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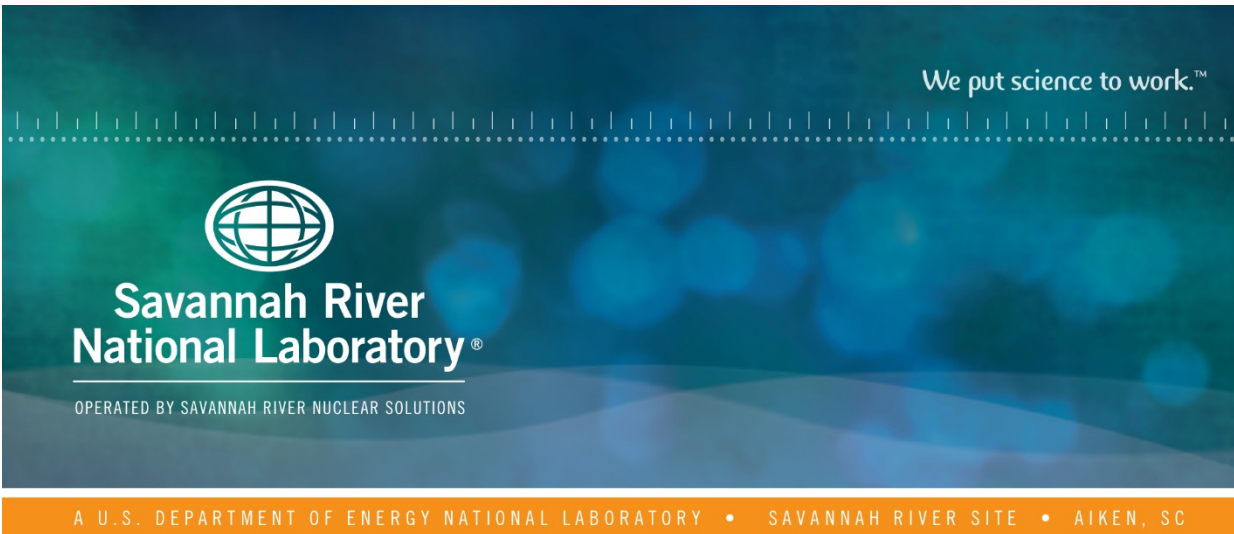
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TANK 22 SETTLED SLUDGE CORE SAMPLE CHARACTERIZATION and TESTING

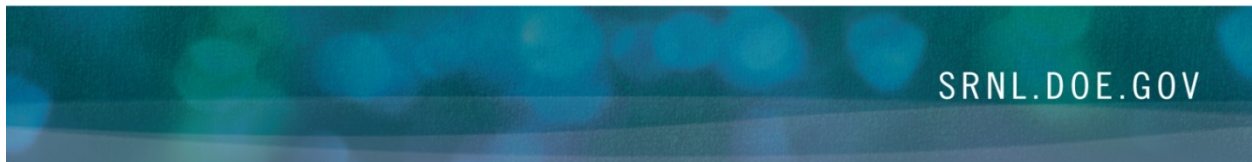
L. N. OJI

J. M. PAREIZS

C. L. TRIVELPIECE

December 2019

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Tank 22 Settled Sludge Core Sample Characterization and Testing

L. N. Oji
J. M. Pareizs
C. L. Trivelpiece

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REVIEWS AND APPROVALS

AUTHORS:

L. N. Oji, Advanced Characterization & Processing	Date
---	------

J. M. Pareizs, Process Technology Programs	Date
--	------

C. L Trivelpiece, Immobilization Technology	Date
---	------

TECHNICAL REVIEW:

W. D. King, Advanced Characterization & Processing <i>Reviewed per Manual E7 Procedure 2.60</i>	Date
--	------

C.A. Nash, Advanced Characterization & Processing <i>Reviewed per Manual E7 Procedure 2.60</i>	Date
---	------

T. B. Peters, Advanced Characterization & Processing <i>Reviewed per Manual E7 Procedure 2.60</i>	Date
--	------

E. K. Hansen, Energy Science & Engineering <i>Reviewed per Manual E7 Procedure 2.60</i>	Date
--	------

APPROVALS:

B. J. Wiedenman, Manager, Advanced Characterization & Processing	Date
--	------

F. Pennebaker, Program Manager, Liquid Waste	Date
--	------

S. D. Fink, Director, Chemical Processing Technologies	Date
--	------

J. E. Occhipinti, Manager, Tank Farm Facility Engineering	Date
---	------

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was requested by Savannah River Remediation (SRR) Engineering (SRR-E) to provide sample characterization and analyses of Tank 22 settled sludge core sample and the supernatant liquids (supernate) in support of Tank 22 re-baseline data, inhalation dose potential/hydrogen generation and suspension/removal of settled sludge from the bottom of Tank 22.

The approximately 9.5 inches of intact Tank 22 core sample from SRR-E, after extrusion in the SRNL Shielded Cells, showed three visually different stratification layers or regions of solids in the extruded core material. Part of the initial physical characterization of these three segments of the Tank 22 core sample included density, weight percent total solids, particle size distribution, X-ray diffractions and scanning electron microscope of each segment material.

Given the dissimilarity of the three Tank 22 segment materials after the physical characterization results and the fact that there was no clear line of demarcation to indicate where each segment began and ended across the entire length of the core sample, SRNL in conjunction with the SRR-E customer decided to blend all three segments of the material to form a composite Tank 22 core sample for further analysis and characterization without taking into consideration the proportional weight or mass contribution of each segment. This compositing approach assumes that the errors introduced in any characterization of the Tank 22 core sample will be comparable to the errors when the three segments are separated and combined proportionally by weight to form the composite Tank 22 sample. This compositing approach maximized the quantity of composited Tank 22 material needed for radionuclide and other physical characterizations.

A composite Tank 22 core sample has been characterized for physical properties, stable elemental constituents, radionuclides, rheological and settling properties. The densities, solids distribution and select radionuclide content of the Tank 22 supernatant liquid was also determined. A summary of the average characterization data, based on one sigma analytical uncertainty where applicable, for the composite Tank 22 core sample and segments includes the following.

The composite Tank 22 sludge bulk wet and bulk dry densities are 1.54 ± 0.20 , and 0.66 ± 0.13 g/mL, respectively.

The measured weight percent total solids for the Tank 22 composite sample was 42.5 ± 3.61 wt% (total sludge basis), while the total dissolved solids were 4.34 wt % (supernatant basis). This gives a calculated insoluble solids value of 39.9 wt % (sludge basis) and wt % soluble solids of 2.61 wt %. The experimentally determined calcined solids was 32.5 ± 1.20 wt % and the maximum calculated calcined solids for the Tank 22 composite material was 32.10 wt %.

The dominant elemental constituents in the Composite Tank 22 sludge material were Fe (6.13 ± 0.11 wt %), Hg ($5.12 \pm 3.66E-01$ wt %), Na (5.03 ± 0.17 wt %), Al (2.49 ± 0.13 wt %), Mn (2.39 ± 0.19 wt %), Si (2.32 ± 0.16 wt %), and Li ($7.33E-02 \pm 5.14E-04$ wt %).

The Fe/Si and Fe/Li mass ratios, respectively, 2.64 and 83.6, which reflects on the fraction of frit in Tank 22, are comparable to the ratios of these elements in previous Tank 22 characterizations.

Total elemental mercury composition in the composite Tank 22 sludge material averaged $5.12 E+00 \pm 0.37$ wt % total solids.

The measurable alpha-emitters in the composite Tank 22 sludge sample are Pu-238 ($2.64E-01 \pm 7.72E-03$ Ci/ gal), Am-241 ($4.10E-02 \pm 1.54E-03$ Ci/gal), Pu-239 ($1.55E-02 \pm 1.47E-03$ Ci/gal), Pu-240 ($4.94 E-03 \pm 1.51E-04$ Ci/gal), and Cm-244 ($3.32E-02 \pm 1.67E-03$ Ci/gal).

The measured total alpha activity concentration at $< 3.90\text{E-}01$ Ci/ gal (<1.03 E-01 Ci/L) is significantly lower than the “Low rem” limit ($8.51\text{E-}01$ Ci/gal or $2.25\text{E-}01$ Ci/L) of the inhalation dose potential determination.

The sum of the activity concentrations of the individually measured alpha emitters (Pu-238, Pu-239, Pu-240, Am-241 and Cm-244) is $9.92\text{E-}02$ Ci/L ($3.76\text{E-}01$ Ci/gal), which is consistent with the measured total alpha result of <1.03 E-01 Ci/L ($3.90\text{E-}01$ Ci/gal).

The primary beta-emitting radionuclides in the composite Tank 22 core sludge sample are Sr-90 ($1.68\text{E+}01 \pm 1.82\text{E+}00$ Ci/gal), Y-90 ($1.68\text{E+}01 \pm 1.82\text{E+}00$ Ci/gal), and Cs-137 ($1.14\text{E+}00 \pm 0.14$ Ci/gal).

The primary gamma-emitting radionuclides in the composite Tank 22 core sample are Ba-137^m, and Co-60 at an average activity concentration of $1.08\text{E+}00 \pm 1.33\text{E-}01$ Ci/gal and $1.10\text{E-}03 \pm 2.3\text{E-}05$ Ci/gal, respectively.

U-238 and Th-232 were present at the highest radionuclide mass concentrations of $1.29\text{E+}00 \pm 2.79\text{E-}02$ and $4.96\text{E-}01 \pm 2.42\text{E-}02$ wt %, respectively.

The total uranium content of the Tank 22 composite core sample is $1.30\text{E+}00$ wt % and the U-235 enrichment is 0.62%.

The total plutonium mass concentration (Pu-238 through Pu-244) for the composite Tank 22 core sample is $2.33\text{E-}03$ wt % total solids.

The XRD data on the mineralogy of both the Tank22 segment samples and the composite Tank 22 sample indicate there are five major crystallographic minerals in these samples, namely, aluminosilicate minerals [nitrated cancrinite ($\text{Na}_{7.6}(\text{AlSiO}_4)_6(\text{NO}_3)_{1.6} \cdot 2\text{H}_2\text{O}$), sodalite ($\text{Na}_6\text{Al}_6\text{Si}_{10} \cdot 12\text{H}_2\text{O}$ and $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$)], boehmite ($\text{AlO}(\text{OH})$), mercuric minerals [montroydite ($\text{Hg}_2\text{NCl} \cdot \text{H}_2\text{O}$) and mercuric oxide (HgO)], iron (Fe_2O_3) and quartz mineral (SiO_2).

The particle size distribution analysis of the three Tank 22 core segment samples (top, middle and bottom) shows that two of these segment samples (top and middle) have large particles sizes, which range from a few microns up to 1000 microns. The particles size in the bottom segment sample averaged about 50 microns.

The particle size distribution (PSD) for the composite Tank 22 core samples showed a bimodal distribution of particles with the larger particles in the 500 to 1000 microns range and the smaller particles averaging about 10 microns.

Larger particles observed in the “as-received” Tank 22 samples (composite and segment samples) may be a sampling artifact resulting from the compaction of smaller particles and the squeezing out of the liquid supernate phase; these larger particles do not represent the particle size distribution in the bulk of the Tank 22 medium.

Simple sonication, for a short time, proved sufficient to de-agglomerate the particles and therefore indexing the pumps in Tank 22 will likely de-agglomerate the particles in the mounds and allow easier suspension of the particles for transfers.

The 2 wt % Composite Tank 22 Sludge settled to less than 10% of the starting height within eight hours; from 38.5 cm to 3.5 cm. Settling stopped after approximately 100 hours at a level of 3.4 cm.

The Tank 22 slurry is generally Newtonian (little or no yield stress) until insoluble solids contents reach >19wt %.

A summary of the average analytical results for the characterization of the Tank 22 supernatant liquid sample follows.

The Tank 22 supernatant liquid and its filtrate densities* are 1.008 ± 0.002 and 1.003 ± 0.006 g/mL, respectively. Densities of the Tank 22 supernatant liquid and its filtrate are almost identical, which means that the supernate contained little or no measurable suspended solids.

The Tank 22 supernatant total mercury and methyl mercury cation concentration are $5.67\text{E-}04 \pm 3.34\text{E-}05$ and $1.03\text{E-}04 \pm 4.45\text{E-}06$ Moles, respectively.

Sodium was the dominant elemental constituent in the Tank 22 supernatant with a concentration of $7.13\text{E-}01 \pm 1.55\text{E-}02$ M. The second, third and fourth most dominant constituents in the supernatant were aluminum, silicon and lithium, with concentrations of $2.15\text{E-}03 \pm 5.89\text{E-}05$ M, $5.73\text{E-}03 \pm 1.44\text{E-}04$ M and $4.26\text{E-}03 \pm 7.80\text{E-}05$ M, respectively.

The predominant anions in this Tank 22 supernatant were nitrite, carbonate, nitrate, sulfate and aluminate, which were present at average concentrations of $3.12\text{E-}01 \pm 5.61\text{E-}03$, $9.49\text{E-}02 \pm 1.14\text{E-}03$, $8.53\text{E-}02 \pm 1.36\text{E-}03$, $3.18\text{E-}03 \pm 6.04\text{E-}05$ and $2.15\text{E-}03 \pm 5.80\text{E-}05$ M, respectively. Free hydroxide concentration in the supernate was less than 0.21 M.

The average concentration of cesium-137 in the Tank 22 supernatant liquid filtrate was $3.07 \text{E+}07 \pm 2.00\text{E+}05$ dpm/mL ($5.23\text{E-}02 \pm 3.41\text{E-}04$ Ci/gal).

The measurable uranium concentrations, U-235 and U-238, were $1.48\text{E-}07$ and $2.09\text{E-}05$ M respectively giving a U-235 enrichment of about 0.71 wt %.

Techecium-99, at an average concentration of $1.50\text{E-}06$ M, was another measurable radionuclide in the Tank 22 supernatant liquid. This ICP-MS data value for Tc-99 may be biased high because both ruthenium and molybdenum isotopes also contribute to atomic mass 99.

* Reported to 4 significant figures because this density measurement only differs in the 4th significant place when compared with that of distilled water or the Tank 22 supernate filtrate.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ARG	Analyzed reference glass
AQR	aqua regia
BSD	back scatter detector
BT	base titration
DMA	Direct Mercury Analysis
DWPF	Defense Waste Processing Facility
EDS	energy-dispersive x-ray spectroscopy
GC/AFS	gas chromatography/atomic fluorescence spectroscopy
LIMS	Laboratory Information Management System
LSC	Liquid Scintillation Counting
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-ES	inductively coupled plasma-emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
IDP	Inhalation Dose Potential
MDA	Minimum Detection Activity
MDL	Minimum Detection Limit
M	mole/Liter
Pa	Pascal
PF	peroxide fusion
PSD	particle size distribution
PUTTA	plutonium extraction with thenoyltrifluoroacetone
RSD	relative standard deviation
SEM	scanning electron microscope
SRNL	Savannah River National Laboratory
SRR-E	Savannah River Remediation-Engineering
SRR	Savannah River Remediation
TAR	Technical Assistance Request
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TTA	thenoyltrifluoroacetone
TTQAP	Technical Task Quality Assurance Plan
TTR	Technical Task Request
UL	Upper Limit
XRD	X-ray diffraction

1.0 Introduction

The Tank 22 core sampling approach involving both mockup testing in the SRNL 723-High Bay and actual sampling from Tank 22 are detailed in another report ¹. Plant information indicates that the Tank 22 core sample was obtained through the 8-inch North East Riser port of Tank 22 with a waste tank liquid level of 168.3 inches and a sludge mound height of 43.2 inches. A commercially available pond sediment sampling tool was utilized to collect a total core sample length of 14.5 inches. This Tank 22 core sample (HTF-22-18-82) was obtained by Savannah River Remediation Engineering (SRR-E) in October 2018 and delivered to SRNL for characterization. The sampler was inserted through the mound until it reached the bottom of the tank.

The serrated sampling edge/head and core catcher were removed from the sampler assembly in the SRNL Shielded Cells during the extruding of the core sample. Extrusion of the sample was initiated by first removing the serrated sampling head. This was followed by pushing the extrusion pin through the bottom of the cylindrical core sampler. This allowed the top section (top segment) of the core sample to be pushed out without contamination. With the subtraction of 2.5 inches of sample in the serrated sampling edge/head and another 2.5 inches of sample in the core catcher from the 14.5 inches of the core sample, about 9.5 inches of the sample remained intact in the cylindrical shaped section of the sampler assembly. The cylindrical core sample, with a diameter of 1.875 inches, weighed about 1000 grams.

After extruding the entire Tank 22 core sludge sample, three visually different stratification layers of solids in the extruded core material were observed. These layers included a top portion of about two inches of more granular sludge, a middle portion which looked like fine settled sticky sludge material (about 5 inches in length) and a remaining third portion which included a very fine deposit of sticky material. The third bottom segment was primarily retrieved from the serrated end of the sampler head. All three portions of this core sludge sample were fully wet with the top portion looking more porous and granular than the other two portions (see inserts in Figure 1-1). The three portions of this Tank 22 core sample, identified as top, middle and bottom segments, were used for initial physical characterizations. These three segments included: 1) the top 1.5 inches of the upper segment, 2) about 1.5 inches of the middle segment and 3) 2 inches of the bottom segment. The three sections of the Tank 22 core samples were each immediately stored in sealed glass containers to minimize moisture loss.

An accompanying 3-L Tank 22 supernatant (supernate), sample HTF-22-18-117, was later delivered to the SRNL Shielded Cells on December 14, 2018. An earlier 500 mL volume of the Tank 22 supernatant sample, sample HTF-22-18-102, was delivered to SRNL in November 19, 2018. This November sample did not meet the analytical requirements for this Tank 22 characterization because it unexpectedly contained more sludge fraction than supernate (60% sludge slurry by volume and about 40 % true liquid supernate volume after settling). During sampling, the sample vital tether accidentally slipped to a lower than desired sampling elevation in the vicinity of the settled sludge layer.

The Tank 22 core sample characterization efforts are governed by a Technical Task Request (TTR)² and a Task Technical and Quality Assurance Plan (TTQAP)³.

Objectives

The customer requested characterization of Tank 22 core sample included solids distribution, densities and radionuclide concentrations to support determination of the Inhalation Dose Potential (IDP) -specifically for input into an IDP calculation. To support waste removal efforts from Tank 22, the customer also requested the rheological properties of the sludge mound material from the bottom of the Tank 22.

The initial task performed with the three Tank 22 segments involved physical characterizations [bulk densities, particle size distribution (PSD), X-ray diffraction (XRD) and scanning electron microscopy (SEM)] which was designed to be used as a guide on the best approach to characterize the original Tank 22 core sample. The Tank 22

supernatant liquid (supernate), sample HTF-22-18-117, was also characterized for weight percent dissolved solids, density, elementals, total mercury and methyl mercury, free-hydroxide and anions.

The primary objectives of this Tank 22 core sludge sample characterization campaign were to quantify the following for the composite Tank 22 material and the supernate, as summarized in Table 1-1.

- Densities of the “as-received” Tank 22 sludge core sample and the supernatant and its filtrate
- The solids distribution of the sludge slurry (total solids, dissolved solids, insoluble solids, soluble solids and calcined solids)
- Anions in the supernatant (supernatant diluted with both deionized water and dilute nitric acid prior to submittal for analyses)
- Inductively coupled plasma-emission spectroscopy (ICP-ES) elemental analysis suite including Na, K, Al, and other elements (Composite digested by peroxide fusion and aqua regia dissolution methods prior to submittal for elemental and radionuclide content)
- Calculate the iron to silicon and iron to lithium ratios for comparison with other Tank 22 data as presented in previous reports.⁴
- Total mercury in the core sludge and supernate
- Particle size distribution and X-ray diffraction patterns for the Tank 22 core sludge material crystalline mineralogy
- Select radionuclides in the “as-received” composite material to including total gamma, total alpha/ beta.
- 2 wt% settling and rheological properties of the composite Tank 22 sludge in a one-Liter capped graduated cylinder using Tank 22 supernatant.

Composite Tank 22 core sample material has been characterized for physical properties, stable elemental constituents, radionuclides, rheological and settling properties.

Table 1-1 . Characterization of the Composited Tank 22 Core Sample and Supernatant

Analysis	Composite Tank 22 sludge	Supernatant	Method
Particle size distribution	x		Diffraction spec
Wet density	x	x	Gravimetric/volumetric
Dry density	x		Gravimetric/volumetric
Solids distribution	x	x	Gravimetric
Elementals	x	X+	ICP-AES
Total mercury	x	x	DMA
Methyl mercury		x	GC/AFS
Sr-90/Y-90	x		Extraction/beta counting
Cs-137/Ba-137m	x		Gamma scan
Co-60, Ce-144, Eu-154, and Am-241	x		Cs-removed gamma scan
Pm-147	x		Extraction/beta counting
Pu-238, 239/240, 241	x		Extraction/alpha spec
Primary isotopes: Pu-239 and Pu-240.	x		Pu-isotope extraction/ICP-MS (Pu-242-244)
Secondary constituents: Ag, Ru, Rh, Pd, Nd, Tc-99, Th-232, U-233, U-234, U-235, U-236, U-238, Np-237.	x		ICP-MS
Cm-244	x		Extraction/alpha spec
Total alpha/beta	x		LSC
Free hydroxide		x	BT
NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , C ₂ O ₄ ²⁻ , HCO ₂ ⁻ , PO ₄ ³⁻ , F ⁻ , Br ⁻		x	IC
CO ₃ ²⁻		x	TIC/TOC analyzer

+ICP-AES analysis of the supernatant phase will provide aluminum concentrations for projecting aluminate [Al(OH)₄⁻] and other elemental concentrations necessary to calculate slurry constituent concentrations on an insoluble solid basis.

ICP-AES = inductively coupled plasma atomic emission spectroscopy; DMA= direct mercury analysis; GC/AFS = gas chromatography/atomic fluorescence spectroscopy; ICP-MS = inductively coupled plasma mass spectroscopy; LSC = liquid scintillation counting; BT = base titration; IC = ion chromatography; and TIC = total inorganic carbon.




	
Top segment of Tank 22 core sample coming out during extrusion	Extruded Tank 22 core sample without the top section and showing part of the bottom section.
Intentionally left blank	
	Tank 22 core bottom sample; unevenly distributed white specks are visible in the bottom sample

Figure 1-1 Photo images of the “as-received” Tank 22 core sludge material after extrusion in the SRNL Shielded cell

2.0 Experimental Setups/Sample description and Preparations/Methodology

A core sample extruding device was used in the SRNL Shielded Cells to extrude the Tank 22 core sample which was delivered to SRNL in October 2018. Details of the development of settled sludge sampling and Shielded Cells sampler head extraction technique necessary for obtaining a settled sludge sample and extracting the sample for analysis in the SRNL Shielded cells are presented in a memo by D. Krementz, S. H. Reboul[†]. These details also include the Tank 22 core sampler and extruding device construction, and evaluation for performance before use.

2.1 Tank 22 individual segment and supernatant initial characterizations

In preparation for sampling of the three Tank 22 core sludge segments (i.e., top, middle and bottom) for PSD, X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis, about 10 grams from each segment sample was washed with a combined total of 300 mL (per sample segment) of Tank 22 simulant[†] solution and inhibited water (0.01 M NaOH); 100 mL of the simulant was used in three sequential washes with each sample followed by filtration with a 0.45 micron Nalgene filter[®]. Washing with Tank 22 simulant was intended to reduce the concentrations of cesium-137 in the solids by diluting the interstitial liquids. The recovered solids from the washing process were air-dried in the cell for about 72 hours before removing 0.15 ± 0.02 grams from each segment for physical characterizations (PSD, XRD and SEM) as presented in Table 1-1.

[†] Sodium nitrite (35.26g/2L), sodium nitrate (10.96 g/2L), sodium hydroxide (154.16 g/2L), sodium sulfate (1.51g/2L), sodium oxalate (0.69g /2L), and sodium carbonate (6.36 g /2L).

The physical characterization of the Tank 22 supernatant liquid and filtrate was based on the December 2018 sample sent to SRNL. All measurements (weight percent solids and densities) were performed in triplicate. The density of the “as-received” Tank 22 supernate was measured directly on the supernate and the total dissolved solids and filtrate density were determined using filtrate from a portion of the “as-received” supernate. A 0.45 μm Nalgene® filter membrane was used for the liquid /solid separation to obtain the filtrate.

2.2 Tank 22 Core Sample Compositing and Sonication for Particle Size Distribution Analysis

Given that the extruded 9.5-inch core Tank 22 sample had three visually distinguishable segments without a clear line of demarcation to indicate where each segment begins and ends across the entire length of the core sample and based on the physical characterization results for each segment, SRNL, in consultation with the SRR-E customer, decided to blend the three segment materials without taking into consideration the proportional weight of each segment. This compositing approach assumed that the errors introduced in any characterization of the Tank 22 core sample will be comparable to the errors when the three segments are separated and combined proportionally by weight to form the composite Tank 22 sample. This compositing approach maximized the quantity of composite Tank 22 material needed for radionuclide and other physical characterizations of the composite material.

In the compositing of the Tank 22 core sample segments (consisting of a top portion, a middle portion and a bottom portion with very fine deposit of sticky material), 300 mL of Tank 22 supernate filtrate was used as a mixing media to re-suspend, mix, and resettle the consolidated core sample solids. The device and set up presented in Appendix A Figure A1, is the mixing equipment used to homogenize the suspended Tank 22 segments material. This mixing set up consists of a motor driven shaft with standard mixing baffles seating inside a 2-liter Teflon® container bearing the Tank 22 sludge components to be suspended and composited. At the end of several days of mixing, settling and decanting of the Tank 22 supernate, which had been used to re-suspend the core sample particles, an almost equal volume and mass of the Tank 22 supernate filtrate (292 mL) used in the re-suspension had been taken out of the composite sample. The liquid fraction from the suspended solids had been carefully decanted with several settling events for several days to give a Tank 22 composite wet cake solids which was used in all composite sample physical, chemical and radiological characterizations.

This compositing approach ensured that the degree of saturation of the composited material was not significantly different from the original saturation of the three Tank 22 individual segment materials used in the compositing.

A small tabletop continuous wave sonicator bath (model PC3 from L&R Ultrasonics, New Jersey), with a 0.5 minute-timer and peak wattage of 50 Watts at 40 KHz was used in the ultrasonic treatment of the washed Tank 22 composite core sample to de-agglomerate the particles. The internal dimensions of the ultrasonic device (sonicator) was 15 x 8.6 x 6.3 cm with a tank capacity of 0.8 L. During the sonication process, about 0.15 grams of the washed Tank 22 composite core sample or other samples under investigation was put into the ultrasonic bath already containing 20 mL of Tank 22 filtered simulant and the mixture mechanically stirred. The sonication of each sample was performed for 120 second. The sonication power density was 2.5 Watts/mL (50 Watt/20 mL) and the power density-time was 300 Watts/mL* sec ((50 Watts/20 mL) *120 seconds)). At the end of each ultrasonic treatment, the 20 mL mixture sample in the ultrasonic bath was transferred into a green shielded cell poly-bottle for cell exit and delivery to Analytical Development (AD) for particles size analysis to be performed within an hour of the sonication process.

2.3 Settling and Rheological Properties of 2 wt % Composite Tank 22 Sludge Material

A settling test slurry was prepared using a combination of composite Tank 22 sludge material containing 2 wt% insoluble solids and 98 wt.% Tank 22 supernatant liquid. The solids settling test was performed in a

graduated cylinder capped to prevent evaporation of supernatant water. The volume capacity of the graduated cylinder was equivalent to the test slurry volume (as mentioned above, the targeted test slurry volume was one liter). The target 2 wt % insoluble solids Tank 22 composite sample used in the preparation of the settling slurry was generated using 50.13 grams of composite Tank 22 sludge without any type of washing to get insoluble solids; since the determined wt% total insoluble solids for the composite Tank 22 sample was 39.90 wt.% and given that the total volume of the test slurry was 1000 g (density of supernatant ~ 1.0 g/mL) with 20 grams constituting 2 wt% of the total volume. Therefore, 20 grams of insoluble solids corresponds to 50.13 grams of composite Tank 22 sludge (20/0.399).

After mixing the settling test slurry to fully suspend all insoluble solid particles, settled sludge volumes were recorded at the following targeted times: every 3 minutes for the first 60 minutes; every 10 minutes for the second 60 minutes; every 30 minutes for the next 2 hours after the initial two hours and every 60 minutes for the remainder of 4 hours. This gives a total of 8 hours of settling within the first day of the settling test. For the remainder of the settling test time of 92 hours, settled sludge volumes were recorded nearly every 24 hours.

At the completion of the settling test (~100 hours), the supernatant phase was decanted off the top of the settled sludge layer, and the yield stress and consistency of the settled sludge was measured, based on flow curves depicting shear stress as a function of shear rate. The weight percent and volume percent of the settled insoluble solids were also determined.

2.4 Preparations and Rheological Properties of 22 wt % Composite Tank 22 sludge material

A 22 wt % insoluble solids slurry was prepared directly using reconstituted composite Tank 22 material containing 22 wt % insoluble solids and 78 wt % Tank 22 supernatant liquid, without washing of any kind. The rheology measurements on the 22 wt % slurry was determined to obtain the yield stress and consistency based on flow curves depicting shear stress as a function of shear rate. The volume percent of the insoluble solids was also determined for the 22 wt % sludge slurry.

Because of insufficient intact composite Tank 22 sludge material left at the end of the processing and characterization of the Tank 22 composite material, it became necessary to resuspend the sticky Tank 22 composite material found in various containers used in the Tank 22 composite material processing and characterizations. This reconstituting of the composite material to obtain enough material necessary for the preparation of the 22 wt % sample involved the resuspension of all trace Tank 22 composite material in different containers using a total of 150 mL volume of the Tank 22 supernatant liquid. In this process, the supernate was used to wash and rinse all the Tank 22 composite material containers to recover all traces of the material into a single container. The single container with the recovered Tank 22 composite sample and a layer of Tank 22 supernate was left to settle for 72 hours. After this settling time, most of the supernate was drained away leaving only the moist reconstituted Tank 22 composite material in the container. The resulting composite material was then air-dried in the shielded cell for 72 hours. After drying, the wt.% total solids and wt % insoluble solids for this reconstituted composite Tank 22 sample was determined. Taking into consideration the measurement uncertainty involved in the determination of the weight percent total solids and insoluble solids, the wt % insoluble solids determined for this reconstituted composite Tank 22 sample (38.26 wt %) is comparable to the wt % insoluble solids of the original Tank 22 composite material (39.90 wt %) before resuspension.

Over all, the rheology of three reconstituted composite Tank 22 samples were measured. First, material following the settling test was removed from the settling vessel (1-L graduated cylinder). The sample was not decanted to the maximum possible amount to ensure the material could be removed from the graduated cylinder. For this sample 1, the post settling slurry, measured wt % total insoluble solids was 10.6%. The second sample was prepared by combining a composite of Tank 22 solids with supernate. 22 wt % insoluble solids was targeted. As shown later, this target of 22 wt % insoluble solids was not attained; what was obtained turned out to be 18.8 wt % solids (a description of the calculations to make this slurry can be found in Appendix A). For the third sample, after rheological measurements, Samples 1 and 2 above were allowed to settle overnight. As much supernatant was decanted as possible (without removing insoluble solids). The samples were then combined to form sample 3, which contained 23.2 wt % insoluble solids. Details of the rheological sample preparations and methodology are presented in Appendix B.

The total solids of each sample were measured, and the insoluble solids was calculated using the dissolved solids of the supernate data presented in Table 4-6.

3.0 Data Quality, Blank and Reference Material Evaluations

Appendix C contains the SRNL Analytical Development Laboratory Information Management System (LIMS) numbers for tracking the analytical data presented in this report. The sample analysis completion dates are tracked in LIMS. Digestion methods such as AQR and PF were performed in the SRNL Shielded Cells prior to taking representative sample aliquots out of the cells for analyses.

In addition to reagent blanks used by the SRNL AD Group, one solid-phase reference material was used during the characterization of Tank 22 composite samples. The solid-phase reference material was an analyzed reference glass (ARG). The elemental chemical composition of the ARG is presented in Appendix A, Table A4. Prior to the processing of the Tank 22 samples, ARG material in a 250-mL capacity poly-bottle was placed at a strategic location in the Shielded Cells to ensure that the material was exposed to the same cell environments as the Tank 22 samples. The ARG container held about 20 grams of the material. The container was opened when the Tank 22 samples were being air-dried or processed and closed at the end of each day of work in the Shielded Cells. At the end of each Tank 22 sample preparations or digestion (air-drying, aqua regia and peroxide fusion digestions), the ARG material was also prepared in the same manner as the preparation of Tank 22 samples and submitted for the same analyses as the actual samples from Tank 22. The ARG sample was used to gauge/ control cell contaminations, if any, in the Shielded Cells.

Acidified (dilute nitric acid) distilled and de-ionized water was used as the liquid reagent media and blanks for digestions performed in the Shielded Cells. The absence of radionuclides in the reference material allowed the materials to additionally be utilized as blanks for radiochemical analyses.

3.1 Data Quality for Routine Radionuclide Constituents

The ICP-MS results are given for each atomic mass and in most cases each mass number represents only one isotope. An example of an exception is mass 238, since both uranium and plutonium are represented by this mass number. However, since the mass contribution of U-238 is significantly greater than that of Pu-238, the 238 signal is used to quantify U-238, not Pu-238. For this reason, Pu-238 was determined by plutonium extraction with thenoyltrifluoroacetone (PUTTA-chemical separation coupled with alpha spectroscopy). See Appendix B for summaries of the methods. In cases where ICP-MS and radiochemistry data give similar results for a species, radiochemistry was typically selected due to better sensitivity and precision.

Routine radionuclide analytical results are also compared between different methods used for characterization of Tank 22 composite samples, specifically comparing results from ICP-MS with results from other methods of analyzing for the routing radionuclide. For example, analytical results for Pu-239 and Pu-240 can be obtained from ICP-MS and from a better analytical technique for these plutonium isotopes using Pu-tracer and plutonium extraction with thenoyltrifluoroacetone (TTA) followed by counting for Pu-239/240.

Using these types of dual analytical approaches (ICP-MS and extraction/ICP-MS, Cs-removed gamma scan, Am/Cm and gamma scan and ICP-MS/ICP-ES), the analytical results for select Tank 22 composite routine radionuclide analytes (Pu-239, Pu-240, Am-241, Am-243 and total Th-232 (assuming no U-232)) have been compared as summarized in Appendix A (Tables A1, A2 and A3) along with the analytical % difference of the values based on the two different methods; where the analytical % difference for each pair of methods is defined as the [(analytical results difference for each isotope by the two methods/average of the analytical results) *100].

The analysis results from direct ICP-MS measurements and separation followed by ICP-MS for Pu-239 in digested Tank 22 composite sludge are quite comparable. The analytical % difference in the analytical result for Pu-239 by the two analytical methods is 10.6% and similarly, the analytical % difference in the analytical result for Pu-240 by the same two analytical methods is 1.5 %, as shown in Appendix A, Table A1.

As shown in Appendix A, Table A2, the analytical results for Am-241 by both Cs-removed gamma scan and Am/Cm separations methods yielded acceptable and comparable results for this isotope. The analytical % difference based on the two methods for Am-241 was 9.0%. The analytical results for Am-243 using these same methods, Cs-removed gamma scan and Am/Cm separations gave results which were below the analytical expectations. In both cases, the analytical result by these two methods were about the same order of magnitude; the % analytical difference was 23.9%. The pooled one sigma percent counting uncertainties for Am-243 by Am/Cm and Cs-removed gamma scan methods were 17.57 and 12.93%, respectively. The counting uncertainties for this isotope are relatively significant for both methods. So, this large analytical difference between the two methods for Am-243 is not unexpected for this isotope. Therefore, it can be concluded that both methods are relatively good in the quantification for Am-243 in the Tank 22 composite sample although the distribution of this isotopes in the composite Tank 22 samples may not have been uniform.

A comparison of total elemental thorium mass concentration obtained from ICP-MS and ICP-ES analysis of Tank 22 composite material, as presented in Appendix A Table A3, shows an excellent agreement, 2.11E-01 and 2.09E-01 wt %, respectively, for the two methods analytical result for Th-232 weight percent total solids. The two values only differ by 1.0%. This relatively small difference provides confidence that the isotopic measurements of ICP-MS and the elemental measurements by ICP-ES are accurate.

3.2 Data Quality and Presentations for Elemental Constituents

A non-radioactive reference material, ARG standard, was digested and analyzed along with the Tank 22 composite materials. Analytical results for the elemental analyses of the ARG reference material were compared against the known reference values⁵.

This comparison of the laboratory results for the cations present in the ARG reference material shows that the laboratory analytical results are in good agreement with the expectations. The typical percent relative deviation (%RD defined as [difference/mean] *100 or the analytical result % difference between the two methods (ICP-MS and ICP-ES) is defined as the [analytical results difference for each cation by the two methods/average of the analytical results] *100.) averages less than 5%. Looking at the analytical results

for the 11 select elemental constituents of the ARG reference sample, Appendix A Table A4, the percent relative deviation for each of the 11 constituents was below 5% and ranged from a low of 0.15 to 4.65 %.

Elemental analytical results were also compared between different methods used for the characterization of Tank 22 composite samples, specifically comparing results from ICP-MS with results from ICP-ES. The total concentrations of select cations (Ba, Co and La) were calculated from ICP-MS analytical data and the resulting concentration values compared with the ICP-ES corresponding results presented in this report. The analytical result % difference for the above cations are presented in Appendix A Tables A5, A6 and A7, respectively. The analytical result % difference between these two complimentary methods of quantifying for Ba, Co and La were 0.7%, 15.6% and 0.9%, respectively. These ICP-ES and ICP-MS analytical results for total Ba, total Co and total La are about the same order of magnitude and the analytical result % differences are within the analytical expectations for these two methods.

3.3 Format of the Reported Results

Mean results, based on the average of all applicable analytical determinations, are reported in this document, along with the percent relative standard deviation (%RSD). The %RSD provides an indication of the measurement variation between triplicate determinations but is typically not an indicator of analytical accuracy. In general, the one sigma analytical uncertainty as reported by Analytical Development was 10%, although it was sometimes lower or higher. Specifically, the one sigma analytical uncertainties reported by AD were: a) ~10% for base titration, IC, ICP-AES, ICP-AES-S, ICP-MS, and TIC/TOC analyses; b) ~20% for DMA analyses; and c) ~5% for Cs-137 determined by gamma spectroscopy. As such, only one to two of the leading digits reported for the AD analysis results should be considered significant.

In the Tank 22 composite sample characterization results presented in tables in this report, values preceded by “<” (less than sign) indicate values were below minimum detection limits (MDLs), and values proceeded by “≤” (less than or equal to sign) indicate that for replicates, at least one of the analysis values was above the instrument detection limit or MDL and at least one of the analysis values was below the detection limit or was an upper limit. Thus, where replicate analyses were both above and below the detection limit, the average of all replicates above and below the detection limit is given a “≤” sign precedes the average value. The standard and percent relative deviations were calculated only for values that were all above the detection limits. The minimum detectable activity (MDA) is defined as the value above which instrument signal can be considered quantitative relative to the signal-to-noise ratio and the upper limit (UL) is defined as activity observed but biased high due to spectral interference or blank contamination. The detection limit (DL) as used in ICP-ES analyses is equivalent to three times the standard deviation of the blank measurements.

Where applicable, the one sigma percent counting uncertainty for each radionuclide reported in the tables is based on the pooled estimate derived from the individual uncertainties for each replicate measurement for that radionuclide using a Microsoft Excel function, $\text{SQRT}((\text{SUMSQ}(x_i)/n))$, where n is the number of replicates and x_i is the individual uncertainty associated with each radionuclide for each analysis. Here it is assumed that the radio-analytical processes, be it counting or other techniques, are of the same precision for each individual measurement.

Occasionally, situations may be encountered where the samples prepared and analyzed in triplicate gave mixed results with one or two of the triplicate analyses results being less than the MDA. In these cases, the reporting of the one sigma percent uncertainty is presented in a slightly different format. In this situation, the individual percent uncertainty associated with each analysis for that radionuclide is reported along with MDA, upper limit values or the DL values as indicated by the analytical method.

In most cases, the preparations for analysis involved the digestion of samples by both Aqua Regia Digestion (AQR) and Sodium Peroxide/Hydroxide Fusion (PF) digestion methods followed by ICP-MS or ICPES analyses. However, the analytical results occasionally are different in magnitude. Thus, the data reported is based on the method with the least uncertainty in the results reported. In some cases, the PF digestions have lower uncertainty values and are thus preferred and reported.

4.0 Results and Discussion

Laboratory analyses were performed on the Tank 22 composite core sludge sample aliquots and Tank 22 supernatant liquid. A combination of routine dissolution/measurement techniques and “tailor-made” digestion/isolation/analysis methods were used to quantify several stable constituents (elements and anions) and select radionuclides. Details of most of the analytical methodologies including weight percent solids and density determinations are summarized in Appendix B. Other physical characterizations of the Tank 22 composite sludge sample included PSD, XRD, SEM and rheological properties. Tank 22 supernatant (supernate) liquid, Tank 22 core sample segments, and Tank 22 composite sample data are presented in the following tables and figures: Table 4-1 (supernate elementals), Table 4-2 (supernate select radionuclides), Table 4-3 (Supernate corrosion chemistry and mercury), Table 4-4 (Tank 22 core segment densities), Table 4-5 (Tank 22 core segment solids distribution), Figure 4-1 (Tank 22 core segment PSD), Figure 4-2 (Tank 22 core segment X-ray diffraction patterns), Figure 4-3 (Tank 22 core segment SEM images); Table 4-6 (Tank 22 composite sample densities and solids distribution), Figure 4-4 (Tank 22 composite sample PSD with and without sonication), Figure 4-5 (Tank 22 slurry supernate sample PSD with and without sonication), Figure 4-6 (Tank 22 composite sample X-ray diffraction pattern), Table 4-7 (Tank 22 composite sample elemental composition), Table 4-8 (Tank 22 composite sample noble metal composition), Table 4-9 (Tank 22 composite sample calcined solids composition), Table 4-10 (Tank 22 composite sample select radionuclide composition), Figures 4-7 and 4-8 (Tank 22 2 wt% insoluble solids initial 8 hours and 100 hours final settling plots) and Table 4-11 (Tank 22 rheological data).

4.1 Tank 22 Supernate Characterization

The “as-received” Tank 22 supernate was analyzed for the following parameters: filtrate elementals, select radionuclides, anions, methyl mercury and total mercury, solids distribution (dissolved solids), and supernate and filtrate densities. The average analytical results are presented in Tables 4-1, 4-2, 4-3, 4-5 and 4-6, respectively.

The free OH^- concentration (< 0.207 molar) was used to calculate the pH value of < 13.3 for the Tank 22 supernate filtrate as reported in the Table 4-3. The pH result was calculated using the following equation:

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

The measured cesium-137 activity in the supernate filtrate was $3.07\text{E}+07$ dpm/mL with 0.65 % RSD.

To check the results, a cation-anion normality balance was performed with the supernate analytical data on cations and anions. The normal concentrations of cations (mainly $\text{Na}^+ + \text{K}^+ + \text{Fe}^{3+} + \text{Li}^+ + \text{Mg}^{2+}$ and Mn^{2+}) were summed, as were the anions (NO_3^- , NO_2^- , SO_4^{2-} , HCO_3^- , Cl^- , CO_3^{2-} , PO_4^{3-} , AlO_2^- , $\text{C}_2\text{O}_4^{2-}$ and free OH^-). The two sums were compared. For the Tank 22 supernate sample, the cations summed to 0.718 M, while the anions summed to < 0.803 M. The differences between the cation and anion molarity values are within $\pm 10\%$ of each other, which is good when one takes into consideration that the nominal uncertainties (1 sigma) for ICP-ES, IC and OH analyses methods are about 10%. The small difference can be attributed to analytical uncertainties and analyte detections limitations.

Additional Tank 22 supernate characterization for radionuclides, using this same Tank 22 supernatant liquid (sample HTF-22-18-117), has been presented in another report.^{6, 7}

Table 4-1 Elemental Analyses of Tank 22 Supernate (Filtrate)

Analyte	Average Concentration M	%RSD n = 3
Ag	<2.70E-06	-
Al	2.15E-03	2.7
B	<2.97E-03	-
Ba	<4.89E-07	-
Be	<1.49E-06	-
Ca	1.22E-05	7.1
Cd	<7.97E-07	-
Ce	<1.95E-05	-
Co	<4.18E-06	-
Cr	<4.74E-06	-
Cu	<8.45E-06	-
Fe	3.56E-05	2.6
Gd	<3.13E-06	-
K	<6.68E-04	-
La	<1.77E-06	-
Li	4.26E-03	1.8
Mg	2.41E-06	4.2
Mn	1.22E-06	2.6
Mo	<2.14E-05	-
Na	7.13E-01	2.2
Ni	<6.48E-06	-
P	<3.45E-04	-
Pb	<6.03E-05	-
S	<5.28E-03	-
Sb	<2.28E-05	-
Si	5.74E-03	2.5
Sn	<5.69E-05	-
Sr	<2.22E-05	-
Th	<8.68E-06	-
Ti	<9.35E-07	-
U	<3.19E-05	-
V	<1.76E-06	-
Zn	<1.37E-05	-
Zr	<9.82E-07	-

n = number of analytical replicates.

Table 4-2 Radionuclide Analyses of Tank 22 Supernate (Filtrate)

Analyte	Average Concentration M	%RSD n = 3
Tc-99*	1.50E-06	1.8
Th-232	<7.24E-07	-
U-233	<4.80E-08	-
U-234	<4.78E-08	-
U-235	1.48E-07	6.3
U-236	<4.74E-08	-
Np-237	<4.72E-08	-
U-238	2.09E-05	6.4
		-
Cs-137, dpm/mL	3.07E+07	1.1

* Tc-99 analytical result is based on ICP-MS method and may be biased high due to mass 99 contributions from ruthenium and molybdenum isotopes.

Table 4-3 Corrosion Chemistry Analyses Results for Tank 22 Supernate (filtrate)

Analyte	Average Concentration M	%RSD n = 3
Fluoride, F	<1.09E-02	-
Formate, HCO₂¹⁻	<4.62E-03	-
Chloride, Cl⁻	<5.85E-03	-
Nitrite, NO₂⁻	3.12E-01	1.8
Nitrate, NO₃⁻	8.53E-02	1.6
Phosphate, PO₄³⁻	<2.19E-03	-
Sulfate, SO₄²⁻	3.18E-03	1.9
Oxalate, C₂O₄²⁻	<2.36E-03	-
Bromide, Br¹⁻	<2.60E-03	-
Free Hydroxide, OH⁻	<0.207	-
Carbonate, CO₃²⁻	9.49E-02	1.2
Aluminate, Al(OH)₄¹⁻	2.15E-03	2.7
Methyl mercury cation	1.03E-04	4.3
Total mercury	5.67E-04	5.9
pH (calculated value)	<13.3	-
*Inorganic carbon, gC/L	1.14E+00	1.2
Organic carbon, gC/L	< 4.15E-01	-
Total carbon, gC/L	<1.25E+00	-

*Gram carbon per Liter (gC/L)

4.2 Tank 22 Segment Sample Characterizations

The physical characterizations which were performed on the core Tank 22 segment and composite sample solids and supernate are listed in Table 1-1. Densities for the Tank 22 segment samples were determined gravimetrically under ambient cell conditions at 26 °C, and the results of these measurements are presented in Table 4-4.

The weight percent total solids, W_{ts} , was measured for each of the three segments of the core sample and the composite Tank 22 core sample. The filtered supernate sample was used to determine the weight percent dissolved solids, W_{ds} . The insoluble solids and soluble solids were calculated from the total and dissolved (filtrate) solids using the following equations:

$$W_{is} = \frac{W_{ts} - W_{ds}}{100 - W_{ds}} \cdot 100 \quad (1)$$

$$W_{ss} = W_{ts} - W_{is} \quad (2)$$

where: W_{ds} = weight fraction dissolved solids in the supernate (filtrate),
 W_{ts} = weight fraction total solids (soluble and insoluble) in the slurry,
 W_{is} = weight fraction insoluble solids in the slurry, and
 W_{ss} = weight fraction soluble solids in the slurry.

Table 4-4 Tank 22 Core Segment Sample Densities

Sample	Average Density, g/mL	Standard Deviation	%RSD, n=3†
Top Segment	1.67	0.07	4.20
Middle Segment	1.58	0.02	1.27
Bottom Segment	1.48	0.06	4.05

† where “n” is the number of replicates

The PSD information, as presented in Figure 4-1, confirms previous conclusions (visual observations and weight percent total solids) on the stratification of the Tank 22 core sample; the top segment is grainy while the bottom segment is composed of fine silt and the middle segment is somewhere between these two extremes. The larger particles in the top and middle segments may be considered an artifact of sampling resulting from compression/compaction of these two regions during sampling and thus leading to the agglomeration of smaller particles to form larger ones. On the other hand, it is also possible that with age, particle deposition effect takes place in the Tank 22; where smaller particles tend to percolate downwards with time, leaving larger particles resulting from physical aggregation at the top regions of the mound. This behavior would seem to be prevalent under conditions where there is poor in-tank mixing.

The weight percent solids distribution data for these three Tank 22 core segment samples is presented in Table 4-5. The %RSD for these triplicate measurements are less than 10%, with the %RSD for weight fraction soluble solids (W_{ss}) being the exception. The %RSD for the weight fraction soluble solids (W_{ss}) ranges from 27 to 91% for the three Tank 22 segments. The large %RSD from W_{ss} calculations may indicate that within each Tank 22 core segment sample, the relative quantity of dissolved solids or the distribution of dissolved solids in the interstitial matter may not be the same. It is also worth noting that W_{ss} is based on the difference or subtraction of weight fraction total solids from weight fraction insoluble solids, as shown in Equation 2 above. Therefore, measurement uncertainties due to the parameters in Equation 2 amplify the %RSD for weight fraction soluble solids.

Table 4-5 Tank 22 Supernatant and Segment Sample: Total Solids Distributions (wt%)

Type	Average wt %	Standard Deviation	%RSD n=3†
Supernate filtrate Dissolved solids	4.34	0.09	2.07
W _{ts} (top segment)	45.05	1.31	2.91
W _{ts} (middle segment)	30.62	2.00	6.53
W _{ts} (bottom segment)	24.00	0.66	2.75
W _{is} (top segment)	42.55	1.38	3.24
W _{is} (middle segment)	27.47	2.09	7.61
W _{is} (bottom segment)	20.55	0.69	3.36
W _{ss} (top segment)	2.50	1.91	76.44
W _{ss} (middle segment)	3.16	2.89	91.46
W _{ss} (bottom segment)	3.46	0.95	27.46
NaCl Reference Standard (5 wt%)	4.92	0.16	3.25

† where “n” is the number of replicates

4.2.1 Particle Size Distributions: Segment Samples

Particle size analysis results are provided in Figure 4-1 for the three segment samples. The PSD for the top segment sample from the Tank 22 core sample is skewed in favor of higher particle sizes in the range of 522 to more than 1000 microns, as shown in Figure 4-1 insert A. The integrated peak summary volume percent is 54% for particles with diameters greater than 584 microns and less than 20% for particles diameters less than 90 microns. The average particle size for this top segment sample is 368 ± 317 microns. It is worth noting that frit material sizes range from 80-200 mesh and an 80-mesh screen has an opening of 177 microns.

For the middle segment sample from the Tank 22 core sample, the PSD is also skewed towards higher particle sizes in the range of 111 to just about 1000 microns. However, the integrated peak summary volume percent for particles with diameters 422 microns and higher is only 33% and about 41% for particles diameters less than 64 microns. Therefore, there are more particles in the middle segment sample with lower particle sizes when compared with top segment sample (Figure 4-1, insert B). The average particle size for the middle segment sample is 175.3 ± 211 microns.

The PSD for the bottom segment sample from the Tank 22 core sample shows a distribution of particles with the mean around 45 microns and a standard deviation of 59 microns (1-sigma). The integrated peak summary volume percent is 22% for particles with diameters greater than 157 microns; 24% for particles with diameters less than 30 microns and 22% for particles with diameter less than 9 microns. Therefore, there are more particles in the bottom segment sample with lower particle sizes when compared with even the middle segment sample (Figure 4-1, insert C).

The PSD information, as presented in Figure 4-1, confirms previous conclusions (visual observations and weight percent total solids) on the stratification of the Tank 22 core sample; the top segment is grainy while the bottom segment is composed of fine silt and the middle segment is somewhere between these two extremes.

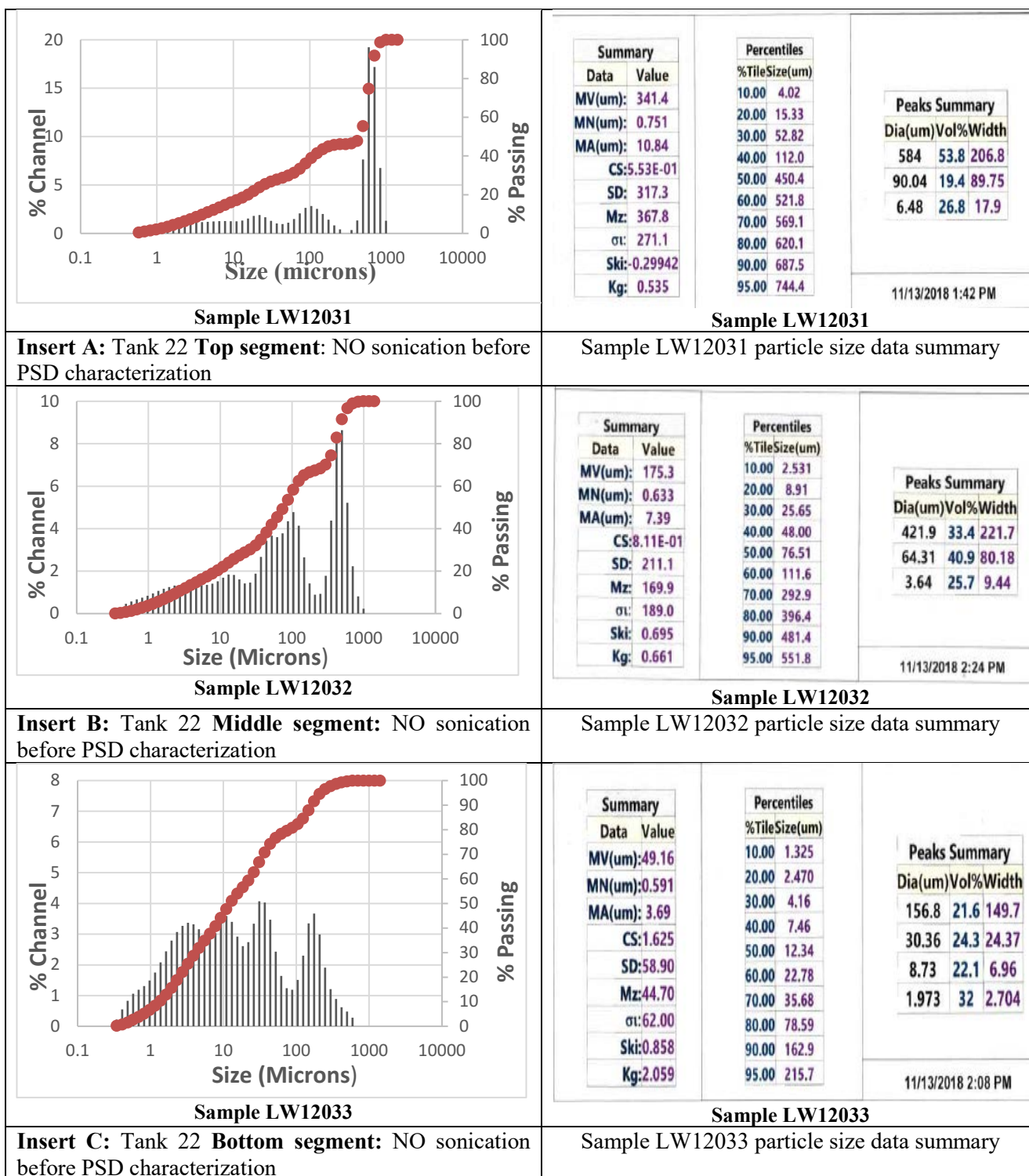


Figure 4-1 Particle size distributions for insert A top, Insert B middle and Insert C bottom segments of the Tank 22 core sample solids. The mean diameters (MV) are 341.4, 175.3 and 49.16, respectively

4.2.2 X-Ray Diffraction: Segment Samples

The results of the XRD analyses on the three segments of the core sample solids are shown in Figure 4-2. All three segments of the Tank 22 core sample contain the same types of mineral phases, which are mainly aluminosilicate minerals [nitrated cancrinite ($\text{Na}_{7.6}(\text{AlSiO}_4)_6(\text{NO}_3)_{1.6} \cdot 2\text{H}_2\text{O}$), sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12} \cdot 12\text{H}_2\text{O}$ and $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$), boehmite ($\text{AlO}(\text{OH})$), mercuric minerals [montroydite ($\text{Hg}_2\text{NCl} \cdot \text{H}_2\text{O}$) and mercuric oxide (HgO)], iron (Fe_2O_3) and quartz mineral (SiO_2). The bulk of the three segments is made up of these five crystalline minerals.

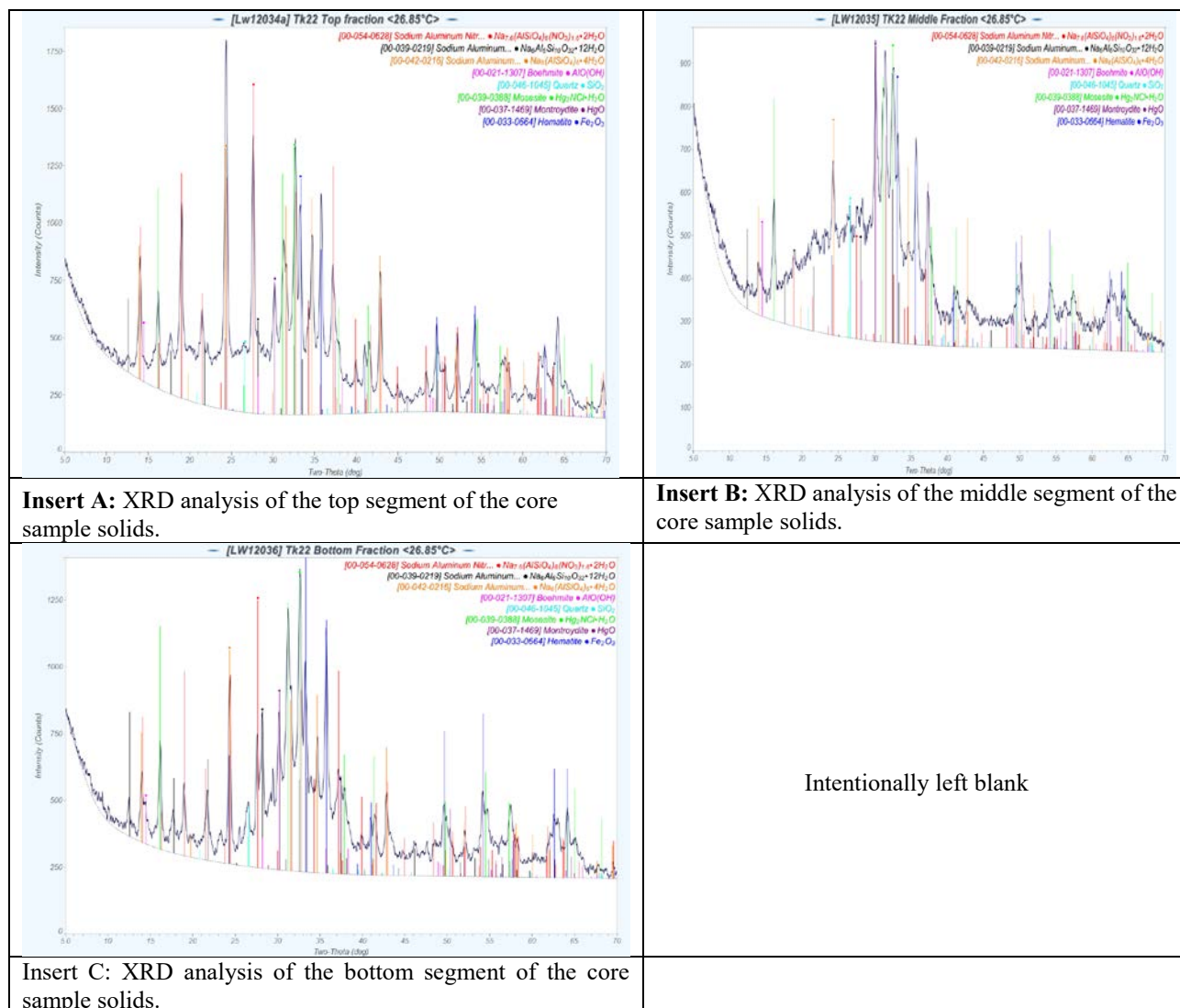


Figure 4-2 X-Ray Diffraction Patterns for Tank 22 Segment Samples (top, middle and bottom segments)

4.2.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy: Segments Samples

SEM and energy-dispersive X-ray spectroscopy (EDS) were used to evaluate the elemental makeup of the various core segments. The results of the SEM/EDS analyses are consistent with the XRD and PSD analyses and are summarized below.

- The particle sizes observed via SEM are consistent with measured PSDs.

- Images of particles from the top segment reveal a graininess in the larger particles that may be indicative of agglomeration of smaller particles (Figure 4-3, insert a) due to the compression of the mound layers during sampling or natural deposition and accumulation with age.
- The largest relative concentrations of mercury (Hg) were observed in the top segment (Figure 4-3, insert b). Mercury is associated with the bright spots in back-scatter detector images (BSD).
- Areas with less Hg have higher relative concentrations of Fe and Mn compared to many other elements.
- The most visibly well-defined crystals in the three samples appeared in the top segment (Figure 4-3, insert c).
- The BSD images of the crystalline areas suggest a high atomic number (Z) material (e.g., Hg) is associated with these crystals (Figure 4-3, insert d).
- Spherical nodules with high relative concentrations of sodium, manganese, and iron ($\text{Na} \approx \text{Mn} > \text{Fe}$) were observed in the middle sample (Figures 4-3 inserts e, and f).
- Less Hg was observed in the middle segment than in the top (Figure 4-3, insert g).
- Aside from the spherical nodules, no well-defined crystalline material was visible in the middle segment at the magnification levels used.
- The least amount of Hg was observed in the bottom sample (Figure 4-3, insert h).
- No visibly well-defined crystals were observed in the bottom segment.
- The elemental ratios of Si, Fe, Al, Mn and Na are approximately constant throughout all segments for areas that do not have significant Hg content.

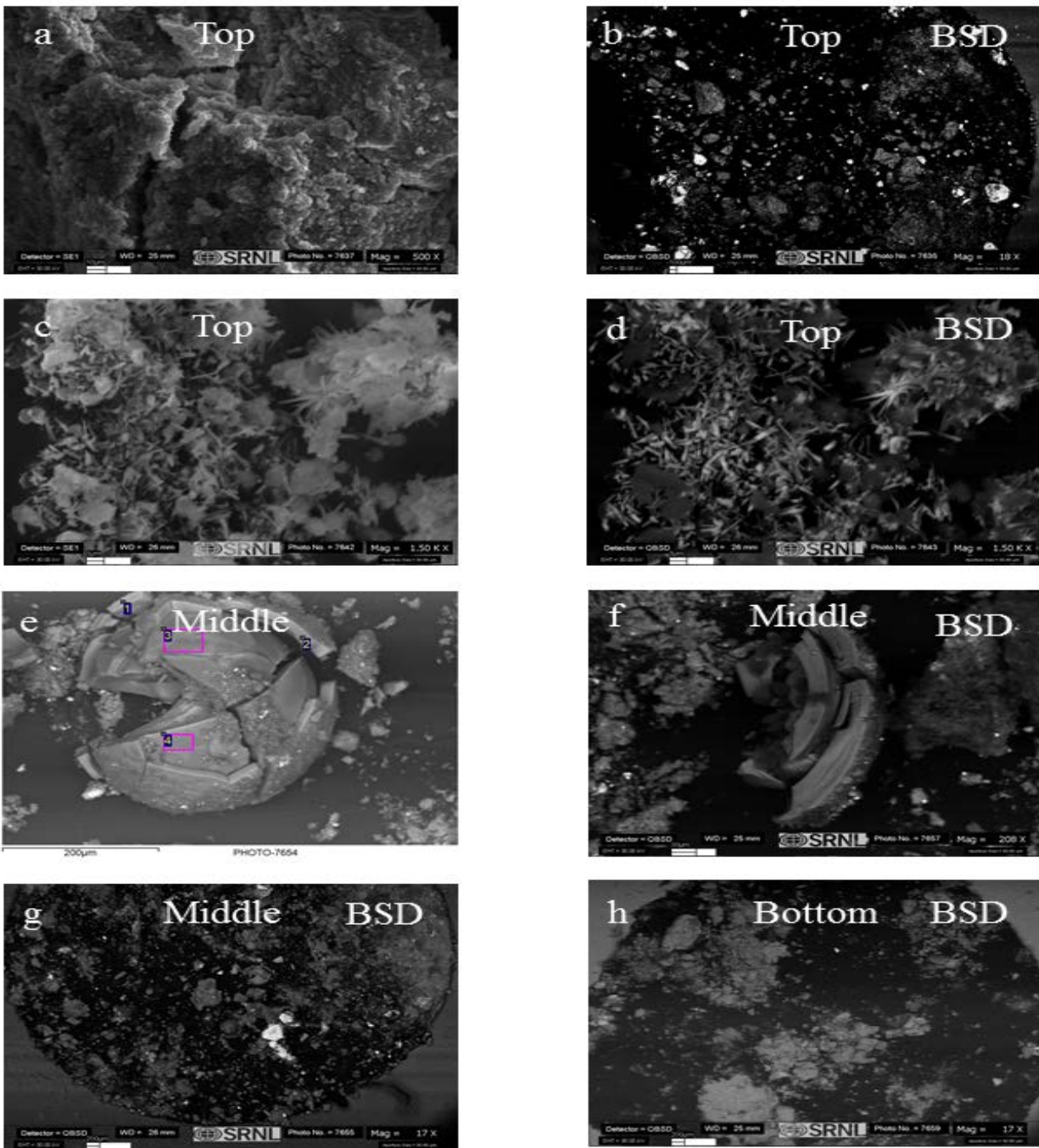


Figure 4-3 a-h: SEM images of the various regions examined from each segment (BSD = back scatter detector, an SEM method in which the image contrast is more dependent on the atomic number of the material being analyzed. Higher Z materials are brighter in such images.)

4.3 Tank 22 Composite Sample Characterizations

4.3.1 Composite Tank 22 Core Sample and Supernatant: Densities and Solids Content

The density determination methods (bulk wet, supernatant and filtrate densities) for both the composite Tank 22 sample and supernate samples are described in Appendix B. The dry density of the composite Tank 22 sludge was obtained after drying a known amount of the material at 110 °C for 72 hours (constant container volume) till constant weight of the dry material was obtained.

The particle density (insoluble mineral solids density for washed and air-dried Tank 22 sludge) was determined by using liquid displacement method with low density/viscosity pure silicon fluid (polydimethylsiloxane; Cas No: 63148-62-9) as the displaced liquid media in a calibrated and graduated glass cylinders. The viscosity, specific gravity and flash point of the silicon fluid was 5 centistokes (cSt), 0.918 and 135 °C, respectively. In this determination of the particle density of Tank 22 washed insoluble solids, each graduated glass cylinder (25 mL capacity glass cylinder with larger interior diameter and a 15 mL capacity glass cylinder with smaller interior diameter) was preloaded with silicon fluid up to known initial levels, 13.4 ± 0.1 mL and 5.2 ± 0.1 mL, respectively, outside the Shielded Cells. While inside the Shielded Cells, known masses of dry Tank 22 insoluble sludge material (2.510 and 1.612 g, respectively) was put into each of the graduated cylinder and the volume of silicon displaced by the insoluble sludge was noted. Knowing the volume of silicon displaced in each cylinder and the corresponding mass responsible for the displacement, the particle density of the insoluble sludge was calculated. These density determinations in the SRNL Shielded Cells occurred at cell temperature of 26 °C.

As expected, an attempt to determine the particle density of the same washed and air-dried Tank 22 sludge using Tank 22 supernatant liquid was not possible because of wetting issues. When known weights of the washed and air-dried Tank 22 sludge were dropped inside graduated cylinders already containing the wetting agent (Tank 22 supernatant liquid), the majority of solid particles failed to mix easily with the supernatant liquid, possibly because of trapped air bubbles in the dried sludge particles or oxidized sites on the particles which could not be wetted easily by the supernatant liquid. As a result, most on the solids particles were still floating on top of the liquid in the graduated cylinders even after 96 hours, as shown in Appendix A, Figure A 2. Unlike particles density measurement with low molecular weight silicon material, where the material instantaneously sank to the bottom of the silicon medium and accompanied by the displacement of measurable volume of the silicon, there was no measurable displacement of the Tank 22 supernatant fluid. After about 120 hours of the test some of the solids particles now imbibed enough liquid and descended to the bottom of the graduated cylinder (Appendix A, Figure A 2, insert C).

The densities and solids distributions for the Tank 22 materials are presented in Table 4-6. The weight percent insoluble solids and soluble solids are calculated quantities from the measured wt % total and dissolved solids (equations 1 and 2 in section 4-2).

Table 4-6 Composite Tank 22 Core Sample Densities and Solids Content

Analyte	Average	%RSD, n = 3	Units
Tank 22 Supernatant density (As-received)	1.008	0.2	g/mL
Supernatant filtrate density	1.003	0.6	g/mL
Composite Tank 22 sample wet bulk density	1.54	13.0	g/mL
Composite Tank 22 sample dry density	0.66	19.7	g/mL
Composite Tank 22 insoluble solid particle density	3.18	1.92	g/mL
Total solids, wt % of sludge	42.51	8.5	Wt %
Dissolved solids, wt % of supernatant	4.35	2.2	Wt %
Insoluble solids, wt % of sludge	39.90	NA*	Wt %
Soluble solids wt % of sludge	2.61	NA*	Wt %

*NA = calculated data.

4.3.2 *Composite Tank 22 Core Sample: Particle Size Distribution*

The PSD for the Tank 22 segment samples, mainly the top and middle segments, as described in section 4.2.1 above, prompted further PSD characterizations with sonication of the samples to verify whether the formation of larger particles in the 200-1000 microns range were due to simple agglomeration of smaller particles due in part to sampling protocols or any other mechanisms.

Tank 22 composite core sample was double washed with Tank 22 simulant followed by washing with inhibited water (0.01 M NaOH). Approximately 0.1 gram of the resulting wet solids was put into a green shielded bottle and 10 mL of filtered Tank 22 simulant was added into the bottle. Another 0.1 gram of the washed wet sample was also put directly into a sonicator basin containing 20 mL of filtered Tank 22 simulant and sonicated for 2 minutes before transfer into a green shielded bottle for immediate PSD analysis by AD. The sonicated sample above was quantitatively split into two separate samples by AD and analyzed for PSD as shown in the PSD results in Figure 4-4, inserts B and C.

As shown in Figure 4-4, insert A, the PSD for the un-sonicated composite Tank 22 washed solids shows a bimodal distribution of particles ranging from 0.5 micron up to 1000 microns. This bimodal PSD characteristic was also observed in the top and middle segments of the un-sonicated Tank 22 segment samples as shown in Figure 4-1, inserts A and B.

In the sonicated Tank 22 composite samples, the PSD for the duplicate analysis ranges from 0.5 to about 20 microns. Sonication had therefore resulted in the breaking up (de-agglomeration) of the agglomerate particles of the composite Tank 22 samples with little efforts in terms of energy applied. This means little energy may be required for dispersing of the agglomerated particles in the mound on the Tank 22 floor because sonication for 2 minutes at 2.5 Wats/mL of solution resulted in the shifting of the particles size distribution from about 1000 microns down to 20 microns or less.

A Tank 22 supernatant sample, containing about 60% of sludge by volume and 40% supernate which was delivered to SRNL in November of 2018 but not used because it contained more sludge than desired for supernate characterization was evaluated for PSD. This sludge laden Tank 22 dip sample was collected by simply dropping the collecting bottle into the tank without any sample compacting. So, it is assumed that the PSD of this dip sample will be more representative of the actual sizes of the particles in Tank 22 overall.

About 20 mL of this Tank 22 supernate slurry dip sample was washed with Tank 22 simulant and inhibited water and the wet washed cake sent to AD for PSD analysis. About 0.1 grams of the washed Tank 22 dip sample was also mixed with 20 mL of filtered Tank 22 simulant and sonicated for 2 minutes before delivery to AD for PSD analysis in duplicate. As presented in the PSD characterization results in Figures 4-5, inserts D, E and F for these samples, the particle size distribution for both the un-sonicated sample (insert D) and sonicated samples (inserts E and F) were similar and ranged between 0.5 and 20 microns. The PSD did not contain particles in the 200-1000 microns range as seen with the un-sonicated composite Tank 22 sample or the top and bottom Tank 22 segment samples.

As earlier mentioned above, the 9.5 inch-Tank 22 core sample was obtained from the Tank 22 floor by inserting the 12-inch sampler through the 43.2-inch high mound. The weight of the ~ 50 lb. sampler assembly was enough to reach the floor without hammering the sampler assembly. The compression of the sample, by allowing the liquid to escape through the sampler vent holes at the top, may have resulted in the agglomeration of the smaller particles into larger ones; up to 1000 microns size sample, as shown in Figure 4-1, inserts A and B for the Tank 22 segment samples and in Figure 4-4, insert A for the composite Tank 22 sample. The SEM characterization of this Tank 22 core sample segments (Figure 4-3 inserts a, c and e for the top and middle segments) also indicate the existence of these large particles in the Tank 22 segment samples; mostly the top and middle segment samples.

Hence, if the above assumption of sampling induced agglomeration holds true, it can be concluded that the larger particles observed in the “as-received” Tank 22 samples (composite and segment samples) may be a sampling artifact resulting from the compaction of smaller particles and squeezing out of the liquid supernate phase. The technical basis in support of this argument include the following: sample densities, solids distributions, and particle size distribution parameters in the segment samples (top, middle and bottom) are highest with the top and middle segments which may have experienced the highest particle to particle contact pressure during sampling of the core Tank 22 material. These top to bottom continuous decreases in densities, solids and particle size distributions in the segment samples are summarized in Tables 4-4, 4-5, and Figures 4-1 inserts A, B and C), respectively. In these tables and figure, the densities for the top, middle and bottom segments averaged 1.67, 1.58 and 1.48 g/ mL, respectively, while the weight percent total solids distributions in each segment averaged 45.1, 30.6 and 24.0 wt %, respectively. This decreasing trend for the segments (top to bottom) is also observed in the particle size distribution where the mean diameters averaged 341, 175 and 49.6 microns, respectively. In addition, the un-sonicated supernate sample that contained 60 volume percent of sludge solids matched the particle size distribution of the sonicated core sample solids.

Therefore, the larger particles observed in the Tank 22 mound sample does not necessarily represent the actual particle size distribution in Tank 22 sludge sample. The reversal of the PSD in the “as-received” Tank 22 composite and segment samples to smaller particles with simple sonication for a short time and the similarity of the resulting PSD to the PSD of the bulk of the Tank 22 slurry/liquid environment could only be so if these particles were **not** chemically bound to each other but rather more of a physical interaction between the particles. As seen with sonicated Tank 22 composite sludge samples, it does not take much energy to de-agglomerate the particles and therefore indexing the pumps in Tank 22 will likely de-agglomerate the particles in the mounds and allow easy suspension of the particles for transfers. The Tank 22 sludge material, with a low sodium concentration, does not contain measurable gel formation chemical agents capable of enhancing gel formation in the Tank and thus Tank 22 sludge is likely similar to any other typical sludge found in other tanks with low sodium concentrations.

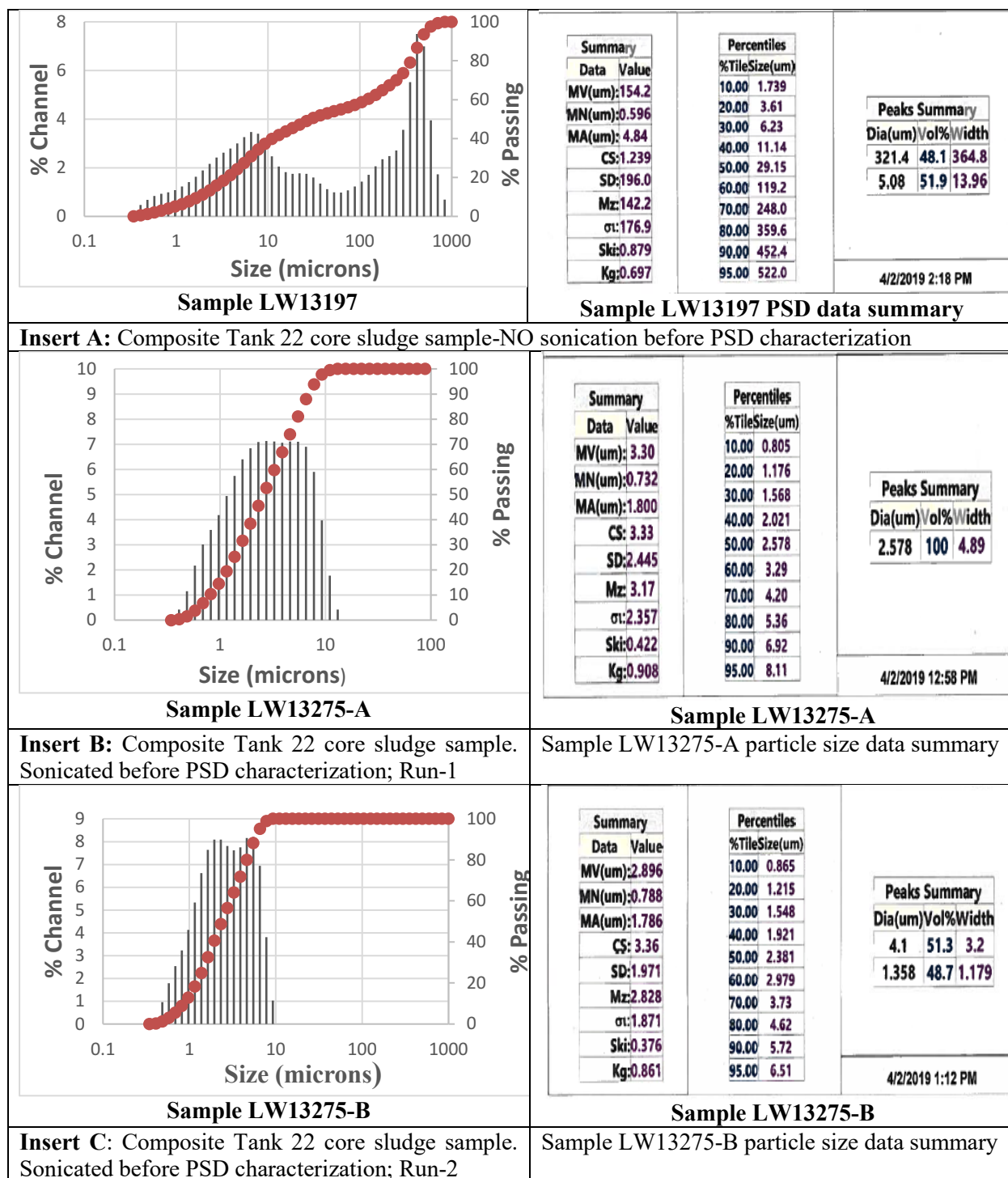


Figure 4-4 Tank 22 Composite Sample PSD, Inserts A (no sonication), B (sonicated sample run-1) and C (sonicated sample run-2). The mean diameters are 154.2, 3.3 and 2.90 μm , respectively.

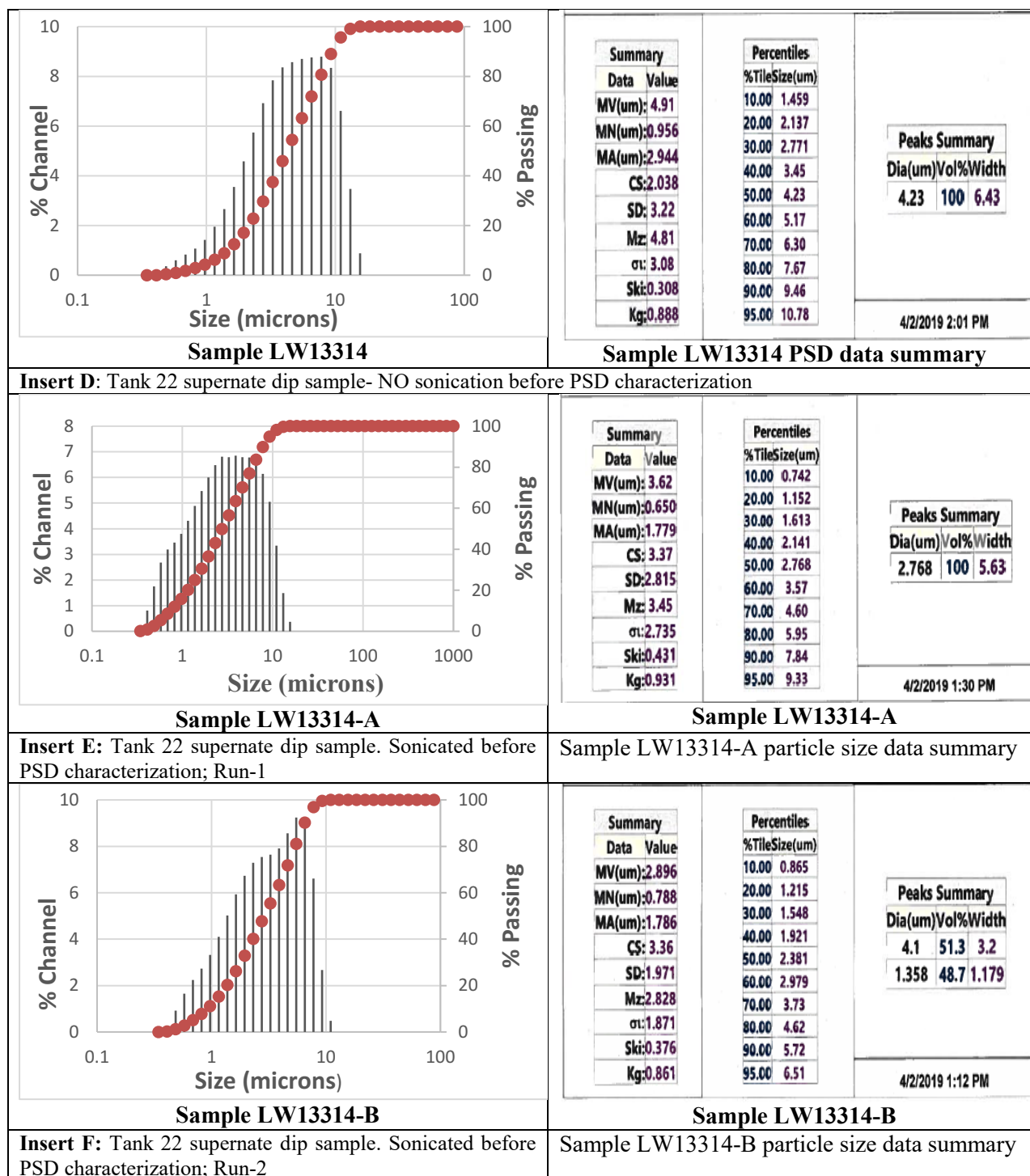


Figure 4-5 Tank 22 Slurry Supernatant Sample PSD, Inserts D (no sonication), E (sonicated sample run-1) and F (sonicated sample run-2). The mean diameters are 4.31, 3.62 and 2.90, respectively.

4.3.3 Composite Tank 22 Core Sample: X-Ray Diffraction

The X-ray diffraction pattern for the composite Tank 22 material is shown in Figure 4-6. This composite Tank 22 core sample, which is a blend of the three Tank 22 segment samples, contain the same type and number of mineral phases as was observed in the individual Tank 22 segment samples as shown in Figure 4-2. There are also five mineral phases, and these are mainly aluminosilicate minerals [nitrated cancrinite ($\text{Na}_{7.6}(\text{AlSiO}_4)_6(\text{NO}_3)_{1.6} \cdot 2\text{H}_2\text{O}$), sodalite ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ and $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$], boehmite ($\text{AlO}(\text{OH})$), mercuric minerals [montroydite ($\text{Hg}_2\text{NCl} \cdot \text{H}_2\text{O}$) and mercuric oxide (HgO)], iron (Fe_2O_3) and quartz mineral (SiO_2).

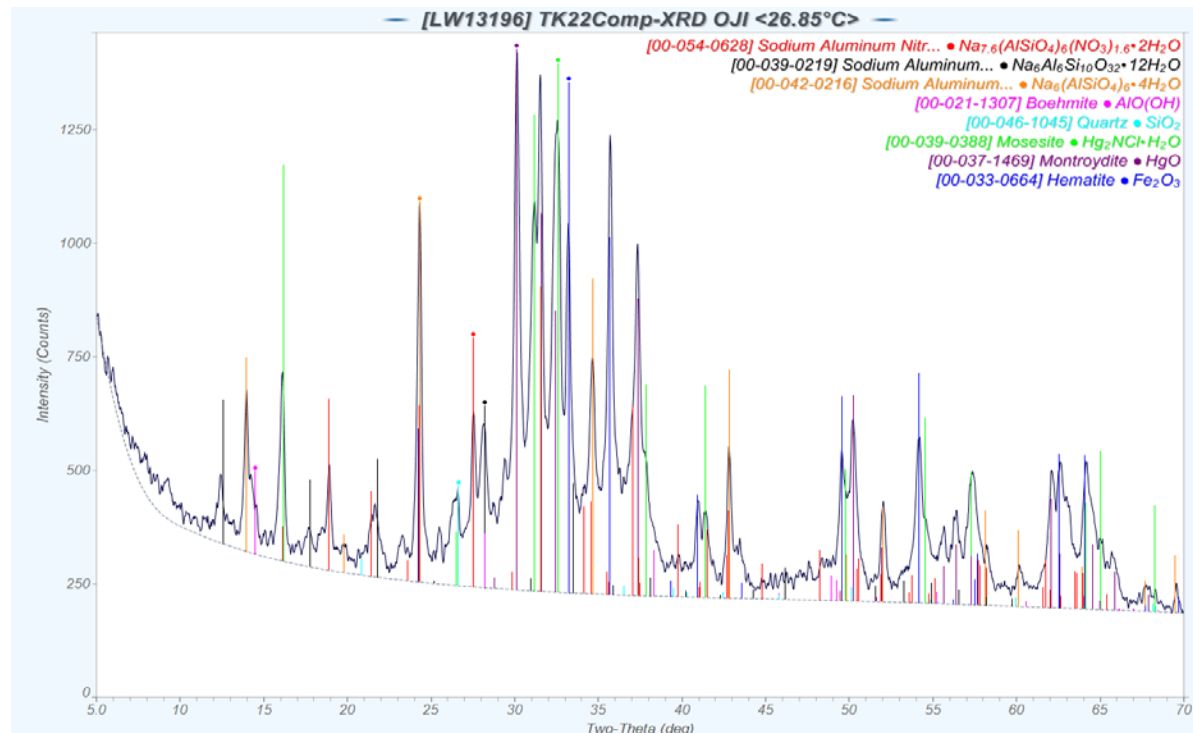


Figure 4-6 X-Ray Diffraction Patterns for Composite Tank 22 Sample

4.4 Tank 22 composite Sample: Elemental Analysis and Weight Percent Calcined Solids Determination

The elemental composition for the Tank 22 composite sample is presented in Table 4-7. The predominant elements in the Tank 22 composite are Fe, Na, Al, Mn and Si at total wt % averages of 6.13, 5.03, 2.49, 2.39 and 2.32, respectively. The secondary cations in concentration are U, Ni, Th and Mg at 0.646, 0.513, 0.209 and 0.164 average wt % total solids, respectively.

In a well-mixed SRS tank environment, because of the excellent solubility for sodium mineral, the distribution of sodium cation is expected to be uniform throughout the entire tank including the sludge material. However, the concentration of sodium cation in the Tank 22 composite sludge material is significantly larger than sodium concentration in the Tank 22 supernatant liquid. The measured values in the Tank 22 composite sludge and the supernate averaged 3.37 ± 0.12 M and 0.71 ± 0.02 M, respectively. The concentration of sodium in the Tank 22 sludge is about a factor of 5 higher in the sludge than in the supernate. Note that the density of the supernate is 1.008 ± 0.002 g/mL and that of the composite Tank 22 sludge is 1.54 ± 0.20 g/mL.

The results for the fission products, Ru, Rh, Pd and Ag, as presented in Table 4-8, are based on a detailed method developed to predict fission product for noble metal concentrations in SRS sludge batches⁸. With this approach, experimentally determined wt % solids data for this Tank 22 composite material are plugged into equations developed by N. Bibler to account for the total concentration of these noble metals taking into consideration all the possible fission product yields. The analytical result for Nd is based on Masses 142,143,144 and 146 from ICP-MS analysis.

A measure of the fraction of frit in the Tank 22 composites sample can be estimated from the Li and Si data as shown in Table 4-7. The Fe-to- Si mass ratio of 2.64 and Fe-to-Li mass ratio of 83.6 from this Tank 22 composite sample characterization is comparable to an earlier Tank 22 characterization data on Tank 22 slurry⁴. These Fe-to- Si and Fe-to-Li mass ratios from the previous analysis of Tank 22 slurry were, 2.4 and 89, respectively. The mass ratios of Fe/B and Li/B are also presented in Table 4-7 are 161 and 1.92, respectively. It is also worth noting that boron, seen in the SEM/EDS data, is derived from Defense Waste Processing Facility (DWPF) processes, where boron is added as a neutron poison.

The weight percent of calcined solids was determined both experimentally and from elemental analysis composition calculations from the Tank 22 composite sludge material.

As presented in Table 4-9, the experimentally determined weight percent calcined solids for the Tank 22 composite material was 32.5 ± 1.20 . The calculated weight percent of calcined solids was based on the elemental compositions and their equivalent oxide conversions for the Tank 22 composite material as presented in Table 4-9. The elemental composition of the Tank 22 composite material with weight percent total solids (wt % total solids) greater than 0.01 wt % was used to calculate the highest limits for the calcined solids. This value was then compared with the experimentally determined wt % calcined solids for the Tank 22 composite material.

The calculated weight percent of calcined solids was 32.1 wt % and the experimentally determined wt % calcined value was 32.5 ± 1.2 , which yields a percent difference of 1.1%. Therefore, the experimentally determined calcined solids value is in good agreement with the calculated value.

Table 4-7 Elemental Composition for Tank 22 Composite Core Sample

Analyte	wt% Total Solids (Average)	%RSD
<i>Ag</i>	<i>5.36E-03</i>	10.6
Al	2.49E+00	5.4
<i>B</i>	<i>3.80E-02</i>	3.0
Ba	2.77E-02	9.3
<i>Be</i>	<i>1.29E-04</i>	21.9
Ca	5.70E-01	6.9
<i>Cd</i>	<i>1.80E-02</i>	10.9
<i>Ce</i>	<i>4.19E-02</i>	9.7
<i>Co</i>	<i>4.20E-03</i>	11.3
Cr	6.41E-02	6.2
Cu	3.08E-02	3.8
Fe	6.13E+00	1.7
<i>Gd</i>	<i>1.79E-02</i>	9.5
<i>K</i>	<i>1.84E-02</i>	22.4
<i>La</i>	<i>1.38E-02</i>	9.1
Li	7.33E-02	0.7
Mg	1.64E-01	4.3
Mn	2.39E+00	8.0
<i>Mo</i>	<i>5.58E-03</i>	8.6
<i>Na</i>	<i>5.03E+00</i>	3.5
Ni	5.13E-01	3.6
<i>P</i>	<i>3.023E-02</i>	26.7
<i>Pb</i>	<i>1.00E-02</i>	8.6
<i>S</i>	<i><6.04E-02</i>	
Sb	7.43E-02	16.1
Si	2.32E+00	6.8
<i>Sn</i>	<i><9.92E-03</i>	
Sr	1.25E-02	2.0
Th	2.09E-01	3.6
Ti	7.03E-02	5.4
<i>U</i>	<i>6.46E-01</i>	7.2
<i>V</i>	<i><1.40E-04</i>	
Zn	2.30E-02	7.6
<i>Zr</i>	<i>1.91E-02</i>	44.3
Hg	5.12E+00	7.1

	Fe/Si	Fe/Li	Fe/B	Li/B
Mass Ratios	2.64	83.63	161.32	1.92

Table 4-8 Concentrations of Noble Metals

(based on total dried solids)		
Noble Metals [#]	Average wt %	Moles/L
Ru	4.94E-02	1.55E-02
Rh	4.63E-03	1.43E-03
Pd	7.68E-04	2.29E-04
Ag	1.27E-02	3.75E-03
Nd*	4.54E-02	1.00E-02

[#] Based on measuring and predicting fission products⁸

*Data from PF /ICP-MS (masses 142,143,144 and 146)

Table 4-9 Elements to Oxides conversions

Element	wt % of Total Solids	Oxide	Element to Oxide Conversion [‡] Factor	Oxide (wt % totals solids)
AL	2.49E+00	Al ₂ O ₃	1.889	4.70E+00
Fe	6.07E+00	Fe ₂ O ₃	1.430	8.68E+00
Na	5.03E+00	Na ₂ O	1.348	6.78E+00
Mn	2.49E+00	MnO ₂	1.583	3.94E+00
Si	2.32E+00	SiO ₂	2.139	4.96E+00
Ni	5.78E-01	NiO	1.273	7.36E-01
Ca	4.89E-01	CaO	1.400	6.85E-01
U	6.46E-01	UO ₂	1.134	7.33E-01
Th	2.51E-01	ThO ₂	1.138	2.86E-01
Mg	1.63E-01	MgO	1.660	2.71E-01
Li	7.95E-02	Li ₂ O	2.153	1.71E-01
P	4.05E-02	P ₂ O ₅	2.292	9.28E-02
K	1.84E-02	K ₂ O	2.405	4.43E-02
La	1.38E-02	La ₂ O ₃	1.173	1.62E-02
Sr	1.33E-02	SrO	1.183	1.57E-02
Pb	1.00E-02	PbO	1.077	1.08E-02
Sum of Wt % Calcined solids				32.13
Experimentally determined wt % calcined solids value				32.48 ± 1.20

[‡] The element-to-oxide conversion, also known as the gravimetric factor, is the ratio of the mass of the oxide to the mass of the element in that oxide. Only cations with wt % total solids greater than 0.01 wt % used for oxide conversion.

4.5 Tank 22 composite Sample: Radionuclide Analysis Results

A measure of the mass and activity concentrations of select radionuclides present in the Tank 22 composite sludge material is presented in Table 4-10. The predominant radionuclide species, in average activity concentrations (Ci/gal), are Sr-90 ($1.68\text{E}+01 \pm 1.82\text{E}+00$), Y-90 ($1.68\text{E}+01 \pm 1.82\text{E}+00$), Cs-137 ($1.14\text{E}+00 \pm 0.14$), Ba-137^m ($1.08\text{E}+00 \pm 1.33\text{E}-01$), Sm-151 ($3.46\text{E}-01 \pm 5.12\text{E}-02$), Pu-238 ($2.64\text{E}-01 \pm 7.72\text{E}-03$), Am-241 ($5.77\text{E}-02 \pm 3.00\text{E}-03$), Cm-244 ($3.32\text{E}-02 \pm 1.675\text{E}-03$), and Pu-239 ($1.55\text{E}-02 \pm 1.47\text{E}-03$). The total alpha and total beta activity concentrations in the Tank 22 composite sludge material are $< 3.90\text{E}-01$ Ci/gal ($<1.03\text{E}-01$ Ci/L) and $3.49\text{E}+01$ Ci/gal (9.22 Ci/L), respectively. This directly measured total alpha in the Tank 22 composite sludge gives a less than value (upper limit of $<1.03\text{E}-01$ Ci/L or $3.90\text{E}-01$ Ci/gal), possibly because of spectral interference peaks. However, a summation of the primary alpha-emitting radionuclides concentrations (Pu-238, Am-241, Pu-240, Pu-239 and Cm-244) based on Table 4-10 activities adds up to $9.92\text{E}-02$ Ci/L ($3.76\text{E}-01$ Ci/gal). This summed total alpha value is just about 2.27 times lower than the empirically defined “Low rem” limit of $2.25\text{E}-01$ Ci/L or $8.51\text{E}-01$ Ci/gal, which is associated with IDP determinations. Thus, a Tank 22 transfer can be considered as a “Low rem” transfer.

The Cs-137 activity in the Tank 22 composite sample and Tank 22 supernatant fluid averaged $4.14\text{E}+08$ dpm/g and $3.07\text{E}+07$ dpm/mL, respectively. Note that the density of the “as-received” Tank 22 supernate averaged 1.008 ± 0.0020 g/mL[§] and that of the composite Tank 22 sludge averaged 1.54 ± 0.20 g/mL. Based on the density values and relative conversions, there is more Cs-137 in the Tank 22 composite sample per gram than there is in the supernatant sample. As earlier noted, sodium concentration in the Tank is also lower in the supernatant fluid which may indicate a poor mixing condition around the mound region of Tank 22.

4.6 Settling and Rheological Properties, Weight and Volume Percent of 2 wt % Composite Tank 22 Sludge Material

A slurry of nominally 2 wt % insoluble solids was prepared by mixing Tank 22 composited solids with Tank 22 supernatant. The slurry was placed into a one-Liter graduated cylinder fitted with a lid so the slurry could be mixed and a centimeter scale to track settling height. The bulk of the settling occurred over the first 8 hours when the settled sludge volume dropped from an initial slurry volume of 1000 mL (38.5 cm [25.974 mL/cm]) down to 90.9 mL (3.5 cm), Figure 4-7. After these hours, settling continued at a much slower settling rate, resulting in settled sludge volume of 88.3 mL (3.4 cm in the graduated cylinder) after a total of about 100 hours settling time, as shown in Figures 4-7 and 4-8 for initial 8 hours settling and over the entire setting time, respectively. Thus, the 2 wt % Composite Tank 22 Sludge settled to less than 10% [8.83%] of the starting height within eight hours and settling stopped after approximately 100 hours.

As presented in Figures 4-7 and 4-8, the relationship between settled sludge volume in units of cm and settling time can be approximated by a biexponential decay with asymptote function. The statistical software package, JMP®, was used to calculate the parameters. The correlation coefficient of the fit, R^2 , was calculated to be 0.989:

[§] Density of the “as-received” Tank 22 supernate reported to 4 significant figures because this density measurement only differs in the 4th significant place when compared with that of distilled water and the Tank 22 supernate filtrate.

Table 4-10 Results of Analyses of Tank 22 Composite Core Sample -Radionuclides

Analyte	Mass Concentration Average wt% Total Solids	Activity Concentration Average Ci/gal of Sludge	Activity Concentration Average Ci/g of Total Solids	%RSD n = 3
Co-60	3.94E-08	1.10E-03	4.45E-07	2.3
Sr-90	4.97E-03	1.68E+01	6.79E-03	10.8
Y-90	1.25E-06	1.68E+01	6.79E-03	10.8
Tc-99	1.14E-03	4.78E-04	1.93E-07	11.5
Cs-134	<6.72E-07	<2.00E-02	<2.71E-10	-
Cs-137	5.30E-04	1.14E+00	4.61E-04	12.3
Ce-144	<1.69E-08	<1.34E-03	<5.39E-07	MDA
Ba-137	8.21E-11	1.08E+00	4.36E-04	12.3
Pm-147	<1.19E-05	<2.74E-01	<1.09E-04	UL
Sm-151	5.30E-04	3.46E-01	1.40E-04	14.8
Eu-152	9.91E-08	4.24E-04	1.71E-07	6.8
Eu-154	1.62E-07	1.08E-02	4.37E-06	5.1
Eu-155	1.26E-07	1.45E-03	5.86E-07	17.2
Th-232	4.96E-01	1.35E-06	5.44E-10	4.9
U-233	2.83E-04	6.79E-05	2.74E-08	8.0
U-234	3.01E-04	4.65E-05	1.88E-08	2.2
U-235	8.03E-03	4.30E-07	1.74E-10	2.9
U-236	5.38E-04	8.63E-07	3.48E-10	5.7
U-238	1.29E+00	1.07E-05	4.32E-09	2.2
Np-237	2.16E-03	3.77E-05	1.52E-08	3.1
Np-239	2.09E-10	1.20E-03	4.86E-07	20.8
Pu-238	6.23E-04	2.64E-01	1.07E-04	2.9
Pu-239	1.01E-02	1.55E-02	6.25E-06	9.5
Pu-240	8.74E-04	4.94E-03	1.99E-06	3.1
Pu-239/240	≤ 9.75E-03	≤ 1.50E-02	≤ 6.06E-06	-
Pu-241	1.61E-05	4.10E-02	1.66E-05	34.4
Pu-242	5.17E-05	4.89E-06	1.97E-09	3.6
Pu-244	≤ 9.36E-07	≤ 4.12E-10	≤ 1.66E-13	-
Am-241	6.71E-04	5.77E-02	2.30E-05	5.2
Am-243	1.92E-04	8.77E-04	3.82E-07	15.21
Am-242m	≤ 7.64E-07	≤ 1.72E-04	≤ 7.43E-08	*MDA/31.9
Cm-242	≤ 1.86E-09	≤ 1.42E-04	≤ 6.14E-08	MDA/31.9
Cm-243	<1.67E-06	<2.62E-03	<8.62E-07	
Cm-244	1.61E-05	3.32E-02	1.30E-05	5.0
Cm-245	<3.27E-04	<1.42E-03	<5.62E-07	-
Cm-247	<6.62E-01	<1.22E-03	<6.14E-07	-
Cf-249	<1.58E-05	<1.31E-03	<6.47E-07	-
Cf-251	<3.15E-05	<9.93E-04	<5.01E-07	-
Total alpha	-	<3.90E-01	<1.58E-04	UL
Total beta	-	3.49E+01	1.41E-02	9.4

* Counting uncertainty (1 sigma % uncertainty) for analytical results which were NOT less than values. MDA = minimum detection activity.

$$y = 3.389 + 33.94e^{-76.15x} + 1.793e^{-4.924x}$$

where, y is sludge height in cm and x is the settling time in days. This equation is shown in the figures as a blue dotted line in both Figures 4-7 and 4-8. The biexponential decay with asymptote function above applies for the entire settling period. Figure 4-7 is plotted in hours (0-8 hours) instead of days (0-0.33 days) for better visual graphics presentation during this fast-settling time period.

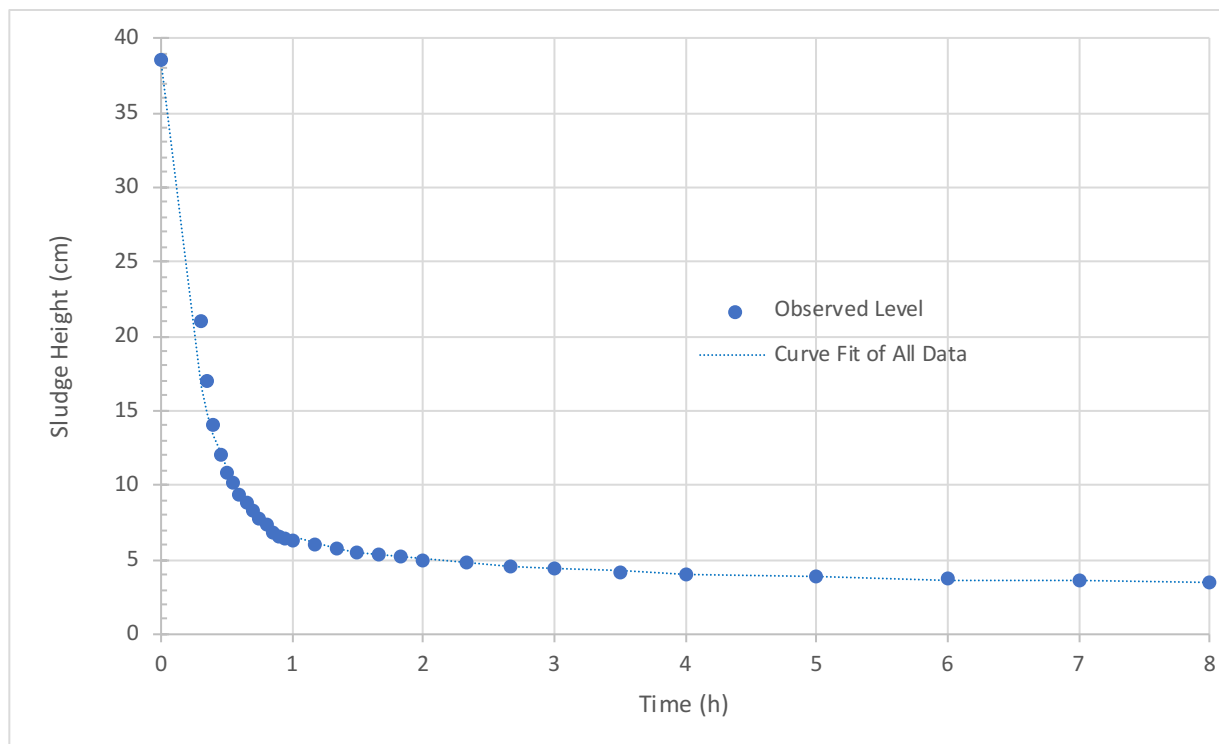


Figure 4-7 Tank 22 (2wt % insoluble solids)- Settling Sludge Volume as a Function of Settling Time; initial 8 hours.

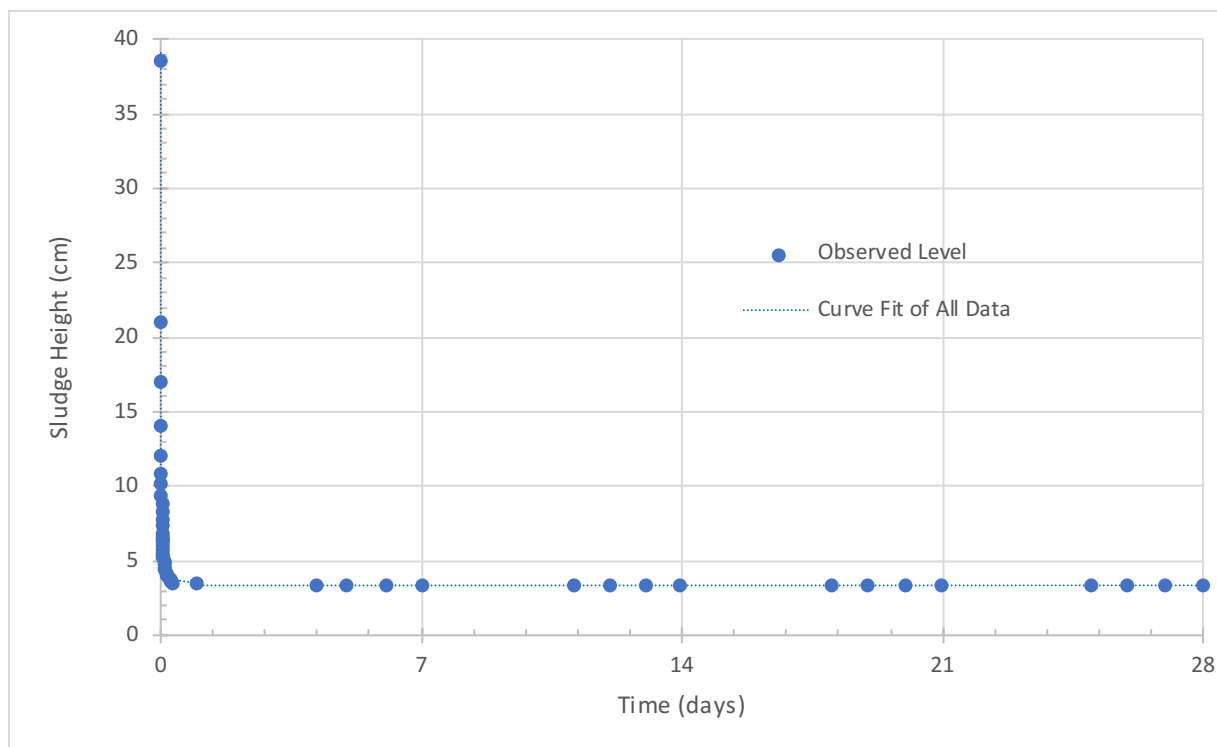


Figure 4-8 Tank 22 (2wt % insoluble solids)- Settling Sludge Volume as a Function of Settling Time; over the entire settling time.

As shown in Table 4-11, the average yield stresses of the three samples with different wt% insoluble solids, respectively at 10.6, 18.8, and 23.2 wt%, ranged from 0.28 to 2.6 Pa, while the average plastic viscosities (consistency) ranged from 3.4 to 7.0 cP. As can be seen, there is virtually no significant difference in magnitude of the yield stress values (0.43 vs. 0.28 Pa) between samples 1 and 2 although the magnitude of insoluble solids in the second sample is nearly twice that of the first sample. Variations between the yield stresses for samples 1 and 2 were thought to be in the normal range of 2 sigma analytical uncertainties, especially when considering that yield stress measurements are impacted by settling and suspension of insoluble solids particles, which can limit measurement stability. While sample 3 has an even higher insoluble solids content (23.2 wt %), the yield stress (the parameter that is typically of most concern with high insoluble solids slurries) is low at 2.6 Pa.

In the case of the average plastic viscosities, the result for sample 1 (3.4 cP, 5%) and sample 3 (7.0 cP, 8%) appear to all be in the same range of the expected analytical uncertainties. However, the result for sample 2 (3.6 cP, 20%) appear to be slightly lower than expected when the magnitude of the wt% insoluble solids content is taken into consideration. Given that the sample densities for all three samples are essentially similar, it is likely that the lower apparent plastic viscosity for the second sample was due to analytical uncertainties, as opposed to true sample variations.

In summary, Tank 22 slurry is generally Newtonian (little or no yield stress) until insoluble solids contents exceed >19 wt %.

Table 4-11 Rheology of Tank 22 Samples at 10.6, 18.8 and 23.2 wt % insoluble solids

Sample	wt % insoluble solids	Plastic viscosity (Consistency) (cP), RSD, n	Yield Stress (Pa), RSD, n
Sample 1 (post setting slurry)	10.6%	3.4, 5%, 2	0.43, 18%, 2
Sample 2 (made from composited solids and supernatant)	18.8%	3.6, 20%, 3	0.28, 10%, 2
Sample 3 (made from decanting samples 1 and 2, then decanting)	23.2	7.0, 8%, 2	2.6, 2%, 2

RSD = Relative Standard Deviation; n = number of replicates

5.0 Conclusions and Recommendations

The Savannah River National Laboratory (SRNL) was requested by Savannah River Remediation (SRR) Engineering (SRR-E) to provide sample characterization and analyses of Tank 22 settled sludge core sample and the supernatant liquids (supernate) in support of Tank 22 re-baseline data, inhalation dose potential/hydrogen generation and suspension/removal of settled sludge from the bottom of Tank 22.

The approximately 9.5 inches of intact Tank 22 core sample from SRR-E, after extrusion in the SRNL Shielded Cells, showed three visually different stratification layers or regions of solids in the extruded core material. Part of the initial physical characterization of these three segments of the Tank 22 core sample included density, weight percent total solids, particle size distribution, X-ray diffractions and scanning electron microscope of each segment material.

Given the dissimilarity of the three Tank 22 segment materials after the physical characterization results and the fact that there was no clear line of demarcation to indicate where each segment began and ended across the entire length of the core sample, SRNL in conjunction with the SRR-E customer decided to blend all three segments of the material to form a composite Tank 22 core sample for further analysis and characterization without taking into consideration the proportional weight or mass contribution of each segment. This compositing approach assumes that the errors introduced in any characterization of the Tank

22 core sample will be comparable to the errors when the three segments are separated and combined proportionally by weight to form the composite Tank 22 sample. This compositing approach maximized the quantity of composited Tank 22 material needed for radionuclide and other physical characterizations.

Composite Tank 22 core sample has been characterized for physical properties, stable elemental constituents, radionuclides, rheological and settling properties. The densities, solids distribution and select radionuclide content of a Tank 22 supernatant liquid was also determined. A summary of the average characterization data for the composite Tank 22 core sample and segments include the following:

The composite Tank 22 sludge bulk wet and bulk dry densities are 1.54 ± 0.20 , and 0.66 ± 0.13 g/mL, respectively.

The measured weight percent total solids for the Tank 22 composite sample was 42.5 ± 3.61 wt % (total sludge basis), while the weight percent total dissolved solids was 4.34 wt % (supernatant basis). This gives a calculated insoluble solids value of 39.9 wt % (sludge basis) and wt % soluble solids of 2.61 wt %. The experimentally determined calcined solids was 32.5 ± 1.20 wt% and the maximum calculated calcined solids for the Tank 22 composite material was 32.1 wt %.

The dominant elemental constituents in the Composite Tank 22 sludge material were Fe (6.13 ± 0.11 wt %), Hg ($5.12 \pm 3.66\text{E-}01$ wt %), Na (5.03 ± 0.17 wt %), Al (2.49 ± 0.13 wt %), Mn (2.39 ± 0.19 wt %), Si (2.32 ± 0.16 wt %), and Li ($7.33\text{E-}02 \pm 5.14\text{E-}04$ wt %).

The Fe/Si and Fe/Li mass ratios, respectively, 2.64 and 83.6, which reflects on the fraction of frit in Tank 22, are comparable to the ratios of these elements in previous Tank 22 characterizations.

Total elemental mercury composition in the composite Tank 22 sludge material averaged $5.12 \text{ E} \pm 0.37$ wt % total solids.

The measurable alpha-emitters in the composite Tank 22 sludge sample are Pu-238 ($2.64\text{E-}01 \pm 7.72\text{E-}03$ Ci/ gal), Am-241 ($4.10\text{E-}02 \pm 1.54\text{E-}03$ Ci/gal), Pu-239 ($1.55\text{E-}02 \pm 1.47\text{E-}03$ Ci/gal), Pu-240 ($4.94 \text{ E-}03 \pm 1.51\text{E-}04$ Ci/gal), and Cm -244 ($3.32\text{E-}02 \pm 1.67\text{E-}03$ Ci/gal).

The measured total alpha activity concentration at $< 3.90\text{E-}01$ Ci/gal ($<1.03 \text{ E-}01$ Ci/L) is significantly lower than the “Low rem” limit ($8.51\text{E-}01$ Ci/gal or 0.225 Ci/L) of the inhalation dose potential determination.

The sum of the activity concentrations of the individually measured alpha emitters (Pu-238, Pu-239, Pu-240, Am-241 and Cm-244) is $9.92\text{E-}02$ Ci/L ($3.76\text{E-}01$ Ci/gal), which is consistent with the measured total alpha result of $<1.03 \text{ E-}01$ Ci/L ($<3.90\text{E-}01$ Ci/gal).

The primary beta-emitting radionuclides in the composite Tank 22 core sludge sample are Sr-90 ($1.68\text{E+}01 \pm 1.82\text{E+}00$ Ci/gal), Y-90 ($1.68\text{E+}01 \pm 1.82\text{E+}00$ Ci/gal), and Cs-137 ($1.14\text{E+}00 \pm 0.14$ Ci/gal).

The primary gamma-emitting radionuclides in the composite Tank 22 core sample are Ba-137^m, and Co-60 at an average activity concentration of $1.08\text{E+}00 \pm 1.33\text{E-}01$ Ci/gal and $1.10\text{E-}03 \pm 2.3\text{E-}05$ Ci/gal, respectively.

U-238 and Th-232 were present at the highest radionuclide mass concentrations of $1.29\text{E+}00 \pm 2.79\text{E-}02$ and $4.96\text{E-}01 \pm 2.42\text{E-}02$ wt %, respectively.

The total uranium content of the Tank 22 composite core sample is 1.30E+00 wt % and the U-235 enrichment is 0.62%.

The total plutonium mass concentration (Pu-238 through Pu-244) for the composite Tank 22 core sample is 2.33E-03 wt % total solids

The XRD data on the mineralogy of both the Tank22 segment samples and the composite Tank 22 sample indicate there are five major crystallographic minerals in these sample, namely, aluminosilicate minerals [nitrated cancrinite ($\text{Na}_{7.6}(\text{AlSiO}_4)_6(\text{NO}_3)_{1.6} \cdot 2\text{H}_2\text{O}$), sodalite ($\text{Na}_4\text{Al}_6\text{Si}_{10} \cdot 12\text{H}_2\text{O}$ and $\text{Na}_6(\text{AlSiO}_4)_6 \cdot 4\text{H}_2\text{O}$)], boehmite ($\text{AlO}(\text{OH})$), mercuric minerals [montroydite ($\text{Hg}_2\text{NCl} \cdot \text{H}_2\text{O}$) and mercuric oxide (HgO)], iron (Fe_2O_3) and quartz mineral (SiO_2).

The particle size distribution analysis of the three Tank 22 core segment samples (top, middle and bottom) shows that two of these segment samples (top and middle) have large particles sizes, which range from a few microns up to 1000 microns. The particles size in the bottom segment sample averaged about 50 microns.

The PSD for the composite Tank 22 core samples showed a bimodal distribution of particles with the larger particles in the 500 to 1000 microns range and the smaller particles averaging about 10 microns.

Larger particles observed in the “as-received” Tank 22 samples (composite and segment samples) may be a sampling artifact resulting from the compaction of smaller particles and the squeezing out of the liquid supernate phase; these larger particles do not represent the particle size distribution in the bulk of the Tank 22 medium.

Simple sonication, for a short time proved sufficient to de-agglomerate the particles and therefore indexing the pumps in Tank 22 will likely de-agglomerate the particles in the mounds and allow easier suspension of the particles for transfers.

The 2 wt % Composite Tank 22 Sludge settled to less than 10% of the starting height within eight hours; from 38.5 cm to 3.5 cm. Settling stopped after approximately 100 hours at a level of 3.4 cm.

The Tank 22 slurry is generally Newtonian (little or no yield stress) until insoluble solids contents reach >19wt %.

A summary of the average analytical results for the characterization of the Tank 22 supernatant liquid sample follows.

The Tank 22 supernatant liquid and its filtrate densities are 1.008 ± 0.002 and 1.003 ± 0.006 g/mL, respectively. Densities of the Tank 22 supernatant liquid and its filtrate are almost identical, which means that the supernate contained little or no measurable suspended solids.

The Tank 22 supernatant total mercury and methyl mercury cation concentration were $5.67\text{E-}04 \pm 3.34\text{E-}05$ and $1.03\text{E-}04 \pm 4.45\text{E-}06$ Moles, respectively.

Sodium was the dominant elemental constituent in the Tank 22 supernatant with a concentration of $7.13\text{E-}01 \pm 1.55\text{E-}02$ M. The second, third and fourth most dominant constituents in the supernatant were aluminum, silicon and lithium, with concentrations of $2.15\text{E-}03 \pm 5.89\text{E-}05$ M, $5.73\text{E-}03 \pm 1.44\text{E-}04$ M and $4.26\text{E-}03 \pm 7.80\text{E-}05$ M, respectively.

The predominant anions in this Tank 22 supernatant were nitrite, carbonate, nitrate, sulfate and aluminate, which were present at average concentrations of $3.12\text{E-}01 \pm 5.61\text{E-}03$, $9.49\text{E-}02 \pm 1.14\text{E-}03$, $8.53\text{E-}02 \pm 1.36\text{E-}03$, $3.18\text{E-}03 \pm 6.04\text{E-}05$ and $2.15\text{E-}03 \pm 5.80\text{E-}05$ M, respectively. Free hydroxide concentration in the supernate was less than 0.207 M.

The average concentration of Cs-137 in the Tank 22 supernatant liquid filtrate is $3.07 \text{E}+07 \pm 2.00\text{E}+05$ dpm/mL ($5.23\text{E-}02 \pm 3.41\text{E-}04$ Ci/gal).

The measurable uranium concentrations, U-235 and U-238, were $1.48\text{E-}07$ M and $2.09\text{E-}05$ Moles, respectively giving a U-235 enrichment of about 0.71 wt %.

Technecium-99, at an average concentration of $1.50\text{E-}06$ M, was another measurable radionuclide in the Tank 22 supernatant liquid. This ICP-MS data value for Tc-99 may be biased high because both ruthenium and molybdenum isotopes also contribute to atomic mass 99.

6.0 Quality Assurance

The TTQAP details the planned activities and associated quality assurance implementing procedures for Tank 22 Core sample characterization and testing (TTQAP, SRNL-RP-2018-00530, Rev. 0, June 25, 2018) task. The documents referenced in the TTQAP include the following: C. Trivelpiece: ELN L7482-00275-05 and L. N. Oji: ELN: L5575-00080-10 (Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and in various AD notebooks contain the analytical data. Other relevant QA documents include the Technical Task Request (HLE-TTR-2013-00002, Rev 1, December. 30, 2018).

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 2.60. This document, including all calculations was reviewed by Design Verification by Document Review^{9, 10}. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

The TTR requested functional classification ("Safety Significant Classification"), the memos, calculations and technical memoranda issued in this Tank 22 characterization effort have received technical review by design verification (E7 Manual, Procedure 2.60, section 5.3). The experimental work, the analyses, and peer check all comply with the customer quality assurance (QA) requirements.

7.0 References

1. D. Kremenz, S. H. Reboul, "Sampler Testing and Simulant Development in Support of Tank 22 Core Sampling", SRNL-L4500-2018-00013, February 2018.
2. "Tank 22 Core Sample(s) Characterization", X-TTR-H-00076, Rev. 2, June 12, 2018.
3. "Task Technical and Quality Assurance Plan for Tank 22 Settled Sludge Core Sample Characterization and Testing", SRNL-RP-2018-00530, Rev. 0, June 25, 2018.
4. J. M. Pareizs "Characterization of Tank Samples HTF-22-14-72 and 73", SRNL-STI-2014-00380, September 2014, Rev. 0.
5. C. J. Coleman, R. A. Dewberry, M. F. Bryant and J. J. Gemmill, "SRL's Performance in Round Robin #6-Analyses of Simulated Defense Waste Glass", WSRC-TR-91-187, Rev. 0, May 31, 1991.
6. "Tank 22 Supernate Sample Characterization", G-TAR-H-00007, Rev. 0, August 5, 2019.

7. L. N. Oji, "Tank 22 Supernatant Sample Characterization for Select Radionuclides", SRNL-L3100-2019-00604, Rev. 0, October 2, 2019.
8. N. E. Bibler, "Measuring and Predicting Fission Products Noble Metals in Savannah River Site High Level Waste Sludges," WSRC-TR-2005-00098, Rev. 0, April 2005.
9. "Technical Reviews", Manual E7, Procedure 2.60, Revision 17, August 25, 2016.
10. "Savannah River National Laboratory Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Revision 2, August 2004.

Appendix A: Weight Percent Calculations, Sludge blending and Particle density Setups and Method comparison for select metals

Calculation of 22 wt. % insoluble solids equivalent in a 100 mL total supernatant volume.

Calculation of the amount of reconstituted composite Tank 22 material needed to prepare 22 wt % insoluble solids equivalent in a 100 mL total supernatant volume.

Tank 22 supernatant liquid (supernate) density = 1.008 g/mL

$$100 \text{ mL} \times \frac{1.008 \text{ g}}{\text{mL}} = 100.8 \text{ g supernate}$$

Let x = the amount of composited solids to add. The wt % insoluble solids is then:

$$0.22 = \frac{x \cdot 0.3826}{100 + x}$$

Rearranging and solving for x,

$$x = \frac{22}{0.3826 - 0.22} = 135.3 \text{ g composited solids}$$

Supernate density is 1.008 g/mL and composited solids density is around 1.54 g/mL (density of original top layer) and assuming volumes are additive,

$$100 \text{ g} \cdot \frac{1 \text{ mL}}{1.008 \text{ g}} + 135.3 \text{ g} \cdot \frac{1 \text{ mL}}{1.54 \text{ g}} = 187 \text{ mL}$$

We don't need that much. So, scale to 100 mL,

$$\frac{100}{187} = 0.535$$

Supernatant:

$$100 \cdot 0.535 = 53.5 \text{ g supernatant}$$

Composited solids:

$$135.3 \cdot 0.535 = 72.4 \text{ g reconstituted composited solids}$$

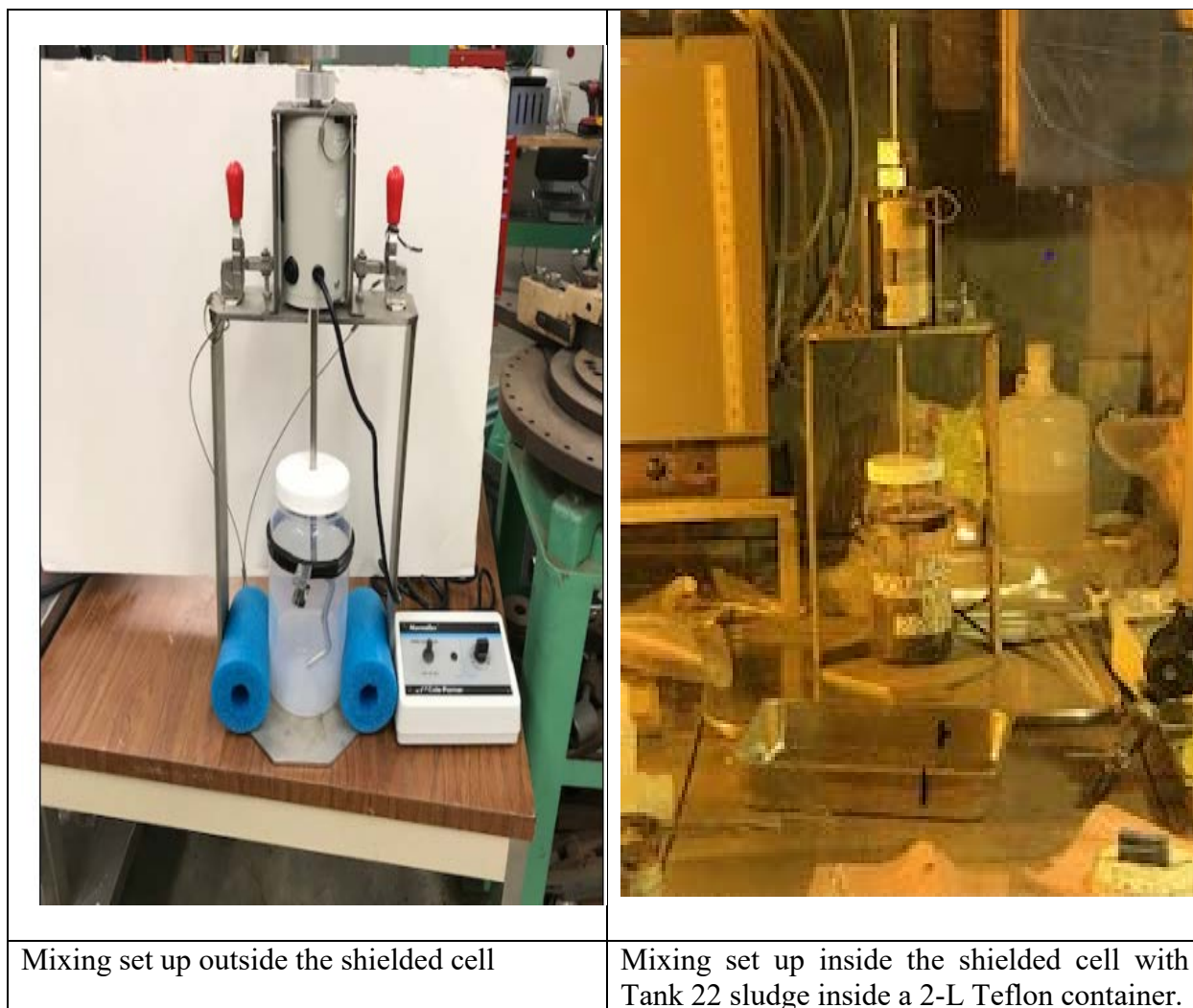


Figure A 1 Sludge mixing device for Tank 22 core sample: The mixing device, as shown above, is a motor driven shaft and controller with mixing impeller blades at the other end.




	
<p>Insert A: Most of the particles failed to descend to the bottom of the cylinder (Day one photo); even with shaking of the contents of the graduated cylinder.</p>	<p>Insert B: No measurable displacement of supernatant liquid even after 96 hours even with shaking of the contents of the graduated cylinder.</p>
	<p>Intentionally left blank</p>
<p>Insert C: There is measurable displacement of supernatant liquid after 120 hours with mild shaking.</p>	

Figure A 2 Particle density determination for washed and air-dried composite Tank 22 sludge in Tank 22 “as-received” supernatant medium.

Table A 1 Pu-239 and Pu-240 Analysis Comparison by Two Methods (ICP-MS vs. Extraction/MS)

LIMS #	Isotope	ICP-MS (masses 239, 240), Average Ci/g TS	Extraction/ICP-MS Average Ci/g TS	Average of Averages, Ci/ g TS	%Diff
LW12270-72	Pu-239	5.62E-06	NA		
LW12262-64	Pu-239	NA	6.25E-06	5.94E-06	10.6
LW12270-72	Pu-240	1.96E-06	NA		
LW12262-64	Pu-240	NA	1.99E-06	1.98E-06	1.5

Table A 2 Am-241 and Am-243 by Cs-removed gamma scan and Am/Cm Analysis Comparisons

LIMS #	Isotope	Cs-removed gamma, Wt % total solids	Am/Cm	Average of averages, Wt % total solids	%Diff.
LW12258-60	Am-241	6.13E-04	NA		
LW13410-12	Am-241	NA	6.71E-04	6.42E-04	9.0
LW12258-60	Am-243	2.44E-04	NA		
LW13410-12	Am-243	NA	1.92E-04	2.18E04	23.8

Table A 3 Total Thorium-232 Analysis Comparison by Two Methods (ICP-MS vs. ICP-ES)

LIMS #	ICP- MS (Mass 232) Average, wt %	ICP-ES Average, wt %
LW12270	0.199	0.201
LW12271	0.217	0.211
LW12272	0.217	0.216
Average of averages, mg/L	0.211	0.209
% difference (MS and ES)*	1.0%	-

- (Difference /average)*100 The percent difference for Thorium-232 concentration by both ICP-ES and ICP-MS methods is 1 %. Differences between the two methods may also be due to contributions from U-232, which was not taken into account for ICP-MS.

Table A 4 Chemical Composition of Analyzed Reference Glass

	Analytical Results for Reference Glass (ARG)	Nominal Recipe for Reference Glass (ARG)[#]	Percent Relative Deviation
Constituent*	wt. %	wt. %	%RD
Al	2.48	2.50	0.20
B	2.67	2.69	0.19
Ca	1.05	1.02	0.72
Fe	10.20	9.79	1.03
Li	1.46	1.49	0.51
K	2.24	2.26	0.22
Mg	0.53	0.52	0.48
Mn	1.50	1.46	0.68
Na	8.57	8.52	0.15
Ni	0.85	0.83	0.69
Ti	0.57	0.69	4.68

* Aqua regia digestion data (AQR: LIMNS # LW13417). [#] Reference values for ARG are reported to the number of digits given in the original citation.

Table A 5 Barium Analysis Comparison by Two Methods (ICP-MS vs. ICP-ES)

LIMS #	ICP- MS (Mass134, 135, 136, 137, 138), mg/L	ICP-ES, mg/L	Average, mg/L	%Difference
LW12270-72	NA	426 (PF digestion)		
LW13414-16	NA	405 (AQR digestion)	416	
LW12270-72	419 (PF digestion)	NA		
LW13414-16	407 (AQR digestion)	NA	413	0.7

The average percent relative deviation (%RD) for total barium concentration by both ICP-ES and ICP-MS methods is < 1 %.

Table A 6 Total Cobalt-60 Analysis Comparison by Two Methods (ICP-MS vs. ICP-ES)

LIMS #	ICP-MS (mass 59), Average, mg/L	ICP-ES, Average, mg/L	Average of Averages, mg/L	% Difference
LW12270-72	54.10	NA		
LW13414-16	53.5	NA	53.80	
LW13414-16	NA	64.70		
LW12262-64	NA	61.1	62.90	15.6

The average percent relative deviation (%RD) for total cobalt concentration by both ICP-ES and ICP-MS methods is 11.03%.

Table A 7 Total Lanthanum Analysis Comparison by Two Methods (ICP-MS vs. ICP-ES)

LIMS #	ICP- MS (Mass 139) Average, mg/L	ICP-ES Average, mg/L	Average of Averages, mg/L	% Difference
LW12262-64	225.00 (AQR)	NA		
LW12270-72	205.00 (PF)	NA	215	
LW13414-16	NA	213.00 (PF)	213	0.9

The average percent relative deviation (%RD) for total lanthanum concentration by both ICP-ES and ICP-MS methods is 0.9 %.

Appendix B: Summary of Analytical, Rheological and Physical Measurement Methods

Aqua Regia Digestions (AQR)

Samples were digested according to procedure L16.1, ADS-2226. In a typical digestion, ~0.5 g of Tank 22 composite sample was placed into a Teflon® digestion vessel. Then, 9 mL (hydrochloric acid) HCl, and 3 mL (nitric acid) HNO₃ were added to the Teflon® vessel. The Teflon® vessel was sealed and heated for a period of no more than 4 hours at 115 °C. The sample was then cooled and diluted to 50 mL. Three aliquot of Tank 22 composite samples were digested by aqua regia.

Sodium Peroxide/Hydroxide Fusions (PF)

Samples were digested according to procedure L16.1, ADS 2502. In a typical digestion, ~2 grams of Tank 22 composite sample were placed into a nickel (Ni) crucible with a known weight. The material in the crucible was dried until two consecutive weights were within ±0.02 grams. The remaining material in the crucible was fused at 675 °C using a mixture of sodium peroxide (6.0 grams) and sodium hydroxide (4.0 grams). After the sample was cooled, water was added to dissolve the fused material and the solution was acidified by the addition of 25 mL HCl. The sample was diluted to 100 mL. Digestions by sodium peroxide fusion using Tank 22 composite samples were performed in triplicate.

Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-ES)

Samples are diluted as necessary to bring analytes within the instrument range. A scandium internal standard is added to all samples after dilution at a concentration of 2 mg/L. The instrument is calibrated daily with a blank and two standards: 5 and 10 mg/L NIST traceable multi-element standards in dilute acid. Background and internal standard correction were applied to the results.

Ion Chromatography for Anions (IC-Anions)

For IC Anions, samples were diluted with a carbonate/bicarbonate diluent as necessary to bring analytes to within instrument calibration. A 3-point calibration curve is run daily on the instrument with concentrations of 10, 25 and 50 µg/mL.

Total mercury was analyzed by DMA.

With DMA method for mercury analysis, controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. With the completion of oxidation, halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.7 nm as a function of mercury concentration.

The typical working range for this method is 0.05-600 ng. The mercury vapor is first carried through a long pathlength absorbance cell and then a short pathlength absorbance cell. (The lengths of the first cell and the second cell are in a ratio of 10:1 or another appropriate ratio.) The same quantity of mercury is measured twice, using two different sensitivities, resulting in a dynamic range that spans at least four orders of magnitude. The instrument detection limit (IDL) for this method is 0.01 ng of total mercury.

Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS)

Samples are diluted as necessary to bring analytes within the instrument range. An internal standard with bismuth and indium is added to all samples after dilution. The instrument is calibrated daily with a blank and a minimum of four calibration standards that are NIST traceable multi-element standards in dilute acid. Background and internal standard correction were applied to the results.

Gross Alpha/Gross Beta

The solid material was too concentrated to be analyzed directly. Aliquots of peroxide fusion dissolution were added to liquid scintillation cocktail and analyzed for gross alpha and gross beta activity using liquid scintillation analysis. Alpha/beta spillover was determined for each aliquot analyzed, and subsequently used for accurately determining alpha and beta activity, via the addition of a known amount of plutonium to an identical aliquot of each sample.

Cs-137, Cs-134

Aliquots of Tank 22 composite samples peroxide fusion and aqua regia dissolutions were analyzed by coaxial high purity germanium gamma-ray spectrophotometers to measure Cs-137 and Cs-134. Cell reagent blanks, Laboratory reagent blanks were run as controls.

Sr-90

Aliquots of Tank 22 composite samples peroxide fusion dissolutions were spiked with an elemental strontium carrier. The strontium species were extracted from the matrix using a crown-ether-based solid phase extractant. Sr-90 concentrations were measured by liquid scintillation analysis. Elemental strontium carrier yields were measured by neutron activation analysis and were used to correct the Sr-90 analyses for any strontium losses from the radiochemical separations. Shielded cell reagent blanks and laboratory reagent blanks and a Sr-90 standard were run as controls.

Co-60, Am-241 (Cs-removed gamma analysis)

Aliquots of Tank 22 composite samples peroxide fusion dissolution were subjected to a Cs-removal process utilizing Bio Rad AMP-1 resin. The Cs-removed solutions were analyzed by coaxial high purity germanium spectrophotometers to measure the gamma-emitting radionuclides listed above. Aliquots of Tank 22 composite samples peroxide fusion dissolution were analyzed for Co-60 and Am-241 following the same protocols as used in the Tank 22 composite sample initial analysis, no additional preparations were required

Pm-147/Sm-151

Aliquots of peroxide fusion and AQR dissolution were spiked with an elemental samarium carrier. The promethium and samarium species were extracted from the matrix using a combination of Octylphenyl-N, N-di-isobutyl carbamoylphosphine oxide/tri-n-butyl phosphate (one CMPO/TBP) and di(2-ethylhexyl) orthophosphoric acid (one HDEHP based). Sm-151 and Pm-147 concentrations were measured by liquid scintillation analysis. The matrix was high in Sm-151, but the short-lived Pm-147 component of the material had decayed below noise levels of the analysis. Elemental samarium carrier yields were measured by neutron activation analysis and were used to correct the analyses for any samarium losses from the radiochemical separations. The separation was designed to extract both Sm and Pm together; a Pm spike was run with the samples to confirm this.

Pu-238, 239/240, 241

Aliquots of Tank 22 composite samples peroxide fusion dissolutions were spiked with Pu-236 tracer. The plutonium was extracted from the matrix using thenoyltrifluoroacetone (TTA) following a series of oxidation-state adjustments. The TTA extracts were mounted on stainless steel counting plates and counted

for Pu-238 and Pu-239/240 using passivated, implanted, planar silicon (PIPs) detectors. Each separation was traced based on the Pu-236 recovery. Aliquots of sample were also subjected to Cs-removal with Bio-Rad Ammonium Molybdophosphate (AMP) resin and extracted using TEVA columns (TEVA Brand name for one of Eichrom's resins). The Pu-containing extracts were measured by liquid scintillation analysis to determine Pu-241 concentrations. Shielded cell reagent blanks, Tank 8 sludge simulant and laboratory reagent blanks and a Pu-238 standard were run as controls.

Pu-239, 240, 242, 244

The plutonium from aliquots of Tank 22 composite samples peroxide fusion dissolutions were extracted using TEVA columns (TEVA Brand name for one of Eichrom's resins). The Pu-containing extracts were then analyzed by ICP-MS to determine Pu-239, Pu-240, Pu-242, and Pu-244 isotopics. The measured Pu-242/Pu-239 ratio was applied to the Pu-239 result obtained from the traced analysis to calculate the Pu-242 quantity. Shielded Cells reagent blank, ARG, and laboratory reagent blanks were run as controls.

Am-242m, 243, Cm-243, 244, 245, 247, 248, Cf-249, 251

Aliquot of Tank 22 composite samples were digested using a sodium peroxide fusion. Additionally, a matrix blank and matrix blank spiked with Am-241 and Cm-244 were prepared using Tank 8 simulated sludge. The americium, curium and californium species were extracted from aliquots of peroxide fusion using a CMPO/tributyl phosphate commercial resin based solid phase extractant and purified further with a proprietary commercial resin called HDEHP based solid phase extractant. Am-241, 243, Cm-243, 245, 247, Cf-249 and 251 concentrations were measured using low energy photon/x-ray, thin-windowed, semi-planar high purity germanium spectrometers. Am-242m, Cm-242, and 244 concentrations were measured using passivated, implanted, planar silicon (PIPS) alpha spectrometers. Cm-245, 247 and 248 ratios to Am-241 were measured using ICP-MS and were applied to the previously quantified Am-241. Am-241 quantities had been measured from the cesium removed gamma analyses, Am, Cm, and Cf results were traced with the Am-241 present in the sample matrix. Shielded cell reagent blanks, Tank 8 simulant, ARG, and laboratory reagent blanks were also run as controls.

Tc-99

AQR digested Tank 22 composite samples were analyzed for Tc-99 by ICP-MS.

U-233, U-234, U-235, U-236 and U-238

The AQR digested samples were analyzed by ICP-MS for U-233, U-234, U-235, U-236, and U-238.

Densities:

Density measurements were conducted at a temperature of ~20 °C. This temperature was governed by the Shielded Cells conditions at the time of the measurements. Densities were measured using weight calibrated balances and 8-9 mL volume-calibrated plastic test tubes. Three individual "as-received" Tank 22 supernate aliquots and three individual supernatant aliquots (filtrate) were utilized in the measurements. The supernatant was generated as a filtrate by passing slurry through a 0.45 µm filtration membrane (note that this generation method was utilized for all the supernatant analyses and not just those used for determining density). The density of a deionized water standard was determined along with the slurry and supernatant determinations, to demonstrate measurement accuracy.

Solids Distribution:

Total solids and dissolved solids determinations were performed by driving water from slurry and supernatant aliquots (respectively) at a nominal temperature of ~110 °C. Three individual slurry aliquots and three individual supernatant aliquots were utilized in the measurements. The mass of each aliquot was ~3.0 g. Insoluble and soluble solids concentrations were calculated based on the total solids and dissolved

solids measurements. The analyses requested included weight fraction solids and density, as well as gross alpha, gross gamma, corrosion chemistry and elementals and select radionuclides. The density and weight percent solids of the “as-received” composite sample and filtrate were completed in the Shielded Cells Facility. Aliquots of the “as-received” composite samples were digested, diluted and removed from the Shielded Cells for analysis by ADS. Except for weight percent solids and density, all analyses were conducted in duplicate. Weight percent solids determinations were performed in the Shielded cell in triplicate with a reference sodium chloride solution.

The specific gravity of the “as-received” sample along with total solids in the slurry and the dissolved solids in the slurry, were measured directly on the “as-received” composite material. The insoluble solids and soluble solids were calculated from the total solids and dissolved solids (filtrate) using the following equations:

$$W_{is} = (W_{ts} - W_{ds}) / (1 - W_{ds}) \text{ and}$$

$$W_{ss} = W_{ts} - W_{is}$$

Where W_{ds} = weight fraction dissolved solids in the supernate,

W_{ts} = weight fraction total solids in the sludge,

W_{is} = weight fraction insoluble solids in the sludge and

W_{ss} = weight fraction soluble solids in the sludge.

Digestions

In preparation for the elemental analyses (prior to submittal to AD), three composite sludge aliquots were digested by the aqua regia (AQR) method and three composite sludge aliquots were digested by the peroxide fusion (PF) method. Note that the AQR method utilized a sealed vessel to prevent loss of volatile constituents. Applicable blanks were also processed through the digestion methods, and multi-element standards were submitted along with the digest solutions, where applicable, for quality assurance purposes. The total solids mass of each sample aliquot was ~0.25 g, and the volume of each final digest solution was 100 mL. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on both the AQR and PF digest solutions, along with the applicable blanks and multi-element standard solution for quality assurance purposes. The ICP-AES measurements provided quantification of most of the elemental constituents reported in this document. The ICP-AES axial sulfur method (ICP-AES-S) was performed on the AQR digest solutions for quantifying sulfur. Direct mercury analysis (DMA) was performed on the AQR digest solutions (along with the AQR blank) for quantifying mercury. The elemental results determined through ICP-AES analyses were based either solely on the AQR digest solutions, solely on the PF digest solutions, or on both the AQR and PF digest solutions, depending on the following factors: potential for interference, magnitude of “blank values,” magnitude of minimum detection limits, consistency of data, and apparent anomalies.

Elemental Analysis of Supernatant:

In preparation for the elemental analyses (prior to AD submittal), three supernatant aliquots were each diluted by a factor of ~21 (on a volume basis), using ~3 M HNO₃. The use of the ~3 M HNO₃ diluent was considered beneficial for minimizing loss of constituents through sorption to the walls of the sample submittal vessels and through potential precipitation reactions. An applicable “acid blank” and a multielement standard were submitted along with the acidified/diluted supernatant, for quality assurance purposes. ICP-AES, ICP-AES-S, and DMA were performed on the acidified/diluted supernatant aliquots, to quantify routine elemental constituents, and mercury, respectively.

Anions in the Supernatant:

In preparation for the anion analyses (prior to AD submittal), three supernatant aliquots were each diluted by a factor of ~21 (on a volume basis), using de-ionized water. IC was performed on the diluted supernatant aliquots, to quantify bromide, chloride, fluoride, formate, nitrate, nitrite, oxalate, phosphate, and sulfate. Total inorganic carbon (TIC) analyses were performed to quantify carbonate, and base titration analyses were performed to quantify free hydroxide. Aluminate was quantified based on the ICP-AES supernatant aluminum concentration, assuming 100% of the aluminum was present as aluminate. Dilution-correction of the results was performed prior to reporting.

Select Radioisotopes in the Composite Solids:

The same AQR digestion method that was used for the elemental analyses was utilized for preparing the composite sludge aliquots for the select radioisotope analyses (three aliquots digested by AQR plus an AQR blank for quality assurance purposes). ICP-MS was performed on the AQR digest solutions to quantify Tc-99, Th-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-239, and Pu-240. Dilution correction of the results was performed prior to reporting.

Select Radioisotopes in the Supernatant:

The same acid dilution method that was used for the supernatant elemental analyses was utilized for preparing the supernatant aliquots for the select radioisotope analyses (three supernatant aliquots acidified and diluted using ~2.0 M nitric acid plus a ~2.0 M acid blank for quality assurance purposes). Gamma spectroscopy was performed on the acidified/diluted supernatant aliquots to quantify Cs-137, and ICP-MS was performed to quantify for Tc-99, U-235-U-238.

Weight Percent and Calcined Solids Measurement

The weight percent total solids in each Tank 22 composite sample were measured in the Shielded Cells using a conventional drying oven at 110 °C. An aliquot of each composite sample was placed in a container. The container was placed in the oven. The weights of the dried sample were checked periodically over 72 hours until two consecutive weights yielded comparable results. The weight fraction solid was calculated by dividing the dry weight of the sample by the initial weight of the sample. A 5% sodium chloride salt solution prepared by dissolving 5 of dried sodium chloride in distilled water was used as the reference matrix for weight percent determinations as described above.

Weight percent calcined solids for the Tank 22 composite material was determined experimentally by heating three aliquots of Tank 22 composite sludge with masses ranging from 1.61 to 2.86 grams in 3 alumina crucibles at 1,100 °C for two hours. After 2 hours of heating, the samples were brought to room temperature inside the furnace and the before and after heating weight of the solids used to calculate the weight percent calcined solids.

The weight percent calcined solids can also be calculated directly from the elemental analysis data for the Tank 22 composite material. In this approach, it is assumed that all the metal cations are converted into the oxides and the anions are driven off during the calcining process at 1,100 °C. The elemental concentrations, now converted into the oxides, are summed into the calcined oxides and now represent the masses of oxides in 100 grams of the total dried solids.

Wet and Dry bulk density and Volume Measurements

The wet bulk density of the “as-received” Tank 22 composite solids was determined using a constant volume cut-out bottom portion of 10-mL capacity glass volumetric flasks. The volumes of several of these cut-outs ranged from 1 to 3 mL. The fixed volume of each cut-out was determined analytically by seating it on a 3-digit balance and filling each cut-out unit with DI water until the water reached the brim of the cut-out (cup) without overflowing. A flat spatula was moved over the top of the cup to remove excess water. This was repeated several times until there was not much water touching the spatula. The weight of the amount of water required to fill the fixed volume cup up to the top was measured by difference. Assuming the density of the water was 1.0 g/mL at the measuring temperature of approximately 25 °C the water mass was considered equal to cup volume.

The wet bulk densities of the “as-received” Tank 22 core sludge solids (segments or the core composite sludge) were individually measured using a constant volume cup described above. Using each of the pre-weighed 1 or 3 mL capacity cups, the solids material was loaded into the cup using a spatula (with the whole assembly seated in a secondary container to prevent contamination and sample spills). Enough solid material was put into the cup until there was a solid material overflow at the top of the cup. The cup and its content was gently tapped or shaken to ensure that much of the solid content had dispersed and seated inside the cup without visible cavities or gaps. A flat head spatula was moved across the top of the cup to uniformly dislodge excess material across the open phase of the cup. At this point, the contents of the cup were flush with the circular cup rim. The cup and contents were seated on a balance and the total weight measured and recorded. Knowing the weight of the material by difference and the volume of the cup, the bulk density of the material was calculated. The measurements were determined three times for each sample and at the end of the measurements the contents of the cup were put back into the original sample container.

Density Measurement for dry composite Tank 22 samples and the mineral solids

Particle density (density of only insoluble mineral solids) was determined by liquid displacement with low density/ viscosity pure silicon fluid (polydimethylsiloxane; Cas No: 63148-62-9) as the displaced liquid media. The viscosity, specific gravity and flash point of the silicon fluid were 5 cSt (centistokes), and 0.918 and 135 °C, respectively. In this determination of the particle density of Tank 22 washed insoluble solids, two initial

levels of the silicon fluid was put into two calibrated/graduated cylinders (25 mL and 15 mL total volume) at levels of 13.4 ± 0.1 mL and 5.2 ± 0.1 mL. Known mass of the dry Tank 22 insoluble sludge material (2.510 and 1.612 g) was put into each of the graduated cylinder and the volume of silicon displaced by the insoluble sludge was read. With the volume of silicon displaced in each cylinder and the corresponding mass responsible for the displacement the particle density of the insoluble sludge was calculated.

In the second approach to determine the particle density of washed and dried Tank 22 composite material, Tank 22 “as-received supernate filtrate was used as the displacement fluid. A known quantity of the washed and air-dried Tank 22 composite sludge was put into a graduated cylinder already containing known volume of the supernate. The volume of supernate displaced with the addition of the dry composite sludge was noted and based on the mass of the material the particles density was again determined. These density determinations in the SRNL shielded cell occurred at cell temperature of 26 °C.

Sonication of Tank 22 composite sample for particle size distribution.

The effectiveness of sonication or cavitation strength, defined as power output (Watt) per unit volume of the liquid (power density) for this batch process was 2.5 Watt/cm³ (Power output = 50 Watt and liquid volume = 20 mL). This sonication of Tank 22 composite core sample particles was performed for a duration of 120 second. After this sonication treatment the resulting sonicated material was sent to AD for particle size analysis. This sonication was performed to evaluate the effect of sonication on agglomerated particles from Tank sampling (breaking the agglomerates).

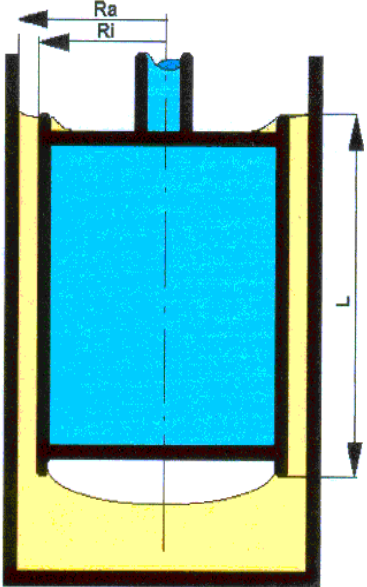
Rheology Measurements

Rheological properties of radioactive samples were determined using a Haake M5/RV30 roto-viscometer. The M5/RV30 is a Searle sensor system, where the bob rotates, and the cup is fixed. The torque and rotational speed of the bob are measured. Heating/cooling of the cup/sample/bob is provided through the holder for the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses. The shear rate for a Newtonian fluid is geometrically determined using the equations of change (continuity and motion). This assumption also assumes that the flow field is fully developed, and the flow is laminar. The shear rate can be calculated for non-Newtonian fluids using the measured data and fitting this data to the rheological model or corrected as recommended by Darby^{**}. In either case, for shear thinning non-Newtonian fluids typical of Savannah River Site (SRS) sludge wastes, the corrected shear rates are greater than their corresponding Newtonian shear rates, resulting in a mathematically thinner fluid. Correcting the flow curves was not performed in this task, resulting in calculations giving a slightly more viscous fluid.

The bob typically used for measuring tank sludge is the MV I rotor. The shape, dimensions, and geometric constants for the MV I rotor are provided in Table 0-1.

^{**} Darby, R., *Chemical Engineering Fluid Mechanics, 2nd edition*. Marcel Dekker: 2001.

Table B-1. MV I and MV II Rotor Specifications and Flow Curve Program

Rotor Design	Dimensions and Flow Curve Program	
	Rotor Type	MV I
	Rotor radius - R_i (mm)	20.04
	Cup Radius - R_a (mm)	21.0
	Height of rotor - L (mm)	60
	Sample Volume (cm^3) minimum	40
	A factor ($\text{Pa}/\% \text{torque}$)	3.22
	M factor ($\text{s}^{-1}/\% \text{RPM}$)	11.7
	Shear rate range (s^{-1})	0 – 600
	Ramp up time (min)	5
	Hold time (min)	1
	Ramp down time (min)	5

Prior to performing the measurements, the rotors and cups were inspected for physical damage. The torque/speed sensors and temperature bath were verified for functional operability using a bob/cup combination with a National Institute of Standards and Technology (NIST) traceable Newtonian oil standard, using the MV I rotor. An N30 oil standard was used to verify system operability prior to the sludge measurements.

The flow curves for the sludge were fitted to the down curves (shear rate ramping down) using the Bingham Plastic rheological model, Equation 0-1, where τ is the measured stress (Pa), τ_o is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa-sec), and $\dot{\gamma}$ is the measured shear rate (sec^{-1}). During these measurements, the sample remained in the cup for the 2nd measurement, due to the limited sample availability.

Equation 0-1 $\tau = \tau_o + \mu_\infty \dot{\gamma}$

Preparation of samples for rheology measurements

The rheology of three samples was measured. First, material following the settling test was removed from the settling vessel (1-L graduated cylinder). The sample was not decanted to the maximum possible amount to ensure the material could be removed from the cylinder.

The second sample was prepared by combining a composite of Tank 22 solids with supernate. 22 wt % insoluble solids were targeted. As can be seen in Table 2-2 (Sample 2) the target was not attained.

For the third sample, after rheological measurements, Samples 1 and 2 were allowed to settle overnight. As much supernatant was decanted as possible (without removing insoluble solids). The samples were then combined to form Sample 3.

The total solids of each sample were measured, and the insoluble solids was calculated using the dissolved solids of the supernatant as shown in Table 4-6.

Appendix C: Tank 22 AD Tracking Numbers for Composite Sample and Supernatant*

Analytes	Method (s)	SRNL AD Tracking Number (LIMS):
Anions	IC	LW12298-LW12300
Free-OH	Free-OH	LW 12302- LW 12304
TIC/TOC	TIC/TOC	LW 12302- LW 12304
Elemental	ICP-ES	LW13414- LW13416, LW12306- LW12308
Select Elements (Ag, Th)	ICP-MS	LW12270- LW12272, LW12306- LW12308
Hg and MHg	DMA	LW12313- LW 12315
Total Alpha	Rad Screen (LSC)	LW12258- LW12260
Non-volatile Beta	Rad Screen (LSC)	LW12258- LW12260
Sr-90/Y-90	Sr90	LW12258- LW12260
Pu-238	Pu-238/241	LW12270- LW12272
Pu-241	Pu-238/241	LW12270- LW12272
Pu-239/ Pu-240	Pu-TTA TEVA separation & ICP-MS	LW12270- LW12272
Cs-134	GAMMA SPEC	LW12258- LW12260, LW13410-LW13412 LW12310-LW12312
Cs-137	GAMMA SPEC	LW12258- LW12260, LW13410-LW13412 LW12310-LW12312
U-233	ICP-MS	LW12270- LW12272, LW12306- LW12308
U-234	ICP-MS	LW12270- LW12272, LW12306- LW12308
U-235	ICP-MS	LW12270- LW12272, LW12306- LW12308
U-236	ICP-MS	LW12270- LW12272, LW12306- LW12308
U-238	ICP-MS	LW12270- LW12272, LW12306- LW12308
Np-237	ICP-MS	LW12270- LW12272, LW12306- LW12308
Co-60	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Sb-126	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Ce-144	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Eu-152	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Eu-154	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Eu-155	GAMMA SPEC Cs REMOVED	LW12258-LW12260
Am-241	Gamma Spec./Am/Cm	LW13410- LW13412, LW12258-LW12260
Cm-244	Am/Cm	LW13410- LW13412
Pm-147/ Sm-151	Pm-147/Sm-151	LW13410-LW13412
Tc-99	ICP-MS	LW12270- LW12272

*Project: IDs: LW-AD-PROJ-170905-1 to Project: ID: LW-AD-PROJ-170905-5

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