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Report on Analyses of WAC Samples of Evaporator Overheads – 2004

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SUMMARY

In March of 2004, the Tank Farm submitted annual samples from 2F, 2H and 3H Evaporator Overhead streams for characterization to verify compliance with the Effluent Treatment Facility (ETF) Waste Acceptance Criteria (WAC) and to look for organic species. With the exception of high silicon in the 2H and slightly high tritium in 2F evaporator overheads, all the overheads samples were found to be in compliance with the Effluent Treatment Facility WAC. The silicon concentration in the 2H-evaporator overhead, at 44 mg/L, was above the ETF WAC limit of 5 mg/L and tritium at 2.11E+05 dpm/mL in 2F overhead sample was above the ETF WAC limit of 1.2E+05 dpm/mL.

INTRODUCTION

All water received into ETF requires characterization versus the 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 arrived at the Savannah River National laboratory in April 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 anion AlO_2^- and a number of elemental species (Ag, B, Ba, Be, Ca, Cd. Cr, Cu, Mg, Mn, Na, Ni, Pb, Sb, Si, and Zn). Atomic Absorption (AA) is used to determine As, Se and K. A 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). Organic carbon was determined using a total organic carbon analyzer. Total suspended solids were measured gravimetrically. A pH meter 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, ^{94}Nb, $^{106}Ru/Rh$, ^{126}Sn, ^{125}Sb, ^{134}Cs, ^{154}Cs, ^{237}Np). 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 "<".

Table 1 provides the measured values for chemical contaminants for the annual samples from the 2F, 2H and 3H evaporator overheads pulled in March and April 2004, along with the limits given in the current revision of the ETF WAC.[1] Organic content analysis for the 3H evaporator overhead is not reported because of the lack of organic samples appropriately sampled and delivered in a glass container. Respectively, only the silicon (44 mg/L) and tritium (2.11E+05 dpm/mL) levels in the 2H and 2F evaporator overheads, were found to be above the waste water collection tank (WWCT) limits of 5 mg/L and 1.2E+05 dpm/mL. Thus, apart from the higher than WWCT feed limits for silicon and tritium concentrations observed in the 2H-evaporator and 2F, respectively, no other species were found to be above the limits in the three evaporators for the annual sample.

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)
Ammonia (NH_4^+)	1.9E+01	3.0E+00	4.0E+00	1.5E+02
Nitrate (NO_3^-)	<1	<1	<1	1.6E+03
Nitrite (NO_2^-)	<1	<1	<1	3E+02
Sulfate (SO_4^{-2})	<5E-01	3 E-01	< 5E-01	4E+01
Aluminate (AlO_2^-)	< 2.1E-01	< 2.1E-01	< 2.1E-01	1E+02
Carbonate (CO_3^{-2})	4.68E+01	2.63E+01	1.43E+01	2E+02
Fluoride (F^-)	< 0.2	< 0.2	< 0.2	1E+02
Oxalate ($C_2O_4^{-2}$)	<1	<1	<1	1E+02
Chloride (Cl^-)	< 2E-01	0.6 E+00	< 2E-01	7E+01
Phosphate (PO_4^{-3})	< 1	<1	<1	10
Silver (Ag)	< 9E-03	<9E-03	<9E-03	1

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	< 5.5E-02	1
Boron (B)	< 1.13E-01	< 1.13E-01	< 1.13E-01	6
Barium (Ba)	< 6.0E-03	< 6.0E-03	< 6.0E-03	2
Beryllium (Be)	< 1.0E-03	< 1.0E-03	< 1.0E-03	5
Calcium (Ca)	5.72 E-01	3.93E-01	<3.4E-02	2.29E+01
Cadmium (Cd)	< 1.4 E-02	< 1.4E-02	< 1.4E-02	6E-01
Chromium (Cr)	< 4.2E-02	< 4.2E-02	< 4.2E-02	5
Copper (Cu)	< 1.10E-02	< 1.10E-02	<1.1E-02	2
Mercury (Hg)	< 1.1E-01	< 1.1E-01	5.12E-01	6
Potassium (K)	<1.5 E-01	<1.5 E-01	2.53 E-01	1E+03
Magnesium (Mg)	6.6E-02	3.4E-02	< 1.0E-02	1.3E+01
Manganese (Mn)	< 6.0E-03	< 6.0E-03	< 6.0E-03	3.1E+01
Sodium (Na)	1.08E+00	4.33E+00	< 2.85E-01	6E+02
Nickel (Ni)	< 5.7E-02	< 5.7E-02	< 5.7E-02	2
Lead (Pb)	< 3.69E-01	< 3.69E-01	< 3.69E-01	2
Antimony (Sb)	< 7.2E-02	< 7.2E-02	< 7.2E-02	4E+01
Selenium (Se)	< 5.5E-02	< 5.5E-02	< 5.5E-02	1
Silicon (Si)	2.2E+00	4.44E+01*	< 1.33E+00	5
Zinc (Zn)	< 1.9E-02	7.8E-02	< 1.9E-02	4E+01
Butanol	2.1E-01	< 5E-02	No sample	--
Benzene	-	-	-	3

* Concentration of Si in blank was less than 1.33 mg/L

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	< 5E+00	<5.0E+00	<5.0E+00	5
Phenol	<1E-01	< 5E-02	**No Sample**	5E+01
Tributyl Phosphate (TBP)	<1E-01	< 5E-02	**No Sample**	5E+01
Dibutyl Phosphate (DBP)	< 1.0E+1	< 1.0E+01	< 1.0E+01	--
Methanol	nd$^{\delta}$	nd$^{\delta}$	nd$^{\delta}$	2
Isopropanol	< 5E-02	< 5E-02	**No Sample**	5E+01
Toluene	0.17E+00	0.17E+00	**No Sample**	
Dioctyl phthalate	4.5E+00			20
Other Volatile Organics	4.5E+00**	< 1E-01	**No Sample**	2E+01
Total Organic Carbon (TOC)	2.19E+01	4.84E+00	1.77E+01	1E+02
Total Suspended Solids (TSS)	< 0.001 wt. %	0.008 wt %	0.001 wt %	4E+01
Particle Size (microns)	χ	χ	χ	3.5E+02
pH (no units)	9.51	5.12	8.38	1 to 12.5

$^{\chi}$ Low total suspended solids, so the particle size distribution was not evaluated.
$^{\delta}$ ADS has no method for methanol. Therefore no concentration is given.
$^{\zeta}$ Toluene was detected in the 2F and 2H samples. However, it was not found in the blank sample.
** Dioctyl phthalate is a common industrial plasticizer, which was probably introduced into the aqueous sample during sampling procedures. This volatile organic was not detected in the blank control sample.

Table 2 gives the annual sample results for radionuclide analyses performed on the samples from the 2F, 2H and 3H Evaporator Overheads.

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	2.11E+05	7.22E+02	1.22E+04	1.2E+05
^{137}Cs	< 4.61E+00	1.96E+02	3.22E+02	1.2E+03
Alpha	< 3.23E+01	< 3.36E+01	< 2.44E+01	1.0E+02
Beta/Gamma (non-volatile)	1.37 E+01	8.75 E+00	8.30 E+00	2.5E+03
^{14}C	< 7.47E+02	< 7.47E+02	< 7.47E+02	2.5E+03
^{59}Ni	< 2.90E+02	< 2.85 E+02	<3.32E+02	2.5E+03
^{60}Co	< 4.9E+00	< 4.44E+00	< 4.14E+00	1.3E+01
^{79}Se	< 9.90E+00	< 1.35E+01	<1.19E+01	5E+01
$^{90}Sr/Y$	< 1.77E+01	< 2.55E+01	< 2.50E+01	1.8E+02
^{94}Nb	< 4.06E+00	< 4.14E+00	< 4.06E+00	6.3E+01
^{99}Tc	< 5.65E+00	<5.65E+00	<5.65E+00	2.5E+03
$^{106}Ru/Rh$	< 3.69E+01	< 4.10E+01	<4.340E+01	7.9E+02
^{126}Sn	< 6.99E+00	< 7.47E+00	<8.36E+00	7E+02
^{125}Sb	<1.08E+01	< 1.30E+01	< 1.52E+01	2.50E+02
^{129}I	< 1.37E+00	< 3.28E-01	< 5.65E-01	1
^{134}Cs	< 4.37E+00	< 4.38E+00	< 4.40E+00	2.5E+03
^{154}Eu	<4.55E+00	<5.56E+00	< 5.71E+00	2.5E+01
^{237}Np	< 1.82E-3	< 1.82E-3	< 1.82E-3	1.3E-01
^{241}Pu	5.84E+00	< 4.17E+00	4.24E+00	1E+02
RCG#	9.14E-04	2.87E-03	4.13E-03	1.2E-02

RCG = (0.145[^{60}Co]+0.0078[^{106}Ru]+0.013[^{125}Sb]+0.022[^{137}Cs]+0.061[^{154}Eu]+0.0705[^{126}Sn])/2200 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-NB-2004-00077.

REFERENCES

[1] "F/H Effluent Treatment Facility Waste Acceptance Criteria," Manual 1S, Procedure 4.02, Revision 3, February 25, 2002.

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