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Tank 8F Sludge Slurry Analysis Results

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Introduction and Summary

Three samples (one surface and two variable depth samples) were taken from Tank 8F in September 2000 and were transported to the Savannah River Technology Center's (SRTC) Shielded Cells facility for analysis.' Upon receipt of the three samples, they were mixed and combined into one sample. This report presents results of weight percent solids, density, nonradioactive composition and noble metal concentrations of that combined sludge slurry and its supernate.

Highlights from this report are:

- The analysis of the total solids from the dried sludge slurry indicates an average Si concentration of 0.54 wt %, a Cr concentration of 0.16 wt %, a Cu concentration of 0.033 wt %, a P concentration of 0.22 wt %, and a Ti concentration of 0.029 wt %.
- The average Hg concentration of the total solids from the dried sludge slurry was 0.115 wt %.
- The weight percent total solids for the combined sludge slurry was 44.0 wt %.
- The weight percent solids dissolved solids for the supernate of the combined sample was
- 29.9 wt %.
- The major elements (excluding oxygen) in the total dried solids were Na, Fe, and Al at concentrations of 23.5,

21.5, and 3.91 wt %, respectively.
- The noble metals, Ru, Rh, Pd, and Ag, in the total dried solids had concentrations of 0.027, 0.0069, 0.00053, and 0.0048 wt %, respectively.
- The concentration of Cl^- in the supernate phase was 0.001 M, F^- was 0.01 M, and the SO_4^{-2} was 0.162 M. The majority of these three ions are expected to be soluble in Tank 8 supernate.

Keywords: Tank Farm, Sludge, Characterization, Tank 8

Results and Discussion

Combination of the Three Sludge Slurry Samples

Three samples of sludge slurry (~80 mL each) were taken from Tank 8F in September 2000. All three samples were obtained approximately one hour after the slurry pumps had been turned off. The samples consisted of a surface sample (SS), a variable depth (VD) sample taken from a middle of the tank (~45 inches), and a variable depth sample taken from near the bottom (~10 inches) of the tank. It was decided by SRTC and High Level Waste Engineering (HLW-E) to combine these samples, so that there would be enough sludge slurry to complete all of the requested analyses.

In order to combine the samples, each sample was thoroughly mixed for approximately five minutes prior to pouring the sludge slurry into the bottle for the combined samples. The two variable depth samples were added to the combined sample bottle first. These sample holders were only approximately 2/3 full of sludge slurry. The mixed sludge slurry appeared to flow easily and no clumps were observed in the slurry from either variable depth sample. Upon opening the surface sample bottle, it was noted that the bottle was full, and that the sludge slurry was very thick and appeared to have the same consistency as the first set of three slurry samples taken from Tank 8 and received at SRTC in May of this year. The surface sample was then poured into the combined sample bottle and small clumps (approximately 1/16" to 1/8" in diameter) were observed in the sludge slurry as the sample was being poured into the combined sample bottle. The first task in the analysis of the combined sludge slurry sample was to determine the weight percent solids and densities of the sludge slurry and its supernate. These results were then compared to those from the first set of Tank 8 samples received in May, 2000.

Measured Weight Percent Total Solids and Densities for the Combined Sludge Slurry and Supernate

Method for Determining Total Solids and Density of the Sludge Slurry

To determine the weight perctent total solids of the combined sludge slurry, triplicate samples of mixed sludge slurry were pipetted out of the combined sludge slurry sample bottle into labeled polymethylpentene (PMP) beakers. These PMP beakers were weighed and then placed into a drying oven at 115°C overnight. Triplicate samples of a 15 wt.% NaCl standard solution were also weighed and dried (in labeled PMP beakers) along with the sludge slurry samples to check the accuracy and precision of the method. All of the samples were allowed to cool for ~15 minutes before they were weighed. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard.

Three density determinations of the combined sludge slurry sample were completed in the Shielded Cells Facility. An 8.25 mL heat sealed pipette tip was used to perform the density measurements. The sealed pipette tip was first weighed and then a mixed sample of sludge slurry was pipetted into the sealed pipette. The sealed pipette tip with the sludge slurry sample was weighed and density was calculated.

Method for Determining Total Solids and Density of the Supernate

A mixed sample of the combined sludge slurry was filtered through 0.45m m Nalgene® filters resulting in clear supernate for the sample. This supernate sample was used to complete the density and the weight percent dissolved solids measurements.

Three density determinations of the supernate sample were completed. An 8.25 mL sealed pipette tip was used to perform the density measurements. The sealed pipette tip was first weighed and then a mixed sample of supernate was pipetted into the sealed pipette. The sealed pipette tip with the supernate sample was weighed and the density was calculated.

After completing the density determinations, the supernate sample was used to complete the weight percent dissolved solids determination. Triplicate determinations were completed for the supernate sample. The supernate sample was pipetted into labeled PMP beakers. These PMP beakers were weighed and then placed into a drying oven at 115°C overnight. Triplicate samples of a 15 wt.% NaCl standard solution were also weighed and dried (in labeled PMP beakers) along with the supernate samples to check the accuracy and precision of the method. All of the samples were allowed to cool for ~15 minutes before they were weighed. The results of the 15 wt.% NaCl standard solutions showed good reproducibility and good agreement with the known value of the standard.

Results for Weight Percent Total Solids and Densities of the Combined Sludge Slurry and Supernate

Table 1 provides the averages of the results of the weight percent total solids, weight percent dissolved solids, and density for the combined sample. The standard deviations and the percent relative standard deviation are provided below the individual values in parentheses. The standard deviations indicate that the results for the combined sample are very precise. Table 1 also presents the averages of the results for three sludge slurry samples from Tank 8 that were received by SRTC in May 2000.

Table 1. Weight Percent Solids Measurements and Density Measurements for the Sludge Slurry and Supernate for the Combined Sample and the First Set of Samples Received in May

Sample ID	Total Solids in the Sludge Slurry[a]	Dissolved Solids in the Supernate[a]	Density for the Sludge Slurry[b]	Density for the Supernate[b]
Combined Sample (September)	44.0 wt.% (± 0.058, 0.13)	34.9 wt% (± 0.31, 0.88)	1.45 g/mL (± 0.01, 0.69)	1.36 g/mL (± 0, 0)
Average of the May Samples	48.1 wt.% (± 1.2, 2.3)	36.9 wt% (± 0.93, 2.5)	1.51 g/mL (± 0.021, 1.4)	1.33 g/mL (± 0.01, 0.75)
Sample VD-1 (May)	46.8 wt.% (± 0.36, 0.76)	35.9 wt.% (± 0.66, 1.8)	1.53 g/mL[c]	1.32 g/mL[c]
Sample VD-2 (May)	48.9 wt.% (± 1.0, 2.1)	37.2 wt.% (± 0.1, 0.27)	1.49 g/mL[c]	1.33 g/mL[c]
Sample SS-3 (May)	48.5 wt.% (± 0.79, 1.6)	37.7 wt.% (± 0.085, 0.22)	1.50 g/mL[c]	1.34 g/mL[c]

[a] Dried overnight at 115°C in drying oven.
[b] Performed in sealed density tips having a known volume of 8.25 mL.
[c] Only one value obtained.

Based on the values in Table 1, the combined sample appears to be lower in total weight percent solids than the first set of samples. This may be due to the addition of water to the tank or actual differences in the solids content at various levels of the tank. Another possible reason for the low weight percent solids obtained for the combined sample could be the sampling technique used to obtain the two variable depth samples. It is possible that the aluminum foil covering on the sample bottles did not have adequate time to dissolve, explaining why the bottles were ~2/3 full and that the consistency of the samples appeared to be thinner upon the addition of the sludge slurry to the combine sample bottle.

Calculation of Insoluble Solids and Soluble Solids for the Combined Sludge Slurry Sample

The soluble and insoluble weight percent solids can be calculated by using the following equations, once the weight percent total solids and dissolved solids have been obtained.

Equation 1: $W_{is} = (W_{ts} - W_{ds}) / (1- W_{ds})$ (Reference)

Equation 2: $W_{ss} = W_{ts} - W_{is}$ (Reference)

W_{ds} – Weight fraction of dissolved solids (weight of dissolved solids/weight of supernate)
W_{ts} – Weight fraction of total solids (weight of total solids/weight of sludge slurry)
W_{is} – Weight fraction of insoluble solids (weight of insoluble solids/weight of sludge slurry)
W_{ss} – Weight fraction of soluble solids (weight dissolved solids/weight of sludge slurry)

The data presented in Table 1 were used to calculate the weight percent insoluble solids and the weight percent soluble solids for the combined sample and for the first set of Tank 8 samples received in May. The results of the calculation are presented in Table 2.

Table 2. Calculated Results of the Insoluble Solids and the Soluble Solids for the Combined Sample and the Variable Depth Samples Taken in May of this Year

Sample ID	Calculated Insoluble Solids for the Sludge Slurry	Calculated Dissolved Solids for the Sludge Slurry
Sample VD-1 (May)	17.0 wt.%	29.8 wt.%
Sample VD-2 (May)	18.7 wt.%	30.2 wt.%
Sample SS-3 (May)	17.3 wt.%	31.2 wt.%
Average of the May Samples	17.7 wt.%	30.4 wt.%
Combined Sample (September)	14.1 wt.%	29.9 wt.%

Concentrations of Major Elements and Noble Metals in the Combined Sludge Slurry Sample

Provided below are the selected results of the analyses for the combined sludge slurry samples. A portion of the mixed sludge slurry sample was taken from the combined sample bottle and dried overnight. This dried sludge slurry was dissolved by the Aqua Regia and Sodium Peroxide Fusion methods along with appropriate standards to check the dissolutions and the analytical methods. After performing the dissolution methods on the sludge slurry, the dissolved sludge slurry was diluted prior to the removal from the Shielded Cells Facility. These diluted samples were sent to Analytical Development Section (ADS) Sample Receiving for analyses to be performed by ADS. Dilution of the sludge slurry samples was required so that only a small portion of the radioactivity was removed from the Shielded Cells. The dissolution results of the standards for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly.

Presented below in Table 3 are the selected cation results obtained from the ICP-ES and the CV-Hg for the dissolved

sludge slurry. The results in Table 3 are the average of eight samples (unless otherwise indicated) and are in the units of weight percent on a dried basis. The standard deviation and the percent relative standard deviation are provided in parentheses.

Table 3. Concentration of Elements Detected by ICP-ES and CV Hg in the Combined Sludge Slurry Sample Presented in Units of Weight Percent

Element	Weight Percent *,[a]	Element	Weight Percent *,[a]
Ag[b]	0.0154(± 0.0023, 15)	Mg	0.572 (± 0.030, 5.3)
Al	3.91 (± 0.15, 3.9)	Mn	1.83 (± 0.13, 7.0)
B[e]	<0.006	Mo[e]	<0.008
Ba[b]	0.023 (± 0.002, 7.4)	Na[b]	23.5 (± 1.0, 4.5)
Ca	0.856 (± 0.045, 5)	Ni	1.01 (± 0.07, 7.1)
Cd[b]	0.0062 (± 0.0008, 13)	P	0.228 (± 0.009, 4.1)
Cr	0.161 (± 0.012, 7.1)	Pb[b]	0.037 (± 0.007, 19)
Cu	0.0330 (± 0.0031, 24)	Si[b]	0.564 (± 0.002, 0.4)
Co[b]	0.0099 (± 0.0022, 22)	Sn[e]	<0.02
Fe	21.5 (± 0.69, 3.2)	Sr	0.012 (± 0.002, 17)
Hg[c,d]	0.115	Ti[b]	0.0289 (± 0.0054, 19)
K	Not analyzed for.	V[b]	0.008 (± 0.002, 27)
La[b]	0.018 (± 0.003,14)	Zn[b]	0.028 (± 0.002, 8.7)
Li	0.0627 (± 0.0046, 7.4)	Zr[b]	0.052 (± 0.003, 6.6)

* The sludge slurry sample was dried overnight at 115°C in a drying oven. Results are presented on a dry total solids basis.

[a] Majority of the results are determined by ICP-ES and are the average of eight sample results when aqua regia and peroxide fusion dissolutions give similar results.

[b] Average of four results only when there is a distinct difference between the aqua regia and peroxide fusion dissolution results.

[c] Only single result available

[d] Result determined by AA method.

[e] Detection Limit of the Instrument.

The peroxide fusion blank results for Si indicated that there was some Si contamination (~0.24 wt.%). To determine the source of contamination, a non-radioactive simulated peroxide fusion sample blank was run on a different instrument and was found to contain no detectable Si. Similar blanks prepared and run previously on the same instrument have indicated ~0.05 to 0.1 wt %. Matrix interference affects are a possibility, but have not been fully examined. Conservatively, the results given in Table 3 should be used without accounting for possible contamination.

The measured concentrations of noble metals based on total dried solids from the combined slurry sample are given in Table 4. These metals were measured by Inductively Coupled Plasma-Mass Spectrometric (ICP-MS) analysis of the solutions resulting from peroxide fusion and aqua regia dissolutions of aliquots of the dried sludge slurry. The elements Ru, Rh, and Pd are in the waste as products from the fission of U-235 in the SRS reactors. Silver (Ag) is natural silver that was put in the waste with the beryl saddles used to capture radioactive iodine upon dissolution of the reactor fuels and targets in the SRS canyons.

Table 4. Concentration of Noble Metals in the Combined Sludge Slurry Sample Presented in Units of Weight Percent[a]

Element	Weight Percent[a]
Ru[b]	0.027
Rh[b]	0.0069
Pd[c]	0.00053
Ag[d]	0.0048

[a] The sludge slurry sample was dried overnight at 115° C in a drying oven. Results are presented on a dry total solids basis. Results are averages of eight samples - four dissolved by peroxide fusion and four by aqua regia dissolution methods. The results from both dissolution methods were similar.
[b] Estimated percent RSD is 13%.
[c] Estimated percent RSD is 16%.
[d] Estimated percent RSD is 10%.

In the ICP-MS analysis, concentrations of isotopes are measured as a function of mass. The noble metal Rh occurs only at mass 103 and the result in Table 4 is the average of the concentrations measured at that mass for the eight samples. In fission product waste solutions the isotopes of Ru occur at masses 101, 102 and 104. The result given in Table 4 is the average of the sum of the concentrations measured at these masses. Natural Ag occurs at masses 107 and 109 and the result in Table 4 is the average of the sum of these concentrations measured at these two masses. Fission product Pd occurs at masses 105, 106, 107, 108 and 110. The only mass in Tank 8 sludge that can be assigned to solely to Pd is mass 105. The natural Ag interferes with a measurement of Pd at mass 107. Natural Cd has isotopes at 106, 108, and 110 that are measured along with the isotopes of fission product Pd at these masses. Analysis of the ICP-MS data indicates that there is indeed natural Cd in the Tank 8 solids. (Natural Cd in the waste results from Cd being added to targets in special charges to the SRS reactors to shape the neutron energy spectrum.) There is too much Cd in this waste to allow a reliable measurement of Pd at masses 106, 108, and 110. Because of these interferences, the total amount of Pd present has to be calculated from the measurement at mass 105. The result in Table 4 for Pd is the average of th concentrations measured at mass 105 in the eight samples combined with the concentrations calculated for the other five appropriate masses in those samples. These calculations are based on the measured concentrations at mass 105 multiplied by the relative fission yields for the other five fission product Pd isotopes. The estimated relative precisions in the footnotes of Table 4 for the four noble metals are based on the range of results of the measured concentrations in the eight samples. For Pd it is the relative standard deviation for the concentrations measured at mass 105.

Concentrations of Major Elements in the Supernate of the Combined Sludge Slurry Sample

Provided below are the results from the analyses of the supernate of the combined sludge slurry sample. A mixed sample of the combined sludge slurry was filtered through a Nalgeneâ filter resulting in a clear supernate. A portion of this supernate was diluted and removed from the Shielded Cells and sent to ADS Sample Receiving so that analyses could be performed by ADS. The dilution of the supernate samples was required so that only a small portion of the radioactivity was removed from the Shielded Cells.

Presented below in Table 5 are the cation results obtained from the ICP-ES for the supernate. The results in Table 5 are the average of three samples and are in the units of molarity and mg/L. The standard deviation and the percent relative standard deviation are also provided in Table 5.

Table 5. Concentrations of Elements Detected by ICP-ES in the Supernate of the Combined Tank 8F Slurry Sample Based on Three Samples of the Supernate

Element [a]	Molarity	mg/L	%RSD
Al	0.406 (±0.002)	10,900 (57)	0.52
B	0.00021 (±0.00002)	2.31 (0.21)	9.1
Cr	0.013 (±0.0001)	693 (5.4)	0.8
Mo	0.00022 (±0.000002)	21.2 (0.19)	0.9
Na	6.42 (±0.03)	148,000 (736)	0.50
P	0.0032 (±0.00003)	98.5 (1.0)	1.0
Pb	0.000062 (±0.000005)	12.8 (0.1)	7.8
Si	0.00011 (±0.00002)	3.1 (0.6)	19
Sn	0.00018 (±0.000004)	20.8 (0.45)	2.2

[a] The following elements were analyzed for and were not detected. Based on the detection limit of the ICP-ES, their concentrations are estimated to be <1 mg/L. The elements were Ag, Ba, Cd, Co, Cu, Ca, Fe, La, Li, Mg, Ni, Sr, Ti, V, Zn, and Zr.

Presented below in Table 6 are the Ion Chromatography results obtained for the supernate. The results in Table 6 are the average of three samples and are in the units of molarity. The standard deviation and the percent relative standard deviation are also provided in Table 6.

Table 6. Concentrations of Soluble Anions Detected by Ion Chromatography in the Supernate of the Combined Tank 8F Slurry Sample Based on Three Samples of the Supernate

Species	Average Molarity	Std. Dev.	%RSD
Fluoride	0.01	0.002	17
Chloride	0.001	0.0001	8
Nitrite	2.16	0.04	1.8
Nitrate	0.920	0.046	5.0
Phosphate	<0.01	-	-
Sulfate	0.162	0.002	1.0
Oxalate	0.002	0.0005	25

All the above results are typical of supernate that is above unwashed sludge.' These two references concern the washing of sludge from Tanks 51 and 42, respectively.

Conclusions

The results of these analyses indicate that the current (September) sludge slurry sample has a lower weight percent solids, particularly insoluble solids, when compared to samples pulled in the spring of 2000. The chemical analyses also indicate that the composite sludge slurry appears similar to slurries analyzed for Macrobatches 1 and 2 in that iron and aluminum would appear to be the major consituents of the sludge.

References

1. E. T. Ketusky, "Tank 8 Sludge Slurry Special Samples", HLE-TTR-2000-046, Revision 1, August 24, 2000.
2. R. F. Swingle, "Task Technical and Quality Assurance Plan for the Characterization of the Tank 8F Dip and Variable Depth Samples", WSRC-RP-2000-00740, October 13, 2000.
3. M. S. Hay and N. E. Bibler, "Characterization and Sludge Washing Studies of Tank 42H Sludge", WSRC-RP-94-730, July 27, 1994.
4. M. S. Hay and N. E. Bibler, "The Characterization and Centrifuge-Settled Washing of a Tank 51H Sludge Sample Obtained in October, 1995", WSRC-RP-95-1003, November 25, 1995.
5. M. S. Hay and N. E. Bibler, "A Laboratory Study of Washing of SRS High-Level Waste Radioactive Sludge - Evidence for Insoluble Sodium and Cesium-137", Proceedings of the International Topical Meeting on Nuclear and Hazardous Waste Management, Spectrum '94, pp. 828-832, American Nuclear Society, La Grange Park, IL

(1994).