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Report on the Analysis of WAC Samples from Evaporator Overheads for 2011

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EXECUTIVE SUMMARY

This report tabulates the chemical analysis of the 3H, 2H and 2F evaporator overhead samples including the inorganic, organic, and radionuclide species according the ETP WAC (rev.4). In addition, the physical properties including pH, total suspended solids, and average particle size are listed for each sample. The report identifies all sample receipt dates, preparation methods, and analyses completed to accumulate these values. All values were found to be within the ETP WAC specifications for WWCT except for the ^{137}Cs concentration for the 2F sample which was slightly above the limit (~5%). However, tank farm personnel sample each tank overhead for beta/gamma prior to transfer using a pulse height analyzer and these field readings were all well within limits. Additional actions will be taken to help understand the reason in the discrepancy of the field measurement versus laboratory analysis.

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LIST OF ABBREVIATIONS

ETP	Effluent Treatment Project
WAC	Waste Acceptance Criteria
ADS	Analytical Development Section
GC/MS	Gas Chromatography/Mass Spectroscopy
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
AA	Atomic Absorption
CVAA	Cold Vapor Atomic Absorption
WWCT	Waste Water Collection Tanks
RCG	Radiological Control Guide

INTRODUCTION

The Tank Farm has submitted the annual samples from 3H (8/16/2011), 2H (8/18/2011), and 2F (5/16/2011) Evaporator Overhead streams for characterization to verify compliance with the ETP WAC[1] and to look for organic species.

EXPERIMENTAL

The annual evaporator overheads samples arrived at the Savannah River National laboratory between May 2011 and August 2011. Sample aliquots were measured and transferred 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. In addition, clean de-ionized water was also submitted as blank samples to assess the background levels of the experiments.

A number of different analytical methods are used by ADS to determine the concentrations of various species in the samples. Both volatile and semivolatile organic species are determined using gas chromatography coupled with mass spectrometry (GC/MS). Ion chromatography (IC) is used to determine a number of anion species (NO_3^-, NO_2^-, SO_4^{2-}, F^-, Cl^-, $C_2O_4^{2-}$ and PO_4^{3-}) as well as the ammonium cation, NH_4^+. Inductively coupled plasma-emission spectrometry (ICP-ES) is used to determine a number of elemental species (Al, Ag, B, Ba, Be, Cd, Cr, Fe, Cu, Mn, Na, Ni, Pb, Sb, and Zn). A wet chemistry method is used to calculate the carbonate concentration. Atomic Absorption (AA) is used to determine the presence and concentration of As, Se and K. A cold vapor AA (CVAA) technique is used to measure the Hg concentration. Organic carbon was determined using a total organic carbon analyzer. Total suspended solids were measured gravimetrically. A TIM900 Titration System was used to measure sample pH. A particle size analysis was not performed due to insufficient insoluble solids.

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, ^{106}Ru, ^{126}Sn, ^{125}Sb, ^{154}Eu). 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. In preparation for this measurement, samples are evaporated down to dry smears and analyzed as such.

In addition to the radionuclide analysis performed by ADS, the tank farm also performs an initial sample screening using a pulse height analyzer.

RESULTS AND DISCUSSION

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

Table 1 provides the measured values for inorganic species contaminants for the annual samples. Table 2 provides the measured values for the organic species contaminants. Table 3 provides the measured values for the physical and chemical properties of the annual samples. Table 4 provides the measured values for the radionuclide contaminants for the annual samples. The samples were submitted from the 2F, 2H, and 3H evaporator overheads, along with the limits given in the current revision of the ETP WAC and a

reference sample to be analyzed in the same manner. Apart from the higher than WWCT feed limits shown in Table 4 for the ^{137}Cs observed in one evaporator overhead sample (2F) which exceeds the deviation,[2] no other species were found to be above the limits in the three evaporators for the annual samples.

Table 1. Results of Chemical Analyses of Inorganic Species
For Evaporator Overhead Samples for 2010

Analyte	**Reference Blank Analysis (mg/L)**	**2F Evap. Overheads (mg/L)**	**2H Evap. Overheads (mg/L)**	**3H Evap. Overheads (mg/L)**	**WWCT Feed Acceptance Limits (mg/L)**
Fluoride (F^-)	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	1.26E+01
Chloride (Cl^-)	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	3.00E+01
Carbonate (CO_3^{2-})	<2.50E+00	2.00E+01	2.00E+01	1.50E+01	1.12E+03
Nitrite (NO_2^-)	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	1.99E+02
Nitrate (NO_3^-)	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	3.40E+03
Phosphate (PO_4^{3-})	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	1.84E+01
Sulfate (SO_4^{2-})	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	1.33E+02
Oxalate ($C_2O_4^{2-}$)	<1.00E+00	<5.00E+00	<1.00E+00	<1.00E+00	2.54E+02
Silver (Ag)	N/A	<2.90E-02	<2.90E-02	<2.90E-02	7.82E+01
Aluminum (Al)	N/A	<6.60E-02	<6.60E-02	<6.60E-02	1.08E+03
Arsenide (As)	N/A	<2.75E-02	<2.75E-02	<2.75E-02	1.50E+00
Boron (B)	N/A	<2.80E-02	<2.80E-02	<2.80E-02	1.50E+01
Barium (Ba)	N/A	<1.30E-02	<1.30E-02	<1.30E-02	5.77E+00
Beryllium (Be)	N/A	<2.00E-03	<2.00E-03	<2.00E-03	2.00E-01
Cadmium (Cd)	N/A	<1.30E-02	<1.30E-02	<1.30E-02	2.58E+00
Chromium (Cr)	N/A	<2.00E-02	<2.00E-02	<2.00E-02	8.40E+00
Copper (Cu)	N/A	<1.30E-02	<1.30E-02	<1.30E-02	9.00E+2
Iron (Fe)	N/A	<1.90E-02	<1.90E-02	<1.90E-02	4.00E+02
Mercury (Hg)	N/A	<1.00E-02	2.65E+00	6.22E-02	3.52E+01
Manganese (Mn)	N/A	<4.00E-03	<4.00E-03	<4.00E-03	9.00E+02
Potassium (K)	N/A	<1.50E-01	<1.50E-01	<1.50E-01	N/A
Sodium (Na)	N/A	2.17E-01	2.45E-01	<1.06E-01	N/A
Nickel (Ni)	N/A	<9.10E-02	<9.10E-02	<9.10E-02	9.52E+01
Lead (Pb)	N/A	<1.43E-01	<1.43E-01	<1.43E-01	3.71E+01
Antimony (Sb)	N/A	<2.13E-01	<2.13E-01	<2.13E-01	1.50E+00
Selenium (Se)	N/A	<5.50E-02	<5.50E-02	<5.50E-02	1.00E+00
Zinc (Zn)	N/A	<1.30E-02	<1.30E-02	<1.30E-02	5.92E+01
Ammonia (NH_3)	N/A	9.00E+00	1.80E+01	5.00E+00	2.00E+01

N/A: Not Available
*3H is same as blank in both 2009 and 2010 samples

Table 2. Results of Chemical Analyses of Organic Species

For Evaporator Overhead Samples for 2010

Analyte	**Reference Blank Analysis (mg/L)**	**2F Evap. Overheads (mg/L)**	**2H Evap. Overheads (mg/L)**	**3H Evap. Overheads (mg/L)**	**WWCT Feed Acceptance Limits (mg/L)**
Phenol	<1.00E+01	<1.00E+01	<1.00E+01	<1.00E+01	3.85E+02
Benzene	<1.00E+00	<1.00E+00	<1.00E+00	<1.00E+00	3.79E+02
Toluene	<1.00E+00	<1.00E+00	<1.00E+00	<1.00E+00	3.85E+02
Trichloroethene	<1.00E+00	<1.00E+00	<1.00E+00	<1.00E+00	2.63E+00
Tetrachloroethene / Perchloroethene (PCE)	<1.00E+00	<1.00E+00	<1.00E+00	<1.00E+00	1.92E+00
PCB	<1.00E-01	<1.00E-01	<1.00E-01	<1.00E-01	9.04E-01
Tetraphenlyborate (TPB)	<5.00E+00	<5.00E+00	<5.00E+00	<5.00E+00	N/A
TOC	1.00E+00	3.00E+00	8.00E+00	1.00E+00	3.85E+02

N/A: No TPB is allowed in these samples
ND: Not Detected

Table 3. Results of Physical/Chemical Properties

For Evaporator Overhead Samples for 2010

Analyte	**Reference Blank Analysis**	**2F Evap. Overheads**	**2H Evap. Overheads**	**3H Evap. Overheads**	**WWCT Feed Acceptance Limits**
Total Suspended Solids (TSS)	N/A	<0.1 wt%$^{\chi}$	<0.1 wt%$^{\chi}$	<0.1 wt%$^{\chi}$	1.00E+02
Particle Size (microns)	N/A	ND	ND	ND	350 microns
pH (no units)	6.54	9.39	9.97	9.42	1 to 12.5

$^{\chi}$ Low total suspended solids, so the particle size distribution was not evaluated.
δ Not Detected: insufficient particles for data.

Table 4. Results of Radionuclide Analyses

For Evaporator Overhead Samples for 2010

Analyte	Reference Blank Analysis (dpm/mL)	2F Evap. Overheads (dpm/mL)	2H Evap. Overheads (dpm/mL)	3H Evap. Overheads (dpm/mL)	WWCT Feed Acceptance Limits (dpm/mL)
Alpha	N/A	<9.23E+00	<4.75E+00	<8.47E+00	2.00E+01
Beta/Gamma	N/A	8.38E+02[α]	2.34E+01	2.05E+02	1.30E+03
^{90}Sr	N/A	<1.62E+01	<1.63E+01	<1.64E+01	1.76E+02
^{3}H	N/A	1.35E+04	5.28E+02	6.75E+03	1.20E+05
^{14}C	N/A	<7.34E+00	<7.34E+00	<7.34E+00	1.91E+03
^{63}Ni	N/A	<1.32E+01	<1.87E+01	<1.14E+01	1.91E+03
^{60}Co	N/A	<2.09E+00	<4.58E+00	<4.89E+00	1.30E+01
^{99}Tc	N/A	<9.26E+00	<9.09E+00	<9.11E+00	2.50E+03
^{106}Ru	N/A	<1.56E+01	<2.54E+01	<2.96E+01	7.92E+02
^{126}Sn	N/A	<9.98E+00	<4.63E+00	<6.16E+00	9.38E+01
^{125}Sb	N/A	<4.24E+00	<8.36E+00	<1.36E+01	4.32E+02
^{129}I	N/A	<4.49E-01	<5.77E-01	<6.06E-01	1.00E+00
^{137}Cs	N/A	1.05E+03[α]	1.76E+01	2.26E+02	1.00E+03[γ]
^{154}Eu	N/A	<3.81E+00	<3.26E+00	<4.32E+00	2.50E+01
^{233}U	N/A	<6.42E-01	<6.42E-01	<6.42E-01	6.60E+01
^{235}U	N/A	<9.60E-05	<9.60E-05	<9.60E-05	6.09E-01
^{238}U	N/A	<2.24E-05	<2.24E-05	<2.24E-05	N/A
^{238}Pu	N/A	<5.44E-01	<7.09E-01	<6.70E-01	N/A
$^{239/240}$Pu	N/A	<6.33E-01	<5.83E-01	<1.03E+00	N/A
^{241}Pu	N/A	<1.71E+01	<1.71E+01	<1.71E+01	2.64E+02
^{237}Np	N/A	<3.13E-02	<3.13E-02	<3.13E-02	1.30E-01
RCG*	N/A	2.56E-02	1.80E-03	7.01E-03	2.57E-02[γ]

*Radiological Control Guide: # RCG = (0.000102[^{60}Co] +0.00000875[^{106}Ru] +0.0000178[^{125}Sb] +0.0000234[^{137}Cs] +0.0000508[^{154}Eu] +0.0000819[^{126}Sn]) 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.

[α] Tank farm PHA shows an average ^{137}Cs concentration of 540 dpm/mL with a max concentration of 603 dpm/mL.[3]

[γ] Deviation to WAC allows values to be 1000 dpm for ^{137}Cs and 2.57E-02 for the RCG value. This is higher than the current WWCT limits of 328 dpm for ^{137}Cs and 7.69E-03 for the RCG value.[2]

N/A: Not Available

CONCLUSIONS

All the overheads samples were found to be in compliance with the Effluent Treatment Project WAC with the exception of the ^{137}Cs value for the 2F evaporator overheads. The ^{137}Cs value for the 2F evaporator sample exceeds the current WAC deviation by 5%.[2] This deviation allows for elevated limits of ^{137}Cs covering the excess beta/gamma in the samples and also increasing the RCG limits. The ^{137}Cs and RCG values are shown in Table 4. Tank farm Operations personnel sample each 2F evaporator overheads tank and measure the beta/gamma concentration using a pulse height analyzer prior to transfer to ETP. The 2F system engineer reviewed the PHA sample results obtained during the period of time that the 2F evaporator was sampled for the annual WAC analysis and all results during this period of time were in the range of 500-600 d/m/ml.[3] Additional actions will be taken to determine if the reason for this discrepancy can be identified.

QUALITY ASSURANCE

Results of the analyses described in this report are documented in SRNL-NB-2010-00013.

REFERENCES

1. "F/H Effluent Treatment Facility Waste Acceptance Criteria," X-SD-H-00009, Revision 5, August 4, 20011.

2. "Request for Deviation to ETP Waste Acceptance Criteria," ETP-RFD-2011-00008, Expires August 2, 2012.

3. Personal email communication with Paul Rogerson. Paul keeps a copy of the operator's log for PHA sample analysis.