Support of SRS Saltstone Regulatory Compliance – 15586

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ABSTRACT

The SRS Saltstone Facility is designed and 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. The Saltstone Processing Facility (SPF) is permitted as a wastewater treatment facility per the South Carolina Department of Health and Environmental Control Regulations (SCDHEC) South Carolina Hazardous Waste Management Regulations (SCHWMR) R.61-67. The Saltstone Disposal Facility is permitted as a solid waste landfill site, as defined by SCDHEC Regulations R61-107.19. The Saltstone Sampling and Analysis Plan provides the SCDHEC with the chemical and physical characterization strategy for the salt solution and saltstone waste form. During operation, samples are collected from Tank 50H on a quarterly basis and are analyzed by the Savannah River National Laboratory (SRNL) for over chemical and radioactive components. The analytical results are compared to the Saltstone waste acceptance criteria in a technical report. SRNL also prepares saltstone samples from the quarterly sample and premix binder materials provided by the SPF to determine the non-hazardous nature of the grout to meet the requirements of the SCDHEC regulation for the “Characteristic of Toxicity”, R.61-79.261.24(b) and the “Universal Treatment Standards”, R.61-79.268.48.4. Saltstone samples are collected, size reduced, packaged, and shipped to an independent United States EPA certified laboratory, or a laboratory that holds an equivalent certification such as one from the National Environmental Laboratory Accreditation Program to perform the EPA Toxicity Characteristic Leaching Procedure (TCLP) extraction of the saltstone sample. SRNL reviews the results of the TCLP analysis and prepares a report detailing the sample preparation and analysis that is used by the Saltstone Facility to demonstrate the nonhazardous nature of the saltstone waste form.

INTRODUCTION

The SRS Saltstone Facility is designed and 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. Low-level waste (LLW) streams from the Effluent Treatment Project (ETP), the H-Canyon general purpose evaporator, and decontaminated solutions from the Modular Caustic Side Solvent Extraction Unit (MCU) are composited in Tank 50H. The composited salt solution is transferred to the Saltstone Facility for treatment and disposal.

The Saltstone Facility is comprised of the Saltstone Production Facility (SPF), which receives and treats the salt solution to produce saltstone grout, and the Saltstone Disposal Facility (SDF), which consists of Saltstone Disposal Units (SDUs) used for the disposal of the saltstone grout. The SPF is permitted as a wastewater treatment facility per the South Carolina Department of Health and Environmental Control Regulations (SCDHEC) R.61-67. The SDF is permitted as a solid waste landfill site, as defined by SCDHEC Regulations R61-107.19. The Saltstone Sampling and Analysis Plan provides the SCDHEC with the chemical and physical characterization strategy for the salt solution and saltstone waste form.

METHODS

During operation, SRS Tank Farm Operations collects samples from Tank 50H—the feed tank for the SPF—on a quarterly basis and transfers the samples to SRNL. Samples consist of a 200 ml dip sample, taken from near the surface, and a 1 L variable depth sample, taken approximately 1.6 m from the tank bottom. The tank is agitated for several hour prior to sampling.

The samples are received into the SRNL Shielded Cells Facility. Samples are analyzed by SRNL for both chemical and radioactive components for compliance with the Waste Acceptance Criteria (WAC) for treatment and disposal at Saltstone. The main objective of the WAC analysis is to support the hazard and accident analyses in the documented safety analysis. For most of the analytes, the method detection limits are below the WAC limits. The requested limits for Ni-59, Nb-94, Cm-247, Cf-249, and Cf-251 are to support Performance Assessment modeling and are below the method detection limits. The requested limits for Norpar 13 and Isopar L to support SDU flammability calculations are also above the requested limits. The WAC also supports the tank corrosion monitoring plan.

SRNL also prepares saltstone samples from the quarterly TCLP sample and premix materials provided by the SPF to determine the non-hazardous nature of the grout to meet the requirements of the SCDHEC regulation for the “Characteristic of Toxicity”, R.61-79.261.24(b) and the “Universal Treatment Standards”, R.61-79.268.48.4.

Waste Acceptance Criteria

After receipt, the surface sample is transferred with glass pipettes to glass vials with Teflon-lined caps to analyze for volatile and semivolatile organic components (VOA and SVOA). The vials were completely filled to minimize the void space and the volatilization of organics. VOA and SVOA constituents are tracked to limits set to protect the Saltstone documented safety analysis for accident scenarios. Lower limits are set for Norpar 13, Isopar L, and tributylphosphate, organic components used at SRS, as well as their decomposition products, to monitor performance with respect to the composite lower flammability limit of the SDUs.

The 1 L variable depth sample is transferred into a 2-L high-density polyethylene bottle. The transferred slurry is left to settle overnight in the bottle. Clear supernate from the settle slurry is returned to the sampler for rinsing. The sample bottle was agitated to disperse the suspended solids into the supernate and aliquots of slurry samples were promptly collected.

Triplicate slurry samples were prepared for the following analyses:

- Six-mL aliquots for Ion Chromatography (IC) analyses for soluble anions and cations.
- Three-mL aliquots for high performance liquid chromatography (HPLC) measurement of tetraphenylborate and ethylenediaminetetraacetate.
- Six-mL aliquots for Total Inorganic Carbon/ Total Organic Carbon (TIC/TOC) analyses.
- Three sets of 70-mL aliquots for radiochemical separations and analyses.
- Twelve-mL aliquots of filtered supernate were prepared by filtering aliquots of supernate using a 0.45 micron syringe filter for TIC/TOC analyses and Total Base analyses.
- Twelve-mL aliquots were digested using an aqua regia method. Visual inspection of the digested sample indicated that all the solids had dissolved. Aliquots of dissolved slurries were analyzed using inductively coupled plasma – emission spectroscopy (ICP-ES), inductively coupled plasma – mass spectrometry (ICP-MS), atomic absorption spectroscopy (AA) for As, K, Na, and Se, and cold vapor atomic absorption spectroscopy (CVAA) for Hg.

The analytical results are compared to the WAC requirements and reported to the Saltstone facility. Table I is the analytes required for analysis and the analytical techniques.

TABLE I. Dry blend mixture of binders used to prepare 7 kg batches.

Method	Analytes
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^+, dibutylphosphate
Wet chemistry titration	CO_3^{2-}, Total Base, Free OH^-, pH
TIC/TOC	Total Organic Carbon, CO_3^-
HPLC	Tetraphenylborate, Phenol, EDTA
GC-MS	Organics (VOA for butanol, isobutanol, isopropanol, benzene, toluene; SVOA for phenol, Isopar L, Norpar 13)
Gross Alpha	Alpha Radiation
Gamma Scan	Cs-137, Cs-134, Co-60, Eu-154, Eu-155, Am-241,
Cs removed Gamma	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	Pu-238, Pu-238, Pu-240, Pu-241
Other Rad Chem	H-3, Ni-59, Ni-63, Se-79, Sr-90, Pm-147, Sm-151, I-129, C-14, Tc-99
Am/Cm	Am-242m, Am-243, Cm-242, Cm-244, Cm-245, Cm-247, Cf-249, Cf-251
Liquid Scintillation	Total Alpha and Beta Radiation

TCLP

Typically, the contents of Tank 50H exceed the regulatory limits for chromium and mercury and therefore must be treated and disposed of in a non-hazardous waste form. Using the processing parameters provided by the Saltstone facility, SRNL prepares a saltstone sample for TCLP analysis. The weight percent solids data used for the mix calculation is taken from the quarterly WAC analyses. Saltstone samples for TCLP are prepared with the Tank 50H blended salt solution and a premix of 10 % ordinary portland cement, 45% blast furnace slag, and 45% thermally beneficiated Class F fly ash. The salt solution is stirred in a container with an agitator and then the dry feeds are added during agitation. The slurry is mixed for approximately three minutes, occasionally pausing the agitator to release entrained air. After mixing, the slurry is cast into a polyethylene zip top bag. The bag is laid flat and the air was expelled prior to sealing. The sample was cured flat in a polypropylene bag to facilitate the size reduction step needed to conform to the particle size requirements of the TCLP. After curing for not less than 28 days, the saltstone is removed from the container and a portion of the saltstone is crushed to particles less than 0.9 centimeters (3/8 inch) as prescribed by Section 7.13 of the TCLP method.[1] The crushed saltstone is packaged into an EPA pre-cleaned container. After the saltstone has been crushed, sieved and packaged, the sample is deemed “collected.” The sample is then shipped to an independent USEPA certified laboratory, or a laboratory that holds an equivalent certification such as one from the National Environmental Laboratory Accreditation Program (NELAP). The independent laboratory performs a TCLP extraction of the saltstone sample. Analysis of the TCLP extracts include the RCRA metals and select underlying hazardous constituents (UHC), antimony, beryllium, nickel, thallium, benzene, phenols, and total and amenable cyanide which could not be eliminated from analysis by process knowledge. SRNL reviews the results of the TCLP analysis and prepares a report detailing the sample preparation and analysis that is used by the Saltstone Facility to demonstrate the nonhazardous nature of the saltstone waste form.

DISCUSSION

Waste Acceptance Criteria

Historically, the analysis for all of the VOA/SVOA analytes have been below the method detection limits. All of the chemical analytes have been below the WAC limits. The radionuclide Ba-137m is the radioactive daughter of 94.6% of the beta decay of Cs-137. 5.4% of the Cs-137 decays to stable ^{137}Ba. The half-life of the parent radionuclide, Cs-137, is six million times longer than its daughter, Ba-137m, therefore the two radionuclides are in secular equilibrium. Radionuclides in secular equilibrium have the same activity associated with their decay. Thus, the activity of Ba-137m is 94.6% of the activity of the Cs-137. The concentration of Cs-135 is calculated by assigning all of the mass at 135 to cesium. It is assumed all

the mass detected at mass 244 is Pu-244. The Pu alpha Pulse Height Analysis (PHA) method does not resolve the alpha activities of Pu-239 and Pu-240. To determine the maximum concentration of each radionuclide, the total activity is assigned to each radionuclide separately. Fig. 1 shows the trend for the analysis of the major anions over several years. The trends show that although Tank 50 receives transfers from variable sources, the overall composition does not vary greatly over time.

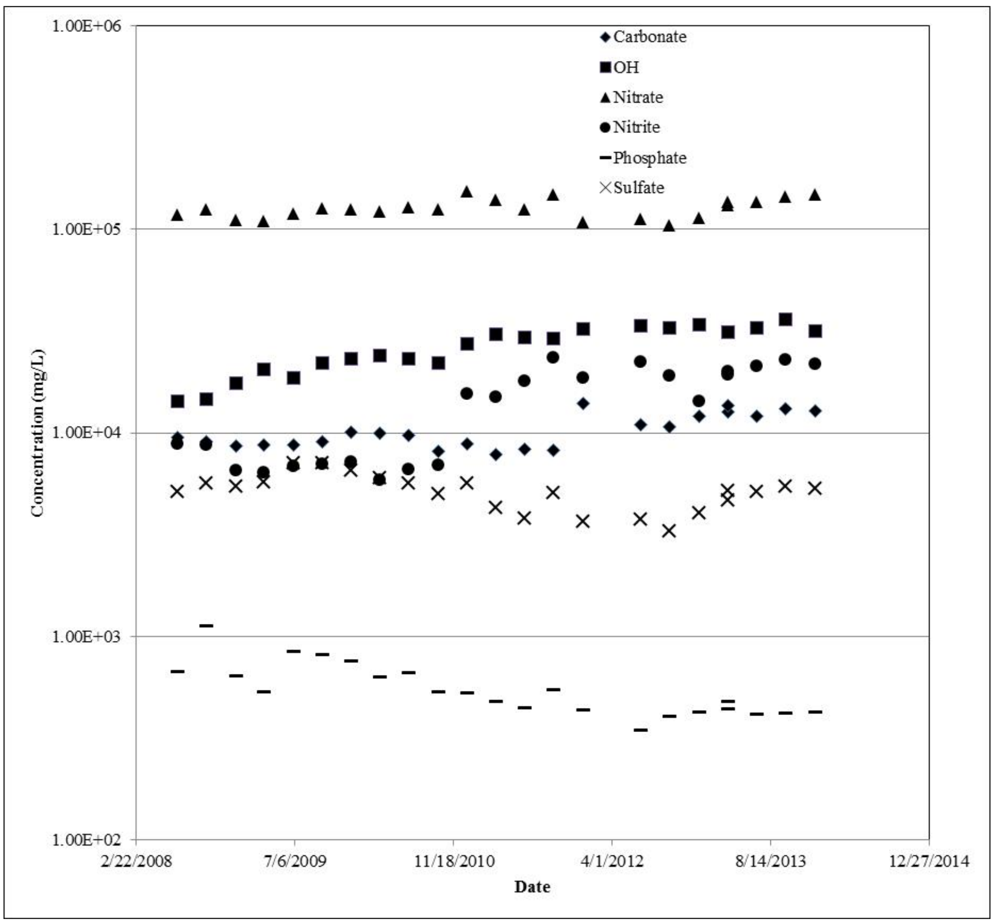

Fig. 1. Trend of analytical results for major anions.

Fig. 2 is a similar plot for radionuclides of interest. The variability in radionuclide concentration, specifically, the marked decrease in Cs-137 and Sr-90 is a result of implementation of the modular caustic side solvent extraction unit at SRS.

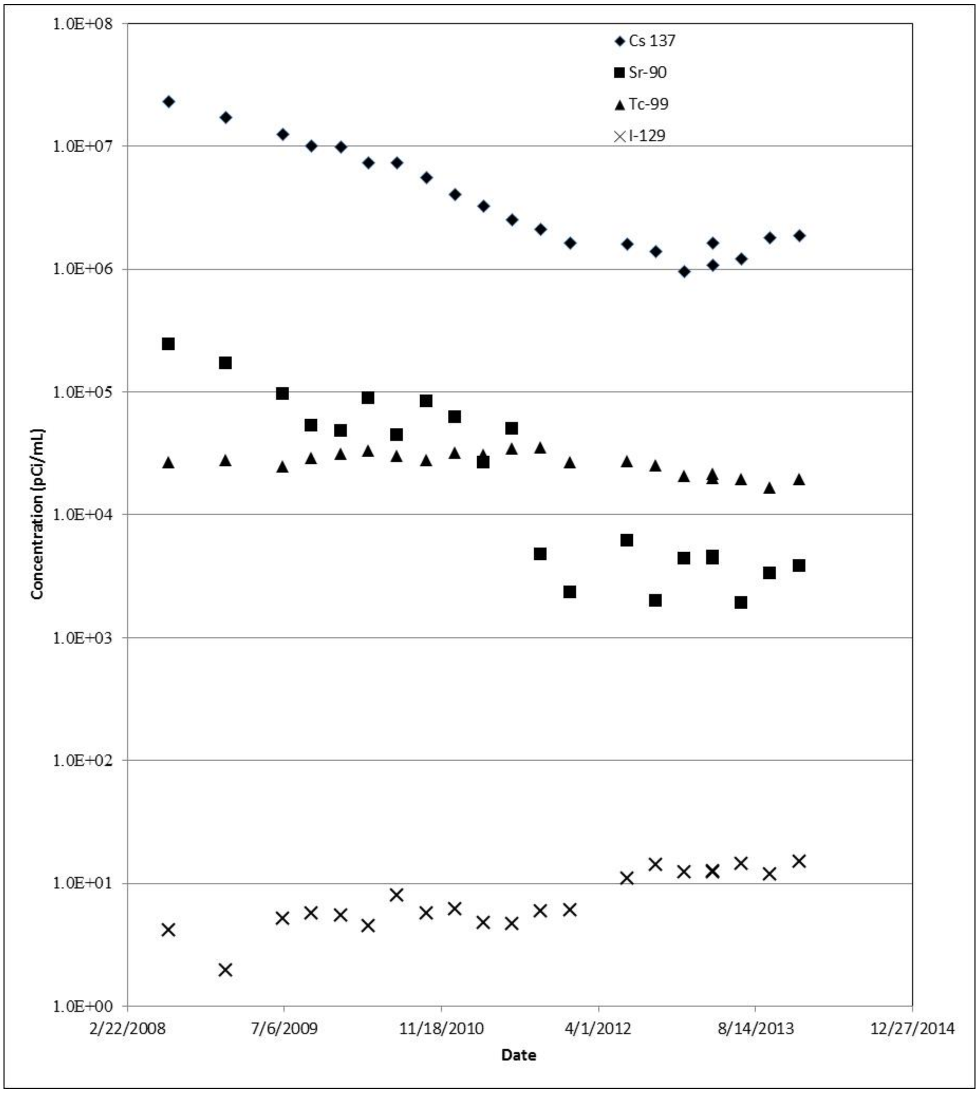

Fig. 2. Rend of analytical results for radionuclides of interest.

TCLP

TCLP testing of the Saltstone samples is currently performed by Southwest Research Institute. The samples are delivered with chain of custody documentation. Sample containers are inspected for visible signs of tampering or breakage.

Samples for the volatile compound benzene are prepared by SW-846 Method 5035 and analyzed according to SW-846 Method 8260B. For total and amenable cyanide, the sample was prepared using SW-846 9010B and analyzed using method 9012B. Since the sample is a solid a manual distillation and colorimetric procedure for total phenol, method SW-846 9065 (phenolics), is performed. For the TCLP metals analysis, the sample was extracted by SW-846 method 1311. Results from method 1311 are designated “modified” since a reduced sample mass is extracted due to the elevated activity in the sample. The extracts are prepared and analyzed for mercury by SW-846 Method 7470A. Extracts are digested according to SW-846 Method 3010A for the remaining metals. Those digestates were analyzed by ICP-AES, SW-846 Method 6010C.

Results from blanks, laboratory control samples, matrix spikes, and matrix spike duplicates are reviewed for quality assurance. The data package also includes data for calibration verifications, interference checks, and serial dilutions performed during the analysis.

CONCLUSIONS

The WAC limits were for the SRS Saltstone Facility have been met for all analyzed chemical and radioactive contaminants with measureable concentration in the salt solution over the time period covered in this work. The detection limits for the radionuclide Ni-59, Nb-94, Cm-247, Cf-249, and Cf-251 are above the requested limits and exceed the desired detection limits.

The saltstone waste form disposed of in the Saltstone Disposal Facility has always met the TCLP requirements and is not characteristically hazardous for toxicity. The concentrations of the eight RCRA metals and UHCs identified in the saltstone waste form is always present at levels below the universal standard. Analyses has consistently met all quality assurance specifications of USEPA SW-846.The saltstone waste form placed in the Saltstone Disposal Facility has always met the SCHWMR R.61-79.261.24(b) RCRA metals requirements for a nonhazardous waste form. The TCLP leachate concentrations were less than 10x the MCLs in SCDHEC Regulations R.61-107.19, Part I C.
The saltstone waste form placed in the Saltstone Disposal Facility has always met the R.61-79.268.48(a) non wastewater treatment standards.

REFERENCES

1. EPA. 1992. *Toxicity Characteristic Leaching Procedure*. *EPA Method 1311*, Revision 0. U.S. Environmental Protection Agency, Washington, D.C.