WSRC-TR-2001-00519, Rev. 0

Keywords: Tank Farm, Characterization, Criticality

Retention Time: Permanent

Characterization of Tank 46F Core Samples

Author (s): L. N. Oji and W. R. Wilmarth

Publication Date: February 5, 2002

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

SUMMARY

In support of criticality analysis for Tank 46F we have analyzed two batches of its core samples. Results of this analysis indicate that the average amount of neutron poisons (Na, Fe, Mn, Cr and Zn) and, therefore, their corresponding poison-to-equivalent U-235 ratios for the "as-received" core samples and insoluble solids from Tank 46F meet the Minimum Safe Ratios of Inherent Saltcake Metals –to-Uranium ratios.

We analyzed Tank 46F samples for the presence of aluminosilicate formation species: silicon, aluminum, sodium and free-OH^-. Of the two batches of Tank 46F "as-received" core samples provided by the plant, the Al/Si ratios in the second batch of core sample was significantly higher than in the first batch of core sample. Similarly, the total sodium concentration in the second batch of the "as-received" Tank 46F core sample was also about twice as high as in the first batch of core samples. The free-OH^- concentration, measured in the liquid fraction from the first batch of Tank 46F core sample, was 11.45 M.

The first batch of Tank 46F-core sample contained both a liquid and a solid fraction, while the second batch was all solid material.

TABLE OF CONTENTS

LIST OF TABLES

1.0 INTRODUCTION

Tank 46F is the current drop tank for the 2F evaporator and contains about190 inches of saltcake. Samples from the High Level Waste (HLW) Evaporator feed and drop tanks are analyzed every six months for criticality safety and scale formation potential. Analysis performed under this program includes analysis for silicon, aluminum, sodium, and free hydroxide concentration (evaluation of scale formation rates) and suite of criticality analyses[1]. The recent minor leaks detected in Tank 5F have also led to HLW engineering to attempt to decide where to send material from Tank 5F. One of the primary options is to transfer Tank 5F material to Tank 46F. In order to support the Tank 5F transfer decision process, data is needed on the uranium isotopic distribution in the salt in Tank 46F.

This Tank 46F characterization complies with the work scope defined in the following plans: L. N. Oji and W. R. Wilmarth, " Task Technical and Quality Assurance Plan for the Periodic Characterization and Analysis of Evaporator Feed and Drop Tanks for Criticality and Scale Formation Potential," WSRC-RP-2001-00679, Rev. 0, May 17, 2001 and Technical Task Request HLE-TTR- 2000-035 from B.L. Lewis titled " Periodic Tank Analysis for Evaporator Monitoring" February 26, 2001.

2.0 EXPERIMENTAL

Two batches of Tank 46F samples were sent to SRTC for characterization. The first batch of Tank 46F-core sample (T46FTF048) supplied by the plant for characterization consisted of distinct liquid and solid phases. Based on our normal procedure for processing salt samples, this as-received Tank 46F-core sample was further separated into solid and liquid fractions using a centrifuge. These two phases were to be characterized separately. However, because preliminary tests showed that the solid fraction completely dissolved in inhibited water (0.015 M NaOH), leaving no solids to wash and characterize, the plant customer provided SRTC with a second batch of Tank 46F-core sample. This second batch of Tank 46F-core sample was mostly salt cake and contained no liquid fraction even with centrifugation. The characterization of the "as-received" sample, third inhibited water wash liquid of the solid fraction, and the dried insoluble core solids were based on this second batch of Tank 46F-core sample provided by the plant. See Table 1 for a summary of analyses requested by the plant.

The characterization of the two batches of Tank 46F samples are presented in the following order: Analysis and characterization of batch II samples (as-received, washed and dried solid Sample and 3rd wash Core sample chemistry), and analysis and characterization of batch 1 samples (As-received sample, as received sample solid fraction and as received sample liquid fraction).

In both cases above, aliquots of the "as-received" Tank 46F core-samples were digested in triplicate by two different methods (aqua regia dissolution and sodium peroxide fusion digestion) and analyzed for various number of different chemical species (Table 1). Using the as-received sample from the second batch of Tank 46F sample, a portion of the "as- received" solid was also washed three times with inhibited water and the resulting solids from inhibited water wash were dried to a constant weight, digested (aqua regia dissolution and sodium peroxide fusion digestion) and analyzed for chemical species.

As mentioned earlier, no residual solids were obtained in preliminary tests for solids when the "as received" solids from the first batch of tank 46F samples was washed with inhibited water.

In the inhibited water washing process used to separate the undissolved salts from the soluble components of the Tank 46F core sample, about 10 grams of the cake was placed into each of four 40-ml centrifuge tubes and 30 ml of inhibited water was added to each tube. The centrifuge tubes were shaken for several minutes and allowed to settle for at least 12 hours. The centrifuge tubes were centrifuged for at least two periods of 15 minutes each, or in some cases more, until consecutive centrifuge runs produced no apparent reduction in volume of undissolved components. After this centrifuging, the salt solution was carefully decanted from each of the four tubes. The washing process was performed three times with each of the four centrifuge tubes. The insoluble solids remaining after three of such washes were dried to a constant weight in a convection oven set to 110 °C.

Both the solid and liquid fractions from the first batch of Tank 46F sample were also separately characterized for chemical species: aqua regia dissolution and sodium peroxide fusion digestion for the solids fraction and analysis of the liquid portion without further treatment.

Table 1 Analyses Conducted on Samples from Tank 46F Core Samples

Analysis/Analytical Method	As-Received Sample **Batches I &II**	solid fraction from liquid separation by centrifuging **Batch I**	I[st] Liquid fraction from liquid separation by centrifuging **Batch I**	3[rd] inhibitor wash liquid of solid fraction **Batch II**	Dried Insoluble Core Solids **Batch II**
Density	X	-	-	-	-
Na_2O_2 Digestion	X	X	-	-	X
Aqua Regia	X	X	-	-	X
U and Pu-isotopes (By ICP-MS)	X	X	X	X	X
Tank 50 Rad Screen for total α and β	X	X	X	X	X
Pu-238 and 241 (PuTTA)	X	X	X	X	X
Aluminates, Carbonates and Free OH	-	-	X	X	-
IC – Anions NO_3, NO_2	-	-	X	X	-
ICP-ES: Al, Si Cr, Na, ,Fe, Mn, Zn	X	X	X	X	X
XRD	-	-	-	-	X (insufficient solid sample)

3.0 RESULTS

3.1 Analytical results

The principal analytical techniques employed by ADS in this characterization include the following techniques: Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)[2] for radiochemical analysis for the actinides, alpha counting for Pu-238/241(PuTTA), Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES)[3], for elemental analysis, wet chemistry (free OH, aluminate and carbonate), IC-anions[4] and Tank 50 rad screen[5] for total alpha and beta activities, and gamma scan for gamma emitting isotopes[6].

The ICP-MS results are given for each atomic mass, and with the exception of a few cases, each mass number represents only one isotope. In the case of mass number-238, however, both uranium and plutonium can be represented by this mass number. Also, mass 241 represents both Pu and Am. Hence, Pu-238 and Pu-241 results were measured by PuTTA to distinguish the values from uranium-238 and americium-241 values, respectively. The total plutonium results reported in each Table are based on Pu-238 and Pu-241 values from PuTTA and ICP-MS actinide results for Pu-239, Pu-240 and Pu-242. Equivalent U-235 was determined using the following summation: U-235+ 4.02(Pu-239 + Pu-241+U-233)[7].

No elemental analysis results are given for sodium, zirconium and silver from peroxide fusion digestions because this technique adds considerable amounts of sodium as a reagent and the digestion crucible is made of zirconium because of high temperature requirements. This technique also introduces significant interference for the determination of silver. Hence, in cases were these elements are not reported for peroxide fusion, the combined average values for these elements are represented by those from aqua regia digestion.

In the Tables, values preceded by "<" (less than sign) were below detection limits and no standard deviation values are provided in these cases. In the ICP-MS summary for actinides a "bdl" is used to indicate below detection limits. In cases where ADS provided results which were below and above detection limits (samples analyzed in triplicate), the actual values and limits of detection are averaged and preceded by "≤", indicating that the average of the results is " less than or equal to" the given result.

The uncertainties reported for the poison/ equivalent U-235 ratios are based on propagation of errors. Likewise, no standard deviations are provided for ratios of elements to equivalent uranium or combined apparent averages based on aqua regia dissolution and peroxide fusion digestion because these two methods are entirely different methods of sample preparation.

For both the "as-received" sample and the digested insoluble solids, concentration units are reported here as follows: Elemental analysis (ICP-ES): weight percent (wt. %), Actinides (ICP-MS): weight percent (wt. %), Rad screen (α and β activity): disintegration per minute per gram solid (dpm/g),
Plutonium (PuTTA): weight percent (wt. %) and disintegration per minute per gram solid (dpm/g).

For the analysis of third wash liquid, concentrations are reported as mg/L for both elemental analysis and ICP-MS for actinides, disintegration per minute per milliliter (dpm/mL) and mg/L for PuTTA, disintegration per minute per milliliter (dpm/mL) for rad screen.

3.2 Analysis of "As-Received" Batch II Tank 46F Core Sample

The density of this batch II Tank 46F core sample is not reported because of difficulties encountered in reproducing the density values. This difficulty stems from the fact that the core sample was hard and could not be compacted uniformly in a density tube.
Without further processing, aliquots of Tank 46F "as-received" core samples were digested in triplicate (Aqua regia dissolution and sodium peroxide fusion digestion) and analyzed for the following species (Table 1): actinides, rad screen for alpha and beta, plutonium isotopes. These analytical results are summarized in Tables 2, and 3.

Table 2 As-Received Core Sample: Batch II Tank 46 Sample.

		Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution **Average dpm/g**
Tk 50 Rad Screen		Av. dpm/g	**St. Dev.**		Av. dpm/g)	**St. Dev.**		
Alpha	<	1.55E+07		<	1.55E+07			< 1.55E+07
Beta		1.78E+09	*4.91E+08*		6.31E+08	*5.02E+07*		1.21E+09
Pu-238/241		**Wt. %**			**Wt. %**			**Wt. %**
Pu-238		2.55E-06	*1.84E-07*		1.73E-06	*3.49E-07*		2.14E-06
Pu-241		2.13E-07	*3.12E-08*	<	4.50E-07			< 3.32E-07
Pu-238/241		**Av. dpm/g**			**Av. dpm/g**			**Av. dpm/g**
Pu-238		9.69E+05	*7.00E+04*		6.57E+05	*1.33E+05*		8.13E+05
Pu-241		4.87E+05	*7.14E+04*	<	1.03E+06			< 7.58E+05
ICP-MS-Act.		Average	**St. Dev.**		Average	**St. Dev.**		Average
		Wt. %			**Wt.%**			**Wt.%**
M-232 (Th)		bdl			bdl			bdl
M-233 (Pa)		bdl			bdl			bdl
M-234 (Th,U)	<	8.36E-06			1.80E-05	*1.652E-05*	<	1.32E-05
M-235 (U)		4.11E-05	6.33E-06		5.46E-05	*4.60E-05*		4.78E-05
M-236 (U)		bdl			bdl			bdl
M-237 (Np)		bdl			9.01E-06			9.01E-06
M-238 (U, Pu)		6.04E-03	7.28E-04		5.79E-03	5.94E-04		5.91E-03
M-239 (Pu)		bdl			bdl			bdl
Total U		6.09E-03	*7.28E-04*		5.87E-03	*6.27E-04*		5.98E-03
Total Pu		2.77E-06	*2.840E-07*		2.18E-06	*4.76E-07*		2.47E-06
U-235/U-total		6.729E-03	*2.63E-04*		9.261E-03	*5.67E-04*		7.995E-03
Equiv. U-235		4.19E-05	*6.34E-06*		5.64E-05	*4.60E-05*		4.91E-05
Na/Equiv.U-235		8.93E+05	*1.80E+05*		NA			8.93E+05
Fe/Equi.U235		3.06E+02	*6.14E+01*		5.59E+02	*4.66E+02*		4.33E+02
Cr/Equi.U235		3.17E+02	*9.19E+01*	<	2.36E+02		<	2.76E+02
Zn/Equi.U235	<	6.80E+01		<	5.06E+01		<	5.93E+01
Mn/Equi.U235	<	2.42E+01		<	1.80E+01		<	2.11E+01

Table 3 As-Received: Batch II of Tank 46 Sample.

	Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution		
ICP-ES		Average	**St. Dev.**		Average	**St. Dev.**		Average	
Species		(Wt. %)			(Wt. %)			(Wt. %)	
Ag	<	5.703E-03			NA		<	5.703E-03	
Al		2.849E+00	*7.993E-01*		1.223E+00	*9.679E-02*		2.036E+00	
B	≤	1.837E-02		<	4.773E-03		≤	1.157E-02	
Ba	<	2.851E-03		<	1.909E-03		<	2.380E-03	
Ca		4.729E-03	*7.889E-04*	<	4.391E-02		≤	2.432E-02	
Cd	<	1.901E-03		<	2.864E-03		<	2.382E-03	
Co	<	6.653E-03		<	1.814E-02		<	1.239E-02	
Cr		1.329E-02	*3.285E-03*	<	1.718E-02		≤	1.523E-02	
Cu		1.642E-03	*1.353E-04*	<	5.727E-03		≤	3.685E-03	
Fe		1.283E-02	*1.689E-03*		3.151E-02	*5.474E-03*		2.217E-02	
La	<	1.236E-02		<	1.098E-01		<	6.106E-02	
Li	<	1.901E-03		<	7.636E-03		<	4.769E-03	
Mg		1.653E-03	*3.457E-04*		3.635E-03	*6.454E-04*	<	2.644E-03	
Mn	<	1.012E-03		<	1.909E-03		<	1.461E-03	
Mo		5.384E-03	*1.265E-03*	<	7.636E-03		≤	6.510E-03	
Na		3.744E+01	*4.992E+00*		NA			3.744E+01	
Ni	<	6.653E-03		<	2.768E-02		<	1.717E-02	
P		5.106E-02	*9.289E-03*	<	4.773E-02		≤	4.939E-02	
Pb	<	2.851E-02		<	2.415E-01		≤	1.350E-01	
Si		NA		<	6.777E-02		≤	7.917E-02	
Sn	<	1.616E-02		<	4.458E-01		<	2.310E-01	
Sr	<	9.504E-04		<	1.909E-03		<	1.430E-03	
Ti	<	9.504E-04		<	2.864E-03		<	1.907E-03	
U		9.186E-02	*8.226E-03*	<	4.649E-01		≤	2.784E-01	
V	<	2.851E-03		<	1.050E-02		<	6.676E-03	
Zn	<	2.851E-03		<	5.727E-03		<	4.289E-03	
Zr	<	1.901E-03			NA		<	1.901E-03	

3.3 Analysis of washed and dried Insoluble Solid: Tank 46F Batch II Core Sample.

The insoluble solids resulting from the three wash processes were dried to a constant weight. Of the 40 g of the Batch II Tank 46 solid cake used in the washing process, only a total of 0.297 grams of dried insoluble core solids was realized. A minimum of 1.5 grams is normally required to analyze the solids in triplicate for the above two characterizations (peroxide fusion and aqua regia digestion). After consulting with the plant customer, the number of analytical replicates was reduced to two for aqua regia digestion and one peroxide fusion due to this limited amount of insoluble solids. For each digestion, an average of 0.094 grams of the dry solid was digested in acid solutions and brought to a final volume of 100 ml with distilled water. The analytical results are summarized in Tables 4, and 5.

The ICP-ES elemental analytical results, Table 4, based on aqua regia digestion for iron (0.17wt %) is significantly different from the complimentary peroxide fusion digestion result for iron (21.87 wt %). A re-analysis of the digested samples showed that the difference is not due to analytical errors. Since this shielded cell work was carefully planned to minimize any sources of external contamination, we can only attribute this difference in iron results to the lack of homogenous blending of the small residual insoluble sample prior to the digestions. The average combined dissolution data is therefore considered more useful in calculating relevant parameters such as iron to equivalent uranium-235 ratio.

The X-ray characterization of the insoluble solids (Table 1) was not performed because of the limited amount of insoluble solids obtained from the wash process.

Table 4 Washed and Dried Solid: Batch II of Tank 46 Sample.

	Aqua Regia Dissolution			Peroxide Fusion Digestion			Average Combined Dissolution	
ICP-ES Species	Average (Wt. %)		**St. Dev.**	Average (Wt. %)		**St. Dev.**	(Wt. %)	
Al		3.026E+01	*4.113E-01*		2.792E+01	NA		2.909E+01
B	<	3.300E-03			6.600E-03	NA	≤	4.950E-03
Ba		4.300E-03	*2.828E-04*		1.050E-02	NA		7.400E-03
Ca		6.930E-02	*4.384E-03*		2.516E-01	NA		1.605E-01
Cd	≤	2.400E-03			1.580E-02	NA	≤	9.100E-03
Co	≤	3.550E-03		<	2.020E-02	NA	≤	1.188E-02
Cr		6.915E-02	*6.293E-03*		9.120E-02	NA		8.018E-02
Cu	≤	4.100E-03			3.120E-02	NA		1.765E-02
Fe		1.710E-01	*2.468E-02*		2.187E+01	NA		1.102E+01
La	<	1.085E-02		<	1.223E-01	NA	<	6.658E-02
Li	<	3.300E-03		<	8.500E-03	NA	<	5.900E-03
Mg		3.700E-03	*1.273E-03*		7.420E-02	NA		3.895E-02
Mn		6.300E-03	*2.828E-04*		8.470E-02	NA		4.550E-02
Mo		1.690E-02	*9.899E-04*		1.980E-02	NA		1.835E-02
Na		5.917E-01	*1.881E-02*		NA	NA		5.917E-01
Ni	≤	1.225E-02			5.410E-02	NA	≤	3.318E-02
P	≤	3.840E-02			1.178E-01	NA	≤	7.810E-02
Pb	≤	5.095E-02		<	2.691E-01	NA	≤	1.600E-01
Si		NA			2.560E+00	NA		2.560E+00
Sn		3.425E-02	*1.485E-03*	<	4.968E-01	NA	≤	2.655E-01
Sr	<	1.100E-03			1.310E-02	NA	≤	7.100E-03
Ti		1.650E-03	*7.071E-05*		5.960E-02	NA		3.063E-02
U		2.908E-01	*7.212E-03*	<	5.181E-01	NA	≤	4.045E-01
V		3.800E-03	*4.243E-04*	<	1.170E-02	NA	≤	7.750E-03
Zn		7.500E-03	*9.899E-04*		3.704E-01	NA		1.890E-01
Zr		4.200E-03	*4.243E-04*		NA	NA		4.200E-03

Table 5 Washed and Dried Solid: Batch II Tank 46F Sample (Continued).

	Aqua Regia Dissolution		Peroxide Fusion Digestion		Combined Dissolution **Average**
Tk 50 Rad Screen	**Av. dpm/g**	**St. Dev.**	**dpm/g**	**St. Dev.**	**Av. dpm/g**
Alpha	2.105E+07	1.747E+07	5.394E+07	NA	3.749E+07
Beta	4.734E+08	3.596E+08	9.053E+08	NA	6.894E+08
Pu-238/241					
Pu-238	3.81E+07	*1.271E+07*	2.88E+07	NA	3.346E+07
Pu-241	1.51E+07	*5.115E+06*	1.02E+07	NA	1.263E+07
Pu-238/241	**Wt. %**		**Wt. %**		**Wt. %**
Pu-238	1.00E-04	*3.35E-05*	7.59E-05	NA	8.81E-05
Pu-241	6.56E-06	*2.22E-06*	4.41E-06	NA	5.48E-06
ICP-MS	Average	**St. Dev.**		**St. Dev.**	Average
	Wt. %		**Wt. %**		**Wt. %**
M-232 (Th)	bdl		5.05E-04	NA	2.53E-04
M-233 (Pa)	bdl		bdl	NA	bdl
M-234 (Th,U)	bdl		4.49E-04	NA	2.24E-04
M-235 (U)	1.22E-03	*2.72E-04*	1.15E-03	NA	1.18E-03
M-236 (U)	bdl		bdl	NA	bdl
M-237 (Np)	bdl		bdl	NA	bdl
M-238 (U, Pu)	2.34E-01	*7.38E-02*	2.11E-01	NA	2.23E-01
M-239 (Pu)	bdl		4.13E-04	NA	2.06E-04
M-240 (Pu)	bdl		bdl	NA	bdl
M-241 (Pu,Am)	bdl		bdl	NA	bdlss
Total U	2.35E-01	*7.38E-02*	2.14E-01	NA	2.24E-01
Total Pu	1.07E-04	*3.57E-05*	4.93E-04	NA	3.00E-04
U-235/U-Tot	5.20E-03	*2.01E-03*	5.42E-03	NA	5.31E-03
Equivalent U-235	1.25E-03	*2.81E-04*	2.82E-03	NA	2.04E-03
Na/Eq. U-235	4.88E+02	*1.25E+02*	NA	NA	4.88E+02
Fe/Eq. U-235	1.38E+02	*1.14E+01*	7.75E+03	NA	3.95E+03
Cr/Eq. U-235	5.62E+01	*7.63E+00*	3.23E+01	NA	4.43E+01
Zn/Eq. U-235	6.07E+00	*5.75E-01*	1.31E+02	NA	6.86E+01
Mn/Eq. U-235	5.15E+00	*9.33E-01*	3.00E+01	NA	1.76E+01

3.4 Analysis of Tank 46 Core Sample Wash Water: Third Wash Chemistry

Only the third wash water from all the three washes with inhibited water was collected and submitted for analysis for the following species: Uranium and plutonium by ICP-MS, Pu-238 and 241, rad screen for total alpha and beta, metal cations by ICP-ES and IC anions. The results are presented in Tables 6 and 7.

Since the first and second wash water samples were not analyzed, variations in the concentration of species as a function of number of washes can not be evaluated.

Table 6. Third Wash Core Sample Chemistry: <u>Batch II Tank 46F Sample</u>

	Average		**St. Dev.**
ICP-ES	Mg/L		
Al		8.003E+01	*5.661E+01*
B		3.767E+00	*2.857E+00*
Ba	<	3.000E-01	
Ca		8.367E+00	*3.157E+00*
Cd	≤	8.333E-01	
Co	<	3.000E-01	
Cr	≤	2.333E+00	
Cu	≤	3.667E-01	
Fe		8.067E+00	*5.707E+00*
La	<	1.000E+00	
Li	<	3.000E-01	
Mg		7.000E-01	*2.65E-01*
Mn	≤	1.667E-01	
Mo		1.000E+00	*7.81E-01*
Na		2.182E+03	*1.44E+03*
Ni	<	9.000E-01	
P	≤	8.300E+00	
Pb	<	4.600E+00	
Si		5.560E+01	*4.479E+01*
Sn	<	1.600E+00	
Sr	<	1.000E-01	
Ti	<	1.000E-01	
U	<	7.700E+00	
V	<	3.000E-01	
Zn		4.700E+00	*4.857E+00*
Zr	<	3.000E-01	

Table 7. Third Wash Core Sample Chemistry: Batch II Tank 46F Sample (continued).

	Average	St. Dev.
Tk 50 Rad Screen	**dpm/ml**	
Alpha	< 4.07E+04	
Beta	7.53E+05	*4.57E+05*
Pu-238/241		
Pu-238	3.80E+03	*1.96E+03*
Pu-241	< 5.53E+03	
Pu-238/241	**Mg/L**	
Pu-238	1.00E-06	*5.17E-07*
Pu-241	< 2.40E-07	
IC-Anions	**Mg/L**	
Cl^-	< 40	
F^-	< 40	
NO_3^-	140	57
NO_2^-	< 200	
SO_4^{-2}	< 100	
PO_4^{-3}	< 200	
CHO_2^-	< 200	
$C_2O_4^{-2}$	< 200	
Wet Chemistry	**Molarity**	
Free OH^-	< 0.4	
CO_3^{-2}	< 0.4	
AlO_2^-	< 0.4	
ICP-MS	Average	
	Mg/L	
M-232 (Th)	bdl	
M-233 (Pa)	bdl	
M-234 (Th,U)	bdl	
M-235 (U)	bdl	
M-236 (U)	bdl	
M-237 (Np)	bdl	
M-238 (U, Pu)	2.387E+00	*6.111E-01*

3.50 Analysis of "As-Received" Batch I Tank 46F Core Sample

The average density of the "as received" batch I slurry from Tank 46F was 1.58 ± 0.02 g/cc at a temperature of 27 ± 1°C inside the shielded cell.

Aliquots of Tank 46F (Batch I) "as-received" core samples were digested in triplicate (Aqua regia dissolution and sodium peroxide fusion digestion) and analyzed for the following species (Table 1): actinides, rad screen for alpha/ beta and plutonium isotopes. These analytical results are summarized in Tables 8 and 9.

Table 8 As-Received Core Sample: <u>Batch I Tank 46</u> <u>Sample .</u>

	Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution Average		
Species	Average		**St. Dev.**	Average		**St. Dev.**			
ICP-ES	(Wt. %)			(Wt. %)			(Wt. %)		
Ag	<	5.000E-03			NA		<	5.000E-03	
Al		1.159E+00	*2.287E-01*		1.053E+00	*1.536E-01*		1.106E+00	
B		1.067E-02	*1.485E-03*		4.467E-02	*3.935E-02*		2.767E-02	
Ba	<	3.000E-03		≤	2.567E-03		≤	2.783E-03	
Ca	<	1.000E-03		<	4.600E-02		<	2.350E-02	
Cd	<	2.000E-03		<	3.000E-03		<	2.500E-03	
Co	<	3.000E-03		<	1.900E-02		<	1.100E-02	
Cr		2.200E-02	*4.313E-03*		3.457E-02	*1.152E-02*		2.828E-02	
Cu	≤	6.033E-03		≤	7.100E-03		≤	6.567E-03	
Fe	≤	6.767E-03			1.100E-01	*7.150E-02*	≤	5.837E-02	
La	<	1.000E-02		<	1.150E-01		<	6.250E-02	
Li	<	3.000E-03		<	8.000E-03		<	5.500E-03	
Mg	<	1.000E-03		≤	3.500E-03		≤	2.250E-03	
Mn	<	1.000E-03			7.400E-03	*5.786E-03*	≤	4.200E-03	
Mo		7.500E-03	*2.263E-03*	≤	8.467E-03		≤	7.983E-03	
Na		2.416E+01	*3.089E+00*		NA			2.416E+01	
Ni	<	9.000E-03		<	2.900E-02		≤	1.900E-02	
P		5.870E-02	*1.959E-02*	≤	1.116E-01		<	8.515E-02	
Pb	<	3.600E-02		<	2.53E-01		<	1.445E-01	
Si		NA			1.071E-01	*1.529E-02*		1.071E-01	
Sn	<	1.600E-02		<	4.670E-01		<	2.415E-01	
Sr	<	1.000E-03		<	2.000E-03		<	1.500E-03	
Ti	<	1.000E-03		≤	3.267E-03		≤	2.133E-03	
V	<	3.000E-03		<	1.100E-02		<	7.000E-03	
Zn	<	3.000E-03		≤	7.900E-03		≤	5.450E-03	
Zr		3.000E-03			NA			3.000E-03	

Table 9 As-Received Core Sample: Batch I Tank 46F Sample.

	Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution Average		
Tk 50 Rad Screen		**Av. dpm/g**	**St. Dev.**		**dpm/g**	**St. Dev.**		**dpm/g**	
Alpha		≤1.67E+06	1.04E+05		≤ 2.68E+06	*1.11E+06*	≤	2.18E+06	
Beta		2.92E+09	9.02E+07		2.58E+09	*3.74E+08*		2.75E+09	
Pu-238/241		**Av. dpm/g**			**Av. dpm/g**			**Av. dpm/g**	
Pu-238		2.67E+05	*4.76E+04*		≤ 7.85E+05	*4.41E+05*	≤	5.26E+05	
Pu-241		1.70E+05	*8.24E+04*		< 1.02E+06		≤	5.87E+05	
Pu-238/241		(Wt. %)	**St. Dev.**		(Wt. %)	**St. Dev.**		(Wt. %)	
Pu-238		7.04E-07	*1.25E-07*		≤ 2.07E-06	*1.16E-06*	≤	1.39E-06	
Pu-241		7.38E-08	*3.57E-08*		< 4.35E-07	*4.24E-07*	≤	2.55E-07	
ICP-MS		Average	**St. Dev.**			**St. Dev.**			
		(Wt. %)			(Wt. %)			(Wt. %)	
M-232 (Th, U)	≤	8.10E-05	*1.40E-04*	≤	2.30E-05	*3.51E-05*	≤	5.20E-05	
M-233 (Pa)		bdl			bdl			bdl	
M-234 (th,U)		bdl			bdl			bdl	
M-235 (U)		bdl		≤	6.80E-05	*1.04E-04*	≤	6.80E-05	
M-236 (U)		bdl			bdl			bdl	
M-237 (Np)		bdl			bdl			bdl	
M-238 (U, Pu)		8.04E-04	*5.14E-04*		2.21E-03	*1.39E-03*		1.51E-03	
M-239 (Pu)		bdl			bdl			bdl	
M-240 (Pu)		bdl			bdl			bdl	
M-241 (Pu,Am)		bdl			bdl			bdl	
Total U		8.85E-04	*5.33E-04*		2.30E-03	*1.39E-03*		1.59E-03	
Total Pu		7.78E-07	*3.57E-08*	≤	2.50E-06	*1.51E-06*		1.64E-06	
Equivalent U-235		2.97E-07	*1.44E-07*		6.98E-05	*1.17E-04*		3.50E-05	
Na/Eq.U-235		9.68E+07	*4.83E+07*		NA			9.68E+07	
Fe/Eq.U-235	≤	3.14E+04	*2.69E+04*		3.20E+04	*2.73E+04*	≤	3.17E+04	
Cr/Eq.U-235		8.77E+04	*4.21E+04*		1.38E+04	*1.43E+04*		5.08E+04	
Zn/Eq.U-235	<	1.25E+04			2.99E+03	*3.82E+03*	≤	7.75E+03	
Mn/Eq.U-235	<	4.17E+03			1.77E+03	*1.95E+03*	≤	2.97E+03	

3.6 Analysis of As-Received Batch I Tank 46F Core Sample -<u>Liquid and Solid Fractions.</u>

About 20 g of the as-received batch I material put tube into a centrifuge tube and centrifuged for 20 minutes followed by vigorously shaking it for 5 minutes. The tube was allowed to settle for 2 hours. The tube was centrifuged for every 15 minutes until there was no apparent changes in volume of the solids between two consecutive centrifuge runs. Without picking up any solid components from the tube, the liquid portion was carefully transferred to a pre-weighed container. An average of 0.25 g portions of the solid fraction from this separation were digested (Aqua regia dissolution and peroxide fusion digestion) in triplicate and analyzed per Table 1. These analytical results are presented in Tables 10, and 11.

Aliquots of the liquid fraction were diluted and submitted for analysis for the species specified in Table 1. These analytical results are summarized in Tables 12 and 13.

Table 10 As-Received Sample solid fraction: <u>Batch I Tank 46F</u> Core Sample.

	Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution Average	
ICP-ES	Average		**St. Dev.**	Average		**St. Dev.**		
Species	(Wt. %)			(Wt. %)			(Wt. %)	
Ag	<	5.188E-03			NA		<	5.188E-03
Al		7.751E-01	*1.658E-01*		7.710E-01	*9.894E-02*		7.730E-01
B		1.256E-02	*4.033E-03*		2.529E-02	*5.476E-03*		1.892E-02
Ba	<	2.843E-03		≤	2.473E-03	*1.086E-03*	≤	2.658E-03
Ca		4.048E-02	*5.410E-02*	<	4.275E-02	*1.301E-03*	<	4.161E-02
Cd	<	7.665E-03			3.801E-03	*1.284E-03*	≤	5.733E-03
Co		3.800E-03	*5.780E-04*	<	1.766E-02	*5.374E-04*	≤	1.073E-02
Cr		1.515E-02	*5.119E-03*		3.345E-02	*9.962E-03*		2.430E-02
Cu	≤	5.036E-03	*3.395E-03*	≤	6.474E-03	*2.387E-03*	≤	5.755E-03
Fe		1.705E-02	*1.182E-02*		7.194E-02	*2.687E-02*		4.450E-02
La	<	9.478E-03		<	1.069E-01	*3.253E-03*	<	5.818E-02
Li	<	2.843E-03		<	7.435E-03	*2.263E-04*	<	5.139E-03
Mg		4.183E-03	*4.812E-03*		2.558E-03	*1.850E-03*		3.371E-03
Mn	≤	1.205E-03	*2.715E-04*		4.866E-03	*2.104E-03*	≤	3.036E-03
Mo		5.902E-03	*1.987E-03*	≤	9.021E-03	*3.024E-03*	≤	7.462E-03
Na		2.165E+01	*1.412E+00*		NA			2.165E+01
Ni	<	8.530E-03		<	2.695E-02	*8.202E-04*	<	1.774E-02
P	≤	3.712E-02	*7.330E-03*	≤	6.056E-02	*3.278E-02*	≤	4.884E-02
pb	<	4.360E-02		<	2.351E-01	*7.156E-03*	<	1.394E-01
Si		NA			1.676E-01	*1.736E-02*		1.676E-01
Sn	<	1.516E-02		<	4.340E-01	*1.321E-02*	<	2.246E-01
Sr	<	9.478E-04		<	1.859E-03	*5.657E-05*	<	1.403E-03
Ti		1.486E-03	*4.644E-04*		1.860E-02	*2.113E-03*		1.004E-02
V	≤	3.791E-03	*1.081E-03*	≤	1.311E-02	*5.934E-03*	≤	8.453E-03
Zn		4.971E-03	*2.630E-03*	≤	6.198E-03	*9.617E-04*	≤	5.585E-03
Zr		4.295E-03	*6.285E-04*		NA			4.295E-03

Table 11 As-Received Sample Solid fraction: Batch I Tank 46F Core Sample.

		Aqua Regia Dissolution			Peroxide Fusion Digestion			Combined Dissolution
Tk 50 Rad Screen		**Av. dpm/g**	**St. Dev.**		**dpm/g**	**St. Dev.**		Average dpm/g
Alpha		≤ 2.80E+06	*1.76E+06*		2.12E+07	*5.97E+06*		1.20E+07
Beta		9.67E+08	*6.45E+08*		5.42E+09	*1.68E+09*		3.20E+09
Pu-238/241								
Pu-238		2.97E+05	*5.36E+04*		5.45E+05	*1.91E+05*		4.21E+05
Pu-241		1.35E+05	*1.61E+04*		2.34E+05	*5.07E+04*		1.85E+05
Pu-238/241		**Wt%**			**Wt.%**			**Wt.%**
Pu-238		7.82E-07	*1.41E-07*		1.44E-06	*5.07116E-07*		1.11E-06
Pu-241		5.92E-08	*7.06E-09*		1.03E-07	*2.24006E-08*		8.09E-08
ICP-MS Act.		Average	**St. Dev.**			**St. Dev.**		Average
		Wt. %			**Wt. %**			**Wt. %**
M-232 (Th,U)		bdl			1.09E-05	*1.03E-06*	≤	1.09E-05
M-233 (Pa)		bdl			bdl			bdl
M-234 (Th, U)		bdl			bdl			bdl
M-235 (U)		bdl			1.5E-05		≤	1.5E-05
M-236 (U)		bdl			bdl			bdl
M-237 (Np)		bdl			bdl			bdl
M-238 (U, Pu)		6.75E-04	*2.58E-04*		1.02E-03	*2.10E-04*		8.46E-04
M-239 (Pu)		bdl			bdl			bdl
M-240 (Pu)		bdl			bdl			bdl
M-241 (Pu, Am)		bdl			bdl			bdl
Tot.U		6.75E-04	*2.58E-04*		1.04E-03	*2.10E-04*		8.59E-04
Tot Pu		8.41E-07	*1.35E-07*		1.54E-06	*1.18E-06*		1.19E-06
Equivalent. U-235		2.38E-07	*7.06E-09*		1.54E-05	*1.03E-07*		7.83E-06
Na/Equiv. U-235		9.10E+07	*6.52E+06*		NA			9.10E+07
Fe/Equiv. U-235		7.17E+04	*4.97E+04*		4.67E+03	*1.21E+03*		3.87E+04
Cr/Equiv. U-235		6.36E+04	*3.39E-01*		2.17E+03	*4.22E+02*		3.29E+04
Zn/Equiv. U-235		2.09E+04	*1.11E+04*		4.02E+02	*3.29E+01*		1.06E+04
Mn/Equiv. U-235	<	5.06E+03		≤	3.16E+02	*9.64E+01*	≤	2.69E+03

Table 12 As-Received Sample Liquid Fraction: Batch I Tank 46F Core Sample.

	Average		St. Dev.
ICP-ES	Mg/L		
Al		1.256E+04	*6.528E+02*
B		4.842E+02	*2.431E+01*
Ba	<	3.000E+00	
Ca		2.440E+01	*7.808E+00*
Cd	<	2.000E+00	
Co	<	3.000E+00	
Cr		4.440E+02	*2.202E+01*
Cu		4.967E+00	*1.343E+00*
Fe		5.313E+01	*6.531E+00*
La	<	1.000E+01	
Li	<	3.000E+00	
Mg	≤	1.433E+00	*4.509E-01*
Mn		5.233E+00	*4.509E-01*
Mo		1.595E+02	*9.717E+00*
Na		3.685E+05	*1.924E+04*
Ni	<	9.000E+00	
P		6.036E+02	*1.760E+01*
Pb	<	4.600E+01	
Si		1.223E+02	*3.335E+01*
Sn	<	1.600E+01	
Sr	<	1.000E+00	
Ti	<	1.000E+00	
V		6.767E+00	*8.963E-01*
Zn		3.540E+01	*3.105E+00*
Zr	<	3.000E+00	

Table 13 As-Received Sample Liquid Fraction: Batch I Tank 46 Core Sample.

	Average	**St. Dev.**
Tk 50 Rad Screen	**dpm/ml**	
Alpha	7.44E+06	*5.96E+05*
Beta	5.91E+09	*3.46E+08*
Pu-238/241		
Pu-238	1.63E+05	*1.22E+04*
Pu-241	6.81E+04	*1.51E+04*
Pu-238/241	Mg/L	
Pu-238	4.29E-03	*3.21E-04*
Pu-241	2.98E-04	*6.60E-05*
IC-Anions	**mg/L**	
Cl^-	2.53E+03	*7.57E+02*
F^-	< 2000	
NO_2^-	3.33E+05	*6.91E+04*
NO_3^-	3.56E+05	*8.55E+04*
SO_4^{-2}	< 5000	
PO_4^{-3}	< 10,000	
CHO_2^-	4.77E+03	*1.10E+03*
$C_2O_4^{-2}$	< 10,000	
Wet Chemistry	**Molarity**	
Free OH^-	1.14E+01	*7.29E-01*
CO_3^{-2}	< 5.33E-01	
AlO_2^-	< 5.33E-01	
ICP-MS Act.	Average	**St. Dev.**
	mg/L	
M-232 (Th)	3.33E-02	*2.31E-02*
M-233 (Pa)	bdl	
M-234 (Th,U)	6.33E-02	*5.77E-03*
M-235 (U)	9.67E-02	*1.53E-02*
M-236 (U)	4.67E-02	*5.77E-03*
M-237 (Np)	3.67E-02	*5.77E-03*
M-238(U,Pu)	5.94E+00	*8.91E-01*
M-239 (Pu)	2.33E-02	*5.77E-03*
Total U	6.18E+00	*8.91E-01*
Total Pu	4.70E-02	*8.17E-03*
Equivalent U-235	2.86E-01	*1.73E-02*
Na/Eq.U-235	1.29E+06	*1.03E+05*
Fe/Eq.U-235	1.86E+02	*2.55E+01*
Cr/Eq.U-235	1.56E+03	*1.22E+02*
Zn/Eq.U-235	1.05E+01	
Mn/Eq.U-235	1.83E+01	*1.93E+00*

4.0 CONCLUSIONS

A summary of the metal poison/equivalent uranium-235 ratios is presented in Table 14 for the two batches of Tank 46F core samples. The average amount of neutron poisons (Na, Fe, Mn Cr and Zn) and therefore, their corresponding poison-to-equivalent U-235 ratios for the "as-received" core sample and insoluble solids meet the Minimum Safe Ratios of Inherent Saltcake Metals to Uranium ratios (Reference vii).

Table 15 shows a summary of the measured average concentrations, in mg/L and weight percent, of the species (silicon, sodium aluminum and free OH^- (Liquid fraction only)) that govern scale formation rates for aluminosilicates in Tank 46F.

Table 14. Total uranium, U-235 enrichment and poison/equivalent U-235 summary.

	"AS-Received" Core Sample Batch II*	**Dry Insoluble Solids From Core Sample Batch II***	**AS-Received" Core Sample Batch 1***	**Solid Fraction from As-Received Core Sample Batch 1***	**Liquid Fraction from As-Received Core Sample Batch 1** **mg/L**
Total Uranium (Wt. %)	5.98E-03	2.24E-01	1.59E-03	8.59E-04	6.18E+00
U-235 Enrichment (U-235/U-total)	7.99E-03	5.31E-03	4.28E-02	1.62E-02	1.56E-02
Total Pu (wt %)	2.47E-06	3.00E-04	1.64E-06	1.189E-06	4.70E-02
Equivalent U-235 (wt. %)	4.19E-05	2.04E-03	3.50E-05	7.83E-06	2.86E-01
Na/equivalent U-235	8.93E+05	4.88E+02	9.68E+07	9.10E+07	1.29E+06
Fe/equivalent U-235	4.33E+02	3.95E+03	3.17E+04	3.87E+04	1.86E+02
Mn/equivalent U-235	< 2.11E+01	1.76E+01	2.97E+03	≤ 2.69E+03	1.83E+01
Zn/equivalent U-235	< 5.93E+01	6.86E+01	≤ 7.75E+03	1.06E+04	< 1.05E+01
Cr/equivalent U-235	< 2.76E+02	4.43E+01	5.08E+04	3.29E+04	1.56E+03

* Values based on combined dissolution average from aqua regia and peroxide fusion digestions.

Table 15 Concentration Summary for Scale Formation Species in Tank 46F

	"AS-Received" Core Sample Batch II	Dry Insoluble Solids From Core Sample Batch II	AS-Received" Core Sample Batch 1	Solid Fraction from As-Received Core Sample Batch 1	Liquid Fraction from As-Received Core Sample Batch 1
Aluminum, mg/L	NA	NA	NA	NA	1.26E+04 ± *6.53E+02* (0.47 moles/L)
Silicon ,mg/L	NA	NA	NA	NA	1.22E+02 ± *3.34E+01* (0.0043 moles/L)
Al/Si ratio	NA	NA	NA	NA	103.28
Sodium, mg//L	NA	NA	NA	NA	3.68E+05 ± *1.92E+04* (16 Moles/L)
Aluminum, wt.%	2.04	29.10	1.11	0.773	NA
Silicon, wt.%	< 0.068	2.56	0.107	0.168	NA
Al/Si ratio	30.1	11.4	10.4	4.60	NA
Sodium, wt.%	37.4	0.590	24.2	21.7	NA
Free OH^- , molarity	NA	NA	NA	NA	1.145E+01 ± 7.287E-01

5.0 QUALITY ASSURANCE

The SRTC Analytical Development Section (ADS) performed all the analytical requirements for this characterization of Tank 46F according to their operating quality assurance procedures. SRTC Shielded Cell operations personnel conducted all the sample preparation protocols per written instructions provided by Waste Processing Technology personnel. Data obtained from this study reside as records in WSRC-NB-2001-00179 and in WSRC-NB-2002-0007, in addition, to several notebooks maintained by ADS.

6.0 ACKNOWLEDGEMENTS

The authors thank Analytical Development Section personnel, in particular, B. Boyce, M. Malek, C. Coleman, R. Ray, D. Diprete, C. Diprete and J. Hart for their analytical assistance in this characterization. We also thank A. Williams, and D. Wheeler for assistance in completing the shielded Cell part of this Tank 46F characterization task.

7.0 APPROVALS/REVIEW

Authors

4/09/02

L. N. Oji, Waste Processing Technology — Date

5/29/02

W. R. Wilmarth, Waste Processing Technology — Date

Design Check

4-16-02

C. J. Martino, Waste Processing Technology — Date

4-24-02

D. C. Bumgardner, Concentration, Storage, Transfer Engineering — Date

(Ref: N-TRC-F-00001) 5/14/02

D. J. Martin, Manager, Concentration, Storage, Transfer Engineering — Date

W. B. Van Pelt 6-17-02

W. B. Van Pelt, Level 4 Manager, Waste Processing Technology — Date

6/17/02

W. L. Tamosaitis, Level 3 Manager, Waste Processing Technology — Date

8.0 REFERENCES

[1] TTR Number: HLE-TTR-20001-035

[2] "Inductively Coupled Plasma-Mass Spectrometer Elemental and Isotopic Analysis for Aqueous Liquid Sample Fisions Plasma Quad II (U),"Manual L16.1, Procedure ADS1543, Rev.1, April 1,1998.

[3] "Inductively Coupled Plasma-Emission Spectrometer Elemental for Aqueous Liquid Sample Analysis," Manual L16.1, Procedure ADS-1509, June 25, 1996.

[4] "Analysis of Solutions by Ion Chromatography U)," Manual L16.1, procedure ADS23-6, Rev. 7, January 30, 1998.

[5] "Gross Alpha/Beta Determination by Liquid Scintillation Counting" Manual L16.1, Procedure ADS-2424, Rev. 5, February 02,1999.

[6] "Gamma Sample Preparation and Analysis (Gamma PHA)," Manual L16.1, Procedure ADS-2420, Rev.1, April1, 1998.

[7] N-NCS-H-00034, Nuclear Criticality Safety Evaluation-"Minimum Safe Ratios of Inherent Saltcake Metals to Uranium," R.H Ross, October 14, 1996.