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

Keywords: Tank Farm
Evaporator
Overheads
ETF
Characterization

Retention Time: Permanent

Report on Analyses of WAC Samples of Evaporator Overheads – 2004

L. N. Oji and S. McCollum

Issue Date: March 18, 2005

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U. S. Department of Energy Under Contract Number DE-AC09-96SR18500

SUMMARY

In November and December of 2004, the Tank Farm submitted annual samples from 2F, 2H and 3H Evaporator Overhead streams for characterization to verify compliance with the new Effluent Treatment Facility (ETF) Waste Acceptance Criteria (WAC) and to look for organic species. With the exception of slightly high ammonia in the 2F evaporator overheads and high radiation control guide number for the 3H and 2F evaporator overhead samples, all the overheads samples were found to be in compliance with the Effluent Treatment Facility WAC. The ammonium concentration in the 2F-evaporator overhead, at 33 mg/L, was above the ETF waste water collection tank (WWCT) limits of 28 mg/L. The RCG # for the 3H and 2F evaporator samples at, respectively, 1.38E-02 and 8.24E-03 were higher than the WWCT limit of 7.69E-03. The analytical detection limits for americium-241 and radium-226 in the evaporator samples were not consistently met because of low WWCT detection limits and insufficient evaporator samples.

INTRODUCTION

All water received into ETF requires characterization versus the newly defined Waste Acceptance Criteria.[1] Currently, much of the water received by ETF comes from the F and H Evaporator Overheads. Concentration, Storage and Transfer Engineering issued a modified list of species to be determined.[2]

DISCUSSION

EXPERIMENTAL

The annual evaporator overheads samples (HTF-E-04-011, HTF-E-04-012, HTF-E-04-013; 3H special 1, 3H special 2, and 3H special-poly-bottle and FTF-409, FTF-410 and FTF-411) arrived at the Savannah River National laboratory in November and December of 2004. Waste Processing Technology (WPT) personnel transferred samples to containers more suitable for transmittal to the Analytical Development Section (ADS). Since these samples were relatively low in activity, no dilution was required prior to submittal for analysis.

A number of different analytical methods are used by ADS to determine the concentrations of various species in the samples. Ion chromatography (IC) is used to determine a number of anion species (NO_3^-, NO_2^-, SO_4^{--}, F^-, Cl^-, $C_2O_4^{--}$ and PO_4^{---}) as well as the cation NH_4^+. A wet chemistry method is used to measure the CO_3^{--} concentration. Inductively coupled plasma-emission spectrometry (ICP-ES) is used to determine the most of the transition metals (Ag, B, Ba, Be, Ca, Cd. Cr, Cu, Mg, Mn, Na, Ni, Pb, Sb, Si, and Zn and others). Atomic Absorption (AA) is used to determine As, Se and K. Acid digestion followed by cold vapor AA (CVAA) technique is used to measure the Hg concentration. Both volatile and semivolatile organic species are determined using gas chromatography coupled with mass spectrometry (GC/MS). Ethylenediaminetetraacetic acid (EDTA) was determined using ion pair chromatography (IPC). Total organic carbon (TOC) was determined using a total organic carbon analyzer. Total suspended solids were measured gravimetrically. A pH meter was used to measure sample pH. Inductively coupled plasma-mass spectrometry (ICP-MS) is used to characterize for ^{237}Np, ^{99}Tc, and the uranium isotopes.

Radionuclide determinations were also made using a number of different methods. Gamma spectrometry was used where possible to determine many radionuclides (^{137}Cs, ^{60}Co, ^{94}Nb, ^{106}Ru/Rh, ^{126}Sn, ^{125}Sb, ^{134}Cs, ^{154}Eu, ^{155}Eu, ^{144}Ce, and ^{94}Nb,). Am/Cm analysis was used to analyze for ^{241}Am, ^{242}Am and ^{243}Cm. Gross alpha and non-volatile beta determinations were made by first removing the tritium and then using liquid scintillation counting. ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{79}Se, ^{14}C, ^{129}I, and ^{241}Pu were determined by chemical separations followed by beta counting. Tritium was determined by beta counting after separating the tritium by distillation.

Annual Sample Results

The results of the analyses provided in the tables below are for a single determination by Analytical Development Section (ADS). For many species the concentration fell below the lower limit of detection. In these cases, ADS reported the lower limit of detection preceded by “<”.

Tables 1 and 2 provide, respectively, the measured values for chemical contaminants and radionuclides for the annual samples from the 2F, 2H and 3H evaporator overheads pulled in November and December of 2004, along with the limits given in the current revision of the new ETF WAC.[1] Apart from the slightly higher than WWCT feed limits for ammonium concentrations observed in the 2F-evaporator sample and high radiation control guide (RCG) number on the 3H and 2F evaporator overhead samples, no other species were found to be above the limits in the three evaporators for the annual sample. The RCG # for the 3H and 2F evaporator samples at, respectively, 1.38E-02 and 8.24E-03 were higher than the WWCT limit of 7.69E-03.

It is difficult in some cases to consistently meet the WWCT limits for some species because of dilution and matrix effects problems, especially in those cases when the WWCT limits are quite low and approach the theoretical instrument detection limits. This happens to be the case with the WWCT limits for Americium-241 for the 2F evaporator (^{241}Am < 1.05E+01 dpm/mL) and radium-226 (< 4.23E+01 and < 4.61E+01 dpm/mL, respectively, for 2F and 3H evaporator samples) where the analytical values obtained are higher than the WWCT limit. This is due in part to insufficient sample available for each analysis. The results reported for plutonium-240 are based on 20% of the value for plutonium-239 analysis.

Table 1. Results of Chemical Analyses for Evaporator Overheads Year 2004 Annual Samples

Species	2F Evap. Overheads (mg/L)	2H Evap. Overheads (mg/L)	3H Evap. Overheads (mg/L)	WWCT Feed Acceptance Limits (mg/L)
Ammonium (NH_4^+)	3.30E+01	4.00E+00	1.20E+01	2.80E+01
Nitrate (NO_3^-)	< 1.00E+00	< 1.00E+00	< 1.00E+00	1.18E+03
Nitrite (NO_2^-)	< 1.00E+00	< 1.00E+00	< 1.00E+00	1.99E+03
Sulfate (SO_4^{-2})	< 5.00E-01	4.00 E-01	< 5.00E-01	1.33E+02
Aluminate (AlO_2^-)	< 2.20E-01	< 2.20E-01	< 2.20E-01	-
Carbonate (CO_3^{-2})	< 1.20E+02	< 1.20E+02	< 1.20E+02	1.12E+03
Fluoride (F^-)	< 2.00E-01	< 2.00E-01	< 2.00E-01	1.26E+01
Oxalate ($C_2O_4^{-2}$)	< 1.00E+00	< 1.00E+00	< 1.00E+00	2.54E+02
Chloride (Cl^-)	< 2.00E-01	4.00E-01	< 2.00E-01	3.00E+01
Phosphate (PO_4^{-3})	< 1.00E+00	< 1.00E+00	< 1.00E+00	1.84E+01

Table 1 (cont'd). Results of Chemical Analyses for Evaporator Overheads Year 2004 Annual Samples

Species	**2F Evap. Overheads (mg/L)**	**2H Evap. Overheads (mg/L)**	**3H Evap. Overheads (mg/L)**	**WWCT Feed Acceptance Limits (mg/L)**
Arsenic (As)	< 5.50E-02	< 5.50E-02	< 5.50E-02	5.77E+00
Silver (Ag)	< 1.10E-02	< 1.10E-02	< 1.10E-02	7.82E+01
Aluminum (Al)	< 1.00E-01	< 1.00E-01	< 1.00E-01	1.08E+03
Boron (B)	1.41E+00*	< 4.00E-02	< 4.00E-02	6.92E+00
Barium (Ba)	< 9.00E-03	< 9.00E-03	< 9.00E-03	5.77E+00
Beryllium (Be)	< 1.00E-03	< 1.00E-03	< 1.00E-03	5.00E+00
Calcium (Ca)	4.19E-01	1.28E+00	3.19E-01	2.12E+01
Cadmium (Cd)	< 2.30 E-02	< 2.30 E-02	< 2.30 E-01	2.58E+00
Cerium (Ce)	< 1.34E-01	< 1.34E-01	< 1.34E-01	-
Chromium (Cr)	< 4.10E-02	< 4.10E-02	< 4.10E-02	8.40E+00
Cobalt (Co)	7.00E-05	3.20E-04	< 2.00E-05	6.92E+00
Copper (Cu)	< 1.30E-02	3.70E-02	<1.30E-02	8.48E+01
Mercury (Hg)	4.28E-01*	< 1.10E-01	2.41E-01	4.06E+01
Iron (Fe)	< 5.60E-02	< 5.60E-02	< 5.60E-02	4.62E+01
Gadolinium (Gd)	< 1.40E-02	< 1.40E-02	< 1.40E-02	-
Potassium (K)	5.18 E-01*	1.18 E-01	6.98 E-01	2.82E+02
Lanthanum (La)	< 4.50E-02	< 4.50E-02	< 4.50E-02	-
Lithium (Li)	< 2.30E-02	< 2.30E-02	< 2.30E-02	6.92E+00
Magnesium (Mg)	4.30E-02	5.30E-02	2.10E-02	-
Manganese (Mn)	< 3.00E-03	< 3.00E-03	< 3.00E-03	6.92E+00
Molybdenum (Mo)	< 1.65E-01	< 1.65E-01	< 1.65E-01	6.92E+00
Sodium (Na)	2.73E+00	2.16E+00	8.34E-01	1.24E+03
Nickel (Ni)	< 3.20E-02	3.30E-02	< 3.20E-02	6.92E+00
Phosphorous (P)	< 8.26E-01	< 8.26E-01	< 8.26E-01	-
Lead (Pb)	< 5.82E-01	< 5.82E-01	< 5.82E-01	3.71E+01
Sulfur (S)	< 2.44E-01	< 2.44E-01	< 2.44E-01	-
Silicon (Si)	7.40E+00*	8.55E+00	1.25E+00	9.92E+01
Antimony (Sb)	< 6.30E-02	< 6.30E-02	< 6.30E-02	2.17E+02
Selenium (Se)	< 5.50E-02	< 5.50E-02	< 5.50E-02	3.46E+00
Tin (Sn)	< 5.09E-01	< 5.09E-01	< 5.09E-01	-
Zinc (Zn)	< 1.10E-02	4.60E-02	< 1.10E-02	7.50E+00
Strontium (Sr)	8.40E-02	2.69E-01	6.80E-02	6.92E+00
Titanium (Ti)	< 8.00E-03	< 8.00E-03	< 8.00E-03	-
Zirconium (Zr)	<1.50E-02	<1.50E-02	<1.50E-02	-
Vanadium (V)	<4.30E-02	<4.30E-02	<4.30E-02	-

* Equivalent amount was detected in the blank samples analyzed with the 2F overhead samples.

Table 1 (cont'd). Results of Chemical Analyses for Evaporator Overheads Year 2004 Annual Samples

Species	**2F Evap. Overheads (mg/L)**	**2H Evap. Overheads (mg/L)**	**3H Evap. Overheads (mg/L)**	**WWCT Feed Acceptance Limits (mg/L)**
EDTA	< 1.50E+01	< 5.00E+01	< 1.50E+01	3.75E+02
Phenol	< 1.00E-01	< 1.00E-01	< 1.00E-01	3.85E+02
Tributyl Phosphate (TBP)	< 1.00E-01	< 1.00E-01	< 1.00E-01	3.85E+02
Dibutyl Phosphate (DBP)	< 1.00E+01	< 1.00E+01	< 1.00E+01	-
Tetraphenylborate (TPB)	< 1.00E+00	< 2.00E-01	< 1.00E+00	-
Dimethyl mercury (DMHg)	< 5.00E-03	4.60E-01*	6.10E-03	-
Polychlorinated Biphenyls (PCBs)	< 1.00E-02	< 2.00E-02	< 1.00E-02	9.04E-01
Methanol	nd$^{\delta}$	nd$^{\delta}$	nd$^{\delta}$	2.25E+02
Isopropanol	< 5.00E-03	< 1.00E-01	< 5.00E-03	3.85E+02
Butanol & Isobutanol	4.00E-02	< 1.00E-03	< 5.00E-03	3.85E+02
Toluene	3.20E +00	< 1.00E-03	1.20E-01	3.85E+02
Benzene	< 5.00E-03	< 1.00E-03	1.50E-02	3.79E+02
Trichloroethylene (TCE)	< 5.00E-03	< 1.00E-03	< 5.00E-03	2.63E+00
Tertrachloroethylene/ Perchlorchloroethylene (PCE)	< 5.00E-03	< 1.00E-03	< 5.00E-03	1.92E+00
Total Organic Carbon (TOC)	< 2.00E+01	< 2.00E+01	< 2.00E+01	3.85E+02
Total Suspended Solids (TSS)	< 1.1E01	< 1.1E01	< 1.1E01	1.00E+02
Particle Size (microns)	< 4 micron	< 1 micron	< 1 micron	350 micron/40 mesh
pH (no units)	9.28	5.57	9.45	1 to 12.5

$^{\delta}$ ADS has no method for methanol. Therefore no concentration is given.

* Equivalent amount was detected in the blank control sample for the 2H-Evaporator overhead.

Table 2. Results of Radionuclide Analyses for Evaporator Overheads Year 2004 Annual Samples

Species	2F Evap. Overheads (dpm/mL)	2H Evap. Overheads (dpm/mL)	3H Evap. Overheads (dpm/mL)	WWCT Feed Acceptance Limits (dpm/mL)
^{3}H	9.95E+04	4.66E+02	1.84E+04	1.20E+05
Alpha	< 9.53E+00	< 1.74E+00	< 2.27E+01	1.00E+02
Beta/Gamma (non-volatile)	3.69E+02	9.94E+01	2.99 E+02	2.50E+03
^{14}C	< 1.81E+01	< 1.19E+02	< 7.79E+00	1.91E+03
^{26}Al	< 1.89E+00	< 1.64E-01	< 1.91E+00	4.87E+01
^{59}Ni	< 8.89E+01	< 3.15E+02	< 1.02E+02	1.91E+03
^{63}Ni	< 4.59E+01	< 1.75E+01	< 4.86E+01	1.91E+03
^{60}Co	< 2.22E+00	< 1.93E-01	< 2.11E+00	1.30E+01
^{79}Se	< 5.83E+01	< 1.24E+01	<1.59E+01	1.76E+03
$^{90}Sr/Y$	< 5.76E+01	< 9.65E+00	<1.51E+01	1.76E+02
^{94}Nb	< 1.89E+00	< 1.84E-01	< 1.80E+00	2.59E+02
^{99}Tc	4.30E+00	5.12E+01	1.28E+01	2.50E+03
$^{106}Ru/Rh$	< 1.75E+01	< 2.07E+00	< 2.06E+01	7.92E+02
^{126}Sn	< 3.05E+00	< 3.27E-01	< 3.63E+00	9.38E+01
^{125}Sb	<7.80E+00	< 9.26E-01	< 9.03E+00	2.50E+02
^{129}I	< 1.91E-01	< 1.35E-01	< 1.13-01	1.00E+00
^{134}Cs	< 2.25E+00	< 2.07E-01	< 2.31E+00	2.50E+03
^{135}Cs	< 5.11E-01	2.30E-01	< 5.11E-01	2.50E+03
^{137}Cs	3.13E+02	1.09E+02	5.48E+02	1.20E+03
^{144}Ce	< 1.12E+01	< 1.26E+00	< 1.25E+01	-
^{147}Pm	< 3.08E+01	< 2.32E+01	< 1.90E+01	2.50E+03
^{151}Sm	< 2.15E+01	< 1.99E+01	< 1.34E+01	3.81E+02
^{154}Eu	< 3.12E+00	< 3.38E-01	< 3.36E+00	2.50E+01

Table 2 (cont'd). Results of Radionuclide Analyses for Evaporator Overheads Year 2004 Annual Samples.

Species	2F Evap. Overheads (dpm/mL)	2H Evap. Overheads (dpm/mL)	3H Evap. Overheads (dpm/mL)	WWCT Feed Acceptance Limits (dpm/mL)
^{155}Eu	< 3.44E+00	< 3.75E-01	< 4.10E+00	1.91E+02
^{226}Ra	< 4.23E+01	< 6.22E+00	< 4.61E+01	8.80E+00
^{230}Th	< 1.51E+01	< 3.16E+00	< 1.51E+01	5.28E+01
^{232}Th	4.74E-06	< 1.68E-05	1.65E-05	8.80E+00
^{233}U	3.85E-01	< 1.48E+00	< 2.14E+00	6.60E+01
^{234}U	1.10E-01	< 9.52E-01	1.10E-01	6.60E+01
^{235}U	< 4.80E-04	< 3.31E-04	< 4.80E-04	6.09E1-01
^{236}U	1.15E-03	< 9.94E-03	2.02E-03	6.60E+01
^{238}U	4.10E-05	< 5.15E-05	1.12E-05	7.92E+01
^{237}Np	< 7.85E-02	< 1.08E-01	9.42E-03	3.96E+00
^{238}Pu	< 2.59E-1	<1.86E-01	< 2.58E-01	5.28E+00
^{239}Pu	< 1.67E-01	< 2.18E-01	< 2.17E-01	3.96E+00
^{240}Pu	< 3.34E-02	< 4.36E-02	< 4.34E-02	3.96E+00
^{241}Pu	< 1.75E+01	< 1.76E+00	3.22E+01	2.64E+02
^{242}Pu	< 8.73E-01	< 6.02E-01	< 8.73E-01	3.96E+00
^{241}Am	< 1.05E+01	< 2.85E+00	< 2.24E+00	3.96E+00
^{242}Cm	< 7.39E-01	< 1.94E-01	< 7.39E-01	-
^{243}Am	< 3.27E+00	< 2.37E+00	< 2.41E+00	3.96E+00
^{244}Cm	< 3.84E+00	< 7.14E-02	< 1.12E+00	7.92E+00
RCG#	8.24E-03	2.65E-03	1.38E-02	7.69E-03

RCG = (0.000102 [Co-60] + 0.00000875 [Ru-106] + 0.0000178 [Sb-125] + 0.0000234 [Cs-137] + 0.0000508 [Eu 154] + 0.0000819 [Sn-126]) where the concentrations are given in dpm/mL Note the results given here assume that any radionuclide concentration results that came back less than detectable are considered to be at the lower limit of detection.

QUALITY ASSURANCE

Results of the analyses described in this report are documented in WSRC-LB-2001-00179.

REFERENCES

[1] A. W. Wiggins, Jr "F/H Effluent Treatment Project Waste Acceptance Criteria (U)" X-SD-H-00009, Rev. 0., December 2004.

[2] C. I. Aponte, "Quarterly Analysis of Evaporator Overheads Samples," HLW-STE-99-0214, Revision 1, November 30, 2001.

APPROVALS

Authors (s)

L. N. Oji, Waste Processing Technology — Date: 3/21/05

S. McCollum, Waste Processing Technology — Date: 3/21/05

Design Check per Manual E7, Procedure 2.40

C. J. Martino, Design Check, Waste Processing Technology — Date: 3-21-05

APPROVALS:

W. R. Wilmarth, Manager, Waste Processing Technology — Date: 3-29-05

A. W. Wiggins, Manager ETP Process Support — Date: 4/13/05

J. M. Russel, Liquid Waste Process Chemistry Engineering — Date: 4-5-05

E. J. Freed, Manager H & F Process Support — Date: 4/13/05

J. C. Griffin, Manager, Waste Processing Technology — Date: 4/14/05

Distribution

C. I. Aponte,	703-H
H. Bui,	703-H
T. E. Britt,	703-H
K. Collins,	703-H
S. D. Fink,	773-A
E. J. Freed,	703-H
J. C. Griffin,	773-43A
M. D. Johnson,	703-H
T. D. Lookabill,	241-168H
C. G. May,	773-42A
D. J. Martin,	703-H
K. B. Martin,	773-42 A
C. J. Martin,	735-11 A
H. A. McGovern,	241-246H
P Rogerson,	703-H
J. M. Russel,	703-H
J Stergion,	703-H
R. F. Swingle,	773-42A
A. W. Wiggins,	241-246H
W. R. Wilmarth,	773-42A
STI	703-43A