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## **Tank 30 and 37 Supernatant Sample Cross-check and Evaporator Feed Qualification Analysis -2012**

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## EXECUTIVE SUMMARY

This report summarizes the analytical data reported by the F/H and Savannah River National Laboratories for the 2012 cross-check analysis for high level waste supernatant liquid samples from SRS Tanks 30 and 37. The intent of this Tank 30 and 37 sample analyses was to perform cross-checks against routine F/H Laboratory analyses (corrosion and evaporator feed qualification programs) using samples collected at the same time from both tanks as well as split samples from the tanks.

Of the eight Tank 30 and 37 samples pulled, two were pulled at the surface of each tank and two others were variable depth samples (Tank 30 pulled from 218 inches and Tank 37 pulled from 340 inches) from each tank. Four of these samples were delivered to SRNL and the other four samples were delivered to F/H Laboratory for characterization and eventual compilation of the data to compare and identify inconsistencies in the analytical results for routine high level waste tank supernate characterization by the two laboratories. These Tanks 30 and 37 samples sent to each laboratory constitute two sets of data; one set from each laboratory. A third set of data, derived from splitting the SRNL sample set into nearly two nearly equal parts, was sent to F/H Laboratory. In all, three sets of Tanks 30 and 37 supernatant liquid samples were analyzed by both laboratories (One half split-sample set from SRNL and two sets from F/H Laboratory) for this cross-check evaluation.

In these analyses, a 20 percent relative deviation was used as the benchmark for measuring the relative difference between the laboratory results for the same component analysis by the two laboratories. Data for the same component analysis from the two laboratories which differed by more than 20 percent relative deviation was considered as not comparable or not in agreement.

In general, the two laboratories were able to produce analytical results for the following components: free-OH, nitrate, nitrite, oxalate, cesium-137, and specific gravity, which were fairly comparable if not considered identical in magnitude in most cases. Unlike in previous cross-check evaluations (2008) the free-OH concentrations obtained at two different acid titration concentrations (0.1 N and 0.01 N acid titrants) by the two laboratories were quite comparable 88% of the time the analyses was performed. The percent relative deviation between the analytical results of the two laboratories for free-OH averaged less than 20%.

On the other hand, the analytical results from both laboratories for carbonates, silicon, sulfate, chloride and phosphates in all three sets of Tank 30 and 37 results from the two laboratories were greater than the 20 percent relative deviation benchmark and methods/analytical techniques will need to be evaluated further by both laboratories to determine the cause of such significant differences in analytical results between the two laboratories. The high sodium concentrations in the original Tanks 30 and 37 samples (averaging 15M) means that a significant dilution of the original sample is required to minimize the impact of high alkali content on analytical instruments performance (for example ICP-ES plasma and IC performance). These large dilutions of the original samples lead to anion and cation concentrations (sulfate, phosphate, silicon and chloride) which are too close to instrument detection limits for these analytes and thus introduce significant errors in measurements.

The inability of the two laboratories to get good agreement in the analyses for carbonate may not only be attributable to dilution effects and the use of different analytical methods, as described, but also to the fact that it is difficult to get reliable analytical values for low carbonate samples in the presence of 15 M sodium hydroxide.

This along with heating of Tanks 30 and 37 samples by F/H Laboratory to match the tank temperatures prior to sampling for analyses may lead to different analytical results when compared to the SRNL-AD results for these components of Tanks 30 and 37. SRNL-AD did not heat the samples. However, it is worth noting that the SRNL-AD reagent or matrix blanks and cell blanks for silicon were high. So, there may be some silicon contamination issues which SRNL-AD need to address.

The large measures of relative differences between the two laboratory results for these anions and cations were also observed in some of the 2008 cross-check measurements.

Based on discussions with the liquid waste customer, none of these results present a significant concern in the current measurement of process samples or the Tank Farm. The measurement of carbonate and anions such as sulfate, phosphate, and chlorides are performed to evaluate impacts in the ionic strength of the samples. If the carbonate and other anions are low, their impact on the ionic strength would be negligible. Also, while silicon is low for these samples, typical measurements at SRNL are performed on the 2H evaporator tanks, which have higher concentration of silicon, which minimizes the impact of the silicon in the blank.

Recommendation to enhance the goals of cross-check comparisons between the two laboratories includes the following:

- Both laboratories (SRNL-AD and F/H laboratories) should work on method improvements to enhance analyzes for both silicon and carbonate at low concentrations.
- Although it is non-routine for SRNL-AD group to heat tank samples to specific tank temperature prior to analysis for cations and anions, it will be useful for the sake of these types of comparative analyses between the two laboratories for SRNL-AD to heat the samples to the same temperature that F/H laboratory treats the samples prior to analysis. This temperature treatment will eliminate the problems associated with changes in sample density, precipitation and uneven sample pipetting and deliveries
- If possible, both laboratories should employ the same analytical methods in all these analyses.

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## LIST OF ABBREVIATIONS

AD	Analytical Development
CC	Corrosion Control
CC/ EFQ	Corrosion Control/Evaporator Feed Qualification
EFQ	Evaporator Feed Qualification
ICP-ES	Inductively Coupled Plasma–Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma–Mass Spectroscopy
LIMS	Laboratory Information Management System
LWO	Liquid Waste Operations
MDA	Minimum Detectable Activity: Minimum detectable activity is the value above which instrument signal can be considered real.
SpG	Specific Gravity
SRNL-AD	Savannah River National Laboratory-Analytical Development
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC/TOC	Total inorganic carbon/Total organic carbon
TTQAP	Task Technical Quality Assurance Plan
TTR	Technical Task Request
VDS	Variable Depth Sample



## 1.0 Introduction

Liquid Waste Processing Engineering personnel requested cross-check analyses of F/H Laboratory sample results for Tank 30 and 37 supernate samples. The intent of this analysis was to compare the analysis results from both SRNL and F/H Laboratories for given tank farm sample components as specified by SRR. These characterizations by both laboratories also includes analyses for evaporator feed qualification. Overall, this task examined Evaporator Feed Qualification (EFQ) and Corrosion Control (CC) parameters of surface and variable depth samples (VDS) pulled from Tanks 30 and 37.

A total of eight samples were pulled from Tanks 30 and 37. Of these samples, two were pulled at the surface of each tank and two others were VDS from each tank. Four of these samples were delivered to SRNL and the other four samples were delivered to F/H Laboratories as summarized in Table 1 below.

**Table 1 Tanks 30 and 37 supernate samples pulled and delivered to the two laboratories.**

Sample ID	Sampling location	Sample Destination	Analyses category
HTF-30-12-1	surface	F/H	CC/EFQ
HTF-30-12-2	218 inches	F/H	EFQ
HTF-37-12-4	surface	F/H	CC/EFQ
HTF-37-12-5	340 inches	F/H	EFQ
HTF-30-12-6	surface	SRNL	CC/EFQ
HTF-30-12-7	218 inches	SRNL	EFQ
HTF-37-12-8	surface	SRNL	CC/EFQ
HTF-37-12-9	340 inches	SRNL	EFQ

where:

CC/EFQ = SpG, nitrate, nitrite, free hydroxide, total gamma (from Cs-137), sulfate, phosphate, oxalate, carbonate, sodium, aluminum, silicon

EFQ = SpG, free hydroxide, sulfate, phosphate, oxalate, carbonate, sodium, aluminum, silicon.

In this report an attempt has been made to compare and identify inconsistencies in the analytical results for routine high level waste tank supernate characterization by the two laboratories. Samples from these two tanks were analyzed in accordance with Technical Task Request (TTR)<sup>1</sup> and the Task Technical and Quality Assurance Plan (TTQAP<sup>2</sup>).

## 2.0 Sample Preparation for Analysis

After opening the four samples assigned to SRNL (HTF-30-12-6, HTF-30-12-7, HTF-37-12-8, HTF-37-12-9), SRNL and F/H Laboratory personnel visually examined the four samples for the existence of solid particles and clarity. The supernate samples seemed fairly clear although with some cloudiness. There were no visible solid particles. However, during transfer of one of the samples from the original steel container (HTF-37-12-8) to a clear poly-methyl pentane secondary container for visual observation with the use of small plastic funnel a small piece of solid salt cake was seen lodged in the funnel vertical transfer duct. This particular sample was then decanted to remove the small salt cake. In accordance with cross-check analyses recommendations from the 2008 cross-check comparisons<sup>3</sup> one half of the split sample unit in labeled stainless steel sample holders was sent to F/H Laboratory for characterization, while SRNL analyzed the other half of the sample set with original sample labels (HTF-30-12-6, HTF-

30-12-7, HTF-37-12-8, HTF-37-12-9). The portion of the four samples sent to F/H Laboratory were sent in labeled 80-mL capacity stainless steel sample holders (HTF-30-12-6-F/H, HTF-30-12-7-F/H, HTF-37-12-8-F/H and HTF-37-12-9-F/H).

In these cross-check analyses, both F/H and SRNL laboratories were required to perform separate sample preparations (duplicate sample preparations) and not rely merely on duplicate measurements of the same sample. F/H Laboratory performed their analyses as usual, meaning, bringing the sample temperature to a given temperature of the tank under consideration. SRNL was not required to heat the sample to mimic F/H procedures, but was required to document shielded cell temperatures during sample preparations as mentioned above. Titration of the samples for free-OH was based on 0.1 M HCL titrant for SRNL and 0.01 M HCL titrant for F/H Laboratory. Both laboratories analyzed for silicon via warm acid strike followed by ICP-ES analysis for silicon. With the exception of F/H Laboratory analyses results for the un-split Tank 30 and 37 samples, all samples were analyzed and reported in duplicate by both laboratories. These Tank 30 and Tank 37 samples respectively, surface samples HTF-30-12-1 and HTF-37-12-4 and variable depth samples (HTF-30-12-2 and HTF-37-12-5) were analyzed by F/H Laboratory only once for each analyte.

Components analyzed for in these supernate samples included free-OH<sup>-1</sup>, NO<sub>2</sub><sup>-1</sup>, NO<sub>3</sub><sup>-1</sup>, SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>, C<sub>2</sub>O<sub>4</sub><sup>-2</sup>, PO<sub>4</sub><sup>-3</sup>, Al, Si, Na, total gamma, and specific gravity.

The SRNL sample sets were prepared in the shielded cell and submitted to SRNL Analytical Development (AD) for the required analyses. The sample preparation, which involved a target sample dilution factor by volume of  $25 \pm 1$  of Tank 30H and 37H supernatant liqueurs with deionized water, were accomplished in the SRNL shielded cells prior to submittal to the SRNL Analytical Development for the required analyses. The shielded cell temperature reading during the initial opening of the sample was 19 °C. During the entire samples processing (Sample opening, decanting, 50/50 partitioning of the samples to be delivered to F/H Laboratory and diluting of samples to take out of the cell) five cell temperature measurements were taken and these ranged from 19.0 °C to 22.2 °C with an average of  $20.2 \pm 1.3$  °C.

Analytical methods employed in these characterizations include atomic absorption (AA) for Na analysis and inductively coupled plasma-emission spectroscopy (ICP-ES) for Si (warm acid strike before ICP-ES) and Al. AD used ion chromatography (IC) to measure several of the anions (NO<sub>2</sub><sup>-1</sup>, NO<sub>3</sub><sup>-1</sup>, SO<sub>4</sub><sup>-2</sup>, C<sub>2</sub>O<sub>4</sub><sup>-2</sup> and PO<sub>4</sub><sup>-3</sup>). A titration method was used for free hydroxide and carbonate analysis. SRNL-AD analyzed for carbonate by total inorganic carbon while F/H Laboratory analyzed for carbonate by titration method.

For this peer reviewed technical report, two sets of Tank 30 and 37 sample characterization data were obtained from F/H Laboratory. The first set from F/H Laboratory was the split Tanks 30 and 37 sample portions [HTF-30-12-6-F/H, HTF-30-12-7-F/H, HTF-37-12-8-F/H and HTF-37-12-9-F/H] provided by SRNL for analyses and the second set were original Tank 30 and 37 samples [HTF-30-12-1, HTF-30-12-2, HTF-37-12-4 and HTF-37-12-5] directly assigned to F/H Laboratory by SRR for characterization. The third sample set, which is part of the split sample from Tanks 30 and 37, were prepared and characterized by SRNL. The cross-check analytical data comparison between the two laboratories are therefore based on component analyses results from these three sets of Tank 30 and 37 samples described above.

### 3.0 Results of Analyses of Tanks 30 and 37 Supernatant Samples

The intent of this Tank 30 and 37 characterizations was to perform cross-checks against routine F/H Laboratory analyses (corrosion and evaporator feed qualification programs) using samples collected at the same time from both tanks as well as split samples from the tanks. An attempt has been made to compare and identify inconsistencies in the analytical results for routine high level waste tank supernate characterization by F/H and SRNL laboratories.

The Tanks 30 and 37 samples (as-received) were almost clear supernatant liqueurs as expected. A visual inspection of the samples showed that each sample was a cloudy solution with no visible suspended fine particles. Components/parameters analyzed for in these Tank 30 and 37 supernatant samples included free  $\text{OH}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ , Al, Si, Na, total gamma scan for Cs-137, and specific gravity.

In all, three sets of Tank 30 and 37 component analytical results from both laboratories have been compiled and compared; two sets of Tank 30 and 37 analytical data from F/H Laboratory and one set from SRNL.

With the exception of one set of F/H Laboratory analyses for Tanks 30 and 37, all analytical results were performed by the two laboratories in duplicate. Silicon and free-OH analysis were performed in triplicate and in the case of free-OH acid titrations were performed at two acid concentrations levels, 0.1 and 0.01 M, by SRNL and F/H Laboratory, respectively. In cases where one or both of the results are below the limit of detection no standard deviation is given. For species where the concentration fell below the lower limit of detection the reported lower limit of detection is preceded by “<”.

In this report, analyses results from both laboratories for a component is flagged when the percent relative deviation, a measure of the relative difference between the laboratory results for the same component analysis, is more than 20%.

The pH results presented in the tables were calculated from the average free- $\text{OH}^-$  concentrations based on the 0.1 and 0.01 M acid titrations for the two tank samples using the following equation:

$$\text{pH} = 14 + \log_{10}(\text{OH}^-)$$

#### 3.1 Analytical Result Presentation

The average analytical results reported by the two laboratories for all the analytes of interest are presented in Tables 2 through Table 5, respectively, for Tank 30 surface and variable depth samples, Tank 37 surface and variable depth samples, Tank 30 split sample (surface and variable depth) and Tank 37 split sample (surface and variable depth). Each table also contains the calculated percent relative deviations (%RD) for the corresponding surface and variable depth samples data information from both laboratories.

Replicate data are presented in Appendices A and B. Appendix C contains the SRNL Analytical Development Tracking numbers (Laboratory Information Management System number) for all Tanks 30 and 37 sample analyses. Blank spaces within the tables followed by a dash are used to indicate those cases where a particular analyte was not measured by a laboratory. The percent relative deviation (%RD) is used as a measure of the relative difference between the laboratory

results for the same analysis. Percent relative deviation was calculated as the difference between the result from two data sets for the same analyte from the two laboratories divided by the mean\*100, as shown below.

$$((A-B)/(A+B)/2)*100.$$

Where: A and B represent magnitude of analysis result for the same analyte by the two laboratories.

For the purpose of this evaluation and comparison, a % relative deviation of 20% was chosen as the criterion for determining if the results from the two laboratories were considered comparable or in agreement. Percent relative deviations values were not calculated for analytical results below detection limits. Percent relative deviations values less than or equal to 20% indicate the analytical data from the two laboratories or replicates are considered to be in reasonable agreement.

### 3.2 Tank 30 and 37 Sample Comparisons: Surface and Variable Depth Samples Acquired at the Same Time.

As described earlier and presented in Table 1, two surface and two variable depth samples from Tanks 30 and 37 (218 and 340 inches, respectively) were collected and delivered to both laboratories for characterization for given analytes as shown in Tables 2 and 3. Since these samples were pulled at the same time and from the same tank levels, one would expect the concentration of the analytes from both laboratories to be same using the similar analytical techniques.

However, based on the average values summarized in Table 2 for the surface and variable depth samples from Tank 30, the percent relative deviations (%RD) calculated from the analytical result data presented by the two laboratories shows that the results are not comparable for a few of the analytes. In other words, the 20 %RD evaluation criterion was not met in component analytical results by the two laboratories for aluminum, sulfate, carbonate, sodium and silicon ions. For the Tank 30 surface sample, the percent relative deviations between the two laboratory analytical results for these analytes (aluminum, sulfate, carbonate, sodium and silicon ions) varied from 39% to 74%. In the variable depth Tank 30 samples these %RD values for aluminum, sulfate, carbonate, sodium and silicon ions varied from 31% to 107%. These percent relative deviations are all well above the 20 %RD criterion.

Free-OH concentration measurements by the two laboratories were comparable in almost all the analyses results for this analyte. Analysis result for free-OH in the variable Tank 30 sample by the two laboratories, at 29% percent relative deviation, was the only instance when the percent relative deviation was outside the 20 % bench mark for free-OH analyses by the two laboratories.

The analytical results presented by the two laboratories for Tank 30 surface samples for specific gravity, nitrite, nitrate, free-OH and cesium-137 concentration are all less than 15 %RD and thus are considered comparable. Tank 30 surface sample result for phosphate by the two laboratories at 19.1 %RD is just on the border line in terms of meeting the 20% RD criterion for acceptability.

F/H Laboratory did not analyze for chloride in the Tank 30 surface and variable samples and also did not analyze for nitrate, nitrite, and cesium-137 in the variable depth Tank 30 samples. The percent relative deviation for specific gravity and phosphate analyses for the Tank 30 variable depth samples components by the two laboratories are considered comparable at percent relative deviations of 0.43 and 9.88, respectively.

Overall, the two laboratories failed to obtain comparable analytical results in the analyses for anion (sulfate, carbonate) and cations (aluminum, sodium and silicon) in both surface and variable depth samples from Tank 30.

In Tank 37 surface and variable depth analyses results for the components presented in Table 3, both laboratories met the expected analytical results for specific gravity, aluminum, phosphate and free-OH concentrations. The %RD for these analytes averaged below 10%. The Tank 37 surface sample analyses results for sodium was just below the criteria for acceptability at 19.4 %RD. Nitrite ion concentrations measured by both laboratories in the Tank 37 surface sample at 21.9%RD were just above the acceptability requirement.

Tank 37 surface and variable depth sample analyses result by both laboratories for carbonate and silicon were not comparable at all. The percent relative deviation calculated from data provided from both laboratories for both variable and surface samples for carbonate averaged above 118 %, while that for silicon averaged above 50%. Thus, analysis results for these two anions by both laboratories failed the 20 %RD criterion for acceptability. Sodium analyses in the variable depth Tank 37 sample by these two laboratories are not also comparable at 25.9 %RD.

F/H Laboratory did not analyze for chloride in both Tank 37 variable depth and surface samples. F/H Laboratory did not also analyze for nitrate, nitrites and cesium-137 in the Tank 37 variable depth sample.

### 3.3 Tank 30 and 37 Sample Comparisons: Split Surface and Variable Depth Samples

The Tank 30 and 37 samples (both surface and variable depth sample) sent to SRNL was split into two nearly equal portions and one half of each split sample unit was sent to F/H Laboratory for characterization, while SRNL analyzed the other halves. As noted in the experimental section, one of the SRNL samples which was split into two equal portions contained visible solid saltcake (Sample HTF-37-12-8). Everything being equal, one would expect the concentration of the analytes from both laboratories to be equivalent.

Characterization results from the two laboratories for Tank 30 split samples (surface and variable depth) for specific gravity, nitrate, nitrite, aluminum, sodium and free-OH are comparable because the calculated percent relative deviation between the results from the two laboratories do not differ by more than 20%; see Table 4. Analyses results for sulfate, silicon and chloride for both surface and variable depth Tank 30 split samples from both laboratories differ by more than 20% and are 54.3% (surface sulfate), 75.3% (VDS sulfate), 63.4% (surface silicon), and 96.2% VDS silicon). The analyses results by the two laboratories for Tank 30 split sample, for carbonate in the surface sample were comparable because the %RD was just under 10% at 9.35%. However, the variable depth analyses result by the two laboratories for the Tank 30 split sample for carbonate anion did not compare favorably because the %RD was 45.8%. Phosphate analyses results for split Tank 30 samples at percent relative deviations of 32% for the surface sample and 36.4% for the variable depth sample do not compare favorably between the two laboratories.

F/H Laboratory did not analyze for cesium-137 in the Tank 30 split variable depth sample. However, F/H Laboratory analyses result for cesium-137 in the Tank 30 split surface sample is comparable with the corresponding analyses result by SRNL at %RD of 1.13%.

Table 5 contains the Tank 37 split samples average analytical results from the two laboratories. Analytical results for Tank 37 split samples (surface and variable depth) from the two laboratories

differ by less than 20% for the following measurements specific gravity, nitrate, nitrite, sodium and free-OH. Hence, these analytical results for the laboratories are comparable. Aluminum analyses in the surface samples by both laboratories have a 20.2%RD, which makes it a borderline case in terms of being comparable. However, both the surface and variable depth analyses results from the two laboratories on carbonate, phosphate, silicon and chloride differ by > 20%RD, and thus are not comparable. F/H Laboratory did not analyze for cesium-137 in the Tank 37 split variable depth sample. However, F/H Laboratory analyses result for cesium-137 in the Tank 37 split surface sample is comparable with the corresponding analyses result by SRNL at %RD of 3.92%.

Again in this split Tank 37 sample, mostly the anions (carbonate, phosphate and chloride) and silicon were not comparable in the analytical results presented by the two laboratories.

### 3.4 Overall Analysis Performance comparison for the Analytes by the two Laboratories.

Table 6 shows a summary of the number of times, in percent, a given analyte analyzed by both laboratories failed to meet the minimum 20 %RD difference criterion between the two laboratory results for that analyte.

With the analysis result for free-OH in Tank 30 variable depth samples and for nitrite in Tank 37 surface samples being the exceptions, the analyses by both laboratories for specific gravity, free-OH, nitrate, nitrite, cesium 137, and possible oxalate anion all met the 20 %RD difference criterion. This means that the analytical data from the two laboratories (SRNL and F/H) are considered to be in a reasonable agreement. It should be noted that these samples were fairly high in hydroxide, which may have enabled easier measurements than previous cross-check characterizations. Free-OH analyses result by both laboratories for variable depth Tank 30 samples has a %RD of 28.6, while nitrite analyses in Tank 37 surface samples has a %RD of 21.9. These %RD for free-OH and nitrite are above the 20% RD benchmark. Since the analyses result for oxalate ion by both laboratories are all less than values the assumption here is that the 20 % RD criterion was met.

In general, species at higher concentrations (0.1 M or higher) compared fairly well between the labs on split samples from SRNL. This may indicate that some of the measurement issues may be related to either sampling, solids in the sample or sample preparation.

The high sodium concentration in the original Tanks 30 and 37 samples (averaging 15M) means that a significant dilution of the original sample to minimize the impact of high alkali content on analytical instruments performance (for example ICP-ES plasma and IC performance) is required. In the case of silicon for example, the required dilution leads to a Na/Si ratio in the order of 8500:1 on mg/L basis. This large dilution of the original samples leads to anion and cation concentrations (sulfate, phosphate, silicon and chloride) which fall close to instrument detection limits for certain analytes and thus impacts biases in measurements. Fifty percent of the time the comparative analyses result for both sulfate and phosphate anions met the 20 %RD criterion when they were analyzed by both laboratories.

In the case where elements were measured at higher concentrations for similar instrumentation (sodium or nitrate) on split samples, the results tended to be more comparable.

However, it is worth noting that the SRNL-AD reagent or matrix blanks and cell blanks for silicon had a measureable bias at 8.52 and 10.3 mg/L silicon, respectively. This is likely the reason for the discrepancy in silicon measurements between the two laboratories. However, the

silicon concentration in these samples was fairly low compared to concentrations that would initiate formation of sodium aluminum silicate solids. This bias at this time would have minimal impact at these concentrations. However, these contamination issues should be reviewed to minimize or eliminate trace silicon.

Carbonate analyses results failed in all cases but in the Tank 30 surface sample split. In some instances, as in the case with carbonate anion, the analysis difference was sometimes even greater than 100%. It is worth noting that SRNL analyzed for carbonate and silicon eight different times, while F/H Laboratories analyzed for these components six and eight times, respectively. The laboratories used different methods to analyze for carbonate. In F/H Laboratory, carbonate was measured by precipitation of carbonate followed by titration. With the high concentration of hydroxide in these samples, washing of the residual solids may not have been sufficient. With the lower concentration of carbonate in these samples, residual hydroxide would potentially bias the titration measurements. However, carbonate and most of the other low concentration anions are primarily measured in the Tank Farm to determine the impact of ionic strength. In each of these cases, the low concentration of the anion will have a negligible impact on the ionic strength.

#### 4.0 Conclusions and Recommendations

In these Tanks 30 and 37 cross-check sample characterizations, results from both laboratories for components were flagged when the percent relative deviation, a measure of the relative difference between the laboratory results for the same component analysis, was more than 20%. In general, the two laboratories were able to produce analytical results for the following components free-OH, nitrate, nitrite, oxalate cesium-137 and specific gravity, which were fairly comparable if not considered identical in magnitude in most cases. Unlike in previous cross-check evaluations (2008)<sup>3</sup> the free-OH concentrations obtained at two different acid titration concentrations (0.1 N and 0.01 N acid titrants) by the two laboratories were quite comparable in about 88% of the time the analyses was performed. The percent relative deviation between the analyses results of the two laboratories for free-OH averaged less than 20%.

On the other hand, the analytical results from both laboratories for carbonates, silicon, sulfate, chloride and phosphates in all three sets of data from the two laboratories fall outside of the 20 percent relative deviation benchmark and can be evaluated further by both laboratories to determine the root cause of such significant differences in analytical results between the two laboratories.

Evaluation of the analytical results from the split sample set also showed that analysis for sulfate, silicon, chloride, carbonates and phosphates from both laboratories were not comparable. For example, in the split Tank 30 samples the percent relative deviations for sulfate, silicon and chloride averaged greater than 65, 80, and 27 %, respectively.. Similarly, for the split Tank 37 samples the percent relative deviations between the two laboratories in the analysis for carbonate, phosphate, silicon and chloride averaged greater than 30, 37, 59, and 42%, respectively. This is likely the result of a significant dilution to levels close to the detection limits for most of these species and low level silicon contamination in the sample preparation.

The inability of the two laboratories to get good agreement in the analyses for carbonate may not only be attributable to dilution effects, as described above, but also to the fact that it is difficult to get reliable analytical values for low carbonate samples in the presence of 15 M hydroxide<sup>a</sup>.

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<sup>a</sup> Both laboratories analyzed for carbonate by two different methods (TIC/TOC by SRNL-AD and titration by F/H Lab).

This along with heating of Tanks 30 and 37 samples by F/H Laboratory to match the tank temperatures prior to sampling for analyses may lead to different analytical results when compared to the SRNL-AD results for these components of Tanks 30 and 37. SRNL-AD did not heat the samples. However, it is worth noting that the SRNL-AD reagent or matrix blanks and cell blanks for silicon were high. So, there may be some silicon contamination issues which need to address by SRNL-AD.

The large measures of relative differences between the two laboratory results for these anions and cations were also observed in some of the 2008 cross-check measurements.

Based on discussions with the liquid waste customer, none of these results present a significant concern in the current measurement of process samples or the Tank Farm. The measurement of carbonate and anions such as sulfate, phosphate, and chlorides are performed to evaluate impacts in the ionic strength of the samples. If the carbonate and other anions are low, their impact on the ionic strength would be negligible. Also, while silicon is low for these samples, typical measurements at SRNL are performed on the 2H evaporator tanks, which have higher concentration of silicon, which minimizes the impact of the silicon in the blank.

Recommendation to enhance the goals of cross-check comparisons between the two laboratories includes the following:

- Both laboratories (SRNL-AD and F/H laboratories) should work on method improvements to enhance analyzes for both silicon and carbonate at low concentrations.
- Although it is non-routine for SRNL-AD group to heat tank samples to specific tank temperature prior to analysis for cations and anions, it will be useful for the sake of these types of comparative analyses between the two laboratories for SRNL-AD to heat the samples to the same temperature that F/H laboratory treats the samples prior to analysis. This temperature treatment will eliminate the problems associated with changes in sample density, precipitation and uneven sample pipetting and deliveries
- If possible, both laboratories should employ the same analytical methods in all these analyses.



Table 2 Cross Check Analysis: Tank 30 Analyses: SRNL and F/H Laboratory Average Result Values Compared-Surface and Variable depth Samples@

SRNL: HTF-30-12-06 and HTF-30-12-07			F/H Lab.: HTF-30-12-01 and HTF-30-12-02				
Analyte	HTF 30-12-06 surface Average	HTF 30-12-07 Variable Depth Average	HTF-30-12-01 surface Average	HTF-30-12-02 Variable Depth Average	%RD Surface	%RD VDS	Units
Specific gravity	1.45	1.46	1.4154	1.4537	2.42	0.43	
pH <sup>+</sup>	14.8	15.0	14.81	14.86	0.0	0.90	
Nitrite, NO <sub>2</sub>	1.93E+00	1.77E+00	2.0061	-	3.81	-	moles/L
Nitrate, NO <sub>3</sub>	1.68E+00	1.28E+00	1.8320	-	8.66	-	moles/L
Aluminum, Al	6.44E-01	7.80E-01	0.4243	0.5195	41.1	40.1	moles/L
Sulfate, SO <sub>4</sub>	6.65E-03	2.888E-03	0.0134	0.0095	67.4	107	moles/L
Carbonate, CO <sub>3</sub>	7.08E-02	4.11E-02	0.1260	0.1238	56.1	100	moles/L
Sodium, Na	1.34E+01	1.47E+01	9.0638	10.7713	38.9	31.1	moles/L
Phosphate PO <sub>4</sub>	7.68E-03	9.69E-03	0.0093	0.0107	19.1	9.9	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	≤2.96E-03	<3.00E-03	<6.84E-03	<6.84E-03			moles/L
Silicon Si	1.52E-03	1.45E-03	7.0E-04	7.0E-04	73.8	69.8	moles/L
Chloride, Cl	1.62E-02	1.78E-02	-	-	-	-	moles/L
Free-OH	6.42	9.63	6.4247	7.2239	0.07	28.6	moles/L
Cs-137	3.57E+09	4.56E+09	3.14E+09	-	12.8		dpm/mL

<sup>+</sup>Based on average [OH]

\*Free-OH @ 0.1 N titrant by SRNL

\*\*Free-OH @ 0.01 N titrant by F/H Lab.

@The following color codes are used for the table contents: Green for highlighted entries for analytes with percent relative deviation greater than 20%, and bold for averages. All subsequent tables have similar color code meanings.

Table 3 Cross Check Analysis: Tank 37 Analyses: SRNL and F/H Laboratory Average Result Values Compared-Surface and Variable depth Samples

SRNL: HTF-37-12-08 and HTF-37-12-09			F/H Lab.: HTF-37-12-04 and HTF-37-12-05				
Analyte	HTF-37-12-08 surface Average	HTF-37-12-09 Variable Depth Average	HTF-37-12-04 surface Average	HTF-37-12-05 Variable Depth Average	%RD Surface	%RD VDS	Units
Specific gravity	1.49	1.51	1.4886	1.4811	0.09	1.93	
pH <sup>+</sup>	15.1	15.1	15.04	15.02	0.20	0.40	
Nitrite, NO <sub>2</sub>	1.42E+00	1.47E+00	1.7724E+00	-	21.9	-	moles/L
Nitrate, NO <sub>3</sub>	1.13E+00	1.24E+00	1.2455E+00	-	9.46	-	moles/L
Aluminum, Al	6.76E-01	6.61E-01	6.156 E-01	6.631E-01	9.35	0.32	moles/L
Sulfate, SO <sub>4</sub>	<2.79E-03	<2.68E-03	<6.3E-03	6.2E-03			moles/L
Carbonate, CO <sub>3</sub>	4.08E-02	3.71E-02	1.608 E-01	1.443 E-01	119	118	moles/L
Sodium, Na	1.61E+01	1.61E+01	13.2644	12.4343	19.4	25.9	moles/L
Phosphate PO <sub>4</sub>	1.37E-02	1.27E-02	1.53E-02	1.41E-02	11.3	10.4	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<3.040E-03	<2.92E-03	<6.86E-03	<6.74E-03			moles/L
Silicon Si	1.33E-03	1.33E-03	7.00E-04	8.00E-04	62.1	49.8	moles/L
Chloride, Cl	2.26E-02	1.70E-02	-	-	-	-	moles/L
Free-OH	11.8*	11.9*	10.9437**	10.4673**	7.28	12.81	moles/L
Cs-137	5.00E+09	5.32E+09	5.45E+09	-	8.61	-	dpm/mL

<sup>+</sup>Based on average [OH]

\*Free-OH @ 0.1 N titrant by SRNL

\*\*Free-OH @ 0.01 N titrant by F/H Lab.

Table 4 Cross Check Analysis: Tank 30 Analyses: SRNL and F/H (SPLIT Sample) Laboratory Results Compared-Surface and Variable depth Samples.

SRNL: HTF-30-12-06 and HTF-30-12-07			F/H Lab.: HTF-30 SPLIT SAMPLE				Units
Analyte	HTF-30-12-06 surface Average	HTF-30-12-07 Variable Depth Average	HTF-30-12-6-F/H surface Average	HTF-30-12-7-F/H Variable Depth Average	%RD Surface	%RD VDS	
Specific gravity	1.45	1.46	1.4591	1.4561	0.63	0.27	
pH	14.8	15.0	14.87	14.96	0.40	0.13	
Nitrite, NO <sub>2</sub>	1.93E+00	1.77E+00	2.1932	2.0576	12.7	15.2	moles/L
Nitrate, NO <sub>3</sub>	1.68E+00	1.28E+00	1.884	1.429	11.2	10.9	moles/L
Aluminum, Al	0.644	0.78	6.037E-01	7.096E-01	6.46	9.45	moles/L
Sulfate, SO <sub>4</sub>	6.65E-03	2.88E-03	1.16E-02	6.35E-03	54.3	75.3	moles/L
Carbonate, CO <sub>3</sub>	7.08E-02	4.11E-02	6.445E-02	6.55E-02	9.35	45.8	moles/L
Sodium, Na	13.44	14.74	12.316	12.714	8.7	14.8	moles/L
Phosphate PO <sub>4</sub>	7.68E-03	9.69E-03	1.06E-02	1.40E-02	32.0	36.4	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	≤2.96E-03	<3.00E-03	<2.81E-03	<2.81E-03			moles/L
Silicon Si	1.52E-03	1.45E-03	7.885E-04	5.085E-04	63.4	96.2	moles/L
Chloride, Cl	1.62E-02	1.78E-02	2.055E-02	2.405E-02	23.9	29.9	moles/L
Free-OH	6.42*	9.63*	7.477**	9.204**	15.2	4.5	moles/L
Cs-137	3.57E+09	4.56E+09	3.53E+09	-	1.13	-	dpm/mL

\*Free-OH @ 0.1 N titrant by SRNL

\*\*Free-OH @ 0.01 N titrant by F/H Lab.

Table 5 Cross Check Analysis: Tank 37 Analyses: SRNL and F/H (SPLIT Sample) Laboratory Results Compared-Surface and Variable depth Samples.

SRNL: HTF-37-12-08 and HTF-37-12-09			F/H Lab.: HTF-37-SPLIT SAMPLE				
Analyte	HTF-37-12-08 surface Average	HTF-37-12-09 Variable Depth Average	HTF-37-12-8- F/H surface Average	HTF-37-12-9-F/H Variable Depth Average	%RD Surface	%RD VDS	Units
Specific gravity	1.49	1.51	1.4933	1.4883	0.22	1.45	
pH	15.1	15.1	15.06	15.07	0.07	0.07	
Nitrite, NO <sub>2</sub>	1.42E+00	1.47E+00	1.6286	1.537	13.5	4.5	moles/L
Nitrate, NO <sub>3</sub>	1.13E+00	1.24E+00	1.2185	1.1715	7.27	6.00	moles/L
Aluminum, Al	6.76E-01	6.61E-01	5.52E-01	6.18E-01	20.2	6.72	moles/L
Sulfate, SO <sub>4</sub>	<2.79E-03	<2.68E-03	0.003	0.0029			moles/L
Carbonate, CO <sub>3</sub>	4.08E-02	3.71E-02	0.0538	0.0514	27.6	32.3	moles/L
Sodium, Na	16.1	16.1	14.085	14.081	13.5	13.6	moles/L
Phosphate PO <sub>4</sub>	1.37E-02	1.27E-02	0.0193	0.0191	34.2	40.2	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<3.040E-03	<2.92E-03	<2.78E-03	<2.76E-03			moles/L
Silicon Si	1.33E-03	1.33E-03	7.0E-04	7.5E-04	62.1	55.8	moles/L
Chloride, Cl	2.26E-02	1.70E-02	2.99E-02	3.08E-02	27.6	57.6	moles/L
Free-OH *	11.77*	11.90*	11.500**	11.68**	2.32	1.87	moles/L
Cs-137	5.00E+09	5.32E+09	5.20E+09	-	3.92	-	dpm/mL

\*Free-OH @ 0.1 N titrant by SRNL

\*\*Free-OH @ 0.01 N titrant by F/H Lab.

**Table 6 Summary of Analytical comparisons between the two laboratories for analytical components of Tank 30 and 37.**

Analyte	Tank 30 surface	Tank 30 VDS	Tank 37 surface	Tank 37 VDS	Tank 30 surface Split	Tank 30 VDS Split	Tank 37 surface Split	Tank 37 VDS Split	Comparative* Analytical Performance, %
<b>Sp. gravity</b>									<b>0.0</b>
<b>pH</b>									<b>0.0</b>
<b>Nitrite</b>			<b>X</b>						<b>12.5</b>
<b>Nitrate</b>									<b>0.0</b>
<b>Aluminum</b>	<b>X</b>	<b>X</b>							<b>25</b>
Sulfate	<b>X</b>	<b>X</b>			<b>X</b>	<b>X</b>			<b>50</b>
Carbonate	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>		<b>X</b>	<b>X</b>	<b>X</b>	<b>87.5</b>
<b>Sodium</b>	<b>X</b>	<b>X</b>		<b>X</b>					<b>37.5</b>
<b>Phosphate</b>					<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>50</b>
<b>Oxalate</b>									<b>0.0</b>
Silicon	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>100</b>
Chloride	-	-	-	-	<b>X</b>	<b>X</b>	<b>X</b>	<b>X</b>	<b>100</b>
<b>Free-OH</b>		<b>X</b>							<b>12.5</b>
<b>Cs-137</b>									<b>0.0</b>

\*As a percent of the number of times analyses was performed by both laboratories for that analyte. A measure of 100% indicates laboratory analytical results were quite different for the same analyte, while a 0 % implies both analytical results were in full agreement in all the analyses results.

X indicates analytical result for that component between the two laboratories (F/H and SRNL) **NOT** comparable, i.e., %RD greater than 20%.

## 5.0 References

- 1) Technical Task Request (TTR) number X-TTR-2012-00016.
- 2) L. N. Oji, "Task Technical and Quality Assurance Plan for the Characterization of Tank Supernate Samples: Cross-Check and Evaporator Feed Quality Analysis for tanks 30 and 37, SRNL-RP-2012-00151, Rev. 0.
- 3) L. N. Oji, "F/H Laboratory and SRNL Cross-check Comparison of High Level Waste Tank 39H Supernatant Sample -2008"  
SRNL-TR-2009-00141, Rev. 0, October 2008.

## Appendix A

**Table 7. Cross Check Analysis for Tanks 30 Samples-Duplicate SRNL analysis: Tank 30 Surface and Variable Depth**

HTF-30-12-06----SRNL: Surface					HTF-30-12-07-----SRNL: Variable Depth				
<b>Analyte</b>	<b>Run-1</b>	<b>Run- 2</b>	<b>Average</b>	<b>St. dev</b>	<b>Run-1</b>	<b>Run- 2</b>	<b>Average</b>	<b>St. dev</b>	<b>Units</b>
Sp. gravity	1.43	1.46	<b>1.45**</b>	0.02	1.450	1.45	<b>1.46**</b>	0.03	
pH	14.8	14.80	<b>14.8*</b>	-	15.0	15.0	<b>15.0</b>	-	
Nitrite, NO <sub>2</sub>	1.94E+00	1.92E+00	<b>1.93E+00</b>	1.37E-02	1.77E+00	1.76E+00	<b>1.77E+00</b>	8.26E-03	moles/L
Nitrate, NO <sub>3</sub>	1.70E+00	1.67E+00	<b>1.68E+00</b>	2.01E-02	1.28E+00	1.29E+00	<b>1.28E+00</b>	6.15E-03	moles/L
Aluminum, Al	6.41E-01	6.48E-01	<b>6.44E-01</b>	5.24E-03	7.85E-01	7.74E-01	<b>7.80E-01</b>	7.86E-03	moles/L
Sulfate, SO <sub>4</sub>	6.87E-03	6.42E-03	<b>6.65E-03</b>	3.18E-04	2.96E-03	2.80E-03	<b>2.88E-03</b>	1.13E-04	moles/L
Carbonate, CO <sub>3</sub>	6.82E-02	7.33E-02	<b>7.08E-02</b>	3.63E-03	4.02E-02	4.20E-02	<b>4.11E-02</b>	1.22E-03	moles/L
Sodium, Na	1.32E+01	1.37E+01	<b>1.34E+01</b>	3.61E-01	1.50E+01	1.44E+01	1.47E+01	4.20E-01	moles/L
Phosphate PO <sub>4</sub>	7.78E-03	7.57E-03	<b>7.68E-03</b>	1.46E-04	9.78E-03	9.61E-03	<b>9.69E-03</b>	1.18E-04	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<b>&lt;0.0E+0</b>	≤2.92E-03	<b>≤2.96E-03</b>		<b>&lt;2.93E-03</b>	<b>&lt;3.05E-03</b>	<b>&lt;2.99E-03</b>		moles/L
Silicon, Si	1.53E-03	1.52E-03	<b>1.52E-03</b>	7.58E-06	1.48E-03	1.42E-03	<b>1.45E-03</b>	4.29E-05	moles/L
Chloride, Cl	1.64E-02	1.59E-02	<b>1.62E-02</b>	3.07E-04	1.82E-02	1.74E-02	<b>1.78E-02</b>	5.47E-04	moles/L
Free-OH	6.73	6.10	<b>6.42</b>	0.45	9.67	9.59	<b>9.63</b>	0.06	moles/L
Cs-137	3.57E+09	3.56E+09	<b>3.57E+09</b>	8.85E+06	4.53E+09	4.59E+09	<b>4.56E+09</b>	3.94E+07	dpm/mL

\*Based on average. [OH]

\*\* Calculated from three values (only two shown).

**Table 8** Cross Check Analysis for Tanks 37 Samples-Duplicate SRNL analysis Tank 37 Surface and Variable Depth

HTF-37-12-08----SRNL: Surface					HTF-37-12-09-----SRNL: Variable Depth				
Analyte	Run-1	Run- 2	Average	St. dev	Run-1	Run- 2	Average	St. dev	Units
Sp. gravity	1.47	1.51	<b>1.49**</b>	<i>0.021</i>	1.50	1.50	<b>1.51**</b>	<i>0.01</i>	-
pH	15.1	15.1	<b>15.1*</b>	<i>0</i>	15.1	15.1	<b>15.1</b>		
Nitrite, NO <sub>2</sub>	1.36E+00	1.48E+00	<b>1.42E+00</b>	<i>8.67E-02</i>	1.56E+00	1.38E+00	<b>1.47E+00</b>	<i>1.21E-01</i>	moles/L
Nitrate, NO <sub>3</sub>	1.08E+00	1.19E+00	<b>1.13E+00</b>	<i>7.76E-02</i>	1.30E+00	1.19E+00	<b>1.24E+00</b>	<i>7.32E-02</i>	moles/L
Aluminum, Al	6.67E-01	6.85E-01	<b>6.76E-01</b>	<i>1.31E-02</i>	6.85E-01	6.37E-01	<b>6.61E-01</b>	<i>3.40E-02</i>	moles/L
Sulfate, SO <sub>4</sub>	<2.71E-03	<2.86E-03	<b>&lt;2.79E-03</b>		<2.70E-03	<2.65E-03	<b>&lt;2.68E-03</b>		moles/L
Carbonate, CO <sub>3</sub>	3.80E-02	4.36E-02	<b>4.08E-02</b>	<i>3.96E-03</i>	3.66E-02	3.76E-02	<b>3.71E-02</b>	<i>7.27E-04</i>	moles/L
Sodium, Na	16.0	16.3	<b>1.61E+01</b>	<i>2.14E-01</i>	1.56E+01	1.67E+01	<b>1.61E+01</b>	<i>8.27E-01</i>	moles/L
Phosphate PO <sub>4</sub>	1.32E-02	1.42E-02	<b>1.37E-02</b>	<i>7.30E-04</i>	1.28E-02	1.26E-02	<b>1.27E-02</b>	<i>1.61E-04</i>	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<2.96E-03	<3.12E-03	<b>&lt;3.04E-03</b>		<2.94E-03	<2.89E-03	<b>&lt;2.92E-03</b>		moles/L
Silicon, Si	1.53E-03	1.13E-03	<b>1.33E-03</b>	<i>2.83E-04</i>	1.33E-03	1.32E-03	<b>1.33E-03</b>	<i>7.58E-06</i>	moles/L
Chloride, Cl	2.20E-02	2.33E-02	<b>2.26E-02</b>	<i>8.80E-04</i>	1.83E-02	1.58E-02	<b>1.70E-02</b>	<i>1.75E-03</i>	moles/L
Free-OH	11.74	11.81	<b>11.77</b>	<i>0.05</i>	12.23	11.57	<b>11.90</b>	<i>0.47</i>	moles/L
Cs-137	5.06E+09	4.93E+09	<b>5.00E+09</b>	<i>9.63E+07</i>	5.36E+09	5.28E+09	<b>5.32E+09</b>	<i>5.91E+07</i>	dpm/mL

\*Based on average [OH]

\*\* Calculated from three values (only two shown).



**Table 9. Check Analysis for Tanks 30 Samples- F/H analysis Tank 30 Surface and Variable Depth.**

HTF-30-12-01----F/H: Surface					HTF-30-12-02-----F/H: Variable Depth				
Analyte	Run-1	Run- 2	Average	St. dev	Run-1	Run- 2	Average	St. dev	Units
Specific gravity	1.4154	NA			1.4537	NA			-
Nitrite, NO <sub>2</sub>	2.0061	NA			NA	NA			moles/L
Nitrate, NO <sub>3</sub>	1.8320	NA			NA	NA			moles/L
Aluminum, Al	0.4243	NA			0.5195	NA			moles/L
Sulfate, SO <sub>4</sub>	0.0134	NA			0.0095	NA			moles/L
Carbonate, CO <sub>3</sub>	0.1260	NA			0.1238	NA			moles/L
Sodium, Na	9.0638	NA			10.7713	NA			moles/L
Phosphate PO <sub>4</sub>	0.0093	NA			0.0107	NA			moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<602	NA			<602	NA			mg/L
Silicon, Si	0.0007	NA			0.0007	NA			moles/L
Free-OH	6.4247	NA			7.2239	NA			moles/L
Cs-137	3.14E09	NA			NA	NA			dpm/mL

**Table 10. Cross Check Analysis for Tanks 37 Samples- F/H analysis Tank 37 Surface and Variable Depth**

HTF-37-12-04----F/H: Surface					HTF-37-12-05-----F/H: Variable Depth				
Analyte	Run-1	Run- 2	Average	St. dev	Run-1	Run- 2	Average	St. dev	Units
Specific gravity	1.4886	NA			1.4811	NA			-
Nitrite, NO <sub>2</sub>	1.7724	NA			NA	NA			moles/L
Nitrate, NO <sub>3</sub>	1.2455	NA			NA	NA			moles/L
Aluminum, Al	0.6156	NA			0.6631	NA			moles/L
Sulfate, SO <sub>4</sub>	<0.0063	NA			0.0062	NA			moles/L
Carbonate, CO <sub>3</sub>	0.1608	NA			0.1443	NA			moles/L
Sodium, Na	13.2644	NA			12.4343	NA			moles/L
Phosphate PO <sub>4</sub>	0.0153	NA			0.0141	NA			moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<604	NA			<593	NA			mg/L
Silicon, Si	0.0007	NA			0.0008	NA			moles/L
Free-OH	10.9437	NA			10.4673	NA			moles/L
Cs-137	5.45E+09	NA			NA	NA			dpm/mL

## Appendix B

Table 11. Cross Check Analysis for Tanks 30 Samples-Duplicate analysis-F/H-SPLIT SAMPLE

HTF-30-12-06----F/H					HTF-30-12-07-----F/H				
Analyte	Run-1	Run- 2	Average	<i>St. dev</i>	Run-1	Run- 2	Average	<i>St. dev</i>	Units
Specific gravity	1.4591	NA	<b>1.46E+00</b>		1.4561	NA	<b>1.46E+00</b>		-
pH	NA	NA			NA	NA			
Nitrite, NO <sub>2</sub>	2.1779	2.2085	<b>2.19E+00</b>	<i>2.16E-02</i>	2.1122	2.003	<b>2.06E+00</b>	<i>7.72E-02</i>	moles/L
Nitrate, NO <sub>3</sub>	1.8623	1.9057	<b>1.88E+00</b>	<i>3.07E-02</i>	1.4562	1.4011	<b>1.43E+00</b>	<i>3.90E-02</i>	moles/L
Aluminum, Al	0.5967	0.6106	<b>6.04E-01</b>	<i>9.83E-03</i>	0.6901	0.7291	<b>7.10E-01</b>	<i>2.76E-02</i>	moles/L
Sulfate, SO <sub>4</sub>	0.0116	0.0116	<b>1.16E-02</b>	<i>0.00E+00</i>	0.0064	0.0063	<b>6.35E-03</b>	<i>7.07E-05</i>	moles/L
Carbonate, CO <sub>3</sub>	0.0580	0.0709	<b>6.45E-02</b>	<i>9.12E-03</i>	0.0592	0.0718	<b>6.55E-02</b>	<i>8.91E-03</i>	moles/L
Sodium, Na	12.3394	12.2923	<b>1.23E+01</b>	<i>3.33E-02</i>	13.161	12.267	<b>1.27E+01</b>	<i>6.32E-01</i>	moles/L
Phosphate PO <sub>4</sub>	0.0105	0.0106	<b>1.06E-02</b>	<i>7.07E-05</i>	0.0144	0.0136	<b>1.40E-02</b>	<i>5.66E-04</i>	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<248	<247			<247	<248			ug/mL
Silicon, Si	0.000701	0.000876	<b>7.89E-04</b>	<i>1.24E-04</i>	0.000564	0.000453	<b>5.09E-04</b>	<i>7.85E-05</i>	moles/L
Chloride, Cl	0.0204	0.0207	<b>2.06E-02</b>	<i>2.12E-04</i>	0.0246	0.0235	<b>2.41E-02</b>	<i>7.78E-04</i>	moles/L
Free-OH	7.5041	7.4498	<b>7.48E+00</b>	<i>3.84E-02</i>	9.3106	9.0982	<b>9.20E+00</b>	<i>1.50E-01</i>	moles/L
Cs-137	3.55E+09	3.51E+09	<b>3.53E+09</b>	<i>2.83E+07</i>	NA	NA			dpm/mL

**Table 12. Cross Check Analysis for Tank 37 Samples-Duplicate analysis F/H-SPLIT SAMPLE**

HTF-37 SPLIT F/H >>> HTF-37-12-8					HTF-37 SPLIT F/H >>> HTF-37-12-9				
Analyte	Run-1	Run-2	Average	St. dev	Run-1	Run-2	Average	St. dev	Units
Specific gravity	1.4933	NA	<b>1.49E+00</b>		1.4883	NA	<b>1.49E+00</b>		-
pH	NA	NA			NA	NA			
Nitrite, NO <sub>2</sub>	1.6039	1.6533	<b>1.63E+00</b>	<i>3.49E-02</i>	1.5561	1.5179	<b>1.54E+00</b>	<i>2.70E-02</i>	moles/L
Nitrate, NO <sub>3</sub>	1.2057	1.2312	<b>1.22E+00</b>	<i>1.80E-02</i>	1.1917	1.1513	<b>1.17E+00</b>	<i>2.86E-02</i>	moles/L
Aluminum, Al	0.5657	0.5382	<b>5.52E-01</b>	<i>1.94E-02</i>	0.6124	0.6232	<b>6.18E-01</b>	<i>7.64E-03</i>	moles/L
Sulfate, SO <sub>4</sub>	0.0029	0.0031	<b>3.00E-03</b>	<i>1.41E-04</i>	0.0029	0.0029	<b>2.90E-03</b>	<i>0.00E+00</i>	moles/L
Carbonate, CO <sub>3</sub>	0.0590	0.0486	<b>5.38E-02</b>	<i>7.35E-03</i>	0.0528	0.0500	<b>5.14E-02</b>	<i>1.98E-03</i>	moles/L
Sodium, Na	14.1006	14.0694	<b>1.41E+01</b>	<i>2.21E-02</i>	14.1489	14.0121	<b>1.41E+01</b>	<i>9.67E-02</i>	moles/L
Phosphate PO <sub>4</sub>	0.0192	0.0193	<b>1.93E-02</b>	<i>7.07E-05</i>	0.0194	0.0188	<b>1.91E-02</b>	<i>4.24E-04</i>	moles/L
Oxalate, C <sub>2</sub> O <sub>4</sub>	<245	<246			<242	<245			ug/mL
Silicon, Si	0.000647	0.000743	<b>6.95E-04</b>	<i>6.79E-05</i>	0.000792	0.00071	<b>7.51E-04</b>	<i>5.80E-05</i>	moles/L
Chloride, Cl	0.0296	0.0302	<b>2.99E-02</b>	<i>4.24E-04</i>	0.0311	0.0305	<b>3.08E-02</b>	<i>4.24E-04</i>	moles/L
Free-OH @	11.3911	11.5981	<b>1.15E+01</b>	<i>1.46E-01</i>	11.7076	11.6583	<b>1.17E+01</b>	<i>3.49E-02</i>	moles/L
Cs-137	5.23E+09	5.17E+09	<b>5.20E+09</b>	<i>4.24E+07</i>	NA	NA			dpm/mL

## Appendix C

### LIMS Numbers for All SRNL Analyses <sup>+</sup>

Analysis	Lims #- HTF 30 and 37	Dilution factor	Comments
HTF-30-12-6-IC-anion-1	300 298622	26.39	
HTF-30-12-6-IC-anion-2	300 298623	25.69	
HTF-30-12-6-Na-AA-1	300 298647	25.70	Including gamma scan Cs-137
HTF-30-12-6-Na-AA-2	300 298648	25.61	Including gamma scan Cs-137
HTF-30-12-6-Si-1	300 298638	+	Dissolution volume = 100 mL
HTF-30-12-6-Si-2	300 298639	+	Dissolution volume = 100 mL
HTF-30-12-6-Free-OH-1	300 298630	26.40	Free-OH and carbonate
HTF-30-12-6-Free-OH-2	300 298631	26.19	Free-OH and carbonate
HTF-30-12-7 IC-anion-1	300 298624	25.79	
HTF-30-12-7 IC-anion-2	300 298625	26.84	
HTF-30-12-7-Na-AA-1	300 298649	25.62	Including gamma scan Cs-137
HTF-30-12-7-Na-AA-2	300 298650	30.20	Including gamma scan Cs-137
HTF-30-12-7-Si-1	300 298640	+	Dissolution volume = 100 mL
HTF-30-12-7-Si-2	300 298641	+	Dissolution volume = 100 mL
HTF-30-12-7-Free-OH-1	300 298632	25.85	Free-OH and carbonate
HTF-30-12-7-Free-OH-2	300 298633	26.34	Free-OH and carbonate
HTF-37-12-8 IC-anion-1	300 298626	26.02	
HTF-37-12-8 IC-anion-2	300 298627	27.49	
HTF-37-12-8-Na-AA-1	300 298651	25.32	Including gamma scan Cs-137
HTF-37-12-8-Na-AA-2	300 298652	25.80	Including gamma scan Cs-137
HTF-37-12-8-Si-1	300 298642	+	Dissolution volume = 100 mL
HTF-37-12-8-Si-2	300 298643	+	Dissolution volume = 100 mL
HTF-37-12-8-Free-OH-1	300 298634	25.30	Free-OH and carbonate
HTF-37-12-8-Free-OH-2	300 298635	32.99	Free-OH and carbonate
HTF-37-12-9 IC-anion-1	300 298628	25.45	
HTF-37-12-9 IC-anion-2	300 298629	25.91	
HTF-37-12-9-Na-AA-1	300 298653	25.18	Including gamma scan Cs-137
HTF-37-12-9-Na-AA-2	300 298654	25.63	Including gamma scan Cs-137
HTF-37-12-9-Si-1	300 298644	+	Dissolution volume = 100 mL
HTF-37-12-9-Si-2	300 298645	+	Dissolution volume = 100 mL
HTF-37-12-9-Free-OH-1	300 298636	25.53	Free-OH and carbonate
HTF-37-12-9-Free-OH-2	300 298637	25.42	Free-OH and carbonate

<sup>+</sup> With the exception of samples for warm acid strike all other samples were diluted before taking them out of the shielded cells for analyses. Warm acid strike samples were digested in the shielded cell, diluted and brought out.