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Task Technical Request HLW/DWPF/TTR-990005:

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Characterization of and Waste Acceptance Radionuclides to be Reported For DWPF Macro Batch 2 (ESP 215-ESP 221) (U)

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1.0 INTRODUCTION AND SUMMARY

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During the period from 1999 through 2002, the Defense Waste Processing Facility (DWPF) received and processed radioactive sludge slurry from High Level Waste Tank 51. The radioactive sludge slurry in Tank 51 was a blend of the remaining sludge slurry from Sludge Batch 1A (Macro Batch 1) and sludge slurry that had been transferred from Tank 42. The combination of these sludges formed Macro Batch 2 or Sludge Batch 1B.

The Savannah River Technology Center (SRTC) has analyzed samples of Sludge Batch 1A [1] and Tank 42 sludge slurry [2] (before Tank 42 was combined with the sludge slurry from Sludge Batch 1A). To meet the reporting requirements as specified in the Waste Form Compliance Plan [3] and the Department of Energy's (DOE) Waste Acceptance Product Specifications (WAPS) [4] for the final glass product, certain analytical information must be provided for a given Macro Batch of material. The DWPF has requested the analyses of sludge slurry samples from Tank 51 (Macro Batch 2) be completed in the Shielded Cells Facility of SRTC to obtain this analytical information [5, 6]. This information will be used to complete the necessary Production Records so that the final glass product, resulting from Macro Batch 2, may be disposed of at a Federal Repository.

The Waste Acceptance Product Specifications (WAPS) [4] 1.2 require that "The Producer shall report the inventory of radionuclides (in Curies) that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total inventory for each waste type indexed to the years 2015 and 3115". As part of the strategy to meet WAPS 1.2, the Defense Waste Processing Facility (DWPF) will report for each waste type, all radionuclides (with half-lives greater than 10 years) that have concentrations greater than 0.01 percent of the total inventory from time of production through the 1100 year period from 2015 through 3115. The initial listing of radionuclides to be included is based on the design-basis glass as identified in the Waste Form Compliance Plan (WCP) [3]. However, it is required that this list be expanded if other radionuclides with half-lives greater than 10 years are identified that meet the greater than 0.01% criterion for Curie content.

Specification 1.6 of the WAPS, IAEA Safeguards Reporting for HLW, requires that the ratio by weights of the following uranium and plutonium isotopes be reported: U-233, U-234, U-235, U-236, U-238, Pu-238, Pu-239, Pu-240, Pu-241, and Pu-242. Therefore, the complete set of reportable radionuclides must also include this set of U and Pu isotopes.

After sludge slurry in Tank 51 was thoroughly mixed, seven dip samples (~80 mL/each) were taken from Tank 51 and sent to the Shielded Cells Facility. Upon receipt of these samples, six of the seven samples (one stainless steel sample bottle was empty) were combined and the final composite was used for the requested analyses [5, 6, & 7].

This report describes the results obtained from the analyses of the combination of six sludge slurry samples taken from Tank 51 and the reportable radionuclides for this Macro Batch of sludge slurry. The combined sludge slurry sample and the supernate were also analyzed for nonradioactive and radioactive elemental composition, weight percent solids and density. The radioactive composition was calculated based on input from time zero (May 1999) to the years 2015 and 3115 in order to determine the reportable radionuclides as required by the WAPS.

Highlights from this report are found below.

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- Twenty-seven radioisotopes were identified as reportable by WAPS 1.2 for Macro Batch 2. The twentyseven radioisotopes met the criteria of having a half-life longer than 10 years and contributing greater than 0.01% of the total radioactivity during the first 1100 years after glass production [3]. Two additional uranium isotopes (U-235 and U-236) were added to the list of reportable radionuclides in order to meet WAPS 1.6. This brings the total number of reportable radionuclides for Macro Batch 2 to twenty-nine.
- 2. The radionuclides C-14, I-129, Cm-246 and Cm-247 were detected in the sludge slurry. This is the first time these radionuclides have been detected and measured in the high level waste sludge slurry.
- 3. The weight percent soluble solids of the supernate for Macro Batch 2 was 2.63 wt. %.
- 4. The density of the supernate for Macro Batch 2 was 1.03 g/mL.
- 5. The weight percent total solids of the sludge slurry for Macro Batch 2 was 18.8 wt.%.
- 6. The density for the sludge slurry for Macro Batch 2 was 1.10 g/mL.
- 7. The concentrations (weight percent based on total solids) of noble metals in Macro Batch 2 are:

Ru	2.18E-02
Rh	4.97E-03
Pd	1.11E-03
Ag	1.40E-02

2.0 COMBINATION OF THE SLUDGE SLURRY SAMPLES

Seven samples (ESP 215 – ESP 221) from Tank 51 were received in 80 mL stainless steel bottles on 1/14/99. These sludge slurry samples were placed into Cell Block A of the Shielded Cells and then combined into a oneliter container labeled "ESP 215-ESP-221 Composite Sample". Prior to the combination of the samples in the one-liter container, the sludge slurry samples were individually mixed by shaking each stainless steel bottle for approximately 5 minutes. To ensure all of the sludge slurry solids had been removed from each stainless steel bottle, the sludge slurry-slurry was allowed to settle in the one-liter container for 2 days. After two days the sludge slurry had settled into two layers, one being a clear supernate layer and the other being a sludge slurry layer. Approximately 5 mL of clear supernate was carefully pipetted into each stainless steel bottle. The stainless steel bottles were recapped and mixed by shaking each bottle for 5 minutes. The caps of the stainless steel bottles were removed after 5 minutes and the volume was returned to the one-liter container. The final volume of sludge slurry was ~454 mL (the sample labeled ESP 215 was empty).

The combined sludge slurry sample was then analyzed as specified in the analytical study plan [7]. Samples required for the analyses were obtained after mixing the sludge slurry for approximately 30 minutes using a magnetic stirrer and new magnetic stir bar. The majority of the analyses were performed by the Analytical Development Section (ADS) with the exception of weight percent solids, calcined solids and density determinations which were performed by qualified Shielded Cells Technicians.

3.0 RESULTS OF THE ANALYSES PERFORMED ON THE SUPERNATE OF THE COMBINED SLUDGE SLURRY SAMPLES

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

Presented below are the results of the Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES) data, Atomic Adsorption (AA) data, Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) data, Ion Chromatography (IC) data, Ion Selective Electrode (ISE) data, Total Organic Carbon (TOC) data, Cold Vapor Mercury (CV Hg) and counting techniques. Also presented below are the weight percent dissolved solids and density determinations of the supernate that was performed in the Shielded Cells Facility.

3.1 IC, ISE, AIO₂⁻, CO₃²⁻, Free OH⁻, TIC / TOC and Total OH⁻ Results for the Supernate

Presented below in Table 1 are the results for the supernate obtained from the following methods: IC, ISE, AIO_2 , CO_3^2 , Free OH, TIC / TOC & Total OH. The results are an average of 4 samples and the standard deviation and the percent relative standard deviation are also provided for each determination.

Method	<u>Average of</u> <u>Resultsª</u>	<u>StDev of</u> <u>Results</u>	<u>% RSD of</u> <u>Results</u>
IC Results for Chloride	3.29E-04 M	± 7.4E-05	23
IC Results for Fluoride	2.03E-03 M	± 1.2E-04	6.0
IC Results for Formate	<1.04E-03 Mb	-	•
IC Results for Nitrate	5.00E-02 M	± 6.2E-04	1.2
IC Results for Nitrite	1.66E-01 M	± 3.0E-03	1.8
IC Results for Phosphate	<4.92E-03 Mb	-	-
IC Results for Sulfate	6.92E-03 M	± 4.7E-04	6.8
IC Results for Oxalate	6.06E-03 M	± 5.1E-04	8.5
ISE Results for Chloride	5.20E-04 M	± 1.8E-04	35
ISE Results for Fluoride	1.92E-03 M	± 5.2E-05	2.7
Results for AIO ₂ -	< 1.28E-02 M ^b	-	-
Results for CO ₃ ²⁻	3.69E-02 M	± 2.1E-03	5.6
Results for Free OH-	3.35E-02 M	± 1.1E-03	3.4
Results for TIC	5.58E02 mg/L	± 2.5E01	4.5
Results for TOC	3.12E02 mg/L	± 5.9E01	19
Results for Total OH-	7.56E-02 M	± 2.5E-03	3.3

Table 1 - IC, ISE, AIO₂, CO_{3²}, Free OH, TIC / TOC and Total OH Results for the Supernate

^a Average of four sample results.

a)

^b Detection Limit of the Instrument.

3.2 ICP-ES, AA and CV Hg Results for the Supernate

Presented below in Table 2 are the results obtained from the ICP-ES, AA and CV Hg for the supernate. The results in Table 2 are the average of 4 sample results (unless otherwise indicated) and are presented in the units of Molarity (moles/Liter) and mg/L. The standard deviations are provided in the parentheses next to each value and percent relative standard deviation for the values are presented in a separate column.

Element	Molarityª (StDev)	mg/Lª (StDev)	% RSD
Ag	2.55E-06 (± 4.5E-07)	2.76E-01 (± 4.8E-02)	18
Al	3.33E-03 (± 7.2E-05)	9.00E01 (± 1.9E00)	2.2
Bd	<2.0E-04	<2.7E00	
Bae	8.13E-07 (± 9.1E-08)	1.12E-01 (± 1.3E-02)	11
Ca	6.66E-05 (± 1.6E-05)	2.67E00 (± 6.2E-01)	23
Cde	5.11E-07 (± 9.6E-08)	5.74E-02 (± 1.1E-02)	19
Со	3.45E-06 (± 7.18E-07)	2.03E-01 (± 4.2E-02)	21
Cr	5.56E-04 (± 1.12E-05)	2.89E01 (± 5.8E-01)	2.0
Cu	3.60E-06 (± 6.15E-07)	2.29E-01 (± 3.9E-02)	17
Fe ^d	<3.0E-06	<1.90E-01	-
Hg⊳	4.08E-05 (± 2.59E-06)	8.18E00 (± 5.2E-01)	6.3
K¢	3.34E-04 (± 6.79E-06)	1.31E01 (± 2.7E-01)	2.0
Lad	<3.0E-06	<4.96E-01	-
Li	2.98E-05 (±4.53E-06)	2.07E-01 (± 3.1E-02)	15
Mg ^d	<1.58E-05	<3.84E-01	-
Mnª	<8.0E-07	<4.63E-02	-
Mo	6.55E-06 (± 2.5E-07)	6.28E-01 (± 2.4E-02)	3.8
Na	3.61E-01 (± 7.5E-03)	8.29E03 (± 1.7E02)	2.1
Nac	3.51E-01 (± 1.2E-02)	8.07E03 (± 2.8E02)	3.5
Ni	4.39E-06 (± 1.5E-06)	2.58E-01 (± 9.0E-02)	35
Р	1.13E-04 (± 1.2E-05)	3.49E00 (± 3.8E-01)	11
Pb	5.66E-06 (± 1.4E-06)	1.17E00 (± 2.8E-01)	24
Si	9.98E-05 (± 7.5E-06)	2.80E00 (± 2.1E-01)	7.5
Sn	4.02E-06 (± 6.7E-07)	4.77E-01 (± 8.0E-02)	17
Sre	<8.0E-07	<7.45E-02	-
Tie	3.17E-06 (± 4.6E-07)	1.52E-01 (± 2.2E-02)	15
V	4.88E-06 (± 7.4E-07)	2.49E-01 (± 3.8E-02)	15
Znd	<7.0E-06	<4.76E-01	-
Zre	3.20E-06 (± 2.9E-07)	2.92E-01 (± 2.7E-02)	9.1

Table 2 – Concentration of Elements Detected by ICP-ES, AA and CV Hg in the Supernate Presented in Units of Moles/Liter and mg/L

^a Majority of the sample results are determined by ICP-ES unless otherwise indicated. Average of 4 sample results unless otherwise indicated.

^b Result determined by Cold Vapor Hg method.

^c Results determined by AA method

^d Detection Limit of the Instrument

e)

e Average of three sample results only. Fourth sample result was at the detection limit of the instrument.

3.3 ICP-MS and Counting Data Results for the Supernate

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Presented in Table 3 are the results for the ICP-MS and counting data for the supernate. The results in Table 3 are the average of 4 samples (unless otherwise indicated). The standard deviation and the relative standard deviation are provided in parentheses.

Element	Results	Units
Sr-90	7.83E-03 (± 4.0E-03, 54)	μCi/mL
Tc-99⁵	2.68E-01 (± 9.8E-03, 3.7)	mg/L
Cs-137ª	2.44E00 (± 6.6E-02, 2.7)	μCi/mL
U-235 ^{b, c}	3.14E-03 (± 2.0E-04, 6.4)	mg/L
U-238 ^b	4.21E-01 (± 2.6E-02, 6.1)	mg/L
Cs-133 ^b	7.17E-02 (± 7.3E-04, 1.0)	mg/L
Cs-135 ^b	1.14E-02 (± 4.1E-04, 3.6)	mg/L
Cs-137 ^{b,d}	3.21E-02 (± 9.3E-04, 2.9)	mg/L
Total W ^{b, e}	9.65E-02	mg/L
Total Alphaf	1.30E-02 (± 7.3E-04, 5.6)	μCi/mL
Total Beta ^f	2.98E00 (± 1.5E-02, 0.51)	μCi/mL

Table 3 – ICP-MS and Counting Data Results for the Supernate

^a Detected by Gamma Scan.

^b Detected by ICP-MS.

^c Average of only 2 sample results.

^d A trace amount of natural Ba was detected in the supernate. Natural Ba has a small amount of Ba-137 in it; however that amount of Ba-137 was so small that it did not significantly affect the calculation of Cs-137 concentration.

e Values for W isotopes (180, 182-184, and 186) were added together.

^f Tank 50 Liquid Scintillation Method.

In Table 3, Cs-133, Cs-135 and Cs-137 were detected in the supernate by ICP-MS. The known fission yields of Cs-133:Cs-135:Cs-137 are 6.77%:6.60%:6.26% respectively. Normalizing the known fission yields to Cs-133 gives the normalized ratios of 1.00 : 0.97 : 0.93. Using the isotopic Cs results obtained for the supernate of the combined sludge slurry sample (7.17E-02 : 1.14E-02 : 3.21E-02), yields a normalized ratio (normalized to Cs-133) of 1.00 : 0.16 : 0.45. This ratio is in agreement with ratios that were previously calculated for 4 salt tanks (1.00 : 0.14 : 0.57) and Tank 42 sludge slurry supernate (1.00 : 0.22 : 0.61) [1]. Assuming the loss of Cs-137 is solely due to decay, the age of the sludge slurry supernate can be calculated. Based on the ratio of 0.45/0.93 for Cs-137, the average age of the supernate for the combined sludge slurry sample was calculated to be 32 years out of the reactor. This implies that the average age of the sludge slurry could be 32 years old. Note that the concentration of Cs-135 is lower than that expected from its fission yield. The reason for this is that isobaric decay chain to Cs-135 decays first to Xe-135 that has a half life of 9.17 hours and a thermal neutron cross section >1000 barns. It thus has time during the irradiation in a reactor to absorb a neutron and become stable Xe-136. Consequently only a portion of the Xe-135 decays to Cs-135.

3.4 Weight Percent Dissolved Solids Determination for the Supernate of the Combined Sludge Slurry Sample

Four 10 mL samples of supernate were pipetted out of the 100 mL bottle containing the filtered supernate and placed into four labeled stainless steel beakers. These stainless steel beakers were weighed and then placed into a drying oven at 115°C overnight. Three 10 mL samples of 15 wt.% NaCl standard solution were also weighed and dried (in labeled stainless steel beakers) along with the supernate samples to check the accuracy and precision of the method. All of the samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard. The average of the calculated results of the weight percent solids for the supernate and 15 wt. % NaCl standard solution are presented in Table 4. The standard deviations (StDev) and the percent relative standard deviations (% RSD) for the data are also presented in Table 4.

3.5 Density Determinations for the Supernate of the Combined Sludge Slurry Sample

Four density determinations of the supernate sample and three density determinations of a standard (water) were completed in the Shielded Cells Facility. An 8.25 mL heat sealed pipette tip was used to perform the density measurements. The sealed pipette tip was first weighed and then a mixed sample of supernate was pipetted into the sealed pipette. The sealed pipette tip with the supernate sample was weighed and a density calculated. The same steps were followed for the standard. The results of the standard showed good reproducibility and good agreement with the known value of 1 g/mL. The results of the supernate sample and standard are presented in Table 4. The standard deviations (StDev) and the percent relative standard deviations (% RSD) for the data are also presented in Table 4.

Type of Determination	<u>Average of</u> <u>Results</u>	<u>StDev of</u> <u>Results</u>	<u>% RSD of</u> <u>Results</u>
Weight Percent Solids of the Supernate ^a	2.63 wt. %	± 5.0E-02	1.76
Weight Percent Solids of the NaCl Standard ^b	15.07 wt. %	± 2.0E-02	0.13
Density of the Supernate ^a	1.03 g/mL	± 3.8 E-03	0.37
Density of the Standard ^a	1.00 g/mL	± 6.8E-03	0.68

Table 4 – Weight Percent Solid Measurements and Density Measurements for the Supernate and the Standards

^a Average of four results

^b Average of three results

4.0 RESULTS OF ANALYSES PERFORMED ON THE COMBINED SLUDGE SLURRY SAMPLES

Provided below are the results of the analyses for the combined sludge slurry samples. A portion of the mixed sludge slurry sample was taken from the one-liter bottle and dried overnight. This dried sludge slurry was dissolved by the Aqua Regia and Sodium Peroxide/Sodium Hydroxide Fusion methods along with appropriate standards to check the dissolutions and the analytical methods. After performing the dissolution methods on the sludge slurry, the dissolved sludge slurry was diluted prior to the removal from the Shielded Cells Facility. These diluted samples were sent to ADS Sample Receiving for analyses to be performed by ADS. Dilution of the sludge slurry samples was required so that only a small portion of the radioactivity was removed from the Shielded Cells. The dissolution results of the standards for the nonradioactive elemental composition were in good agreement with the known values indicating that the analytical methods were complete and performed correctly.

Presented below in the following sections are the results of the Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES) data, Atomic Adsorption (AA) data, Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) data, Ion Chromatography (IC) data, Ion Selective Electrode (ISE) data, Total Organic Carbon (TOC) data, and counting techniques. Also presented below are the weight percent solids, conversion factor for determining calcined solids, and density determinations of the sludge slurry that was performed in the Shielded Cells Facility.

4.1 ICP-ES, and AA Results for the Combined Sludge Slurry Sample

Presented below in Table 5 are the cation results obtained from the ICP-ES and AA for the dissolved sludge slurry. The results in Table 5 are the average of 8 samples (unless otherwise indicated) and are in the units of weight percent on a dry basis. The standard deviation and percent relative standard deviation for each element are provided in parentheses.

Element	Weight Percent *, a	Element	Weight Percent *, a
Ag ^b	1.85E-02 (± 8.8E-04, 4.8)	Mg	1.15E00 (± 3.9E-02, 3.9)
Al	7.66E00 (± 2.2E-01, 2.9)	Mn	3.30E00 (± 1.2E-01, 3.5)
₿Þ	5.49E-03 (± 1.7E-03, 30)	Mo ^b	4.61E-03 (± 3.5E-04, 7.6)
Ba⁵	4.61E-02 (± 1.3E-03, 2.7)	Na ^ь	5.78E00 (± 2.4E-01, 4.2)
Ca	2.18E00 (± 1.1E-01, 5.0)	Ni	3.41E-01 (± 1.4E-02, 4.0)
Cd	1.10E-01 (± 3.7E-03, 3.4)	Р	6.55E-01 (± 1.6E-01, 24)
Cr	1.32E-01 (± 5.4E-03, 4.1)	Pb⁵	7.48E-02 (± 3.8E-03, 5.1)
Cu	2.97E-02 (± 1.1E-03, 3.8)	Si⁵	1.34E00 (± 1.2E-02, 0.93)
Co ^b	7.64E-03 (± 6.3E-04, 8.2)	Sn⊳	9.60E-03 (± 7.0E-04, 7.3)
Fe	2.15E01 (± 6.9E-01, 3.2)	Srb	1.93E-02 (± 7.1E-04, 3.7)
Hg ^{c, d}	8.61E-01 (± 4.2E-02, 4.9)	TiÞ	1.70E-02 (± 6.1E-04, 3.6)
K ^{d, e}	<5.0E-02	VÞ	7.84E-03 (± 6.6E-04, 8.4)
La ^b	2.13E-02 (± 6.3E-04, 3.0)	Zn⁵	3.60E-02 (± 2.1E-03, 5.8)
Lip	6.57E-03 (± 3.7E-03, 5.7)	ZrÞ	2.13E-02 (± 2.2E-03, 11)

Table 5 – Concentration of Elements Detected by ICP-ES and AA in the Combined Sludge Slurry Sample Presented in Units of Weight Percent

* The sludge slurry sample was dried overnight at 115°C in a drying oven. Results are present on a dry total solids basis.

^a Majority of the results are determined by ICP-ES unless otherwise indicated and are the average of eight sample results.

^b Average of four results only.

Average of three results only.

^d Results determined by AA method.

e Detection Limit of the Instrument.

The TTR requested estimates for Be, TI, and Sb. These were not detected. Based on the detection limits, their concentrations were less than 0.001 wt.% in the dried sludge slurry.

4.2 ICP-MS Results and Counting Data for the Combined Sludge Slurry Sample

Presented in Table 6 are the results for the ICP-MS and counting data for dissolved samples of the dried combined sludge slurry samples. The results in Table 6 are the average of three samples unless otherwise indicated. The standard deviation and the relative standard deviation are provided in parentheses. These data will be used as input to determine the reportable radionuclides for Macro Batch 2. Most of the results in Table 6 are from direct ICP-MS analyses of the dried slurry samples dissolved by aqua regia. The radioactive counting results are from analyses of solutions from both dissolution methods. For some radionuclides whose concentrations were low, special separation techniques were necessary in order to detect and analyze these radionuclides. These techniques will now be discussed for the respective radionuclides.

4.2.1 Separation and Analysis for Pu-241

Pu-241 is a beta emitting Pu isotope that cannot be measured directly in the dissolved sludge slurry solutions because of its low concentration. Pu-241 has a relatively short half-life (15 years). Its concentration was determined by isolating Pu from each solution by a thenoyltrifluoroacteone extraction procedure. The extracted Pu was then analyzed by beta and alpha counting to determine the ratio of beta activity from Pu-241 to the alpha activity from the other isotopes of Pu (Pu-238, Pu-239, Pu-240, and Pu-242). In the original dissolution solutions, the total alpha activity from the Pu isotopes was determined by alpha counting and ICP-MS. Knowing the total alpha activity from Pu in the solutions resulting from the extraction allows the concentration of Pu-241 in the original dissolution solutions to be calculated using the beta/alpha ratio determined in the extracted solution.

4.2.2 Separation and Analyses for Am-243 and Cm-243, Cm-244, Cm-246 and Cm-247

Am-243, Cm-243, Cm-244, Cm-245, Cm-246 and Cm-247 are neutron activation products produced in the SRS reactors. These isotopes are difficult to measure because of their low concentrations in the sludge slurry and the dilutions necessary to get the dissolved slurry samples out of the Shielded Cells. These isotopes were not detected directly in any of the solutions by ICP-MS or any of the radioactive counting techniques. The Analytical Development Section (ADS) has developed a method for isolating Am and Cm in a dissolved sludge slurry solution by using a commercially available ion exchange resin. The resulting solution is then analyzed by gamma spectroscopy for Am-241, Am-243 and Cm-243, alpha spectroscopy for Cm-244, and ICP-MS for Am-241, Am-243, Cm-245, Cm-246 and Cm-247. Cm-245 was not detected, but the other isotopes were.

The concentrations Am-241, Am-243, Cm-243 and Cm-244 in the separation solution were calculated from the gamma and alpha counting data. By knowing the measured ratios of

Table 0 - 101 -110 and counting bata results for the complified sludge sturry sample	Table 6 – ICP-MS and Counting	Data Results for	r the Combined Slud	ge Slurry Sample
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Element	Results	Units*	Element	Results	Units*
C-14 ⁱ	9.91E-08 (± 5.7E-08, 57)	Wt. %	Ba-137°	8 53E-03 (+ 2 9E-04, 3.4)	Wt. %
Ni-59	5.92-05 (± 6.1E-06.10.)	Wt. %	Cs-137ª.b	1.84E-04 (+ 5.6E-06, 3.0)	Wt. %
Ni-631	1.63E-05 (± 1.2E-06.7.1)	Wt. %	Ba -138°	2.43E-02 (+ 4.1E-04, 1.7)	Wt. %
Co-60 ^{a,b}	6.44E-08 (± 4.4E-09, 7,1)	Wt. %	La-139°	1.63E-02 (+ 5.9E-04, 3.6)	Wt. %
Sr-86°	1.29E-03 (± 1.3E-04, 10)	Wt. %	Ce-140 ^c	$6.34E-02 (\pm 8.2E-04, 1.3)$	Wt. %
Sr-87¢	1.67E-03 (± 1.1E-04, 6.3)	Wt. %	Pr-141°	1.43E-02 (+ 4.4E-04, 3.1)	Wt. %
Sr-88°	1.67E-02 (± 2.5E-04, 1.5)	Wt. %	Ce-142 ^c	2.10E-02 (± 3.7E-04, 1.8)	Wt. %
Y-89°	7.17E-03 (± 1.8E-04, 2.5)	Wt. %	Nd-143°	1.25E-02 (±3.1E-05; 0.25)	Wt. %
Sr-90 ^d	3.10E-03 (± 7.9E-05, 2.5)	Wt. %	Nd-144°	1.48E-02 (± 2.4E-04, 1.6)	Wt. %
Sr/Zr-90°	4.99E-03 (± 7.6E-04, 15)	Wt. %	Nd-145°	8.90E-03 (± 1.5E-04, 1.7)	Wt. %
Zr-91°	2.12E-03 (± 5.9E-04, 28)	Wt. %	Nd-146°	7.44E-03 (± 2.9E-04, 3.8)	Wt. %
Zr-92°	2.23E-03 (± 6.3E-04, 28)	Wt. %	Sm-147°	4.45E-03 (± 8.2E-05, 1.9)	Wt. %
Zr-93¢	3.27E-03 (± 9.9E-04, 30)	Wt. %	Nd-148°	4.51E-03 (± 2.6E-04, 5.8)	Wt. %
Zr-94°	2.32E-03 (± 5.2E-04, 22)	Wt. %	Sm-149°	2.41E-04 (± 2.3E-05, 9.7)	Wt. %
Mo-95°	2.91E-04 (± 6.3E-06, 2.2)	Wt. %	Nd-150°	3.85E-03 (± 1.2E-04, 3.1)	Wt. %
Zr-96°	2.60E-03 (± 7.5E-04, 29)	Wt. %	Sm-151°	2.40E-04 (± 2.2E-05, 9.0)	Wt. %
Mo-97°	3.32E-04 (± 2.5E-08, 0.007)	Wt. %	Sm-152°	1.20E-03 (± 6.5E-05, 5.4)	Wt. %
Mo-98°	2.98E-04 (± 1.4E-05, 4.7)	Wt.%	Eu-154ª,b	3.89E-06 (± 1.2E-07, 3.2)	Wt. %
Tc-99°	1.10E-03 (± 6.7E-05, 6.1)	Wt. %	Eu-155ª,b	3.12E-07 (± 5.1E-08, 16)	Wt. %
Mo-100°	4.72E-04 (± 1.1E-04, 24)	Wt. %	Th-232 ^{c,f}	3.10E-01 (± 1.4E-02, 4.6)	Wt. %
Ru-101°	8.72E-03 (± 5.4E-04, 6.2)	Wt. %	U-233 ^{c,g}	4.52E-04 (± 1.8E-05, 4.0)	Wt. %
Ru-102°	8.57E-03 (± 2.1E-04, 2.5)	Wt. %	U-234 ^{c,g}	4.65E-04 (± 4.3E-05, 9.2)	Wt. %
Rh-103°	4.97E-03 (± 5.2E-05, 1.0)	Wt. %	U-235 ^{c,(}	1.30E-02 (± 4.8E-04, 3.7)	Wt. %
Ru-104º	4.50E-03 (± 1.5E-04, 3.2)	Wt. %	U-236 ^{c,1}	1.14E-03 (± 8.4E-05, 7.4)	Wt. %
Pd-105°	6.74E-04 (± 6.9E-05, 10)	Wt. %	Np-237¢,f	1.83E-03 (± 9.6E-05, 5.3)	Wt. %
Cd-106°	1.89E-03 (± 2.2E-04, 12)	Wt. %	U-238 ^{c,f}	1.92E00 (± 7.9E-02, 4.1)	Wt. %
Ag-107¢	7.24E-03 (± 1.9E-04, 2.6)	Wt. %	Pu-238 ^h	5.81E-04 (± 4.8E-05, 8.3)	Wt. %
Cd-108º	1.13E-03 (± 1.1E-04, 9.8)	Wt. %	Pu-239⁰	7.87E-03 (± 2.6E-04, 3.3)	Wt. %
Ag-109°	6.74E-03 (± 2.6E-04, 3.8)	Wt. %	Pu-240⁰	7.82E-04 (± 7.5E-05, 9.5)	Wt. %
Cd-110°	1.31E-02 (± 6.7E-04, 5.1)	Wt. %	Pu-241 ⁱ	2.75E-05 (± 2.9E-06, 11)	Wt. %
Cd-111°	1.31E-02 (±7.1E-04, 5.4)	Wt. %	Pu-242⁰	9.41E-05 (± 1.7E-05, 18)	Wt. %
Cd-112°	2.47E-02 (± 1.5E-03, 6.0)	Wt. %	Am-241ª	1.94E-04 (± 1.1E-05, 5.1)	Wt. %
Cd-113º	1.20E-02 (± 7.3E-04, 6.0)	Wt. %	Am-243 ⁱ	2.84E-05 (± 2.4E-06, 8.6)	Wt. %
Cd-114º	2.78E-02 (± 1.0E-03, 3.6)	Wt. %	Cm-243 ⁱ	2.72E-07(± 1.0E-08, 3.8)	Wt. %
Sb-125 ^{a,e}	2.58E-08 (± 3.0E-9, 13)	Wt. %	Cm-244 ⁱ	5.46E-06 (± 3.3E-07, 6.1)	Wt. %
I-127¢	1.26E-03 (± 6.0E-05, 4.8)	Wt. %	Cm-246 ^{i,e}	1.32E-05	Wt. %
I-129ª,i	6.16E-04 (± 2.1E-04, 34)	Wt.%	Cm-247 ^{i,e}	2.48E-06	Wt. %
Cs-133º	6.49E-04 (± 4.9E-05, 7.5)	Wt. %	Total Alphai	1.16E02 (± 5.5E00, 4.8)	μCi/g
Ba-134º	9.16E-04 (± 2.6E-05, 2.8)	Wt. %	Total Betai	9.06E03 (± 3.1E02, 3.4)	μCi/g
Ba-135⁰	9.94E-04 (± 8.8E-05, 8.8)	Wt. %			
Ba-136°	1.15E-03 (± 4.6E-05, 4.0)	Wt. %			

* The sludge slurry was dried overnight at 115°C in a drying oven. All results presented on a dry total solids basis.

^a Detected by Gamma Scan.

^b Average of eight results.

° Detected by ICP-MS.

^d Sr-90 Method. Average of four results.

e Only one value obtained.

[†] Average of four results.

9 Average of two results.

^h Calculation based on Total Alpha results.

ⁱ Special separation technique. See Section 4.2 for explanation.

1 Tank 50 Liquid Scintillation Counting Method.

k Values taken from WSRC-RP-98-01400 [8] and multiplied by sludge dilution factor of 3.0 to convert from a glass basis to a dry sludge slurry basis. Am-243, Cm-243 and Cm-244 to the Am-241 in that solution and knowing an accurate concentration of Am-241 in the original sludge slurry solution by gamma counting, the concentrations of these isotopes in the original sludge slurry solution could be calculated. The results of the ICP-MS analysis gave the concentrations of Am-241, Am-243, Cm-244, Cm-246 and Cm-247 in the separation solution. Again knowing the ratio of Am-241 in the separation solution to that in the original sludge slurry solution allowed the concentration of Am-243, Cm-244, Cm-246 and Cm-247 to be calculated in the original sludge slurry dissolution. The results for Am-243 by the two methods (gamma counting and ICP-MS) agreed within 4%. The results for Cm-244 by the two methods (alpha counting and ICP-MS) agreed within 10%. This good agreement supports the reliability of the analytical method.

4.2.3 Separation and Analysis for C-14

C-14 is a beta emitter with a half life of 5730 years that could have been produced in the SRS reactors from a neutron-proton displacement reaction with N-14. This reaction involves hitting N-14 with a neutron so that it releases a proton to form C-14. In order to detect C-14 in the waste a special separation technique was developed by ADS [9]. In this method samples of dried sludge slurry were dissolved with HNO₃ in glass vessels that were inside sealed Teflon pressure vessels. The Teflon pressure vessels each had a basic solution in the bottom of the vessel which acted as a capture agent for the carbon dioxide which was generated from the dissolving the sample. The basic solutions were then transferred from the Shielded Cells and purified further. The base was acidified and the liberated carbon dioxide was captured in an amine-based capture agent. The agent was then slurried over into a liquid scintillation cocktail and analyzed by liquid scintillation analysis. A C-14 spike solution was run through the process in parallel with the sample and the sample was run in triplicate. The C-14 recovery result from the spike solution was used to correct the sample results for the separation yield. Based on the concentration of the spike, the C-14 recovery was 25%. A blank was also run in sequence with the samples. Results for the blank indicated that it contained a negligible amount of C-14. The liguid scintillation spectra of the three samples clearly indicated the presence of C-14 based on detection and counting to the characteristic C-14 beta particles that have an average energy of 0.0495 MeV and a maximum energy of 0.1565 MeV. The spectra were solely due to C-14 and were clear of any beta activity from other radioactive isotopes.

4.2.4 Separation and Analysis for I-129

I-129 is a long lived fission product ($t_{1/2}$ = 1.6E07 years) that emits beta particles and gamma rays. I-129 was not detected by the ICP-MS or gamma counting in the dissolved dried sludge slurry samples because its concentration was too low. ADS then developed a special procedure to determine the I-129 present [10]. Three samples of the dried sludge slurry were dissolved in presence of a known amount of KI carrier. The resulting solution was further treated to remove Cs-137 and actinide elements. The solution was then treated with AgNO₃ in order to precipitate the iodide ion as AgI. The precipitate was removed from the Shielded Cells and counted by gamma spectroscopy to determine the amount of I-129 present. I-129 was detected by its characteristic gamma ray.

The amount of I-129 recovered in the dissolution and precipitation processes was determined by comparing the amount of iodide ion added originally and the amount precipitated. This analysis was performed by neutron activation. The average and standard deviation of the three results for I-129 are presented in Table 6. It was determined, however, that the complete separation of I-129 from the other gamma emitters in the sludge slurry was not achieved. Consequently, the value in Table 6 may be biased high.

4.2.5 Separation and Analysis for Ni-59 and Ni-63

This separation is based on isolation of Ni from the dissolved sludge using a column containing dimethylglyoxime as an extractant. Details of this technique have been reported [8]. Nickel was then eluted from the extractant. The Ni-59 was measured by its characteristic x-rays and Ni-63 by its beta particles. Total Ni in the eluted sample was measured by ICP-ES. This was compared to the total Ni measured in the dried sludge slurry (see Table 5) to calculate the total Ni-59 and Ni-63 in the dried slurry.

4.2.6 Separation and Analysis for Sn-121m

The fission product Sn-121m with its 55 year half life needs to be considered as a reportable radionuclide. Its concentration could not be measured in the dried sludge slurry because of its low concentration in the solids. The concentration of Sn-121m was estimated based on the measured ratio Sn-121m activity to Sn-126 activity. This ratio was measured on a sample of HLW salt supernate using a low energy gamma analysis. This analysis was carried out on a sample of SRS Waste Tank 37 supernate which had been pre-treated to reduce Cs-137 levels. This pretreatment took enough Cs-137 out supernate so that the radioactive Sn isotopics in this SRS supernate could be measured using the low energy gamma assay. The Sn-121m activity was determined from the 37.2 keV gamma ray, and verified from the 26.2 and 29.7 keV x-rays arising from the decay to Sn-121m to Sb-121. The Sn-126 activity was determined from the 64.3 keV gamma ray, and the 86.94 and 87.57 keV gamma–ray multiplet. From that measurement, an activity ratio of Sn-121m/Sn-126 was 81.

The experimentally determined activity ratio was then used to calculate the activity of Sn-121m in the dried slurry by knowing the activity of Sn-126 in the dried slurry. The Sn-126 activity was calculated from the estimated concentration (wt%) of Sn-126 in the dried slurry. The method for calculating this estimate is described later in Section 6.1. The concentration of Sn-121m was then calculated using its activity in the dried slurry.

4.3 Weight Percent Total Solids Determination for the Combined Sludge Slurry Sample

Four 10 mL samples of mixed sludge slurry were pipetted out of the one-liter container and placed into four labeled platinum crucibles. These platinum crucibles were weighed and then placed into a drying oven at 115°C overnight. Three 10 mL samples of 15 wt.% NaCl standard solution were also weighed and dried (in labeled stainless steel beakers) along with the sludge slurry samples to check the accuracy and precision of the method. All of the samples were removed from the oven and were allowed to cool for ~5 minutes before they were weighed. The calculated results of the weight percent solids for the sludge slurry and 15 wt. % NaCl standard solution are presented in Table 7. The results of the standard solutions showed good reproducibility and good agreement with the known value of the standard.

4.4 Factor for Determining Calcined Solids for the Combined Sludge Slurry Sample

The dried sludge slurry from the weight percent solids determination was used for determining the calcine factor for the sludge slurry. The platinum crucibles containing the dried sludge slurry were first weighed and then placed into a muffle furnace that had been heated to 650°C. The crucibles were heated for 15 minutes, removed from the furnace and allowed to cool. The crucibles were weighed and a calcine conversion factor was calculated.

The calcine conversion factor is used to convert an element in the sludge slurry on a dry basis to a weight percent calcined solids basis. Once the calcined solids for the sludge slurry have been calculated and the amount of frit oxides needed to make glass is known, a waste loading calculation for the glass can be completed. The results of the calcine conversion factor are presented in Table 7.

4.5 Density Determinations for the Combined Sludge Slurry Sample

Four density determinations of the combined sludge slurry sample and three density determinations of a standard were completed in the Shielded Cells Facility. An 8.25 mL heat sealed pipette tip was used to perform the density measurements. The sealed pipette tip was first weighed and then a mixed sample of sludge slurry was pipetted into the sealed pipette. The sealed pipette tip with the sludge slurry sample was weighed and a density calculated. The same steps were followed for the standard. The results of the standard showed good reproducibility and good agreement with the known value. The results of the combined sludge slurry sample and standard are presented in Table 7.

Table 7. – Weight Percent Total Solid Measurements, Calcined Solids Conversion Factor and Density Measurements for the Combined Sludge Slurry Sample and the Standards

<u>Type of Determination</u>	<u>Average of</u> <u>Results</u>	<u>StDev of</u> <u>Results</u>	<u>% RSD of</u> <u>Results</u>
Weight Percent Total Solids of the Sludge Slurry ^a	18.80 wt. %	± 5.50E-02	0.29
Weight Percent Solids of the NaCl Standard ^b	15.11 wt. %	± 1.20E-02	0.08
Calcined Solids Conversion Factor ^a	8.48E-01	± 7.10E-03	0.84
Density of the Sludge Slurryª	1.10 g/mL	± 1.41 E-02	1.28
Density of the Standard ^{a, c}	1.00 g/mL	± 6.8E-03	0.68

^a Average of four results

^b Average of three results

^c Same value as in Table 4.

4.6 Calculation of Weight Percent Soluble Solids and Weight Percent Insoluble Solids for the Combined Sludge Slurry Sample

The soluble and insoluble weight percent solids can be calculated by using the following equations [2] once the weight percent total solids and dissolved solids have been obtained.

Equation 1: $W_{is} = (W_{ts} - W_{ds}) / (1 - W_{ds}) [2]$

Equation 2: $W_{ss} = W_{ts} \cdot W_{is}$ [2]

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

Substituting the values of the known components

 $W_{ds} = 0.0263$ $W_{ts} = 0.188$ $W_{is} = ?$ $W_{ss} = ?$

Solving Equation 1:

 $W_{is} = (0.188 - 0.0263) / (1 - 0.0263)$

 $W_{is} = 0.166$

Converting to weight percent (multiply 100):

W_{is} = 16.6 wt %

Solving Equation 2:

 $W_{ss} = W_{ts} - W_{is}$

 $W_{ss} = 0.188 - 0.166$

 $W_{ss} = 0.022$

Converting to weight percent (multiply 100):

 W_{ss} = 2.20 wt. %

4.7 Calculation of Total Noble Metals Concentrations in Macro Batch 2 (Sludge Batch 1B)

The noble metals in Macro Batch 2 sludge are Ru, Rh, Pd, and Ag. All of these resulted from the fission of U-235 in the SRS reactors while they were operating. Results indicated that there was also natural Ag and natural Cd in the Macro Batch 2 sludge. The Ag resulted from Ag being used to scavenge fission product iodine when irradiated reactor fuels and targets were dissolved. Cadmium was used in some reactor targets as a neutron absorber. The metals Ru, Rh, and Pd were never used in any chemical processes at the site; thus, they resulted in the waste only from being formed in the reactors by fission of U-235. The total Ru and total Pd in the waste are comprised of more than one isotope while Rh has only one. The total Ru in the sludge consists of the three nonradioactive isotopes, Ru-101, Ru-102, and Ru-104. Thus the total Ru concentration is the sum of the concentrations of these three isotopes measured by the ICP-MS (see Table 6). The single isotope for Rh is Rh-103. The total Pd is comprised of five isotopes. These are Pd-105, Pd-106, Pd-107, Pd-108, and Pd-110. Of these, only the Pd-107 is radioactive. Because of natural Ag and also natural Cd being in the Tank 7 sludge, only one Pd isotope, Pd-105, could be measured in Macro Batch 2 samples. Isotopes of natural Ag and Cd have masses of 106,107,108, and 110 and thus interfere with the ICP-MS determination of the Pd isotopes at these masses. The concentrations of each of the isotopes of Pd that could not be measured was calculated by multiplying the measured concentration of Pd-105 by the ratio of the fission yield for that specific isotope relative to the fission yield for Pd-105. The total Pd is then the sum of these five concentrations. The total Ag is comprised of isotopes with masses 107 and 109. The total concentration of Ag is then the sum of the measured concentrations of Ag-107 and Ag-109. The isotopic distribution of the Ag agreed very well with the distribution for natural Ag. The total concentration of each noble metal for Macro Batch 2 sludge is given in Table 8.

Metal	Results
Ru	2.18E-02
Rh	4.97E-03
Pd	1.11E-03
Ag	1.40E-02

Table 8 – Total Noble Metal Concentration in Macro Batch 2 (Sludge Batch 1B) (Weight Percent based on Total Solids in the Dried Slurry)^a

*See Table 6 in Section 4.2 for results of the individual isotopes of the noble metals.

5.0 FISSION YIELD SCALING FACTOR (FYSF) AND U-235 FISSION PRODUCTS MEASURED IN THE COMBINED SLUDGE SLURRY SAMPLE

The FYSF is used to estimate concentrations of U-235 fission products that may be reportable but cannot be detected. In order to calculate the FYSF, as many as possible of the U-235 fission products were measured in the four sludge slurry samples. The fission products in SRS high level waste primarily result from the fission of U-235 used in the SRS reactors to make neutrons or of the U-235 in the uranium irradiated to make Pu-239. The relative amounts (fission yields) of these products occur in a low and a high mass fraction and their yields are well known from many studies. A compilation of these yields has been published [11]. The measured concentrations of the low mass fission products measured in the sludge slurry are plotted as solid circles in Figure 1 as a function of mass number. Results for the high mass fission products appear in Figure 2. All the concentrations in both Figures were measured by ICP-MS. The solid squares in both Figures are the weight percent concentration for the fission product of that mass calculated using the FYSF. Determination of this factor for sludge slurry will be discussed later.

Assignment of specific isotopes to these mass numbers is done by considering the half lives of the various radionuclides in the respective isobaric fission chains from fission of U-235. The isotopes in each of these chains are originally neutron rich immediately after the fission. They then beta decay - increasing in atomic number while the atomic mass remains constant. In each chain usually the element with the longest half life is assigned to that mass. These assignments have been discussed in four other publications [1, 12, 13 & 14] where the fission product concentrations in the sludges in two other SRS waste tanks as well as Tank 51 were measured and presented in the same format.

Calculation of the fission yield scaling factor will now be discussed. The FYSF is simply a factor that relates the concentration of a fission product to its fission yield and the atomic mass of the fission product. The atomic mass has to be included in the equation because fission yields are given in terms of atoms produced per 100 fissions of U-235 and the FYSF is defined in terms of weight percent. The equation for the concentration is then

Concentration (wt%)=FYSF (fission yield X atomic mass)

Thus the FYSF for each isotope can be calculated from the equation

FYSF=wt%/(fission yield X atomic mass)

For those isotopes that meet following five criteria this factor should be a constant. The isotopes had to have low solubilities in NaOH and thus occur predominantly in the sludge. They had to have long half lives and thus had not decayed significantly since the waste was generated. The isotopes had to have low neutron cross sections and thus were not transmuted in the SRS reactors during their operation. The isotopes could not be formed in the reactors by neutron absorption. Lastly, the isotopes had to have masses where interferences such as those from oxides formed in the Ar plasma did not create a problem. Eleven isotopes meet these criteria. These isotopes are Ru-101, Ru-102, Rh-103, La-139, Pr-141, Nd-143, 144, 145, 146, Sm-147, and Nd-148. Note that isotopes from both the low mass and high mass fractions of the fission of U-235 are included. The fission yield scaling factor for each isotope was calculated. The average FYSF based on the eleven isotopes was 1.67E-05±1.9E-06 wt%/(fy atomic mass) with a 11% RSD.

For the eleven isotopes that meet the above five criteria, the measured concentration agree well with the calculated as expected for both the low and high masses in Figures 1 and 2. For the other isotopes the measured concentrations are above or below the calculated concentrations. Those measured concentrations that are significantly above the scaled fission yields in the Figures indicate that something of this mass had been added to waste that is in the this tank. For those isotopes that are below, they may be soluble in caustic and be primarily in the salt tanks at SRS or they may have appreciable thermal neutron cross sections and be transmuted while being irradiated in the SRS reactors.









In Figure 1 for the low mass fission products, the disagreement at masses 86, 87, and 88 resulted from natural Sr in the sludge possibly added as an impurity with the NaOH during processing at SRS. The low concentrations at masses 90, 91, 92, 94 and 96 have the relative concentrations of isotopes in natural Zr. The concentrations at masses 95, 97, and 98 follow the relative abundances for natural Mo rather than fission product Mo. Perhaps natural Mo had been added to the tank from some processing impurity. The deviations from this curve at masses 106 to 112 are due to natural isotopes of Ag and Cd being present in the waste. Silver results from the silver saddles that that were used to scavenge radioactive iodine isotopes released when the fuel or targets were dissolved at SRS. Cadmium was used in some instances in the SRS reactors to shape the neutron energy spectrum. The Cd was then dissolved with the fuel or target rods and eventually added to the waste.

In Figure 2 for the high mass fission products, the isotopes at masses 136, 137, and 138 correspond to natural Ba. Perhaps a small amount of Ba was added as an impurity with some process chemical. The concentration at mass 137 is too high to be only the natural Ba. Isotopes at this mass could also be Cs-137 and Ba-137 resulting from decay of Cs-137 ($t_{1/2}$ = 30 years). The concentrations at masses 140 and 142 are in proportion to the abundance of Ce-140 and 142 in natural Ce, again possibly added as an impurity. The concentrations at masses 149 and 151 result from Sm-149 and Sm-151. Their concentrations are lower than the scaled fission yield because they have been transmuted in the SRS reactors due to their large isotopic thermal neutron absorption cross sections. This accounts for the relatively high concentrations of Sm-150 and Sm-152 compared to the scaled fission yield curve. At masses 153 and above, the concentrations do not agree with the scaled fission yields due to the contributions of the heavy metal oxides formed in the plasma. For example, 138 BaO+ with a total mass of 154 contributes to the response at this mass and makes the measured concentration at the mass higher than the predicted concentration of Sm-154. Also, 139 LaO+ with a total mass of 155 contributes to the response at this mass 104 is slightly above the calculated value, possibly due to the formation of the 88 SrO+ ion with a mass of 104.

6.0 IDENTIFICATION AND DETERMINATION OF REPORTABLE RADIONUCLIDES FOR MACRO BATCH 2

In order to determine the reportable radionuclides for Macro Batch 2, a list of radioisotopes that may meet the criteria as specified by the Department of Energy's (DOE) Waste Acceptance Product Specification (WAPS) was developed [4]. All radioactive U-235 fission products and all radioactive activation products that could be in the SRS HLW were considered. The WAPS states that all "significant" long-lived radioisotopes must be quantified for all waste packages that will be stored in a Federal Repository [4]. "Significant" refers to radioisotopes that have a half-life longer than 10 years and contribute greater than 0.05% of the total radioactivity (Becquerels or Curie basis) during the first 1100 years after production. The DWPF's Waste Form Compliance Plan (WCP) has extended the criteria to include all radioisotopes that have a half-life longer than 10.01% of the total radioactivity during the first 1100 years after glass production [3].

Table 9 presents the list of radioisotopes considered for the determination. The list was derived from the analysis of the combined sludge slurry, and the estimation of certain radioisotopes (see Section 6.1), that may be in the sludge slurry but could not be detected by current techniques. Some of the radioisotopes could be deleted from the list in Table 9 using the previous arguments as established by reference 15. The radioisotopes that were deleted from the list and the arguments that support that decision are presented in Table 10.

Radioisotope	Radioisotope	Radioisotope	Radioisotope
C-14ª	Sn-126 ^b	Ac-227d	Pu-241ª
Ni-59ª	I-129 ^b	Th-229d	Pu-242 ^a
Co-60ª	Cs-135 ^b	Th-230d	Am-241ª
Ni-63ª	Cs-137 ^b	Pa-231d	Am-242m ^a
Se-79 ^b	La-138 ^{b,c}	Th-232°	Am-243ª
Rb-87 ^b	Ce-142 ^{b,c}	U-232ª	Cm-243ª
Sr-90 ^b	Nd-144 ^{b,c}	U-233ª	Cm-244 ^a
Zr-93 ^b	Sm-147 ^{b,c}	U-234d	Cm-245ª
Nb-93m ^b	Sm-149 ^{b,c}	U-235°	Cm-246 ^a
Nb-94ª	Nd-150 ^{b,c}	U-236ª	Cm-247ª
Zr-96 ^{b,c}	Sm-151 ^b	Np-236 ^a	Cm-248ª
Tc-99 ^b	Eu-152 ^{a,b}	Np-237a	Cf-250 ^a
Cd-113 ^{b,c}	Eu-154 ^{a,b}	U-238°	
Pd-107 ^b	Bi-210m ^d	Pu-238ª	
In-115 ^{b,c}	Pb-210 ^d	Pu-239ª	
Sn-121mb	Ra-226 ^d	Pu-240ª	

Table 9 - List of Radioisotopes Considered for Macro Batch 2

a Activation Product

^b Fission Product

^c Naturally Occurring Radionuclide that Resulted in the Waste from Processing at SRS

^d Decay Product of an Actinide Isotope in SRS Waste

Radioisotope	Radioisotope		
Nb-941	Eu-1521		
Zr-96 ²	Np-236 ³		
La-138 ²	U-2324		
Ce-142 ²	Am-242m ³		
Nd-144 ²	Cm-245 ⁵		
Sm-147 ²	Cm-248 ⁵		
Sm-149 ²			

Table 10 – Radioisotopes Not Considered for the Determination of Reportable Radioisotopes for Macro Batch 2

- 1. "Nb-94 and Eu-152 are shielded isotopes: the isobaric fission product decay chain for these stops at a stable isotope before reaching these. They are therefore produced predominately by secondary processes, and are present only in very small amounts. They have not been observed in the sludge slurry"[15].
- 2. Zr-96, La-138, Ce-142, Nd-144, Sm-147 and Sm-149 were deleted because their long half -lives (> 1.05E11 years) make their activities negligible at all times [15].
- 3. "No data was available for Np-236 or Am-242m, but these are known to be made in only very small amounts in reactor irradiations. Np-236 is a minor product of fast neutron spallation; Am-242m can be produced from neutron capture in Am-241, but has a high cross-section for neutrons and is rapidly removed. Both were neglected" [15].
- 4. "U-232 is present only in very small amounts and decays rapidly compared to other actinide isotopes that are much more abundant (It is primarily obtained as a contaminant at a few ppm from the reactor irradiation of Th-232)" [15].
- 5. Cm-245 and Cm-248 were deleted from the list due to the inability of the ICP-MS to detect these isotopes (used the special separation techniques as discussed in Section 4). This indicates the distribution of Cm for Macro Batch 2 is different than that assumed for Macro Batch 1. However if Cm-245 and Cm-248 are detected during analysis of a DWPF glass pour stream sample from Macro Batch 2, a revision to this report will be made at that time. This scenario is unlikely due to the Cm isotopes being diluted (factor of 3) by the addition of frit during the vitrification process.

6.1 Estimation of Se-79, Rb-87, Nb-93m, Pd-107, In-115, Sn-121m, Sn-126, Cs-135, Th-230 and Cf-250 Concentrations in the Combined Sludge Slurry Sample

Some of the radioisotopes in the sludge slurry can not be detected by available instrumentation for one or more of the three following reasons:

- 1. The isotopes have low concentrations and can not be detected by analytical instruments as a result of the dilution of the samples.
- 2. There is an interference of another isotope at the same mass.
- 3. The isotope cannot be detected due to its long half-life and thus its low specific activity.

When an isotope fits the one of the three criteria listed above, an estimate of the concentration of the isotopes must be made by calculating concentrations based on the information available. Presented in Table 11 are the values estimated for Se-79, Rb-87, Nb-93m, Pd-107, I-115, Sn-121m, Sn-126, Cs-135, Th-230 and Cf-250 for the combined sludge slurry sample.

Element	Results	Units
Se-79ª	<5.97E-05	Wt. %
Rb-87ª	3.74E-03	Wt. %
Nb-93m ^b	2.28E-08	Wt. %
Pd-107°	1.03E-04	Wt. %
In-115ª	2.43E-05	Wt.%
Sn-121m ^d	<2.15E-06	Wt.%
Sn-126 ^a	<1.25E-04	Wt. %
Cs-135 ^e	6.54E-05	Wt.%
Th-230 ^f	4.70E-08	Wt. %
Cf-2509	2.60E-08	Wt.%

Table 11 - Values Estimated for Se-79, Rb-87, Nb-93m, Pd-107, I-115, Sn-121m, Sn-126, Cs-135, Th-230 and Cf-250 Concentrations for the Combined Sludge Slurry Sample Assuming the Sludge Slurry is Approximately 32 Years Old

^a Calculated by multiplying the fission yield (a known yield value from the fission of U-235) by the average of the fission yield scaling factor (FYSF) and the atomic mass of the fission product. The average FYSF is determined by calculating a FYSF (wt%/(fisson yield X atomic mass) for appropriate low and high mass fission products (See Section 5.0). This calculation can give only an upper limit for the concentration. (See discussion in Reference 1.)
 ^b Daughter of decay of Zr-93. Calculated assuming the waste is 32 years out of the reactor.

^c Calculated by multiplying the measured concentration of Pd-105 by the ratio of fission yields for Pd-105 and Pd-107.

Equation: wt% Pd-105 (FY Pd-107/Fy-105)

^d Calculated as described in Section 4.2.6 using the measured ratio of Sn-121m activity to the Sn-126 activity and the upper limit for the weight percent estimated for Sn-126.

^e The ratio of Cs-135:Cs-137 was used to calculate the amount of Cs-135 in the combined sludge slurry sample. See the discussion after Table 3 on page 12.

f Th-230 grows into the waste as a decay product of U-234. The concentration was calculated using the appropriate decay calculation assuming the average age of the waste is 32 years old.

9 Estimated by adding Cm distribution (wt.%) and multiplying by 1.0E-03 as indicated in reference 15.

6.2 Identification of Reportable Radionuclides

The complete list of radionuclides and their activities that were considered in the determination of reportable radionuclides are provided in Table 12. For those radionuclides with measured concentrations, the initial activities were calculated by using the weight percent reported for each radioisotope (converted to number of atoms), and its half-life by the following equation: $A_0 = N_0 \cdot \lambda$ where: A_0 = Initial Activity, N_0 = initial number of atoms, and λ = 0.693/half-life [16].

Several radionuclides were not included in Table 12 due to their very low concentrations and insignificant activities. These included Rb-87 (5.97E-03 wt% and a half-life of 4.90E+10 years), Cd-113 (1.20E-02 wt% and a half-life of 9.3E+15 years), In-115 (2.43E-05 wt% and a half-life of 4.40E+15 years), Th-230 (4.70E-08 wt% and a half-life of 7.70E+04 years), and Cf-250 (2.60E-08 wt% and a half-life of 13.08 years).

Radionuclide	Curies per	Bequerels per
	Kilogram	Kilogram
C-14	4.41E-06	1.63E+05
Ni-59	4.78E-05	1.77E+06
Co-60	7.27E-04	2.69E+07
Ni-63	8.42E-03	3.12E+08
Se-79	4.16E-05	1.54E+06
Sr-90	4.24E+00	1.57E+11
Zr-93	8.22E-05	3.04E+06
Tc-99	1.88E-04	6.96E+06
Pd-107	5.30E-07	1.96E+04
Sn-126	1.42E-05	5.27E+05
I-129	1.09E-06	4.02E+04
Cs-135	7.54E-07	2.79E+04
Cs-137	1.59E-01	5.90E+09
Sm-151	6.32E-02	2.34E+09
Eu-154	1.05E-02	3.89E+08
Th-232	3.41E-07	1.26E+04
U-233	4.35E-05	1.61E+06
U-234	2.89E-05	1.07E+06
U-235	2.81E-07	1.04E+04
U-236	7.38E-07	2.73E+04
Np-237	1.29E-05	4.77E+05
U-238	6.46E-06	2.39E+05
Pu-238	9.95E-02	3.68E+09
Pu-239	4.89E-03	1.81E+08
Pu-240	1.78E-03	6.57E+07
Pu-241	2.84E-02	1.05E+09
Am-241	6.65E-03	2.46E+08
Pu-242	3.73E-06	1.38E+05
Am-243	5.65E-05	2.09E+06
Cm-243	1.41E-04	5.20E+06
Cm-244	4.43E-03 ·	1.64E+08
Cm-246	4.05E-05	1.50E+06
Cm-247	2.30E-09	8.51E+01
TOTAL	4.82E+00	1.78E+11

Table 12 – List of Radionuclides and Activities used as Input to the Radioactive Decay Calculator.

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The initial activities for 33 isotopes were entered into the "**Radioactive Decay Calculator**" [17] and the results of calculations with time periods 16 years (2015) and 1116 years (3115) are presented in Tables 13 and 14. Those radionuclides that are reportable are indicated by a yes in the reportable column. Additional calculations were performed for every 200 years up to 1116 years. The results of these calculations have not been included in this report. Excel spreadsheets were used to calculate the total activity (Curies/Kilogram of dried sludge slurry) at each time and the percent of the activity that each of the radionuclides contributed.

One of the radionuclides (Sn-121m) is not part of the database within the **"Radioactive Decay Calculator**". Consequently, the calculations for the decay of Sn-121m, with a half-life of 55 years, were performed separately and then added to the output of the Calculator for each calculation.

The calculations performed by the "**Radioactive Decay Calculator**" and the calculation for Sn-121m were verified by R. A. Sigg [18] using a a separate program called "**RadDecay for Windows**"[19]. A comparison between the output of the two programs showed equivalence for all of the reportable radionuclides out to 3115.

Table 13. Activities in Curies/Kilogram of Dried Sludge in Year 2015

Instance	Curies	Fraction	
Isotopes	per Kg	of Activity	керопаріе
C-14	4.40E-06	7.15E-07	
Ni-59	4.78E-05	7.77E-06	
Co-60	8.87E-05	1.44E-05	
Ni-63	7.54E-03	1.22E-03	yes
Se-79	4.16E-05	6.76E-06	
Sr-90	2.88E+00	4.67E-01	yes
Y-90	2.88E+00	4.68E-01	_
Zr-93	8.22E-05	1.34E-05	
Nb-93m	4.37E-05	7.11E-06	
Tc-99	1.88E-04	3.05E-05	
Pd-107	5.30E-07	8.61E-08	
Sn-121m	9.43E-04	1.53E-04	yes
Sn-126	1.42E-05	2.31E-06	
Sb-126m	1.42E-05	2.31E-06	
Sb-126	1.99E-06	3.23E-07	
1-129	1.09E-06	1.77E-07	
Cs-135	7.54E-07	1.23E-07	
Cs-137	1.10E-01	1.79E-02	yes
Ba-137m	1.04E-01	1.69E-02	
Sm-151	5.59E-02	9.08E-03	yes
Eu-154	2.98E-03	4.84E-04	
Th-232	3.41E-07	5.54E-08	
Ra-228	2.91E-07	4.73E-08	
Ac-228	2.91E-07	4.73E-08	
Th-228	2.67E-07	4.34E-08	
Ra-224	2.67E-07	4.34E-08	
Rn-220	2.67E-07	4.34E-08	
Po-216	2.67E-07	4.34E-08	
Pb-212	2.67E-07	4.34E-08	
Bi-212	2.67E-07	4.34E-08	
TI-208	9.60E-08	1.56E-08	
Po-212	1.71E-07	2.78E-08	
U-233	4.35E-05	7.07E-06	·····
Th-229	6.57E-08	1.07E-08	
Ra-225	6.54E-08	1.06E-08	
Ac-225	6.54E-08	1.06E-08	
Fr-221	6.54E-08	1.06E-08	
At-217	6.54E-08	1.06E-08	
Bi-213	6.54E-08	1.06E-08	
TI-209	1.41E-09	2.30E-10	
Pb-209	6.54E-08	1.06E-08	
Po-213	6.40E-08	1.04E-08	
U-234	3.31E-05	5.38E-06	

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	Curies	Fraction	
Isotopes	per Kg	of Activity	Reportable
Th-230	4.47E-09	7.27E-10	
Ra-226	1.51E-11	2.46E-12	
Rn-222	1.51E-11	2.45E-12	
Po-218	1.51E-11	2.45E-12	
Pb-214	1.51E-11	2.45E-12	
Bi-214	1.51E-11	2.45E-12	
Po-214	1.51E-11	2.45E-12	
Pb-210	2.20E-12	3.57E-13	
Bi-210	2.19E-12	3.55E-13	
Po-210	1.98E-12	3.22E-13	
U-235	2.81E-07	4.57E-08	
Th-231	2.81E-07	4.57E-08	
Pa-231	8.36E-11	1.36E-11	
Ac-227	1.81E-11	2.94E-12	
Fr-223	2.50E-13	4.06E-14	
Ra-223	1.78E-11	2.90E-12	
Rn-219	1.78E-11	2.90E-12	
Po-215	1.78E-11	2.90E-12	
Pb-211	1.78E-11	2.90E-12	
Bi-211	1.78E-11	2.90E-12	
TI-207	1.78E-11	2.89E-12	
Th-227	1.77E-11	2.87E-12	
Po-211	6.70E-16	1.09E-16	
U-236	7.39E-07	1.20E-07	· · · · · · · · · · · · · · · · · · ·
Np-237	1.29E-05	2.10E-06	· · · · · · · · · · · · · · · · · · ·
Pa-233	1.29E-05	2.10E-06	
U-238	6.46E-06	1.05E-06	·
Th-234	6.46E-06	1.05E-06	
Pa-234m	6.46E-06	1.05E-06	· ··· · ···
Pa-234	1.03E-08	1.68E-09	1.
Pu-238	8.77E-02	1.42E-02	yes
Pu-239 ·	4.89E-03	7.94E-04	yes
Pu-240	1.78E-03	2.90E-04	yes
Pu-241	1.32E-02	2.14E-03	yes
Am-241	6.98E-03	1.13E-03	yes
Pu-242	3.73E-06	6.06E-07	
Am-243	5.64E-05	9.17E-06	
Np-239	5.64E-05	9.17E-06	
Cm-243	9.56E-05	1.55E-05	
Cm-244	2.40E-03	3.90E-04	yes
Cm-246	4.04E-05	6.56E-06	
Cm-247	2.30E-09	3.74E-10	
Pu-243	2.30E-09	3.74E-10	

	Curies	Fraction	
Isotopes	per Kg	of Activity	Reportable
C-14	3.85E-06	4.56E-04	yes
Ni-59	4.73E-05	5.60E-03	yes
Co-60	1.38E-67	1.63E-65	
Ni-63	3.71E-06	4.40E-04	yes
Se-79	4.11E-05	4.87E-03	yes
Sr-90	7.65E-12	9.05E-10	
Y-90	7.65E-12	9.05E-10	
Zr-93	8.22E-05	9.72E-03	yes
Nb-93m	8.22E-05	9.72E-03	yes
Tc-99	1.87E-04	2.22E-02	yes
Pd-107	5.30E-07	6.27E-05	
Sn-121m	9.02E-10	1.07E-07	
Sn-126	1.41E-05	1.67E-03	yes
Sb-126m	1.41E-05	1.67E-03	-
Sb-126	1.97E-06	2.33E-04	
I-129	1.09E-06	1.29E-04	yes
Cs-135	7.54E-07	8.92E-05	
Cs-137	1.17E-12	1.39E-10	
Ba-137m	1.11E-12	1.31E-10	
Sm-151	1.17E-05	1.39E-03	yes
Eu-154	7.13E-41	8.44E-39	
Th-232	3.41E-07	4.04E-05	
Ra-228	3.41E-07	7 4.04E-05	
Ac-228	3.41E-07	4.04E-05	
Th-228	3.41E-07	4.04E-05	
Ra-224	3.41E-07	4.04E-05	
Rn-220	3.41E-07	4.04E-05	
Po-216	3.41E-07	4.04E-05	
Pb-212	3.41E-07	4.04E-05	
Bi-212	3.41E-07	4.04E-05	
TI-208	1.23E-07	1.45E-05	·
Po-212	2.18E-07	2.59E-05	
U-233	4.34E-05	5.13E-03	yes
Th-229	4.34E-06	5.14E-04	yes
Ra-225	4.34E-06	5.14E-04	
Ac-225	4.34E-06	5.14E-04	
Fr-221	4.34E-06	4.34E-06 5.14E-04	
At-217	4.34E-06	5.14E-04	
Bi-213	4.34E-06	5.14E-04	
TI-209	9.38E-08	1.11E-05	
Pb-209	4.34E-06	5.14E-04	
Po-213	4.25E-06	5.03E-04	-
U-234	6.44E-05	7.63E-03	yes

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Table 14. Activities in Curies/Kilogram of Dried Sludge in Year 3115

Isotones	Curies	Fraction	Benertable
isotopes	per Kg	of Activity	Reportable
Th-230	6.05E-07	7.16E-05	
Ra-226	1.20E-07	1.42E-05	
Rn-222	1.20E-07	1.42E-05	_
Po-218	1.20E-07	1.42E-05	-
Pb-214	1.20E-07	1.42E-05	
Bi-214	1.20E-07	1.42E-05	
Po-214	1.20E-07	1.42E-05	
Pb-210	1.13E-07	1.34E-05	
Bi-210	1.13E-07	1.34E-05	
Po-210	1.13E-07	1.34E-05	
U-235	2.86E-07	3.39E-05	
Th-231	2.86E-07	3.39E-05	
Pa-231	5.83E-09	6.90E-07	
Ac-227	5.66E-09	6.70E-07	
Fr-223	7.82E-11	9.25E-09	
Ra-223	5.66E-09	6.70E-07	
Rn-219	5.66E-09	6.70E-07	
Po-215	5.66E-09	6.70E-07	
Pb-211	5.66E-09	6.70E-07	
Bi-211	5.66E-09	6.70E-07	
TI-207	5.65E-09	6.68E-07	
Th-227	5.53E-09	6.55E-07	
Po-211	2.09E-13	2.47E-11	
U-236	7.94E-07	9.40E-05	
Np-237	1.42E-05	1.68E-03	yes
Pa-233	1.42E-05	1.68E-03	
U-238	6.46E-06	7.65E-04	yes
Th-234	6.46E-06	7.65E-04	
Pa-234m	6.46E-06	7.65E-04	
Pa-234	1.03E-08	1.22E-06	<u> </u>
Pu-238	1.48E-05	1.75E-03	yes
Pu-239	4.74E-03	5.61E-01	yes
_Pu-240	1.59E-03	1.89E-01	yes
Pu-241	1.34E-25	1.59E-23	
Am-241	1.27E-03	1.51E-01	yes
Pu-242	3.80E-06	4.50E-04	yes
Am-243	5.09E-05	6.02E-03	yes
Np-239	5.09E-05	6.02E-03	
Cm-243	2.31E-16	2.74E-14	
Cm-244	1.26E-21	1.49E-19	
Cm-246	3.44E-05	4.07E-03	yes
Cm-247	2.30E-09	2.72E-07	
Pu-243	2.30E-09	2.72E-07	

Twenty-seven radionuclides have been identified as reportable for DWPF Sludge Batch 1B (Macro Batch 2) as specified by WAPS 1.2. Consistent with the strategy detailed in the WCP and WQR, each of these radionuclides has a half-life greater than 10 years and contributes more than 0.01 % of the radioactivity on a Curie basis at some point from production through the 1100-year period between 2015 and 3115. The 27 reportable radionuclides are:

C-14	Ni-59	Ni-63	Se-79	Sr-90	Zr-93
Nb-93m	Tc-99	Sn-121m	Sn-126	l-129	Cs-137
Sm-151	Th-229	U-233	U-234	Np-237	U-238
Pu-238	Pu-239	Pu-240	Am-241	Pu-241	Pu-242
Am-243	Cm-244	Cm-246			

Table 15 – Reportable Radionuclides in Macro Batch 2 (Sludge Batch 1B)

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The WCP and WQR require that all of the radionuclides present in the Design Basis glass be considered as the initial set of reportable radionuclides. For Sludge Batch 1B (Macro Batch 2) all of the radionuclides in the Design Basis glass are reportable except for three radionuclides: Pd-107, Cs-135, and Th-230. At no time through the calendar year 3115 did any of these three radionuclides contribute to more than 0.01 % of the radioactivity on a Curie basis.

Two additional uranium isotopes (U-235 and U-236) must be added to the list of reportable radionuclides in order to meet WAPS 1.6. All of the Pu isotopes and other U isotopes (U-233, U-234 and U-238) identified in WAPS 1.6 were already determined to be reportable according to WAPS 1.2. This brings the total number of reportable radionuclides for Sludge Batch 2 to twenty-nine.

The WQR requires that the relative concentrations of the uranium and plutonium isotopes be provided from the analysis of each Macro Batch (in this case Sludge Batch 1B) in order to meet the WAPS IAEA Safeguards Reporting for HLW Specification (WAPS 1.6). The results are in Table 16.

Isotope	Mass No.	% Distribution	Wt %
U-233	233	2.34E-02	4.52E-04
U-234	234	2.40E-02	4.65E-04
U-235	235	6.72E-01	1.30E-02
U-236	236	5.89E-02	1.14E-03
U-238	238	9.92E+01	1.92E+00
Total		1.00E+02	1.94E+00

Isotope	Mass No.	% Distribution	Wt%
Pu-238	238	6.21E+00	5.81E-04
Pu-239	239	8.41E+01	7.87E-03
Pu-240	240	8.36E+00	7.82E-04
Pu-241	241	2.94E-01	2.75E-05
Pu-242	242	1.01E+00	9.41E-05
Total		1.00E+02	9.35E-03

Table 17 – Plutonium Isotopics Macro Batch 2 (Sludge Batch 1B)

The total Curie content of the dried sludge in the year 2015 is 6.15 Curies/Kilogram. This value is greater than the 4.63 Curies/Kilogram total represented by the reportable radionuclides in Table 6. The difference is due to the significant contribution to the activity from radionuclides having half-lives shorter than 10 years. These radionuclides include Co-60, Y-90, Ba-137m, Pm-147, and Eu-154. The total curie content reduces to 0.0085 Curies/Kilogram in the year 3115. This is a reduction by a factor of 727 over this 1100 year period.

7.0 <u>Conclusions</u>

- 1. The composition (radioactive and nonradioactive), density and weight percent solids of DWPF Macro Batch 2 have been determined.
- The following 27 radioisotopes were identified as being reportable by WAPS 1.2 for Macro Batch 2: C-14, Ni-59, Ni-63, Se-79, Sr-90, Zr-93, Nb-93m, Tc-99, , Sn-121m, Sn-126, I-129 Cs-137, Sm-151, Th-229, U-233, U-234, Np-237, U-238, Pu-238, Pu-239, Pu-240, Pu-241, Am-241, Pu-242, Am-243, Cm-244, and Cm-246.
- Two additional uranium isotopes (U-235 and U-236) must be added to the list of reportable radionuclides in order to meet WAPS 1.6. This brings the total number of reportable radionuclides to 29.

8.0 <u>References</u>

- 1. N.E. Bibler, W.F. Kinard, R.A. Dewberry, and C.J. Coleman, "A Method for the Determination of Waste Acceptance Radionuclides in DWPF Glass and Demonstration of that Method Using SRS Tank 51 Radioactive Sludge and Glass (U)", WSRC-TR-94-0505, Rev.0, October 20, 1994.
- 2. M.S. Hay and N.E. Bibler, "Characterization and Decant of the Tank 42 Sludge Sample ESP-200 (U)", WSRC-RP-98-00406, Rev.0, June, 12,1998.
- 3. Westinghouse Savannah River Company, "DWPF Waste Form Compliance Plan (U)", WSRC-IM-91-116-0, Rev.7, (June 2003).
- 4. Office of Environmental Restoration and Waste Management, "Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms", USDOE Document DOE/EM-0093, Rev. 2, (12/96).
- 5. S.L. Marra and M. Norton, Technical Task Request, HLW/DWPF/TTR-990005, Rev. 0, October, 1998.
- 6. T.L. Fellinger, "Technical and QA Plan: Characterization of DWPF Radioactive Dip Samples for Sludge Batch 1B (U)", WSRC-RP-98-01473, Rev. 0, December 1998.

7. T.L. Fellinger, "Analytical Study Plan: Characterization of DWPF Radioactive Dip Samples for Sludge Batch 1B (U)", WSRC-RP-98-01478, Rev. 0, December 1998.

1 6

- 8. N.E. Bibler and T.L. Fellinger, "DWPF Glass Results for the Analysis of a Pour Stream Sample Taken During the Pouring of the 409th Canister (Canister S00834) in Macro Batch 1 (U)", WSRC-RP-98-01400, Rev.0, April 13, 1999.
- 9. D.P. Diprete, "Results C-14 Analyses on High Level Caves Sludge (U)", SRT-ADS-99-1110, March 16, 1999.
- 10. D.P. Diprete, "Results I-129 Analysis of High Level Waste Sludge (U)", SRT-ADS-98-1429, December 18, 1998.
- 11. W.H. Walker, "Review Paper 11a for the IAEA Panel on Fission Product Nuclear Data", Bologna, Italy, 11/26 11/30, 1973, (IAEA-169, Volume 1, 285{1974}).
- N.E. Bibler, W.F. Kinard, W.T. Boyce, and C.J. Coleman, "Determination of Long Lived Fission Products and Actinides in Savannah River Site HLW Sludge and Glass for Waste Acceptance", Journal of Radioanalytical and Nuclear Chemistry, Vol. 234, p.159-163 (1998).
- N.E. Bibler, C.J. Coleman, and W.F. Kinard, "Relative Yields of U-235 Fission Products Measured in a High Level Waste Sludge at Savannah River Site", Nuclear and Hazardous Waste Management, spectrum "92, American Nuclear Society, Inc., LaGrange, IL., (1992), 952.
- 14. W.F. Kinard, N.E. Bibler, C.J. Coleman and S.B. Wyrick, "Inductively Coupled Plasma-Mass Spectroscopy Studies of the Chemistry of Fission Products and Actinides in High Level Waste: Lessons that can be Applied to Environmental Measurements, Radiochimica. Acta., 66/67, (1994) 259.
- 15. M.L. Hyder, "Waste Acceptance Radionuclides to be Reported in Tank 51 Sludge Only Glass (U)", WSRC-TR-95-0485, Rev.0, December 12, 1995.
- 16. W.D. Ehmann and D.E. Vance, "Radiochemistry and Nuclear Methods of Analysis", John Wiley & Sons, Inc., New York, 1991.
- 17. "Radioactive Decay Calculator," D.W. James & Associates, North Oaks, MN 55127.
- 18. R. A. Sigg, Technical Review of, "Characterization of and Waste Acceptance Radionuclides to be Reported for DWPF Macro Batch 2, (ESP215-ESP22)," SRT-ADS-2003-0410, August 5, 2003.
- 19. "RadDecay for Windows," Version 1.13, Grove Engineering, Rockville, Maryland.

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