Demonstration of the Tank Farm Washing Process and the DWPF SRAT Cycle with Sludge Batch 3 Simulant and Precipitated Pu/Gd Mixture from H-Canyon Tank 18.3

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1.0 INTRODUCTION AND SUMMARY

The Nuclear Materials Management Division (NMMD) has proposed that certain Pu solutions stored in H-Canyon be disposed to H-Tank Farm. These solutions contain significant inventories of plutonium. Prior to discharging the acidic solutions, the acid is neutralized to >1 M free hydroxide. The plan is to send the neutralized Pu solutions to H-Tank Farm (Tank 51) as a slurry containing precipitated Pu with sufficient Gd to prevent the possibility of criticality.

The Pu/Gd mixture (along with the sludge slurry from Tank 7 and Am/Cm solution) will be processed as a part of Sludge Batch 3. Sludge Batch 3 is the next sludge batch of feed for the Defense Waste Processing Facility (DWPF). In order to prepare the feed for DWPF, the sludge slurry will be washed to ~0.55 M Na in the supernate. NMMD issued a Task Technical Request (TTR- NMMD-HTS-2002-010[1]) requesting an evaluation of the processing impacts to the Tank Farm and DWPF. In response to the request in TTR- NMMD-HTS-2002-010, a matrix was developed identifying processing impacts. This report addresses the glove box work with a Sludge Batch 3 simulant and a Pu/Gd mixture precipitated from H-Canyon Tank 18.3[2, 3]. The main objective of this experimental work was to determine the behavior of the Pu and Gd during the Tank Farm washing process and the SRAT process. Since this was the main objective of the experimental work, no additions of sodium oxalate, mercury, or noble metals (related to H_2 production in the SRAT) were made to the Sludge Batch 3 simulant. The washing issues surrounding sodium oxalate, and the SRAT cycle issues of the H_2 production (noble metals effect the H_2 production during the SRAT) and the steam stripping efficiency of mercury are specific issues related to Sludge Batch 3. These issues will be investigated as a part of the Sludge Batch 3 nonradioactive work conducted at the Aiken County Technology Laboratory (ACTL) and radioactive work conducted in the Shielded Cells facility with the qualification samples. Highlights from this report are found below.

- Up to 0.95% of the Gd and 0.20% of the Pu was soluble during the glove box demonstration of the Tank Farm Washing Process. The majority of the Gd (99 %) and Pu (99.8%) were insoluble and stayed with the sludge solids.
- The small quantities of leached plutonium during the sludge washing tests do not present a criticality safety concern and are not sufficient to adversely impact the Effluent Treatment Facility or Saltstone operations.
- No significant problems were encountered during the washing process. Based on analytical results, the Pu/Gd mixture appeared to be uniformly distributed throughout the sludge.
- Approximately 2.64% of the Gd and ~0.16% of the Pu was soluble after the glove box demonstration of the DWPF SRAT cycle. The majority of the Gd (97 %) and Pu (99.8%) was insoluble and stayed with the sludge solids.
- No significant processing problems were encountered during the processing of this material through the first of two SRAT cycles.
- The nitrite was less than 102 ppm at the end of the SRAT cycle. The DWPF requirement is <1000 ppm at the end of the SRAT cycle.
- Upon lowering the pH of the SRAT product to ~3, approximately 4.84% of the Gd and 0.15% of the Pu was soluble after the glove box demonstration of the DWPF SRAT cycle. The majority of the Gd (95 %) and Pu (99.8%) was insoluble and stayed with the sludge solids.
- Two extra additions of antifoam were made during the 12 hour boiling period of the second SRAT cycle (pH~3) to control foaming.
- As a well mixed slurry in the DWPF (for both SRAT scenarios studied in this experiment), there is enough Fe with the fissile Pu to not cause a criticality concern (i.e. Fe:Pu ratio must be greater than 160:1).

Table 1 provides a summary of the Gd and Pu behavior during the Tank Farm Process and the DWPF SRAT cycle.

Table 1 – Summary of the Gd and Pu Behavior for the Tank Farm Washing Process and the SRAT Cycles

Top Sample – First Wash[a] (pH~14)	Element	% Soluble in the Supernate	% Insoluble in the Sludge Solids
	Gd	0.70 %	99.30 %
	Pu-239	0.15 %	99.85 %
	Pu-240	0.14 %	99.86 %
Bottom Sample – First Wash[a] (pH~14)	**Element**	**% Soluble in the Supernate**	**% Insoluble in the Sludge Solids**
	Gd	0.40%	99.60 %
	Pu-239	0.19%	99.81 %
	Pu-240	0.20%	99.80 %
Top Sample – Second Wash[b] (pH~12.6)	**Element**	**% Soluble in the Supernate**	**% Insoluble in the Sludge Solids**
	Gd	0.65%	99.35 %
	Pu-239	0.11%	99.89 %
Bottom Sample – Second Wash[b] (pH~12.6)	**Element**	**% Soluble in the Supernate**	**% Insoluble in the Sludge Solids**
	Gd	0.95%	99.05 %
	Pu-239	0.02%	99.98 %
First SRAT Cycle[c] (ph~3.9)	**Element**	**% Soluble in the Supernate**	**% Insoluble in the Sludge Solids**
	Gd	2.64 %	97.36 %
	Pu-239	0.06 %	99.94 %
	Pu-240	0.06 %	99.94 %
	Pu-242[e]	0.17 %	99.83 %
Second SRAT Cycle[d] (ph~3.2)	**Element**	**% Soluble in the Supernate**	**% Insoluble in the Sludge Solids**
	Gd	4.84 %	95.16 %
	Pu-239	0.15 %	99.85 %
	Pu-240	0.13 %	99.87 %

[a] Assumptions used for calculation: Total volume of 1561 mL, 14.75 wt.% total solids, slurry density 1.12 g/mL, 9.83 wt.% dissolved solids, and 1.08g/mL supernate density.
[b] Assumptions used for calculation: Total volume of 1735 mL, 7.23 wt.% total solids, slurry density 1.05 g/mL, 3.66 wt.% dissolved solids, and 1.03 g/mL supernate density.
[c] Assumptions: Total volume of 300 mL, 17.5 wt.% total solids, slurry density 1.155 g/mL, 7.89 wt.% dissolved solids, and 1.07g/mL supernate density.
[d] Assumptions: Total volume of 245 mL, 17.3 wt.% total solids, slurry density 1.16 g/mL, 7.67 wt.% dissolved solids, and 1.07g/mL supernate density.
[e] Due to the low concentrations of Pu, this difference is attributed to analytical error.

Outside of the sodium oxalate, noble metals, and mercury issues identified as specific issues related to Sludge Batch 3, other issues concerning Sludge Batch 3 were identified when performing this work. They are listed below and should be considered prior to performing the nonradioactive work and radioactive work for Sludge Batch 3.

1. Resolve the issues surrounding the method of determining TIC/TOC for the sludge slurries that have coal added to them. The TIC concentration is an input for the acid calculations for the SRAT cycle. The TOC concentration will affect the final redox of the melter (Fe^{2+}/Fe^{tot}) which directly affects the amount of formic acid added during the SRAT cycle.
2. Revise the spreadsheet for the SRAT acid calculations to incorporate sludge slurries that have coal/carbon in them.
3. Resolve the differences observed between the Gd concentrations obtained from the radioactive ICP-ES versus the concentrations obtained from the radioactive ICP-MS. The Gd values from the ICP-ES appeared to be biased high by 20%.

4. Determine if coal/carbon ring forms above the sludge slurry for the nonradioactive and radioactive Sludge Batch 3 testing. If coal/carbon remains behind in the vessel, it could impact the ability to reliably predict the redox of the glass.
5. Determine if sand is observed on the bottom of the SRAT vessel for the nonradioactive scoping SRAT runs.
6. Verify the Fe to fissile material in the washed sludge slurry and the SRAT product is greater than 160:1 for the radioactive testing in the Shielded Cells.
7. Analyze the supernate at the end of the SRAT cycle to determine what species have dissolve from the sludge solids for the radioactive testing in the Shielded Cells.

2.0 TANK FARM WASHING PROCESS

As noted in Section 1.0, the objective of the Tank Farm washing process was to study the behavior of the Pu/Gd during this process. Since that was the main objective of the washing process, no sodium oxalate was added to the Sludge Batch 3 simulant. The following sections below provide a description of the Tank Farm washing process that was completed in a glove box at SRTC with a nonradioactive Sludge Batch 3 simulant and a Pu/Gd mixture precipitated from a sample of acidic solution from H-Canyon Tank 18.3[4]. Also presented in the following sections are the analytical data obtained during the washing process.

2.1 Selection and Adjustment of the Sludge Batch 3 Simulant

Based on the predicted composition of Sludge Batch 3[5], Tank 8 (nonradioactive) sludge slurry simulant was selected for the glove box testing. This simulant was selected because the composition closely matched that of Sludge Batch 3 of the available nonradioactive sludge slurries on hand. Table 2 presents the composition of the Tank 8 simulant compared to the predicted Sludge Batch 3 composition.

Table 2 – Comparison of the Composition of the Tank 8 Simulant versus the Predicted Composition of Sludge Batch 3[b]

Element	Wt. % for Tank 8 Simulant[a]	Wt. % for Sludge Batch 3[b]
Al	9.30	9.89
Ba	0.20	0.23
Ca	2.22	2.67
Cr	0.22	0.26
Cu	0.13	0.16
Fe	26.2	29.1
K	0.01	0.37
Mg	0.12	0.11
Mn	2.55	5.74
Na	6.0	8.15
Ni	2.81	1.31
Pb	0.10	0.29
Si	0.89	1.01
Sr	0.08	-
Zn	0.22	0.34
Zr	0.37	0.59

[a] Per E-mail from D.C. Koopman. Sample was dried at 110°C overnight and then dissolved.
[b] Reference WSRC-TR-2002-00145, "An Assessment of the Impacts of Adding Pu/Gd and Am/Cm Waste Streams to Sludge Batch 3 (SB3) on DWPF H_2 Generation rates and Glass Properties (U)[5].

To match the starting sodium molarity of Sludge Batch 3 in Tank 51, the Tank 8 simulant was "dewashed" from ~ 0.57 M Na to ~5 M Na concentration in the supernate by adding Na_2CO_3, NaCl, NaOH, $NaNO_2$, $NaNO_3$, and Na_2SO_4. Representative amounts of sand (20-28 mesh Tyler screen or 600 to 800 micron) and coal (20-28 mesh Tyler screen or 600-800 micron) were added to the "de-washed" Tank 8 simulant (Tank 8 simulant will be referred to as Sludge Batch 3 simulant). Presented below in Table 3 are the "de-washed" weight percent solids, density, and the major elements and anions detected

in the supernate of the Sludge Batch 3 simulant. The standard deviation and the percent relative standard deviation are presented below the value in parentheses.

Table 3 – Weight Percent Solids, Density, and Major Elements and Anions of the Supernate for the "De-Washed" Sludge Batch 3 Simulant

Weight Percent Solids of the Sludge Batch 3 Simulant[a]	32.6 wt. % (± 1.1E00, 3.3E00)
Weight Percent Solids of the Sludge Batch 3 Supernate[a, c]	23.7 wt.% (± 7.0E-01, 3.1E00)
Density of the Sludge Batch 3 Simulant[b]	1.29 g/mL (± 4.0E-03, 3.1E-01)
Density of the Sludge Batch 3 Supernate[b, c]	1.20 g/mL (± 3.0E-03, 2.9E-01)
Al[c]	6.85E03 µg/mL of Supernate (± 1.1E02, 1.7E00)
Ca[c]	5.98E00 µg/mL of Supernate (± 4.0E-02, 6.7E-01)
Cr[c]	1.29E00 µg/mL of Supernate (± 1.0E-02, 7.8E-01)
K[c]	1.72E02 µg/mL of Supernate (± 1.5E00, 8.9E-01)
Na[c]	1.07E05 µg/mL of Supernate (± 5.8E02, 5.4E-01)
Chloride[c]	1.07E04 µg/mL of Supernate (± 1.5E02, 1.4E00)
Nitrite[c]	9.26E04 µg/mL of Supernate (± 6.7E02, 7.2E-01)
Nitrate[c]	1.54E04 µg/mL of Supernate (± 8.4E02, 5.5E00)
Sulfate[c]	5.74E03 µg/mL of Supernate (±6.5E01, 1.1E00)

[a] Average of three results.
[b] Average of four results.
[c] A sample of mixed sludge slurry was filtered to obtain the supernate. Results are the average of three values.

2.2 Addition of the Pu/Gd Mixture to the Sludge Batch 3 Simulant and Washing Strategy

To a calibrated washing vessel, 575 mL of mixed "de-washed" Sludge Batch 3 simulant was added and transferred into a glove box. Based on the expected final washed volume of the sludge slurry (calculated from an Excel spreadsheet), a calculation was performed to determine how much Pu/Gd mixture had to be added to represent 170 kg of Pu in Tank 51. It was determined that 63.3 g of the Pu/Gd mixture had to be added to the "de-washed" Sludge Batch 3 simulant. The Pu/Gd mixture that was added to the Sludge Batch 3 simulant had been precipitated from a sample of Tank 18.3 from H-Canyon[4].

After the addition of 63.4 grams (target 63.3 g actually added 63.4 g) of the Pu/Gd mixture, the Sludge Batch 3 simulant was thoroughly mixed by capping and shaking the contents of the washing vessel by hand. The vessel was then uncapped and the first addition of inhibited water (1000 mL of 0.015 M NaOH and 0.015 M $NaNO_2$ solution) was added. The cap for the washing vessel was replaced and the contents were thoroughly mixed by hand. The washing vessel was then placed on a stir plate and the stir plate was turned on to mix the contents of the washing vessel for sampling (A magnetic stir bar had been placed in the vessel after the "de-washed" Sludge Batch 3 had been added to the washing vessel.). The contents were allowed to stir for approximately 10 minutes prior to taking sludge slurry samples from the top and bottom of the washing vessel. Top and bottom samples were taken for each wash to show that there were no differences in the composition (i.e. Pu/Gd segregates or settles). After taking the samples, the stir plate was turned off and the cap was placed back on the washing vessel to prevent evaporation. The Sludge Batch 3 simulant was then allowed to sit undisturbed for ~5 days so the sludge could settle prior to decant.

At the end of 5 days, the sludge slurry in the washing vessel had separated into two layers. One being a clear supernate layer and the other being a sludge layer. Approximately 1000 mL of the clear supernate was removed during the first decant. After the decant was complete, the second addition of inhibited water (1200 mL of 0.015 M NaOH and 0.015 M $NaNO_2$ solution) was added and the same sampling technique (top and bottom samples) was used as in the first wash. At the end of the 5 day settling period, approximately 1200 mL of clear supernate was removed. Upon receiving the weight percent solids results (13.5 wt.%), another 85 mL of supernate was removed to target a higher weight percent solids value (15.3 wt.%) for the DWPF SRAT cycle.

2.3 Analytical Results of the Top Sample and Bottom Sample of the Sludge Batch 3 Simulant for the First Wash and Second Wash

Provided below are the results of the analyses for the top sample and bottom sample from the first wash and second wash of the Sludge Batch 3 simulant. The samples were allowed the same contact time of 5 days with the inhibited water, as in the washing vessel, prior to analysis.

2.3.1 Total Weight Percent Solids Measurements for the Top Samples and Bottom Samples for the First and Second Washes of Sludge Batch 3 Simulant

Triplicate measurements of the total weight percent solids for the sludge slurry were completed. Mixed portions of a sample of sludge slurry were pipetted into three labeled, pre-weighed vessels. After the addition of the mixed sludge slurry, the vessels were weighed and placed into a drying oven at 110°C overnight. The samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. The averages of the calculated results of the weight percent solids for the sludge slurry are presented in column two of Table 4. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are presented in column three and column four respectively of Table 4.

Table 4 – Total Weight Percent Solids Measurements for the Top Sample and Bottom Sample for the First and Second Wash of Sludge Batch 3 Simulant

Sample ID	Total Weight Percent Solids (wt.%)	Std. Dev.	% RSD
Top Sample – First Wash	14.75	± 8.3E-02	5.6E-01
Bottom Sample – First Wash	14.76	± 1.4E-01	9.6E-01
Top Sample – Second Wash	7.28	± 8.0E-02	1.1E00
Bottom Sample – Second Wash	7.17	± 9.9E-02	1.4E00

2.3.2 Comparison of the Nonradioactive Composition for Top and Bottom Samples for the First Wash and the Top and Bottom Samples for the Second Wash

For each sample, triplicate portions of mixed sludge slurry were taken and dried overnight in a drying oven at 115°C. These samples of the dried sludge slurry were dissolved by the Aqua Regia methods[6] along with a glass standard (ARG) to check the dissolutions and the analytical methods. After performing the dissolution methods on the sludge slurry, the samples were sent to Analytical Development Section (ADS) Sample Receiving for analyses to be performed by ADS. The dissolution results of the standard glass for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly. Table 5 presents the Gd concentration and elements (excluding oxygen) with concentrations >0.1 weight percent for the top and bottom samples for the first wash of the Sludge Batch 3 simulant obtained from the Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES). Table 5 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value. Table 6 presents the Gd concentration and elements (excluding oxygen) with concentrations >0.1 weight percent for the top and bottom samples for the second wash of the Sludge Batch 3 simulant obtained from the Inductively Coupled Plasma- Emission

Spectroscopy (ICP-ES). Table 6 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

Table 5 – Gd Concentration and Elements (excluding oxygen) with Concentrations >0.1 Weight Percent in the Top and Bottom Samples from the First Wash of the Sludge Batch 3 Simulant (Presented in Units of Weight Percent of Total Dried Solids)

Element	Top Sample – First Wash Wt.% (Std. Dev., %RSD)[b]	Bottom Sample – First Wash Wt.% (Std. Dev., %RSD)[b]
Al	4.40E00 (± 1.1E-01, 2.6E00)	4.40E00 (± 5.2E-02, 1.2E00)
Ba	1.16E-01 (± 3.2E-03, 2.8E00)	1.15E-01 (± 4.6E-03, 4.0E00)
Ca	1.01E00 (± 2.1E-02, 2.1E00)	1.01E00 (± 7.1E-03, 7.0E-01)
Fe	1.16E01 (± 2.5E-01, 2.1E00)	1.17E01(± 9.8E-02, 8.4E-01)
Gd	3.87E-02 (± 6.8E-04, 1.8E00)	3.85E-02 (± 5.8E-04, 1.5E00)
Mn	1.33E00 (± 3.9E-02, 2.9E00)	1.33E00 (± 7.6E-02, 5.7E00)
Na	2.48E01 (± 6.5E-01, 2.6E00)	2.47E01 (± 2.1E-01, 8.7E-01)
Ni	1.32E00 (± 2.9E-02, 2.2E00)	1.32E00 (± 1.1E-02, 8.3E-01)
Si[a]	6.0E-01 (± 1.9E-03, 3.1E-01)	6.5E-01 (± 5.3E-02, 8.2E00)
U	1.49E-01 (± 1.8E-03, 1.2E00)	1.51E-01 (± 2.6E-03, 1.7E00)
Zn	1.22E-01 (± 2.1E-03, 1.7E00)	1.22E-01 (± 1.7E-03, 1.4E00)

[a] Si was added to the table because it exceeded the 0.1 wt.% criteria. However, this number should not be used because it is known that this dissolution method does not dissolve all of the Si.
[b] Results are determined by ICP-ES and are the averages of results of three samples of dissolved dried slurry. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

Table 6 – Gd Concentration and Elements (excluding oxygen) with Concentrations >0.1 Weight Percent in the Top and Bottom Samples from the Second Wash of the Sludge Batch 3 Simulant (Presented in Units of Weight Percent of Total Dried Solids)

Element	Top Sample – Second Wash Wt.% (Std. Dev., %RSD)[b]	Bottom Sample – Second Wash Wt.% (Std. Dev., %RSD)[b]
Al	5.60E00 (± 5.7E-02, 1.0E00)	5.70E00 (± 9.8E-02, 1.7E00)
Ba	2.02E-01 (± 6.0E-03, 3.0E00)	2.10E-01 (± 2.7E-03, 1.3E01)
Ca	1.81E00 (± 3.2E-02, 1.7E00)	1.85E00 (± 3.8E-02, 2.1E00)
Cr	1.27E-01 (± 3.0E-03, 2.4E00)	9.08E-02 (± 2.6E-03, 2.9E00)
Cu	1.07E-01 (± 1.6E-03, 1.5E00)	1.10E-01 (1.9E-03, 1.7E00)
Fe	2.13E01 (± 2.7E-01, 1.2E00)	2.16E01(± 5.3E-01, 2.4E00)
Gd	7.32E-02 (± 3.7E-03, 5.1E00)	7.08E-02 (± 1.5E-03, 2.1E00)
Mg	1.12E-01 (± 4.9E-04, 4.4E-01)	1.15E-01 (± 5.30E-04, 4.6E-01)
Mn	2.29E00 (± 9.0E-02, 3.9E00)	2.40E00 (± 6.3E-02, 2.6E00)
Na	1.74E01 (± 1.7E-01, 9.7E-01)	1.77E01 (± 4.0E-01, 2.2E-01)
Ni	2.35E00 (± 2.6E-02, 1.1E00)	2.40E00 (± 5.5E-02, 2.3E00)
Pb	1.20E-01 (± 5.2E-03, 4.3E00)	1.15E-01 (± 4.4E-03, 3.8E00)
Si[a]	1.04E-01 (± 2.5E-03, 2.4E00)	9.85E-02 (± 3.6E-03, 3.7E00)
U	2.59E-01 (± 1.2E-02, 4.5E00)	2.44E-01 (± 8.1E-03, 3.3E00)
Zn	2.15E-01 (± 2.6E-03, 1.2E00)	2.18E-01 (± 4.8E-03, 2.2E00)

[a] Si was added to the table because it exceeded the 0.1 wt.% criteria. However, this number should not be used because it is known that this dissolution method does not dissolve all of the Si.
[b] Results are determined by ICP-ES and are the averages of results of three samples of dissolved dried slurry. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

The results for the Sludge Batch 3 simulant in Table 5 and Table 6 show good agreement between the first wash top and bottom samples and second wash top and bottom samples. This good agreement suggests that the samples were well mixed when the top and bottom samples were taken, and that the Pu/Gd mixture is evenly distributed throughout the Sludge Batch 3 simulant in the washing vessel. The values presented in Table 6 are higher than those presented in Table 5 except for Na. This is due to the removal of Na and associated soluble anions during the washing process.

The concentration of the Gd in Table 5 and Table 6 can be compared to the concentrations predicted from the amount of Pu/Gd added to the Sludge Batch 3 simulant, and the dried total solids predicted from the Excel Washing spreadsheet for both washes. The predicted weight percent of Gd in the first wash for the Sludge Batch 3 simulant was 3.08E-02 wt.% (7.96E-02g of Gd/258g of dried total solids*100). The predicted weight percent of Gd in the second wash for the Sludge Batch 3 simulant was 5.85E-02 wt.% (7.72E-02g of Gd/ 132g of dried solids*100). The Gd values presented in Table 5 and Table 6 are approximately 20% to 23% higher than the calculated value of 3.08E-02 wt.% and 5.85E-02 wt.% respectively. This may be due to a systematic analytical error. A comparison of the ICP-ES data to the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) data for Gd will be completed in Section 2.3.3 to see if higher concentrations for Gd are also obtained.

2.3.3 ICP-MS and Counting Results for the Top and Bottom Samples for the First and Second Washes for the Sludge Batch 3 Simulant

Presented below in Table 7 and Table 8 are the results from the ICP-MS and radioactive counting methods for the top and bottom samples for the first and second wash of the Sludge Batch 3 simulant. The dissolution solutions described in Section 2.3.2 were used for the analyses. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 7 – ICP-MS Results and Counting Results for the Top and Bottom Samples for the First Wash of Sludge Batch 3

ICP-MS Results	Top Sample – First Wash[a]	Bottom Sample – First Wash[a]
Gd-152	8.97E-05 wt.% (± 3.7E-06, 4.1E00)	8.87E-05 wt.% (± 1.4E-06, 1.6E00)
Gd-154	8.36E-04 wt.% (± 3.9E-05, 4.6E00)	7.95E-04 wt.% (± 1.3E-05, 1.6E00)
Gd-155	4.73E-03 wt.% (± 1.9E-04, 4.0E00)	4.48E-03 wt.% (± 1.1E-04, 2.5E00)
Gd-156	6.38E-03 wt.% (± 2.1E-04, 3.2E00)	6.08E-03 wt.% (± 1.3E-04, 2.2E00)
Gd-157	4.82E-03 wt.% (± 1.6E-04, 3.2E00)	4.56E-03 wt.% (± 1.1E-04, 2.4E00)
Gd-158	7.69E-03 wt.% (± 2.8E-04, 3.6E00)	7.28E-03 wt.% (± 1.9E-04, 2.6E00)
Gd-160	6.67E-03 wt.% (± 2.8-04, 4.2E00)	6.31E-03 wt.% (± 1.5-04, 2.3E00)
Th-232	4.42E-05 wt.% (± 9.4E-06, 2.1E01)	3.82E-05 wt.% (± 8.6E-07, 2.3E00)
U-234	2.59E-05 wt.% (± 8.8E-07, 3.4E00)	2.57E-05 wt.% (± 2.9E-06, 1.1E01)
U-235	3.62E-05 wt.% (± 3.9E-06, 1.1E01)	3.42E-05 wt.% (± 4.2E-06, 1.2E01)
U-236	9.55E-06 wt.% (± 1.9E-06, 2.0E01)	9.00E-06 wt.% (± 3.9E-07, 4.3E00)
Np-237	9.07E-05 wt.% (± 3.1E-06, 3.5E00)	8.98E-05 wt.% (± 5.7E-06, 6.4E00)
U-238	2.68E-04 wt.% (± 9.1E-06, 3.4E00)	2.53E-04 wt.% (± 8.0E-06, 3.2E00)
Pu-239	2.10E-02 wt.% (± 7.2E-04, 3.4E00)	2.01E-02 wt.% (± 6.3E-04, 3.1E00)
Pu-240	2.09E-03 wt.% (± 9.5E-05, 4.5E00)	1.99E-03 wt.% (± 5.7E-05, 2.8E00)
Am-241[b]	2.42E-04 wt.% (± 1.3E-05, 5.5E00)	2.28E-04 wt.% (± 1.3E-05, 5.7E00)
Pu-242	4.65E-05 wt.% (± 2.2E-06, 4.8E00)	4.31E-05 wt.% (± 3.7E-06, 8.6E00)
Counting Data Results	**Top Sample – First Wash[a]**	**Bottom Sample – First Wash[a]**
Cs-137	7.91E-09 wt.% (± 6.7E-10, 8.4E00)	6.35E-09 wt.% (± 7.2E-10, 1.1E01)
Am-241	1.09E-04 wt.% (± 2.3E-06, 2.1E00)	1.09E-04 wt.% (± 2.4E-06, 2.2E00)
Total Alpha	4.01E00 µCi/g (± 2.1E-01, 5.1E00)	3.80E00 µCi/g (± 3.5E-01, 9.5E00)

[a] Results are determined by ICP-MS and counting methods and are the averages of results of three samples of dissolved dried slurry. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

[b] The concentration reported for mass 241 may be high due to Am-241 and Pu-241 being detected by the ICP-MS. No special separation techniques were performed to determine the Pu-241 concentration.

Table 8 - ICP-MS Results and Counting Results for the Top and Bottom Samples for the Second Wash of Sludge Batch 3

ICP-MS Results	Top Sample – Second Wash[a]	Bottom Sample – Second Wash[a]
Gd-152	1.48E-04 wt.% (± 1.3E-06, 9.0E-01)	1.44E-04 wt.% (± 1.1E-05, 7.6E00)
Gd-154	1.49E-03 wt.% (± 2.5E-05, 1.7E00)	1.48E-03 wt.% (± 7.8E-05, 5.3E00)
Gd-155	9.14E-03 wt.% (± 7.3E-05, 8.0E-01)	9.06E-03 wt.% (± 4.0E-04, 4.4E00)
Gd-156	1.26E-02 wt.% (± 1.2E-04, 9.5E-01)	1.25E-02 wt.% (± 5.3E-04, 4.2E00)
Gd-157	9.56E-03 wt.% (± 9.1E-05, 9.5E-01)	9.48E-03 wt.% (± 4.0E-04, 4.3E00)
Gd-158	1.53E-02 wt.% (± 1.3E-04, 8.5E-01)	1.52E-02 wt.% (± 6.6E-04, 4.4E00)
Gd-160	1.33E-02 wt.% (± 1.1-04, 8.6E-01)	1.32E-02 wt.% (± 5.6-04, 4.3E00)
Th-232	7.62E-05 wt.% (± 7.9E-06, 1.0E01)	7.57E-05 wt.% (± 1.2E-06, 1.5E00)
U-234	4.88E-05 wt.% (± 8.7E-07, 1.8E00)	4.54E-05 wt.% (± 4.9E-06, 1.1E01)
U-235	7.04E-05 wt.% (± 2.2E-06, 3.1E00)	7.48E-05 wt.% (± 8.0E-06, 1.1E01)
U-236	2.00E-05 wt.% (± 2.0E-06, 9.9E00)	1.90E-05 wt.% (± 2.5E-06, 1.3E01)
Np-237	1.94E-04 wt.% (± 5.3E-06, 2.8E00)	2.02E-04 wt.% (± 1.8E-05, 9.0E00)
U-238	4.80E-04 wt.% (± 1.3E-05, 2.7E00)	4.81E-04 wt.% (± 2.5E-05, 5.3E00)
Pu-239	4.15E-02 wt.% (± 1.5E-04, 3.7E-01)	4.14E-02 wt.% (± 2.3E-03, 5.6E00)
Pu-240	4.07E-03 wt.% (± 2.6E-05, 6.3E-01)	4.07E-03 wt.% (± 2.0E-04, 5.0E00)
Am-241[b]	4.55E-04 wt.% (± 7.3E-06, 1.6E00)	4.54E-04 wt.% (± 2.5E-05, 5.4E00)
Pu-242	8.82E-05 wt.% (± 6.6E-06, 7.5E00)	8.89E-05 wt.% (± 5.5E-06, 6.1E00)
Counting Data Results	**Top Sample – Second Wash**	**Bottom Sample – Second Wash**
Cs-137[c]	<5.8E-09 wt.%	<3.3E-09 wt.%
Am-241[a]	2.37E-04 wt.% (± 4.4E-05, 1.9E01)	2.10E-04 wt.% (± 3.7E-06, 1.8E00)
Total Alpha[a]	7.46E00 μCi/g (± 1.3E-01, 1.7E00)	7.34E00 μCi/g (± 5.2E-01, 7.1E00)

[a] Results are determined by ICP-MS and counting methods and are the averages of results of three samples of dissolved dried slurry. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[b] The concentration reported for mass 241 may be high due to Am-241 and Pu-241 being detected by the ICP-MS. No special separation techniques were performed to determine the Pu-241 concentration.
[c] Detection limit of the method.

The responses for masses 152, 154 through 158, and 160 were attributed to Gd because they followed the natural abundance for Gd. Adding these masses together in Table 7 yielded an average Gd value, for the top and bottom samples, of 3.04E-02 wt.% versus 3.86E-02 wt.% obtained by ICP-ES. This value was then compared to the predicted weight percent value for Gd for the first wash. The difference between the predicted weight percent and ICP-MS values were 1.3% versus the 20% obtained with the ICP-ES data. The same method was used to compare the Gd values in
Table 8. The average Gd values in
Table 8 were 6.13E-02 Wt.%. This value was then compared to the predicted weight percent value for Gd for the second wash. The difference between the predicted weight percent and ICP-MS values were 4.8% versus the 23% obtained with the ICP-ES data. Based on this data, it appears the ICP-MS values are more accurate than the ICP-ES results for Gd. An investigation of the ICP-ES Gd data is being conducted to resolve the differences observed between the ICP-ES and ICP-MS data.

The same comparison of the Pu in the Sludge Batch 3 simulant was completed for the first and second wash. The predicted amount of Pu for the first wash was 2.20E-2 wt.% (5.68E-02g of Pu/258g of dried total solids*100). The predicted amount of Pu for the second wash was 4.18E-02 wt.% (5.51E-02g of Pu/ 132g of dried solids*100). Adding the Pu isotopes (239, 240, 242) together for Table 7 yields a value of 2.26E-02 wt.% and 4.56E-02 wt.% respectively. The differences between the predicted Pu weight percent and the actual weight percents for the first and second wash are 2.7% and 9.1%.

The ratio of the Gd to the Pu for the Pu/Gd mixture is 1.40 to 1[4]. Using the analytical data for the Gd and Pu in Table 7 the ratio of Gd to Pu is 1.34:1. The differences in the ratios from the predicted ratio are reasonable, and are probably due to analytical error surrounding the measurement of the low concentrations of Gd and Pu in the sludge slurry.

2.3.4 Comparison of the Nonradioactive Composition for the Supernate of the Top and Bottom Samples for the First Wash and the Top and Bottom Samples for the Second Wash

Provided below are the results from the analyses of the supernate of the top and bottom samples for both washes of the Sludge Batch 3 simulant. Mixed samples of the sludge slurry were filtered through a Nalgene® filter (0.45µm) resulting in clear supernate solutions. The supernate solutions were then diluted to make sure the Na concentration was within the limits of analytical method. Elemental standards were also submitted with the supernate samples to check the analytical methods. These diluted samples were sent to ADS Sample Receiving so that analyses could be performed by ADS. The results for the elemental standards submitted with the supernate indicated good agreement with the known values of the standards. Table 9 presents the elements with concentrations >1 ppm (mg/L of supernate) in the supernate for the top and bottom samples for the first wash of the Sludge Batch 3 simulant obtained from the ICP- ES and the Ion Chromatography (IC). Table 9 also presents the standard deviation and the percent relative standard deviation in parentheses next to the ppm value. Table 10 presents the elements with concentrations >1 ppm (mg/L of supernate) in the supernate for the top and bottom samples for the second wash of the Sludge Batch 3 simulant obtained from the ICP- ES (ICP-ES) and the Ion Chromatography (IC). Table 10 also presents the standard deviation and the percent relative standard deviation in parentheses next to the ppm value.

Table 9 – ICP-ES and IC Supernate Results for Top and Bottom Samples for the First Wash of the Sludge Batch 3 Simulant

ICP-ES Results	Top Sample – First Wash[c]	Bottom Sample – First Wash[c]
Al	4.70E03 mg/L Supernate (± 5.7E01, 1.2E00)	4.63E03 mg/L Supernate (± 3.6E01, 7.8E-01)
B	5.99E01 mg/L Supernate (± 5.1E-01, 8.5E-01)	5.51E01 mg/L Supernate (± 3.6E-01, 6.6E-01)
Ca	7.39E00 mg/L Supernate (± 3.3E-01, 4.5E00)	8.63E00 mg/L Supernate (± 2.6E-01, 3.1E00)
Cr	3.34E00 mg/L Supernate (± 7.0E-02, 2.2E00)	3.13E00 mg/L Supernate (± 3.0E-02, 8.5E-01)
Gd[a]	3.7E-01 mg/L Supernate (± 6.0E-02, 1.7E01)	<2.3E-01 mg/L Supernate[b]
Mo	2.64E00 mg/L Supernate (± 2.0E-02, 6.9E-01)	2.31E00 mg/L Supernate (± 2.0E-02, 8.7E-01)
Na	3.91E04 mg/L Supernate (± 2.3E03, 5.8E00)	3.89E04 mg/L Supernate (± 4.6E03, 1.2E00)
P	1.28E01 mg/L Supernate (± 2.2E00, 1.7E01)	1.26E01 mg/L Supernate (± 1.0E00, 7.9E00)
Pb	3.58E00 mg/L Supernate (± 1.8E-01, 5.0E00)	2.45E00 mg/L Supernate (± 1.4E-01, 5.8E00)
Sn	5.04E00 mg/L Supernate (± 7.7E-01, 1.5E01)	4.09E00 mg/L Supernate (± 3.2E-01, 7.9E00)
U	7.30E00 mg/L Supernate (± 2.4E-01, 3.3E00)	3.81E00 mg/L Supernate (± 3.0E-01, 7.8E00)
Zn	1.63E00 mg/L Supernate (± 3.0E-02, 1.7E00)	1.35E00 mg/L Supernate (± 3.0E-02, 2.0E00)
IC Results	**Top Sample – First Wash[c]**	**Bottom Sample – First Wash[c]**
Flouride[b]	<32 mg/L Supernate	<35 mg/L Supernate
Formate[b]	<158 mg/L Supernate	<174 mg/L Supernate
Chloride	2.59E03 (± 9.1E00, 3.5E-01)	2.50E03 (± 2.2E02, 8.8E00)
Nitrite	2.86E04 (± 1.8E02, 6.4E-01)	2.96E04 (± 2.3E03, 7.8E00)
Nitrate	1.06E04 (± 1.0E03, 9.7E00)	1.06E04 (± 1.3E03, 1.2E01)
Phosphate[b]	<158 mg/L Supernate	<174 mg/L Supernate
Sulfate	1.96E03 mg/L Supernate (± 9.1E00, 4.7E-01)	1.89E03 mg/L Supernate (± 1.8E02, 9.3E00)
Oxalate[b]	<158 mg/L Supernate	<174 mg/L Supernate

[a] Gd was added to the table since this is a Study of Pu/Gd solubility during the washing process.
[b] Detection limit of the analytical method.
[c] Results are determined by ICP-ES and IC and are the averages of results of three samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

Table 10 - ICP-ES and IC Supernate Results for Top and Bottom Samples for the Second Wash of the Sludge Batch 3 Simulant

ICP-ES Results	Top Sample – Second Wash[b]	Bottom Sample – Second Wash[b]
Al	1.43E03 mg/L Supernate (± 1.8E00, 1.3E-01)	1.41E03 mg/L Supernate (± 5.5E01, 3.9E00)
B	1.77E01 mg/L Supernate (± 1.4E-01, 7.8E-01)	1.83E01 mg/L Supernate (± 2.0E-01, 1.1E-01)
Ca	9.41E00 mg/L Supernate (± 5.7E-01, 6.1E00)	7.39E00 mg/L Supernate (± 1.2E00, 1.7E01)
Cr	1.30E00 mg/L Supernate (± 1.7E-01, 1.3E01)	1.62E00 mg/L Supernate (± 8.0E-02, 4.8E00)
Gd	3.1E-01 mg/L Supernate[c]	4.5E-01 mg/L Supernate (± 9.0E-01, 1.9E01)
Mo	9.40E-01 mg/L Supernate (± 6.0E-02, 5.9E-01)	1.06E00 mg/L Supernate (± 4.0E-02, 3.3E00)
Na	1.34E04 mg/L Supernate (± 1.3E02, 9.6E-01)	1.26E04 mg/L Supernate (± 4.3E02, 3.4E00)
P	7.35E00 mg/L Supernate (± 6.6E-01, 9.0E00)	7.56E00 mg/L Supernate (± 9.5E-01, 1.3E01)
Pb	1.38E00 mg/L Supernate (± 5.5E-01, 4.0E01)	1.79E00 mg/L Supernate (± 2.2E-01, 1.3E01)
Sn	3.19E00 mg/L Supernate (± 2.3E-01, 7.2E00)	3.07E00 mg/L Supernate (± 7.0E-02, 2.3E00)
U	3.35E00 mg/L Supernate (± 1.8E00, 5.2E01)	7.45E00 mg/L Supernate (± 1.2E00, 1.6E01)
IC Results	**Top Sample – First Wash[b]**	**Bottom Sample – First Wash[b]**
Flouride[a]	<37 mg/L Supernate	<34 mg/L Supernate
Formate[a]	<184 mg/L Supernate	<169 mg/L Supernate
Chloride	7.13E02 (± 1.1E01, 1.5E00)	5.99E02 (± 9.8E00, 1.6E00)
Nitrite	9.22E03 (± 1.1E02, 1.2E00)	7.82E03 (± 2.5E01, 3.3E-01)
Nitrate	3.34E03 (± 1.8E02, 5.5E-01)	2.82E03 (± 9.8E00, 3.5E-01)
Phosphate[a]	<184 mg/L Supernate	<169 mg/L Supernate
Sulfate	5.71E02 mg/L Supernate (± 7.6E-06, 1.3E-06)	4.92E02 mg/L Supernate (± 0, 0)[d]
Oxalate[a]	<184 mg/L Supernate	<169 mg/L Supernate

[a] Detection limit of the analytical method.
[b] Results are determined by ICP-ES and IC and are the averages of results of three samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[c] Only one value obtained.
[d] Same value recorded for all sulfate numbers.

2.3.5 ICP-MS and Counting Results of the Supernate for the Top and Bottom Samples for the First and Second Washes for the Sludge Batch 3 Simulant

Presented below in Table 11 and Table 12 are the results of the supernate from the ICP-MS and radioactive counting methods for the top and bottom samples for the first and second wash of the Sludge Batch 3 simulant. The supernate solutions described in Section 2.3.4 were used for the analyses. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 11 – ICP-MS and Counting Results of the Supernate for the First Wash Top and Bottom Samples of the Sludge Batch 3 Simulant

ICP-MS Results	Top Sample – First Wash[a]	Bottom Sample – First Wash[a]
U-234	4.55E-03 mg/L Supernate (± 5.7E-04, 1.2E01)	6.91E-03 mg/L Supernate (± 5.1E-04, 7.3E00)
U-235	7.48E-03 mg/L Supernate (± 5.7E-04, 7.6E00)	1.0E-02 mg/L Supernate (± 4.1E-04, 4.1E00)
Np-237	7.24E-03 mg/L Supernate (± 5.5E-04, 7.6E00)	7.77E-03 mg/L Supernate (± 4.9E-04, 6.3E00)
U-238	2.78E-02 mg/L Supernate (± 1.2E-03, 4.4E00)	3.80E-02 mg/L Supernate (± 2.7E-03, 7.2E00)
Pu-239	5.32E-02 mg/L Supernate (± 3.0E-03, 5.6E00)	6.57E-02 mg/L Supernate (± 5.7E-03, 8.6E00)
Pu-240	4.97E-03 mg/L Supernate (± 9.7E-05, 1.9E00)	6.57E-03 mg/L Supernate (± 7.88E-04, 1.2E01)
Counting Data Results	**Top Sample – First Wash[a]**	**Bottom Sample – First Wash[a]**
Cs-137	9.20E-04 µCi/mL Supernate (± 5.6E-05, 6.1E00)	8.88E-04 µCi/mL Supernate (± 6.1E-05, 6.9E00)
Total Alpha	1.53E04 dpm/mL Supernate (± 8.6E02, 5.6E00)	1.65E04 dpm/mL Supernate (± 1.3E03, 7.7E00)

[a] Results are determined by ICP-MS and counting methods and are the averages of results of three samples. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

Table 12 - ICP-MS and Counting Results of the Supernate for the Second Wash Top and Bottom Samples of the Sludge Batch 3 Simulant

ICP-MS Results	Top Sample – Second Wash[a]	Bottom Sample – Second Wash[a]
U-238	4.33E-03 mg/L Supernate (± 1.5E-03, 3.4E01)	3.60E-03 mg/L Supernate (± 3.7E-04, 1.0E01)
Pu-239	3.55E-03 mg/L Supernate (± 2.7E-04, 7.5E00)	6.61E-03 mg/L Supernate (± 3.3E-04, 5.0E00)
Counting Data Results	**Top Sample – Second Wash[a]**	**Bottom Sample – Second Wash[a]**
Cs-137	3.26E-04 µCi/mL Supernate (± 3.3E-05, 1.0E01)	2.73E-04 µCi/mL Supernate (± 4.8E-05, 1.8E01)
Total Alpha	2.54E03 dpm/mL Supernate (± 1.3E02, 5.2E00)	2.57E03 dpm/mL Supernate (± 7.1E01, 2.8E00)

[a] Results are determined by ICP-MS and counting methods and are the averages of results of three samples. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

No Gd was detected by the ICP-MS at masses 152, 154 through 158, and 160 in Table 11 and Table 12. The ICP-ES data indicates that Gd is present in the supernate except for the bottom sample from the first wash. As indicated earlier in Section 2.3.3, the ICP-ES data may be biased high.

2.4 Summary of the First Wash and Second Wash Results for the Sludge Batch 3 Simulant

Two washes of the Sludge Batch 3 simulant were completed with no processing problems. The first wash lowered the Na molarity of the supernate from 4.64M (see Table 3 for ppm value) to 1.79M (Table 9 for ppm value). The second wash lowered the Na molarity of the supernate from 1.79M to 0.57M (Table 10 for ppm value). This was outside of the Na molarity range of 0.45M to 0.55M specified in the Task Plan[2]. After discussion with Waste Disposition Engineering and Process Engineering, permission was obtained to proceed forward with the SRAT cycle using the Sludge Batch 3 simulant with a Na concentration of 0.57M[7].

A summary of the Gd and Pu solubility during the first and second wash are presented below in Table 13. Table 13 presents the grams of Pu and Gd that became soluble during the washing process. These values are presented on a sludge slurry basis.

Table 13 – Amount of Pu and Gd that Became Soluble During the Washing Process

Top Sample – First Wash[a]	**Element**	**Grams in the Dried Sludge Slurry**	**Grams in the Supernate on a Sludge Slurry Basis**	**% Soluble**
	Gd	8.05E-02[c]	5.66E-04[d]	0.70 %
	Pu-239	5.42E-02[c]	8.14E-05[c]	0.15 %
	Pu-240	5.39E-03[c]	7.61E-06[c]	0.14 %
Bottom Sample – First Wash[a]	**Element**	**Grams in the Dried Sludge Slurry**	**Grams in the Supernate on a Sludge Slurry Basis**	**% Soluble**
	Gd	8.11E-02[c]	3.06E-04[d]	0.40%
	Pu-239	5.19E-02[c]	1.01E-04[c]	0.19%
	Pu-240	5.14E-03[c]	1.01E-05[c]	0.20%
Top Sample – Second Wash[b]	**Element**	**Grams in the Dried Sludge Slurry**	**Grams in the Supernate on a Sludge Slurry Basis**	**% Soluble**
	Gd	8.04E-02[c]	5.28E-04[d]	0.65%
	Pu-239	5.47E-02[c]	6.05E-05[c]	0.11%
Bottom Sample – Second Wash[b]	**Element**	**Grams in the Dried Sludge Slurry**	**Grams in the Supernate on a Sludge Slurry Basis**	**% Soluble**
	Gd	8.04E-02[c]	7.66E-04[d]	0.95%
	Pu-239	5.45E-02[c]	1.13E-05[c]	0.02%

[a] Assumptions used for calculation: Total volume of 1561 mL, 14.75 wt.% total solids, slurry density 1.12 g/mL, 9.83 wt.% dissolved solids, and 1.08g/mL supernate density.
[b] Assumptions used for calculation: Total volume of 1735 mL, 7.23 wt.% total solids, slurry density 1.05 g/mL, 3.66 wt.% dissolved solids, and 1.03 g/mL supernate density.
[c] ICP-MS values used to calculate total grams.
[d] ICP-ES values used to calculate total grams.

Since the ICP-MS did not detect Gd in the supernate, the grams of Gd noted in the fourth column of Table 13 are calculated from the concentrations obtained from the ICP-ES. The ICP-ES results could be biased high based on results observed earlier for the sludge slurry. The Gd results from the ICP-ES (in the fourth

column) provided a conservative estimate for the amount of Gd that was soluble during this washing test. For the first wash, the fraction of Gd ranged from 0% (using the ICP-MS data) to 0.70% (using ICP-ES data) and the fraction of Pu ranged from 0.14% – 0.20% (using ICP-MS data). For the second wash, the fraction of Gd ranged from 0% (using ICP-MS data)– 0.95% and the fraction of Pu ranged from 0.02% - 0.11% (using ICP-MS data).

The amount of Pu that is soluble during the washing process is important, because it contributes alpha activity to the supernate. The decanted supernate solutions from the washing process are evaporated in the High Level Waste evaporator system and the overheads are sent to the Effluent Treatment Facility (ETF). The bottoms from the evaporator will be sent to Saltstone for processing. To estimate the alpha activity of the wash solutions from this experiment, the counting results for the total alpha activity (highest value between the two results were used) in Table 11 and Table 12 were used. Referencing engineering position paper - HLW-SDT-2001-00244[8], a decontamination factor of 1.0E04[9] was assumed for the solution entrained in the evaporator vapor stream. The estimated activities for the first wash and second wash in the evaporator overheads are 1.7 dpm/mL and 2.6E-01 dpm/mL respectively. The alpha activities in the evaporator overheads should not be an issue for ETF, because they meet the ETF acceptance criteria of 100 dpm/mL[10]. Prior to processing the bottoms from the evaporator through Saltstone, the solutions will be treated with a sorbant to remove the alpha emitters to meet the 20nCi/g acceptance criteria for Saltstone[11].

The Pu concentrations obtained from the experimental washing study were also compared to the results obtained from an Excel spreadsheet model that predicted Pu solubility. A direct comparison between the predicted and measured concentrations was not possible since the hydroxide concentration was not measured during the washing tests. However, the measured plutonium concentrations in Table 11 and Table 12 fall within the predicted range of plutonium solubilities (3.77E-03 to 1.67E-01 mg/L reported by D. Hobbs for Sludge Batch 3[12]). Based on the quantity of added co-precipitated Pu/Gd solids in the laboratory tests, between 0.02 and 0.20 wt % of the available plutonium leached from the solids. This percentage of leached plutonium is also within the range of 0.0018 to 0.42 wt % predicted during washing[11]. These results indicate that the co-precipitated Pu/Gd solids do not exhibit any unusual chemical behavior during sludge washing. The small quantities of leached plutonium during the sludge washing tests do not present a criticality safety concern and are not sufficient to adversely impact Salt Processing operations.

3.0 ANALYTICAL RESULTS OF THE FINAL WASHED SLUDGE BATCH 3 SIMULANT

The sections below provide a brief description of the analyses and results obtained from the final washed Sludge Batch 3 simulant and supernate. To obtain the supernate for the required analyses, a portion of the mixed sludge slurry was filtered.

3.1 Weight Percent Solids and Density Measurements for the Final Washed Sludge Batch 3 Simulant and Supernate

Weight percent solids measurements were completed for the sludge slurry and supernate as described in Section 2.3.1. The averages of the calculated results of the weight percent solids for the sludge slurry and the supernate (only one value obtained due to amount of sample available) are presented in column two and column three of Table 14 respectively. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two and column three of Table 14.

Density measurements were completed 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 and supernate. The sealed pipette tip was first weighed and then a sample of the sludge slurry or supernate was pipetted into the sealed pipette tip. The sealed pipette tip containing the sludge slurry or supernate sample was weighed and a density calculated. The results of the sludge slurry and supernate for the final washed Sludge Batch 3 simulant are presented in column four and column five of Table 14. The standard deviations (Std. Dev.)

and the percent relative standard deviations (% RSD) for the data are also presented in column four and column five of Table 14.

Table 14 - Weight Percent Solids and Density Measurements for the Final Washed Sludge Batch 3 Simulant and Supernate

	Wt. % Total Solids for the Sludge Batch 3 Simulant[a]	Wt. % Dissolved Solids for the Supernate[b]	Density Measurements for the Sludge Batch 3 Simulant[c]	Density Measurements for the Supernate[c]
Average	15.30 wt.%	3.32 wt.%	1.14 g/mL	1.02 g/mL
Std. Dev.	± 1.33E-01	-	± 1.7E-03	± 8.0E-03
%RSD	8.70E-01	-	1.5E-01	7.9E-01

[a] Sample(s) were dried at 110°C overnight.
[b] Only one value obtained due to amount of sample available.
[c] Average of four values.

3.2 Nonradioactive Composition of the Final Washed Sludge Batch 3 Simulant

Provided below are the results from the analyses of the dissolved sludge slurry. The sludge slurry was dissolved via the Aqua Regia method[6] and the Peroxide Fusion[13] method. The same protocol was followed as described in Section 2.3.2. Dissolution results of the standard glass for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly. Table 15 presents the elements including Gd (excluding oxygen) with concentrations >0.1 weight percent for the final washed Sludge Batch 3 simulant obtained from the ICP-ES. Table 15 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value. The supernate results of the final washed Sludge Batch 3 supernate are the same as the supernate for the second wash. These results can be found in Table 10.

Table 15 – ICP-ES Results for the Final Washed Sludge Batch 3 Simulant

Element[a]	Wt.% (Std. Dev., % RSD)
Al	5.98E00 (± 2.7E-01, 4.5E00)
Ba	2.73E-01 (± 1.1E-02, 4.0E00)
Ca	2.38E00 (± 6.9E-02, 2.9E00)
Cu	1.50E-01 (± 3.0E-03, 2.0E00)
Fe	2.71E01 (± 1.5E00, 5.4E00)
Gd	8.90E-02 (± 4.7E-03, 5.3E00)
Mg	1.38E-01 (± 1.7E-02, 1.2E01)
Mn	3.01E00 (± 2.2E-01, 7.2E00)
Na[b]	6.79E00(± 2.0E-01, 3.0E00)
Ni	3.05E00 (± 1.4E-01, 4.6E00)
Pb[c]	1.53E-01 (± 5.3E-03, 3.5E00)
Si[c]	1.06E00 (± 1.1E-01, 1.1E01)
U[b]	3.38E-01 (± 1.5E-02, 4.5E00)
Zn	3.14E-01 (± 2.7E-02, 8.7E00)

[a] Results are determined by ICP-ES and are the average of results of six samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[b] Average of three results.

3.3 Radioactive Composition of the Final Washed Sludge Batch 3 Simulant

Presented below in Table 16 are the results from the ICP-MS and radioactive counting methods for the final washed Sludge Batch 3 simulant. The aqua regia dissolution solutions described in Section 3.2 were used for the ICP-MS analyses. Both dissolution solutions were used for the counting methods. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 16 – ICP-MS and Counting Data for the Final Washed Sludge Batch 3 Simulant

ICP-MS Results[a]	Wt.% (Std. Dev., % RSD)
Gd-152	2.40E-04 (± 7.3E-06, 3.0E00)
Gd-154	2.26E-03 (± 7.6E-05, 3.4E00)
Gd-155	1.18E-02 (± 2.2E-04, 1.9E00)
Gd-156	1.58E-02 (± 3.2E-04, 2.0E00)
Gd-157	1.23E-02 (± 2.6E-04, 2.1E00)
Gd-158	1.88E-02 (± 3.4E-04, 1.8E00)
Gd-160	1.64E-02 (± 2.3E-04, 1.4E00)
Th-232	1.12E-04 (± 8.1E-07, 7.2E-01)
U-234	5.91E-05 (± 1.9E-06, 3.3E00)
U-235	8.81E-05 (± 1.0E-05, 1.2E01)
U-236	2.16E-05 (± 1.9E-06, 8.8E00)
Np-237	2.32E-04 (± 4.8E-06, 2.0E00)
U-238	7.31E-04 (± 4.4E-05, 6.0E00)
Pu-239	5.48E-02 (± 1.8E-04, 3.3E-01)
Pu-240	6.06E-03 (± 1.7E-04, 2.8E00)
Am-241[b]	6.88E-04 (± 1.6E-05, 2.3E00)
Pu-242	1.30E-04 (± 4.2E-06, 3.3E00)
Counting Data Results[c]	**Units**
Cs-137[d]	<4.2E-09 wt.%
Am-241	2.74E-04 wt.% (± 5.4E-06, 2.0E00)
Total Alpha	9.08E00 µCi/g (± 5.7E-01, 6.3E00)

[a] Average of three results.
[b] The concentration reported for mass 241 may be high due to Am-241 and Pu-241 being detected by the ICP-MS. No special separation techniques were performed to determine the Pu-241 concentration.
[c] Average of six results.
[d] Detection limit of the analytical method.

The ratio of Gd to Pu for the final washed Sludge Batch 3 Simulant can be calculated by adding up the concentrations of the Gd isotopes and the concentrations of the Pu isotopes in Table 16. The next step is to divide the Gd by the Pu concentration to obtain the ratio. The ratio for the final washed Sludge Batch 3 simulant is 1.27:1. This ratio is different from the predicted ratio of 1.40:1[4] and the calculated ratio of 1.34:1 for both washes. The differences in the ratios from the predicted ratio are reasonable, and are probably due to analytical error surrounding the measurement of the low concentrations of Gd and Pu in the sludge slurry.

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

As noted previously in Section 1.0, the SRAT cycle was completed to determine the behavior of the Pu and Gd during the SRAT process. Since this was the main objective of the SRAT run, no additions of noble metals (related to H_2 production in the SRAT) or mercury were made to the Sludge Batch 3 simulant. These issues are specifically related to Sludge Batch 3 and will be investigated as a part of the Sludge Batch 3 nonradioactive work conducted at the ACTL, and the radioactive work conducted in the Shielded Cells facility with the Sludge Batch 3 qualification samples.

To determine the behavior of the Pu/Gd under normal operating conditions in the DWPF SRAT vessel, a SRAT product with an ending pH of 7 was selected. To determine the behavior of the Pu/Gd under extreme acidic conditions in the DWPF SRAT vessel, a SRAT product with an ending pH of 3 was selected. For the extreme acidic condition scenario, the SRAT product with the ending pH of 7 was reheated and then the necessary amounts of nitric and formic acids were added to reach the ending pH of 3. By testing both of these scenarios, information about the dissolution of Pu/Gd as a function of pH could be obtained. To obtain the concentrations of the Pu/Gd in the SRAT product and the SRAT product supernate for both scenarios, samples will be taken and analyzed for nonradioactive and radioactive composition.

The sections below provide a description of the system used in the glove box to perform the SRAT cycle using the Sludge Batch 3 Simulant 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 8 inches in height and 3 inches wide. The SRAT/SME vessel has a capacity of approximately 1 liter, 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, purge line, etc.) and for the addition of chemicals (acids, antifoam, 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. A chiller unit is used to supply the chilled water for the condenser. Since this was a solubility test, no offgas data were collected. Figure 1 is a picture taken in the glove box of the system during the SRAT run.

Figure 1 – Picture of the SRAT/SME Vessel in the Glove Box

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 to determine how much nitric acid and formic acid to add for the SRAT cycle. The analytical data, presented in this section and previous sections, were entered into an Excel spreadsheet to determine the amounts of nitric and formic acids.

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 on two portions (~5 g each) of mixed sludge slurry. The first step in the procedure was to weigh each individual portion of the sludge slurry. The next step was to add a known volume of 1 N nitric acid to the sludge slurry. The sludge slurry was then mixed, and a pH recorded once the readout from the pH probe stabilized. The volume of nitric acid was also recorded after each addition to the sludge slurry. The titration was considered complete once the pH of the sludge slurry was below a pH of 3. This procedure was repeated on the remaining portion of sludge slurry. The results of the titration for the two portions of sludge slurry are presented in Figure 2. Figure 2 is a graph of the pH of the sludge slurry (y axis) and the Eq/L of nitric acid added (x axis). Table 17 provides the data recorded for each titration.

Figure 2 - Graph of the Sludge Slurry Titrations Performed for the Washed Sludge Batch 3 Simulant (pH of Sludge Slurry vs. Eq/L of Nitric Acid Added)

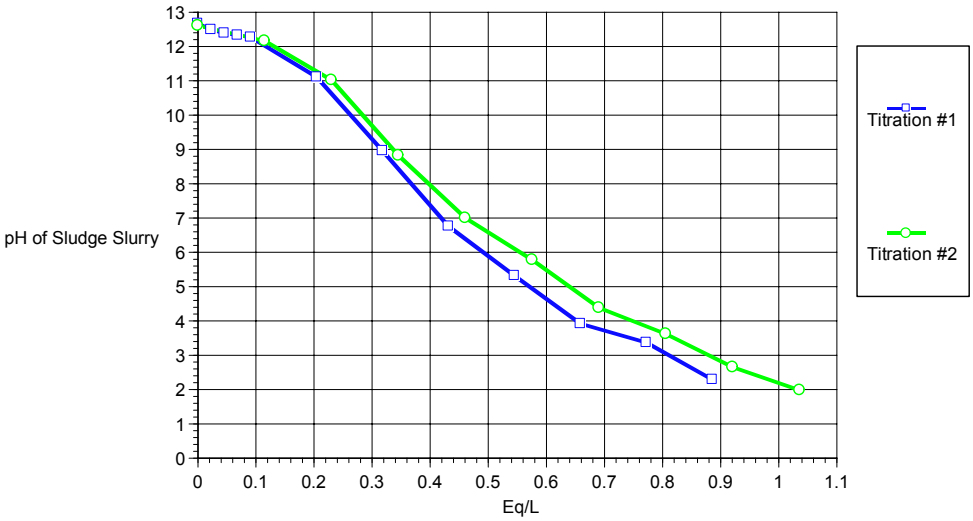


Table 17 - Titration Data for Two Samples of Washed Sludge Batch 3 Simulant

Titration #1 Amount of Acid Added (mL)	pH of Sludge After Addition	**Factor for Eq/L=2.27E-01** [a] Eq/L Sludge Slurry
0	12.67	0.00E+00
0.1	12.49	2.27E-02
0.2	12.39	4.54E-02
0.3	12.33	6.81E-02
0.4	12.27	9.08E-02
0.9	11.11	2.04E-01
1.4	8.96	3.18E-01
1.9	6.76	4.32E-01
2.4	5.32	5.45E-01
2.9	3.92	6.59E-01
3.4	3.37	7.72E-01
3.9	2.29	8.86E-01
Titration #2 Amount of Acid Added (mL)	pH of Sludge After Addition	**Factor for Eq/L=2.30E-01** [a] Eq/L Sludge Slurry
0	12.61	0.00E+00
0.5	12.16	1.15E-01
1.0	11.02	2.30E-01
1.5	8.82	3.45E-01
2.0	7.00	4.61E-01
2.5	5.78	5.76E-01
3.0	4.38	6.91E-01
3.5	3.62	8.06E-01
4.0	2.65	9.21E-01
4.5	1.98	1.04E00

[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).

The differences in the titration curves could be attributed to the amount of nitric acid added and the amount of time given for the pH reading to stabilize prior to the pH being recorded. For example in titration #1, 1.9 mL of nitric acid was added and a pH reading of 6.76 was obtained. In titration #2, 2.0 mL of nitric acid

was added and pH of 7.00 was obtained. For the acid calculations, a pH value of 7.00 was used. The Eq/L value from titration #1 and Titration #2 were averaged together (0.440 Eq/L) and used in Table 18.

4.2.2 TIC Concentration for the Washed Sludge Batch 3 Simulant

To obtain the TIC concentration, approximately five milliliters of the mixed washed Sludge Batch 3 simulant were placed into two bottles and sent to ADS for analysis. The average of the two samples is 2745 ppm. The standard deviation is ± 5.0E01 and the percent relative standard deviation is 1.8E00.

An observation was made about the TIC/TOC (total inorganic carbon/total organic carbon) numbers obtained from ADS. The TOC numbers ranged from 12,080 ppm to 2540 ppm. After discussing the TOC results with ADS, it was found that the TIC and TOC determinations were not independent. The TOC number is obtained by subtracting the amount of TIC from the total carbon. It was thought at the time that the TIC numbers were valid based on the fact that they were analyzed by a different procedure than the total carbon. A request was made to repeat the analyses, but a decision was made to go forward with the SRAT cycle and Bounding test using the available TIC numbers due to project time constraints. Based on these results, any further investigation of sludge slurries containing coal warrants obtaining repetitive results for TIC/TOC.

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 10.2M (49.6 wt.%) and the formic acid results were 22.7 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 percentage used to determine the amount of nitric acid and formic acid for the glove box Cells run was 125%. This percentage was selected based on previous testing completed for Sludge Batch 2. For the Sludge Batch 2 testing, a target of 125% stoichiometry met the requirements of the list below, and also ensured the destruction of nitrite during SRAT processing.

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 2.0 and 4.0) for the weight percent total solids, density, hydroxide (at a pH of 7 from the titration curves, see Section 4.2.1), manganese, nitrite, mercury (no mercury in the feed), 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. Although coal was added to the Sludge Batch 3 simulant, no credit was taken for it as a reductant when targeting a value of $Fe^{2+}/Fe^{tot} = 0.2$ for melter redox. The issue of coal in the Sludge Batch 3 and how it affects the final redox in the melter will have to be addressed separately in the ACTL and Shielded Cells work for Sludge Batch 3. After entering all of the required data, the amounts of the nitric acid and formic acid were determined to be 180 gallons (DWPF basis) and 331 gallons (DWPF basis) respectively. These 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. The volume of acids has increased compared to a prototypic amount of 90 –100 gallons of nitric acid and 190-210 gallons of formic acid for Sludge Batch 2. This increase is due mainly to the TIC value. See Section 4.2.2 for more information. To scale the amounts of nitric acid and formic acid from a DWPF basis to a glove box basis, the volume of each acid was converted to milliliters and then multiplied by a value of 1.32E-5 (See Appendix A). Table 18 is a copy of the spreadsheet used to determine the amounts of nitric acid and formic acid for the glove box SRAT cycle.

Table 18 - Excel Spreadsheet for Determining Nitric Acid and Formic Acid Requirements for the SRAT Cycle

revised 3/31/02

SRAT Batch 2 Shielded Cell Runs Acid Requirements - computed March 31, 2001 By T.L. Fellinger

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

SRAT Conditions and Analyses	
(lab ID 2000xxxxx)	Receipt
Volume [gal]	6,000
spG	1.140
Wt% solids	15.30
Hydroxide [eq/L]	0.440
Nitrite [ppm]	8,509
Mercury [ppm]	0
Manganese [wt%]	3.38
Manganese (sol) [ppm]	0
TIC [ppm]	2,745
Formate [ppm]	0
Nitrate [ppm]	3,072

Formic Acid Addition Volume	
Volume [gal]	331
spG	1.192
Wt%	87.7
Molar	22.71

Nitric Acid Tank	
spG	1.3
Wt%	49.6
Molar	10.22

g-moles C 2279 4558

-> 5,171.40 ppm 2112 ppm

Calculated SRAT Quantities		Nitric Required	Formic Required		
SRAT mass [lbs]	57,080				
MnO2 [g-moles]	2,437.1	1,949.6	974.8		
HgO [g-moles]	0.	0.	0.		
NO2 [g-moles]	4,788.2	2,394.1	1,197.		
CO3 [g-moles]	5,917.6	11,835.2	0.		
OH [g-moles]	9,992.4	9,992.4	0.	OH [ppm]	15,439
Total Acid [g-moles] at 125%		32,714.2	2,714.8	35,429.	total
Total Volume [gal]		**845**	**32**		

From Marek calculational algorithm at 125% of stoichiometry:		
mFA	2,715	Formic Acid Requirement [g-moles]
mA	+ 32,714	Additional Acid Required [g-moles]
mDFA	- 28,456	Direct Formic Acid Addition [g-moles]
mHNO3	= 6,973	g-moles Nitric Acid
VHNO3	**180**	gallons

Specify the following quantities in the SRAT procedure:

180	**gallons of 50 wt% nitric acid**
331	**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.

Glovebox Calc		
NITRIC	**682.14551 L**	
FORMIC	**1252.835 L**	
Scale Factor =	**1.321E-05**	
NITRIC	**9.0112 mL**	**11.7145** g
FORMIC	**16.5500 mL**	**19.7276** g

5.0 DESCRIPTION OF THE SRAT CYCLE

Transfer of Washed Sludge Slurry to the SRAT Vessel
The washed sludge slurry was mixed and approximately 300 mL was poured into the SRAT vessel.

Initiation – Heating and Agitation
The SRAT Cycle began on 2 April 2002 at 0640 with the start of the agitator and heating mantle. When the vessel reached 50°C (0740), antifoam was added. During this heating period, the agitator speed was increased because the sludge slurry appeared to be very viscous with no visible surface movement.

Nitric Acid Addition
At 0847, vessel temperature reached 90°C, and nitric acid addition was initiated. Based on the acid calculations (see Section 4.2.4), 9 mL of 50wt% nitric acid was added to the vessel at the flow rate of 0.1 mL/min (added by 500 lambda pipette every 5 minutes). The acid addition was completed by 1013. During the addition of the nitric acid, the pH of the sludge slurry dropped from 12.1 (~90°C) to 8.9 (~90°C). At the completion of the addition, the sludge slurry was visually examined. The surface appeared smooth but thick.

Formic Acid Addition
Prior to the start of the formic acid addition, an antifoam addition was made to the SRAT vessel. At 1030, the formic acid addition began. A total of 16.6 mL of 90wt% formic acid (see Section 4.2.4 for acid calculations) was added at a flow rate of 0.10 mL/min (added by 500 lambda pipette every 5 minutes). During the addition of the formic acid, the pH of the sludge slurry dropped from 8.9 (~90°C) to 3.0 (~90°C). The surface of the sludge slurry reacted with a rise in level (foamy bubbles) with each addition of formic acid until the pH dropped below 5. The rise in level quickly dissipated shortly after the addition. Also, as the pH of sludge slurry dropped, the mixing of the sludge slurry in the vessel improved. The entire surface (around the thermocouples and pH probe) of the sludge slurry was moving with ease and a vortex was noticed around the agitator shaft. The formic acid addition was completed at 1254.

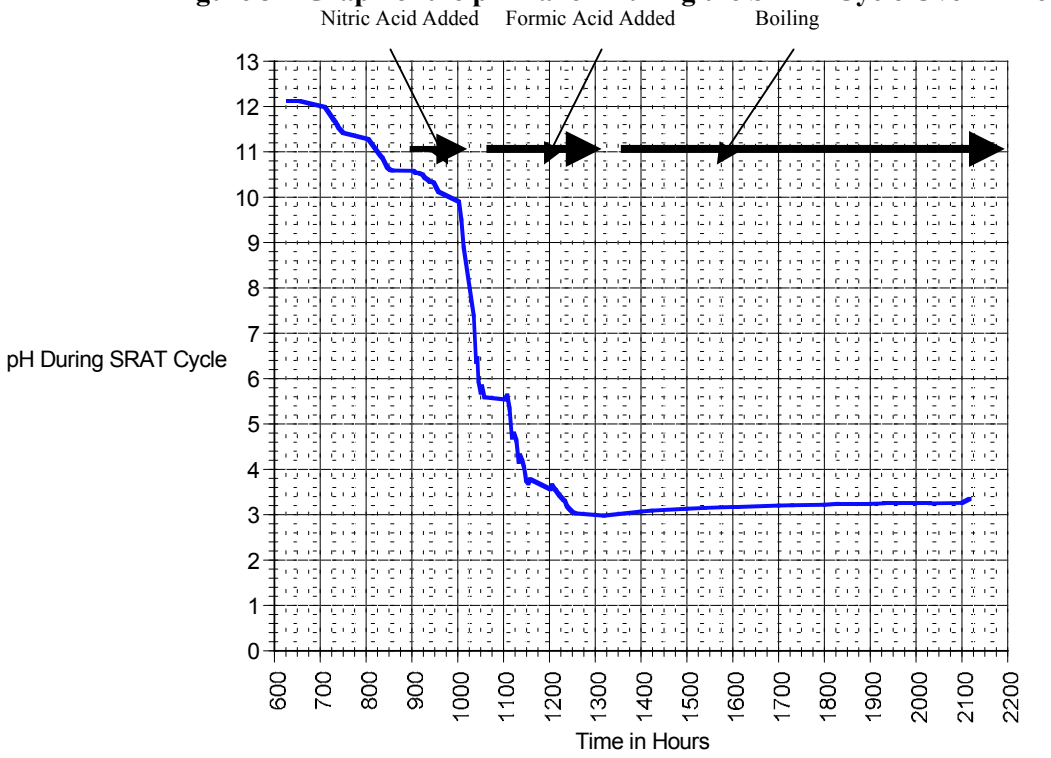
Concentration and Reflux
The vessel was heated to boiling to remove the volume of liquid added during the acid additions, and then to reflux for eight hours. Condensate collection (i.e. boiling) began at approximately 1319. During boiling, it was noticed that a ring of fine black particles was forming around the 400-450 mL mark in the SRAT vessel. The ring of black particles resembled the coal (carbon) that was initially added to the "de-washed sludge slurry". The SRAT run was terminated at 2100 with only eight hours of boiling completed.

Figure 3 is a graph of the pH taken during the SRAT cycle verses time. From 0850 to 1254 the SRAT pH dropped due to the addition of nitric and formic acids. During the eight hour boiling period, the pH of the SRAT product begins to slowly rise.

The vessel was reheated to boiling at 0805 the next morning, April 3, 2002. The contents of the SRAT vessel were boiled for another 4 hours to meet the DWPF 12 hour boiling requirement for the SRAT cycle. The vessel was allowed to cool and samples were taken for analyses. The ending pH was 3.79 (~50°C). This low pH can be explained by the amount of acid added during the SRAT cycle (See Section 4.2.4) and the lack of noble metals in the Sludge Batch 3 simulant. The noble metals catalytically decompose the formic acid to produce CO_2 and H_2.

Antifoam Addition
Antifoam was added when the vessel temperature reached 50°C, prior to formic acid addition, prior to boiling, and then every eight hours thereafter per the current DWPF antifoam strategy.

Figure 3 – Graph of the pH Taken During the SRAT Cycle Over Time



6.0 SRAT CYCLE RESULTS

Presented below are the results obtained from the SRAT cycle. These include the weight percent solids, density, and final composition of the SRAT product. To obtain the supernate for the required analyses, a portion of the mixed sludge slurry was filtered.

6.1 Weight Percent Solids and Density Measurements for the SRAT Product

Weight percent solids measurements were completed for the SRAT product and the SRAT supernate as described in Section 2.3.1. The averages of the calculated results of the weight percent solids for the sludge slurry and the supernate are presented in column two and column three of Table 19 respectively. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two and column three of Table 19.

Density measurements were completed for the SRAT product and the SRAT supernate as described in Section 3.1. The results of the SRAT product and supernate are presented in column four and column five of Table 19. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column four and five of Table 19.

Table 19 – Weight Percent Solids and Density Measurements for the SRAT Product

	Wt. % Total Solids for the SRAT Product[a]	Wt. % Dissolved Solids for the SRAT Supernate	Density Measurements for the SRAT Product[b]	Density Measurements for the SRAT Supernate[b]
Average	17.55 wt.%	7.89 wt.%	1.16 g/mL	1.07 g/mL
Std. Dev.	± 2.00E-01	± 1.30E-01	± 2.0E-03	± 2.0E-03
%RSD	1.14E00	1.65E00	1.4E-01	1.7E-01

[a] Sample(s) were dried at 110°C overnight.
[b] Average of four values.

6.2 Nonradioactive Composition of the SRAT Product and the SRAT Supernate

Provided below are the results from the analyses of the dissolved SRAT product. The SRAT product was dissolved via the Aqua Regia method[6]. The same protocol was followed as described in Section 2.3.2. The dissolution results of the standard glass for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly. Table 20 presents the elements (excluding oxygen) with concentrations >0.1 weight percent for the final washed Sludge Batch 3 simulant obtained from the ICP-ES. Table 20 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

The SRAT product was filtered to obtain the supernate (See Section 2.3.4 for details). Table 21 presents the elements with concentrations >1 ppm (mg/L of supernate) in the supernate for the SRAT supernate samples obtained from the ICP- ES and the IC. Table 21 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

Table 20 – ICP-ES Results for the SRAT Product

Element[a]	Wt.% (Std. Dev., % RSD)
Al	5.55E00 (± 2.7E-02, 4.8E-01)
Ba	2.56E-01 (± 2.2E-03, 8.5E-01)
Ca	2.11E00 (± 1.4E-02, 6.7E-01)
Cr	1.66E-01 (± 4.0E-03, 2.4E00)
Cu	1.35E-01 (± 4.8E-04, 3.6E-01)
Fe	2.59E01 (± 1.5E-01, 5.7E-01)
Gd[b]	9.06E-02 (± 7.5E-04, 8.3E-01)
Mg	1.41E-01 (± 1.5E-03, 1.0E00)
Mn	2.81E00 (± 2.8E-02, 1.0E00)
Na	5.74E00(± 1.5E-02, 2.7E-01)
Ni	2.85E00 (± 2.0E-02, 6.9E-01)
Pb	1.40E-01 (± 3.3E-03, 2.3E00)
U	3.57E-01 (± 9.0E-03, 2.5E00)
Zn	2.68E-01 (± 7.5E-04, 2.8E-01)

[a] Results are determined by ICP-ES and are the average of results of three samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[b] Gd was added to the table since this is a Study of Pu/Gd solubility during the washing process.

Table 21 – ICP-ES and IC Results for the SRAT Supernate

ICP-ES Results	SRAT Supernate[c]
Al	1.08E03 mg/L Supernate (± 0, 0)
B	2.27E01 mg/L Supernate (± 3.1E-01, 1.4E00)
Ba	8.57E00 mg/L Supernate (± 4.0E-02, 5.0E-01)
Ca	4.15E03 mg/L Supernate (± 4.2E01, 1.0E00)
Co	4.13E00 mg/L Supernate (± 2.0E-02, 3.8E-01)
Cr	5.47E00 mg/L Supernate (± 4.0E-02, 6.7E-01)
Cu	2.56E02 mg/L Supernate (± 5.9E-01, 2.3E-01)
Fe	1.73E02 mg/L Supernate (± 5.7E00, 3.3E00)
Gd	1.70E01 mg/L Supernate (± 2.1E-01, 1.2E00)
La	3.36E00 mg/L Supernate (± 4.0E-01, 1.2E00)
Mg	3.08E02 mg/L Supernate (± 2.4E00, 7.6E-01)
Mn	5.72E03 mg/L Supernate (± 5.4E01, 9.4E-01)
Na	1.39E04 mg/L Supernate (± 0, 0)
Ni	3.49E03 mg/L Supernate (± 2.6E01, 7.0E-01)
P	1.09E01 mg/L Supernate (± 1.0E-01, 9.3E-00)
Pb	1.20E01 mg/L Supernate (± 1.0E-01, 8.5E-01)
Si	1.50E01 mg/L Supernate (± 4.4E-01, 3.0E00)
Sn	2.15E00 mg/L Supernate (± 8.0E-02, 3.6E00)
Sr	1.78E02 mg/L Supernate (± 5.9E-01, 3.3E-01)
U	1.48E01 mg/L Supernate (± 4.1E-01, 2.8E00)
Zn	3.42E02 mg/L Supernate (± 1.8E00, 5.2E-01)
IC Results	**SRAT Supernate[c]**
Flouride[a]	<2 mg/L Supernate
Formate[b]	3.73E04 mg/L Supernate (± 7.2E01, 1.9E-01)
Chloride	1.16E03 mg/L Supernate (± 5.9E00, 5.1E-01)
Nitrite[c]	<1.02E02 mg/L Supernate
Nitrate	2.81E04 (± 5.9E01, 2.1E-01)
Phosphate[c]	<102 mg/L Supernate
Sulfate	1.15E02 mg/L Supernate (± 2.9E01, 2.6E01)
Oxalate[c]	<102 mg/L Supernate

[a] Detection limit of the analytical method.
[b] Average of two results.
[c] Results are determined by ICP-ES and IC and are the averages of results of three samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

One of the requirements for the DWPF SRAT cycle is to destroy the nitrite. From Table 21, the value for nitrite is <102 ppm. This meets the DWPF criteria of having < 1000 ppm of nitrite at the end of the SRAT cycle.

6.3 Radioactive Composition for the SRAT Product and SRAT Supernate

Presented below in Table 22 are the results from the ICP-MS and radioactive counting methods for the SRAT product. The aqua regia dissolution solutions described in Section 6.2 were used for the ICP-MS analyses. The dissolution solution was used for the counting methods. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 22 – ICP-MS and Counting Results for the SRAT Product

ICP-MS Results[a]	Wt.% (Std. Dev., % RSD)
Gd-152	2.20E-04 (± 4.0E-06, 2.0E00)
Gd-154	1.94E-03 (± 3.1E-05, 1.6E00)
Gd-155	9.70E-03 (± 1.2E-04, 1.2E00)
Gd-156	1.32E-02 (± 1.8E-04, 1.4E00)
Gd-157	1.00E-02 (± 1.8E-04, 1.8E00)
Gd-158	1.59E-02 (± 2.2E-04, 1.4E00)
Gd-160	1.38E-02 (± 1.9E-04, 1.3E00)
Th-232	9.22E-05 (± 3.1E-06, 3.4E00)
U-234	4.42E-05(± 4.2E-06, 9.5E00)
U-235	5.99E-05 (± 3.7E-06, 6.2E00)
U-236	1.58E-05 (± 1.3E-06, 8.4E00)
Np-237	2.03E-04 (± 2.9E-06, 1.4E00)
U-238	5.53E-04 (± 1.0E-05, 1.8E00)
Pu-239	5.07E-02 (± 1.3E-03, 2.5E00)
Pu-240	5.28E-03 (± 1.4E-04, 2.6E00)
Am-241[b]	5.96E-04 (± 1.7E-05, 2.9E00)
Pu-242	1.16E-04 (± 3.7E-06, 3.2E00)
Counting Data Results[a]	**Units**
Cs-137[c]	<1.3E-09 wt.%
Am-241	2.52E-04 wt.% (± 2.8E-06, 1.1E00)
Total Alpha	8.90E00 μCi/g (± 2.7E-01, 3.0E00)

[a] Average of three results.
[b] The concentration reported for mass 241 may be high due to Am-241 and Pu-241 being detected by the ICP-MS. No special separation techniques were performed to determine the Pu-241 concentration.
[c] Detection Limit of the method.

The ratio of Gd to Pu for the SRAT Product can be calculated by adding up the concentrations of the Gd isotopes and the concentrations of the Pu isotopes in Table 22 and then dividing Gd by the Pu. The ratio for the SRAT product is 1.16:1. This ratio is different from the expected ratio of 1.40:1[4] and the ratio of 1.27:1 for final washed Sludge Batch 3 simulant. Because of this difference, a calculation was completed to determine if the amount of Gd or Pu determined by ADS was causing the ratio to change. The total grams of Gd and Pu in the final washed Sludge Batch 3 Simulant were 0.0406g and 0.0319g (based on the volume, density, and weight percent solids of the sludge slurry) respectively. The total grams of Gd and Pu for the SRAT product are 0.0393g and 0.0340g (based on the volume, density, and the weight percent solids of the SRAT product) respectively. There was a decrease in the amount of Gd and an increase in amount of Pu in the SRAT product when compared to the grams of Gd and Pu determined for the final washed sludge slurry. The differences in the amount of Gd and Pu are reasonable, and are probably due to analytical error surrounding the measurement of the low concentrations of Gd and Pu in the sludge slurry.

Presented below in Table 23 are the results from the ICP-MS and radioactive counting methods for the SRAT supernate. The supernate samples obtained in Section 6.2 were used for the ICP-MS analyses and the counting methods. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 23 – ICP-MS and Counting Results for the SRAT Supernate

ICP-MS Results[a]	mg/L Supernate (Std. Dev., % RSD)
Gd-152	9.96E-03 (± 5.8E-04, 6.0E00)
Gd-154	8.89E-02 (± 1.8E-03, 2.0E00)
Gd-155	5.28E-01 (± 1.1E-02, 2.0E00)
Gd-156	7.31E-01 (± 1.7E-02, 2.4E00)
Gd-157	5.58E-01 (± 1.2E-02, 1.8E00)
Gd-158	8.82E-01 (± 2.2E-02, 2.5E00)
Gd-160	7.74E-01 (± 1.9E-02, 2.4E00)
U-233	8.75E-04(± 2.7E-05, 3.1E00)
U-234	6.79E-02(± 1.8E-03, 2.6E00)
U-235	9.64E-02 (± 9.8E-04, 1.0E00)
U-236	2.63E-02 (± 3.1E-05, 1.2E00)
Np-237	2.09E-02 (± 2.2E-06, 1.1E00)
U-238	3.58E-01 (± 2.3E-03, 6.3E-01)
Pu-239	6.29E-02 (± 1.5E-03, 2.4E00)
Pu-240	6.80E-03 (± 4.7E-04, 6.9E00)
Am-241	6.61E-03 (± 1.0E-03, 1.6E01)
Pu-242[b]	4.17E-04 (± 1.3E-04, 3.2E01)
Counting Data Results[a]	**Units**
Cs-137[b]	2.73E-04 μCi/mL of supernate (± 2.4E-05, 8.6E00)
Am-241	2.79E-01 μCi/mL of supernate (± 3.0E-02, 1.1E01)
Total Alpha	6.23E04 dpm/mL of supernate (± 3.2E03, 5.2E00)

[a] Average of three results.
[b] Average of two numbers.

Using ICP-ES data from Table 20 and Table 21, the percentage of Al, Ca, Fe, Mg, and Mn that became soluble during the SRAT cycle can be determined. Using the ICP-MS data from and Table 23, the percentage of Gd and Pu that became soluble during the SRAT cycle can be determined. Table 24 presents the grams of Al, Ca, Fe, Mg, Mn, Gd, and Pu that were soluble after the completion of the SRAT process. These values are presented on a sludge slurry basis.

Table 24 – Amount of Al, Ca, Fe, Mg, Mn , Gd, and Pu Soluble After the SRAT Cycle

SRAT Cycle[a]	Element	Grams in the Dried SRAT Product	Grams in the Supernate on a Sludge Slurry Basis	% Soluble
	Al	3.37E00	3.14E-01	9.30 %
	Ca	1.28E00	1.21E00	94 %
	Fe	1.57E01	5.03E-02	0.32 %
	Mg	8.58E-02	8.98E-02	105 %
	Mn	1.71E00	1.66E00	97 %
	Gd	3.94E-02	1.04E-03	2.64 %
	Pu-239	3.08E-02	1.83E-05	0.06 %
	Pu-240	3.21E-03	1.98E-06	0.06 %
	Pu-242	7.05E-05	1.21E-07	0.17 %

[a] Assumptions: Total volume of 300 mL, 17.5 wt.% total solids, slurry density 1.155 g/mL, 7.89 wt.% dissolved solids, and 1.07g/mL supernate density

From Table 24, it appears that essentially all of the Mg, Mn, and Ca was soluble at a pH of 3.79. A small percentage of the Al and Gd were soluble and very little of the Fe or Pu was soluble at this pH. This indicates that the majority of the Pu was insoluble along with the Fe and Gd. It also appeared, from Table 24, that more of the Gd was dissolved than the Pu. As a well mixed slurry in the DWPF, there is enough Fe with the fissile Pu to not cause a criticality concern (i.e. Fe:Pu ratio must be greater than 160:1[14]). No experimental data was obtained for a settled SRAT product to prove the Pu (from the Pu/Gd mixture) does not preferentially settle if the agitation in the DWPF SRAT vessel was stopped. A calculation is being

performed to prove that the Pu does not preferentially settle and that the Fe and other neutron poisons in the settled sludge are sufficient to prevent a criticality if agitation were stopped.

The fractions for the Pu isotopes in Table 24 should agree, but they do not. The likely reason for the higher solubility of the Pu-242 is analytical error surrounding the ICP-MS method.

7.0 LOWERING OF THE pH OF THE SRAT PRODUCT TO ~ 3

After the SRAT cycle was completed and the samples were taken, the vessel was heated again and the pH was lowered to ~3. This was completed in order to study the Pu/Gd mixture under very acidic conditions in the SRAT vessel. Table 25 provides the amount of acid to be added to lower the pH to 3. The same input variables were used as in except for the TIC value and the total OH^-. The total OH^- was obtained from Figure 2, and the TIC value used is an average of four values. The nitric acid and the formic acid values in Table 25 were subtracted from the values in to obtain the amount of nitric acid and formic acid needed for addition. Presented below are the results from this experiment.

7.1 Description of the pH 3 SRAT Cycle

Initiation – Heating and Agitation
The SRAT Cycle began on 4 April 2002 at 0615 with the start of the agitator and heating mantle. When the vessel reached 50°C (0740), antifoam was added. The sludge slurry surface appeared to be well mixed with a lot of surface movement.

Nitric Acid Addition
At 0802, vessel temperature was at 90°C, and nitric acid addition was initiated. Based on the acid calculations (see Section 4.2.4 and Section 7.0), 2 mL of 50wt% nitric acid was added to the vessel at the flow rate of 0.1 mL/min (added by 500 lambda pipette every 5 minutes). The acid addition was completed by 0824. During the addition of the nitric acid, the pH of the sludge slurry dropped from 3.90 (~25°C) to 3.12 (~90°C). At the completion of the addition, the sludge slurry was visually examined. The surface appeared smooth with a lot of surface movement.

Formic Acid Addition
Prior to the start of the formic acid addition an antifoam addition was made to the SRAT vessel. At 0832, the formic acid addition began. A total of 3.7 mL of 90 wt% formic acid (see Section 4.2.4 and Section 7.0 for acid calculations) was added at a flow rate of 0.10 mL/min (added by 500 lambda pipette every 5 minutes). During the addition of the formic acid, the pH of the sludge slurry dropped from 3.12 (~90°C) to 2.76 (~90°C). The formic acid addition was completed at 0902.

Concentration and Reflux
The vessel was heated to boiling to remove the volume of liquid added during the acid additions, and then to reflux for twelve hours. Condensate collection (i.e. boiling) began at approximately 0935. Two extra additions of antifoam were made during the 12 hour boiling period due to foaming in the vessel. It is believed that the excess acid in the vessel may be consuming the antifoam or rendering it ineffective over time. The SRAT cycle was complete 2130 04 April 2002. Figure 4 presents the pH for the SRAT cycle over time. From 0807 to 0902 the SRAT pH dropped due to the addition of nitric and formic acids. During the twelve hour boiling period, the pH of the SRAT product begins to slowly rise.

All of the sludge slurry was transferred from the SRAT vessel to sample bottles for analyses the next day (4/5/2002). After transferring the sludge slurry out of the SRAT vessel, the bottom of the vessel was inspected for solids. White solids in the form of several small clumps (~1mm) were found on the bottom of the vessel. These solids appeared to be coated with sludge slurry. See Figure 5 for a picture of the white solids (coated with sludge slurry). There is evidence (see Section 7.5) that at least a portion of these white clumps coated with sludge slurry

were the sand that had been added to the initial "de-washed' sludge slurry. Samples of these solids were obtained and submitted for analyses. Also, samples of the SRAT product were pulled for analyses to assess the chemical behavior of the Pu/Gd mixture in the sludge slurry.

Table 25 - Excel Spreadsheet for Determining Nitric Acid and Formic Acid Requirements to Lower the pH of the SRAT Product to 3

revised 3/31/02

SRAT Batch 2 Shielded Cell Runs Acid Requirements - computed March 31, 2001 By T.L. Fellinger

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

SRAT Conditions and Analyses	
(lab ID 2000xxxxx)	Receipt
Volume [gal]	6,000
spG	1.140
Wt% solids	15.30
Hydroxide [eq/L]	0.846
Nitrite [ppm]	8,509
Mercury [ppm]	0
Manganese [wt%]	3.38
Manganese (sol) [ppm]	0
TIC [ppm]	2,048
Formate [ppm]	0
Nitrate [ppm]	3,072

Formic Acid Addition Volume	
Volume [gal]	404
spG	1.192
Wt%	87.7
Molar	22.71

Nitric Acid Tank	
spG	1.3
Wt%	49.6
Molar	10.22

g-moles C 2279 4558

2112 ppm

-> 5,171.40 ppm

Calculated SRAT Quantities		Nitric Required	Formic Required	
SRAT mass [lbs]	57,080			
MnO2 [g-moles]	2,437.1	1,949.6	974.8	
HgO [g-moles]	0.	0.	0.	
NO2 [g-moles]	4,788.2	2,394.1	1,197.	
CO3 [g-moles]	4,415.	8,830.	0.	
OH [g-moles]	19,212.7	19,212.7	0.	OH [ppm] 29,684
Total Acid [g-moles] at 125%		40,483.1	2,714.8	43,197.9 total
Total Volume [gal]		**1,046**	**32**	

From Marek calculational algorithm at 125% of stoichiometry:		
mFA	2,715	Formic Acid Requirement [g-moles]
mA	+ 40,483	Additional Acid Required [g-moles]
mDFA	- 34,732	Direct Formic Acid Addition [g-moles]
mHNO3	= 8,466	g-moles Nitric Acid
VHNO3	**219**	gallons

Specify the following quantities in the SRAT procedure:

219	**gallons of 50 wt% nitric acid**
404	**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.

Glovebox Calc

NITRIC	**828.21024 L**	
FORMIC	**1529.14 L**	
Scale Factor =	**1.321E-05**	
NITRIC	**10.9407 mL**	**14.2229** g
FORMIC	**20.2000 mL**	**24.0784** g

Figure 4 - Graph of the pH Taken During the SRAT Cycle (pH~ 3) Over Time

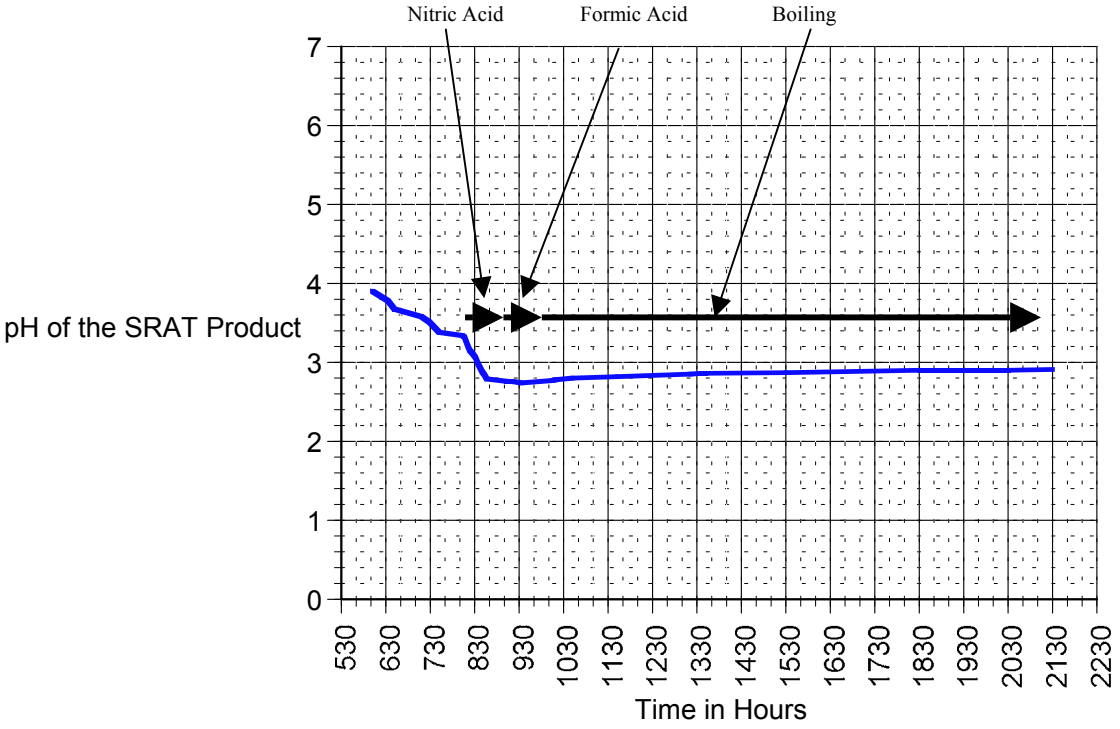


Figure 5 – Picture of the White Solids (Coated with Sludge Slurry) Found on the Bottom of the SRAT Vessel

7.2 Weight Percent Solids and Density Results for the pH 3 SRAT Product

Weight percent solids measurements were completed for the SRAT product and the SRAT supernate as described in Section 6.1. The averages of the calculated results of the weight percent solids for the sludge slurry and the supernate are presented in column two and column three of Table 26 respectively. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column two and column three of Table 26.

Density measurements were completed for the SRAT product and the SRAT supernate as described in Section 6.1. The results of the SRAT product and SRAT supernate are presented in column four and column five of Table 26. The standard deviations (Std. Dev.) and the percent relative standard deviations (% RSD) for the data are also presented in column four and column five of Table 26.

Table 26– Weight Percent Solids and Density Measurements for the SRAT Product (pH of ~3)

	Wt. % Total Solids for the SRAT Product[a]	Wt. % Dissolved Solids for the SRAT Supernate[a]	Density Measurements for the SRAT Product[b]	Density Measurements for the SRAT Supernate[b]
Average	17.29 wt.%	7.67 wt.%	1.16 g/mL	1.07 g/mL
Std. Dev.	± 2.38E-01	± 2.06E-01	± 4.0E-03	± 2.0E-03
%RSD	1.38E00	2.69E00	3.8E-01	1.8E-01

[a] Sample(s) were dried at 110°C overnight.
[b] Average of four values.

7.3 Nonradioactive Composition of the SRAT Product and the SRAT Supernate

Provided below are the results from the analyses of the dissolved SRAT product. The SRAT product was dissolved via the Aqua Regia method[6] and Sodium Peroxide Fusion method[12]. The same protocol was followed as described in Section 3.2. The dissolution results of the standard glass for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly. Table 27 presents the elements (excluding oxygen) with concentrations >0.1 weight percent for the final washed Sludge Batch 3 simulant obtained from the ICP-ES. Table 27 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

The SRAT product was filtered to obtain the supernate (See Section 2.3.4 for details). Table 28 presents the elements with concentrations >1 ppm (mg/L of supernate) in the supernate for the SRAT supernate samples obtained from the ICP- ES and the IC. Table 28 also presents the standard deviation and the percent relative standard deviation in parentheses next to the weight percent value.

Table 27 – ICP-ES Results for the SRAT Product (pH of ~3)

Element[a]	Wt.% (Std. Dev., % RSD)
Al	5.27E00 (± 2.9E-01, 5.4E00)
Ba	2.44E-01 (± 1.2E-02, 4.9E00)
Ca	2.09E00 (± 5.4E-02, 2.6E00)
Cr	1.73E-01 (± 6.7E-02, 3.9E00)
Cu	1.34E-01 (± 3.9E-03, 2.9E00)
Fe	2.38E01 (± 1.3E00, 5.6E00)
Gd[b]	7.79E-02 (± 3.8E-03, 4.9E00)
Mg	1.22E-01 (± 1.5E-02, 1.3E01)
Mn	2.63E00 (± 1.9E-01, 7.8E00)
Na[c]	5.99E00(± 1.2E-01, 2.0E00)
Ni	2.71E00 (± 1.5E-01, 5.4E-01)
Pb	1.33E-01 (± 5.5E-03, 4.1E00)
U	2.89E-01 (± 3.1E-02, 1.1E01)
Zn	2.82E-01 (± 2.4E-02, 8.6E00)

[a] Results are determined by ICP-ES and are the average of results of six samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.
[b] Gd was added to the table since this is a Study of Pu/Gd solubility during the washing process.
[c] Average of three values.

Table 28 – ICP-ES and IC Results for the SRAT Supernate (pH of ~3)

ICP-ES Results	SRAT Supernate[b]
Al	2.14E03 mg/L Supernate (± 2.1E01, 9.7E-01)
B	2.02E01 mg/L Supernate (± 2.6E-01, 1.3E00)
Ba	6.05E00 mg/L Supernate (± 3.0E-02, 5.0E-01)
Ca	3.70E03 mg/L Supernate (± 4.0E01, 1.1E00)
Co	3.71E00 mg/L Supernate (± 2.0E-02, 5.6E-01)
Cr	5.09E00 mg/L Supernate (± 6.0E-02, 1.2E00)
Cu	2.65E02 mg/L Supernate (± 1.2E00, 4.4E-01)
Fe	4.43E02 mg/L Supernate (± 3.1E00, 6.9E-01)
Gd	1.82E01 mg/L Supernate (± 1.5E-01, 8.4E-01)
La	3.06E00 mg/L Supernate (± 7.0E-02, 2.2E00)
Mg	2.75E02 mg/L Supernate (± 1.7E00, 6.3E-01)
Mn	4.60E03 mg/L Supernate (± 5.1E01, 1.1E00)
Na	1.26E04 mg/L Supernate (± 1.7E02, 1.4E00)
Ni	3.33E03 mg/L Supernate (± 3.2E01, 9.6E-01)
P	9.98E00 mg/L Supernate (± 5.0E-02, 4.6E-01)
Pb	2.01E01 mg/L Supernate (± 1.0E-01, 5.0E-01)
Si	2.0E01 mg/L Supernate (± 1.2E-01, 5.8E-01)
Sn	3.19E00 mg/L Supernate (± 1.2E-01, 3.6E00)
Sr	1.56E02 mg/L Supernate (± 5.8E-01, 3.7E-01)
U	1.78E01 mg/L Supernate (± 3.0E-01, 1.7E00)
Zn	3.46E02 mg/L Supernate (± 1.8E00, 5.2E-01)
IC Results	**SRAT Supernate[b]**
Flouride[a]	<20 mg/L Supernate
Formate	4.36E04 mg/L Supernate (± 1.02E02, 2.0E00)
Chloride	1.18E03 mg/L Supernate (± 1.1E02, 9.0E00)
Nitrite[a]	<1.0E01 mg/L Supernate
Nitrate	2.94E04 (± 9.5E02, 3.2E00)
Phosphate[a]	<1.0E01 mg/L Supernate
Sulfate	1.20E02 mg/L Supernate (± 0E00, 0E00)
Oxalate[a]	<1.0E01 mg/L Supernate

[a] Detection limit of the analytical method.
[b] Results are determined by ICP-ES and IC and are the averages of results of three samples unless otherwise indicated. The standard deviation and the percent relative standard deviation are presented in parentheses next to each value.

7.4 Radioactive Composition for the SRAT Product and SRAT Supernate

Presented below in Table 29 are the results from the ICP-MS and radioactive counting methods for the SRAT product. The aqua regia dissolution solutions described in Section 7.3 were used for the ICP-MS analyses. Both dissolution solutions were used for the counting methods. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 29 – ICP-MS and Counting Results for the SRAT Product (pH~3)

ICP-MS Results[a]	Wt.% (Std. Dev., % RSD)
Gd-152	2.03E-04 (± 1.1E-06, 5.6E-01)
Gd-154	1.96E-03 (± 3.0E-05, 1.5E00)
Gd-155	9.99E-03 (± 5.8E-05, 5.9E-01)
Gd-156	1.36E-02 (± 1.1E-04, 7.9E-01)
Gd-157	1.02E-02 (± 1.1E-04, 1.1E00)
Gd-158	1.62E-02 (± 1.6E-04, 9.6E-01)
Gd-160	1.42E-02 (± 1.9E-04, 1.4E00)
Th-232	9.38E-05 (± 3.2E-06, 3.4E00)
U-234	4.39E-05(± 3.6E-06, 8.2E00)
U-235	6.25E-05 (± 1.8E-06, 2.8E00)
U-236	1.56E-05 (± 8.8E-07, 5.7E00)
Np-237	1.95E-04 (± 5.2E-06, 2.7E00)
U-238	5.57E-04 (± 1.6E-05, 2.9E00)
Pu-239	4.87E-02 (± 1.1E-03, 2.3E00)
Pu-240	5.03E-03 (± 6.3E-05, 1.3E00)
Am-241[b]	5.63E-04 (± 7.62E-06, 1.4E00)
Pu-242	1.09E-04 (± 4.6E-06, 4.2E00)
Counting Data Results[a]	**Units**
Cs-137[c]	<1.3E-09 wt.%
Am-241[d]	2.37E-04 wt.% (± 1.2E-05, 5.0E00)
Total Alpha[d]	8.94E00 μCi/g (± 2.0E-01, 2.2E00)

[a] Average of three results.
[b] The concentration reported for mass 241 may be high due to Am-241 and Pu-241 being detected by the ICP-MS. No special separation techniques were performed to determine the Pu-241 concentration.
[c] Detection Limit of the method.
[d] Average of six values.

The ratio of Gd to Pu for the SRAT Product can be calculated by adding up the concentrations of the Gd isotopes and the concentrations of the Pu isotopes in Table 29 and then dividing Gd by the Pu. The ratio for the SRAT product is 1.23:1. This ratio is different from the expected ratio of 1.40:1 and is between the ratio of 1.27:1 for final washed Sludge Batch 3 simulant and the ratio of the first SRAT product of 1.16:1. As noted earlier in this document, the difference in the Gd/Pu ratios can be explained by the analytical error surrounding both the Gd and Pu values.

Presented below in Table 30 are the results from the ICP-MS and radioactive counting methods for the SRAT supernate. The supernate samples obtained in Section 7.3 were used for the ICP-MS analyses and the counting methods. The units used for the ICP-MS results and the counting methods are presented next to each value. The standard deviation and the percent relative standard deviations for the values are presented in parentheses.

Table 30 – ICP-MS and Counting Results for the SRAT Supernate (pH~3)

ICP-MS Results[a]	mg/L Supernate (Std. Dev., % RSD)
Gd-152	1.54E-02 (± 7.6E-04, 5.0E00)
Gd-154	1.56E-01 (± 9.0E-04, 5.7E-01)
Gd-155	9.79E-01 (± 6.3E-03, 6.4E-01)
Gd-156	1.38E00 (± 1.9E-02, 1.4E00)
Gd-157	1.03E00 (± 6.9E-03, 6.7E-01)
Gd-158	1.64E00 (± 1.5E-02, 9.4E-01)
Gd-160	1.43E00 (± 7.3E-03, 5.1E-01)
U-233[b]	1.37E-03(± 1.5E-04, 1.1E01)
U-234	6.77E-02(± 3.4E-03, 5.0E00)
U-235	9.61E-02 (± 2.2E-03, 2.3E00)
U-236	2.53E-02 (± 6.6E-04, 2.6E00)
Np-237	1.15E-02 (± 1.2E-03, 1.0E01)
U-238	3.94E-01 (± 2.2E-03, 5.6E-01)
Pu-239	1.50E-01 (± 7.0E-03, 4.6E00)
Pu-240	1.33E-02 (± 9.2E-04, 7.0E00)
Am-241	1.23E-02 (± 3.4E-04, 2.8E00)
Counting Data Results[a]	**Units**
Cs-137	2.71E-04 µCi/mL of supernate (± 3.7E-05, 1.4E01)
Am-241	3.96E-01 µCi/mL of supernate (± 7.0E-03, 1.7E00)
Total Alpha	1.62E05 dpm/mL of supernate (± 1.4E04, 8.6E00)

[a] Average of three results.
[b] Average of two numbers.

Using ICP-ES data from Table 27 and Table 28, the percentage of Al, Ca, Fe, Mg, and Mn that became soluble during the second SRAT cycle can be determined. Using the ICP-MS data from Table 29 and Table 30, the percentage of Gd and Pu that became soluble during the SRAT cycle can be determined. Table 31 presents the grams of Al, Ca, Fe, Mg, Mn, Gd, and Pu that were soluble after the completion of the SRAT process. These values are presented on a sludge slurry basis.

Table 31 – Amount of Al, Ca, Fe, Mg, Mn, Gd, and Pu Soluble After the SRAT Cycle (pH~3)

SRAT Cycle[a]	Element	Grams in the Dried SRAT Product	Grams in the Supernate on a Sludge Slurry Basis	% Soluble
	Al	2.59E00	5.09E-01	19.7 %
	Ca	1.03E00	8.82E-01	85.9 %
	Fe	1.17E01	1.06E-01	0.90 %
	Mg	5.99E-02	6.55E-02	109 %
	Mn	1.29E00	1.10E00	84.8 %
	Gd	3.26E-02	1.58E-03	4.84 %
	Pu-239	2.39E-02	3.57E-05	0.15 %
	Pu-240	2.47E-03	3.14E-06	0.13 %

[a] Assumptions: Total volume of 245 mL, 17.3 wt.% total solids, slurry density 1.16 g/mL, 7.67 wt.% dissolved solids, and 1.07g/mL supernate density

From Table 31, it appears the majority of the Mg, Mn, and Ca was soluble at a pH of 3.2. A small percentage of the Al and Gd were soluble and very little of the Fe or Pu was soluble at this pH. This would indicate that the majority of the Pu was insoluble along with the Fe and Gd. Upon comparing the results in Table 24 to Table 31 it appears that more of the Gd and Pu became soluble as the pH was lowered to 3. The results also indicate that more Gd is soluble than Pu. As a well mixed slurry in the DWPF, there is enough Fe with the fissile Pu to not cause a criticality concern (i.e. Fe:Pu ratio must be greater than 160:1[13]). The ratio of Fe:Pu for this experiment was 442:1, which exceeds the ratio of 160:1. No experimental data was obtained for a settled SRAT product to prove the Pu (from the Pu/Gd mixture) does not preferentially settle if the agitation in the DWPF SRAT vessel was stopped. A calculation is being performed to prove that the Pu does not preferentially settle and that the Fe and other neutron poisons in the settled sludge are sufficient to prevent a criticality if agitation were stopped.

There are slight differences in the solubility of the Pu-239 versus Pu-240. This is contributed error surrounding the ICP-MS method rather than an isotope effect.

7.5 Analytical Results of the Black Ring and White Solids (Coated with Sludge Slurry) Found in the SRAT Vessel

Several samples of the black ring and white solids were taken from the SRAT vessel for analysis by X-Ray Diffraction (XRD) and Contained Scanning Electron Microscopy (CSEM). The CSEM results of the coated white solids showed that the solids were mainly a sludge slurry matrix (Fe, Na, Al, Ni, Zr etc.) with Si. No Pu was detected in the samples of the solids submitted for analyses.

The CSEM cannot detect carbon, but a sample of the black ring was submitted to make sure no Pu was in the black ring. The results of the CSEM for that sample showed a sludge slurry matrix with no Pu detected in the sample. The XRD results of the black ring and white solids showed that the solids were mainly sand (Quartz - SiO_2), Calcite ($CaCO_3$), and Copper Formate ($Cu(CHO_2)_2$). No carbon and no Pu were detected in the sample.

8.0 SUMMARY OF THE SRAT TESTING

The first SRAT cycle was completed with no significant processing problems noted. An ending pH of 7 was targeted for the first SRAT cycle, but pH of 3.9 (~25°C) was obtained. The lower pH can be explained by the amount of acid added during the SRAT cycle (See Section 4.2.4) and the lack of noble metals in the Sludge Batch 3 simulant. The noble metals catalytically decompose the formic acid to produce CO_2 and H_2. Although the pH was lower than expected, the amount of Gd and Pu dissolved, as noted in Table 24, was small and the majority of the Pu (99.9%) and Gd (97%) remained insoluble.

The second SRAT cycle was completed with no significant processing problems noted. Two extra additions of antifoam were made during the 12 hour boiling period due to foaming in the vessel. It was believed that the excess acid in the vessel may be consuming the antifoam or rendering it ineffective over time. An ending pH of 3 was targeted for the second SRAT cycle, but pH of 3.2 (~25°C) was obtained. It was noticed that there was a small increase in the amount of Gd and Pu dissolved from the sludge solids, as noted in Table 31, but the majority of the Pu (99.8%) and Gd (95%) remained insoluble. Table 32 compares the fractions of elements soluble after the SRAT process for both SRAT products.

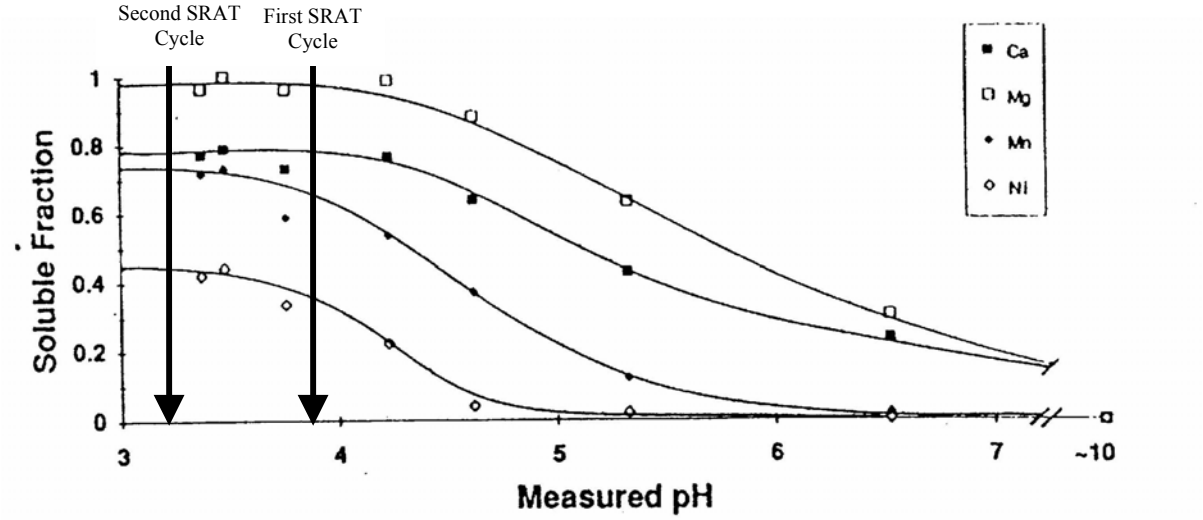
Table 32 – Fraction of Selected Elements Soluble After the First SRAT Cycle and the Second SRAT Cycle

First SRAT Cycle[a] (ph~3.9)	Element	% Soluble in the Supernate	% Insoluble in the Sludge Solids
	Al	9.30 %	90.7 %
	Ca	94 %	6 %
	Fe	0.32 %	99.68 %
	Mg	105 %	-
	Mn	97 %	3 %
	Gd	2.64 %	97.36 %
	Pu-239	0.06 %	99.94 %
	Pu-240	0.06 %	99.94 %
	Pu-242	0.17 %	99.83 %
Second SRAT Cycle[b] (ph~3.2)	Al	19.7 %	80.3 %
	Ca	85.9 %	14.1 %
	Fe	0.90 %	99.1 %
	Mg	109 %	-
	Mn	84.8 %	15.2 %
	Gd	4.84 %	95.16 %
	Pu-239	0.15 %	99.85 %
	Pu-240	0.13 %	99.87 %

[a] Assumptions: Total volume of 300 mL, 17.5 wt.% total solids, slurry density 1.155 g/mL, 7.89 wt.% dissolved solids, and 1.07g/mL supernate density.
[b] Assumptions: Total volume of 245 mL, 17.3 wt.% total solids, slurry density 1.16 g/mL, 7.67 wt.% dissolved solids, and 1.07g/mL supernate density

The fractions in Table 32, were then compared to a previous study[15] conducted with Tank 51 radioactive sludge slurry. Figure 6 is a graph of the results obtained from a dissolution study with Tank 51 sludge slurry and nitric acid. The results in Table 32 essentially agree with the fractions at a pH of 3.9 and 3.2 in Figure 6.

Figure 6 - Graph of pH Versus Elemental Fraction Dissolved During Nitric Acid Addition for Tank 51 Sludge Slurry



As a well mixed slurry in the DWPF (for both SRAT scenarios studied in this experiment), there is enough Fe with the fissile Pu to not cause a criticality concern (i.e. Fe:Pu ratio must be greater than 160:1[13]). The ratio of Fe:Pu for the first SRAT cycle and second SRAT cycle was 446:1 and 442:1 respectively. These ratios exceed the required ratio of 160:1 that is documented in DWPF criticality safety analysis summary report for sludge only operations (WSRC-RP-94-1132[13]). No experimental data was obtained for a settled SRAT product to determine if the Pu (from the Pu/Gd mixture) preferentially settles if the agitation in the DWPF SRAT vessel was stopped. The issue of preferential settling of Pu has been addressed in a separate memo[16].

From performing these SRAT cycles, some issues that are specific to Sludge Batch 3 have been identified. They are listed below, and should be addressed as part of the nonradioactive work conducted at the ACTL and radioactive work conducted in the Shielded Cells for Sludge Batch 3.

1. Resolve the issues surrounding the method of determining TIC/TOC for the sludge slurries that have coal added to them. The TIC concentration is an input for the acid calculations for the SRAT cycle. The TOC concentration will affect the final redox of the melter (Fe^{2+}/Fe^{tot}) which directly affects the amount of formic acid added during the SRAT cycle.
2. Revise the spreadsheet for the SRAT acid calculations to incorporate sludge slurries that have coal/carbon in them.
3. Resolve the differences observed between the Gd concentrations obtained from the radioactive ICP-ES versus the concentrations obtained from the radioactive ICP-MS. The Gd values from the ICP-ES appeared to be biased high by 20%.
4. Determine if coal/carbon ring forms above the sludge slurry for the nonradioactive and radioactive Sludge Batch 3 testing. If coal/carbon remains behind in the vessel, it could impact the ability to reliably predict the redox of the glass.
5. Determine if sand is observed on the bottom of the SRAT vessel for the nonradioactive scoping SRAT runs. Should also determine if the particle size of the sand is too large for the sampling system used in DWPF.
6. Verify the Fe to fissile material in the washed sludge slurry and the SRAT product is greater than 160:1 for the radioactive testing in the Shielded Cells.
7. Analyze the supernate at the end of the SRAT cycle to determine what species have dissolve from the sludge solids.

9.0 CONCLUSIONS

- Up to 0.95% of the Gd and 0.20% of the Pu was soluble during the glove box demonstration of the Tank Farm Washing Process. The majority of the Gd (99 %) and Pu (99.8%) were insoluble and stayed with the sludge solids.
- The small quantities of leached plutonium during the sludge washing tests do not present a criticality safety concern and are not sufficient to adversely impact the Effluent Treatment Facility or Saltstone operations.
- No significant problems were encountered during the washing process. Based on analytical results, the Pu/Gd mixture appeared to be uniformly distributed throughout the sludge.
- Approximately 2.64% of the Gd and ~0.16% of the Pu was soluble after the glove box demonstration of the DWPF SRAT cycle. The majority of the Gd (97 %) and Pu (99.8%) was insoluble and stayed with the sludge solids.
- No significant processing problems were encountered during the processing of this material through the first of two SRAT cycles.
- The nitrite was less than 102 ppm at the end of the SRAT cycle. The DWPF requirement is <1000 ppm at the end of the SRAT cycle.
- Upon lowering the pH of the SRAT product to ~3, the fractions soluble were approximately 4.84% of the Gd and 0.15% of the Pu was soluble after the glove box demonstration of the DWPF SRAT cycle. The majority of the Gd (95 %) and Pu (99.8%) was still insoluble and stayed with the sludge solids.
- Two extra additions of antifoam were made during the 12 hour boiling period of the second SRAT cycle (pH~3) to control foaming.
- As a well mixed slurry in the DWPF (for both SRAT scenarios studied in this experiment), there is enough Fe with the fissile Pu to not cause a criticality concern (i.e. Fe:Pu ratio must be greater than 160:1).

10.0 APPENDIX A

Scaling Factor for Glove Box

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Glove Box:	0.30	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= 0.3 Liters / 22710 Liters

Ratio= 1.32E-05

Nitric Acid Addition Flow Rate for Glove Box

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Glove Box:	0.30	Liters
Volume of Sludge Receipt for the DWPF:	6000	Gallons
or Volume of Sludge Receipt for the DWPF:	22710	Liters
DWPF Flow Rate for Ntric Acid:	2	Gallons/min
or DWPF Flow Rate for Ntric Acid:	7.57	Liters/min

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

Ratio= (0.3 Liters X 7.57 Liters/min) / 22710 Liters

Glove Box Flow Rate = 0.00010 Liters/min
or
Glove Box Flow Rate= 0.10 mL/min

Formic Acid Flow Rate for Shielded Cells

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Glove Box:	0.30	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= (0.3 Liters X 7.57 Liters/min) / 22710 Liters

Glove Box Flow Rate = 0.00010 Liters/min
or
Glove Box Flow Rate = 0.10 mL/min

Dow Corning Antifoam Additions for Shielded Cells

	Amount	Units
Volume of Sludge Receipt for the Glove Box:	0.300	Liters
Density of Sludge:	1.14	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:	2.5	g
Water Required:	45	g
Total Solution wt:	50	g
Check of calculations:	(2.5/50)*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)*(100 ppm)*(1000 mL/L) / 1000000 g Slurry

Grams of antifoam= 0.0342 g

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

mL of Antifoam Solution to Add= 0.68 mL

Purge Rate for the SRAT Cycle

Assumptions for Scaling Factor:

	Amount	Units
Volume of Sludge Receipt for the Glove Box:	0.300	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= (0.3 Liters* 5324160 sccm) / 22710 Liters

Shielded Cells Purge Rate for SRAT/SME Vessel= 70.3 sccm

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