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Characterization of High-Level Waste Saltcake Stored at the Savannah River Site (U)

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INTRODUCTION

Approximately 34 million gallons of high-level nuclear waste (HLW) are stored at the Savannah River Site (SRS) in 51 underground storage tanks. Facilities have been constructed to permanently dispose of this waste. The radioactive components will be separated from the bulk of the waste into a small volume fraction and vitrified in the Defense Waste Processing Facility (DWPF). The remaining, much larger volume fraction will be incorporated into a cement wasteform in the Saltstone facility.

Most of the radioactivity in the HLW is present in a solids fraction referred to as sludge. These solids are produced upon addition of sodium hydroxide to the acidic waste solutions to provide a highly alkaline slurry. The highly alkaline condition is necessary to prevent corrosion of the carbon steel storage tanks. After allowing the sludge solids to settle, the waste solutions are decanted and evaporated to conserve storage space in the tanks. Upon cooling, salts are crystallized from the evaporated wastes. The crystallized salts are referred to as saltcake.

The saltcake will be dissolved in water and processed through the In-Tank Precipitation (ITP) process to remove cesium and strontium radioisotopes. After removal of the radioactivity, the decontaminated salt solution will be transferred to the Saltstone facility and disposed as a low-level waste. The concentrated radioactive fraction will be transferred to the DWPF and vitrified with the sludge fraction of the HLW.

Several nuclear safety issues have arisen associated with the dissolution of saltcake presently stored in Tank 41H. Based on estimates of the inventory of plutonium and uranium in the tank, the accumulation of a critical mass of uranium and, to a lesser extent, of plutonium is postulated if the fissile materials do not completely dissolve. To determine the total plutonium and uranium content and the isotopics for each, saltcake samples were taken from the tank and analyzed. Other chemical and radiochemical analyses were carried out to provide data for planning ITP operations with salt solution prepared from this saltcake.

EXPERIMENTAL

Samples of the saltcake were taken from Tank 41H using a simple tool (see Figure 1). A sample cup approximately 3.8 cm in diameter and 10 cm in length was attached to the end of two 150 cm lengths of galvanized steel pipe. The sample cup was driven into the saltcake filling the sample cavity (see Figure 2). After removing the tool from the waste, the sample cup was separated from the tool, placed into a plastic bag and shielded container, and transported to the laboratory. The as-received samples were removed from the sample cups and stored in glass jars. Because of the high radioactivity, all sampling operations were carried out remotely in shielded cells. Liquid samples after dilution were removed from the shielded cells for chemical analyses.

In March 1993, a single 3.8 cm depth saltcake sample was taken from the B-3 riser on Tank 41H and analyzed[Sample #1-1]. In July 1993, three additional saltcake samples were taken. These samples were taken from the E-1 riser, which is located on the other side of the center support column of the tank from the B-3 riser. Sample #2-1 is the first (top) sample taken on July 12, #2-2 is the second (middle) sample also taken on July 12, and #2-3 is the third (bottom) sample taken on July 13. It was estimated that the total depth of saltcake sampled on July 12 and 13 was 30 centimeters.

Figure 1. Diagram of Sampling Tool

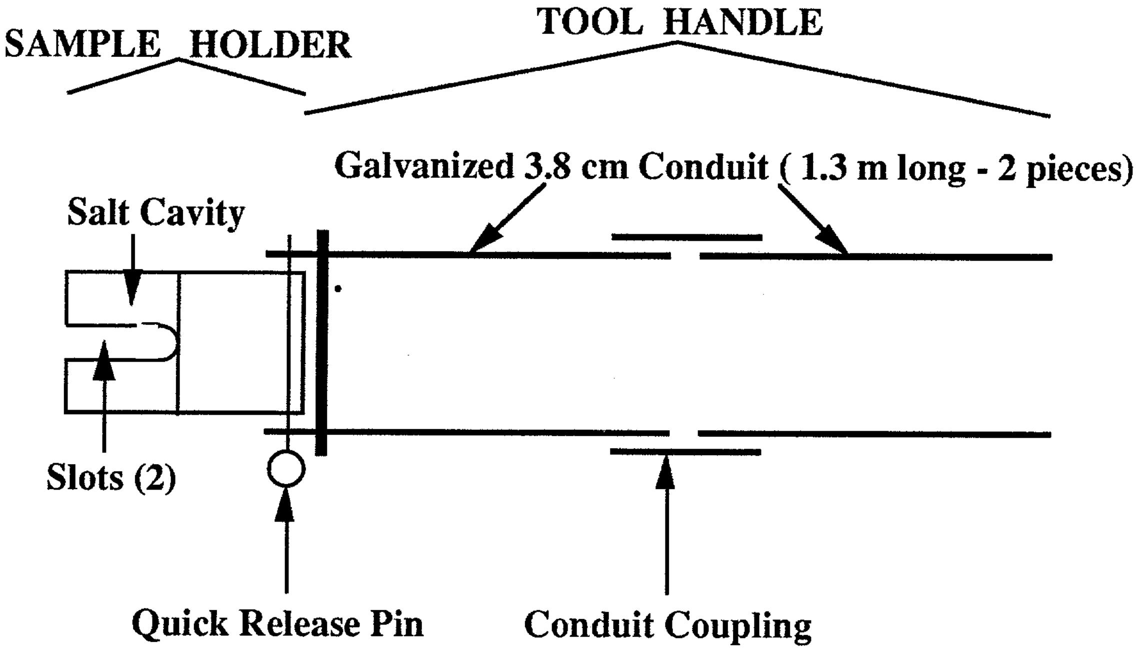
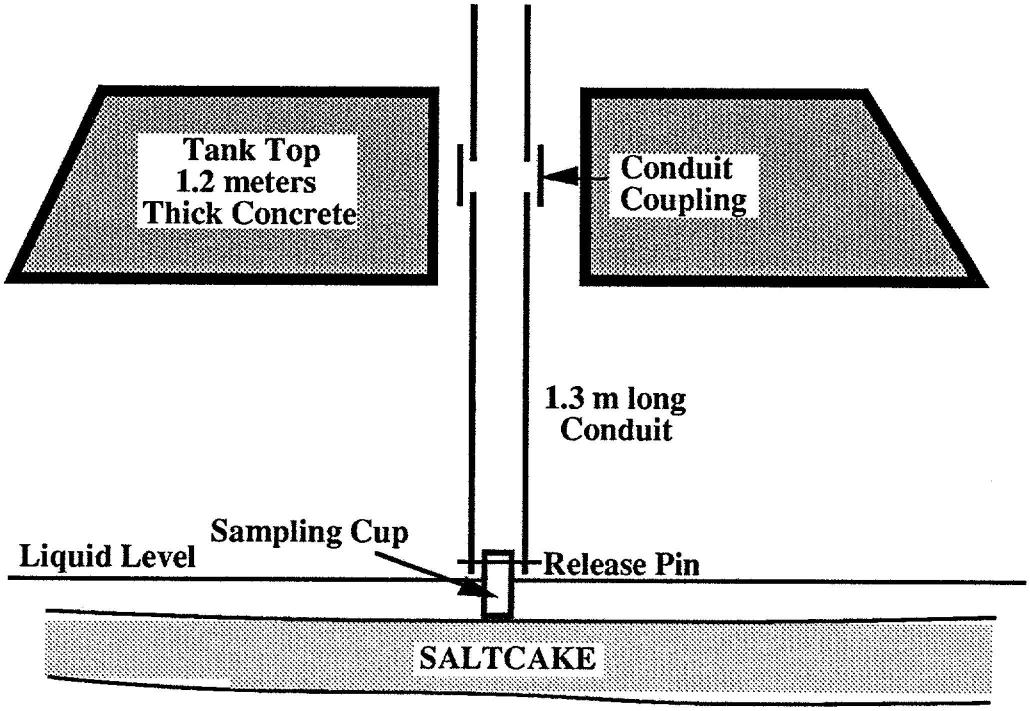


Figure 2. Tank Sampling Diagram



The methodology used for the analysis of each sample consisted of the following: (1) visually inspect the as-received samples, (2) dissolve sub-samples of the as-received samples in 2M nitric acid and perform liquid phase analyses, and (3) dissolve sub-samples of the as-received samples in water, separate liquid phase and any undissolved solids and determine chemical composition of each fraction. The plutonium and uranium content and isotopics were determined by inductively-coupled plasma mass spectrometry (ICP/MS), thermal ionization mass spectrometry (TIMS), and by alpha spectrometry (α-PHA). Elemental composition was determined by inductively-coupled plasma emission spectroscopy (ICP/ES).

Water solubility tests were conducted using a dilute sodium hydroxide (0.015M) solution. The water solubility tests consisted of weighing a known quantity of the saltcake sample into a graduated centrifuge tube, adding increasing amounts of inhibited water, and measuring the volume of undissolved solids. After the final inhibited water addition, the sample was centrifuged, and the clear solution removed from the undissolved solids. The undissolved solids were rinsed with two small portions of inhibited water and dried at 100°C. The dried solids were either submitted for x-ray diffraction (XRD) analysis to identify crystalline phases present or dissolved in 2M nitric acid and analyzed for radiochemical and chemical composition.

RESULTS AND DISCUSSION

General Sample Characteristics and Properties

The saltcake samples contained a mixture of light-colored and dark-colored solids. The density of the saltcake was determined to be 1.9 g/cm^3. The weight percent solids for the samples ranged from about 86% to 89% (see Table I). Sodium nitrate and sodium carbonate were the only crystalline phases identified by XRD in the as-received samples. These findings are consistent with the ion chromatography and ICP/ES results, that indicated that sodium, nitrate, and carbonate are the predominant components of the saltcake.

Table I. Weight Percent Solids and X-Ray Diffraction Results

Date	Sample ID	wt % Solids[1]	Crystalline Phases Identified by XRD
3/93	#1-1	86.3 ± 1.3	$NaNO_3$, Na_2CO_3, $Na_2CO_3 \cdot H_2O$
7/93	#2-1	89.0 ± 3.6	$NaNO_3$, Na_2CO_3, $Na_2CO_3 \cdot H_2O$
7/93	#2-2	nd	nd
7/93	#2-3	89.2 ± 2.4	$NaNO_3$

[1] of the as-received saltcake sample nd = not determined

Saltcake Dissolution Characteristics

The as-received saltcake samples readily dissolved in nitric acid with the evolution of gases (carbon dioxide and nitrogen oxides). The light-colored solids, but not the dark-colored solids rapidly dissolved in water. At a 1:1 volume ratio of water to saltcake, approximately 50% of the saltcake dissolved. At a 2:1 ratio, 70% of the saltcake dissolved and at a 3:1 ratio, 90% of the saltcake dissolved. There was no visible colloidal material, and the dark insoluble solids were observed to settle in the dissolved salt solution after standing overnight or centrifuging for 30 minutes.

Chemical Composition

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. The results for each of these elements for the total sample and the water-soluble fraction are presented in Table II. The potassium:sodium (K:Na) weight ratio in the soluble fraction of the saltcake sample was determined to range from a factor of 4 to 10 lower than that reported for average concentrated salt solution. Consequently, much less potassium tetraphenylborate precipitate (10-25%) will be produced from salt solution resulting from the dissolution of Tank 41H saltcake having the K:Na ratios measured in these samples.

Results from the ion chromatographic and gravimetric methods to determine anion content of the water-soluble solids are also provided in Table II. Nitrate and carbonate were the major anions in the saltcake sample. These results are consistent 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 form carbonate in the aged waste.

The total cation, total anion, and insoluble solids contents for each sample were summed to determine a total solids content for the as-received samples (see Table III). The calculated total solids content was then compared to that determined by drying the as-received sample at 100 °C. Fairly good agreement between the two totals was obtained for each of the samples. This indicated that the overall elemental and chemical analyses of the samples were consistent and that no major component(s) had not been identified.

The total equivalents for cations and anions were calculated for each sample. Both should be the same to maintain an overall neutral charge. For sample #1-1, excellent agreement in the cation and anion equivalents was observed. For samples #2-1 and #2-3, the agreement was not as good, and suggested that not all of the anionic species had been accounted for in the chemical analyses. The unaccounted anionic species may be carbonate. For samples #2-1 and #2-3, the carbonate content was about half of that found in sample #1-1. All other anionic species were similar for each of the samples.

Table II. Chemical Composition of Saltcake Samples

Element/Anion	#1-1	#2-1	#2-2	#2-3
		Weight %		
		Total Sample		
Na	28.0	27.9	26.6	27.3
Al	0.21	0.11	0.25	0.10
P	0.41	0.37	0.43	0.33
Zn	0.059	0.014	0.21	0.069
Cr	0.058	0.092	0.079	0.058
K	0.032	0.019	0.031	0.024
		Water-Soluble Fraction		
Na	25.8	27.0	nd	27.1
Al	0.21	0.093	nd	0.095
P	0.37	0.34	nd	0.25
Zn	0.040	0.0021	nd	0.026
Cr	0.0088	0.021	nd	0.0068
K	0.034	0.014	nd	0.020
Nitrate	40.6	44.1	nd	46.3
Carbonate	11.3	6.5	nd	4.7
Hydroxide	2.0	1.0	nd	1.5
Aluminate	1.0	0.22	nd	0.70
Nitrite	0.98	0.50	nd	0.80
Phosphate	0.71	0.98	nd	0.54
Sulfate	1.2	<0.038	nd	0.65
Oxalate	0.17	<0.076	nd	<0.077
Chloride	0.024	0.020	nd	0.020
Total Anion	58.0	53.3	nd	55.2

nd = not determined

Table III. Saltcake Solids Mass and Charge Balance

	Concentration (wt %)		
	#1-1	**#2-1**	**#2-3**
Total Cation	28.0	27.9	27.3
Total Anion	58.0	53.3	55.2
Insoluble Solids	1.7	0.89	0.77
CalculatedTotal Solids Content	87.7	82.1	83.3
Measured Total Solids Content	86.3	89.0	89.2
	Concentration (mole/100 g saltcake)		
Total Cation Equivalents	1.22	1.21	1.19
Total Anion Equivalents	1.23	1.03	1.05

Radiochemical Analyses

The as-received samples and the water soluble solids were analyzed for radiochemical content. The results are given in Table IV. Radionuclides detected included ^{137}Cs, ^{134}Cs, ^{90}Sr, and ^{99}Tc. ^{137}Cs was the predominant radioactive material found in all of the samples. The concentration of ^{90}Sr was fairly low, most of which was not soluble in inhibited water. Because of the low concentration, removal of ^{90}Sr would not be necessary to meet the recommended Saltstone feed requirements.

Table IV. Radiochemical Analytical Results

	Concentration of As-Received Saltcake Sample (µCi/g)			
Radionuclide	**#1-1**	**#2-1**	**#2-2**	**#2-3**
^{137}Cs	108	65	175	40
^{134}Cs	0.11	0.047	0.16	0.042
^{90}Sr	0.012	nd	nd	nd
^{99}Tc	0.013	nd	nd	nd
^{106}Ru	<0.057	nd	nd	nd
^{154}Eu	<0.22	nd	nd	nd
^{155}Eu	<0.22	nd	nd	nd
^{126}Sn	<0.18	nd	nd	nd

nd = not determined

Uranium and Plutonium Content and Isotopic Abundance

The average concentrations determined for the total uranium and plutonium content and abundances for selected uranium and plutonium isotopes are presented in Table V. The average total uranium content of the three July samples was determined to be 4.5 ± 1.7 µg/g, which is similar to that found for the March sample (5.7 ± 0.44 µg/g). The uranium isotopic abundances for the March and July samples were also very similar. The maximum ^{235}U abundance was determined to be 16% at the 95.2% (2σ) confidence level. Since the March and July samples were taken from two different riser on opposite sides of the tank, it appears that the uranium is distributed uniformly radially in the top 12 inch layer of the tank. The similarity of the isotopic distribution in all of the samples indicates that the uranium is from the same source.

At the 95.2% (2σ) confidence level, the total uranium content for samples #2-1 and #2-2 are not statistically different, but are statistically different from sample #2-3. These results suggest that there is some inhomogeneity in the distribution of the uranium in the 30 cm vertical sampling profile. Based on the July samples, the total uranium content varied by a factor of about two over the 30 cm vertical segment.

The average total plutonium content of the July samples was determined to be 0.033 ± 0.0081 µg/g, which is about half of that found in the March sample (0.065 ± 0.0098 µg/g). The average ^{238}Pu and ^{239}Pu abundances were determined to be considerably different for the March and July samples. However, at the 95.2% (2σ) confidence level, there was no statistically significant differences between the March and July samples because of the greater uncertainty in the March sample results. Because of the greater variation in the plutonium concentrations, it cannot be determined if there was any difference in the vertical distribution of plutonium.

The factor of two difference in the plutonium content between the March and July samples is attributed to the difference in the amount of water-insoluble solids. For both the March and July samples, 95% or more of the total plutonium in the saltcake samples is associated with the insoluble solids fraction. The quantity of insoluble solids in the July samples was about one-half of that found in the March sample. Thus, it follows that the lower plutonium content is due to the lower insoluble solids content in the July samples.

Table V. Average Uranium and Plutonium Concentrations and Isotopic Abundances

	Average Concentration (µg/g)		Isotopic Abundance			
Sample ID	Total U	Total Pu	% ^{235}U	% ^{238}U	% ^{238}Pu	% ^{239}Pu
1-1	5.7	0.065	13	77	58	35
2-1	6.0	0.027	11	80	75	20
2-2	4.8	0.042	11	80	78	18
2-3	2.7	0.029	11	80	77	17
Ave. #2	4.5	0.033	11	80	77	18

Characterization of Water-Insoluble Solids

Crystalline phases in the insoluble solids were identified by x-ray diffraction analysis. Sodium nitrate was found in all the samples. Other crystalline phases found included sodium aluminum silicate, zinc sodium phosphate, sodium fluorophosphate, and zinc sodium silicate (see Table VI). The composition of the dark solids is not identical for all samples indicating some degree of heterogeneity for the insoluble solids among the axial and 30 cm vertical profiles. The insoluble solids were determined to be comprised of chiefly sodium, chromium, zinc, iron, phosphorous, aluminum, silicon, and calcium by ICP-ES. A list of the major elements (≥0.1 wt%) in decreasing concentration for each sample is also provide in Table VI. Chromium, iron, and calcium apparently are present as amorphous solids, since crystalline phase containing these elements were not identified by XRD.

Upon dissolution of the Tank 41H saltcake for the ITP process, insoluble solids will be present. Based on the soluble sodium concentration and the insoluble solids content determined for the March and July samples, the concentration of insoluble solids in the dissolved salt solution is calculated to range from 580 to 7900 mg/L at a sodium ion concentration of 5.2M. Process Requirements for ITP currently limit the insoluble solids content to 400 mg/L. Thus, the insoluble solids content in the dissolved salt solution may exceed the current limit. The insoluble solids limit is provided to minimize possible impacts on filter performance by insoluble solids other than monosodium titanate and tetraphenylborate salts. Removal of the insoluble solids from the dissolved salt solution may be required to prevent any impact on the performance of the ITP filters.

Table VI. Solids Content and Crystalline Phases of the Water Insoluble Solids

Sample ID	wt % Solids Wet Basis[1]	XRD Results	Major Elements
#1-1	1.7	$Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O$ $NaNO_3$ $Zn_2NaP_3O_{16} \cdot 9H_2O$	Na, Zn, Cr, P, Al, Fe, Ca, Si
#2-1	0.52	$NaNO_3$ $Na_8(Al_6Si_6O_{24})(S_2O_3) \cdot 3H_2O$	Na, Cr, Ca, Fe, Zn, P, Al, Si
#2-3	0.76	$NaNO_3$ Na_2ZnSiO_4 $Na_7F(PO_4)_2 \cdot 19H_2O$	Na, Cr, Fe, P, Ca, Zn, Al, Si

[1] % dark solids in as-received saltcake sample.

Determination of Water-Soluble and Insoluble Uranium and Plutonium Content

The uranium and plutonium content of the water soluble and insoluble solids is given in Table VII. From the ICP/MS data, there was no detectable plutonium in the soluble fraction of the July samples, indicating all of the plutonium was associated with the insoluble solids. Alpha-PHA spectrometry indicated that the soluble solids did have a small amount of plutonium activity. It is estimated that no more than 5% of the total plutonium present in the July saltcake samples was associated with or remained in the dissolved salt solution. Between 63% and 89% of the total uranium present in the saltcake is associated with soluble solids fraction.

Table VI. Uranium and Plutonium Concentration and Percent of Total Content in Water-Soluble and Water-Insoluble Solids

	Concentration and % of Total					
	#1-1		#2-1		#2-3	
	µg/g	% of Total	µg/g	% of Total	µg/g	% of Total
Soluble U	4.68	89	3.7	82	1.4	63
Insoluble U	32.8	11	620	18	98	37
Soluble Pu	1.24E-3	4.7	0	0	0	0
Insoluble Pu	1.45	95	11.8	100	3.46	100

SUMMARY AND CONCLUSIONS

The saltcake at the top of Tank 41H has a total uranium concentration of between 3.0 and 7.3 µg/g and ^{235}U abundance of 16% and total plutonium concentration of between 0.034 and 0.061 µg/g and ^{239}Pu abundance of 32%. Based on the low plutonium and uranium concentrations, the low ^{235}U abundance, and the fill history of Tank 41H, up to 1.5 meters of saltcake may be safely dissolved without further sampling and characterization of saltcake. Accumulation of the water-insoluble solids in the tank during saltcake dissolution is not 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 be required before processing this saltcake in the ITP process to prevent impacting filter performance. The low ^{90}Sr concentration in the saltcake samples indicates that the removal of ^{90}Sr will not be necessary upon processing this saltcake in the ITP process. Due to the low potassium concentration, it is estimated that only 10-25% of the flowsheet amount of potassium tetraphenylborate precipitate will be produced upon processing this saltcake in the ITP process.

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