WSRC-TR-2002-00076

Technical Task Request HLW/DWPF/TTR-00-0016, Rev. 1:

Confirmation Run of the DWPF SRAT Cycle Using the Sludge-Only Flowsheet with Tank 40 Radioactive Sludge and Frit 200 in the Shielded Cells Facility (U)

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DISCLAIMER

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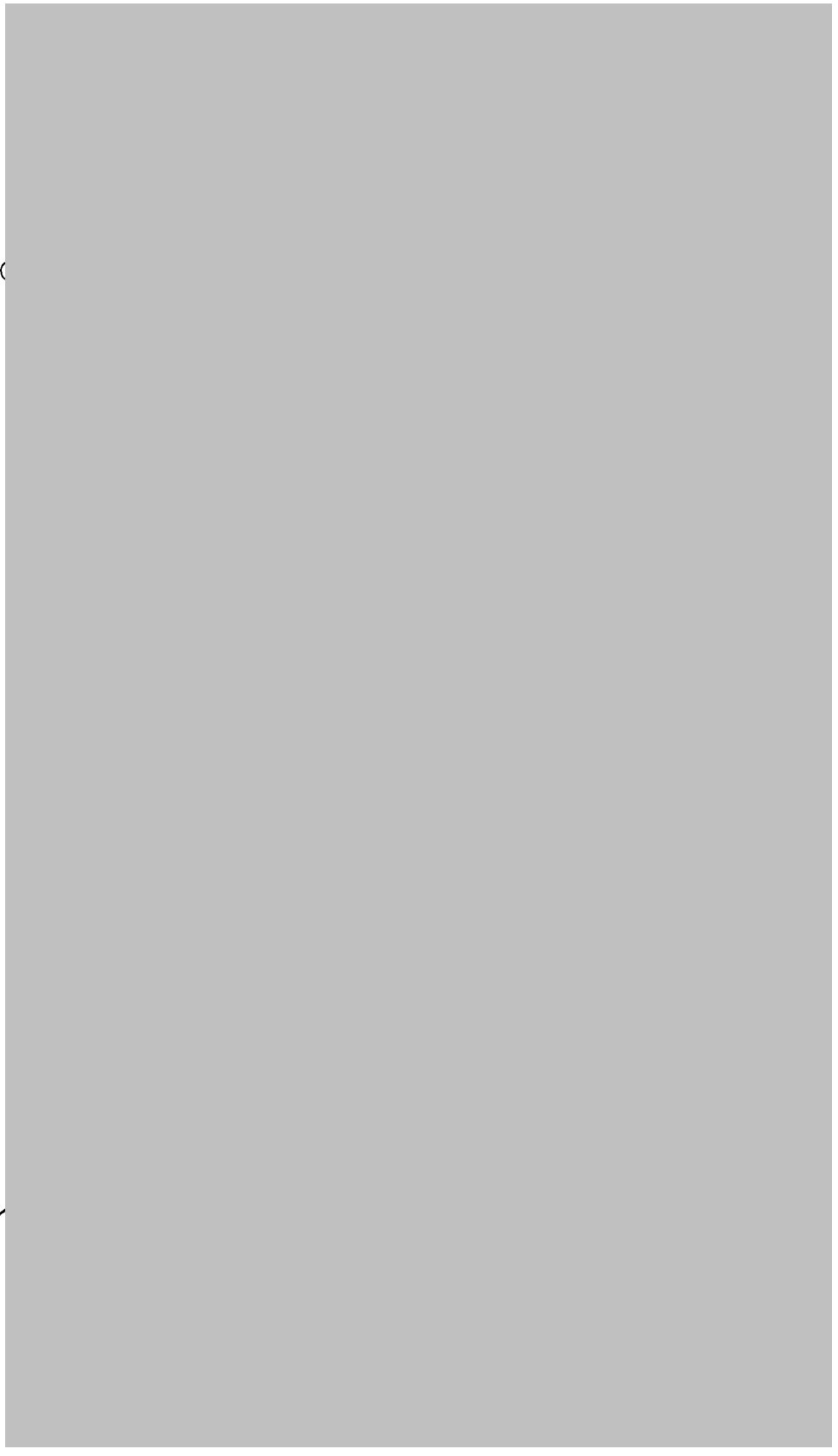
APPROVALS



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1.0 SUMMARY

Several basic data reports[1, 2, 3] have been issued concerning the recent demonstration of the Defense Waste Processing Facility (DWPF) Sludge Receipt and Adjustment Tank (SRAT) Cycle and Slurry Mix Evaporator (SME) Cycle, conducted at the Savannah River Technology Center (SRTC). The SRTC demonstration was completed using the DWPF "Sludge-Only" flowsheet with washed Tank 40 sludge slurry (Sludge Batch 2 or Macrobatch 3) in the Shielded Cells facility. The DWPF "Sludge-Only" flowsheet[4] calls for processing radioactive sludge slurry using nitric acid, concentrated formic acid, and frit 200. This demonstration was requested by the DWPF through a Technical Task Request (HLW/DWPF/TTR-00-0016, Rev. 1)[5].

The basic data reports contained tables of data that allowed the DWPF to perform the essential evaluations in order to expedite processing of Sludge Batch 2. This report provides the detail that was omitted from the basic data reports[1, 2]. Highlights from this report are found below.

- The SRAT cycle was successfully completed by adding the prescribed amounts of nitric acid and concentrated formic acid.
- Foaming was encountered during the formic acid addition during the SRAT cycle. An extra addition of 100 ppm of IIT747 antifoam was added to the vessel, successfully mitigating the observed foam. See recommendation below.
- The maximum hydrogen production rate on a DWPF basis was 0.00076 lb H_2/hr during the SRAT cycle, well below the DWPF hydrogen design basis rate of 0.65 lb/hr for the SRAT Cycle.
- Nitrite was destroyed (95%) by the end of the SRAT cycle.
- During the SRAT cycle 91.6% of the Hg was removed from the sludge.
- The iron to fissile material ratios in the washed Tank 40 sludge slurry and the resulting SRAT product exceeded the minimum required to ensure criticality safety. On this basis, the DWPF can process Tank 40 sludge slurry with negligible risk of a nuclear criticality.

Recommendation (See Sections 5.0 and 8.0):

- Recommendation for new IIT747 Antifoam Addition for the SRAT Cycle*:* Follow the prescribed antifoam strategy except add 100 ppm of antifoam prior to the formic acid addition[4]. As prescribed, refresh the antifoam every 8 hours of processing[4].

2.0 INTRODUCTION

The DWPF is currently processing and immobilizing radioactive sludge slurry into a durable borosilicate glass. After successfully processing Sludge Batch 1B (Macrobatch 2) for approximately 3 years, the DWPF was in need of a new batch of radioactive sludge slurry to continue canistered waste form production. The next batch of radioactive sludge slurry to be processed by the DWPF is called Sludge Batch 2 (Macrobatch 3). Sludge Batch 2 is a mixture of the sludge slurry that was transferred from Tank 8 and the sludge slurry that already existed in Tank 40. Tank 40 is one of the two tanks (the other feed tank is Tank 51) that directly feed the DWPF.

Prior to processing a new sludge batch in DWPF, SRTC-Immobilization Technology Section (ITS) must analyze and confirm that each sludge batch produces an acceptable glass[6]. The first step in this confirmation is to complete a glass variability study using nonradioactive simulants and frit (glass

forming chemicals) to obtain glass properties for various blends of the simulant and frit together[7]. The second step is to perform process testing using nonradioactive sludge slurry simulants[4]. The last step is to confirm steps one and two by targeting a glass composition and processing the actual radioactive sludge slurry from the tank[5, 8, 9, 10].

To perform the last step, twelve (220 mL/each dip sample) dip samples, totaling 2.6 L, were obtained from Tank 40 and sent to the SRTC Shielded Cells Facility. The samples were combined and an initial composition of the radioactive sludge slurry was obtained. Since the Na concentration of the sludge slurry did not meet the DWPF acceptance criteria, a demonstration of the Tank Farm's Extended Sludge Processing (ESP) was performed by the Waste Processing Technology Section (WPTS). The sludge slurry was washed to have a final supernate sodium concentration in the range of 0.53 M to 0.60 M to meet the acceptance criteria of the DWPF. Upon receipt of the washed sludge slurry from WPTS, a demonstration of the DWPF "Sludge-Only" flowsheet was performed using approximately one liter of sludge slurry. The DWPF "Sludge-Only" flowsheet calls for processing radioactive sludge slurry using nitric acid, concentrated formic acid, and frit 200 through the Chemical Processing Cell (CPC) of DWPF.

Information concerning processing, offgas data, and analyses of the final washed sludge slurry composition and final SRAT product obtained during this cycle are provided in this report. Information concerning the SME cycle, vitrification, and Product Consistency Test results can be found in WSRC-TR-2002-00096[11].

3.0 RESULTS OF THE ANALYSES PERFORMED ON THE WASHED TANK 40 RADIOACTIVE SLUDGE SLURRY AND SUPERNATE

Provided below are the results from the analyses of the washed Tank 40 sludge slurry and washed Tank 40 supernate. Analyses include density measurements, weight percent solids measurements, calcined solids measurement for the sludge slurry, nonradioactive and radioactive compositions of the supernate, and dissolution procedures to obtain the nonradioactive and radioactive compositions of the sludge slurry. Details of the ESP washing of this sludge slurry, performed by the WPTS, will be published at a later date.

3.1 Total Weight Percent Solids, Calcined Solids Measurements, Density Measurements, and Nonradioactive and Radioactive Compositions for the Washed Tank 40 Sludge Slurry

The sections below provide a brief description of the analyses and results obtained from portions of the washed Tank 40 sludge slurry sample.

3.1.1 Total Weight Percent Solids Measurements for the Washed Tank 40 Sludge Slurry

Quadruplicate measurements of the total weight percent solids for the sludge slurry were completed remotely in the Shielded Cells Facility. Mixed portions of a sample of sludge slurry were pipetted into four labeled, pre-weighed PMP® beakers. After the addition of the mixed sludge slurry, the PMP® beakers were weighed and placed into a drying oven at 115°C overnight. The samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. To check the accuracy and precision of the method, three samples of a 15 wt% NaCl standard solution were also weighed and dried (in labeled PMP® beakers) along with the sludge slurry samples. The results of the standard solutions showed good reproducibility and good agreement with the known value of

the standard. The averages of the calculated results of the weight percent solids for the sludge slurry are presented in column two of Table 1. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two of Table 1.

3.1.2 Calcined Solids Measurements for the Washed Tank 40 Sludge Slurry

Duplicate measurements of the calcined solids were completed in the Shielded Cells Facility for the sludge slurry. Mixed portions of a sample of sludge slurry were pipetted into two pre-weighed alumina crucibles. The crucibles were weighed and then dried overnight at 115°C in a drying oven to avoid any loss of the material during the calcining process. The samples were removed from the drying oven and allowed to cool for ~5 minutes before they were weighed. The samples were then placed into a muffle furnace and heated to 1000°C. The samples were held at 1000°C for ~ 2 hours. The muffle furnace was turned off and the samples were allowed to cool inside of the muffle furnace. The samples were then removed from the muffle furnace, weighed, and the calcined solids were calculated. The averages of the calculated results of the calcine solids for the sludge slurry are presented in column three of Table 1. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column three of Table 1.

3.1.3 Density Measurements for the Washed Tank 40 Sludge Slurry

Density measurements were completed remotely in the Shielded Cells Facility by using heat sealed pipette tips. The pipette tips are first sealed and then calibrated with water to obtain the volume. Four density measurements were completed for the sludge slurry. The sealed pipette tip was first weighed and then a mixed sample of sludge slurry was pipetted into the sealed pipette tip. The sealed pipette tip containing the sludge slurry sample was weighed and a density calculated. The results of the sludge slurry for the washed Tank 40 sample are presented in column four of Table 1. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column four of Table 1.

Table 1 - Weight Percent, Calcined Solids, and Density Measurements for the SRTC Washed Tank 40 Sludge Slurry

	Weight Percent Total Solids for the Tank 40 Sludge Slurry [a, b]	Calcined Solids for the Tank 40 Sludge Slurry [c]	Density Measurement for the Tank 40 Sludge Slurry [b]
Average	18.4 wt%	15.7 wt%	1.12 g/mL
Std. Dev.	± 3.9E-02	± 2.7E-01	± 2.3E-02
% RSD	2.1E-01	1.7E00	2.1E00

[a] The samples for weight percent solids measurements were dried overnight in a drying oven at 115°C.
[b] Average of four results.
[c] Average of two results. Samples heated to 1000°C.

3.1.4 Nonradioactive Composition for the Washed Tank 40 Sludge Slurry

Provided below are the results of the analyses for the washed Tank 40 sludge slurry sample. Eight portions of a mixed sludge slurry sample were taken and dried overnight in a drying oven at 115°C. This dried sludge slurry was dissolved by the Aqua Regia[12] and Sodium Peroxide/Sodium Hydroxide Fusion[13] methods along with appropriate standards to check the dissolutions and the analytical methods. After performing the dissolution methods on the sludge slurry, the dissolved sludge slurry was removed from the Shielded Cells Facility. These diluted samples were sent to Analytical

Development Section (ADS) Sample Receiving for analyses to be performed by ADS. The dissolution results of the standards for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly. Table 2 presents the elements (excluding oxygen) with concentrations >0.1 weight percent in the SRTC washed Tank 40 sludge slurry obtained from ADS methods (Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES) and Atomic Adsorption (AA)). Table 2 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

Table 2 - Elements (excluding oxygen) with Concentrations >0.1 Weight Percent in the SRTC Washed Tank 40 Sludge Slurry Presented in Units of Weight Percent of Total Dried Solids

Element	Weight Percent [*, a]	Element	Weight Percent [*, a]
Al	5.77E00 (± 8.6E-02, 1.5E00)	Mg	1.84E00 (± 3.8E-02, 2.1E00)
Ca	2.34E00 (± 8.1E-02, 3.5E00)	Mn	3.21E00 (± 1.4E-01, 4.2E00)
Cd	1.39E-01 (± 5.1E-03, 3.7E00)	Na[b]	7.80E00 (± 5.6E-02, 7.0E00)
Cr [b]	1.57E-01 (± 6.5E-04, 4.0E-01)	Ni[b]	1.19E00 (± 1.0E-02, 9.0E-01)
Fe	2.36E01 (± 5.0E-01, 2.1E00)	P	6.36E-01 (± 1.9E-02, 3.0E00)
Hg [b, c]	1.95E-01 (± 1.1E-02, 3.2E00)	Si[b]	1.19E00 (± 6.4E-02, 5.4E00)
		U [b]	7.61E00 (± 4.5E-02, 6.0E-01)

*The sludge slurry sample was dried overnight at 115°C. Results are presented on a dry total solids basis.
a Results are determined by ICP-ES unless otherwise indicated and are the average of results of seven dissolved samples of dried slurry.
b Average of four results.
c Results determined by AA method.

3.1.5 Radioactive Composition of the Washed Tank 40 Sludge Slurry

To obtain the radioactive composition, the dissolution solutions discussed in Section 3.1.4 were used. Portions of the dissolution solutions were submitted to ADS for the following methods: Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) and counting techniques. Table 3 presents the concentrations of the radionuclides requested in the Technical Task Request to meet the DWPF Radiological Program and the DWPF TSR/WAC requirements. The concentration of C-14 required for solid waste characterization is not included in Table 3 and has been estimated and published previously[1]. Additional radionuclides such as Ni-59, Ni-63, and I-129, required for repository waste acceptance will be measured and results will be published later. The concentrations in Table 3 are presented in weight percent in the dried sludge slurry and in microcuries per gram of dried sludge slurry. The concentrations with the prefix of the less than symbol (<) were too small to be measured because of the short half-life of the radionuclides. These concentrations are upper limits based on the detection limit of the analytical method. The measured concentrations are averages based on the analysis of four to eight samples of the dissolved sludge slurry. The standard deviation and percent relative standard deviations for these measured concentrations are presented in columns four and five. The results in the last column are curies per gallon based on 18.4 wt% total solids and a density of 1.12 g/mL for the sludge slurry.

Table 3 - Radioactive Results for the Washed Tank 40 Sludge Slurry

Radionuclide	wt%	µCi/g Dried Sludge Slurry	Std. Dev. (µCi/g)	%RSD	Ci/gal in Sludge Slurry based on measured wt% solids in SRTC washed sludge
H-3	<2.0E-10	<1.9E-02	N/A	N/A	<1.5E-05
Co-60(a)	4.8E-07	5.5E+00	4.6E-01	8.4E+00	4.3E-03
Sr-90(b)	3.3E-03	4.5E+03	4.4E+02	9.6E+00	1.7E+00
Tc-99(c)	7.4E-04	1.3E-01	3.2E-03	2.6E+00	9.8E-05
Ru-106	<3.7E-08	<1.2E+00	N/A	N/A	<4.9E-04
Sb-125	<4.5E-08	<4.6E-01	N/A	N/A	<3.6E-04
Te-125m	<2.6E-09	<4.6E-01	N/A	N/A	<3.6E-04
Cs-134	<6.8E-09	<8.8E-02	N/A	N/A	<6.8E-05
Cs-137(a)	3.2E-04	2.8E+02	2.1E+01	7.8E+00	1.1E-01
Ce-144	<2.7E-08	<8.7E-01	N/A	N/A	<3.4E-04
Pm-147(b)	1.4E-05	1.3E+02	2.4E-06	1.7E+01	1.0E-01
Eu-154(a)	3.0E-06	8.0E+00	3.3E-01	4.1E+00	6.3E-03
Eu-155(a)	9.6E-07	4.5E+00	6.2E-01	1.4E+01	3.5E-03
U-233(c)	1.1E-04	1.1E-02	5.1E-04	4.8E+00	8.3E-06
U-234(c)	5.7E-04	3.6E-02	9.2E-04	2.6E+00	2.8E-05
U-235(c)	3.0E-02	6.6E-04	1.4E-05	2.1E+00	5.1E-07
Np-237(c)	1.9E-03	1.3E-02	7.0E-05	5.4E-01	1.0E-05
U-238(c)	7.5E+00	2.5E-02	9.5E-04	3.7E+00	2.0E-05
Pu-238(d)	2.3E-04	3.9E+01	1.7E+00	4.5E+00	3.0E-02
Pu-239(c)	1.2E-02	7.7E+00	1.7E-01	2.2E+00	6.0E-03
Pu-240(c)	1.1E-03	2.4E+00	4.2E-02	1.8E+00	1.9E-03
Pu-241(b)	2.7E-05	2.8E+01	1.2E+00	4.2E+00	2.2E-02
Am-241(a)	9.5E-04	3.3E+01	2.5E+00	7.7E+00	2.6E-02
Cm-244(c)	4.8E-05	3.9E+01	2.0E+00	5.1E+00	3.0E-02
Total alpha	N/A	1.2E+02	3.0E+00	2.5E+00	9.5E-02
Total beta	N/A	1.2E+04	7.9E+02	6.8E+00	9.0E+00
Total gamma	N/A	3.3E+02	1.9E+01	5.9E+00	2.5E-01
Total beta-gamma	N/A	1.2E+04	7.7E+02	6.5E+00	9.3E+00

(a) Measured by Direct Gamma Counting
(b) Measured by Beta Counting after Special Separation
(c) Measured by Inductively Coupled Mass Spectroscopy
(d) Measured by Alpha Counting after Special Separation

3.2 Weight Percent Solids, Density Measurements, and Nonradioactive and Radioactive Compositions for the Washed Tank 40 Supernate

The sections below provide a brief description of the analyses and results obtained from portions of the washed Tank 40 supernate sample. To obtain the supernate needed for all of the analyses mentioned in Section 3.2, a mixed sample of the sludge slurry was filtered through a Nalgene® filter resulting in a clear supernate.

3.2.1 Weight Percent Solids Measurements of the Washed Tank 40 Supernate

Mixed samples of the supernate were pipetted into four labeled, pre-weighed PMP® beakers and the same procedure was followed for the supernate samples as for the sludge slurry samples (see Section 3.1.1). To check the accuracy and precision of the method, three samples of a 15 wt% NaCl standard solution were also weighed and dried (in labeled PMP® beakers) along with the supernate samples. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard. The averages of the calculated results of the weight percent solids for the supernate are presented in column two of Table 4. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two of Table 4.

Table 4 - Weight Percent Solids and Density Measurements for the Washed Tank 40 Supernate

	Weight Percent Dissolved Solids for the Tank 40 Supernate [a, b]	Density Measurement for the Tank 40 Supernate [b]
Average	3.39 wt%	1.03 g/mL
Std. Dev.	± 7.3E-02	± 4.0E-03
% RSD	2.1E00	3.5E-01

[a] The samples for weight percent solids measurements were dried overnight in a drying oven at 115°C.
[b] Average of four results.

3.2.2 Density Measurements for the Washed Tank 40 Supernate

Density measurements for the supernate were completed remotely in the Shielded Cells Facility by using heat sealed pipette tips. To obtain the supernate needed for the analyses, a mixed sample of the sludge slurry was filtered through a Nalgene® filter resulting in a clear supernate. The pipette tips were sealed and then calibrated as described in Section 3.1.3. Four density measurements (see Section 3.1.3) were completed for the supernate. The results of the supernate for the washed Tank 40 sample are presented in column three of Table 4. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column three of Table 4.

3.2.3 Nonradioactive Composition of the Washed Tank 40 Supernate

Provided below are the results from the analyses of the supernate of the washed Tank 40 sample. A mixed sample of the combined sludge slurry was filtered through a Nalgene® filter resulting in a clear supernate. A portion of this supernate was diluted and removed from the Shielded Cells along with elemental standards to check the analytical methods. These diluted samples were sent to ADS Sample Receiving so that analyses could be performed by ADS. The dilution of the supernate samples was required so that only a small portion of the radioactivity was removed from the Shielded Cells. The results for the elemental standards submitted with the supernate indicated good agreement with the known values of the standards. This indicates that the analytical methods were complete and performed correctly.

Presented in Table 5 and Table 6 are the results of the Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES) data, Ion Chromatography (IC) data, Total Inorganic Carbon (TIC), Total Organic Carbon (TOC), free OH^-, total OH^-, CO_3^{2-}, and AlO_2^-. The results are averages of three values unless otherwise indicated. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) are provided in columns three and four for each table.

Table 5 - Concentration of Elements Detected by ICP-ES in the Washed Tank 40 Supernate

Element	Molarity [a] (mol/L Supernate)	Std. Dev.	% RSD	Weight Percent of Total Solids
Ag	1.39E-06	± 1.3E-07	9.5E00	6.68E-05
Al	2.32E-02	± 1.4E-04	6.2E-01	2.79E-01
B	1.64E-04	± 1.5E-05	9.1E00	7.90E-04
Ba [b]	<6.2E-07	-	-	<3.79E-05
Ca	3.67E-05	± 4.7E-06	1.3E01	6.56E-04
Cd [c]	7.7E-07	± 7.5E-08	9.7E00	3.86E-05
Co [c]	3.19E-06	2.5E-07	7.9E00	8.38E-05
Cr	7.62E-04	± 6.0E-06	7.9E-01	1.77E-02
Cu [c]	1.88E-06	± 1.0-07	5.5E00	5.32E-05
Fe	4.39E-06	5.8E-07	1.3E01	1.09E-04
La [b]	<2.6E-06	-	-	<1.61E-04
Li [c]	1.07E-06	± 1.8E-07	1.7E01	3.31E-06
Mg [c]	3.30E-06	± 2.2E-07	6.6E00	3.58E-05
Mn [b]	<5.4E-07	-	-	<1.32E-05
Mo	1.35E-05	± 3.3E-07	2.4E-01	5.77E-04
Na	5.65E-01	± 1.1E-02	1.9E00	5.79E+00
Ni [b]	<4.5E-06	-	-	<1.18E-04
P	1.11E-04	± 5.7E-06	5.1E00	1.53E-03
Pb [b]	<6.5E-06	-	-	<6.00E-04
Si	1.42E-04	± 5.0E-06	3.5E00	1.78E-03
Sn	6.33E-06	± 4.5E-07	7.2E00	3.35E-04
Sr [b]	<3.4E-07	-	-	<1.33E-05
Ti	1.69E-06	± 5.7E-07	3.4E01	3.61E-05
U [c]	1.52E-05	± 2.0E-06	1.3E01	1.61E-03
V	4.49E-06	± 8.2E-07	1.8E01	1.02E-04
Zn [b]	<2.7E-06	-	-	<7.87E-05
Zr	1.81E-06	± 4.4E-07	2.4E01	7.36E-05

[a] Average of three samples unless otherwise indicated.
[b] Detection limit of the analytical method
[c] Average of two samples

Table 6 - IC, AlO_2^-, CO_3^{2-}, Free OH^-, TIC / TOC, and Total OH^- Results for the Washed Tank 40 Supernate

Method	Average of Results*	Std. Dev.	% RSD	mg/kg of Slurry (ppm)
IC Results for Chloride	3.96E-04 M	± 1.7E-06	4.0E-01	1.15E+01
IC Results for Fluoride	3.94E-03 M	± 7.6E-05	1.9E00	6.14E+01
IC Results for Formate	7.49E-04 M	± 3.1E-06	4.2E-01	2.77E+01
IC Results for Nitrate	7.54E-02 M	± 2.8E-03	3.7E00	3.83E+03
IC Results for Nitrite	1.64E-01 M	± 6.3E-03	3.9E00	6.19E+03
IC Results for Phosphate [a]	<3E-04 M	-	-	<2E+01
IC Results for Sulfate	1.12E-02 M	± 3.3E-04	3.0E00	8.82E+02
IC Results for Oxalate	7.35E-03 M	± 1.9E-04	2.6E-01	5.31E+02
Results for $AlO2^-$	9.33E-02 M	± 2.06E-02	2.2E01	4.51E+03
Results for $CO32^-$	3.44E-02 M	± 3.64E-03	1.1E01	1.69E+03
Results for Free OH^-	3.82E-02 M	± 6.0E-04	1.6E00	5.33E+02
Results for TIC	4.54E+02 mg/L	± 1.1E01	2.5E00	3.72E+02
Results for TOC	3.04E+02 mg/L	± 4.8E01	1.6E01	2.49E+02
Results for Total OH^-	1.31E-01 M	± 2.1E-02	1.6E01	1.83E+03

* Average of three results for each method unless otherwise indicated.
[a] Detection limit of the analytical method.

3.3 Calculation of the Insoluble and Soluble Solids for the Washed Tank 40 Sludge Slurry

The soluble and insoluble weight percent solids can be calculated by using the following equations[14] once the weight percent total solids and dissolved solids have been obtained.

$$W_{is} = \frac{(W_{ts} - W_{ds})}{(1 - W_{ds})} \qquad \text{Eq. 1}$$

$$W_{ss} = W_{ts} - W_{is} \qquad \text{Eq. 2}$$

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

Converting the weight percent total and dissolved solids from Table 1 and Table 4 into weight fractions and inserting into Equations 1 and 2 yields:

$$W_{is} = \frac{(0.184 - 0.0339)}{(1 - 0.0339)} = 0.155$$

$$W_{ss} = 0.184 - 0.155 = 0.029$$

Multiplying the above results by 100 to convert to percent yields:

15.5 wt% insoluble solids
2.9 wt% soluble solids.

3.4 Comparison of the HLWD Washed and SRTC Washed Tank 40 Sludge Slurries

As stated in Section 2.0, SRTC personnel washed and characterized a sludge slurry sample form Tank 40 to be used as feed for the SRAT cycle in the SRTC Shielded Cells. The washing targeted a final sodium concentration in the supernate of 0.53 M to 0.60 M[15]. After washing the entire contents of Tank 40, High Level Waste Division (HLWD) personnel submitted a sample to SRTC for sodium concentration and weight percent solids measurement[16]. Results of these measurements are given in Table 7 below.

Table 7 – Sodium Concentration and Weight Percent Solids Results of the HLWD Washed and SRTC Washed Tank 40 Sludge Slurries

	HLWD Washed Tank 40 Sludge Slurry	SRTC Washed Tank 40 Sludge Slurry
Sodium (mol/L supernate)	0.534	0.565
Slurry Density (g/mL)	1.12	1.12
Supernate Density (g/mL)	1.03	1.03
Weight Percent Total Solids of Slurry	20.5	18.4
Weight Percent Dissolved Solids	3.10	3.39
Weigh Percent Insoluble Solids	17.9	15.5
Weight Percent Soluble Solids	2.55	2.9

As can be seen from the above table, the HLWD and SRTC washed sludge slurries are very similar. More importantly, the comparison shows that the HLWD sludge slurry is more washed (lower sodium concentration) than the SRTC sample. This shows that in terms of sodium concentration, the SRTC washing/SRAT cycle/SME cycle/glass fabrication demonstration bounds Sludge Batch 2 (Macrobatch 3) processing in the DWPF. It should be noted that the weight percent total solids of the HLWD washed sludge slurry (20.5 wt%) exceeded the DWPF Waste Acceptance Criteria (13 to 19 wt% total solids). This higher weight percent total solids will not affect the final DWPF glass product, but it may have other processing consequences.

4.0 DESCRIPTION OF THE SYSTEM USED TO PERFORM THE SRAT CYCLE AND ACID CALCULATIONS FOR THE SRAT CYCLE

The sections below provide a description of the system used in the Shielded Cells to perform the Tank 40 demonstration and the data used to calculate the amounts of nitric acid and formic acid required to complete the SRAT cycle.

4.1 System Description

The SRAT/SME vessel used in this confirmation run is a glass cylinder approximately 13 inches (33 cm) in height and 6 inches (15 cm) wide. The SRAT/SME vessel has a capacity of approximately 2 liters, and the top of the SRAT/SME vessel has a series of ports and openings. These ports and openings are for the installation of equipment (i.e. pH probe, thermocouple, agitator, etc.) and process lines (acid addition, air purge, etc.). The condenser, mercury/condensate trap, and cold trap connected to the SRAT/SME vessel are also made out of glass.

To supply heat to the SRAT/SME vessel, a heating mantle is used. Also, a laboratory chiller unit is used to supply the chilled water for the condenser. Figure 1 is a picture taken in the Mockup Cells of the system prior to installation in the Shielded Cells. Figure 2 is a picture of the top portion of the vessel showing the ports/openings for the SRAT/SME vessel.

The SRAT/SME is purged using air with 0.5% (nominal) helium. By measuring the helium in the vessel purge, gas generation rates can be calculated. The purge gas composition is measured using a Varian CP-2002 Micro-GC gas chromatograph (GC). Column A contains a Molsieve 5A column with argon carrier gas. It measures helium, hydrogen, oxygen, and nitrogen. Column B contains a PoraPlot Q column with nitrogen carrier gas. It separates and detects carbon dioxide and nitrous oxide. The GC is located in a radiohood behind the Shielded Cells.

Figure 1 - Picture of the SRAT/SME Vessel in the Mockup Cells of the Shielded Cells Facility

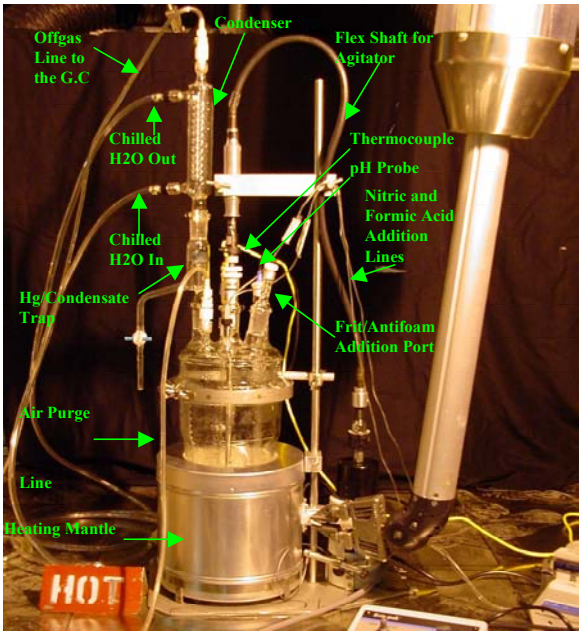
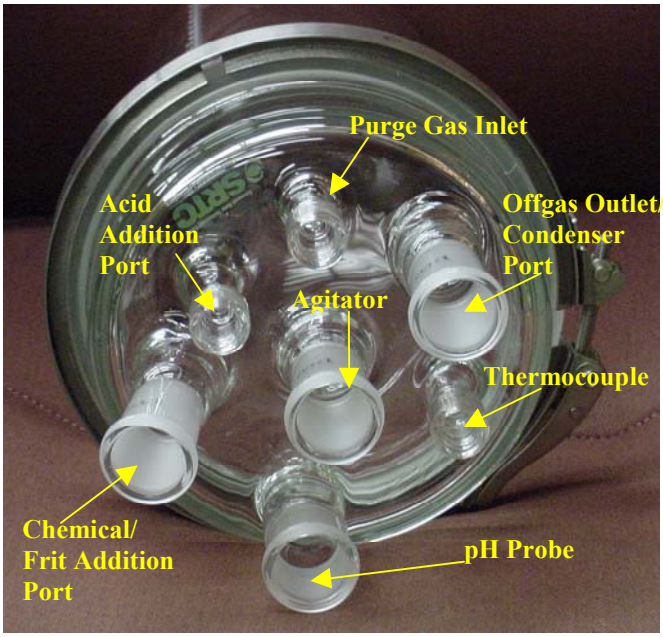


Figure 2 - Picture of the Top View of the Connections/Ports for the SRAT/SME Vessel Prior to Entry into the Shielded Cells



4.2 Acid Calculations for the SRAT Cycle

The sections below describe the analytical methods performed on the sludge slurry to obtain the remaining data in order to perform the acid calculations for the SRAT cycle. The analytical data, presented in this section and previous sections, were entered into a spreadsheet* and the amounts of nitric and formic acids were determined.

4.2.1 Titration of the Washed Sludge Slurry to Obtain the Concentration of Hydroxide

To obtain the concentration of hydroxide (in equivalents per liter (Eq/L)) for the washed sludge slurry, a titration was completed in the Shielded Cells on three portions of mixed sludge slurry. The first step in the procedure was to weigh each individual portion of the sludge slurry to obtain the weight. The next step was to add a known volume of 1.05 N nitric acid to the sludge slurry. The sludge slurry was then mixed, and a pH recorded as soon as the readout from the pH probe stabilized. The volume of nitric acid added was also recorded after each addition to the sludge slurry. The procedure was considered complete when the pH of the sludge slurry was less than or equal to four. This procedure was repeated on the remaining two portions of sludge slurry. The results of the titration procedure for the three portions of sludge slurry are presented in Figure 3 and Figure 4. Figure 3 is a graph of the pH of the sludge slurry (y axis) and the milliliters of nitric acid added (x axis). Figure 4 is a graph of the pH of the sludge slurry (y axis) and the Eq/L of nitric acid added (x axis). Table 8 provides the data recorded for each titration. From Figure 4, the total hydroxide is estimated by determining the amount of acid required to reduce the pH of each slurry sample to pH 7.0. The result for each test is summarized in Table 8. The average of these three tests is 0.308 Eq/L.

* Microsoft Excel 97

Table 8 - Titration Data for Three Samples of Washed Tank 40 Sludge Slurry

Tank 40 Titrations		
Titration #1		**Factor for Eq/L=3.82E-02** [a]
Amount of Acid Added (mL)	pH of Sludge After Addition	Eq/L Sludge Slurry
0	12.83	0.00E+00
2	12.5	7.65E-02
4	11.69	1.53E-01
6	9.71	2.29E-01
8	7.14	3.06E-01
10	5.81	3.82E-01
12	5.23	4.59E-01
14	4.73	5.35E-01
16	4.39	6.12E-01
18	4.09	6.88E-01
20	3.91	7.65E-01
Titration #2		**Factor for Eq/L=5.28E-02** [a]
Amount of Acid Added (mL)	pH of Sludge After Addition	Eq/L Sludge Slurry
0	12.89	0.00E+00
2	12.28	1.06E-01
4	10.36	2.11E-01
6	6.83	3.17E-01
8	5.58	4.22E-01
10	4.56	5.28E-01
12	4.16	6.33E-01
14	3.9	7.39E-01
Titration #3		**Factor for Eq/L=5.37E-02** [a]
Amount of Acid Added (mL)	pH of Sludge After Addition	Eq/L Sludge Slurry
0	12.81	0.00E+00
0.929	12.74	4.99E-02
2.816	11.85	1.51E-01
4.774	9.51	2.56E-01
6.557	6.61	3.52E-01
7.464	5.84	4.01E-01
9.22	4.94	4.95E-01
11.12	4.48	5.97E-01
13.802	4.00	7.42E-01

[a] The Factor for Eq/L is used to convert from mL of acid added to Eq/L of sludge slurry.

$$\text{Factor for Eq/L} = \frac{\text{Density of Sludge Slurry} \times \text{normality of acid}}{\text{weight of sludge slurry used in titration}}$$, with the units being Eq/mL acid/L sludge slurry.

Figure 3 - Graph of the Sludge Slurry Titrations Performed in the Shielded Cells (pH of Sludge Slurry vs. mL of Nitric Acid Added)

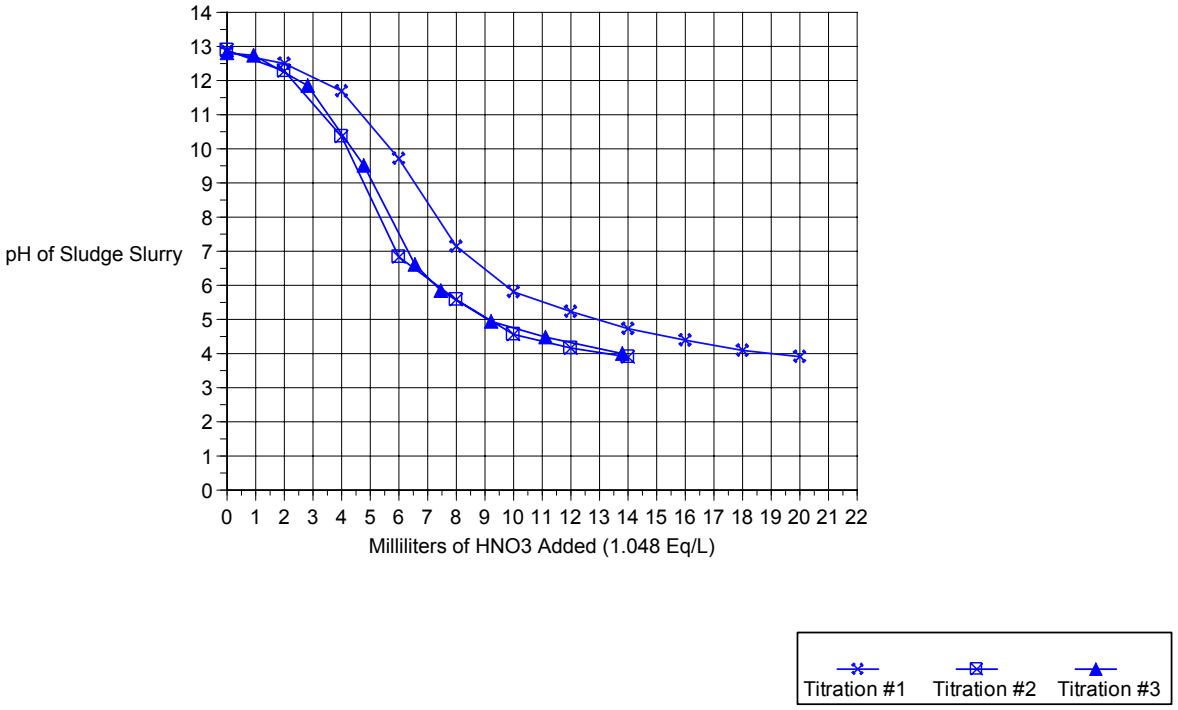
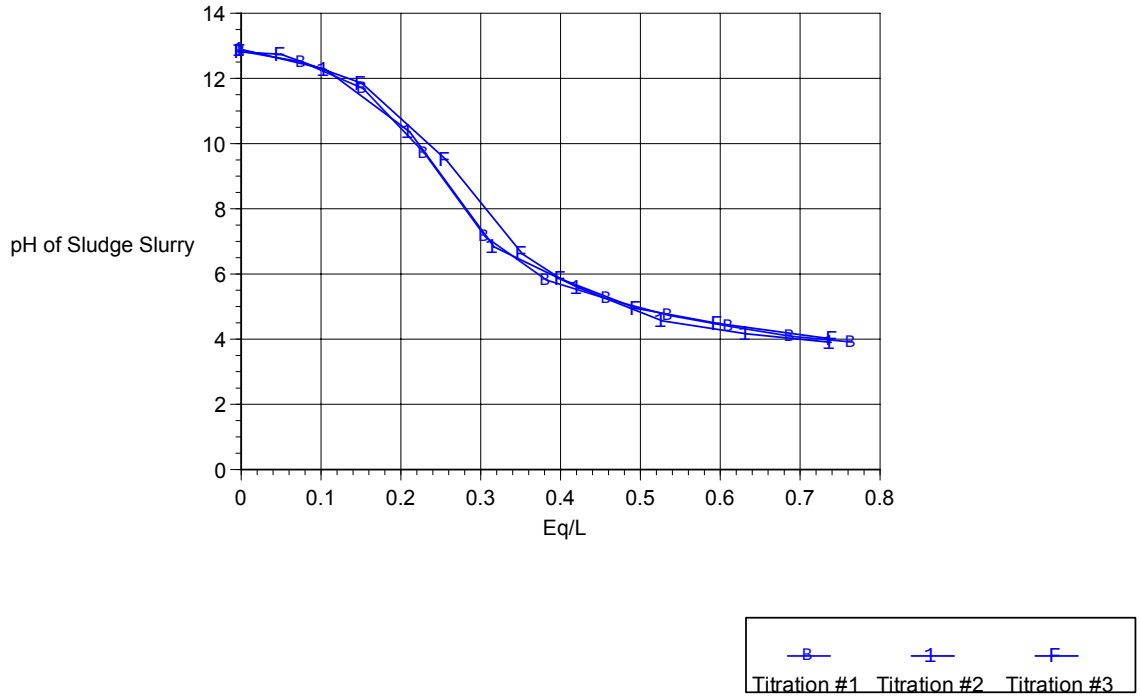


Figure 4 - Graph of the Sludge Slurry Titrations Performed in the Shielded Cells (pH of Sludge Slurry vs. Eq/L of Nitric Acid Added)



4.2.2 TIC Concentration for the Washed Sludge Slurry

To obtain the TIC concentration, a few drops of the mixed washed sludge slurry were placed into shielded bottles. Shielded bottles were used for these samples due to the radioactivity of the sludge slurry. These samples were removed from the Shielded Cells and submitted to ADS for analysis. The average TIC concentration of the two samples was 866 ppm. The standard deviation was ± 5.0E00 and the percent relative standard deviation was 6.0E-03.

4.2.3 Nitric Acid and Formic Acid Results

Samples of the nitric and formic acids used in this demonstration were submitted for analyses. The results of the analyses for the nitric acid were 10.29M (49.9 wt%) and the formic acid results were 22.8 M (88.03 wt%). The specific gravity for the nitric acid and the formic acid at the indicated molarities were 1.30 and 1.19 respectively.

4.2.4 Acid Calculations for the SRAT Cycle

The stoichiometric target used to determine the amount of nitric acid and formic acid for the Shielded Cells run was 125%. This target was recommended based on nonradioactive simulant testing[4]. During the nonradioactive simulant testing, a target of 125% stoichiometry met the following requirements:

1. Acid base neutralization reactions - destruction of hydroxides and carbonates.
2. Reaction with Sodium Nitrite - Destruction of nitrite.
3. Some reduction of MnO_2 to MnO.
4. Reduction of Mercury - This reduces HgO to Hg.
5. Appropriate balance of nitric and formic for final redox in the melter.

The analytical results (located in Sections 3.0 and 6.0) for the weight percent total solids, density, hydroxide, manganese, nitrite, mercury, and TIC in the washed sludge slurry were entered into the spreadsheet. The results of the nitric acid and formic acid additions were also entered. To ensure the appropriate redox in the melter, a value of $Fe^{2+}/Fe^{tot} = 0.2$ was used in the spreadsheet. After entering all of the required data, the amounts of the nitric acid and formic acid were determined to be 91 gallons (DWPF basis) and 206 gallons (DWPF basis) respectively (5.0 moles formic acid to 1 mole nitric acid). The amounts of nitric acid and formic acid obtained from the spreadsheet were required to complete the necessary reactions and meet the redox in the melter. To scale the amounts of nitric acid and formic acid from a DWPF basis to a Shielded Cells basis, the volume of each acid was converted to milliliters and then multiplied by a value of 4.16E-05 (See Appendix B). Table 9 is a copy of the spreadsheet used to determine the amounts of nitric acid and formic acid for the Shielded Cells SRAT cycle[17].

Table 9 - Excel Spreadsheet for Determining Nitric Acid and Formic Acid Requirements for the SRAT Cycle

revised 10/2/01

SRAT Batch 2 Shielded Cell Runs Acid Requirements - computed October 2, 2001 by M.A. Rios-Armstrong

(NOTE: to be used for Sludge Batch 2 only, and incorporates revised F-3N redox model)

SRAT Conditions and Analyses	
(lab ID 2000xxxxx)	Receipt
Volume [gal]	6,000
spG	1.120
Wt% solids	18.40
Hydroxide [eq/L]	0.308
Nitrite [ppm]	7,529
Mercury [ppm]	359
Manganese [wt%]	3.16
Manganese (sol) [ppm]	0
TIC [ppm]	866
Formate [ppm]	0
Nitrate [ppm]	4,678

-> 5,814.40 ppm

Formic Acid Addition Volume	
Volume [gal]	206
spG	1.192
Wt%	88.03
Molar	22.80

Nitric Acid Tank	
spG	1.3
Wt%	49.9
Molar	10.29

Calculated SRAT Quantities		Nitric Required	Formic Required		
SRAT mass [lbs]	56,078				
MnO2 [g-moles]	2,692.	2,153.6	1,076.8		
HgO [g-moles]	45.5	0.	45.5		
NO2 [g-moles]	4,162.4	2,081.2	1,040.6		
CO3 [g-moles]	1,834.1	3,668.3	0.		
OH [g-moles]	6,994.7	6,994.7	0.	OH [ppm]	11,000
Total Acid [g-moles] at 125%		18,622.2	2,703.7	21,325.9	total
Total Volume [gal]		478	31		

From Marek calculational algorithm at 125% of stoichiometry:		
mFA	2,704	Formic Acid Requirement [g-moles]
mA	+ 18,622	Additional Acid Required [g-moles]
mDFA	- 17,776	Direct Formic Acid Addition [g-moles]
mHNO3	= 3,550	g-moles Nitric Acid
VHNO3	91	gallons

Specify the following quantities in the SRAT procedure:

91	gallons of 50 wt% nitric acid
206	gallons of 90 wt% formic acid
6,300	gallon SRAT concentration endpoint
12	hours of additional reflux
6,000	gallon SRAT reflux endpoint/final SRAT slurry level

Notes:
Adjust formic acid volume (F5) with Goal Seek function to make target glass redox (L8) = 0.2.
Blue numbers in yellow-shaded cells indicate user input.

5.0 DESCRIPTION OF THE TRANSFER OF WASHED TANK 40 SLUDGE SLURRY TO THE SRAT VESSEL AND THE SRAT CYCLE

Transfer of Washed Sludge Slurry to the SRAT Vessel

The washed sludge slurry was mixed for approximately four hours prior to the transfer to the SRAT vessel. Upon completion of the transfer of approximately one liter to the vessel, the sludge slurry was allowed to settle for one hour. Upon lifting the vessel up for inspection of the level, it was noticed that the sludge slurry had separated into three distinct layers. A foamy layer was on top, clear supernate in the middle, and sludge on the bottom. Figure 5 is a picture of the three layers in the SRAT vessel. The foam layer appeared to be about 30% of the total volume.

It was hypothesized that if the sludge slurry was allowed to settle over the weekend that the foamy layer would dissipate with time. On the following Monday, the SRAT vessel was raised again and the foamy layer was still present on top of the supernate. The vessel was tapped several times and the agitator blades were raised and lowered to make the foamy layer dissipate. Figure 6 is a picture of the sludge slurry in the SRAT vessel after the foamy layer dissipated.

Figure 5- Picture of the Three Layers in the SRAT Vessel

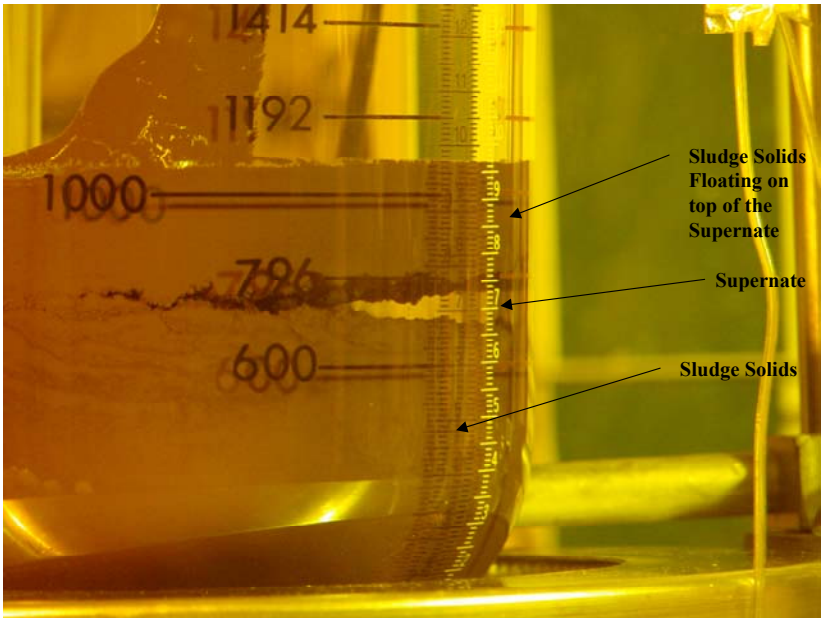
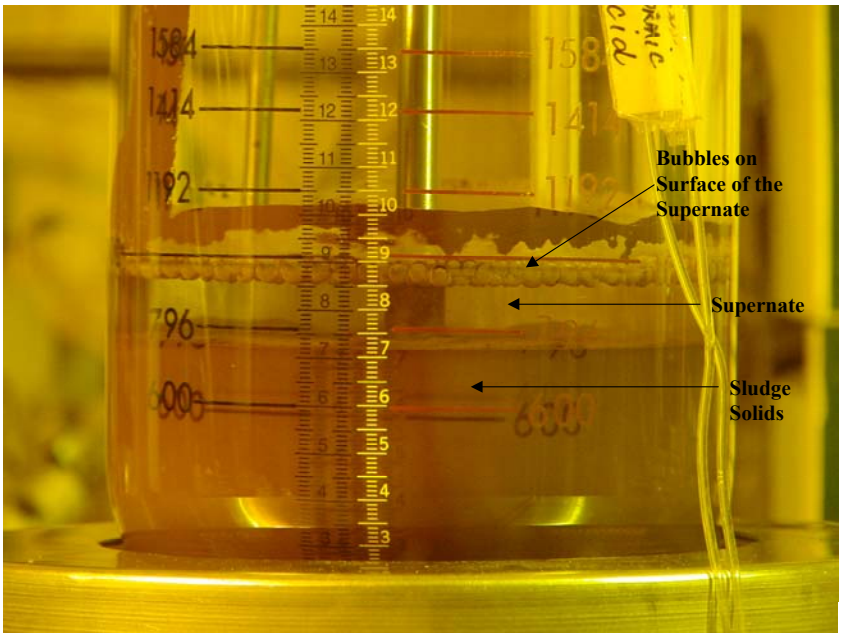


Figure 6 - Picture of the Sludge Slurry in the SRAT Vessel After the Foamy Layer Dissipated



Initiation - Heating and Agitation
The SRAT Cycle began on 3 October 2001 at 0730 with the start of the agitator and heating mantle to heat the SRAT/SME vessel. When the vessel reached 50°C (0912), antifoam was added. During this heating period, hydrogen concentration in the offgas increased as the radiolytic hydrogen that was dissolved in the sludge slurry was released.

Nitric Acid Addition
At 1154, the vessel temperature was at 93°C, and the nitric acid addition was initiated. Based on the acid calculations (see Section 4.2.4), 14.31mL of 50 wt% nitric acid was added to the vessel at a flow rate of 0.31 mL/min (See Appendix B). The acid addition was completed by 1245. During the addition, a small amount of carbon dioxide was produced, and the pH decreased slightly (see Figure 7). At the completion of the addition, the sludge slurry was visually examined. The surface appeared smooth but thick.

Formic Acid Addition
At 1321, the formic acid addition began. A total of 32.45 mL of 90wt% formic acid was added at a flow rate of 0.31 mL/min (see Section 4.2.4 for acid calculations and Appendix B for flow rate calculation). After approximately forty minutes of formic acid addition, the pH had decreased from above 9 to below 6, CO_2 and N_2O concentrations were increasing, and foam was observed in the vessel. An unscheduled antifoam addition was made to mitigate the foam formation. This caused the foam to rapidly dissipate.

The formic acid addition was completed at 1531. The addition took approximately 25 minutes longer than planned due to difficulties in removing the last few drops of formic acid from the supply bottle. At this point, the minimum pH in the SRAT cycle was reached (3.8); H_2 concentration in the purge gas was declining; CO_2 concentration had peaked and was beginning to decline; and N_2O concentration was still increasing.

Concentration and Reflux
The vessel was heated to boiling to remove the volume of liquid added during the acid additions, and allowed to reflux for twelve hours. Condensate collection (i.e. boiling) began at approximately 2100. Condensate collection ended at 0930 on 4 October 2001, and reflux began. The long period between the end of formic acid addition and the end of the concentration (approximately 5.5 hours to reach boiling and 12.5 hours for concentration) was due to careful, small changes in heater settings. DWPF heatup and concentration time is typically twelve hours.

While heating the vessel to boiling (1531 to 2100 on 3 October 2001), H_2 concentration in the purge gas reached a minimum and began to slowly increase; the CO_2 concentration steadily decreased; and the N_2O concentration peaked shortly after formic acid addition, and then decreased. During the reflux period, these trends continued, with the H_2 concentration stabilizing near the end of the reflux period.

After twelve hours of reflux, the heating mantle was turned off.

Antifoam Addition
Antifoam was added per the current DWPF antifoam strategy of adding antifoam at 50°C (before boiling) and to refresh every 8 hours. One unscheduled 100 ppm addition (See Appendix B for calculation of amount of antifoam) was made during formic acid addition due to foaming observed in the vessel. No foam was observed during concentration and reflux.

6.0 SRAT CYCLE RESULTS

Presented below are the results obtained from the SRAT cycle. These include the final composition of the SRAT product, SRAT offgas generation data, nitrate and nitrite balance, and carbon balance.

6.1 Results of the Analyses Performed on the Tank 40 Radioactive SRAT Product and Supernate

Provided below are the results from the analyses of the Tank 40 SRAT Product and Tank 40 SRAT supernate. Analyses include density measurements, weight percent solids measurements, calcined solids measurement for the SRAT product, nonradioactive and radioactive compositions of the SRAT supernate, and dissolution procedures to obtain the nonradioactive and radioactive compositions of the SRAT product.

6.1.1 Total Weight Percent Solids, Calcined Solids Measurements, Density Measurements, and Nonradioactive and Radioactive Compositions for the Tank 40 SRAT Product

The sections below provide a brief description of the analyses and results obtained from portions of the washed Tank 40 SRAT product.

6.1.1.1 Total Weight Percent Solids Measurements for the Tank 40 SRAT Product

Quadruplicate measurements of the total weight percent solids for the SRAT product were completed remotely in the Shielded Cells Facility. Mixed portions of a sample of SRAT product were pipetted into four labeled, pre-weighed PMP® beakers. After the addition of the mixed SRAT product, the PMP® beakers were weighed and placed into a drying oven at 115°C overnight. The samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. To check the accuracy and precision of the method, three samples of a 15 wt% NaCl standard solution were also weighed and dried (in labeled PMP® beakers) along with the SRAT product samples. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard. The averages of the calculated results of the weight percent solids for the SRAT product are presented in column two of Table 10. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two of Table 10.

6.1.1.2 Calcined Solids Measurements for the Tank 40 SRAT Product

Duplicate measurements of the calcined solids were completed in the Shielded Cells Facility for the SRAT product. Mixed portions of a sample of SRAT product were pipetted into two pre-weighed alumina crucibles. The crucibles were weighed and then dried overnight at 115°C in a drying oven to avoid any loss of the material during the calcining process. The samples were removed from the drying oven and allowed to cool for ~5 minutes before they were weighed. The samples were then placed into a muffle furnace and heated to 1000°C. The samples were held at 1000°C for ~ 2 hours. The muffle furnace was turned off and the samples were allowed to cool inside of the muffle furnace. The samples were then removed from the muffle furnace, weighed, and the calcined solids were calculated. The averages of the calculated results of the calcine solids for the SRAT product are presented in column three of Table 10. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column three of Table 10.

6.1.1.3 Density Measurements for the Tank 40 SRAT Product

Density measurements were completed remotely in the Shielded Cells Facility by using heat sealed pipette tips. The pipette tips are first sealed and then calibrated with water to obtain the volume. Four density measurements were completed for the SRAT product. The sealed pipette tip was first weighed and then a mixed sample of SRAT product was pipetted into the sealed pipette tip. The sealed pipette tip containing the SRAT product was weighed and a density calculated. The results for the washed Tank 40 SRAT product are presented in column four of Table 10. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column four of Table 10.

Table 10 - Weight Percent, Calcined Solids, and Density Measurements for the SRTC Tank 40 SRAT Product

	Weight Percent Total Solids [a, b]	Calcined Solids [c]	Density Measurement [b]
Average	20.2 wt%	15.7 wt%	1.15 g/mL
Std. Dev.	± 1.1E-01	± 1.0E-02	± 4.0E-03
% RSD	5.4E-01	9.0E-02	3.0E-01

[a] The samples for weight percent solids measurements were dried overnight in a drying oven at 115°C.
[b] Average of four results.
[c] Average of two results. Samples heated to 1000°C.

6.1.1.4 Nonradioactive and Radioactive Composition for the Tank 40 SRAT Product

Provided below are the results of the analyses for the SRAT product. Eight portions of a mixed sludge slurry sample were taken and dried overnight in a drying oven at 115°C. This dried SRAT product was dissolved by the Aqua Regia[12] and Sodium Peroxide/Sodium Hydroxide Fusion[13] methods along with appropriate standards to check the dissolutions and the analytical methods. After performing the dissolution methods on the SRAT product, the dissolved samples were removed from the Shielded Cells Facility. These diluted samples were submitted to ADS Sample Receiving for analyses to be performed by ADS. The dissolution results of the standards for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly[18]. Table 11 presents the elements (excluding oxygen) with concentrations >0.1 weight percent in the SRTC washed Tank 40 SRAT product obtained from ADS methods (Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES) and Atomic Adsorption (AA)). Table 11 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

Comparing Table 11 with Table 2 in Section 3.1.4, most of the concentrations in Table 11 are slightly lower. The difference in the concentrations is attributed to the increase in total weight percent of total solids (18.4% in the washed Tank 40 sludge, and 20.2% in the SRAT product). The increase is likely due to the nitric and formic acids added during the SRAT cycle (the nitric acid contributes nitrate and the formic acid contributes formate). The mercury concentration is particularly low. This is due to the removal of mercury during the 12 hour reflux period of the SRAT cycle. The 12 hour reflux period resulted in 91.6% of the mercury being removed from the sludge slurry. Appendix C shows a direct comparison of grams fed to the SRAT (washed Tank 40 sludge) to grams in the SRAT product for most of the elements in Table 11.

Table 11 - Elements (excluding oxygen) with Concentrations >0.1 Weight Percent in the Tank 40 SRTC SRAT Product Presented in Units of Weight Percent of Total Dried Solids

Element	Weight Percent *, [a]	Element	Weight Percent *, [a]
Al	5.56E00 (± 1.8E-01, 2.0E-01)	Mg	1.77E00 (± 9.3E-02, 5.3E00)
Ca	2.19E00 (± 6.1E-02, 2.8E00)	Mn	2.97E00 (± 1.2E-01, 4.0E00)
Cd	1.30E-01 (± 4.7E-03, 3.6E00)	Na[b]	7.88E00 (± 8.4E-02, 1.1E00)
Cr	1.78E-01 (± 3.7E-02, 2.1E01)	Ni	1.13E00 (± 4.6E-02, 4.0E00)
Fe	2.23E01 (± 1.1E+00, 4.7E00)	P	5.81E-01 (± 3.8E-02, 6.6E00)
Hg [b, c]	1.64E-02 (± 1.6E-03, 9.9E00)	Si[b]	9.94E-01 (± 1.8E-02, 1.8E00)
		U [b]	6.85E00 (± 5.7E-01, 8.3E00)

* The SRAT product slurry was dried at 115°C. Results are presented on a dry total solids basis.
[a] Results are determined by ICP-ES unless otherwise indicated and are the averages of results of eight samples of dissolved dried slurry. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[b] Average of four results.
[c] Results determined by AA method.

To obtain the radioactive composition, the dissolution solutions discussed in the first paragraph of this section were used. Portions of the dissolution solutions were submitted to ADS for the following methods: Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) and counting techniques. Table 12 presents the averages of the concentrations of select radionuclides for the Tank 40 SRAT product. Columns three and four of Table 12 present the standard deviation and percent relative standard deviation respectively.

Table 12 - Concentrations of Select Radionuclides for the Tank 40 SRAT Product

Element	Average (wt%)	Std. Dev.	% RSD
Sr-90[a]	2.77E-03	± 1.7E-04	6.2E00
Cs-137[b]	2.79E-04	± 1.3E-06	4.5E-01
U-233[c]	1.44E-04	± 9.0E-06	6.2E00
U-235[c]	3.91E-02	± 2.1E-03	5.4E00
U-236[c]	1.82E-03	± 1.1E-04	6.2E00
Np-237[c]	2.29E-03	± 1.3E-04	5.7E00
U-238[d]	6.85E00	± 5.7E-01	8.3E00
Pu-239[c]	1.47E-02	± 1.3E-03	8.7E00
Pu-240[c]	1.20E-03	± 1.2E-04	9.8E00
Pu-241[e]	2.41E-05	± 1.7E-06	7.3E00

[a] Sr-90 Analytical Method. Average of four results.
[b] Gamma Counting Method. Average of four results.
[c] Detected by ICP-MS. Average of three results.
[d] Detected by ICP-ES. Average of four results.
[e] Measured by Beta Counting after Special Separation. Average of four results.

6.1.2 Weight Percent Solids, Density Measurements, and Nonradioactive and Radioactive Compositions for the Tank 40 SRAT Product Supernate

The sections below provide a brief description of the analyses and results obtained from portions of the Tank 40 SRAT supernate sample. To obtain the supernate needed for all of the analyses mentioned in Section 6.1, a mixed sample of the SRAT product was filtered through a Nalgene® filter resulting in a clear supernate.

6.1.2.1 Weight Percent Solids Measurements of the Tank 40 SRAT Product Supernate

Mixed samples of the SRAT supernate were pipetted into four labeled, pre-weighed PMP® beakers and the same procedure was followed for the SRAT supernate samples as for the SRAT product (see Section 6.1.1.1). To check the accuracy and precision of the method, three samples of a 15 wt% NaCl standard solution were also weighed and dried (in labeled PMP® beakers) along with the SRAT supernate samples. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard[18]. The averages of the calculated results of the weight percent solids for the supernate are presented in column two of Table 13. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two of Table 13.

Table 13 - Weight Percent Solids and Density Measurements for the Tank 40 SRAT Product Supernate

	Weight Percent Dissolved Solids [a, b]	Density Measurement [b]
Average	6.08 wt%	1.04 g/mL
Std. Dev.	± 2.1E-01	± 1.3E-02
% RSD	3.4E00	1.2E00

[a] The samples for weight percent solids measurements were dried overnight in a drying oven at 115°C.
[b] Average of four results.

6.1.2.2 Density Measurements for the Tank 40 SRAT Product Supernate

Density measurements for the SRAT supernate were completed remotely in the Shielded Cells Facility by using heat sealed pipette tips. To obtain the SRAT supernate needed for the analyses, a mixed sample of the SRAT product was filtered through a Nalgene® filter resulting in a clear supernate. The pipette tips were sealed and then calibrated as described in Section 6.1.1.3. Four density measurements (see Section 6.1.1.3) were completed for the supernate. The results of the supernate for the Tank 40 SRAT product are presented in column three of Table 13. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column three of Table 13.

6.1.2.3 Nonradioactive and Radioactive Composition of the Tank 40 SRAT Product Supernate

Provided below are the results from the analyses of the supernate of the SRAT product. A mixed sample of the combined sludge slurry was filtered through a Nalgene® filter resulting in a clear supernate. A portion of the SRAT supernate was diluted and removed from the Shielded Cells along with elemental standards to check the analytical methods. These diluted samples were submitted to ADS Sample Receiving for analyses. The dilution of the supernate samples was performed so that only a small portion of the radioactivity was removed from the Shielded Cells. The results for the

elemental standards submitted with the supernate indicated good agreement with the known values of the standards[18]. This indicates that the analytical methods were complete and performed correctly.

Presented below in Table 14, Table 15, and Table 16 are the results of the ICP-ES data, Ion Chromatography (IC) data, ICP-MS, and counting data. The results are averages of three values unless otherwise indicated. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) are provided in columns three and four for each table.

Table 14 - Concentration of Elements Detected by ICP-ES in the Tank 40 SRAT Product Supernate

Element	Molarity [a]	Std. Dev.	% RSD	Weight Percent of Total Solids
Al	2.38E-04	± 7.1E-05	3.0E01	2.60E-03
B	6.18E-04	± 8.0E-05	1.3E01	2.70E-03
Ba [b]	<3.9E-06	-	-	<2.2E-04
Ca	5.20E-02	± 8.6E-04	1.7E00	8.43E-01
Cd	1.16E-04	± 5.8E-06	5.0E00	5.27E-03
Cr [c]	4.91E-05	± 7.6E-06	1.6E01	1.03E-03
Fe	2.80E-05	± 6.6E-06	2.4E01	6.32E-04
La[c]	2.25E-05	± 6.0E-06	2.7E01	1.26E-03
Li	6.24E-04	± 2.5E-05	4.0E00	1.75E-03
Mg	9.33E-02	± 2.7E-03	2.9E00	9.17E-01
Mn	7.44E-03	± 2.1E-04	2.9E00	1.65E-01
Na	7.28E-01	± 6.1E-03	8.4E-01	6.77E+00
Ni	7.60E-05	± 1.8E-05	2.4E01	1.80E-03
Si	2.79E-03	± 1.4E-04	4.8E00	3.17E-02
Sn	3.04E-05	± 7.4E-06	2.4E01	1.46E-03
Sr	1.0E01	± 2.5E-01	2.5E00	3.54E+02

a Average of three samples unless otherwise indicated.
b Detection limit of the analytical method
c Average of two samples

Table 15 - Ion Chromatography Results for the Tank 40 SRAT Product Supernate

Species Analyzed	Average*	Std. Dev.	% RSD	mg/kg of Slurry (ppm)
Chloride [a]	<7E-04 M	-	-	<2.03E+01
Fluoride [a]	<1E-03 M	-	-	<1.55E+01
Formate	6.31E-01 M	± 4.6E-02	7.3 E00	2.32E+04
Nitrate	2.60E-01 M	± 7.8E-03	3.0E00	1.32E+04
Nitrite	8.81E-03 M	± 3.3E-05	3.7E-01	3.31E+02
Phosphate [a]	<3E-04 M	-	-	<2.33E+01
Sulfate	6.44E-03 M	± 3.25E-05	5.0E-01	5.05E+02
Oxalate [a]	<2E-03 M	-	-	<1.44E+02

* Average of three results for IC method.
[a] Detection limit of the instrument.

Table 16 - ICP-MS and Counting Data Results for the Tank 40 SRAT Product Supernate

Isotope	Average*	Std. Dev.	%RSD	Weight Percent of Total Solids
Sr-90[a]	2.30E02 µCi/mL	2.6E01	1.2E01	6.82E-04
Tc-99[b]	3.31E-01 mg/L	4.7E-03	1.4E00	1.34E-04
Cs-133[b]	4.99E-01 mg/L	1.9E-03	3.82E-01	2.02E-04
Cs-135[b]	6.95E-02 mg/L	1.2E-03	1.8E00	2.81E-05
Cs-137[b]	2.36E-01 mg/L	3.9E-03	1.7E00	9.54E-05
Cs-137[c]	2.11E01 µCi/mL	2.1E-01	1.0E00	9.81E-05
U-235[b]	2.81E-02 mg/L	3.2E-04	1.1E00	1.14E-05
U-236[d]	1.47E-03 mg/L	3.1E-04	2.1E01	5.95E-07
Np-237[b]	7.07E-01 mg/L	9.7E-03	1.4E00	2.86E-04
U-238[b]	7.40E00 mg/L	1.6E00	2.2E01	2.99E-03
Pu-240[d]	1.50E-03 mg/L	2.8E-04	1.9E01	6.07E-07
Total Alpha [e,f]	8.0E-01 µCi/mL	-	-	N/A
Total Beta [e]	5.48E02 µCi/mL	8.9E00	1.6E00	N/A

[a] Sr-90 Method. Average of three results.
[b] Detected by ICP-MS. Average of three results.
[c] Detected by Gamma Scan. Average of three results.
[d] Detected by ICP-MS. Average of two results.
[e] Tank 50 Liquid Scintillation Method.
[f] Upper Limit of Detection for the Method.

In Table 16, there are two results given for Cs-137 based on two different analytical methods. Upon converting the units of mg/L to µCi/mL for Cs-137, the two analytical methods agree well with each other (21.1 µCi/mL versus 20.5 µCi/mL).

6.1.3 Calculation of the Insoluble and Soluble Solids for the Tank 40 SRAT Product

Equation 1 and equation 2 in Section 6.1.3 were used to calculate the weight percent insoluble solids and the weight percent soluble solids for the SRAT product. The weight fraction of insoluble solids was determined to be 0.1503 and the weight fraction of soluble solids was determined to be 0.0517. The fractions were then multiplied by 100 to calculate the weight percent solids. This yielded 15.03 weight percent insoluble solids and 5.17 weight percent soluble solids for the SRAT product.

6.2 SRAT Cycle Gas Production

The SRAT vessel was purged using air with 0.5% (nominal) helium. The helium was used as a tracer to calculate flow out of the vessel and gas generation rates. The composition of the gas produced in the SRAT vessel was measured using a GC located in a hood outside of the SRTC Shielded Cells. The GC was capable of measuring helium, hydrogen, oxygen, nitrogen, carbon dioxide, and nitrous oxide. It should be noted that many of the oxides of nitrogen were likely produced in the SRAT cycle, but the GC was only capable of measuring nitrous oxide.

Figure 7 shows the hydrogen (H_2), carbon dioxide (CO_2), and nitrous oxide (N_2O) concentrations during the SRAT cycle. Table 17 lists the maximum concentrations and generation rates, on a DWPF basis, of H_2, CO_2, and N_2O (see Appendix A for details of conversion from SRTC to DWPF basis).

During initial heat up, prior to ~1130 on 10/3/01, radiolytic hydrogen was released from the sludge via agitation and heating of the sludge. At the conclusion of the nitric acid addition, there was a rapid increase in CO_2 concentration, followed by an almost equally as rapid decrease. During the increase, an unscheduled antifoam addition was required. After the start of the formic acid addition, the rate of decrease in CO_2 concentration slowed, while N_2O concentration increased. During the reflux period, both CO_2 and N_2O concentrations gradually decreased, while the H_2 concentration slowly increased, stabilizing after about eight hours of reflux.

Figure 7 - SRTC Scale Hydrogen, Carbon Dioxide, and Nitrous Oxide Concentrations and pH in the Offgas During the SRAT Cycle

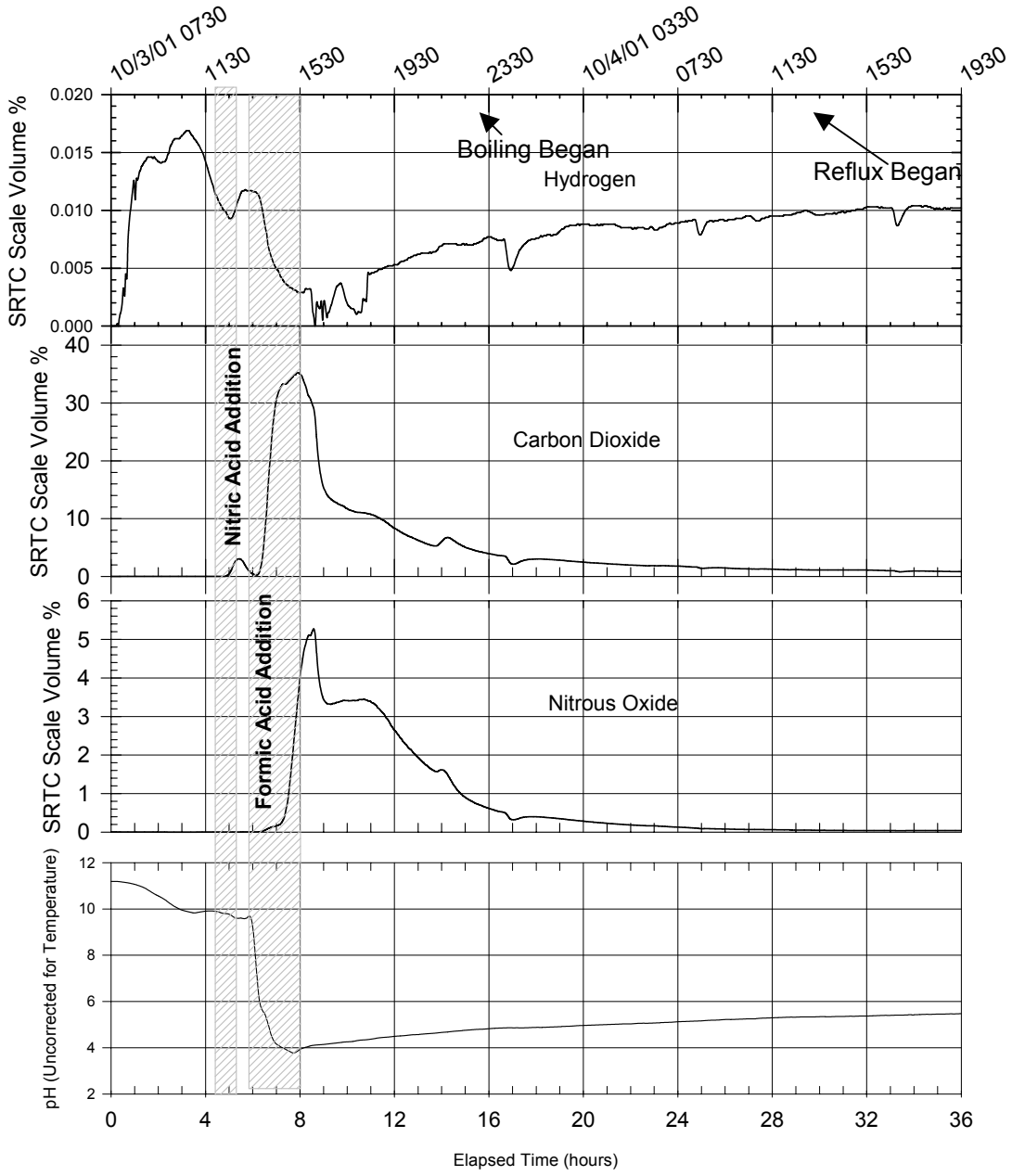


Table 17 - Maximum Hydrogen, Carbon Dioxide, and Nitrous Oxide Concentration and Generation Rate During the SRAT Cycle on a DWPF Basis

Gas	Maximum Gas Concentration (vol%)	Maximum Gas Generation Rate (lb/hr)
H_2	0.0013	0.00076
CO_2	4.4	81
N_2O	0.66	12

6.2.1 Hydrogen Generation

One of the requirements of the Technical Task Request was to collect and verify that the H_2 generation rate for the SRAT cycle was less than design basis rates currently used in DWPF. Table 17 shows both the maximum H_2 concentration and generation rates for the SRAT cycle on a DWPF basis. The maximum generation rate of 0.00076 lb/hr is well below the design basis rate of 0.65 lb/hr.

Hydrogen is primarily produced through the catalytic decomposition of formic acid and the radiolytic decomposition of water:

$$HCOOH \xrightarrow{\text{catalyst}} H_2 + CO_2 \qquad \text{Eq. 3}$$

$$2H_2O \xrightarrow{\text{radiolysis}} 2H_2 + O_2 \qquad \text{Eq. 4}$$

The formic acid decomposition reaction is catalytically promoted by fission product noble metals in the sludge slurry. Table 18 presents the calculated concentrations of noble metals for the isotopes of Ru, Pd, and Rh using the ICP-MS data from the washed Tank 40 sludge slurry. Also, summarized below are the key conclusions from previous surrogate studies characterizing noble metal catalyzed hydrogen production from the destruction of formic acid from Hutson[19] and Hsu and Ritter[20], respectively.

From Hutson[19],

- "The relative catalytic activity of the fission product noble metals is Rh>>Ru>>Pd."
- "The rate of reaction is highly dependent on the temperature of the vessel."
- "The amount of the nitrite (NO_2^-) ion present in the sludge affects the induction period for the initiation of hydrogen evolution."
- "The amount of hydrogen is dependent on the amount of excess formic acid added to the sludge material."

From Hsu and Ritter[20],

- "Rhodium was responsible for the peak hydrogen generation rate, whereas the sustained hydrogen generation was due to ruthenium. Palladium showed very little catalytic activity in the sludge simulant."
- "The hydrogen generation rate peaked only after all of the nitrite was destroyed."

Considering the Hsu and Ritter conclusion that hydrogen rate peaks after all the nitrite is destroyed and noting that the maximum H_2 concentration was observed during reflux (see Figure 7), it is likely that the majority of nitrite was destroyed prior to reflux. The decrease in N_2O concentration, a product of nitrite destruction, to nearly zero before reflux supports this conclusion. Also note from Figure 7 that the N_2O concentration was declining as the H_2 concentration was increasing.

Table 18 - Noble Metal Concentrations for the Washed Tank 40 Sludge Slurry

Element	Weight Percent of Total Solids *, [a]
Ru	3.32E-02 (±8.3E-04, 2.5E00)
Pd	8.85E-04 (±5.7E-05, 6.4E00)
Rh	7.77E-03 (±2.2E-04, 2.8E00)
Ag	1.06E-02 (± 1.5E-04, 1.4E00)

* The sludge slurry sample was dried at 115°C in an oven. Results are presented on a dry total solids basis.
[a] Results are calculated from the ICP-MS data (four samples). The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

Hydrogen from the radiolytic decomposition of water cannot be quantified with the data from the SRAT cycle. However, it is present as evidenced by the relatively large amount of hydrogen observed when the vessel was first agitated and heating began.

6.2.2 NO_x and Carbon Dioxide Evolution

The purpose of acid addition in the SRAT cycle is to destroy nitrite; to reduce mercury and manganese; and to acidify the sludge to adjust rheology. As the acids react with the nitrite and carbonate, CO_2 and NO_x are produced. A summary of reactions is given below.

Nitrite Destruction

$$2H_3O^+ + 3NO_2^- \rightarrow NO_3^- + 2NO + 3H_2O \quad \text{Eq. 5}$$

Oxidation/Reduction Reactions

$$MnO_2 + HCOOH \rightarrow MnO + CO_2 + H_2O \quad \text{Eq. 6}$$

$$HgO + HCOOH \rightarrow Hg + CO_2 + H_2O \quad \text{Eq. 7}$$

Acidification Reactions

$$2H_3O^+ + CO_3^{2-} \rightarrow CO_2 + 3H_2O \quad \text{Eq. 8}$$

$$H_3O^+ + OH^- \rightarrow 2H_2O \quad \text{Eq. 9}$$

Because both nitric and formic acids are used in the SRAT cycle for acidification, the potential exists for denitration. However, this denitration reaction occurs at a pH less than three[21]. During the SRAT cycle in the SRTC Shielded Cells, pH varied from just under 4 to over 11 (see Figure 7). Therefore, no denitration was expected. Although one cannot definitively state that there was no denitration, nitrates were produced during the SRAT cycle (see Equation 5 and Table 19), implying that any denitration was minor.

6.2.2.1 Nitrite and Nitrate Balance

As can be seen from Equation 5, nitric oxide (NO) is produced during the SRAT cycle. It should be noted, however, that Equation 5 is a summation of the following reactions[22].

$$2H_3O^+ + 2NO_2^- \rightarrow 2HNO_2 + 2H_2O \quad \text{Eq. 10}$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad \text{Eq. 11}$$

$$HNO_3 + NO_2^- \rightarrow HNO_2 + NO_3^- \quad \text{Eq. 12}$$

In addition to the above reactions, many other reactions involving nitrogen occur. Given below are some of the reactions that may be occurring.

$$2HNO_2 + 2HCOOH \rightarrow N_2O + 2CO_2 + 3H_2O \quad \text{Eq. 13}$$

$$2HNO_2 \leftrightarrow NO_2 + NO + H_2O \quad \text{Eq. 14}$$

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{Eq. 15}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \quad \text{Eq. 16}$$

$$2NO_2 \leftrightarrow N_2O_4 \quad \text{Eq. 17}$$

The exact extent of the above reactions cannot be quantified; of the nitrogen oxide gasses, only N_2O could be measured with the GC. Table 19 summarizes the nitrogen balance for the SRAT cycle.

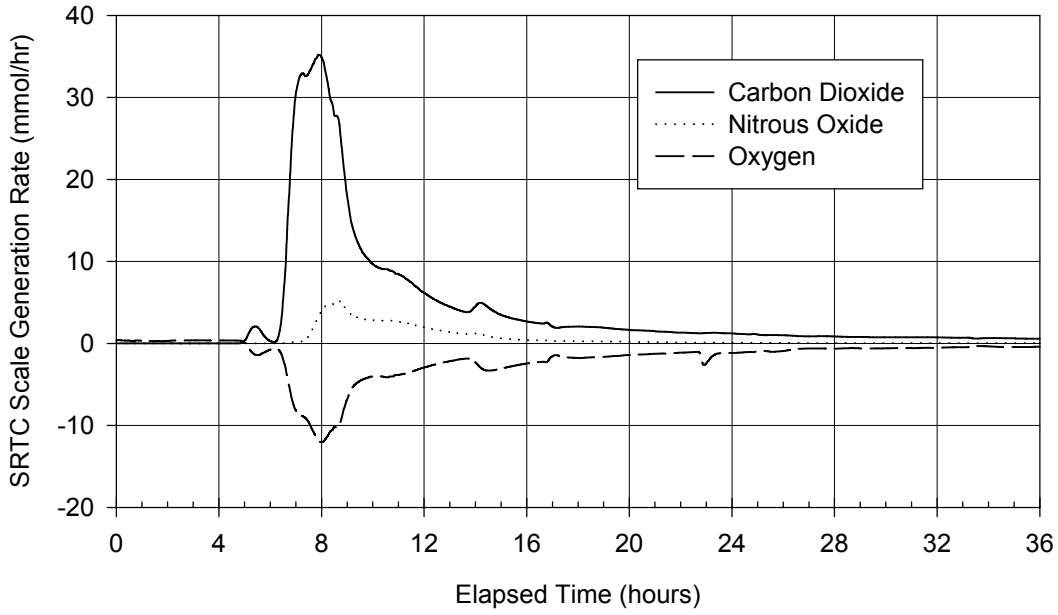
Table 19 - SRAT Cycle Nitrogen (N) Balance

	Input (SRAT Feed, Acid Addition) as mmol N	**Output (SRAT Product, Gas Generation) as mmol N**	**Generation (Output – Input) as mmol N [a]**
NO_2^-	142	7.78	- 134
NO_3^-	213.1 [b]	230	16.9
N_2O	0	42.6	42.6 [c]
Other	0	not measured	74.5 [d]

[a] A positive value denotes generation, while a negative value represents a consumption.
[b] 65.1 mmol from NO_3^- in feed, and 148 mmol from nitric acid addition.
[c] N_2O produced was calculated by converting measured concentration (Figure 7) to a generation rate, and then integrating under the resulting curve.
[d] The amount of "Other" is calculated by adding the nitrogen from the destroyed nitrite to the nitrogen from the nitrate and nitrous oxide.

As can be seen from Table 19, over 50% of the nitrite is converted to nitrate and compounds other than N_2O. A significant amount likely reacted to form NO, with subsequent oxidation in the vessel vapor space to form NO_2 (see Equation 15). A plot of gas generation rate (Figure 8) shows that oxygen is being consumed as CO_2 and N_2O are being produced. This suggests that NO may be forming and consuming oxygen as it oxidizes.

Figure 8 - SRTC Carbon Dioxide, Nitrous Oxide, and Oxygen Generation Rates During the SRAT Cycle



Although there is some uncertainty as to the exact products from nitrite destruction, the following observations can be made from the nitrogen balance:

- 95% of the input nitrite was destroyed (mmol NO_2^- consumed/mmol NO_2^- input).
- 12% of the input nitrite was converted to nitrate (mmol NO_3^- produced/mmol NO_2^- input).
- 15% of the input nitrite was converted to nitrous oxide (mmol N_2O produced/[2 x mmol NO_2^- input]).
- 79% of the input nitrogen in the SRAT feed was measured and accounted for in the SRAT product and offgas.

6.2.2.2 Carbon Balance

The sources of carbon in the SRAT process are inorganic carbon (carbonate) in the sludge slurry and formate from the formic acid addition to the sludge slurry. Carbon dioxide is produced from the catalytic decomposition of formic acid (Equation 3); during the reduction of manganese and mercury (Equations 6 and 7); and from the acidification of carbonate (Equation 8). Carbon dioxide may also be produced from reaction of formic acid and nitrous acid (Equation 13). Table 20 summarizes the carbon balance for the SRAT cycle.

Table 20 - SRAT Cycle Carbon (C) Balance

	Input (SRAT Feed, Acid Addition)	Output (SRAT Product, Gas Generation)	Generation (Output – Input)[a]
Inorganic Carbon	76.0 mmol	0 mmol [a]	- 76.0 mmol
Formate	758 mmol [b]	557 mmol	- 201 mmol
CO_2	0	146 mmol	146 mmol
Other	0	Not measured	131 mmol [c]

[a] The final pH of the SRAT product was less than 7. Therefore, the total inorganic carbon was assumed to be zero.
[b] 0.6 mmol in feed, and 757 mmol from formic acid addition.

Like the nitrite destruction, there is some uncertainty as to the exact products from the destruction of carbon compounds. The following observations can be made from the carbon balance:

- 26% of the input formate was destroyed (mmol formate consumed/mmol formate input).
- 50% of the consumed carbon formed CO_2 (- mmol CO_2 generated/[mmol inorganic carbon generated + formate generated + oxalate generated])
- 83% of the input carbon in the SRAT feed was measured and accounted for in the SRAT product and offgas.

7.0 CRITICALITY SAFETY BASIS AND DISCUSSION OF ELEMENTS DISSOLVED FROM THE SLUDGE SOLIDS DURING THE SRAT CYCLE

Section 7.1 contains the evaluation of the criticality safety basis for the washed Tank 40 SRAT feed and Tank 40 SRAT product using data presented in previous sections. Section 7.2 discusses the elements dissolved from the sludge solids during the SRAT cycle.

7.1 Criticality Safety Basis

Based on the DWPF criticality safety analysis summary report for sludge only operations, WSRC-RP-94-1132[23], SRTC is to confirm that the sludge batch is safe from a criticality standpoint. This is completed by verifying that the ratio of Fe to fissile material in the washed SRAT feed and SRAT product is >160. This parameter has to be met to ensure that the correct amount of neutron absorber is present in order to prevent a criticality. Table 21 shows the ratios of Fe to fissile materials for washed Tank 40 SRAT feed and for Tank 40 SRAT product compared to the safe weight ratios for each.

Table 21 - Ratio of Fe to Fissile Materials in the Washed Tank 40 Sludge Slurry and Tank 40 SRAT Product Compared to the Safe Weight Ratios

	Safe Weight Ratio for SRAT Feed	Ratio for the Washed Tank 40 SRAT Feed (1)	Safe Weight Ratio for the SRAT Product	Ratio for the Tank 40 SRAT Product (2)
Fe/ Equivalent Pu-239 (3) ratios	1.6E2	5.60E2	1.6E2	4.13E02

Notes:

(1) These values were derived from the analysis of the washed Tank 40 SRAT feed. See Table 2 and Table 3.
(2) These values were derived from the analysis of the washed Tank 40 SRAT product. See Table 11 and Table 12.
(3) Equivalent Pu-239 is defined as a simple sum of U-233, U-235, Pu-239, and Pu-241, according to WSRC-RP-94-1132[23]

Evaluating the washed SRAT feed and the SRAT product ratios to the criteria listed above, the following conclusion can be made:

- Based on the Fe to equivalent Pu-239 ratios (160:1) criteria for the SRAT feed and the SRAT product, the washed SRAT feed and the SRAT product exceeded the minimum required to ensure the criticality safe weight ratio for Fe (washed SRAT feed = 560:1 and the SRAT product = 413:1). Based on this, the DWPF can process Tank 40 sludge slurry with a negligible risk of a nuclear criticality.

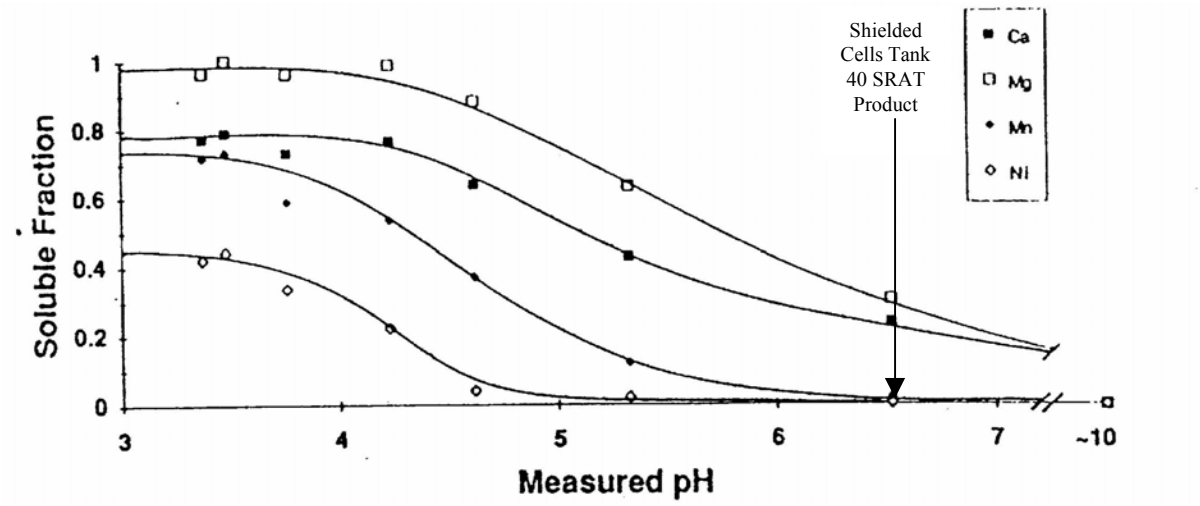
7.2 Elements Dissolved from the Sludge Solids During the SRAT Cycle

In the SRAT process, evidence has been obtained for the dissolution of certain species from the sludge solids as the pH of the sludge slurry is lowered by the addition of nitric and formic acids[24, 25]. For the Tank 40 demonstration, the ending pH of the SRAT product was 6.5. Upon analysis of the Tank 40 SRAT supernate (see Section 6.1.2), measurable amounts of Na, Sr-90, Mg, Ca, Cs-137, Mn, and Ni were dissolved from the sludge solids. Table 22 presents the fractions of elements soluble after the SRAT process using experimental results in Section 6.1 of this report. Figure 9 is a graph of the results obtained from a dissolution study with Tank 51 sludge slurry and nitric acid. The results in Table 22 indicate that 85.9% of the Na is dissolved from the sludge solids. In the study with Tank 51 sludge slurry, it was determined that all the Na dissolved at a pH of 6.5 or less (See Figure 9). The fractions in Table 22 essentially agree with the fractions at a pH of 6.5 in Figure 9. Also, the results in Table 22 indicated that the Fe and U-235 present in the Tank 40 sludge slurry is relatively insoluble after the SRAT process and stay with the sludge solids.

Table 22 - Fraction of Selected Elements Soluble After the SRAT Process

Element	Total (as Wt% of Total Dried Solids)	Quantity in the Supernate (as Wt% of Total Dried Solids)	Fraction Soluble After the SRAT Cycle
Al	5.56E00	2.60E-03	4.68E-04
Ca	2.19E00	8.43E-01	3.85E-01
Fe	2.23E01	6.32E-04	2.83E-05
Mg	1.77E00	9.17E-01	5.18E-01
Mn	2.97E00	1.65E-01	5.56E-02
Na	7.88E00	6.77E+00	8.59E-01
Ni	1.13E00	1.80E-03	1.59E-03
Sr-90	2.77E-03	6.82E-04	2.46E-01
Cs-137	2.79E-04	9.54E-05	3.42E-01
U-235	3.91E-02	1.14E-05	2.92E-04
U-236	1.82E-03	5.95E-07	3.27E-04
Np-237	2.29E-03	2.86E-04	1.25E-01
U-238	6.85E00	2.99E-03	4.36E-04
Pu-240	1.20E-03	6.07E-07	5.06E-04

Figure 9 - Graph of pH Versus Elemental Fraction Dissolved During Nitric Acid Addition for Tank 51 Sludge Slurry



8.0 RECOMMENDATIONS

Recommendation for new IIT747 Antifoam Addition for the SRAT Cycle: Follow the prescribed antifoam strategy except add 100 ppm of antifoam prior to the formic acid addition[4]. As prescribed, refresh the antifoam every 8 hours[4].

9.0 QUALITY ASSURANCE

The following certified NIST traceable standard gases (from Air Liquide) were used to calibrate the GC for the SRAT cycle:

	He	H_2	O_2	N_2O	CO_2	N_2
CalGas 1	0.80	1.00	12.00	15.00	25.00	Balance
CalGas 2	0.20	0.10	20.00	0.10	1.00	Balance

Each calibration gas was sampled until a steady reading on the GC was obtained to establish a calibration curve for each species immediately before the SRAT cycle started.

All samples generated in the Shielded Cells for this task were tracked per L1 2.21 Procedure, "Radioactive Sample Receiving, Labeling and Tracking". All sludge dissolution samples were submitted with standards to check that dissolutions were complete and the analytical procedures were performed correctly[8, 9].

Data are recorded in notebooks WSRC-NB-2000-00166[17], WSRC-NB-2001-00162[26] and WSRC-NB-2001-00163[18].

10.0 CONCLUSIONS

- No significant processing problems were encountered during the processing of this material through the SRAT cycle.
- Foam was experienced in the SRAT cycle of this confirmation run that required an extra 100 ppm addition of IIT747 during the formic acid addition. Foam was noted during the initial transfer of slurry into the SRAT vessel. This foam was difficult to break.
- The hydrogen production rate on a DWPF basis was 0.00076 lb H_2/hr during the SRAT cycle, which was well below the DWPF hydrogen design basis rate of 0.65 lb H_2/hr for the SRAT cycle.
- The maximum hydrogen and nitrous oxide concentrations observed on a DWPF basis were 0.0013 volume % and 0.66 volume %, respectively.
- Final SRAT product nitrite levels indicate that at least 95% of the starting nitrite was destroyed.
- No significant loss of nitrate occurred during the SRAT cycle.
- Approximately 91.6% of the Hg in the sludge was removed during the SRAT cycle.
- Using IC measurements for nitrite and GC data to estimate total N_2O, it was calculated that about 15% of the original nitrite in SRAT feed was converted (reduced) to gaseous N_2O during the SRAT cycle.
- The safe weight ratio for Fe exceeds the minimum (>160) for the Tank 40 SRAT feed and the Tank 40 SRAT product. Based on this, the DWPF can process Tank 40 sludge slurry with a negligible risk of a nuclear criticality.

11.0 REFERENCES

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APPENDIX A - INPUTS AND ASSUMPTIONS USED FOR CALCULATING THE OFFGAS DATA FOR THE SRAT CYCLE

Table A-1 - SRTC and DWPF Sludge Volumes and Purge Rates Used for the SRAT Cycle

	SRAT Cycle SRTC Basis	SRAT Cycle DWPF Basis
Sludge Volume	0.945 L	22710 L (6000 gal)
Purge Rate (F_{in})	27.7 sccm	5.324E06 sccm (188 scfm)

Definition of Standard Conditions:

Temperature = 21.1°C or 70°F (This is the temperature used by SRS flow calibration personnel)

Pressure=1 atm

Assumption: The gasses produced during the SRAT cycle behave as ideal gasses, i.e. volume %=mole %, and 1 mole = 2.41×10^4 cc (calculated using ideal gas law PV=nRT, with P = 1 atm and T = 21.1°C)

Conversion of the SRTC Volume % to DWPF Volume %

To convert from SRTC to DWPF scale volume %, one must adjust for differences in sludge volumes and purge rates.

$$Volume\,\%\ Conversion = \frac{DWPF\ Sludge\ Volume}{SRTC\ Sludge\ Volume} \cdot \frac{SRTC\ Purge\ Rate}{DWPF\ Purge\ Rate} \tag{A-1}$$

For the SRAT cycle:

$$\frac{22710\,\text{L DWPF Sludge}}{0.945\,\text{L SRTC Sludge}} \cdot \frac{27.7\,\text{sccm SRTC purge}}{5.324\times10^{6}\,\text{sccm DWPF purge}} = 0.125\,\frac{\text{vol\% DWPF}}{\text{vol\% SRTC}} \tag{A-2a}$$

Calculation of Gas Generation Rate

The DWPF scale gas generation rate is calculated by
1. Calculating the flow out of the SRTC vessel
2. Calculating the gas generation rate in the SRTC vessel by multiplying the measured volume % by the flow rate out of the vessel
3. Converting the SRTC generation rate from cc/min to lb/hour
4. Scaling the SRTC rate to DWPF basis

1. The flow rate out of the vessel is calculated by a helium balance. The vessel purge gas contains 0.46% helium. Therefore, the flow rate out of the vessel is:

$$F_{out} = F_{in} \cdot \frac{0.46}{x_{He}} \tag{A-3}$$

where F_{in} is flow into vessel (purge rate) and x_{He} is the measured volume % helium

2. The SRTC gas generation rate is then:

$$SRTC\ Gas\ gen\ rate = \frac{x_i}{100} \cdot F_{out} \tag{A-4}$$

where x_i is the measured vol % of gas *i*.

3. The SRTC gas generation rate (SGGR) is then converted from cc/min to lb/hr:

$$SGGR\ \text{sccm} \cdot \frac{\text{mol}}{2.41\text{E}4\ \text{cc}} \cdot \frac{M_i\ \text{g}}{\text{mol}} \cdot \frac{1\ \text{lb}}{454\ \text{g}} \cdot \frac{60\ \text{min}}{1\ \text{hour}} \tag{A-5}$$

where M_i is the molecular weight of gas *i*.

4. To scale the gas generation rate from SRTC to DWPF, the ratio of sludge volumes is used:

$$Gen\ Rate\ Scale\ Factor = \frac{DWPF\ Sludge\ Volume}{SRTC\ Sludge\ Volume} \tag{A-6}$$

Combining the above:

$$DWPF\ Gas\ Gen\ Rate = F_{in} \cdot \frac{x_i}{100} \cdot \frac{0.46}{x_{He}} \cdot \frac{\text{mol}}{2.41\text{E}4\ \text{cc}} \cdot \frac{M_i\ \text{g}}{\text{mol}} \cdot \frac{1\ \text{lb}}{454\ \text{g}} \cdot \frac{60\ \text{min}}{1\ \text{hour}} \cdot \frac{DWPF\ Sludge\ Vol}{SRTC\ Sludge\ Vol} \tag{A-7}$$

Inputting known values and combining terms, the above expression reduces to:

$$DWPF\ Gas\ Gen\ Rate = F_{in} \cdot \frac{x_i}{x_{He}} \cdot M_i \cdot \frac{DWPF\ Sludge\ Volume}{SRTC\ Sludge\ Volume} \cdot 2.5225 \times 10^{-8} \tag{A-8}$$

For the SRAT cycle:

$$DWPF\ Gas\ Gen\ Rate = x_i \cdot \frac{M_i}{x_{He}} \cdot 1.68 \times 10^{-2} \qquad \text{(A-9a)}$$

Table A-2. SRAT Cycle Maximum Gas Concentrations and Generation Rates

	H_2[†]	**CO_2**	**N_2O**
Molecular Weight (M_i)	2.0	44.0	44.0
He Vol. % at Maximum Gas Concentrations (x_{He})	0.46	0.32	0.33
SRTC Scale Vol. % (x_i)	1.04E-02	3.52E01	5.3E00
DWPF Scale Vol. % (Factor From Eq. 2a)	1.3E-03	4.4E00	6.6E-01
DWPF Scale Generation Rate (lb/hr) (Eq. 9a)	7.6E-04	8.1E01	1.2E01

[†] Higher hydrogen concentrations were detected when vessel agitation and heating began as the radiolytic hydrogen that was dissolved in the sludge was released.

APPENDIX B - CALCULATIONS COMPLETED FOR THE SRAT CYCLE

Scaling Factor for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Shielded Cells:	0.94	Liters
Volume of Sludge Receipt for the DWPF:	6000	Gallons
or Volume of Sludge Receipt for the DWPF:	22710	Liters

Ratio= Volume of Sludge Receipt for the Shielded Cells / Volume of Sludge Receipt for the DWPF

Ratio= 0.944 Liters / 22710 Liters

Ratio= 4.16E-05

Nitric Acid Addition Flow Rate for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Shielded Cells:	0.94	Liters
Volume of Sludge Receipt for the DWPF:	6000	Gallons
or Volume of Sludge Receipt for the DWPF:	22710	Liters
DWPF Flow Rate for Nitric Acid:	2	Gallons/min
or DWPF Flow Rate for Nitric Acid:	7.57	Liters/min

Ratio= (Volume of Sludge Receipt for the Shielded Cells)*(DWPF Flow Rate for Nitric Acid) / Volume of Sludge Receipt for the DWPF

Ratio= (0.944 Liters X 7.57 Liters/min) / 22710 Liters

Shielded Cells Flow Rate = 0.00031 Liters/min
or
Shielded Cells Flow Rate= 0.31 mL/min

Formic Acid Flow Rate for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Shielded Cells:	0.94	Liters
Volume of Sludge Receipt for the DWPF:	6000	Gallons
or Volume of Sludge Receipt for the DWPF:	22710	Liters
DWPF Flow Rate for Formic Acid:	2	Gallons/min
or DWPF Flow Rate for Formic Acid:	7.57	Liters/min

Ratio= (Volume of Sludge Receipt for the Shielded Cells)*(DWPF Flow Rate for Formic Acid) / Volume of Sludge Receipt for the DWPF

Ratio= (0.944 Liters X 7.57 Liters/min) / 22710 Liters

Shielded Cells Flow Rate for Formic Acid= 0.00031 Liters/min
or
Shielded Cells Flow Rate for Formic Acid= 0.31 mL/min

Dow Corning Antifoam Additions for Shielded Cells

	Amount	Units
Volume of Sludge Receipt for the Shielded Cells:	0.945	Liters
Density of Sludge:	1.12	g/mL
Concentration of Antifoam :	100	ppm
Weight percent solution wanted:	5	wt.%
Approximate Density of Antifoam Solution:	1	g/mL

To make 50 mLs of 5 wt.% antifoam solution, you will need to add the following:

Antifoam Required:	5	g
Water Required:	95	g
Total Solution wt:	100	g
Check of calculations:	(5/100)*100	
Wt. % of Antifoam:	5	wt.%
Density of Antifoam	1	g/mL

Calculation for Amount of Antifoam to be Added During SRAT and SME Cycles

Grams of antifoam= (Volume of Sludge L)*(Density of Sludge)*(100ppm)*(1000mL/L) / 1000000 g Slurry

Grams of antifoam= 0.1058 g

mL of Antifoam Solution to Add= (Grams of Antifoam Required) / (Made up Solution)*(Density of Solution)

mL of Antifoam Solution to Add= 2.12 mL

Purge Rate for the SRAT Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Shielded Cells:	0.945	Liters
Volume of Sludge Receipt for the DWPF:	6000	Gallons
or Volume of Sludge Receipt for the DWPF:	22710	Liters
DWPF Air Purge Rate:	188.00	scfm
or DWPF Air Purge Rate:	5324160	sccm

Ratio= (Volume of Sludge Receipt for the Shielded Cells)*(DWPF Air Purge Rate) / Volume of Sludge Receipt for the DWPF

Ratio= (0.945 Liters* 5324160 sccm) / 22710 Liters

Shielded Cells Purge Rate for SRAT/SME Vessel= 221.5 sccm
Purge Rate Used for the Shielded Cells Run to See H2 (1/8 of DWPF purge) 27.7 sccm

APPENDIX C - MASS BALANCE OF SELECTED ELEMENTS FOR THE SRTC MACROBATCH 3 SRAT CYCLE DEMONSTRATION

Below is a table showing the as analyzed grams fed to the SRAT and the as analyzed grams in the SRAT product for selected elements (those with a concentration of >1 wt% in the feed total solids). The intent of this table is to show that, for the most part, the analytical results of the feed and product were good. Note that for the elements in the table, grams fed should equal the grams in the product.

Element	SRAT Feed (Wt% of Total Solids)	SRAT Product (Wt% of Total Solids)	SRAT Feed (grams)	SRAT Product (grams)	Percent Difference
Al	5.77E+00	5.56E+00	1.12E+01	1.21E+01	8.6
Ca	2.34E+00	2.19E+00	4.53E+00	4.78E+00	5.5
Fe	2.36E+01	2.23E+01	4.57E+01	4.87E+01	6.5
Mg	1.84E+00	1.77E+00	3.56E+00	3.87E+00	8.4
Mn	3.21E+00	2.97E+00	6.22E+00	6.49E+00	4.3
Na	7.80E+00	7.88E+00	1.51E+01	1.72E+01	13.9
Ni	1.19E+00	1.13E+00	2.31E+00	2.47E+00	7.0
Si	1.19E+00	9.94E-01	2.31E+00	2.17E+00	-5.8
U	7.61E+00	6.85E+00	1.47E+01	1.50E+01	1.5

Wt Fraction Total Solids	0.184	0.202
Density (g/mL)	1.12	1.15
Volume (mL)	940	940

Notes to Table
The SRAT feed is Tank 40 Washed Sludge Slurry.

$$Percent\ Difference = \frac{grams\ in\ product - grams\ in\ feed}{grams\ in\ feed} \times 100$$