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## DWPF Decon Frit: Supernate Analysis

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## EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) has been requested to perform analyses on samples of the Defense Waste Processing Facility (DWPF) decon frit slurry (i.e., supernate samples and sump solid samples). Four 1-L liquid slurry samples were provided to SRNL by Savannah River Remediation (SRR) from the ‘front-end’ decon activities. Additionally, two 1-L sump solids samples were provided to SRNL for compositional and physical analysis. This report contains the results of the supernate analyses, while the solids (sump and slurry) results will be reported in a supplemental report.

The analytical data from the decon frit supernate indicate that all of the radionuclide, organic, and inorganic concentrations met the limits in Revision 4 of the Effluent Treatment Plant (ETP) Waste Acceptance Criteria (WAC) with the exception of boron. The ETP WAC limit for boron is 15.0 mg/L while the average measured concentration (based on quadruplicate analysis) was 15.5 mg/L. The measured concentrations of Li, Na, and Si were also relatively high in the supernate analysis. These results are consistent with the relatively high measured value of B given the compositional make-up of Frit 418.

Given these results, it was speculated that either (a) Frit 418 was dissolving into the supernate or aqueous fraction and/or (b) fine frit particulates were carried forward to the analytical instrument based on the sampling procedure used (i.e., the supernate samples were not filtered – only settled with the liquid fraction being transferred with a pipette). To address this issue, a filtered supernate sample (using a 0.45 um filter) was prepared and submitted for analysis. The results of the filtered sample were consistent with “unfiltered or settled” sample – relatively high values of B, Li, Na, and Si were found. This suggests that Frit 418 is dissolving in the liquid phase which could be enhanced by the high surface area of the frit fines or particulates in suspension.

Based on the results of this study, it is recommended that DWPF re-evaluate the technical basis for the B WAC limit (the only component that exceeds the ETP WAC limit from the supernate analyses) or assess if a waiver or exception can be obtained for exceeding this limit. Given the possible dissolution of B, Li, Na, and Si into the supernate (due to dissolution of frit), DWPF may need to assess if the release of these frit components into the supernate are a concern for the disposal options being considered.

It should be noted that the results of this study may not be representative of future decon frit solutions or sump/slurry solids samples. Therefore, future DWPF decisions regarding the possible disposal pathways for either the aqueous or solid portions of the Decon Frit system need to factor in the potential differences. More specifically, introduction of a different frit or changes to other DWPF flowsheet unit operations (e.g., different sludge batch or coupling with other process streams) may impact not only the results but also the conclusions regarding acceptability with respect to the ETF WAC limits.

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## LIST OF ABBREVIATIONS

AA	Atomic Absorption
AD	Analytical Development
CV	Cold Vapor
DWPF	Defense Waste Processing Facility
EDS	Energy Dispersive Spectroscopy
ETP	Effluent Treatment Plant
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
IC	Ion Chromatography
PSD	Particle Size Distribution
RCG	Radiation Control Guide
SEM	Scanning Electron Microscopy
SLUSOL	Slurry Solids
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi-Volatile Organic Analysis
SUMPSOL	Sump Solids
SUP	Supernate
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TTR	Task Technical Request
TTQAP	Task Technical and Quality Assurance Plan
VOA	Volatile Organic Analysis
WAC	Waste Acceptance Criteria
WWCT	Waste Water Collection Tank
XRD	X-Ray Diffraction



## 1.0 Introduction

The Defense Waste Processing Facility (DWPF) process improvement commitments for the current Savannah River Remediation (SRR) contract include the implementation of a water separation technology to separate the frit solids from the decon frit slurry transferred from the canister decontamination system to the Slurry Mix Evaporator (SME). Currently, all of the spent frit slurry from the canister decontamination process, which contains approximately 98% water by volume, is transferred to the SME resulting in additional cycle time associated with boiling off the water, as well as significant burden on the DWPF recycle waste system. The current process produces a ‘front-end’ frit slurry as well as a rinse/flush dilute solution. The combined volume of these processes is ~ 800 – 1,000 gallons per canister. It is proposed that a water separation technology be utilized to minimize the amount of water being sent to the SME which should alleviate the SME boil-down times (i.e., “dry” frit additions to the SME are the goal). Generically, the underflow (solids) will still be transferred to the SME, and the overflow (liquid) will be transferred to the Effluent Treatment Plant (ETP), or an alternate treatment facility. Since the spent frit slurry also contains the oxide layer removed from the stainless steel canister surface during the decontamination process (estimated to be 70 g of material in 800 gallons of slurry (Hutsell 2010), and the overflow (liquid) stream may still contain traces of contaminated frit, it is unknown whether or not the overflow would be acceptable for transfer to ETP or an alternate treatment facility.

The Savannah River National Laboratory (SRNL) has been requested to perform analyses on samples of the decon frit slurry (i.e., supernate samples and sump solid samples) as defined by Hutsell (2010). Four 1-L liquid slurry samples were provided to SRNL by SRR from the ‘front-end’ decon activities. Additionally, two 1-L sump solids samples were provided to SRNL for compositional and physical analysis. Hutsell (2010) also indicated that even though the as-received decon frit slurry samples will represent a bounding case with respect to meeting the ETP Waste Acceptance Criteria (WAC) requirements, a sample of the supernate (after settling of the as-received samples) should also be taken and analyzed. The supernate sample is expected to more closely mimic the overflow stream (liquid) and should provide a more realistic representation of the waste stream proposed to be transferred to ETP, or an alternate treatment facility. The results from the analyses will be used to evaluate the compatibility of the front-end decon frit slurry with ETP WAC requirements as defined by Martin (2009), Revision 4.

In response to the SRR request, Crawford and Peeler (2010) provided a Task Technical and Quality Assurance Plan (TTQAP) with an outline of the sample preparation techniques, task responsibilities spanning the various organizations associated with the task, a high-level overview of the task, and a detailed analytical study plan with corresponding sample and analytical controls to be used.

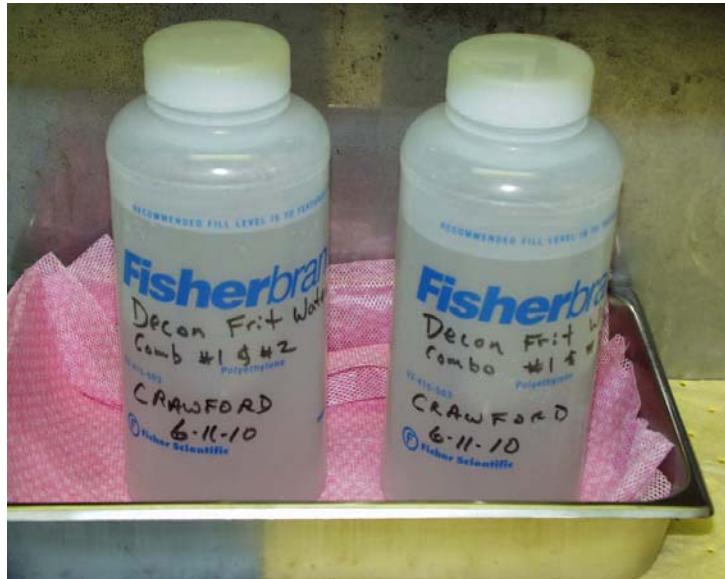
In this report, the results of the supernate samples (samples decanted from the liquid slurry samples received from SRR after settling for ~ 3 days) are reported and compared to the ETP WAC. The results of the solids analysis (both sump solids and supernate solids) will be provided in a separate report.

## 2.0 Experimental Procedure

Although the results of the supernate are the sole focus of this report, a general description of the “as received” samples and the protocols used to generate the supernate, sump solids, and slurry solids samples are fully described in this section. Information regarding the sample preparation, analytical requests, and results can be found in WSRC-NB-99-00002 and SRNL-NB-2010-00033.

### 2.1 Receipt of Samples

On June 8, 2010, SRNL received six 1-L polybottles from SRR. Four 1-L bottles (labeled #1 through #4) contained the liquid slurry samples. The contents were generally described or classified as “clear” with a small amount of visible solids on the bottom. Figure 1 shows examples of two of the four liquid slurry bottles. (Note these photos were taken after Bottles #1 and #2 were composited, redistributed into two 1-L bottles, and allowed to settle for ~ 3 days).



**Figure 1. Examples of “As Received” Liquid Slurry Samples.  
(after Bottles #1 and #2 were composited and allowed to settle for ~ 3 days).**

Two of the six 1-L bottles received from SRR contained sump solids. These bottles contained primarily solids (e.g., frit) and had a small but visible clear liquid layer on the top of the solids. These two bottles were labeled #5 and #6 and are shown in Figure 2.



**Figure 2. “As Received” Sump Solids Samples.  
(Note clear liquid fraction on top of the solids)**

## 2.2 Sample Preparation

Based on dose readings ( $< 1$  mrem/hr), sample preparation and handling of all of the frit decon samples (both solids and liquids) could be performed in a radiochemical hood. The following sections describe the sample preparation process that was used to produce the supernate, slurry solids, and sump solids samples ultimately submitted to Analytical Development (AD).

### 2.2.1 *Liquid Slurry Samples*

Two of the four liquid slurry samples (Bottles #1 and #2) were combined and then reallocated into separated 1-L polybottles and allowed to settle over an approximate 3 day period. Figure 3 shows one of the liquid slurry samples after 3 days of settling. Note the visible solids on the bottom of the polybottle. To obtain the supernate fraction of these samples, a pipette was used to transfer most of the liquid from each bottle working from top to bottom to minimize the potential for any of the settled solids from being transferred. (These samples were not filtered – only transferred with a pipette into a separate polybottle).

To provide quadruplicate analysis, four aliquots were obtained and labeled (i.e., SUP\_1, SUP\_2, SUP\_3 and SUP\_4)<sup>a</sup> for AD analysis. These four samples are referred to throughout this report as the “supernate” samples. It should also be noted that the pH of the supernate was  $\sim 9$  (based on the use of indicator strips ranging from 5 – 10).

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<sup>a</sup> “SUP” refers to the supernate fraction (decanted but not filtered) from the four liquid slurry samples.



**Figure 3. Liquid Slurry Sample After 3 Days of Settling.**  
(Note solids settled on bottom of polybottle)

### 2.2.2 Slurry Solids Samples

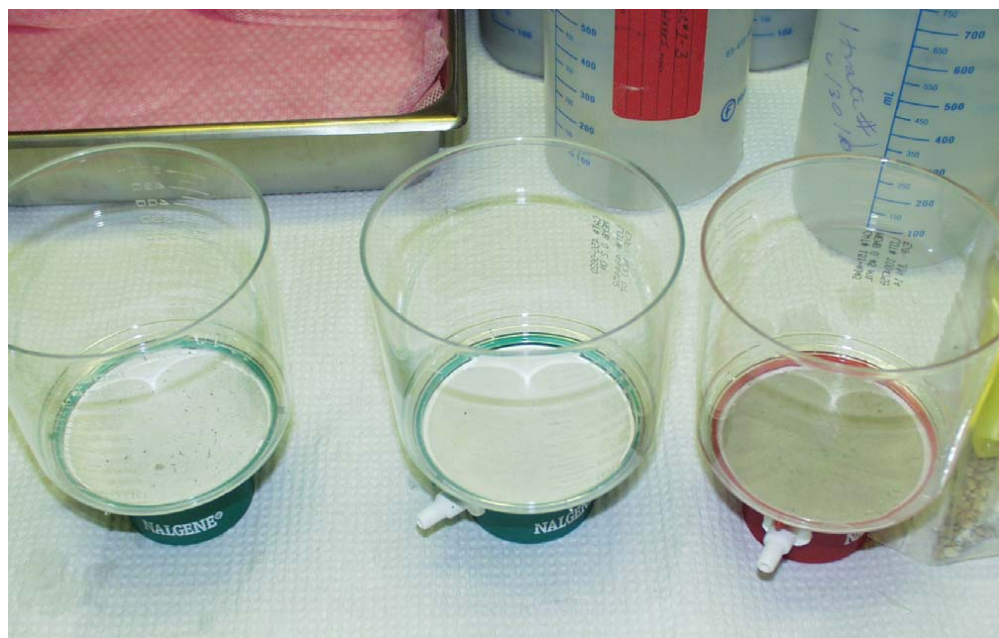
The two remaining “as received” liquid slurry bottles (#3 and #4) were combined with the remaining liquid and trace solids from Bottles #1 and #2 (those used to generate the supernate samples as noted in Section 2.2.1). The liquid–solid sample was slurried and then filtered (using a 0.2 or 0.45 micron filter) to obtain the insoluble solids from the liquid slurry Bottles #1 through #4.

Figure 4 shows the dispersed solids (top portion) and clear filtrate (below) during the filtration process. The solids (from Bottle #1 – Bottle #4) were collected on 3 filters – see Figure 5. The two leftmost filters were collected on 6/30/10 and air-dried overnight. The last filter (right) was collected on the day the photo was taken (7/1/10) and appears darker in color due to moisture content in the filter. All of the solids were continuously air-dried until 7/5/10. At that point, the solids were combined and four samples were obtained (labeled as SLUSOL-1, SLUSOL-2, SLUSOL-3, and SLUSOL-4)<sup>a</sup> to support the required chemical analyses. Additional samples were taken to support the physical analysis (i.e., particle size (PSD), x-ray diffraction (XRD), and scanning electron microscopy (SEM)). These samples are referred to as the “slurry solids” throughout this report.

<sup>a</sup> “SLUSOL” referring to the slurry (slu) solids (sol) which were filtered.



**Figure 4. Filtration of the Liquid Slurry Samples with Dispersed Solids (top) and Clear Filtrate (below).**



**Figure 5. Filtered Solids from the Liquid Slurry Samples (Bottles #1-#4).**

### 2.2.3 Sump Solids

The final set of samples was obtained from the two 1-L polybottles (#5 and #6) containing the sump solids (refer to Figure 2 for “as received” sump solids). The water/liquid layer on the top of the solids was decanted (to remove as much of the “free” water as possible) resulting in about 250 mL (approximately 125 mL from each bottle).

After decanting, approximately 20 grams of damp/wet solids was removed from each bottle and transferred to a weigh pan yielding approximately 40 grams of sump solids (see Figure 6). The sump solids were described as being similar to beach sand. The sump solids were air-dried in a radiohood for approximately 4 days.

Four sump solid samples were obtained for AD chemical analysis (labeled as SUMPSOL-1, SUMPSOL-2, SUMPSOL-3, and SUMPSOL-4). Additional sump solids samples were taken to support the physical analysis (i.e., PSD, XRD, and SEM).



**Figure 6. Sump Solids Transferred to Weigh Pan (Prior to Air-Drying).**

### 2.3 Requested Analysis

The supernate and solid (slurry and sump) samples were submitted to AD for physical and chemical characterization. As specified by the Task Technical Request (TTR) (Hutsell 2010) and outlined by the TTQAP (Crawford and Peeler 2010, Revision 1), chemical and physical properties or analysis required to support programmatic objectives were:

- Anions:  $\text{CO}_3^{-2}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{C}_2\text{O}_4^{-2}$ ,  $\text{PO}_4^{-3}$ , and  $\text{SO}_4^{-2}$
- Cation:  $\text{NH}_4^+$

- Elementals (at least the following): Ag, Al, As, B, Ba, Be, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Si, and Zn
- Radionuclides: total alpha, total beta/gamma, H-3, C-14, Ni-63, Co-60, Sr-90, Tc-99, Ru-106, Sn-126, Sb-125, I-129, Cs-137, Eu-154, U-233, U-235, Pu-241, and Radiation Control Guide (RCG) as defined in Attachment 8.2 of X-SD-H-00009 (Martin 2009).<sup>a</sup>
- Volatile Organic Analysis (VOA) and Semi-Volatile Organic Analysis (SVOA)
- Particle size distribution (only for slurry and sump solids)
- pH (only for the liquid supernate samples)
- Weight percent total solids

Crawford and Peeler (2010) provide a synopsis of the sample preparation, types of analyses to be performed, methods/instrumentation to be used for specific analytes, and the analytical controls implemented.

### 3.0 Results and Discussion: Supernate Samples

In this section the results of the supernate samples are provided and compared to the WAC limits as defined by Martin 2009, Revision 4. As previously noted, the results of the sump and slurry solids will be reported in a separate document.

#### 3.1 Inorganic Results

Table 1 provides a summary of the supernate results for the inorganic species as defined by Martin (2009). This table shows the specific inorganic species and the acceptance limits for the specified chemical contaminants as defined in Attachment 8.1 of the ETP WAC (Martin 2009). Acceptance limits for the Waste Water Collection Tank (WWCT) are also provided. The supernate results are the average of the four or quadruplicate supernate sample analysis (i.e., average of SUP\_1, SUP\_2, SUP\_3, and SUP\_4).

Comparing the averaged supernate results with the acceptance criteria for WWCT, all but one of the inorganic species (i.e., B) satisfy the requirements. The averaged B concentration for the supernate samples is 15.5 mg/L compared to WWCT feed criterion of 15 mg/L. It should be noted that the composition of Frit 418 (the frit being used by DWPF when the decon frit samples were pulled) is 8 wt% B<sub>2</sub>O<sub>3</sub>, 8 wt% Na<sub>2</sub>O, 8 wt% Li<sub>2</sub>O, and 76 wt% SiO<sub>2</sub>. From a glass perspective, the increased levels of B in the supernate samples could be an indication of either: (a) Frit 418 dissolving into the supernate or liquid as it sits in the sump and/or (b) fine frit particulates being carried forward to the analytical instrument (i.e., the supernate samples were not filtered as described in Section 2.2.1 – only settled with the liquid fraction being transferred with a pipette).

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<sup>a</sup> C-14 was removed from the analysis request based on communications from J. Bricker to D. Peeler (personnel communication via email on June 23, 2010 – see WSRC-NB-2009-00002, page 44 for more details).

**Table 1. Acceptance Limits for Chemical Contaminants as Defined by Martin (2009).  
 (Attachment 8.1 in X-SD-H-00009, Revision 4)**

Inorganic Species	Supernate Average - AD Analytical Results (mg/L)	WWCT Feed Acceptance Limits (mg/L)	Analytical Technique <sup>a</sup>
Ammonia (NH <sub>3</sub> )	< 5.00E+00	2.00E+01	IC
Carbonate (CO <sub>3</sub> <sup>-2</sup> )	1.52E+02	1.12E+03	TIC/TOC
Chloride (Cl <sup>-</sup> )	1.48E+00	3.00E+01	IC
Fluoride (F <sup>-</sup> )	< 1.00E+00	1.26E+01	IC
Nitrate (NO <sub>3</sub> <sup>-</sup> )	< 2.00E+00	3.40E+03	IC
Nitrite (NO <sub>2</sub> <sup>-</sup> )	< 1.00E+00	1.99E+03	IC
Oxalate (C <sub>2</sub> O <sub>4</sub> <sup>-2</sup> )	< 1.00E+00	2.54E+02	IC
Phosphate (PO <sub>4</sub> <sup>-3</sup> )	< 1.00E+00	1.84E+01	IC
Sulfate (SO <sub>4</sub> <sup>-2</sup> )	3.68E+00	1.33E+02	IC
Ag	< 4.30E-02	7.82E+01	ICP-AES
Al	< 1.88E-01	1.08E+03	ICP-AES
As	< 2.75E-02	1.50E+00	AA
B	1.55E+01 <sup>b</sup>	1.50E+01	ICP-AES
Ba	< 4.70E-02	5.77E+00	ICP-AES
Be	< 1.40E-02	2.00E-01	ICP-AES
Cd	< 5.10E-02	2.58E+00	ICP-AES
Cr	< 2.80E-02	8.40E+00	ICP-AES
Cu	< 4.90E-02	9.00E+02	ICP-AES
Fe	5.33E-01	4.00E+02	ICP-AES
Hg	< 5.00E-02	3.52E+01	CVAA
Mn	< 2.20E-02	9.00E+02	ICP-AES
Ni	< 1.86E-01	9.52E+01	ICP-AES
Pb	< 1.46E-01	3.71E+01	ICP-AES
Sb	< 2.08E-01	1.50E+00	ICP-AES
Se	< 5.50E-02	1.00E+00	AA
Zn	1.14E-01	5.92E+01	ICP-AES

Table 2 provides additional analysis of inorganic species from the supernate samples. These results are being reported for information only as they are not listed in the ETP WAC Revision 4.

<sup>a</sup> Analytical techniques used by AD to report measured concentrations. Techniques include: IC (Ion Chromatography), TIC/TOC (total inorganic carbon / total organic carbon), AA (atomic absorption), CV (cold vapor), ICP-AES (inductively coupled plasma – atomic energy spectroscopy).

<sup>b</sup> The reported B concentration for each of the four supernate samples was 15.5 mg/L with a relatively standard deviation of 10% (1-sigma). More specifically, the boron values for SUP-1, SUP-2, SUP-3 and SUP-4 were 15.5, 15.5, 15.5, and 15.5 mg/L, respectively.



**Table 2. Additional Supernate Results (Inorganics) Reported by ICP-AES Analysis.**  
 (All analytes measured by ICP-AES).

	Supernate Average (mg/L)
Inorganic Species	AD Analytical Results
Ca	< 3.06E-01
Ce	< 2.62E-01
Co	< 3.40E-02
Gd	< 4.20E-02
K	< 6.98E-01
La	< 4.00E-02
Li	1.75E+01
Mg	2.43E-01
Mo	< 8.50E-02
Na	4.22E+01
Si	1.13E+02
Sn	< 8.60E-02
Sr	< 1.00E-02
Th	< 4.72E-01
Ti	< 2.20E-02
U	< 8.89E-01
V	< 2.40E-02
Zr	< 3.60E-02

The increased levels of Na and Si (17.5 mg/L and 113 mg/L respectively) are consistent with the relatively high measured value of B (see Table 1) given the compositional make-up of Frit 418. As previously mentioned, although the supernate was allowed to settle for ~ 3 days, it is possible that fines were still in suspension when the liquid fraction was transferred with the pipette which could have resulted in the increased B concentrations in solution (i.e., particulates carried forward to the supernate the Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) analysis). Another possibility is that some fraction of Frit 418 has dissolved into the liquid/water while in the sump. Dissolution of the frit (which would lead to enhanced concentrations of Si, B, Li, and Na in solution) would be expedited or aided by the high surface area for reaction (i.e., fines or particulates). Physical characterization of the sump solids and slurry solids were available at the time this report was written and may provide insight into this issue (see discussion below).

SEM analysis of the slurry solids indicates that there is a larger fraction of fines associated with the slurry solids (Figure 7) as compared to the sump solids (Figure 8). This would be expected given the settling of fines would take longer in the supernate samples. It should be pointed out that Figure 7 represents the slurry solids that had been filtered from a composited sample and does not represent the size fraction that may have been transferred to the supernate samples

during pipetting. The intent of comparing Figure 7 and Figure 8 is to demonstrate the presence of fines associated with the slurry solids and leading to the potential for the increased Si, B, Na, and Li values observed in the ICP-AES measurements. Although not shown in this report, PSD measurements confirm a larger fraction of fines in the slurry solids.

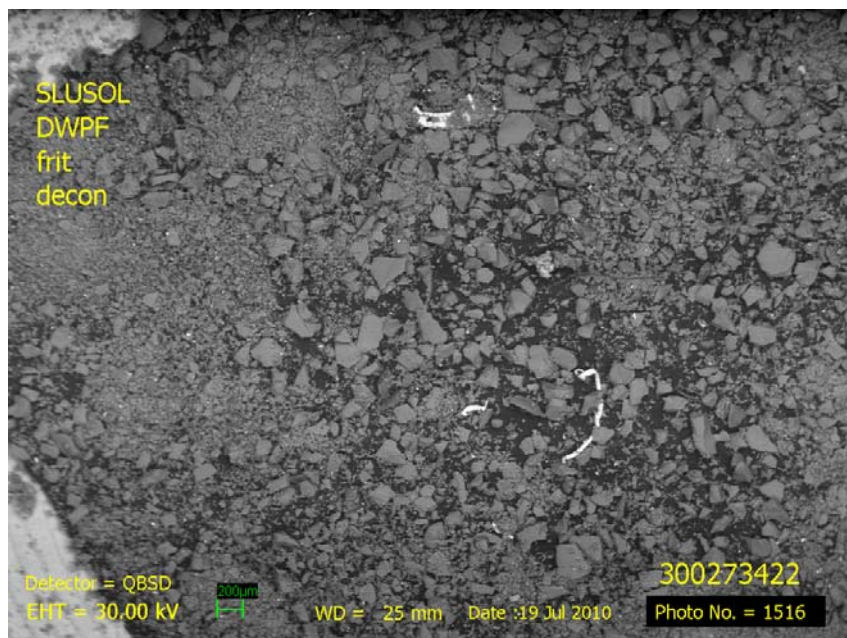


Figure 7. SEM Photo of Slurry Solids (17x).

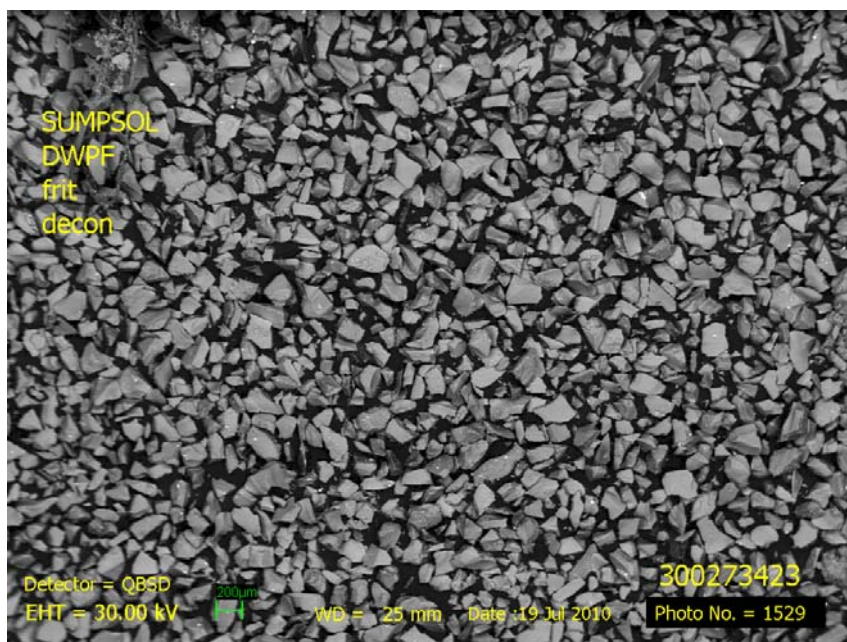


Figure 8. SEM Photo of Sump Solids (17x).

Although the SEM and PSD data provide some insight into the presence of fines in the slurry samples which could have lead to the increased concentrations of the four frit components, the results do not directly answer the question of dissolution versus carry-through. To provide more definitive insight, a composited supernate sample was filtered through a 0.45 micron filter and the filtrate was submitted to AD for ICP-AES analysis. There were no visible solids on the filter paper. Table 3 summarizes the ICP-AES results of the filtered supernate sample. Note the elements are divided into two groups based on those inorganic species reported in Revision 4 (Table 3a) and those not (Table 3b).

The results indicate that enhanced concentrations of B, Si, Na, and Li are present after filtration. This suggests that dissolution of Frit 418 is occurring into the aqueous fraction of the frit decon process. As reported in Section 2.2.1, the pH of the liquid slurry samples was measured to be 9 (also reported in Table 6 of Section 3.3). The increase in pH is consistent with the glass dissolution mechanism as ion exchange between the aqueous phase and the frit drives Na<sup>+</sup> and Li<sup>+</sup> into solution increasing the pH. As the pH increases there is more attack on the Si-O-Si bonds (the glass's structural back-bone) in the frit which enhances the dissolution. For comparison, when a DWPF glass is tested for durability (as defined by the Product Consistency Test), crushed glass (100 to 200 mesh) is placed in a fixed amount of deionized water (initial pH of ~ 6.8) and heated to 90°C. After the 7-day test, the pH of the solution is typically on the order of 10 – 11. The increased concentrations of B, Si, Li, and Na in the supernate samples is consistent with this phenomena – especially if there are fines with high surface area available for reaction, a limited (and static) aqueous media, and time.

**Table 3a. Elemental (as specified in Revision 4) Results (in mg/L) of the Filtered Supernate Sample. (All analytes measured by ICP-AES)**

	<b>Filtered Supernate</b>
<b>Elemental</b>	<b>(mg/L)</b>
Ag	< 0.0428
Al	< 0.188
B	16.7
Ba	< 0.0236
Be	< 0.014
Cd	< 0.0256
Cr	< 0.0278
Cu	< 0.0494
Fe	0.0924
Mn	< 0.044
Ni	< 0.186
Pb	< 0.146
Sb	< 0.208
Zn	0.195

**Table 3b. Elemental (not specified in Revision 4) Results (in mg/L) of the Filtered Supernate Sample. (All analytes measured by ICP-AES)**

	<b>Filtered Supernate</b>
<b>Elemental</b>	<b>(mg/L)</b>
Ca	0.154
Ce	< 0.353
Co	< 0.0592
Gd	< 0.0424
K	< 0.698
La	< 0.0432
Li	19.4
Mg	0.203
Mo	< 0.0854
Na	45.2
P	< 0.674
S	< 2
Si	119
Sn	< 0.172
Sr	< 0.016
Th	< 0.472
Ti	< 0.022
U	< 0.889
V	< 0.024
Zr	< 0.0356

### 3.2 Radionuclide Results

Table 4 summarizes radionuclide results from the supernate samples. The reported values are averages from quadruplicate analysis (i.e., SUP-1, SUP-2, SUP-3, and SUP-4). Also shown in Table 4 are the ETP WAC limits as reported in Revision 4 by Martin (2009). All of the reported radionuclide values meet the WAC limits.

**Table 4. Radionuclide Results for the Supernate and WAC Acceptance Criteria (dpm/mL).<sup>a</sup>**

<b>Radionuclide</b>	<b>Supernate Average - AD Analytical Results</b>	<b>WWCT Feed Acceptance Limits</b>
Alpha	< 9.15E+00	1.00E+02
Nonvolatile Beta (Beta/Gamma)	1.43E+02	2.50E+03
H-3	< 5.99E+00	1.20E+05
C-14 <sup>b</sup>	NA	1.91E+03
Ni-63	< 7.77E+00	1.91E+03
Co-60	< 1.42E-01	1.30E+01
Sr-90	4.57E+01	1.76E+02
Tc-99	< 1.25E+00	2.50E+03
Ru-106	< 3.29E-01	7.92E+02
Sb-125	< 3.73E-01	4.32E+02
Sn-126	< 3.29E-01	9.38E+01
I-129	< 6.56E-02	1.00E+00
Cs-137	1.80E+01	3.28E+02
Eu-154	< 2.43E-01	2.50E+01
U-233	< 2.14E+00	6.60E+01
U-235	4.80E-04	6.09E-01
Pu-241	< 6.41E+00	2.64E+02
RCG <sup>c</sup>	4.79E-04	7.69E-03

<sup>a</sup> For the radionuclide concentrations that were reported by AD as a less than (“<”) value (or detection limit), the value reported in Table 4 is the highest detection limit of the four supernate replicates. This provides a conservative value for each radionuclide when making comparisons to the WTP WAC limits.

<sup>b</sup> C-14 was not analyzed for in the supernate samples based on customer request (see WSRC-NB-99-00002, page 44 for more information).

<sup>c</sup> RCG = (0.000102 [Co-60] + 0.00000875 [Ru-106] + 0.0000178 [Sb-125] + 0.0000324 [Cs-137] + 0.0000508 [Eu-154] + 0.0000819 [Sn-126]) (concentration in dpm/mL). For those radionuclides which were reported as “<” values, the highest detection limit was used in the RCG calculation to provide a conservative number.

As with the inorganic species, additional radionuclide results were reported by AD that were not listed in Revision 4 of the ETP WAC. Table 5 summarizes those radionuclides and their measured values.

**Table 5. Additional Radionuclides Reported by AD but Not Listed in ETP WAC Revision 4.**

<b>Radionuclide</b>	<b>Supernate Average</b>
	<b>AD Analytical Results (dpm/mL)</b>
Pu-238	< 3.85E-01
Pu-239/240	< 7.97E-01
K-40	1.49E+01

### 3.3 Organic Species

Table 6 summarizes the results of the supernate organic analyses. Again the results are averaged values from the quadruplicate supernate samples (i.e., SUP-1, SUP-2, SUP-3, and SUP-4). AD reported most of the VOA and SVOA results under an overarching category (i.e., VOA and SVOA were reported as “not detected” and a detection limit was provided). The reported detection limits for VOA and SVOA were 0.5 and 1.0 mg/L, respectively. Although the VOA and SVOA analysis may have encompassed more analytes than shown in Table 6, those called out in Revision 4 are summarized under the appropriate category (VOA or SVOA).

All of the organic species measured in the supernates meet the Revision 4 WAC criteria. It should be pointed out that although the tetraphenylborate (TPB) concentration (or detection limit of 5 mg/L) is listed in Table 6, the ETP WAC indicates that:<sup>a</sup> “Tetraphenylborate (TPB) is a constituent in the Saltstone WAC. Since TPB usage was restricted to Tanks 48, 49, and 50, TPB cannot be present in ETP influent because these tanks are either isolated or have been cleaned of TPB. If TPB is believed present in the waste stream, a deviation will be required prior to disposal at ETP.”

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<sup>a</sup> In Revision 4 of the ETP WAC, the reader is referred to Section 5.2.1.c for a discussion on TPB. The following quotation is from that section.

**Table 6. Organic Results for the Supernate as Compared to Revision 4 ETP WAC Acceptance Values.**

Constituent/Property	Supernate Average (mg/L)	WWCT Feed Acceptance Limits (mg/L)
VOA (all analytes)	< 5.00E-01	
Benzene	< 5.00E-01	3.79E+02
Toluene	< 5.00E-01	3.85E+02
Trichloroethylene (TCE)	< 5.00E-01	2.63E+00
Tetrachloroethylene (PCE)	< 5.00E-01	1.92E+00
SVOA (all analytes)	< 1.00E+00	
Phenol	< 1.00E+01	3.85E+02
PCBs (all analytes)	< 9.04E-01	9.04E-01
Tetraphenylborate (TPB)	< 5.00E+00	See footnote <sup>a</sup>
TOC	< 1.25E+00	3.85E+02
pH	9	1 – 12.5

#### 4.0 Conclusions/Recommendation

The analytical data from the decon frit supernate indicate that all of the radionuclide, organic, and inorganic concentrations meet the limits in Revision 4 of the ETP WAC with the exception of boron. The ETP WAC limit for boron is 15.0 mg/mL while the average measured concentration (based on quadruplicate analysis) was 15.5 mg/mL. The measured concentrations of Li, Na, and Si were also relatively high in the supernate analysis. These results are consistent with the relatively high measured value of B given the compositional make-up of Frit 418.

Given these results, it was speculated that either (a) Frit 418 was dissolving into the supernate or aqueous fraction and/or (b) fine frit particulates were carried forward to the analytical instrument based on the sampling procedure used (i.e., the supernate samples were not filtered – only settled with the liquid fraction being transferred with a pipette). To address this issue, a filtered supernate sample (using a 0.45 um filter) was prepared and submitted for analysis. The results of the filtered sample were consistent with “unfiltered or settled” sample – relatively high values of B, Li, Na, and Si were found. This suggests that Frit 418 is dissolving in the liquid phase which could be enhanced by the high surface area of the frit fines or particulates in suspension and/or increased temperatures.

Based on the results of this study, it is recommended that DWPF re-evaluate the technical basis for the B WAC limit (the only component that exceeds the ETP WAC limit from the supernate analyses) or assess if a waiver or exception can be obtained for exceeding this limit. Given the possible dissolution of B, Li, Na, and Si into the supernate (due to dissolution of frit), DWPF may need to assess if ETP WAC limits for these components need to be defined. It should be noted

<sup>a</sup> In Revision 4 of the ETP WAC, the reader is referred to Section 5.2.1.c for a discussion on TPB.

that the results of this study may not be representative of future decon frit solutions or sump/slurry solids samples. Therefore, future DWPF decisions regarding the possible disposal pathways for either the aqueous or solid portions of the Decon Frit system need to factor in the potential differences. More specifically, introduction of a different frit or changes to other DWPF flowsheet unit operations (e.g., different sludge batch or coupling with other process streams) may impact not only the results but also the conclusions regarding acceptability with respect to the ETF WAC limits.

## **5.0 Future Work**

SRNL will document the chemical and physical results of the slurry and sump solids in a separate report, which were also part of the scope of the technical request.

DWPF should ensure representative Decon Frit samples are taken for characterization (as DWPF continues processing) to support future decisions regarding disposal options.

## **6.0 References**

**Crawford, CL and DK Peeler. 2010.** Task Technical and Quality Assurance Plan for DWPF Water Separation from Decon Frit: Analysis of Spent Decon Frit Slurry Sample, SRNL-RP-2010-00497, Revision 1, Savannah River National Laboratory, Aiken, South Carolina.

**Hutsell. 2010.** DWPF Water Separation from Decon Frit: Analysis of Spent Decon Frit Slurry Sample, DJ Hutsell and JM Bricker, HLW-DWPF-TTR-2010-0005, Revision 0, January 2010.

**Martin. 2009.** F/H Effluent Treatment Project Waste Acceptance Criteria, DJ Martin, Effluent Treatment Project Engineering, X-SD-H-0009, Revision 4, Effective Date: April 2, 2009.



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