

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.



Characterization of the As-Received Sludge Batch 9 Qualification Sample (HTF- 51-15-81)

J. M. Pareizs

September 2015

SRNL-STI-2015-00442



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Keywords: *TANK FARM, TANK 51H,
SLUDGE BATCH 9*

Retention: *Permanent*

Characterization of the As-Received Sludge Batch 9 Qualification Sample (HTF-51-15-81)

J. M. Pareizs

September 2015

Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.



REVIEWS AND APPROVALS

AUTHORS:

| <u>Signature on file</u> | |
|--|------|
| J. M. Pareizs, Process Technology Programs | Date |

TECHNICAL REVIEW:

| <u>Signature on file</u> | |
|---|------|
| J. D. Newell, Process Technology Programs, Reviewed per E7 2.60 | Date |

APPROVAL:

| <u>Signature on file</u> | |
|---|------|
| M. E. Stone, Manager Process Technology Programs | Date |

| <u>Signature on file</u> | |
|--|------|
| A. P. Fellingner, Manager Environmental & Chemical Process Technology Research Programs | Date |

| <u>Signature on file</u> | |
|---|------|
| E. J. Freed, Manager SRR DWPF/Saltstone Facility Engineering | Date |

| <u>Signature on file</u> | |
|--|------|
| J. S. Contardi, Manager SRR Tank Farm Engineering | Date |

| <u>Signature on file</u> | |
|--|------|
| R. E. Edwards, Manager SRR Nuclear Safety and Engineering Integration | Date |

ACKNOWLEDGEMENTS

The author would like to acknowledge the excellent support of the Savannah River National Laboratory (SRNL) Shielded Cells technicians and management. The author would also like to acknowledge the support of SRNL Analytical Development.

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) personnel have been requested to qualify the next sludge batch (Sludge Batch 9 – SB9) for processing at the Defense Waste Processing Facility (DWPF). To accomplish this task, Savannah River Remediation (SRR) has sent SRNL a 3-L slurried sample of Tank 51H (HTF-51-15-81) to be characterized, washed, and then used in a lab-scale demonstration of the DWPF flowsheet (potentially after combining with Tank 40H sludge). This report documents the first steps of the qualification process – characterization of the as-received Tank 51H qualification sample. These results will be used to support a reprojection of SB9 by SRR from which final Tank 51H washing, frit development, and Chemical Processing Cell (CPC) activities will be based.

TABLE OF CONTENTS

| | |
|--|------|
| LIST OF TABLES | viii |
| LIST OF ABBREVIATIONS | ix |
| 1.0 Introduction | 1 |
| 2.0 Experimental Procedure | 1 |
| 2.1 Sample Receipt ant Subsampling | 1 |
| 2.2 Weight Percent Solids and Density | 1 |
| 2.3 Sample Preparations for Total Solids Characterization..... | 1 |
| 2.4 Sample Preparations for Supernatant Characterization | 2 |
| 2.5 Sample Preparations for Oxalate Analysis (Slurry Dilutions)..... | 2 |
| 2.6 SRNL-AD Methods..... | 2 |
| 2.7 Quality Assurance | 3 |
| 3.0 Results and Discussion | 4 |
| 3.1 Density and Wt% Solids..... | 4 |
| 3.2 Supernatant Analytical Results | 4 |
| 3.3 Slurry Oxalate | 5 |
| 3.4 Analysis of Total Solids | 6 |
| 3.5 Calculation of Wt% Calcined Solids..... | 8 |
| 4.0 Recommendations..... | 9 |
| 5.0 References..... | 10 |

LIST OF TABLES

| | |
|--|---|
| Table 2–1. Analyses Performed by SRNL-AD..... | 3 |
| Table 2–2. Analytes from SRNL-AD Methods | 3 |
| Table 3–1. Densities and Wt% Solids..... | 4 |
| Table 3–2. Supernatant Results..... | 5 |
| Table 3–3. Slurry Oxalate Concentration | 6 |
| Table 3–4. Elemental Composition of Total (Dried) Solids | 7 |
| Table 3–5. Cs-137, Uranium Isotopes, and Pu Isotopes | 7 |
| Table 3–6. Elements to Oxides Conversion..... | 8 |
| Table 4–1. Comparison Between Tank Farm Projections and Measurements for the Tank 51 SB9 Qualification Sample | 9 |

LIST OF ABBREVIATIONS

| | |
|---------|--|
| AF | alkali fusion |
| AR | aqua regia |
| CPC | Chemical Process Cell |
| CVHG | SRNL-AD method – cold vapor atomic absorption for Hg |
| DWPF | Defense Waste Processing Facility |
| IC | ion chromatography |
| ICPES | SRNL-AD method RADICPES (inductively coupled plasma – electron spectroscopy) |
| ICPES-S | ICPES special method for sulfur |
| ICPMS | SRNL-AD method RAD ICPMS (inductively coupled plasma – mass spectroscopy) |
| n | number of replicates |
| RSD | relative standard deviation |
| SB9 | Sludge Batch 9 |
| SRNL | Savannah River National Laboratory |
| SRNL-AD | Savannah River National Laboratory Analytical Development |
| SRR | Savannah River Remediation |
| TIC | total inorganic carbon |
| Tit | SRNL-AD method T BASE/OH/OTHER BASE EXC CO ₃ ²⁻ |
| TOC | total organic carbon |
| TTQAP | Task Technical and Quality Assurance Plan |
| TTR | Technical Task Request |
| wt% | weight percent |

1.0 Introduction

Savannah River National Laboratory (SRNL) personnel have been requested to qualify the next sludge batch (Sludge Batch 9 – SB9) for processing at the Defense Waste Processing Facility (DWPF).¹ To accomplish this task, Savannah River Remediation (SRR) sent SRNL a 3-L slurried sample of Tank 51H to be characterized, washed, and then used in a lab-scale demonstration of the DWPF flowsheet (potentially after combining with Tank 40H sludge). This report documents the first steps of the qualification process – characterization of the as-received Tank 51H qualification sample. These results will be used to support a reprojection of SB9 by SRR from which final Tank 51H washing, frit development, and Chemical Processing Cell (CPC) activities will be based. This task is governed by a Task Technical and Quality Assurance Plan (TTQAP).²

2.0 Experimental Procedure

2.1 Sample Receipt and Subsampling

SRNL received the Tank 51H SB9 qualification sample (HTF-51-15-81) on July 23, 2015. The sample was transferred from the Tank Farm sampler to a one gallon glass bottle. Sample volume was just under 3 L and sample mass was 3,685 g. The bulk sample was well mixed and a subsample of approximately 500 mL was taken using a peristaltic pump with Tygon[®] chemical tubing. From this subsample, another approximately 100 mL subsample was taken. A portion of the original subsample was filtered to obtain filtrate for weight percent (wt%) dissolved solids. The 100 mL subsample was allowed to settle over a weekend; the aqueous phase was decanted and used for supernatant analyses. A decanted supernatant better represents Tank Farm operations compared to filtering, although filtrate and supernatant are chemically equivalent. Decanted supernatant was used in this case because time (a weekend) was available for settling prior to sample preparations. All other analyses utilized well mixed slurry from the first 500 mL subsample.

2.2 Weight Percent Solids and Density

Aliquots of slurry and filtrate were dried to a constant weight at 110 °C for wt% total solids and wt% dissolved solids, respectively. Filtrate was obtained by filtering slurry through a 0.45 µm nylon filter. Filtrate, instead of supernatant, was used in this measurement to facilitate drying samples over a three day weekend; using decanted supernatant would have required waiting over the weekend for a sludge sample to settle. Wt% insoluble and soluble solids were calculated from the total and dissolved solids measurements.

Slurry and supernatant densities were determined gravimetrically from sample weights in vessels of known volume. As stated in Section 2.1, supernatant was obtained by decanting from a sub-sample of slurry that was allowed to settle over a weekend.

Based on previous experience, a direct measurement of wt% calcined solids may not be possible with a high sodium sample such as this Tank 51H material. Also, the calcining furnace in the Shielded Cells is temporarily not functional, preventing an attempt at a measurement. Therefore, wt% calcined solids were calculated from elemental analyses of the total solids and the wt% total solids. This methodology and calculation are described in Section 3.5.

2.3 Sample Preparations for Total Solids Characterization

To characterize the solids of the Tank 51H sample, aliquots of slurry were digested and submitted to Savannah River National Laboratory-Analytical Development (SRNL-AD). Slurry samples were digested by two methods, aqua regia (AR) and alkali fusion (AF). For the AR digestions, aliquots of slurry were mixed with aqua regia and heated. The resulting liquids were diluted to 100 mL and submitted to SRNL-AD for analysis. For the AF digestions, aliquots of slurry were dried and fused at 675 °C with sodium peroxide. The fusions were then dissolved with water and nitric acid. The resulting liquids were diluted to 100 mL. The SRNL-AD results were then converted from a slurry basis to a wt% total solids basis using the measured wt% total solids. In general,

aqua regia results have better detection limits compared to alkali fusions; alkali fusions must be diluted more prior to analysis due to the sodium used in the sample preparation. The alkali fusion is a more rigorous digestion, and is better for some forms of aluminum (e.g., boehmite) and silicon. In addition to slurry samples, reagent blanks and digested glass of known composition were processed. Results of these samples were used in evaluating AR and AF results of the slurry digestions. The SRNL-AD analyses performed on the digestions are given in Table 2-1.

2.4 Sample Preparations for Supernatant Characterization

The required results of supernatant characterization include various elements, anions, Cs-137, and free hydroxide. Supernatant, decanted from a subsample of settled slurry, was diluted by approximately 30X with deionized water to reduce personnel radioactivity exposure prior to submission to SRNL-AD. Supernatant was diluted in quadruplicate, and the water used in the dilutions was submitted as a blank. The analyses performed on the diluted supernatant are given in Table 2-1.

2.5 Sample Preparations for Oxalate Analysis (Slurry Dilutions)

Sodium oxalate solubility increases significantly as aqueous sodium concentration decreases.³ This behavior was used to determine total oxalate. A slurry aliquot was diluted with water by ~3x, lowering sodium to below 1 M (near the projected end point). A second slurry aliquot was diluted with water by ~50x; at the resulting sodium concentration, nearly all sodium oxalate should be soluble and measurable in the aqueous phase. The aqueous phases of the dilutions were then submitted to SRNL-AD in quadruplicate for oxalate quantification (see Table 2-1) by Ion Chromatography (IC). The SRNL-AD results and slurry dilution factors were then used to calculate slurry oxalate concentration on a slurry basis.

2.6 SRNL-AD Methods

Given in Table 2-1 are the types of samples (described above) and the SRNL-AD methods used for characterization. Table 2-2 lists the SRNL-AD methods and the analytes reported from these methods.

Table 2–1. Analyses Performed by SRNL-AD

| SRNL-AD Method | Supernatant Dilutions | Slurry Dilutions (Aqueous Phase, for Oxalate) | Aqua Regia Digestions | Alkali Fusion Digestions |
|---|------------------------------|--|------------------------------|---------------------------------|
| RAD Inductively Coupled Plasma – Electron Spectroscopy (ICPES) LEEMAN | X | – | X | X |
| RAD ICPES SULFUR (ICPES-S) AXIAL | X | – | X | – |
| Cold Vapor Atomic Absorption (CVHG) | | – | X | – |
| CVHG DIGESTED | X | – | – | – |
| IC ANIONS | X | X | – | – |
| T BASE/OH/OTHER BASE EXC CO ₃ ²⁻ | X | – | – | – |
| Total Inorganic Carbon/Total Organic Carbon (TICTOC) | X | – | – | – |
| RAD Inductively Coupled Plasma – Mass Spectroscopy (ICPMS) | – | – | X | – |
| GAMMA SCAN | X | – | – | X |
| PU238/241 | – | – | – | X |

X: Sample prep submitted to SRNL-AD; –: Sample prep not submitted to SRNL-AD for this analysis.

Table 2–2. Analytes from SRNL-AD Methods

| SRNL-AD Method | Expected Results to Satisfy TTR Requirements |
|---|---|
| RAD ICPES LEEMAN | Ag, Al, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Sr, Th, Ti, U, V, Zn, Zr |
| RAD ICPES SULFUR AXIAL | S |
| CVHG and CVHG DIGESTED | Hg |
| IC ANIONS | Bromide, Chloride, Fluoride, Formate, Nitrate, Nitrite, Oxalate, Phosphate, Sulfate |
| T BASE/OH/OTHER BASE EXC CO ₃ ²⁻ (Titr) | Free OH ⁻ |
| TICTOC | Total inorganic carbon (CO ₃ ²⁻ is calculated from TIC result) |
| RAD ICPMS | Mass numbers are used to calculate Pd, Ru, Rh, Nd, Th-232, U-233, U-235, U-236, U-238, Pu-239 |
| GAMMA SCAN | Cs-137 |
| PU238/241 | Pu-238, Pu-241 |

2.7 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Density and Wt% Solids

Presented in Table 3–1 are the density and wt% solids results. As stated in Section 2.2, decanted supernatant was used for supernatant density, and filtrate was used for wt% dissolved solids.

The wt% insoluble solids and soluble solids are calculated from the measured wt% total and dissolved solids.⁴ Wt% calcined solids were calculated from elemental analyses of the total solids and the wt% total solids. This methodology and calculation is described in Section 3.5.

Table 3–1. Densities and Wt% Solids

| Property | Result | RSD* |
|---|--------|------|
| Slurry Density (g/mL) | 1.22 | 0.5% |
| Supernatant Density (g/mL) | 1.14 | 0.4% |
| Wt% Total Solids (Slurry Basis) | 27.4 | 0.2% |
| Wt% Dissolved Solids (supernatant basis) | 17.2 | 0.4% |
| Wt% Insoluble Solids (Slurry Basis) | 12.3 | NA |
| Wt% Soluble Solids (Slurry Basis) | 15.1 | NA |
| Wt% Calcined Solids (Slurry Basis) | 19.8 | NA |

* RSD = relative standard deviation with number of measurements (n) = 4. NA = not applicable; result is calculated.

3.2 Supernatant Analytical Results

Presented in Table 3–2 are supernatant results. These analytes were determined from analysis of water-diluted supernatant (nominally 30X). Anions (with the exception of carbonate and hydroxide) were determined by IC. Cs-137 was determined by γ -scan. Carbonate was determined from a TIC analysis by assuming all TIC was carbonate. Free hydroxide was determined from a titration. Mercury was determined by a digestion technique performed by SRNL-AD followed by cold vapor atomic absorption (SRNL-AD method CVHG). The remaining elements were quantified by ICPES. Specific analytical technique for each analyte is reiterated in the table.

As has been seen in Tank Farm samples, sulfate by IC is approximately 75% of the total sulfur as measured by ICPES-S (see, for example, the Tank 40 Sludge Batch 8 composition report where sulfate was 79% of the sulfur, on a molar basis⁵). This difference is likely due to non-sulfate species in the sludge slurry. Therefore, it is recommended that sulfur be projected and tracked with sulfur via ICPES instead of by IC, particularly if sulfur content approaches DWPF limits.

Silicon is not reported for the supernatant. It was detected. However, silicon is known to be present in colloidal form, and not accurately measureable without a digestion method.⁶ A digestion of supernatant for silicon quantification was not performed since silicon was not requested in the TTR.¹ Elements that were less than the detection limit by ICPES were Ba, Be, Cd, Ce, Co, Cu, Gd, Mg, Mn, Ni, Pb, Sb, Sn, Sr, Th, Ti, U, V, Zn, and Zr, with detection limits ranging between 0.1 and 41 mg/L, depending on the element.

Table 3–2. Supernatant Results

| Analyte | Analytical Method* | Units | Result | RSD[†] |
|----------------|---------------------------|--------------|---------------|------------------------|
| Bromide | IC | M | <0.02 | NA |
| Chloride | IC | M | <0.008 | NA |
| Fluoride | IC | M | <0.02 | NA |
| Formate | IC | M | <0.006 | NA |
| Nitrate | IC | M | 0.529 | 0.7% |
| Nitrite | IC | M | 1.04 | 1% |
| Oxalate | IC | M | 0.014 | 2% |
| Phosphate | IC | M | <0.003 | NA |
| Sulfate | IC | M | 0.023 | 1% |
| Carbonate | TIC | M | 0.124 | 9% |
| Free OH | Tit. | M | 0.855 | 4% |
| Hg | CVHG | mg/L | 195 | 9% |
| Cs-137 | γ-scan | dpm/mL | 5.67E+08 | 3% |
| Al | ICPES | M | 0.195 | 0.5% |
| B | ICPES | M | 4.27E-03 | 0.3% |
| Ca | ICPES | M | 1.92E-05 | 19% |
| Cr | ICPES | M | 6.40E-04 | 0.6% |
| Fe | ICPES | M | 4.49E-05 | 12% |
| K | ICPES | M | 0.0122 | 1% |
| La | ICPES | M | 5.14E-06 | 6% |
| Li | ICPES | M | 4.26E-04 | 23% |
| Mo | ICPES | M | 3.00E-04 | 3% |
| Na | ICPES | M | 3.15 | 0.3% |
| P | ICPES | M | 1.48E-03 | 4% |
| S | ICPES-S | M | 0.0305 | 0.7% |

*IC = ion chromatography; TIC = total inorganic carbon (all inorganic carbon is assumed to be carbonate);

Tit. = titration; ICPES = inductively coupled plasma-electron spectroscopy; ICPES-S = ICPES for sulfur;

CVHG = cold vapor atomic absorption for mercury; γ-scan = gamma scan

[†] RSD = relative standard deviation with number of measurements (n) = 4.

3.3 Slurry Oxalate

Sodium oxalate solubility increases significantly as aqueous sodium concentration decreases.³ To determine total oxalate, the sodium concentration in slurry was decreased by diluting slurry aliquots with water. Two dilutions were done: a 3x and a 50x (nominal). The aqueous phases of the dilutions were then submitted to SRNL-AD for oxalate quantification by IC. The SRNL-AD results and slurry dilution factors were then used to calculate oxalate concentration on a slurry basis. Results are presented in Table 3–3. The soluble oxalate in the as-received supernatant reported in Table 3–2 above corresponds to 950 mg oxalate per kg slurry. Thus, 90% of the oxalate in the as-received sample is insoluble. However, as shown by the 3x dilution (diluent Na concentration is comparable to the SB9 wash endpoint), most of the oxalate will become soluble as the wash endpoint is reached.

Table 3–3. Slurry Oxalate Concentration

| Nominal Slurry Dilution | Oxalate Concentration (mg/kg slurry) | RSD[†] |
|--------------------------------|---|------------------------|
| 3X | 9,110 | 3% |
| 50X | 9,390 | 1% |

[†] RSD = relative standard deviation with number of measurements (n) = 4.

3.4 Analysis of Total Solids

Presented in Table 3–4 are elemental analyses of the total dried solids of the Tank 51H sample. As described above, slurry was digested by both aqua regia and alkali fusion. Both digestions were submitted for RAD ICPEs; aqua regia digestions were submitted for CVHG and ICPMS; and alkali fusions were submitted for SRNL-AD's γ -scan and PU238-241 methods. In addition to the slurry samples, reagent blanks and digestions of a reference glass were analyzed by RAD ICPEs.⁷ The results of the blanks and reference glass digestions were used in evaluating slurry results (as discussed below).

- The element Hg was determined from aqua regia digestions and SRNL-AD method CVHG.
- For the elements Al, Ba, Cr, Cu, Fe, Gd, Li, Mg, Mn, Ni, Sr, Ti, and Zn, both RAD ICPEs from aqua regia and alkali fusions were used because there was no significant difference between the digestions.
- For Ca, results from the aqua regia digestion were used because the alkali fusion results were high in the reference glass digestion (likely due to a Ca impurity in the reagent chemicals).
- For Ce, the alkali fusion results were used. The results from the alkali fusions were almost ten times higher than the result from the aqua regia results. No Ce was detected in the reagent blank or the reference glass, thus, this high result, compared to the aqua regia result, is likely not due to reagent impurities. It is possible that the aqua regia digestion did not completely digest the Ce in the sludge.
- For Na and Zr, the aqua regia digestion results were used; alkali fusions utilize Na as a reagent and they are performed in Zr crucibles.
- For Si, results from the alkali fusion digestion were used because the aqua regia results were low in the reference glass digestion.
- Several elements were determined from RAD ICPMS results from aqua regia digestions. Rh was determined from mass 103. Ru was calculated from the sum of masses 101, 102, and 104. Pd was calculated from mass 105 and fission yield values from masses 105-108 and 110.⁸ U was calculated from the sum of masses 233-236 and 238. Th was determined from mass 232.
- The remaining elements and those below detection limits were obtained from aqua regia digestions.

Table 3–4. Elemental Composition of Total (Dried) Solids

| Element | Dig, Analytical Method* | wt% of Total Solids | RSD, n [‡] | Element | Dig, Analytical Method* | wt% of Total Solids | RSD, n [‡] |
|---------|-------------------------|---------------------|---------------------|---------|-------------------------|---------------------|---------------------|
| Ag | AR, ES | 0.00572 | 4%, 4 | Mo | AR, ES | 0.0146 | 4%, 4 |
| Al | AR/AF, ES | 5.25 | 3%, 8 | Na | AR, ES | 25.1 | 2%, 4 |
| B | AR, ES | 0.0131 | 14%, 4 | Ni | AR/AF, ES | 0.455 | 5%, 8 |
| Ba | AR/AF, ES | 0.03 | 5%, 8 | P | AR, ES | 0.120 | 1%, 4 |
| Be | AR, ES | 0.00085 | 1%, 4 | Pb | AR, ES | 0.0209 | 14%, 4 |
| Ca | AR, ES | 0.613 | 2%, 4 | Pd | AR, MS [†] | 0.00116 | 6%, 4 |
| Cd | AR, ES | 0.00942 | 1%, 4 | Rh | AR, MS [†] | 0.00528 | 4%, 4 |
| Ce | AF, ES | 0.105 | 12%, 4 | Ru | AR, MS [†] | 0.0299 | 6%, 4 |
| Co | AR, ES | 0.00512 | 1%, 4 | S | AR, ES-S | 0.303 | 4%, 4 |
| Cr | AR/AF, ES | 0.0651 | 6%, 8 | Sb | AR, ES | <0.03 | NA |
| Cu | AR/AF, ES | 0.0227 | 3%, 8 | Si | AF, ES | 1.03 | 2%, 4 |
| Fe | AR/AF, ES | 10.6 | 2%, 8 | Sn | AR, ES | <0.008 | NA |
| Gd | AR/AF, ES | 0.0428 | 11%, 8 | Sr | AR/AF, ES | 0.0135 | 4%, 8 |
| Hg | AR, CVHG | 1.88 | 1%, 4 | Th | AR, MS [†] | 0.467 | 4%, 4 |
| K | AR, ES | 0.162 | 8%, 4 | Ti | AR/AF, ES | 0.0195 | 5%, 8 |
| La | AR, ES | 0.0140 | 2%, 4 | U | AR, MS [†] | 1.83 | 3%, 4 |
| Li | AR/AF, ES | 0.0435 | 4%, 8 | V | AR, ES | <0.0003 | NA |
| Mg | AR/AF, ES | 0.128 | 7%, 8 | Zn | AR/AF, ES | 0.0178 | 3%, 8 |
| Mn | AR/AF, ES | 3.47 | 4%, 8 | Zr | AR, ES | 0.0284 | 5%, 4 |

* Dig, Analytical Method: AR=Aqua Regia; AF=Alkali Fusion; ES= ICPES; ES-S=ICPES-S; MS=ICPMS; CVHG=cold vapor atomic absorption for mercury

[†] For the elements quantified by MS: Rh is determined from mass 103; Ru is calculated by summing masses 101, 102, and 104; Pd is calculated from mass 105 and fission yields from masses 105-108 and 110; Th is determined from mass 232; and U is calculated from the sum of masses 233-236 and 238.

[‡] RSD = relative standard deviation; n = number of replicates.

Gamma scan, ICPMS, and alpha counting were used to quantify Cs-137, and the isotopes of uranium and plutonium. Those results are presented in Table 3–5. Cs-137 was determined from gamma scan. U-233, U-235, U-238, and Pu-239 were determined from ICPMS. Pu-238 was quantified by alpha counting. Pu-241 was determined from liquid scintillation counting. Pu-240 was calculated from the difference of alpha counting result (the sum of Pu-239 and Pu-240) and the ICPMS Pu-239 result.

Table 3–5. Cs-137, Uranium Isotopes, and Pu Isotopes

| Isotope | Result | RSD [†] |
|--------------------------------|----------|------------------|
| Cs-137 (dpm/g of total solids) | 2.54E+09 | 3% |
| U-233 (Wt% of Total Solids) | 4.27E-04 | 4% |
| U-235 (Wt% of Total Solids) | 2.62E-02 | 4% |
| U-238 (Wt% of Total Solids) | 1.80E+00 | 3% |
| Pu-238 (Wt% of Total Solids) | 4.41E-04 | 7% |
| Pu-239 (Wt% of Total Solids) | 3.82E-03 | 3% |
| Pu-240 (Wt% of Total Solids) | 2.33E-04 | NA |
| Pu-241(Wt% of Total Solids) | 1.66E-05 | 9% |

[†] RSD = relative standard deviation with number of measurements (n) = 4.

3.5 Calculation of Wt% Calcined Solids

Based on previous experience, a direct measurement of wt% calcined solids may not be possible with a high sodium sample such as this Tank 51H material. Also, the calcining furnace in the Shielded Cells is temporarily not functional. Instead, the wt% calcined solids is calculated. First, the elements detected at greater than 0.1 wt% from Table 3–4, with the exception of Hg, were converted to oxides and summed (see Table 3–6). In this calculation, it is assumed that these elements are converted to oxides and all Hg and anions such as nitrite, nitrate, and hydroxide are driven off in the calcining process. Therefore, this sum represents the mass of oxides (calcined solids) in 100 g of total dried solids. The sum was then used to calculate the wt% calcined solids (slurry basis):

$$\frac{72.3 \text{ g oxides}}{100 \text{ g total dried solids}} \times \frac{27.4 \text{ g total dried solids}}{100 \text{ g slurry}} \times 100 = 19.8\%$$

Table 3–6. Elements to Oxides Conversion

| Element | Wt% of Total Solids | Oxide | El. to Oxide Conv.* | Oxide (wt% of total solids) |
|----------------|----------------------------|--------------------------------|----------------------------|------------------------------------|
| Al | 5.246 | Al ₂ O ₃ | 1.8895 | 9.91 |
| Ca | 0.613 | CaO | 1.3992 | 0.858 |
| Ce | 0.105 | Ce ₂ O ₃ | 1.1713 | 0.123 |
| Fe | 10.6 | Fe ₂ O ₃ | 1.4297 | 15.1 |
| K | 0.162 | K ₂ O | 1.2046 | 0.195 |
| Mg | 0.128 | MgO | 1.6583 | 0.212 |
| Mn | 3.47 | MnO | 1.5825 | 5.48 |
| Na | 25.1 | Na ₂ O | 1.3480 | 33.8 |
| Ni | 0.455 | NiO | 1.2726 | 0.579 |
| P | 0.120 | P ₂ O ₅ | 2.2914 | 0.275 |
| S | 0.303 | SO ₄ | 2.9959 | 0.907 |
| Si | 1.03 | SiO ₂ | 2.1393 | 2.19 |
| Th | 0.467 | ThO ₂ | 1.1379 | 0.531 |
| U | 1.83 | U ₃ O ₈ | 1.1792 | 2.16 |
| | | Total | | 72.3 |

* The Element to Oxide Conversion factor (El. to Oxide Conv), also known as the gravimetric factor, is the ratio of the mass of the oxide to the mass of the element in that oxide.

4.0 Recommendations

The results of this characterization are comparable to projections (see Tank Farm planning spreadsheet SB9_072115.xlsm), suggesting the as received sample is representative of Tank 51H. Therefore, it is recommended that SRNL proceed with SB9 qualification using this sample. See Table 4–1 for a comparison between projections and measurements for several analyses.

Table 4–1. Comparison Between Tank Farm Projections and Measurements for the Tank 51 SB9 Qualification Sample

| | Projection | Measurement | Difference |
|----------------------------|------------|-------------|------------|
| Wt% Insoluble Solids | 10.77 | 12.3 | 14% |
| Wt% Total Solids | 26.33 | 27.4 | 4% |
| Supernatant Density (g/mL) | 1.118 | 1.14 | 2% |
| Sodium (M) | 2.944 | 3.15 | 7% |
| Nitrite (M) | 1.059 | 1.04 | -2% |
| Nitrate (M) | 0.517 | 0.529 | 2% |
| Free Hydroxide (M) | 0.956 | 0.855 | -11% |

$$\text{Difference} = (\text{Measurement} - \text{Projection}) / \text{Projection} \times 100$$

5.0 References

1. Rios-Armstrong, M. A. *Sludge Batch 9 Qualification, Confirmatory, and Waste Acceptance Product Samples*; U-TTR-S-00009, Rev. 0; Savannah River Site: Aiken, SC, 2015.
2. Pareizs, J. M. *Task Technical and Quality Assurance Plan for Sludge Batch 9 Qualification, Confirmatory, and Waste Acceptance Product Specification Samples*; SRNL-RP-2015-00120; Savannah River National Laboratory: Aiken, SC, 2015.
3. Kilpatrick, L. L. *Solubility of Sodium Oxalate and Sodium Tetraphenyl Borate in DWPF Supernate*; DPST-84-00341; 1984.
4. Marek, J. C. *Correction Factor for Soluble and Insoluble Solids (U)*; SRTC-PTD-92-0040, Rev. 0; Savannah River Site: Aiken, SC, 1992.
5. Bannochie, C. J. *Tank 40 Final Sludge Batch 8 Chemical Characterization Results*; SRNL-STI-2013-00504; Savannah River National Laboratory: Aiken, SC, 2013.
6. Pennebaker, F. M.; Coleman, C. J.; Jones, M. A.; Wilmarth, W. R.; Jantzen, C. M.; Click, D. R. *Evaluation of Warm Acid Strike Treatment for Silicon Analysis in High Level Waste*; WSRC-TR-2003-00036, Rev. 0; 2003.
7. Smith, G. L. *Characterization of Analytical Reference Glass – 1 (ARG-1)*; PNL-8992; Pacific Northwest National Laboratory: Richland, WA, 1993.
8. Bibler, N. E. *Measuring and Predicting Fission Product Noble Metals in Savannah River Site High Level Waste Sludges*; WSRC-TR-2005-00098; Savannah River Site: Aiken, SC, 2005.

Distribution:

A Fellingner/SRNL/Srs
Timothy Brown/SRNL/Srs
Michael Stone/SRNL/Srs
Samuel Fink/SRNL/Srs
Elizabeth Hoffman/SRNL/Srs
Frank Pennebaker/SRNL/Srs
Bill Wilmarth/SRNL/Srs
Fabienne Johnson/SRNL/Srs
Tommy Edwards/SRNL/Srs
ORG_L3130
Helen Boyd/SRR/Srs
Jonathan Bricker/SRR/Srs
John Contardi/SRR/Srs
Terri Fellingner/SRR/Srs
Eric Freed/SRR/Srs
Jeffrey Gillam/SRR/Srs
Maria Rios-Armstrong/SRR/Srs
Barbara Hamm/SRR/Srs
Bill Holtzscheiter/SRR/Srs
John Iaukea/SRR/Srs
Vijay Jain/SRR/Srs
Chris Martino/SRNL/Srs
Jeff Ray/SRR/Srs
Paul Ryan/SRR/Srs
Hasmukh Shah/SRR/Srs
David Sherburne/SRR/Srs
Christie Sudduth/SRR/Srs
Ryan Mcnew/SRR/Srs
Jason Vitali/SRR/Srs
Arthur Wiggins/SRR/Srs
Patrick Jackson/DOE/Srs
Jeffrey Crenshaw/DOE/Srs
Michael02 Smith/SRR/Srs
Donald Mcwhorter/SRR/Srs

Posted by
John Pareizs
Entered on
09/28/2015

Generic Approval Routing

Tracking Number
GenAppr-2015-00024
Status: Approved

Title SRNL-STI-2015-00442, Revision 0 - Characterization of the As-Received Sludge Batch 9 Qualification Sample (HTF-51-15-81),

Attachments



SRNL-STI-15-442 Rev 0.docx

Approval Routing: Approved on 10/15/2015

| Approvers | Title | Assigned | Received | Status Changed | Status |
|----------------------|------------------------|------------------------|------------------------|------------------------|----------|
| Michael Stone | Manager, PTP | 10/07/2015 04:20:29 PM | 10/08/2015 08:24:22 PM | 10/08/2015 08:26:06 PM | Approved |
| John Pareizs | Author | 10/07/2015 04:20:29 PM | 10/07/2015 04:35:00 PM | 10/13/2015 02:50:07 PM | Approved |
| David Newell | Technical Reviewer | 10/07/2015 04:20:29 PM | 10/13/2015 02:32:49 PM | 10/13/2015 02:33:16 PM | Approved |
| A Fellingner | Manager, ERPS | 10/07/2015 04:20:29 PM | 10/07/2015 04:27:01 PM | 10/15/2015 10:45:01 AM | Approved |
| Maria Rios-Armstrong | Customer - Tank Farm | 10/07/2015 04:20:29 PM | 10/07/2015 04:26:34 PM | 10/08/2015 03:43:44 PM | Approved |
| Helen Boyd | Customer - DWPF | 10/07/2015 04:20:29 PM | 10/08/2015 08:34:46 AM | 10/08/2015 10:07:54 AM | Approved |
| Eric Freed | SRR Saltstone/DWPF Eng | 10/07/2015 04:20:29 PM | 10/07/2015 04:33:24 PM | 10/08/2015 11:57:32 AM | Approved |
| John Contardi | SRR-Tank Farm Eng | 10/07/2015 04:20:29 PM | 10/07/2015 04:23:06 PM | 10/07/2015 04:23:13 PM | Approved |
| Richard Edwards | SRR-NS&EI | 10/07/2015 04:20:29 PM | 10/13/2015 11:39:33 AM | 10/13/2015 11:41:42 AM | Approved |

Previous Process - Approval Routing: Denied on 09/29/2015

| Approvers | Title | Assigned | Received | Status Changed | Status |
|----------------------|--------------------|------------------------|------------------------|------------------------|----------|
| Michael Stone | Manager | 09/28/2015 05:07:01 PM | 09/28/2015 05:08:11 PM | - | - |
| John Pareizs | Author | 09/28/2015 05:07:01 PM | 09/28/2015 05:27:01 PM | 09/29/2015 08:05:54 AM | Denied |
| David Newell | Technical Reviewer | 09/28/2015 05:07:01 PM | 09/29/2015 07:54:11 AM | 09/29/2015 08:01:58 AM | Approved |
| A Fellingner | Customer | 09/28/2015 05:07:01 PM | - | - | - |
| Maria Rios-Armstrong | Customer Manager | 09/28/2015 05:07:01 PM | 09/28/2015 05:07:21 PM | - | - |
| Helen Boyd | | 09/28/2015 05:07:01 PM | - | - | - |
| Eric Freed | | 09/28/2015 05:07:01 PM | 09/29/2015 06:09:41 AM | - | - |
| John Contardi | | 09/28/2015 05:07:01 PM | 09/29/2015 05:33:20 AM | - | - |
| Richard Edwards | | 09/28/2015 05:07:01 PM | 09/29/2015 07:55:32 AM | - | - |

Reviewers

| Name | Date Time | Action |
|--------------|----------------------|----------|
| John Pareizs | 9/29/2015 8:41:02 AM | Reviewed |