Measurements Taken in Support of Qualification of Processing Savannah River Site Low-Level Liquid Waste into Saltstone – 10160

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ABSTRACT

The Saltstone Facility at the Savannah River Site (SRS) immobilizes low-level liquid waste into Saltstone to be disposed of in the Z-Area Saltstone Disposal Facility, Class Three Landfill. In order to meet the permit conditions and regulatory limits set by the South Carolina Department of Health and Environmental Control (SCDHEC), the Resource Conservation and Recovery Act (RCRA) and the Environmental Protection Agency (EPA), both the low-level salt solution and Saltstone samples are analyzed quarterly. Waste acceptance criteria (WAC) are designed to confirm the salt solution sample from the Tank Farm meets specific radioactive and chemical limits. The toxic characteristic leaching procedure (TCLP) is used to confirm that the treatment has immobilized the hazardous constituents of the salt solution. This paper discusses the methods used to characterize the salt solution and final Saltstone samples from 2007 – 2009.

INTRODUCTION

The Saltstone Facility at the Savannah River Site (SRS) treats low-level liquid waste (LLW) and solidifies it in a cementitious waste form known as Saltstone. To meet the South Carolina Department of Health and Environmental Control (SCDHEC), the Resource Conservation and Recovery Act (RCRA) and the Environmental Protection Agency (EPA) regulatory limits, both the salt solution from Tank 50 and the final waste form, Saltstone, must be analyzed for radionuclide and chemical constituents as well as leaching of hazardous constituents.

Savannah River Remediation (SRR), which operates the Tank Farm and Liquid Waste Operations (LWO) at SRS, contracts Savannah River National Laboratory (SRNL) to perform the quarterly sample analyses. The measurements taken in support of the waste acceptance criteria (WAC) include analysis of the salt solution for 74 alpha, beta, and gamma emitting radionuclides, volatile and nonvolatile organics, total inorganic and organic carbon, total base and 23 metal contaminants. Compliance of the analyses with the Saltstone WAC ensures that the regulatory limits will be met for the low-level waste transferred to the Saltstone Disposal Facility for permanent disposal. In addition, the WAC limits provide both near and long-term protection of onsite personnel, offsite populations, the environment, and groundwater resources from unnecessary radiological and/or chemical hazards and toxins. The liquid waste sample is combined with premix materials as specified by the density and weight percent solids of the salt solution and cured to form Saltstone.

The toxic characteristic leaching procedure (TCLP) is used to assess the effectiveness of the treatment of the cured Saltstone sample. The amounts of the eight toxic metals as specified by RCRA; arsenic, barium, cadmium, chromium, mercury, lead, selenium, and silver are determined as well as the levels of four additional metals; antimony, beryllium, nickel and thallium, which are designated as underlying hazardous constituents (UHC). The grout sample is also analyzed for total content of benzene, phenols and total and amenable cyanide, which are also designated as UHCs.

SALTSTONE FACILITY

The Saltstone Facility is designed as an interim facility that allows staging of LLW processing prior to completion and startup of the Salt Waste Processing Facility (SWPF) that will operate at a higher capacity than the Saltstone Facility [1]. The Saltstone Facility is permitted to immobilize and dispose of low-level radioactive and hazardous liquid waste (salt solution) remaining from the processing of radioactive material at the Savannah River Site to maintain sufficient tank space for continued uninterrupted sludge processing at the Defense Waste Processing Facility (DWPF) [1]. It is comprised of two facility segments: the Saltstone Production Facility (SPF) and the Saltstone Disposal Facility (SDF). At the SPF, the contents of Tank 50 are combined with dry premix that consists of 45 wt% slag, 45 wt% fly ash, and 10 wt% cement to form a self-leveling grout slurry that is pumped to the SDF. The SDF is comprised of above ground storage vaults where the grout slurry solidifies to form a free-standing cementitious waste form.

WASTE ACCEPTANCE CRITERIA (WAC)

According to the SCDHEC permit, the salt solution transferred to the Saltstone Facility must be analyzed quarterly to ensure the WAC requirements are met. These WAC are applicable to any aqueous waste transferred to the Saltstone Facility through an inter-area transfer line that connects to the Salt Feed Tank (SFT) in Z-Area during Interim Salt Disposition Project (ISDP) operations [1]. The WAC are designed to ensure that the aqueous waste sent to the Saltstone Facility meets the safety basis and permit requirements; produces Saltstone that meets TCLP requirements and is certified as non-hazardous; protects workers from unnecessary radiological and chemical hazards; and provides near and long-term protection of off-site populations, the environment, and groundwater resources [1].

To provide results for all the required analytes, the aqueous samples are submitted for high performance liquid chromatography (HPLC) analyses, volatile/semi-volatile organic analyses (VOA/SVOA), ion chromatography (IC), wet chemistry titrations, total inorganic/total organic carbon analyses (TIC/TOC), radiochemical analyses (which will perform digestions of the slurry for specific radiochemical methods), and aqua regia digestions of the slurry samples for analyses by atomic absorption spectroscopy (AA), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-ES). Table I lists the various analyses that are performed on the samples to meet WAC requirements and the analytes that are measured by that technique as of the third quarter 2009.

Table I. Analytes Required for Analysis and the Analytical Methods Used.

Method	Analytes
Total Solids	---
Dissolved Solids	---
ICP – ES	Ag, Al, B, Ba, Be, Ca, Cd, Ce, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Si, Sn, Sr, Ti, Tl, U, Zn, Zr
ICP – MS	Isotopes at mass 81 to 252 and Co-59
AA	As, Hg, K, Na, Se
IC	NO_3^-, NO_2^-, SO_4^-, PO_4^{3-}, Cl^-, F^-, $C_2O_4^{2-}$, CHO_2^-, NH_4^+
Wet Chemistry Titration	CO_3^{2-}, Total Base, Free OH^-, pH
TIC/TOC	Total Organic Carbon, CO_3^{2-},
HPLC	Tetraphenlyborate, Phenol, Organics, EDTA
GC – MS	Organics (VOA for butanol, isobutanol, isopropanol, benzene, toluene; SVOA for phenol, Isopar L, and Norpar 13)
Gross Alpha	Alpha radiation
Gamma Pulse Height Analysis	Cs-137, Cs-134, Co-60, Eu-154, Eu-155, Am-241
Cs Removed Gamma Pulse Height Analysis	Al-26, Na-22, Co-60, Nb-94, Ru/Rh-106, Sb-125, Sn-126, Ce-144, Eu-152, Eu-155, Pb-214, Ra-226, K-40, Ag-108m, Ba-133, Bi-207, Ac-227, Ra-228, Th-228, Pa-231
Pu-238/241 Separation and Analyses	Pu-238, Pu-239/240, Pu-241
Other Radiochemistry Techniques	H-3, Ni-59/63, Se-79, Sr-90, Pm-147, Sm-131, I-129, C-14, Tc-99
Am/Cm Separation and Analysis	Am-242m, Am-243, Cm-242, Cm-244, Cm-245, Cm-247, Cf-249, Cf-251
Liquid Scintillation	Total Alpha and Beta Radiation

Many of the WAC analytes can be measured by the methods listed in Table I. For those, the WAC report issued by SRNL provides the analyte of interest, the method used for measuring that analyte, the average concentration of the analyte based on triplicate samples (unless otherwise noted), the %RSD of the average, and, the WAC target or requested limit for the analyte concentration. However, several of the analytes have concentrations so small that they can not currently be detected in the samples. For these, the method reporting limit (MRL) is cited in the report. Five radionuclides (Y-90, Nb-93m, Te-125m, Sb-126, and Ba-137m) are in secular equilibrium with their radioactive parents; thus their activities are determined by calculation from the measured values of their parents [2].

Several radionuclides cannot be measured directly in the Tank 50 WAC solutions because of their low concentrations or the interferences from other radionuclides in the solutions. However their maximum concentrations can be reliably estimated from the results of the other analyses of the solution. The isotopes Pu-239 and Pu-240 are two radionuclides specified in the WAC whose concentrations must be determined. Their half lives are 2.41E04 and 6.56E03 years, respectively. The mass concentrations of both radionuclides could be measured by ICP-MS at masses 239 and

240. However concentration of each is usually too small in the quarterly Tank 50 solutions to be reliably measured by this technique; but, the combined alpha activity resulting from the radioactive decay of each of these radionuclides can be measured reliably by a Pu-239/Pu-240 radiochemical separation and alpha pulse height counting technique. This technique relies on the solvent extraction of the Pu radionuclides Pu-238, Pu-239, Pu-240, and Pu-241 from the other radionuclides in the solution. (Each of these Pu radionuclides has a WAC limit in Tank 50.) The resulting Pu solution is then analyzed for beta activity and for alpha activity. The beta activity is a measure of the concentration of Pu-241 which is a beta emitter. The alpha activity is resolved as a function of the energy of the alpha particles. The Pu-238 alpha particles have energies of 5.5 MeV and can be easily resolved from the alpha particles from Pu-239 and Pu-240 whose energies are in the range of 5.1 to 5.2 MeV. These energies are too close to be resolved by this technique. Consequently, the Pu-238 concentration can be measured directly; however, only the total activity from Pu-239 and Pu-240 can be measured. To determine the maximum activity of each of the two, the total activity Pu-239 and Pu-240 is assigned separately to Pu-239 and to Pu-240. This represents the maximum each could have in this solution. As an example, results for all the Pu radionuclides measured in the third quarter 2009 Tank 50 sample along with their WAC limits are presented in Table II. Note that all the concentrations are less than their respective WAC limits [1].

Table II.. Measured or Maximum Concentrations and WAC Limits for Pu Radionuclides in the 3rd Quarter 2009 Tank 50 Sample.

Radionuclide	Meas.Conc. or Upper Limit (pBq/mL)	WAC Limit (pBq/mL)
Pu-238	1.32E+14	9.25E+15
Pu-239	< 8.14E+12	9.25E+15
Pu-240	< 8.14E+12	9.25E+15
Pu-241	< 3.02E+13	3.10E+16

Until the third quarter of 2009, the samples were analyzed only semi-annually for radionuclide contaminants and analyzed quarterly for chemical contaminants. However, in order to more accurately support Saltstone operations, such as vault inventories, the samples are now analyzed for both radionuclide and chemical contaminants every quarter. In addition, several radionuclides not currently in the WAC required quantification. As a result, K-40, Ag-108m, Ba-133, Bi-207, Ac-227, Ra-228, Pa-231, Cm-247, Cf-249, and Cf-251 concentrations are now included in the Saltstone WAC analyses and reports.

Expanded support of the radionuclide inventory reporting requirements required reduced detection limits (DL) for several of the radionuclides. As a result, the detection limits for Na-22, Al-26, Ni-59, Nb-94, Ru-106, Ce-144, Eu-152, Eu-155, and Ra-226 have been lowered for the third quarter 2009 (3Q09) and future reports by increasing the measurement sensitivity primarily through increasing the sample aliquot size. Some examples are given in Table III. Although the requested detection limits for Nb-94 and Ra-226 by SRR are not currently achievable by SRNL Analytical Development (AD), the reported values for those radionuclides are below the estimated limits established by SRNL AD as well as the WAC limits [3, 4].

Table III. Changes to the Reported Detection Limits for Selected Radionuclides as of 3Q09.

Radionuclide	DL Prior to 3Q09 (pBq/mL)	3Q09 Requested DL (pBq/mL)	3Q09 Estimated DL (pBq/mL)
Nb-94	2.43E+11	7.40E+07	1.62E+10
Ru-106 (and Rh-106)	5.85E+12	3.70E+12	3.92E+11
Ce-144	5.70E+12	3.70E+11	3.81E+11
Eu-155	2.17E+12	3.70E+12	2.01E+11
Ra-226	2.27E+13	8.14E+11	1.51E+12

The WAC aims to limit the concentration of specific chemicals and organics in the SDF vaults to avoid producing a highly flammable vapor mix in the vaults. Table IV lists the chemical and organic contaminants that impact vault flammability [1]. For the organic contaminants (butanol, tributylphosphate, isopropanol, methanol and Norpar 13), the WAC limits are designed such that the volatiles in salt solution shall contribute less than 10% to the Composite Lower Flammability Limit (CLFL) at peak CLFL concentrations [1].

Table IV. Chemical and Organic Contaminants that Impact Vault Flammability and their Associated WAC Limits.

Chemical Name	Chemical Formula	Molecular Weight (grams/mole)	WAC LIMIT
Isopar L	----	163	1.10E+01 ppm
Tetraphenlyborate (TPB)	$B(C_6H_5)_4^-$	319.22	5.00E+00 mg/L
Ammonium	NH_4^+	18.04	2.12E+02 mg/L
Butanol	C_4H_9OH	163	7.50E-01 mg/L
Tributylphosphate	$(C_4H_9O)_3PO$	266.32	1.00E+00 mg/L
Isopropanol	C_3H_7OH	319.22	2.50E-01 mg/L
Methanol	CH_3OH	32.04	2.50E-01 mg/L
Norpar 13	----	187	1.00E-01 mg/L

However, the preparation and analysis methods for semi-volatile and volatile organic contaminant analysis (SVOA and VOA respectively) can cause inaccurate results or have higher detection limits than the WAC limits for the organic analytes. For Isopar L, isopropanol, and Norpar 13 specifically, the WAC limits listed in Table IV are lower than the achievable MRL based on current AD capabilities. Isopar L and Norpar 13 have limited solubility in aqueous solutions making it difficult to obtain consistent and reliable sub-samples. The values reported in the WAC reports are the concentrations in the sub-sample as detected by the GC/MS; however, the results may not accurately represent the concentrations of these analytes in the sample received by SRNL. Currently, method development is being performed to lower detection limits and increase sub-sample reliability for these and other analytes for future WAC reports.

TOXIC LEACHING CHARACTERISTIC PROCEDURE (TCLP)

The SPF in Z-Area is permitted by SCDHEC as a wastewater treatment facility that converts mixed aqueous waste into a saltstone grout that is not classified as hazardous waste. The SDF is a solid waste landfill facility permitted by SCDHEC for the disposal of solid waste. The SDF cannot be used for the disposal of hazardous waste and the non-hazardous nature of saltstone grout must be certified by an SCDHEC-certified laboratory by testing samples of solid saltstone using the Toxicity Characteristic Leach Procedure (TCLP) [1,9]. The Saltstone Grout Sampling plan provides SCDHEC with the chemical and physical characterization strategy for the salt solution which is to be disposed of in the Z-Area Industrial Solid Waste Landfill (ISWLF) [5]. LLW salt solution samples are collected from which grout samples are prepared to determine that the solidification treatment meets the requirements of the South Carolina Hazardous Waste Management Regulations (SCHWMR) R.61-79.261.24(b) and R.61-79.268.48(a). Table V shows the sample results and regulatory limits for the eight RCRA metals and four UHCs that are analyzed as part of the quarterly TCLP analysis. Each quarter, the WAC results for the analytes listed in Table V are compared to their associated regulatory limit. If the concentrations of any of the RCRA metals are above the limit, it is necessary to perform TCLP analysis on a representative Saltstone sample for that quarter. As indicated in Table V, the concentration of chromium, mercury and nickel are above their regulatory limits and therefore TCLP is performed to ensure the hazardous analytes are immobilized in Saltstone.

Table V. Sample Results of TCLP Metals from WAC Analysis and the Corresponding Regulatory Limits for RCRA Metals and UHCs Analyzed frm othe TCLP for the First Quarter 2009.

-	Sample WAC Results (mg/L)	Regulatory Limits (mg/L)
-	**1Q09**	**Toxicity[a]**
As	< 0.105	5
Ba	0.458	100
Cd	< 0.456	1
Cr	44.3	5
Pb	0.489	5
Hg	11.2	0.2
Se	< 0.211	1
Ag	< 0.936	5
--	--	**UHC[b]**
Sb	< 5.31	1.15
Be	< 0.0357	1.22
Ni	15.9	11
Tl	< 0.215	0.20
-	-	**(mg/kg)**
benzene	< 0.50	10
phenol	< 0.10	5.2
cyanide (total)	NM	1.2
cyanide (amenable)	NM	0.86

[a] SCHWMR R.61-79.261.24(b) "Characteristic of Toxicity."
[b] SCHWMR R.61-79.268.48 "Universal Treatment Standards."

The Saltstone samples for TCLP testing are made under the same process conditions as it is in the Saltstone Facility for the quarter of interest and cured for at least 28 days. After the designated curing time, the sample is shipped to an SCDHEC certified laboratory, Babcock & Wilcox Technical Services Group – Radioisotope and Analytical Chemistry Laboratory (B&WTSG-RACL), to perform the TCLP and subsequent extract analysis on Saltstone samples for the analytes required for the quarterly analysis [6]. In addition to the eight toxic metals (arsenic, barium, cadmium, chromium, mercury, lead, selenium and silver) analytes included the underlying hazardous constituents (UHC) antimony, beryllium, nickel, and thallium which could not be eliminated from analysis by process knowledge [7]. B&WTSG-RACL provided subsamples to GEL Laboratories, LLC for analysis for the UHCs benzene, phenols and total and amenable cyanide. Figure 1 shows the process of preparing and analyzing the quarterly TCLP samples.

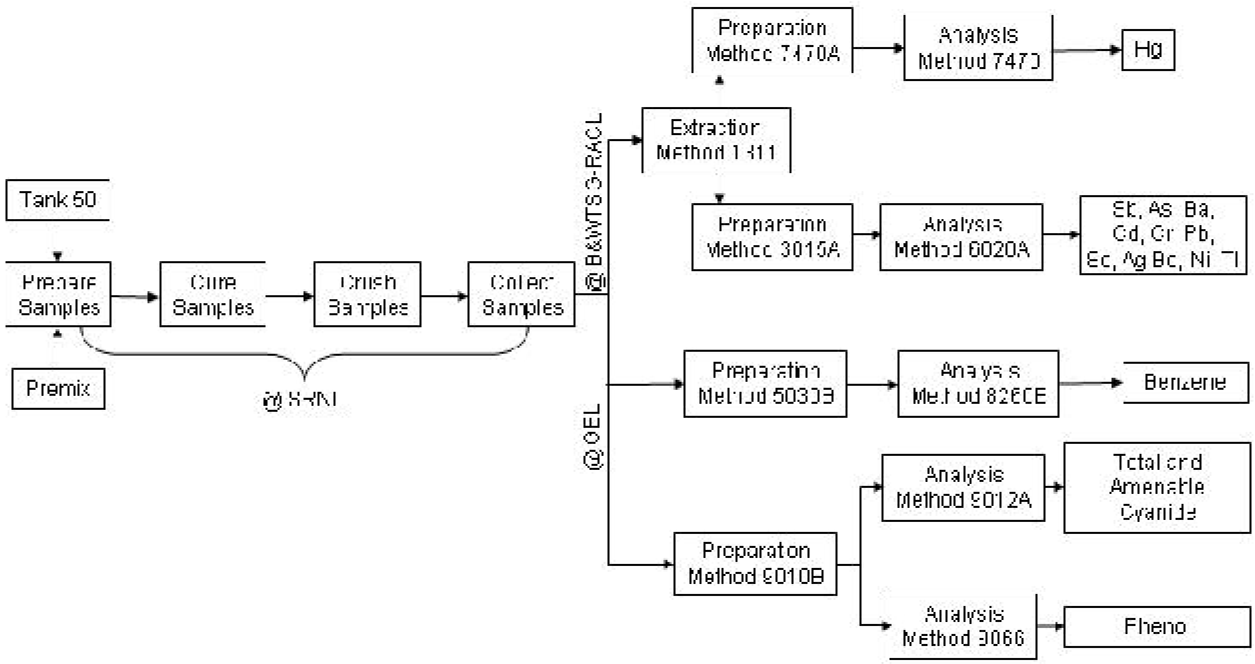

Figure 1. Flowchart of Saltstone sample preparation and analysis.

The Metals method 6020A analysis was performed on an X-7 Series Inductively Coupled Plasma – Mass Spectrometer (ICP-MS). The instrument measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Mass interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Metals method 7470A analysis was performed on a Leman PC 200 II instrument which consists of a cold vapor atomic absorption spectrometer (CVAA) set to detect mercury at a wavelength of 253.7 nm. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. Method 8260B analysis was performed with an HP6890/HP5973 gas chromatograph/mass spectrometer using a J&W1DB-624 column and methods 9012A and 9066 were performed using a Lachat QuickChem FIA+ 8000 Series.

Table VI shows the Saltstone TCLP results and corresponding regulatory limits. The first quarter 2009 sample is used as an example. Table V includes the SCHWMR R.61-79.261.24(b) limits above which a waste is to be considered characteristically hazardous for toxicity and the SCHWMR R.61-79.268.48 Universal Treatment Standards (UTS) for hazardous constituents. In addition, Maximum Contaminant Levels (MCLs) from the State Primary Drinking Water Regulations have been included [5,8]. The MCL is the limit for a constituent in drinking water. The MCL is used to determine the class of landfill required. At 10x MCL, a Class 3 landfill is required. The SDF vaults are permitted as a Class 3 landfill [8].

Table VI. Saltstone TCLP Results and Corresponding Regulatory Limits.

-	Sample TCLP Results (mg/L)	Regulatory Limits		
SRS ID	**1Q09**	**Toxicity[a]**	**UTS[b]**	**MCL[c]**
B&W ID	**0905003-01A**	**(mg/L)**	**Nonwastewater Standard (mg/L TCLP)**	**(mg/L)**
Sb	3.90E-03	-	1.15	0.006
As	9.90E-03	5	5	0.010
Ba	3.53E-01	100	21	2
Cd	2.90E-04	1	0.11	0.005
Cr	6.60E-03	5	0.6	0.1
Pb	9.80E-03	5	0.75	0.015[d]
Hg	2.00E-04	0.2	0.025	2E-03
Se	1.13E-01	1	5.7	0.05
Ag	6.00E-05	5	0.14	0.1[e]
Be	1.60E-04	-	1.22	4E-03
Ni	5.90E-03	-	11	-
Tl	3.50E-04	-	0.20	2E-03

[a] R.61-79.261.24(b) "Characteristic of Toxicity."
[b] R.61-79.268.48 "Universal Treatment Standards."
[c] SCDHEC State Primary Drinking Water Regulation Maximum Contaminant Levels (MCL).
[d] Lead action level from SCDHEC 61-58.11.B.
[e] Secondary drinking water parameter.

As indicated in Table VI, the sample TCLP results are orders of magnitude lower than the WAC results in Table V, which indicates Saltstone immobilizes the hazardous contaminants. The TCLP leachate RCRA metal concentrations were below the SCHWMR R.61-79.261.24(b) limits for characteristically hazardous toxic waste. Similarly, all results were less than the UTS Nonwastewater Standard. Although selenium was above the MCL, none of the analyses were greater than 10x the MCL.

CONCLUSION

To date, none of the analyzed radionuclide or chemical constituents in the LLW salt solution have been measured at concentrations that exceeded their WAC limits. However, reported detection limits for some organic contaminants have been above their WAC limits for vault flammability analysis (Isopar L and Isopropanol). Through process knowledge (allowed by the Saltstone WAC when analytical methods are not sensitive enough to demonstrate compliance), it has been shown via evaluation that the organic contaminant concentrations are within WAC limits. In addition, none of TCLP samples have surpassed the SCDHEC and EPA regulatory limits; therefore the Saltstone waste form disposed of in the Saltstone Disposal Facility is non-hazardous and non-toxic. The concentrations of the eight RCRA metals and UHCs identified as possible in the Saltstone waste form were present at levels below the universal treatment standards (UTS).

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