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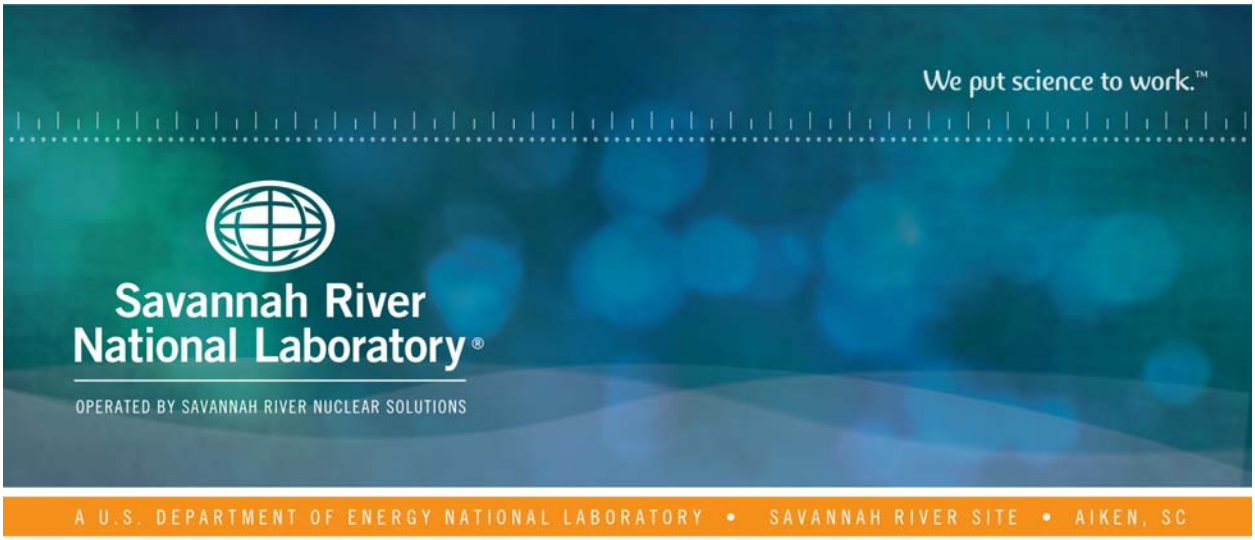

Characterization Results of SRS Tank 26 Samples FTF-26-19-12 and -13

J. M. Pareizs

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EXECUTIVE SUMMARY

Savannah River Remediation (SRR) has requested that the Savannah River National Laboratory (SRNL) characterize several samples from the Savannah River Site (SRS) Tank Farm in preparation for Sludge Batch (SB) 10. This report documents the characterization of Tank 26 material received by SRNL in May of 2019. SRR pulled 2 × 200 mL samples (FTF-26-19-12 and FTF-26-19-13) with Tank 26 slurry pumps at 60 inches. Two samples were taken to ensure SRNL has adequate material for the requested analyses. Because both samples were taken at the same time and at the same tank level, SRNL combined the two Tank Farm samples into one sample prior to analyses.

Results presented in this report include: weight percent solids, density, elemental composition of supernate and slurry, Cs-137 in supernate and slurry, and slurry total alpha and beta.

The sample contained higher than expected total sulfur with a significant insoluble fraction, prompting SRR-E to request a washing study to predict how sulfur will be removed during Tank Farm washing.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AR	aqua regia
DMA	direct mercury analysis
HDPE	high density polyethylene
ICP-ES	inductively coupled plasma-emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry
n	number of replicates
NA	not applicable
PF	peroxide fusion
RSD	relative standard deviation
SB	Sludge Batch
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TIC	total inorganic carbon
TOC	total organic carbon
TTQAP	task technical and quality assurance plan
TTR	technical task request
WD	water dilution

1.0 Introduction

Savannah River Remediation (SRR) has requested that the Savannah River National Laboratory (SRNL) characterize several samples from the Savannah River Site (SRS) Tank Farm in preparation for Sludge Batch (SB) 10.[1] This report documents the characterization of Tank 26 material received by SRNL in May of 2019. SRR pulled 2 × 200 mL samples (FTF-26-19-12 and FTF-26-19-13) with Tank 26 slurry pumps at 60 inches. Two samples were taken to ensure SRNL has adequate material for the requested analyses. Because both samples were taken at the same time and at the same tank level, SRNL combined the two Tank Farm samples into one sample prior to analyses.

For Tank 26, SRR requested different sets of analyses based on slurry pump position at the time of sampling. This material was taken with slurry pumps at 60 inches[2], requiring weight percent solids; density; and supernate elementals, anions, and total gamma; and slurry total alpha, beta, and gamma.[3] SRR subsequently requested elemental analysis of the dried solids.[3]

Note that weight percent solids; density; and supernate anions, gamma, Na, Al, and Si have previously been reported.[4]

2.0 Experimental Procedure

2.1 Sample Receipt and Supernate Acquisition

SRNL received two slurry samples from Tank 26 (FTF-26-19-12 and FTF-26-19-13) from the SRS Tank Farm on May 14, 2019. The two samples were poured into a 500 mL high density polyethylene (HDPE) bottle. The total amount of Tank 26 material was 584 g.

Supernate was obtained by decanting supernate from a 200 mL subsample that was allowed to settle 24 hours. Roughly 45 g (35 mL) of supernate was decanted; this was the most supernate that could be decanted at that time without disturbing the insoluble solids. It should be noted that supernate from slurry samples is often obtained by filtering. Consistent with the TTQAP, decanting was used for this analysis to ensure colloidal silicon would not be removed from the supernate.

2.2 Density and Weight Percent Solids

Slurry and supernate densities were determined gravimetrically from sample weights in vessels of known volume.

Aliquots (nominally 3 g) of slurry and supernate were dried to a constant weight at 110 °C for weight percent total solids and weight percent dissolved solids, respectively. Weight percent insoluble and soluble solids were calculated from the total and dissolved solids measurements.

2.3 Supernate Preparations

Two supernate analytical preparations were done in the SRNL Shielded Cells. First, aliquots were diluted with water by a nominal factor of 50 (WD) to reduce dose rate and then submitted to SRNL-Analytical Development (AD) for anion analysis. Samples were diluted and submitted in triplicate.

Second, supernate was digested by the warm acid strike method.[1, 5] A reagent blank and three silicon standard solutions were submitted for analysis with the samples. Samples were submitted for inductively coupled plasma-emission spectroscopy (ICP-ES) and gamma scan. The warm acid preparation is used to ensure any colloidal silicon is dissolved and measured.

2.4 Digestions

Aliquots of the well mixed slurry sample were prepared for analysis using the aqua regia (AR) and sodium peroxide fusion (PF) in zirconium crucibles digestion methods[6] by AD. Quadruplicate aliquots of the slurry were prepared with each digestion method along with a reagent blank. The sodium peroxide digested samples were submitted to AD for analysis by ICP-ES and Rad Screen. The aqua regia digestions were submitted to AD for analysis by ICP-ES, direct mercury analysis (DMA), and inductively coupled plasma-mass spectrometry (ICP-MS) analyses. Due to instrument problems in AD's 773-A lab, samples were sent to F/H Laboratories for ICP-ES.

2.5 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. This review meets the acceptable criteria to comply with the TTR classification for this work as safety class.[1, 3] Data are recorded in the electronic laboratory notebook system as notebook/experiment number L3293-00022-34.

3.0 Results and Discussion

3.1 Characterization Results

Presented in Table 3-1 are the density and weight percent solids results.

Table 3-1. Densities and Weight Percent Solids

Property	Average	RSD, n=4*
Slurry Density @ 26 °C (g/mL)	1.39	0.3%
Supernate Density @ 26 °C (g/mL)	1.34	1.0%
Wt% Total Solids (Slurry Basis)	40.8	0.3%
Wt% Dissolved Solids (Supernate Basis)	35.2	0.5%
Wt% Insoluble Solids (Slurry Basis)	8.6	NA
Wt% Soluble Solids (Slurry Basis)	32.2	NA

*RSD = relative standard deviation; n = number of measurements;
NA = not applicable because result is calculated.

Supernate results are presented in Table 3-2 and Table 3-3. Table 3-2 shows the anions and total organic carbon (TOC) measured from the water dilutions of the supernate, and the gamma scan results from the warm acid strike. Included in the table are the AD methods – ion chromatography (IC), total inorganic carbon (TIC), titration (Titr), TOC, and gamma scan. It was assumed all TIC was carbonate.

The elemental composition of the supernate is given in Table 3-3. All results were determined by ICP-ES from the warm acid strike preparation method. Results are presented in both mg/L and M. Per the warm acid method protocol, silicon standards were also analyzed. Results of the standards were within 10% of the as-made concentrations.

As a quality check of the supernate results, the sum of the anions was compared to the major cation, sodium. Summing the anions (assuming Al is in the form of $Al(OH)_4^-$) yields a result of 7.83 M, which agrees within 5% of the sodium molarity of 8.00, indicating good data quality in the measurements.

Table 3-2. Supernate Anions, Organic Carbon, and Gamma Scan Results

Analyte	AD Method†	Units	Result	RSD, n=3‡	AD 1-σ Uncertainty
F^-	IC	M	<0.03	NA	NA
CHO_2^-	IC	M	<0.01	NA	NA
Cl^-	IC	M	<0.02	NA	NA
NO_2^-	IC	M	0.809	0.8%	10%
NO_3^-	IC	M	1.99	0.8%	10%
PO_4^{3-}	IC	M	<0.006	NA	NA
SO_4^{2-}	IC	M	0.267	0.8%	10%
$C_2O_4^{2-}$	IC	M	<0.007	NA	NA
Br^-	IC	M	<0.007	NA	NA
CO_3^{2-} ††	TIC	M	0.461*	1.6%	10%
Free OH^-	Titr.	M	3.27	0.8%	10%
Organic Carbon	TIC	mg/L	<1,200	NA	NA
Cs-137	γ-scan	dpm/mL	7.81E+08	0.5%	5%
Ba-137m			7.39E+08	0.5%	5%

†IC = ion chromatography; TIC = Total Inorganic Carbon; Titr. = titration; γ-scan = gamma scan;
‡RSD = relative standard deviation; n = number of measurements.
* TIC was detected in the blank (the water used as the diluent). Therefore, this result may be biased high.
NA = not applicable.

Table 3-3. Supernate Elements

Element	Result (mg/L)	Result (M)	RSD, n=3	AD 1-σ Uncertainty
Ag	<7.8E-01	<7.3E-06	NA	NA
Al	8.18E+03	3.03E-01	0.9%	10%
B	1.12E+02	1.04E-02	0.5%	10%
Ba	<7.8E-02	<5.7E-07	NA	NA
Be	<1.1E-01	<1.2E-05	NA	NA
Ca	8.28E+00	2.07E-04	24.6%	10%
Cd	<7.4E-01	<6.5E-06	NA	NA
Ce	<3.8E+00	<2.7E-05	NA	NA
Co	<7.4E-01	<1.2E-05	NA	NA
Cr	2.05E+02	3.95E-03	0.8%	10%
Cu	<2.2E+00	<3.5E-05	NA	NA
Fe	2.12E+01	3.79E-04	20.8%	10%
Gd	<1.1E+00	<6.7E-06	NA	NA
K	1.60E+03	4.10E-02	0.5%	10%
La	<5.4E-01	<3.9E-06	NA	NA
Li	<7.6E-01	<1.1E-04	NA	NA
Mg	9.59E-01	3.95E-05	10.6%	10%
Mn	5.14E+00	9.35E-05	2.4%	10%
Mo	4.39E+01	4.58E-04	2.3%	10%
Na	1.84E+05	8.00E+00	1.1%	10%
Ni	<1.5E+00	<2.5E-05	NA	NA
P	2.87E+02	9.26E-03	2.8%	10%
Pb	<2.4E+01	<1.1E-04	NA	NA
S	9.74E+03	3.04E-01	1.0%	10%
Sb	<6.1E+00	<5.0E-05	NA	NA
Si	<1.3E+01	<4.5E-04	NA	NA
Sn	<1.5E+01	<1.3E-04	NA	NA
Sr	<5.1E-02	<5.8E-07	NA	NA
Th	<2.0E+00	<8.5E-06	NA	NA
Ti	<1.2E-01	<2.5E-06	NA	NA
U	<2.5E+01	<1.0E-04	NA	NA
V	<1.5E+00	<2.9E-05	NA	NA
Zn	6.13E+00	9.37E-05	3.9%	10%
Zr	<7.4E-01	<8.1E-06	NA	NA

Presented in Table 3-4 is the elemental composition of the Tank 26 solids. As stated above, slurry samples were digested and submitted for ICP-ES, ICP-MS, and DMA. The results were then converted to a dried solids basis using the weight percent total solids from Table 3-1. Digestions were done in quadruplicate. However, Cr, Fe, and Ni concentrations in one of the PF digestions were approximately twice that of the other replicates. It is believed that cross contamination occurred in the replicate. Therefore, this replicate was not used (i.e., there were four AR digestions and three PF digestions used in these results).

For the elements Ag, B, Ba, Be, Ce, Co, Cu, Gd, La, Li, Mo, P, Pb, Sb, Sn, Sr, Ti, V, and Zr, results from ICP-ES of the AR digestions were used either because the detection limit was lower in the AR results or the element was not detected in the PF digestion. For Cd and Zn, the detection limit in the PF digestion was reported since the PF detection limit was lower than that in the AR digestion. For Ca, K, and Na, results from the ICP-ES of the AR digestions were used because these elements were detected in

significant quantities in the PF reagent blank. The PF digestion method utilizes sodium hydroxide, which, in addition to Na, likely has Ca and K impurities. For Hg, results from DMA analysis of the AR digestions was used. For Th and U, ICP-MS from the AR digestions was used. Th was not detected by ICP-ES, and U had a relatively high (30%) uncertainty form the ICP-ES. Mass number 232 was used for Th, and masses 234, 235, and 238 were summed for U.

Table 3-5 shows Cs-137, total alpha, total beta, and Cs-removed total beta from PF slurry digestions. Results are presented on a Ci/gal of slurry basis. Total alpha results are an "upper limit". That is, alpha was detected, but is likely biased high due to high beta, which interferes with the alpha measurement, in the sample. Total beta is a measurement of all beta emitters in the sample, including Cs-137. This method measures electron activity and is likely biased high compared to a sum of the activities of beta emitters if quantified separately. The Cs-removed total beta result is obtained by the same method as total beta, but after Cs-137 removal. The major beta emitters in SRS sludge that would be captured in this analysis would be Sr-90 and Y-90. Other beta emitters such as Tc-99, Pu-241, H-3, Sm-151, Eu-154, Eu-155, etc., would also contribute to the Cs-removed total beta number. Note that Cs-137 was the only radionuclide reported by AD from the gamma scan.

Table 3-4. Elemental Composition of Total Dried Solids*

Element	Dig meth	Result (wt% of Dried Solids)	RSD	n	AD 1-σ Uncertainty
Ag	AR	< 5E-03	NA	NA	NA
Al	AR, PF	1.52E+00	3.7%	7	10%
B	AR	1.40E-02	3.1%	4	10%
Ba	AR	5.74E-03	1.6%	4	10%
Be	AR	< 5E-03	NA	NA	NA
Ca	AR	3.43E-01	3.5%	4	10%
Cd	PF	< 8E-03	NA	NA	NA
Ce	AR	4.72E-03	2.7%	4	10%
Co	AR	< 5E-03	NA	NA	NA
Cr	AR, PF	2.80E-01	3.4%	7	10%
Cu	AR	< 5E-03	NA	NA	NA
Fe	AR, PF	2.85E+00	5.6%	7	10%
Gd	AR	< 5E-03	NA	NA	NA
Hg	AR	7.88E-02	14%	NA	20%
K	AR	2.36E-01	3.3%	4	10%
La	AR	< 5E-03	NA	NA	NA
Li	AR	< 5E-03	0.0%	NA	NA
Mg	AR, PF	1.21E-01	6.6%	7	10%
Mn	AR, PF	1.60E-01	4.8%	7	10%
Mo	AR	< 1E-02	0.0%	NA	NA
Na	AR	3.35E+01	1.7%	4	10%
Ni	AR, PF	4.75E-02	6.1%	7	10%
P	AR	5.20E-02	0.9%	4	10%
Pb	AR	< 5E-03	NA	NA	NA
S	AR, PF	2.84E+00	4.5%	7	10%
Sb	AR	< 5E-03	NA	NA	NA
Si	AR, PF	8.96E-02	7.2%	7	10%
Sn	AR	< 5E-03	NA	NA	NA
Sr	AR	< 5E-03	NA	NA	NA
Th	AR	2.42E-04	5.5%	4	10%
Ti	AR	< 5E-03	NA	NA	NA
U	AR	2.11E+00	0.7%	4	10%
V	AR	< 5E-03	NA	NA	NA
Zn	PF	< 8E-03	NA	NA	NA
Zr	AR	< 5E-03	NA%	NA	NA

* Results determined from digestions of slurry and then converted to total dried solids basis using the weight percent total solids measurement (see Table 3-1).

Table 3-5. Rad Screen Results of slurry

	Result (Ci/gal)	RSD	AD 1-σ Uncertainty
Cs-137	1.37E+00	1.9%	5%
Total Alpha	< 3.70E-02	NA	NA
Total Beta	2.35E+00	0.8%	10%
Cs-Removed Total Beta	5.49E-01	1.6%	10%

3.2 Insoluble Sodium and Sulfur

The amount of sulfur in the supernatant and in the total solids of the Tank 26 sample was higher than expected resulting in a projected 1.45 wt% sulfate in the final SB10 glass.* The projection is based on washing sulfur from the supernatant, leaving insoluble sulfur unchanged. The original DWPF sulfate limit in glass was 0.4 wt%[7], however, sulfate has been administratively controlled since SB3 to 0.6-0.65 wt.% based on experimental sulfate solubility testing for a given sludge batch.[8-15] As shown in the table below, almost 40% of the sulfur was insoluble at room temperature (25-30 °C) in the cells. This high sulfur in glass, if it is not significantly reduced during washing, could impact the SB10 batch recipe and, at a minimum, require studies to evaluate this level of sulfur in glass. Because a significant portion of the sulfur is insoluble in the sample, sulfur removal predictions during washing are difficult. It is possible that a portion of the sulfur in the insoluble solids is burkeite, and should dissolve during Tank Farm washing in the time periods between water additions and decants (see for example work with Tank 4[7]). In burkeite, the sodium to sulfur ratio is 3:1. In the insoluble solids of Tank 26, the sodium to sulfur ratio is nearly 3:1, suggesting **it could be** burkeite. With the uncertainty of the form of sulfur in the insoluble solids and whether it could be washed out by the time it reaches 1M Na in the supernate, SRR-E has requested that SRNL perform a washing study focused on sulfur removal.[8]

Table 3-6. Soluble Sodium and Sulfur in the Tank 26 sample

Basis: 100 g slurry		
Element	Na	S
Total, g	13.7	1.16
Soluble, g	12.6	0.664
% Soluble	91.8%	57.3%
Moles Insoluble	0.049	0.015

4.0 Conclusions

The characterization results for this material are consistent with unwashed slurry samples – greater than 1% of the total solids results for sodium, iron, aluminum, and uranium. Supernate Na was 8 M, with free OH concentration greater than 3 M. Digestion of the slurry showed sodium to be the main component of the total dried solids of the sample followed by iron, uranium, and aluminum. The sum of the major cations versus the sum of the major anions from the analysis of the supernate showed a difference of <5% indicating good data quality for the supernatant analysis.

The sample contained higher than expected total sulfur with a significant insoluble fraction, prompting SRR-E to request a washing study to predict how sulfur will be removed during Tank Farm washing.

* This projected concentration was provided by SRR-E.

5.0 References

1. Fellinger, T. L. *Technical Task Request: Sample Analysis for Sludge Batch 9B/10 Assembly*; X-TTR-S-00050, Rev. 0; Savannah River Remediation: Aiken, SC, 2016.

2. *Waste Tank Equipment Manual*; Manual SW11.1-WTE, Section 7.8; Savannah River Remediation: Aiken, SC.

3. Pareizs, J. M. *Task Technical and Quality Assurance Plan for Tank 26 Characterization Samples*; SRNL-RP-2019-00208, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2019.

4. Pareizs, J. M. *Analytical Results of SRS tank 26 Samples FTF-26-19-12 and -13 for Corrosion Control and Evaporator Qualification*; SRNL-L3300-2019-00021, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2019.

5. 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.

6. Savannah River National Laboratory *Analytical Development Section Analytical Operating Procedures*; Manual L16.1; Savannah River National Laboratory: Aiken, SC.

7. Edwards, T. B. *SME Acceptability Determination for DWPF Process Control (U)*; WSRC-TR-95-00364, Rev. 6; Savannah River National Laboratory: Aiken, SC, 2017.

8. Lorier, T. H.; Reamer, I. A.; Workman, R. J. *Initial Sulfate Solubility Study for Sludge Batch 4 (SB4)*; WSRC-TR-2005-00213, Rev. 0; 2005.

9. Fox, K. M.; Edwards, T. B.; Peeler, D. K. *Sulfate Retention in High Level Waste (HLW) Sludge Batch 4 Glasses: A Preliminary Assessment*; WSRC-STI-2006-00038, Rev. 0; 2006.

10. Raszewski, F. C.; Best, D. R.; Peeler, D. K. *An Assessment of the applicability of the 0.6 wt% SO_4^{2-} PCCS limit for the Frit 418-SB5 system*; SRNL-L3100-2008-00023, Rev. 0; Savannah River National Laboratory: Aiken, SC, September 2008.

11. Billings, A. L. *DWPF Sulfate Limit Verification for SB6*; SRNL-STI-2010-00191, Rev. 0; 2010.

12. Billings, A. L. *Sulfate Solubility Limit Verification for DWPF Sludge Batch 7a*; SRNL-STI-2011-00197, Rev. 0; 2011.

13. Billings, A. L.; Fox, K. M. *Sulfate Solubility Limit Verification for DWPF Sludge Batch 7b*; SRNL-STI-2011-00482, Rev. 0; 2011.

14. Kot, W. K.; Pegg, I. L. *Determination of Sulfate Solubility Limit for Defense Waste Processing Facility (DWPF) Sludge Batch 8*; VSL-13L2580-3, Rev. 0; 2013.

15. Johnson, F. C. *Recommendation for the Sludge Bach 9 Sulfate Solubility Limit*; SRNL-L3100-2016-00044, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2016.

Distribution:

timothy.brown@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
c.diprete@srnl.doe.gov
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samuel.fink@srnl.doe.gov
nancy.halverson@srnl.doe.gov
erich.hansen@srnl.doe.gov
connie.herman@srnl.doe.gov
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Gregg.Morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
Amy.Ramsey@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
michael.stone@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
bill.wilmarth@srnl.doe.gov
Records Administration (EDWS)
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
tony.polk@srs.gov
patricia.suggs@srs.gov
celia.aponte@srs.gov
timothy.baughman@srs.gov
earl.brass@srs.gov
Richard.Edwards@srs.gov
Azikiwe.hooker@srs.gov
Thomas.Huff@srs.gov
Ryan.McNew@srs.gov
phillip.norris@srs.gov
Christine.Ridgeway@srs.gov
Azadeh.Samadi-Dezfouli@srs.gov
Vijay.Jain@srs.gov
arthur.wiggins@srs.gov
terri.fellinger@srs.gov
hasmukh.shah@srs.gov
jeffrey.gillam@srs.gov