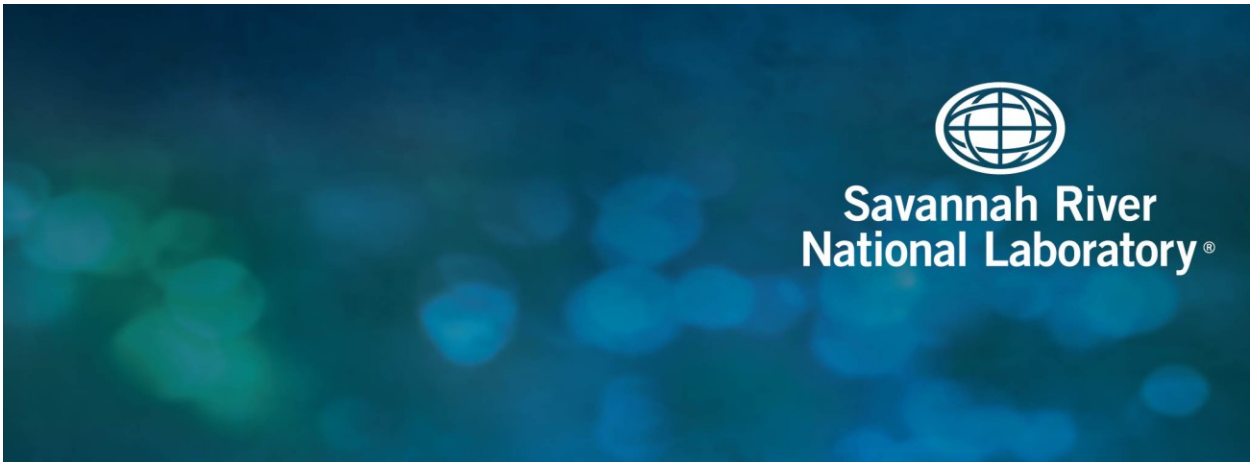
Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:



A U.S. DEPARTMENT OF ENERGY NATIONAL LAB • SAVANNAH RIVER SITE • AIKEN, SC • USA

IDP Analysis of Tank 9H Mined Well Samples

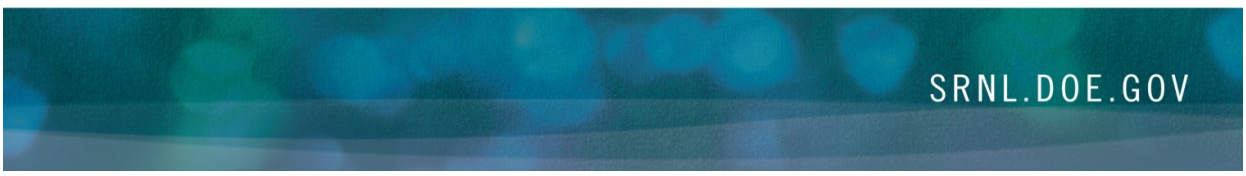
R. A. Pierce

K. M. L. Taylor-Pashow

C. J. Coleman

February 2022

SRNL-STI-2022-00052, Revision 0



DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2022-00052
Revision 0

Keywords: *tank, insoluble solids, analysis, sludge, slurry*

Retention: *Permanent*

IDP Analysis of Tank 9H Mined Well Samples

R. A. Pierce
K. M. L. Taylor-Pashow
C. J. Coleman

February 2022

Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

REVIEWS AND APPROVALS

AUTHORS:

_____
R. A. Pierce, Separation Sciences and Engineering Date

_____
K. M. L. Taylor-Pashow, Separation Sciences and Engineering Date

TECHNICAL REVIEW:

_____
T. C. Shehee, Separation Sciences and Engineering, Reviewed per E7 2.60 Date

APPROVAL:

_____
B. J. Wiedenman, Manager Date
Separation Sciences and Engineering

_____
F. M. Pennebaker, Manager Date
Chemical Processing

_____
M. C. Clark, Waste Removal & Tank Closure Date

EXECUTIVE SUMMARY

The Savannah River Site (SRS) Tank Farm Transfer Control Program Description Document (PDD) requires Inhalation Dose Potential (IDP) testing to determine whether a transfer qualifies as a "HIGH-REM" (> 2.08E+08 rem/gal) or a "LOW-REM" (≤ 2.08E+08 rem/gal) waste transfer. Due to the unexpected presence of solids in a variable depth sample taken from Tank 9H, transfers from salt tanks potentially containing insoluble solids are currently being assessed as sludge slurry transfers. The insoluble solids concentration of such samples were requested to be adjusted to 16.7 wt% for the results to be used to bound future transfers from that tank.

Two samples, HTF-09-21-100 and -101, were received from Tank 9H for analysis to determine IDP. The initial percent insoluble solids concentrations of HTF-09-21-100 and -101 were measured at 4.04 wt% and 6.23 wt%, respectively. Sample HTF-09-21-101 was adjusted to a target of at least 16.7 wt% insoluble solids by removing supernate.

Analysis measured the adjusted insoluble solids concentration at 19.0 wt%. A representative sample was obtained for analysis. Then, based on calculations, supernate was added back to HTF-09-21-101 to achieve a percent insoluble solids concentration of 17.1 wt%, and a representative sample was collected for analysis. Based on duplicate analyses at 17.1 wt% and 19.0 wt% insoluble solids, the samples contain less than 0.0012 Ci/L of gross alpha activity. Therefore, the Tank 9H material can be transferred as a "LOW REM" transfer.

TABLE OF CONTENTS

LIST OF TABLES vi
LIST OF FIGURES vi
LIST OF ABBREVIATIONS vii
1.0 Introduction 8
2.0 Experimental Procedure 8
2.1 Sample Preparation and Analysis 8
2.2 Quality Assurance 9
3.0 Results and Discussion 9
3.1 Receipt of the Sample 9
3.2 Sample Weights 10
3.3 Measurement of Percent Insoluble Solids 10
3.4 IDP Measurements 11
4.0 References 12

LIST OF TABLES

Table 3-1. Initial Sample Masses 10
Table 3-2. Weight Percent of Wet Solids 10
Table 3-3. Percent Total, Dissolved, and Insoluble Solids 11
Table 3-4. Alpha Activity in Tank 9H Slurry Samples 12
Table 3-5. Beta Activity in Tank 9H Slurry Samples 12

LIST OF FIGURES

Figure 3-1. Samples in Plastic Beakers 9
Figure 3-2. Adjusted HTF-09-21-101 in the Original Sample Bottle 11

LIST OF ABBREVIATIONS

IDP	Inhalation Dose Potential
IS	insoluble solids
LSC	liquid scintillation counting
PDD	Program Description Document
PMP	polymethylpentene
SaM	Sensing and Metrology
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
%DS	weight percent dissolved solids
%IS	weight percent insoluble solids
%TS	weight percent total solids

1.0 Introduction

The Savannah River Site (SRS) Tank Farm Transfer Control Program Description Document (PDD) requires Inhalation Dose Potential (IDP) testing to determine whether a transfer qualifies as a "HIGH-REM" (> 2.08E+08 rem/gal) or a "LOW-REM" (≤ 2.08E+08 rem/gal) waste transfer.[1] Due to the unexpected presence of solids in a variable depth sample taken from Tank 9H during a bulk saltcake dissolution,[2] transfers from salt tanks potentially containing insoluble solids (IS) are currently being assessed as sludge slurry transfers. The PDD allows for the sampling of solids from a salt tank at the bottom of a mined well as a means of demonstrating future transfers meet the "LOW-REM" criteria.[1] The solids concentration of such samples must be adjusted to a reasonably conservative value (16.7 wt %) in order for the results to be used to bound future transfers from that tank.[1]

Savannah River Remediation (SRR) requests analysis of such samples from the bottom of mined wells in salt tanks by Savannah River National Laboratory (SRNL) to provide information for determination of the IDP for such samples.[3]

2.0 Experimental Procedure

2.1 Sample Preparation and Analysis

This work was performed according to Task Technical and Quality Assurance Plan (TTQAP) SRNL-RP-2021-05243.[4] Two samples were received from Tank 9H for analysis to determine IDP (see Figure 3-1). The two samples can be used in conjunction to create a single sample for analysis. It is required that the IDP analysis occur on a sample with more than, but close to 16.7 wt% insoluble solids (%IS). SRR Engineering requested that the following methodology be used to assess an IDP sample for any waste tank with mined wells.

1. Measure the total solids of a representative aliquot of each sample.
2. Filter aliquots of each sample and measure the dissolved solids in each filtrate.
3. Calculate the %IS for each of the as-received samples.
4. Based on Step 3, determine the adjustments required to each sample to achieve 16.7 wt% IS.
5. Adjust at least one of the samples by adding or removing supernate, as appropriate. Supernate from one sample can be added to the other sample to make the adjustment.
6. Measure the %IS in the adjusted sample to confirm it is at least 16.7 wt% IS.
7. Digest and analyze the concentrated slurry to assess IDP by determining the total alpha in the sample, reporting results in Ci/L.

After observing the characteristics of the samples, efforts were made to break apart large crystals with a spatula or rod. The sample was transferred to a 250-mL polymethylpentene (PMP) beaker. A Teflon-coated stir bar was added to the beaker, and the beaker was placed on a stirrer. While stirring vigorously, a slurry pipette with the tip cut off was used to transfer ~3 g of sample to a separate weighed beaker. The weight of the beaker and sample were measured. Another aliquot (~3 g) of the sample being stirred was filtered through a 0.2-µm cellulose nitrate filter. The filtrate was transferred to its own weighed beaker, and the beaker with the sample was weighed. The unused sample was returned to the initial sample bottle.

$$Wt\%_{totalsolids} = [(Wt_{fullsample} - Wt_{dry,fullsample}) / Wt_{fullsample}] * 100 \quad (1)$$

$$Wt\%_{dissolvedsolids} = [(Wt_{supernate} - Wt_{dry,supernate}) / Wt_{supernate}] * 100 \quad (2)$$

$$Wt\%_{insoluble} = (Wt\%_{totalsolids} - Wt\%_{dissolvedsolids}) / (100 - Wt\%_{dissolvedsolids}) \quad (3)$$

The two beakers with samples were placed in a Lindbergh drying oven at 125 °C. The samples were periodically removed, weighed, and the weights recorded. When the difference between two consecutive measurements was essentially unchanged, drying discontinued and the final weight recorded. The weight

percent of total solids (%TS) was calculated using Equation 1, the weight percent dissolved solids (%DS) was calculated with Equation 2, and the weight percent insoluble solids (%IS) was calculated according to Equation 3.

Since both samples were below 16.7 wt% IS, calculations determined the amount of supernate that must be removed from each sample to achieve at least 16.7 wt% IS. Both samples were stored without mixing to allow solids to settle prior to the removal of supernate. Sample HTF-09-21-101 was adjusted to a target of 17.0 wt% IS. It was subsequently mixed vigorously, sampled, and re-analyzed to determine the adjusted %IS.

When HTF-09-21-101 was shown to be in the targeted range, the sample was vigorously mixed with a stirrer and magnetic stir bar and then sampled with a modified slurry pipette. The sample was submitted to Sensing and Metrology (SaM) for sample digestion using heated HNO_3-HF and analysis for total alpha activity using liquid scintillation counting (LSC).

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 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. This work was performed following the applicable Task Technical and Quality Assurance Plan (TTQAP).[4] The Task Technical Request (TTR) associated with this work[5] requested a functional classification of Safety Class (see section 9.5 of the TTQAP entitled "Clarification of Safety Significant Functional Classification"). To match the requested functional classification, this report and calculations within received a technical review by design verification.[5] Data are recorded in the Electronic Laboratory Notebook (ELN) system.[6]

3.0 Results and Discussion

3.1 Receipt of the Sample

Two samples collected from the mined salt well in Tank 9H were received at SRNL on 10/27/21. The samples are HTF-09-21-100 and -101. The two samples were collected with slightly different methods. They were both collected from the same area of the tank, but the sampler was covered with foil during the collection of HTF-09-21-101 while the container for HTF-09-21-100 was uncovered. Consequently, there may be a difference in %IS between the two samples.

The samples were high dose and had to enter the cells through pulling of a cell plug. The samples were opened and photographed on 11/9/21 and were found to contain large pieces of what appeared to be salt. Both vials contained salt solids stuck in the bottom of the vial. The solids were able to be transferred to the beaker by breaking up with a slurry pipette and repeated rinsing with supernate from the original sample. It was noted that the solids settle quickly when no stirring is applied

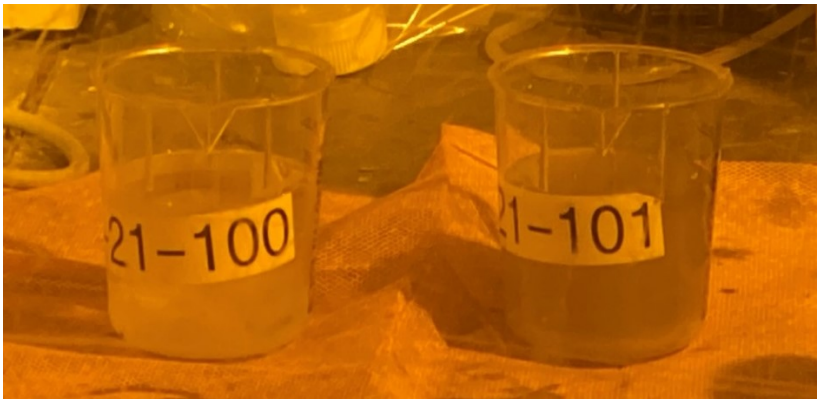


Figure 3-1. Samples in Plastic Beakers

After observing the characteristics of the samples, efforts were made to break apart large crystals with a spatula or rod. Despite this, the Tank 9H samples still contained coarse crystals which sank readily to the bottom of the bottle.

3.2 Sample Weights

Initial weight of the samples and the sample bottles were obtained by using a calibrated balance to weigh the sample in the bottle and the bottle without the sample. The data are provided in Table 3-1.

Table 3-1. Initial Sample Masses

Sample	Bottle + Sample (g)	Bottle (g)	Sample (g)
HTF-09-21-100	334.938	38.823	296.115
HTF-09-21-101	347.257	38.718	308.539

As a first assessment of the %IS, the samples were left unmixed for solids to settle. Next, each bottle and sample were weighed. After, the supernate was decanted, and the weight of the remaining wet solids in the bottle was obtained. The data for the percent wet solids is shown in Table 3-2. Although not necessarily related to the %IS, these data provide an indication that the %IS measurements will be below 16.7%.

Table 3-2. Weight Percent of Wet Solids

Sample	Bottle + Wet Solids (g)	Bottle (g)	Wet Solids (g)	Wt. % Wet Solids
HTF-09-21-100	78.457	38.823	39.634	13.38
HTF-09-21-101	92.565	38.718	53.847	17.45

3.3 Measurement of Percent Insoluble Solids

To measure %IS, the entire sample was transferred from the bottle to a 250-mL PMP beaker. A Teflon-coated stir bar was added to the beaker, and the beaker was placed on a stirrer. The sample was stirred vigorously, sufficient to achieve a good vortex in the sample. While being mixed, striations were observed in the sample, likely due to the larger crystals. The sample also had a few black particles. Using a slurry pipette with the tip cut off to enable the transfer of large particles, approximately 3 grams of sample was transferred to a weighed Pyrex beaker. This sample was dried to determine the %TS in the sample. Duplicate samples were transferred to separate beakers for analysis.

Similarly, another aliquot of the sample was withdrawn, but this time it was passed through a 0.2-µm cellulose nitrate filter to obtain a filtered liquid sample. The filtered liquid was transferred to a separate weighed Pyrex beaker. This sample was dried to determine the %DS in the liquid portion of the sample. Duplicate samples were transferred to separate beakers for drying and measurement of the solids content.

The Pyrex beakers were heated in a drying oven at 125 °C until a constant weight was achieved. Because of the potential for the samples to reabsorb moisture in the shielded cells, and because there is no desiccator in the cells, the beakers were removed from the drying oven one at a time. The beaker was cooled for two minutes, and then it was weighed. Because of air flow and moisture sensitivity in the cells, deciding when a sample was at "constant" weight was a decision based on the experience of the analyst.

The data for the total solids and dissolved solids measurements are provided in Table 3-3. The average of the two values was calculated and the averages were used in Equation 3 to calculate %IS. After the first measurement, the difference between the %DS analyses for the two samples was noted. Although a difference in the %TS might be expected between the two samples, the %DS should be essentially the same because the solution is saturated. Therefore, the %DS for both samples was re-analyzed and the %IS

recalculated. The initial %IS concentrations of HTF-09-21-100 and -101 were measured at 4.04 wt% and 6.23 wt%, respectively.

Since both samples were below 16.7 wt% IS, calculations were made to determine the amount of supernate that must be removed from each sample to achieve the target %IS. Sample HTF-09-21-101 was adjusted to a target of 17.0 %IS by the removal of 63.4% of the total sample mass as supernate. A picture of the adjusted sample is shown in Figure 3-2. Calculations indicate that the %IS for HTF-09-21-101 was adjusted 16.9%.

The remaining HTF-09-21-101 sample was subsequently mixed vigorously in the sample bottle with a magnetic stir bar, sampled, and re-analyzed to determine the adjusted %IS. Analysis measured the adjusted %IS at 19.0 wt%. The sample ("Adjusted") was mixed vigorously with a stir bar and sampled for analysis. The slurry density was also determined to be 1.63 g/mL by measuring the mass of 10.0 mL of sample; the density is the average of two measurements.

Table 3-3. Percent Total, Dissolved, and Insoluble Solids

Sample	Condition	%TS1	%TS2	%TS3	%TS-AVG	%DS1	%DS2	%DS-AVG	%IS
09-21-100	As-received	52.78	52.16	---	52.47	47.62	46.16	46.89	10.51
09-21-101	As-received	53.93	53.31	---	53.62	50.36	51.03	50.70	5.93
09-21-100	As-received*	52.78	52.16	---	52.47	50.83	50.11	50.47	4.04
09-21-101	As-received*	53.93	53.31	---	53.62	50.39	50.69	50.54	6.23
09-21-101	Adjusted	60.10	61.45	58.26	59.94	previous analysis		50.54	19.01
09-21-101	Diluted	Added 9.630 g of supernate to 85.170 g of adjusted sample							17.07

%TS = % Total Solids %DS = % Dissolved Solids %IS = % Insoluble Solids
* Repeat of %DS measurements

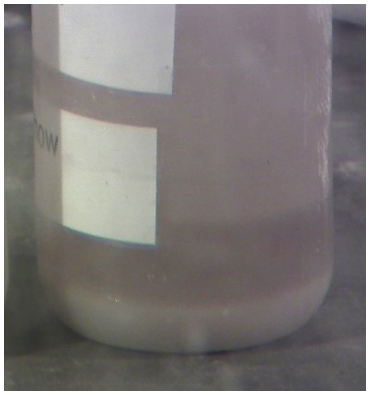


Figure 3-2. Adjusted HTF-09-21-101 in the Original Sample Bottle

Then, based on calculations, supernate was added back to dilute HTF-09-21-101 to achieve a %IS concentration of 17.1 wt%. The sample ("Diluted") was mixed vigorously with a stir bar and sampled for analysis. The solution density was measured at 1.62 g/mL by measuring the mass of 10.0 mL of sample; the density is the average of two measurements. Samples were submitted to SaM for sample digestion and analysis of total alpha activity using LSC. The data for the adjusted and diluted samples are in Table 3-3.

3.4 IDP Measurements

The HTF-09-21-101-Adjusted and 09-21-101-Diluted samples (see Table 3-3) were analyzed in duplicate. The results of the analyses are provided in Table 3-4.

Table 3-4. Alpha Activity in Tank 9H Slurry Samples

Sample	Condition	%IS	Slurry Alpha Activity (dpm/g)*	Slurry Alpha Activity (Ci/g)	Slurry Density (g/mL)	Slurry Alpha Activity (Ci/L)
09-21-101	Adjusted-a	19.01	<1.57E+06	<7.07E-07	1.63	<0.00115
	Adjusted-b		<1.55E+06	<6.98E-07		<0.00114
09-21-101	Diluted-a	17.07	<1.61E+06	<7.25E-07	1.62	<0.00117
	Diluted-b		<1.29E+06	<5.81E-07		<0.00094
* Upper limit value						

A bounding assessment determined that gross alpha sample analysis results less than 0.2247 Ci/L qualify as a "LOW-REM" waste transfer.[1] Based on duplicate analyses at 17.1 wt% and 19.0 wt% insoluble solids, the samples contain less than 0.0012 Ci/L of gross alpha activity. Therefore, the Tank 9H material can be transferred as a "LOW REM" transfer.

While not needed for the IDP calculation, LSC also provides the total beta activity in the samples and those results are provided below in Table 3-5.

Table 3-5. Beta Activity in Tank 9H Slurry Samples

Sample	Condition	%IS	Slurry Beta Activity (dpm/g)	Slurry Beta Activity (Ci/g)	Slurry Density (g/mL)	Slurry Beta Activity (Ci/L)
09-21-101	Adjusted-a	19.01	1.64E+09	7.39E-04	1.63	1.20
	Adjusted-b		1.60E+09	7.21E-04		1.17
09-21-101	Diluted-a	17.07	1.56E+09	7.03E-04	1.62	1.14
	Diluted-b		1.47E+09	6.62E-04		1.07

4.0 References

1. D. G. Harris, "Tank Farm Transfer Control Program, Pump Tank Transfer Jet Control Program, and Waste Tank Chemical Cleaning Program", WSRC-TR-2002-00403, Rev. 32, August 2021.
2. K. M. L. Taylor-Pashow, "Characterization of Tank 9H Dissolution Batches is Support of Tank Closure Cesium Removal (TCCR) 1A Batch 1 Preparations", SRNL-STI-2021-00385, August 2021.
3. M. C. Clark, "IDP Sample Analysis from Waste Tanks with Mined Wells", Liquid Waste Technical Task Request U-TTR-H-00067, October 26, 2021.
4. K. M. L. Taylor-Pashow, "Task Technical and Quality Assurance Plan for Analysis of Samples from Waste Tanks with Mined Wells for Inhalation Dose Potential", SRNL-RP-2021-05243, December 2021.
5. Savannah River Site Manual E7 "Conduct of Engineering", Procedure 2.60 Rev. 18 "Technical Reviews", December 2, 2019.
6. SRNL Electronic Laboratory Notebook #E7518-00472-05.

Distribution:

cj.bannochie@srnl.doe.gov
William.bates@srnl.doe.gov
marion.cofer@srnl.doe.gov
alex.cozzi@srnl.doe.gov
connie.herman@srnl.doe.gov
brady.lee@srnl.doe.gov
Joseph.Manna@srnl.doe.gov
Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
William.Ramsey@srnl.doe.gov
Marissa.Reigel@srnl.doe.gov
eric.skidmore@srnl.doe.gov
michael.stone@srnl.doe.gov
william.swift@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
bill.clark@srs.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
Curtis.Gardner@srs.gov
timothy.littleton@srs.gov
Anna.Murphy@srs.gov
tony.polk@srs.gov
Anthony.Robinson@srs.gov
mark-a.smith@srs.gov
patricia.suggs@srs.gov
thomas.temple@srs.gov
celia.aponte@srs.gov
timothy.baughman@srs.gov
Richard.Edwards@srs.gov
Azikiwe.hooker@srs.gov
Ryan.McNew@srs.gov
phillip.norris@srs.gov
Christine.Ridgeway@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
Vijay.Jain@srs.gov
Bruce.wiersma@srnl.doe.gov
arthur.wiggins@srs.gov
terri.fellinger@srs.gov
gregory.arthur@srs.gov
Eric.Barrowclough@srs.gov
Carl.Scherman@srs.gov
Azikiwe.Hooker@srs.gov
seth.campbell@srs.gov

Records Administration (EDWS)