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Characterization of High Level Nuclear Wastes Stored at the Savannah River Site

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1.0 Abstract

The Savannah River Site (SRS) currently stores over 125 million liters of high-level nuclear waste (HLW). Approximately 20 million liters of the HLW consists of water-insoluble solids referred to as sludge. The remainder consists of a mixture of crystallized salts and concentrated supernatant liquid produced from the evaporation of alkaline aqueous solutions. Retrieval, pretreatment and disposal operations and the closure of emptied storage tanks at the SRS require characterization of the HLW. This paper will present requirements, experiences and results obtained from the sampling and analysis of (1) sludges prepared for the first two batches of feed vitrified in the Defense Waste Processing Facility, (2) residual sludge heels in two HLW tanks prior to closure of the tanks, (3) saltcake for the determination of fissile content prior to dissolution and retrieval and (4) supernatant liquid wastes processed through HLW evaporators at the SRS.

2.0 Introduction and General Overview of High-Level Waste Flowsheet

High-level nuclear wastes (HLW) are stored at the SRS in two areas, referred to as F-Area and H-Area Tank Farms, at the SRS. Influents include low heat and high heat wastes from both F-Canyon and H-Canyon chemical separation operations, a recycle stream from the Defense Waste Processing Facility (DWPF), the Receipt Basin for Offsite Fuels (RBOF), waste from the 299-H decontamination facility, reactor basins waste water, and miscellaneous laboratory waste from the Savannah River Technology Center and Analytical Laboratories. Historically, the bulk of the HLW originated from F-Canyon and H-Canyon.

Because of the high alkalinity, most of the metal components precipitate in a solid oxide or hydrous oxide phase referred to sludge. Upon standing, the precipitated solids settle to the bottom of the storage tanks. Operations decants the supernatant liquid from the solids and evaporates at atmospheric pressure to reduce the volume of waste. The concentrated liquid waste transfers to a separate tank and cooled. Upon cooling, salts crystallize from solution. After a period of time, operations decants the supernatant liquid from the crystallized solids, referred to as saltcake, and returns the liquid to the evaporator feed tank for further concentration.

The Savannah River Site (SRS) stores over 125 million liters of HLW in 49 underground carbon-steel tanks. Processing facilities will permanently disposition this waste, by separating the radioactive components from the bulk into a small volume fraction followed by vitrification in the Defense Waste Processing Facility (DWPF). Operations will incorporate the remaining, much larger volume fraction into a cement wasteform in the Saltstone facility.

Most of the radioactivity in the HLW resides in a solid fraction referred to as sludge. These solids form upon addition of sufficient sodium hydroxide to the acidic waste solutions to provide a highly alkaline slurry. The highly alkaline condition prevents corrosion of the carbon-steel storage tanks. After allowing the sludge solids to settle, the operations include decanting and evaporating the waste solutions to conserve storage space. Upon cooling, salts (e.g., sodium nitrate, sodium carbonate and sodium aluminate) crystallize from the evaporated wastes. The crystallized salts are referred to as saltcake.

Processing saltcake involves dissolving the salt in dilute NaOH solution (0.015 M), combining with supernatant liquid and removing cesium, strontium, and alpha-emitting radioisotopes. After removal of the radioactivity, the decontaminated salt solution transfers to the Saltstone facility for disposal as a low-level waste. The concentrated radioactive fraction transfers to the DWPF for vitrification with the sludge fraction of the HLW.

3.0 Characterization of Saltcake Samples

3.1 Introduction

Nuclear safety issues required resolution prior to dissolution of saltcake presently stored in Tank 41H. Fissile isotopes such as ^{235}U and ^{239}Pu currently exist in dilute concentrations and in the presence of high concentrations of neutron poisons (e.g., Na, Fe, Cr, Mn and Zn) relative to the fissile isotopes in the saltcake prohibiting the assembly of a critical mass. However, during salt dissolution, if the fissile isotopes do not completely dissolve or precipitate post dissolution, sufficient inventory of uranium and possibly plutonium exist to accumulate as a critical mass in the tank. Therefore, personnel obtained and analyzed saltcake samples to determine the isotopic distributions, the total plutonium and uranium content, the concentrations of neutron poisons, and the characteristics of the insoluble solids.

3.2 Experimental

Personnel obtained four saltcake samples from Tank 41H using a simple tool consisting of a sample cup approximately 3.8-cm in diameter and up to 10-cm in length, attached to the end of 150-cm lengths of galvanized steel pipe. The sample cavity fills as the tool drives into the saltcake. After removing the tool from the waste, personnel separated the sample cup from the remainder of the tool, placed the cup into a plastic bag and shielded container and transported the container to the laboratory. At the laboratory, personnel opened the containers, removed and placed the saltcake material in glass jars.

Personnel obtained the first sample from the B-3 riser on Tank 41H to a depth of 3.8-cm from the saltcake surface. We obtained three additional saltcake samples from the E-1 riser, located on the opposite side of the center support column of the tank from the B-3 riser. The second sampling campaign employed a modified sampling tool consisting of successively smaller cups and a pipe insert for directing the sampling tool to the same location and obtaining successively deeper samples. We estimated that the total depth of saltcake sampled at 30-cm.

The analysis of each sample consisted of the following: (1) visually inspect the as-received samples, (2) dissolve subsamples in 2M nitric acid and perform liquid phase analyses, and (3) dissolve subsamples in dilute sodium hydroxide solution (0.015 M), separate the liquid phase from any undissolved solids and determine chemical composition of each fraction. Analytical methods included gamma spectroscopy, alpha spectroscopy, beta

spectroscopy, ion chromatography, inductively-coupled plasma emission spectroscopy (ICP-ES), inductively-coupled plasma mass spectroscopy (ICP-MS), cold vapor atomic absorption spectroscopy (CV-AAS), acid-based titration, scanning electron microscopy, particle size distribution and X-ray diffraction (XRD).

3.3 Results

The saltcake samples contained a mixture of light-colored and dark-colored solids. The XRD analysis identified sodium nitrate and sodium carbonate as the only crystalline phases in the as-received samples.

The as-received saltcake samples readily dissolved in nitric acid with the visible evolution of gases, presumably carbon dioxide and nitrogen oxides from the decomposition of carbonate and nitrite, respectively. The light-colored solids, but not the dark-colored solids, rapidly dissolved in water. At a 3:1 ratio of water to solids, approximately 90% of the saltcake dissolved.

The predominant elements found in the as-received samples and the water-soluble fraction of the saltcake samples included Na, P and Al, with smaller amounts of Zn, Cr, and K. Table 3-1 provides the ion chromatographic and gravimetric analyses of the water-soluble solids. These analyses identified nitrate and carbonate as the major anions in the saltcake sample. These results agree with the XRD results that identified sodium nitrate and sodium carbonate crystalline phases in the dried saltcake samples. The relatively high carbonate concentration reflects the absorption of atmospheric carbon dioxide and reaction with hydroxide to produce carbonate in the aged waste.

Summing the total cation, total anion, and insoluble solids contents for each sample provides a total solids content for the as-received samples. The authors compared the calculated total solids content to that determined by drying the as-received sample at 100 °C. Fairly good agreement existed between the two totals for each sample. This agreement indicated consistent overall elemental and chemical analyses of the samples and that the analyses identified all major components.

Table 3.1 Analytical Results for Water-Soluble Solids

	Concentration (wt %)[a]				
Species	**B-3 Riser**	**E-1 Riser #1**	**E-1 Riser #3**	**E-1 Riser Average**	**%RSD**
Na	25.8	27.0 ± 1.2	27.1 ± 1.2	27.1 ± 0.071	0.26
Al	0.21	0.093 ± 0.0050	0.095 ± 0.057	0.094 ± 0.0014	1.5
P	0.37	0.34 ± 0.0024	0.25 ± 0.073	0.30 ± 0.064	22
Zn	0.040	0.0021 ± 0.0011	0.026 ± 0.030	0.014 ± 0.017	120
Cr	0.0088	0.021 ± 0.0032	0.0068 ± 0.0010	0.014 ± 0.010	72
K	0.034	0.014 ± 0.0043	0.020 ± 0.0011	0.017 ± 0.0042	25
Free OH^-	2.0 ± 0.16	1.0 ± 0.0090	1.5 ± 0.0061	1.3 ± 0.35	27
$Al(OH)_4^-$	1.0 ± 0.15	0.22 ± 0.012	0.70 ± 0.17	0.46 ± 0.34	74
CO_3^{2-}	11.3 ± 0.60	6.5 ± 0.79	4.7 ± 0.92	5.6 ± 1.3	23
NO_3^-	40.6 ± 1.6	44.1 ± 1.5	46.3 ± 0.00034	45.2 ± 1.6	3.4
NO_2^-	0.98 ± 0.048	0.50 ± 0.0089	0.80 ± 0.026	0.65 ± 0.21	32
PO_4^{3-}	0.71 ± 0.20	0.98(± 0.11	0.54 ± 0.043	0.76 ± 0.31	41
SO_4^{2-}	1.2 ± 0.20	<0.038 ± 0.0020	0.65 ± 0.14	0.34 ± 0.43	130
$C_2O_4^{2-}$	0.17 ± 0.016	<0.076(± 0.0040	<0.077 ± 0.0010	<0.077 ± 0.00071	0.9
Cl^-	0.024 ± 0.0056	0.020 ± 0.00031	0.020 ± 0.0066	0.020 ± 0.00	0
Total Anion	58.0 ± 3.0	53.3 ± 2.4	55.2 ± 1.3	54.3 ± 1.3	2.4

[a] Average concentrations and standard deviations (1σ) of as-received samples.
Average E-1 Riser equals the average of samples #1 and #3 taken from the E-1 Riser.
% RSD equals the standard deviation divided by the average multiplied by 100.

Radionuclides detected in the samples included isotopes of uranium and plutonium, ^{137}Cs, ^{134}Cs, ^{90}Sr and ^{99}Tc (see Table 3-2). The ^{137}Cs proved the dominant radioactive material found in all of the samples. The average total uranium content of the three samples taken from riser E-1 measured 4.5 ± 1.7 µg/g, similar to that found for the sample taken from riser B-3, 5.7 ± 0.44 µg/g. Table 3-2 also provides the relative abundances for selected uranium and plutonium isotopes. The uranium isotopic abundances for the four samples agreed well. The maximum ^{235}U abundance measured 16% at the 95.2% (2s) confidence level. Since the two sets of samples came from different risers located on opposite sides of the tank, the uranium appears uniformly distributed radially in the top 30-cm of the tank. The similarity of the isotopic distribution in all of the samples indicates that the uranium comes from the same source.

The total uranium contents for the samples differed statistically. These results suggest inhomogeneity in the distribution of the uranium in the 30-cm vertical sampling profile. Based on the second set of samples (E-1 riser), the total uranium content varied by a factor of about two over the 30-cm vertical segment. The analytical results indicate that the approximately 95% of the plutonium exists in the water-insoluble fraction of the saltcake. The factor of two difference in the plutonium content between the samples from the different risers likely reflects the difference in the amount of water-insoluble solids. The quantity of insoluble solids in the samples taken from the E-1 riser represents about one-half of that found in the sample taken from the B-3 riser. Thus, it follows that the lower plutonium content mirrors the lower insoluble solids content in the set of samples taken from the E-1 riser. Results also indicated that the mole ratio of the various elements to uranium appears similar for both the final rinse and soak solutions. This indicates no significant preferential dissolution of any of the elements.

The XRD analysis identified several crystalline phases in the insoluble solids. Sodium nitrate existed in all the samples. Other crystalline phases found included sodium aluminum silicate, zinc sodium phosphate, sodium fluorophosphate, and zinc sodium silicate. The composition of the insoluble solids differs for all samples indicating a degree of heterogeneity for the solids among the axial and 30 cm vertical profiles. Elements identified in the solids included: chromium, iron, aluminum, silicon, sodium, calcium, zinc, phosphorous and uranium. Scanning electron microscopy

revealed that the majority of the solids particles range in diameter from about 1 µm to 10 µm. Particles enriched in uranium were detected. The range of the other solids present in the samples bound the particle size of the uranium-enriched particles.

Gravity settling and decanting is the current method employed at the SRS to remove insoluble solids from the feed solution to salt processing operations. Table 3.3 provides settling rates to remove the insoluble solids from salt solutions upon dissolution of the Tank 41H saltcake. Suspending insoluble solids in one of two salt solutions having different densities and measuring the turbidity as a function of time allowed the determination of these rates. With the exception of the value for 50% removal, the rates follow the expected trend of decreasing at the higher solution density. Based on the measurements, we estimate settling times of 10 – 60 days are necessary to affect the required solids removal.

Table 3.2 Selected Isotope Concentrations and Percent Abundance

	Concentration (% Abundance) [a]					
Isotope	**B-3 Riser**	**E-1 Riser #1**	**E-1 Riser #2**	**E-1 Riser #3**	**E-1 Riser Ave.**	**% RSD**
^{235}U	7.5 ± 0.52 E-01 (13 ± 1.8 %)	6.8 ± 1.4 E-01 (11 ± 1.1%)	5.5 ± 0.84 E-01 (11 ± 1.2 %)	3.1 ± 0.48 E-01 (11 ± 1.2%)	5.1±1.9 E-01 (11 ± 0.0%)	37 0
^{238}U	4.4 ± 0.35 E+00 (77 ± 0.32 %)	4.8 ±0.39 E+00 (80 ± 1.8 %)	3.9 ± 0.11 E+00 (80 ± 2.0 %)	2.1 ± 0.070 E+00 (80 ± 1.9 %)	3.6±1.3 E+00 (80 ± 0.0 %)	36 0
Total U	5.7 ± 0.44 E+00	6.0 ±0.63 E+00	4.8 ± 0.25 E+00	2.7 ± 0.15 E+00	4.5±1.7 E+00	38
^{238}Pu	3.8 ± 0.45 E-02 (58 ± 23 %)	2.0 ±0.13 E-02 (75 ± 5.6 %)	3.3 ± 0.69 E-02 (78 ± 24 %)	2.3 ± 0.15 E-02 (77 ± 8.7 %)	2.5±0.67 E-02 (77 ± 1.5 %)	27 2.0
^{239}Pu	2.3 ± 0.15 E-02 (35 ± 14 %)	5.3 ±1.6 E-03 (20 ± 6.1 %)	7.6 ± 1.6E-03 (18 ± 5.7 %)	5.1 ± 1.5E-03 (17 ± 4.4 %)	6.0±1.4 E-03 (18 ± 1.5 %)	23 8.3
^{240}Pu	3.3 ± 0.45 E-03 (5.1 ± 2.1)	1.1 ± 0.30 E-03 (4.1 ± 1.1 %)	1.5 ± 0.95 E-03 (3.6 ± 2.4 %)	1.0 ± 0.25 E-03 (3.5 ± 0.89 %)	1.2± 0.26 E-03 (3.7 ± 0.32 %)	22 8.6
Total Pu	6.5 ± 2.5 E-02	2.7 ± 0.085 E-02	4.2 ± 0.97 E-02	2.9 ± 0.27 E-02	3.3±0.81 E-02	25
^{137}Cs	108 ± 4	65 ± 14	175 ± 11	40 ± 2	93 ± 72	77
^{134}Cs	0.11 ± 0.01	0.047[b]	0.16 ± 0.02	0.042 ± 0.015	0.083 ± 0.067	81
^{90}Sr	0.012 ± 0.001	nd	nd	nd	-	-
^{99}Tc	0.013 ± 0.001	nd	nd	nd	-	-

[a] Uranium and plutonium concentration units are µg/g of as-received saltcake sample. All other radioisotopes are in units of µCi/g of as-received saltcake sample. Values are averages of duplicate measurements of two different dissolutions in nitric acid, except sample from B-3 riser, which represents duplicate measurements of five different dissolutions. % RSD equals the standard deviation divided by the average value multiplied by 100.
[b] single result above detection limit reported
nd = not determined

Table 3.3 Settling Rates for the Insoluble Solids Present in the Tank 41H Saltcake

	Settling Velocity (cm/d)	
% Solids Removal	Low Density[a]	High Density[b]
50	38	64
90	9.1	8.1
95	5.3	4.3
98	3.3	2.8

[a] density = 1.2 g cm^{-3}
[b] density = 1.4 g cm^{-3}

3.4 Summary and Conclusions

The saltcake in the top 30-cm of Tank 41H contains uranium at a concentration between 3.0 and 7.3 µg/g with a ^{235}U abundance of 16%. The total plutonium concentration measures between 0.034 and 0.061 µg/g with a ^{239}Pu abundance of 32%. The low ^{90}Sr concentration in the saltcake samples indicates no need to remove ^{90}Sr prior to disposing the waste.

Dissolution of the Tank 41H saltcake will produce insoluble solids. Accumulation of the water-insoluble solids in the tank during saltcake dissolution does not pose a nuclear criticality concern because of the presence of neutron poisons (e.g., Fe, Cr, and Zn). Removal of insoluble solids upon dissolution of the saltcake may prove necessary before processing this saltcake to maintain good filter performance in salt processing operations. Settling times will range from 10 – 60 days to achieve the necessary solids removal.

Based on the particle sizes and settling velocities of the water-insoluble solids, we conclude uranium cannot segregate from the bulk of the insoluble solids during salt dissolution operations by gravity settling. Selective dissolution of uranium and neutron absorbers (e.g., Cr, Fe, Mn, and Zn) did not occur upon contacting the insoluble solids with 0.015M NaOH solution or deionized, distilled water. Thus, we conclude that the formation of a solid phase consisting of uranium without significant amounts of Cr, Fe, Mn, and Zn will not occur during the dissolution of saltcake in dilute sodium hydroxide solution. Based on the characterization results for these samples and the fill history of Tank 41H, dissolution of as much as 1.5 meters of saltcake may safely proceed without further sampling and characterization.

4.0 Characterization of Sludge Samples

4.1 Introduction

Prior to vitrification in the DWPF, sludge is retrieved from storage tanks, placed in large tanks equipped for chemical processing and treated with dilute sodium hydroxide solution to remove soluble salts by dilution and solid/liquid separation using gravity settling and decanting of the supernatant liquid. Sludges containing high aluminum concentrations are first treated with concentrated sodium hydroxide at elevated temperature to dissolve the hydrous aluminum oxide solids. These operations are referred to as Extended Sludge Processing or ESP.

Prior to vitrification in the DWPF, each sludge batch will be sampled in the processing tanks and extensively characterized for chemical composition before and after washing with inhibited water. This information provides guidance to the ESP facility in preparing the sludge and assurance that acceptable glass can be produced from the material in the DWPF. Data obtained includes the fate of various radioactive and non-radioactive species present in the sludge during the washing operation.

4.2 Experimental

Personnel used a specially designed device to obtain the sludge samples. The sampler is lowered into the sludge mixture in the open position, which allows the mixture of solids and liquid to flow into the internal cavity of the

device. After a period of time to allow complete filling of the cavity, an outer sleeve releases closing the cavity and retaining the sludge. The sampler is raised above the sludge, rinsed with water while still in the tank to remove material adhering to external surfaces, removed from the tank and placed in a shipping cask for transport to the laboratory.

At the laboratory, personnel remove the sampler from the shipping cask and place the sampler into the Shielded Cells Facility that can safely handle highly radioactive materials. The sampler is opened and the sample allowed to flow into a storage vessel. Subsamples from the storage vessel are retrieved and prepared for chemical analyses and washing studies. Washing tests utilized a dilute sodium hydroxide solution (0.01 M). Solid-liquid separations utilized gravity settling and centrifugation. Radiochemical and chemical analyses included the following methods: gamma spectroscopy, beta spectroscopy, alpha spectroscopy, inductively coupled plasma emission spectroscopy, inductively coupled plasma mass spectroscopy, atomic absorption spectroscopy, ion chromatography, ion selective electrode, and acid/base titration.

4.3 Results

Personnel obtained samples from two tanks, Tank 42H and 51H. These tanks provide the first two macro batches of sludge for vitrification in the DWPF. The sludges transferred into these tanks from their original storage tanks, 15H, 18F and 21H. The Tank 15H sludge transferred into Tank 42H and was treated in 1983 with strong caustic solution at elevated temperature to remove hydrous aluminum oxide solids.

Table 4-1 presents the weight percent dissolved solids and insoluble solids for the sludge samples obtained from Tanks 42H and 51H. The Tank 42H sample exhibited a higher insoluble solids content before and after washing than the Tank 51H sample. However, the Tank 51H sample exhibited a more concentrated supernatant liquid than that measured in the Tank 42H sample.

Table 4-1. Soluble and Insoluble Solids Content in Tanks 42H and 51H Sludge Samples

	Unwashed Tank 42H	Washed Tank 42H	Unwashed Tank 51H	Washed Tank 51H
wt % Dissolved Solids [1]	8.46	0.80	11.4	4.91
wt % Soluble Solids [2]	6.52	0.60	9.70	4.20
wt % Insoluble Solids [3]	23.0	20.5	15.1	13.6
wt % Total Solids [4]	29.5	21.1	24.8	17.8

[1] wt % dissolved solids in supernatant liquid
[2] wt % dissolved solids in sludge slurry
[3] wt % insoluble solids in sludge slurry
[4] wt % total dried solids in sludge slurry

Personnel determined the isotopic abundance for uranium and plutonium isotopes. Table 4-2 provides the results for ^{235}U, ^{238}U and ^{239}Pu. The analytical results indicate the same uranium and plutonium isotopic abundance at the 95% confidence level for both sludge materials. The isotopic abundance results indicate the uranium is depleted uranium and that the source of plutonium is predominantly from weapons-grade plutonium production.

Table 4-2. Uranium and Plutonium Isotopic Abundances in Tanks 42H and 51H Sludge Samples

	Tank 42H	Tank 51H
% ^{235}U	0.56 (5.5)	0.45 (12)
% ^{238}U	99.4 (0.1)	99.5 (0.1)
% ^{238}Pu	6.27 (12)	4.31 (15)
% ^{239}Pu	85.4 (1.1)	87.1 (2.6)
% ^{240}Pu	7.06 (0.5)	8.19 (20)

numbers in parenthesis are the percent relative standard deviation

Table 4-3 presents selected elemental and radionuclide concentrations for the total dried solids before and after washing each sludge sample. The bulk of the sludge solids consist of iron, aluminum, sodium and manganese. The high concentration of these metals relative to those of fissile uranium and plutonium indicate that the sludge processing does not constitute a critical concern.

Gravity settling and decanting is the reference method employed in the Extended Sludge Processing operations. Centrifugation allows for much more rapid processing of samples in laboratory washing studies. Analytical results for the Tank 42H sludge sample employing the centrifugation method for solid/liquid separation method exhibited no statistically significant differences than those measured using gravity settling and decanting. Based on the Tank 42H results, centrifugation is an acceptable laboratory method for the separation of sludge solids and supernatant liquids.

With exception of sodium, the elemental concentration ratios of the washed to unwashed sludge slurry is greater than one and generally close to the predicted value of 1.2. The bulk of the sodium present in the unwashed sludge slurry originates from dissolved sodium salts in the supernatant liquid. Thus, sludge washing dilutes the sodium concentration. The other elements listed in Table 4-3 originate in the solids that exhibit very low solubility under alkaline conditions. Other water-soluble components in the unwashed sludge slurry (e.g., nitrate, nitrite, hydroxide, sulfate, oxalate, carbonate, phosphate and halides) decrease in concentration during washing as expected due to dilution.

Unlike the Tank 42H sample, the ^{137}Cs content in the Tank 51H sludge solids increased upon washing. Cesium ions are very soluble in alkaline solutions and should dissolve in the wash solution.

The Tank 51H results suggest that a significant fraction of cesium is present in a low-solubility phase (e.g., zeolite or other aluminosilicate phase such as cancrinite).

4.4 Summary and Conclusions

Analytical results of the Tanks 42H and 51H sludge solids agree with those expected for sludges produced from Purex processing and aluminum-leached HM processing of irradiated nuclear fuels. The relatively low concentrations of fissile isotopes and high concentrations of neutron poisons confirm that the sludge does not present a criticality safety concern. Uranium and plutonium concentrations in the wash water decants are lower than that predicted based on dilution. The lower concentrations may indicate the presence of colloidal uranium and plutonium in this sludge. Washing results indicate no evidence for the dissolution of constituents present in the sludge solids. The washing studies also indicate that the soluble components in the supernatant liquid follow a simple dilution model. Based on these results, we conclude that both of these sludges could be washed to the requirements for feed to the DWPF and produce acceptable HLW glass for disposal.

Table 4-3. Selected Elemental and Radionuclide Concentrations of Tanks 42H and 51H Sludge Samples

Element	Unwashed Tank 42H Slurry (wt %)	Washed Tank 42H Slurry (wt %)	Ratio of Washed to Unwashed	Unwashed Tank 51H Slurry (wt %)	Washed Tank 51H Slurry (wt %)	Ratio of Washed to Unwashed
Fe	21.2	26.0	1.23	22.1	25.8	1.17
Al	7.76	9.17	1.18	5.57	6.36	1.14
Na	8.52	3.90	0.46	14.4	9.40	0.65
Mn	3.52	4.36	1.24	2.34	2.61	1.12
Ca	2.20	2.99	1.36	2.15	2.39	1.11
U	2.66	3.22	1.21	3.11	3.21	1.03
Mg	1.23	1.54	1.25	1.07	1.20	1.12
Hg	0.94	1.17	1.24	0.14	0.16	1.14
P	0.94	1.16	1.23	0.48	0.55	1.15
Ni	0.34	0.43	1.26	0.27	0.33	1.22
Cr	0.13	0.14	1.08	0.16	0.19	1.19
Cu	0.027	0.034	1.26	0.024	0.038	1.58
Ti	0.016	0.021	1.31	0.013	0.016	1.23
Pu	0.0092	0.011	1.20	0.012	0.012	1.00
	(µCi/g)	(µCi/g)		(µCi/g)	(µCi/g)	
^{90}Sr	5630	6190	1.10	564	627	1.11
^{137}Cs	156	180	1.15	70.1	62.1	0.88
^{154}Eu	16.2	17.8	1.10	1.17	1.38	1.18

5.0 Characterization of Residual Heel Material in Tanks Prior to Closure

5.1 Introduction

SRS began decommissioning of HLW tanks in 1997. To date, two Type IV tanks, Tank 17F and 20F, have been decommissioned. Type IV tanks do not have cooling coils or secondary containment and historically stored only low activity waste that did not require external cooling. These tanks represent the easiest of the four SRS tank designs to decommission. Lessons learned during the closure of these tanks will prove invaluable in decommissioning the remaining tanks.

The general methodology used to decommission a tank includes the following: (1) remove bulk of waste from tank, (2) clean internal tank surfaces, (3) fill tank with inert material and (4) close all openings into the tank. An important consideration of waste removal and cleaning is ‘how clean is clean’. Prior to decommissioning the tank, we assess the impact of the release of the residual radioactivity on the environment. Thus, the radionuclide composition in the residual material must be known to determine if the tank is sufficiently clean to decommission. We report the results of the analysis of supernatant liquid and solids taken from Tank 17F in support of tank closure.

5.2 Experimental

Personnel obtained one supernatant liquid and two solid samples from Tank 17F. The solids sampling device consisted of a remotely maneuverable, floating suction pump with an intake hose that extends to the bottom of the tank. The pump discharge travels to a filter. Liquid passes through the filter and returns to the tank. The retained solids fall by gravity into a sample vial attached below the filter unit.

Samples from Tank 17F transferred to laboratories designed to handle highly radioactive material. At this point, personnel removed the samples from the sample containers, visually inspected the samples and prepared subsamples for a variety of chemical and radiochemical analyses. Analytical methods included gamma spectroscopy, alpha spectroscopy, beta spectroscopy, ion chromatography, inductively-coupled plasma emission spectroscopy (ICP-ES), inductively-coupled plasma mass spectroscopy (ICP-MS), cold vapor atomic absorption spectroscopy (CV-AAS), and

acid-based titration.

Personnel dried the solids to constant weight at 110 ° C and employed two different methods to dissolve subsamples for analysis: closed container heating in aqua regia and high temperature sodium peroxide fusion. After the heat treatment, addition of hydrochloric acid followed by deionized, distilled water brought each sample to constant volume.

5.3 Results

Table 5-1 presents the predominant species found in the supernatant liquid sample. The concentrations of these species agreed well with samples previously taken from this tank. The high hydroxide, high nitrite and low nitrate concentrations indicate that the supernatant liquid in Tank 17F is not corrosive. Most of the radioactivity in the supernatant liquid is ^{137}Cs and ^{3}H. ^{99}Tc and actinide concentrations are very low.

Table 5-1. Tank 17F Supernatant Liquid Analytical Results

Species	Concentration	Units
NO_3^-	0.004	M
NO_2^-	0.22	M
PO_4^{3-}	0.002	M
CO_3^{2-}	0.20	M
$Al(OH)_4^-$	0.016	M
OH^-	0.23	M
Na	0.97	M
B	26	mg/L
Cr	1.0	mg/L
Si	6.5	mg/L
As	1.4	mg/L
Se	2.3	mg/L
^{137}Cs	2.0E-4	µCi/mL
^{3}H	3.4	µCi/mL
^{99}Tc	7.4E-4	µCi/mL
^{238}U	1.2E-6	µCi/mL
^{239}Pu	1.5E-4	µCi/mL
^{237}Np	1.1E-6	µCi/mL

Table 5-2 provides the average analytical results for the two Tank 17F solids samples. Generally the results are averages of replicate samples from both dissolution methods (total of 12 analyses). However, in some cases we report only the replicates from a single dissolution method. An example is sodium. The sodium peroxide fusion method adds too much sodium to the sample to allow an accurate sodium determination. Thus, we used only the aqua regia dissolutions for determination of sodium.

The composition of the Tank 17F samples agrees with expected for sludge solids produced from the processing of irradiated fuel at the Savannah River Site. Iron is the major constituent with smaller amounts of aluminum, manganese, silicon, and uranium. Based on the analytical results for the solids and the supernatant liquid samples, approximately 99% of the ^{99}Tc, ^{90}Sr and ^{237}Np exist in the solid phase. The low ^{137}Cs concentration in the supernatant liquid is consistent with the multiple additions of inhibited water to the tank contents. The ^{137}Cs content in the solids may reflect absorption of the cesium onto zeolite or other aluminosilicate phases.

Table 5-2. Tank 17F Solids Analytical Results

Species	Concentration	% RSD	Units
Ca	8.7E-01	8.5	wt %
Cd	9.2E-01	4.7	wt %
Mg	1.6E+00	4.1	wt %
Mn	2.4E+00	34	wt %
Zn	3.1E-02	9.6	wt %
Al	3.9E+00	31	wt %
Fe	2.4E+01	9.7	wt %
Na	9.5E+00	12	wt %
Ni	3.0E-02	26	wt %
Cr	3.1E-02	3.7	wt %
Si	1.8E+00	26	wt %
Hg	7.5E-03	28	wt %
^{137}Cs	9.6E+00	15	µCi/g
^{154}Eu	7.6E-02	21	µCi/g
^{60}Co	3.9E-01	29	µCi/g
^{241}Am	4.5E+00	1.9	µCi/g
^{90}Sr	6.0E+01	26	µCi/g
^{99}Tc	4.6E-01	4.6	µCi/g
^{237}Np	7.1E-03	9.7	µCi/g
^{238}U	3.4E-03	11	µCi/g
^{238}Pu	3.3E+01	*	µCi/g
^{239}Pu	7.5E+00	33	µCi/g
^{240}Pu	1.7E+00	18	µCi/g
^{241}Pu	1.5E+02	*	µCi/g

* calculated from average values

5.4 Summary and Conclusions

Analysis of the Tank 17F supernatant liquid indicates that the liquid phase contains sufficient corrosion inhibitors to protect the tank from stress corrosion cracking and pitting corrosion. Composition of the solids indicates the bulk of the materials are metal oxides from the reprocessing of irradiated fuels. Although present in relatively low concentrations, the extremely long half-lives of ^{99}Tc, ^{237}Np and most of the plutonium isotopes make the levels of these radionuclides important in determining the long-term environmental impact of the residual material in the tank. Based on the quantities measured in the Tank 17F samples, personnel determined the allowable quantity of residual material for tank closure.

6.0 Characterization of Evaporator System Samples

6.1 Introduction

From early 1990 through 1997, SRS collected samples and analyzed samples from the H- and F-Area High Level Waste Evaporator system tanks to elucidate the chemistry of plutonium and uranium during waste evaporation. This information would confirm if a mechanism exists to accumulate sufficient quantities of plutonium and uranium to pose a nuclear criticality concern. The solubility of plutonium and uranium in alkaline solutions is sufficiently small to be well below a safe concentration. However, it is possible that plutonium and uranium solids could form upon evaporation. Accumulation of solids enriched in uranium and plutonium in the evaporator would then pose a nuclear criticality concern.

The design of the HLW evaporators precludes obtaining samples of concentrated liquids and solids, if formed, except during shutdown. Shut down of the evaporator on a routine basis to obtain samples is not practical due to lost operating time. Thus, personnel obtained supernatant liquid samples from the respective feed (Tanks 26F and 43H) and concentrate receipt tanks (Tanks 46F and 38H). Personnel analyzed these samples for uranium and plutonium content

to determine if there exists any evidence for accumulation of uranium and plutonium in the evaporator.

6.2 Experimental

HLW Operations obtained dip samples from the tanks and delivered them to the Shielded Cells Facility in the Savannah River Technology Center. Personnel first determined the density of the liquid samples by emptying the contents of the dip bottles into pre-weighed 100-mL graduated cylinders with the accuracy of the graduated cylinders verified to ± 0.5% at 100 mL. Following density determination, personnel removed representative aliquots and diluted in 0.2 M nitric acid with a dilution factor of ~100. A second dilution to a combined dilution factor of ~10,000 occurred using distilled water. The Analytical Development Section performed analyses for ^{137}Cs activity by gamma spectroscopy and actinide concentrations by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

6.3 Results

Tank 43H and Tank 26F are the respective evaporator feed tanks and Tank 38H and 46F the respective concentrate receipt tanks for the two evaporator systems. Table 6.1 provides the average values for supernatant samples taken from these tanks for the time period of early 1991 through 1997. The average values indicate higher ^{137}Cs and ^{238}U concentrations in F-Area and higher ^{235}U concentrations in H-Area. The higher ^{235}U content in the H-Area system and higher ^{238}U content in F-Area agree with that expected for fuel reprocessing operations in each canyon. H-Canyon processes enriched uranium fuels and thus releases uranium containing a much higher ^{235}U isotopic abundance than that in F-Area. F-Area processes weapons grade plutonium which is diluted with depleted uranium to reduce the concentration of fissile isotopes. Consequently, F-Area waste contains more uranium, but with a lower ^{235}U enrichment.

Comparing the average uranium and plutonium concentrations between the evaporator feed and concentrate receipt tanks indicates a small increase in the cesium and uranium concentrations in the H-Area system and decrease in uranium concentrations in the F-Area system. The increase in the H-Area system reflects concentration of the waste due to evaporation. The uranium decrease in the F-Area reflects crystallization of uranium salts in the evaporator concentrate receipt tank, Tank 46F. During this time period, H-Area operations limited the water removal in the H-Area system to prevent formation of saltcake. Thus, formation of uranium salts would be less likely than in F-Area where saltcake was produced.

Table 6.1 Average Density, ^{137}Cs, ^{235}U, ^{238}U and ^{239}Pu Concentrations in Evaporator Feed and Concentrate Tank Samples

		Concentration[b]			
Tank	Density[a] (g/mL)	^{137}Cs (Ci/L)	^{235}U (mg/L)	^{238}U (mg/L)	^{239}Pu (mg/L)
43H	1.26 (0.11)	0.43 (0.27)	0.35 (0.19)	2.6 (1.5)	0.023 (0.01)
38H	1.38 (0.085)	0.68 (0.44)	0.51 (0.24)	3.3 (1.5)	0.021 (0.020)
26F	1.38 (0.086)	0.90 (0.37)	0.062 (0.047)	24 (20)	0.10 (0.21)
46F	1.39 (0.033)	0.80 (0.13)	0.030 (0.007)	10 (1.7)	0.011 (0.005)

[a] measured at ambient cell temperature of approximately 20 °C, numbers in parenthesis are 1σ standard deviations.
[b] numbers in parenthesis are 1σ standard deviation.

Figures 6.1, 6.2, and 6.3 provide plots of the density, ^{137}Cs concentration and ^{238}U concentration, respectively, for each of the four waste tank samples over the entire sampling period. The H-Area tanks exhibited an increase in sample density over the course of the sampling period. Tank 43H sample density peaked about 1993, remained constant through 1995 and decreased beginning in 1996. We attribute the decrease in 1996 with the startup of the Defense Waste Processing Facility (DWPF), which sends a relatively dilute waste stream to the H-Area tank farm. With decreased fuel reprocessing at the SRS, the DWPF became the major waste generator. The F-Area tanks exhibited no

discernible trends during this time period.

Both the H and F-Area evaporator feed and concentrate receipt tanks generally exhibited very similar ^{137}Cs concentrations. During this time period the ^{137}Cs concentration varied by up to a factor of thirty. Based on waste volumes processed and the volumes of condensed overheads, concentration factors during the time period averaged a factor of three. Since the variation of ^{137}Cs concentrations is greater than the average concentration factor, the ^{137}Cs concentration is not a useful indicator of solids accumulation in the evaporator.

Non-fissile uranium (i.e., ^{238}U) concentrations in Tank 43H generally are slightly lower than the corresponding sample in Tank 38H. This result is consistent with an increase in uranium concentration upon evaporation of the waste without the significant formation of uranium solids. If significant uranium solids formed, then the ^{238}U concentrations in the Tank 38H samples would be lower than that observed in the Tank 43H samples.

Samples taken from Tank 26F exhibited much higher ^{238}U concentrations than that observed in Tank 43H. Analytical results for the F-Area evaporator concentrate receipt tank (Tank 46F) are available only for the time period of mid-1994 through 1997. Over this time period only three samples exhibited a significant difference. For two of the samples, the Tank 46F samples analyzed lower than the 26F. For one sample, the Tank 46F sample analyzed higher than the 26F sample. Given these results and assuming a threefold concentration during evaporation, about 67% of the uranium deposits in the evaporator concentrate tank, Tank 46F.

Figure 6.1 Tank Sample Density over Sampling Period

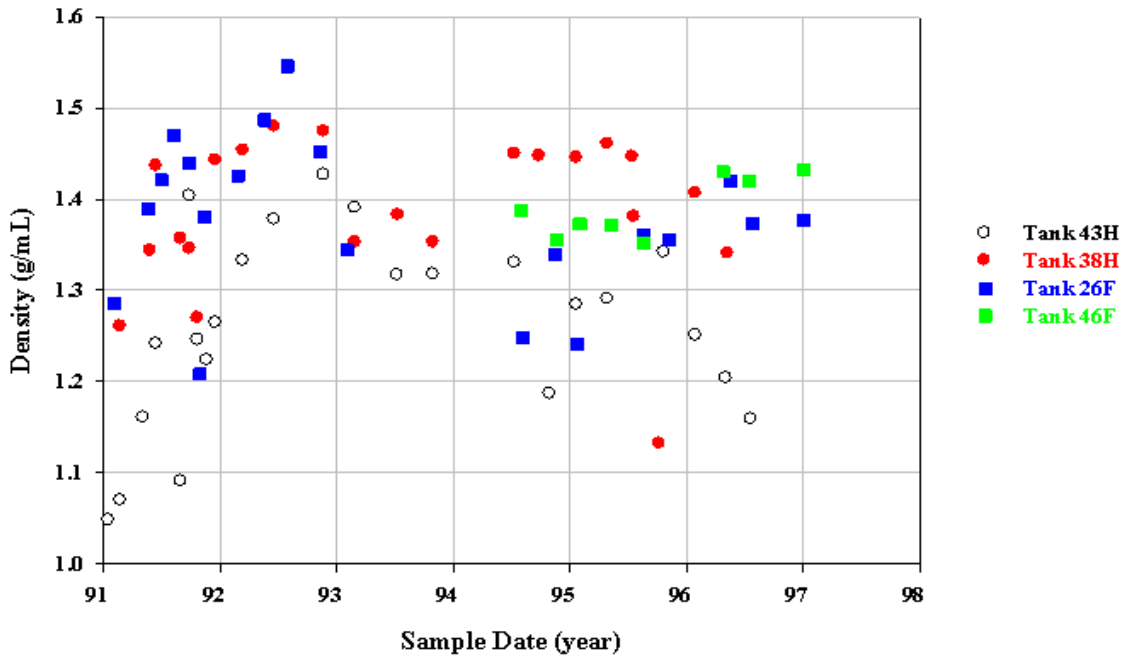


Figure 6.2 Tank Sample ^{137}Cs Concentration over Sampling Period

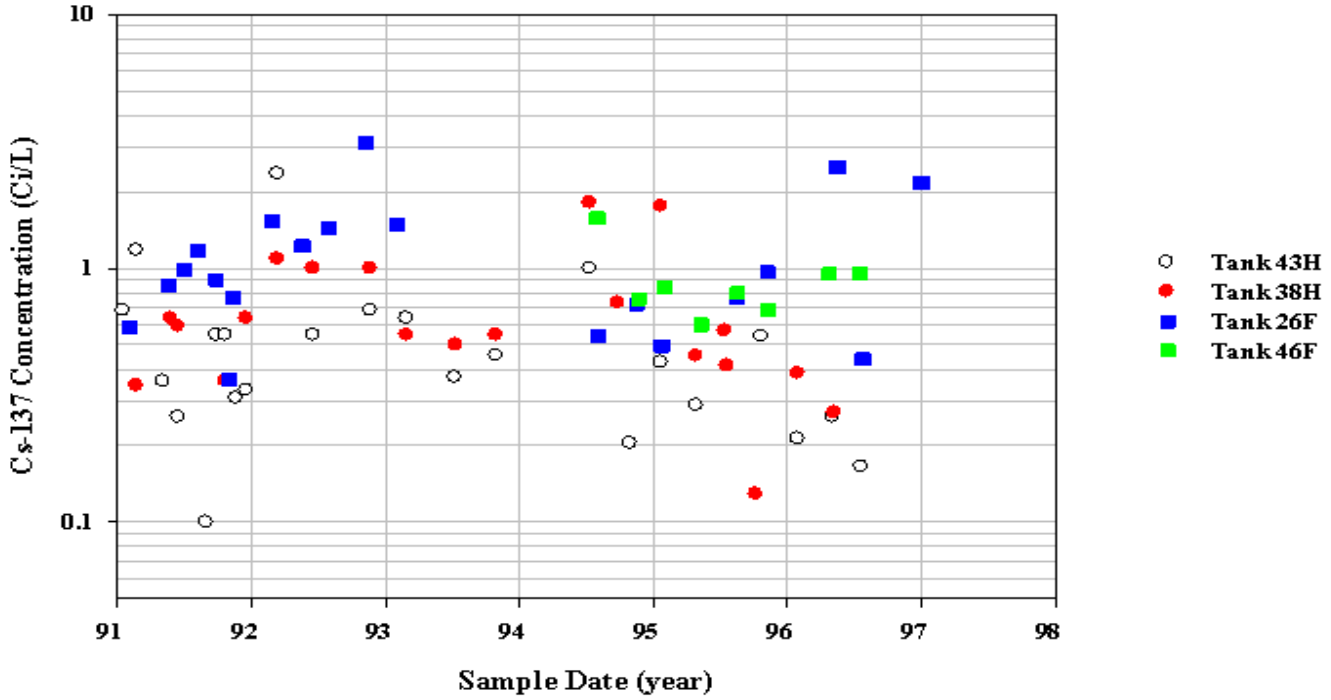
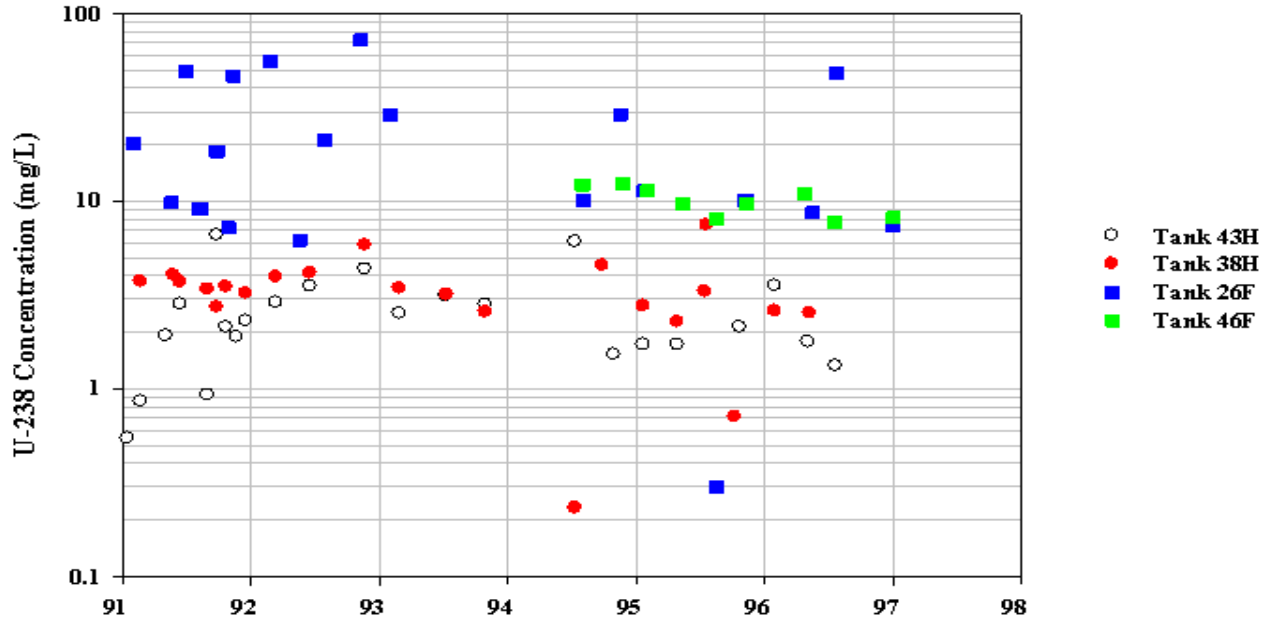


Figure 6.3 Tank Sample ^{238}U Concentration over Sampling Period



6.4 Summary and Conclusion

Analytical results for supernate samples taken from the 2H and 2F evaporator systems indicate the presence of uranium and plutonium at expected concentrations and isotopic abundances. The isotopic abundances are characteristic of the source of the waste material. For example 2H samples contains uranium more highly enriched in ^{235}U and plutonium that is primarily ^{238}Pu, whereas the 2F samples contain uranium depleted in ^{235}U and primarily ^{239}Pu. CSome concentration of both actinidesuranium occurs upon cooling of evaporation ofored waste solutions. The amount of concentration is not significant and does not present a nuclear safety concern.

7.0 References

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