR	NR
P	<161	245	NR	NR	241
Pb	<15	<7.16	NR	NR	NR
S	199 ± 53	244	NR	NR	280
Sb	<22.0	<10.7	NR	NR	6.87
Si	<9.0	6.57	<125	4.675	6.84
Sn	<11.6	<5.61	<77	NR	4.92
Sr	<0.1	<0.05	NR	NR	NR
Ti	<0.3	<0.38	<1	NR	NR
U	<67.4	<32.7	<50	NR	NR
V	<1.0	<0.08	NR	NR	0.889
Zn	5.47 ± 1.35	5.97	NR	NR	5.41
Zr	<0.5	<0.55	<2	NR	NR

The lowest LOD is provided when both duplicates provide LOD values.

### 3.3 In-Cell Slurry Sample Results

Personnel measured solids contents and densities in the Shielded Cells because of the high activity of the samples.

### 3.3.1 Slurry and Filtrate Density

Filtrate from the Nalgene® cup filters was checked for visible solids, and none were seen in all cases for this work. Table 19 shows that filtrate density is consistent across the duplicate measurements but higher than previous measurements. Slurry density was simply determined by measuring the weight of well-mixed samples in density tubes of measured and traceable volumes (8.506 mL in both cases here). Both slurry and filtrate densities for HTF-48-12-20/24 are consistently higher than all past densities.

**Table 19. Comparison of Densities of Tank 48H Slurry and Filtrate**

Sample Number	Slurry Density, g/mL, Std Dev	Filtrate Density, g/mL, Std Dev
HTF-48-12-20/24 Test A	1.226	1.205
HTF-48-12-20/24 Test B	1.211	1.190
Average for HTF-48-12-20/24	1.219 ± 0.011	1.198 ± 0.01
HTF-E-05-021 (current measurement)	NM	1.15 (single measurement)
HTF-E-05-021 (2005) <sup>3</sup>	1.165 ± 0.002	1.14 ± 0.06
HTF-E-04-49,50 (2004) <sup>2</sup>	1.16 ± 0.009	1.164 ± 0.001
HTF-E-03-73 (2003) <sup>1</sup>	1.12 ± 0.021	1.148 ± 0.0056
HTF-E-03-127 (2003) <sup>1</sup>	1.14 ± 0.003	1.148 ± 0.0056

### 3.3.2 Soluble and Insoluble Solids

SCO measured the Tank 48H filtrate density as 1.198 ± 0.01 g/mL.

The dissolved solids concentration of the HTF-48-12-20/24 Tank 48H filtrate was 22.08 ± 0.40 wt %. The dissolved solids concentration of the August 24, 2004 filtrate was 16.28 ± 0.27 wt %. The dissolved solids concentration of the June 3, 2003 and September 23, 2003 filtrate was 16.6 wt %. The 2005 work appears to use the 2004 result.

Insoluble solids concentration was measured a second time after mixing of the carboy was determined to be inadequate for the first sampling. Based on triplicate analysis of the well-mixed carboy, the slurry total solids is 23.23 ± 0.06% and the filtrate dissolved solids content is 22.08 ± 0.40%. The second dissolved solids measurement is slightly high when compared with the other two. Table 20 shows the gravimetric results from triplicate samples analysis. The value for the insoluble solids (1.467 ± 0.873 wt %) is calculated using the following formula.

$$\text{Insoluble Solids} = (\text{total solids} - \text{dissolved solids}) / (1 - \text{dissolved solids}/100)$$

$$\text{Insoluble Solids} = (23.23 - 22.08) / (1 - 22.08 / 100) = 1.47 \pm 0.873 \text{ wt } \%$$

Based on this calculation, the insoluble solids measurement is consistent with previous analyses (1.69 ± 0.22 wt %, <sup>2</sup> 2.18 ± 0.61 wt %, <sup>1</sup> and 2.3 wt %<sup>8</sup>). The soluble solids content is higher than past work consistent with the current finding that filtrate density is higher than measurements made years ago (see previous section).

**Table 20. Comparison of Solids Data with those of Previous Samples**

Sample Number	wt % Total Solids	wt % Dissolved Solids	wt % Insoluble Solids
HTF-48-12-20/24 Test A	23.16	21.87	1.651
HTF-48-12-20/24 Test B	23.24	22.55	0.891
HTF-48-12-20/24 Test C	23.28	21.83	1.855
Average for HTF-48-12-20/24	23.23 ± 0.06	22.08 ± 0.40	1.467 ± 0.873*
HTF-E-05-021 (2005) <sup>3</sup>	20.19 ± 0.08	17.68 ± 0.14	3.05 ± 0.15
HTF-E-04-49,50 (2004) <sup>2</sup>	19.08 ± 0.08	17.68 ± 0.14	1.69 ± 0.22
HTF-E-03-127 (2003) <sup>1</sup>	18.42 ± 0.205	16.60 ± 0.402	2.18 ± 0.607
HTF-E-03-73 (2003) <sup>1</sup>	17.77 ± 0.117	16.55 ± 0.123	1.46 ± 0.24

\* Insoluble solids for this method is reported with uncertainty at 95% confidence (2-sigma)

#### 4.0 Analysis of Data

An ion balance for the filtrate (Table 21) shows that when the historically high carbonate (by TIC) for the current sample is accounted for, the sum of anion concentration significantly exceeds the cation concentration. This contrasts with the 2005 sample HTF-E-05-021 results where the total cation charge was 3.87 M and total anion charge was 3.14 M. Further examination of the current carbonate level may be needed since it is indicated to be significantly higher than historical measurements for Tank 48H.

**Table 21. Tank 48H Filtrate Anion/Cation Balance**

<b>Analyte</b>	<b>Normal</b>	<b>1<math>\sigma</math> Uncertainty, Normal</b>	<b>Method</b>
Al(OH) <sub>4</sub> <sup>-</sup>	0.076	0.0057	ICP-ES
BO <sub>3</sub> <sup>3-</sup>	0.128	0.0305	ICP-ES
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.024	0.0211	IC
Cl <sup>-</sup>	0.0053	0.0004	IC
CO <sub>3</sub> <sup>2-</sup>	2.77	0.058	TIC/TOC
NO <sub>2</sub> <sup>-</sup>	0.535	0.016	IC
NO <sub>3</sub> <sup>-</sup>	0.180	0.0232	IC
OH <sup>-</sup>	1.02	0.02	Titration
PO <sub>4</sub> <sup>3-</sup>	0.0044	0.001	IC
SO <sub>4</sub> <sup>2-</sup>	0.0043	0.0064	IC
<b>Total Anion Charge</b>	<b>4.77</b>		<b>Calculation</b>
K <sup>+</sup>	0.007	0.00058	ICP-ES
Na <sup>+</sup>	3.73	0.334	ICP-ES
<b>Total Cation Charge</b>	<b>3.74</b>	<b>0.334</b>	<b>Calculation</b>



## 5.0 References

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<sup>1</sup> D. P. Lambert, T. B. Peters, M. E. Stallings, and S. D. Fink, “Analysis of Tank 48H Samples HTF-E-03-73 (June 03, 2003) and HTF-E-03-127 (September 17, 2003)”, WSRC-TR-2003-00720, January 20, 2004.

<sup>2</sup> D. P. Lambert, T. B. Peters, M. J. Barnes, and S. D. Fink, “Analysis of Tank 48H Samples HTF-E-04-49 and HTF-E-04-50 (August 23, 2004)”, WSRC-TR-2004-00514, November, 2004.

<sup>3</sup> F. F. Fondeur, D. P. Lambert, and S. D. Fink, “Analysis of Tank 48H Sample HTF-E-05-021”, WSRC-TR-2005-00358, October 3, 2005.

<sup>4</sup> K. Subramanian, TTR “Technical Task Request – Sampling and Characterization of Tank 48H Waste”, G-TTR-H-00004, Rev. 0, October 20, 2011.

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