

**WESTINGHOUSE SAVANNAH RIVER COMPANY
ETP ENGINEERING**

**X-WCP-H-00002
Revision: 9**

Keywords:
Waste Acceptance Criteria,
WAC, WCP, ETF, ETP, Tank
Farms

**F/H EFFLUENT TREATMENT PROJECT WASTE
CONCENTRATE REGULAR WASTE COMPLIANCE PLAN (U)**

Retention: Permanent

Classification:
UNCLASSIFIED
No classification review required

ISSUED: February 2008

A.W. Wiggins
A. W. Wiggins, Author, ETP Engineering Lead

Date: 2/25/08

H. Kindel
H. Kindel, Technical Reviewer, ETP Engineering

Date: 2/26/08

L.W. Lunden
L. W. Lunden, Technical Reviewer, LW Process Engineering

Date: 02/27/08

A.W. Wiggins FOR C.J. WARD PER TELECON
C. J. Ward, Manager, Environmental Support

Date: 2/27/08

R.L. Salizzoni
R. L. Salizzoni, Tank Farm Chief Engineer

Date: 2/27/08

C.L. Atseff
C. L. Atseff, Manager, Liquid Waste Process Engineering

Date: 2/27/08

Hugh M. McGovern
H. A. McGovern, Manager, Effluent Treatment Project

Date: 2/27/08

M.N. Borders
M. N. Borders, Manager, H Tank Farm Facility

Date: 2/27/08



Revision Summary

Revision 0 (3/03)	Initial Issue
Revision 1 (8/04)	Revised to include current Saltstone WAC limits and Tank 50 Requirements
Revision 2 (11/04)	Incorporated results from baseline sample.
Revision 3 (4/05)	Added LW Environmental Engineering approval, identified air pollutants in table 2.1, revised Al, Hg, Sr-90 and U-235 limits on Tables 2.1 and 2.2, added temperature section 6.2 and to table 1, and revised hydroxide concentration verification in section 6.1.
Revision 4 (3/06)	Added Liquid Waste Disposition Project (LWDP) Linking Document Database (LDD) references, deleted the discussion of the Tank 50 valve box NCSE from section 6.6, and updated sample results.
Revision 5 (10/06)	Changed Liquid Waste Disposition Project (LWDP) Linking Document Database (LDD) references to Specific Admin Controls.
Revision 6 (2/07)	Revised section on Ammonia Flammability. Added oxalate to quarterly WCT sample.
Revision 7 (11/07)	Added NO _{eff} for hydrogen generation rate determination. Revised section on Ammonia Flammability to credit lowering Tank 50 HLLCP.
Revision 8 (1/08)	Revised section on Ammonia Flammability to remove controls that are the responsibility of HTF.
Revision 9 (2/08)	Revised section on Ammonia Flammability to document ammonia limit based on Tank 50 temperature and level controls that are the responsibility of HTF.

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Requirement: This document meets the CST requirements of the following:

- CST Admin Control 5.8.2.13
- CST SAC 5.8.2.15
- CST SAC 5.8.2.25
- JCO WSRC-TR-2003-00083, 5.0.2

1.0 Background and Waste Generator Responsibilities

The F/H Area Effluent Treatment Project (ETP) treats routine wastewater (primarily evaporator overheads) from the F and H Tank Farms and F and H Canyons and Outside Facilities. The ETP treatment process splits the influent waste stream into a high volume treated effluent and a low volume waste concentrate. This Waste Compliance Plan (WCP) is for the transfer of the ETP low volume waste concentrate from the waste concentrate tanks (WCT) to H Tank Farm via the Tank 50 valve box to Tank 50 or through HDB-8 to one of the other H Tank Farm tanks. The volume of each transfer will be approximately 1300-1500 gallons. Typically there will be 1-3 transfers per week. The WCP is based on past ETP operating experience and process data as well as sample analyses of Tank 50 material processed at Saltstone.

Liquid Waste Disposition Engineering (LWDE) has established a Waste Acceptance Criteria (WAC)¹ to control receipts of liquid waste into the 241 F/H Tank Farms. The WAC requires the waste generators to develop a Waste Compliance Program document which describes the waste generating process and the controls that ensure the stream(s) comply with all WAC requirements. The WCP documents the waste stream composition such that LWDE can determine the waste acceptability. The WAC and the WCP combine to bridge the interface between the tank farms and the waste generator to ensure all wastes transferred to the Tank Farms can be safely stored and processed for disposal.

The 241 F/H Tank Farm WAC designates the waste generator as being responsible for:

- ◆ Developing a documented WCP that includes the following elements:
 - a description of the waste generating process; including flow sheet information (e.g. transfer volumes and frequencies) and the transfer route to the Tank Farms;
 - a description and inventory of chemicals (and radionuclides if applicable) used in the waste generating process (i.e. species that could affect the waste stream composition);

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- the waste stream definition and complete characterization;
 - the justification for any deviation from the WAC;
 - a description of the program activities that ensures compliance with the WAC;
 - a description of the self-assessment program that ensures compliance with the WAC;
 - a description of waste minimization activities; and
 - a description of any future improvement activities.
- ◆ Designating a primary contact, known as the “Liquid Waste Generator Representative” (LWGR), for all communications with LWDE regarding the responsibilities assigned to the generator;
 - ◆ Preparing all waste for transfer to the Tank Farm so that all WAC requirements are met;
 - ◆ Maintaining records demonstrating compliance with the WAC and WCP, and providing LWDE a copy of all available waste characterization data;
 - ◆ Conducting a self-assessment program to ensure compliance with the WCP;
 - ◆ Reporting a WAC non-compliance to LWDE, no matter how small, and assisting with any investigation (e.g. NCR, SIRIM, etc.);
 - ◆ Financing any additional evaluations or other measures required to accept Special Waste (SW);
 - ◆ Financing any corrective action resulting from the generator’s failure to meet the WAC; and
 - ◆ Participating in quarterly reviews of the proposed waste transfers.

Note: All items above are included in this document.

2.0 Process Description

The ETP collects radioactively and chemically contaminated wastewater (primarily evaporator overheads), treats and discharges it either to the environment and/or transfers it for eventual storage in the Z-Area Saltstone Vaults. The wastewater is primarily generated by the F and H Canyons and Outside Facilities and the F and H Tank Farm evaporators. ETP waste receipts are controlled by the ETP WAC², which has as one of its bases the Tank Farm WAC. The ETP treatment process

splits the “influent wastewater” stream into two streams: the high volume “treated effluent” and the low volume “waste concentrate.”

The ETP treatment plant decontaminates the influent wastewater through a series of steps consisting of pH adjustment, sub-micron filtration, heavy metal ion exchange and organic removal activated carbon, reverse osmosis, and a polishing cation exchange. After the treatment steps remove specific species, the treatment effluent is analyzed and discharged to the environment through a National Pollution Discharge Elimination System (NPDES) permitted outfall. The treatment steps concentrate the contaminants into a smaller volume of secondary waste, which is further concentrated by evaporation. Various chemicals are added to restore the process efficiency and the spent solutions are also sent to the evaporator. The evaporator bottoms (waste concentrate) are pH adjusted to >12 and then sent to Tank 50 for eventual disposal at Saltstone or to the Tank Farm (through HDB-8).

The ETP process consists of several unit operations, or treatment steps. Attachment 1 contains an ETP process diagram. The principal unit operations are summarized below:

Wastewater Collection and pH Adjustment - Wastewater is received and aluminum nitrate (15-25 mg/L Al) and nitric acid are added as a pretreatment. The pH is adjusted between 6.0 and 9.0.

Micro-filtration - Wastewater is pumped through porous ceramic tubes. Filtrate passes from inside the tube, through the porous ceramic wall, and into a filtrate collection tank. The concentrate (solids) passes down the length of the tubes and collects in the filter concentrate tank.

Mercury Removal - The filtered wastewater is passed through columns filled with ion exchange resin to remove mercury.

Organic Removal - Effluent from the mercury removal columns is pumped through columns containing activated carbon to remove organic contaminants.

Carbon Filtration - Effluent from the organic removal column is passed through a cartridge filter to remove any carbon fines.

Reverse Osmosis - Reverse osmosis (RO) consists of a membrane system composed of high rejection seawater membranes. Clean permeate passes through the membrane, while ionic contaminants are rejected.

Cesium Removal - The RO permeate is passed through columns filled with cation exchange resin to remove Cesium-137.

Evaporation - The filtration and RO concentrates, ion exchange regenerate solutions, cleaning solutions, and sump water are fed to a forced-circulation flash evaporator for waste volume reduction. Also, some special wastes are fed directly to the evaporator. The evaporator overheads are fed back to the process, while the concentrated bottoms (30 wt.% dissolved solids) are collected, pH adjusted with 50 wt.% caustic ($\text{pH} > 12.0$, $\text{OH}^- > 1.1 \text{ M}$), and transferred to the Tank Farm (through HDB-8) or Tank 50.

This WCP covers the transfer of the ETP evaporator bottoms concentrate to the H Tank Farm.

3.0 Chemical Inventory

Since the ETP is a waste treatment facility, the principal chemicals present are the wastewater streams being treated. The ETP adds chemicals such as 40 wt% nitric acid, 50 wt% sodium hydroxide, oxalic acid, sodium metabisulfite, sodium hypochlorite, and aluminum nitrate to adjust wastewater pH and chemistry or as cleaning agents. The amount of each chemical used varies depending on the waste composition or the amount of equipment cleaning required. Any new chemical additions will be evaluated on a case by case basis for acceptability and compliance with the Tank Farm WAC prior to use.

4.0 Waste Stream Categories and Characterization

The ETP evaporator bottoms concentrate meets the specification for a Regular Waste (RW). The identification number for this waste stream is ETP-RW-001. This waste is generated as part of the routine operation of the ETP process.

Characterization of this stream was done by analyzing a waste concentrate sample per the Saltstone WAC. A complete characterization of this material is shown in Attachment 2 of this WCP and can also be found in the ETP folder in the WG08/HLW-WRT folder.

5.0 Compliance Strategy

Compliance with the Tank Farm WAC will be accomplished by periodic sampling of the waste concentrate stream. Table 1 shows the sampling schedule and analyses performed. The waste is sampled and the pH analyzed before every transfer. If the pH is too low to provide sufficient corrosion control, additional sodium hydroxide is added to the tank to increase pH to above 12. The existing

ETP procedures that are currently used to sample the waste and document the results are given in References 5 and 6.

TABLE 1
 Transfer Sampling Schedule

Prior to Every Transfer	After Every Transfer	Monthly	If Beta/Gamma > 40,000 dpm/ml	Quarterly
pH	Total beta/gamma	Arsenic	Co-60	VOC
Temperature	Total alpha	Barium	Pu-106	NO3
Hydroxide	Total suspended solids	Cadmium	Sb-125	NO2
NH ₃	Density	Chromium	Sn-126	Oxalate
		Lead	Cs-137	
		Mercury	Eu-154	
		Selenium	Sr-90	
		Silver		
		Chlorides		

6.0 Specific Criteria for High Level Liquid Waste Receipts

6.1 Requirements for Corrosion Prevention [*A/C* CST Admin Control 5.8.2.13]

The minimum pH requirement for the Tank Farms is 9.5.¹ The pH is verified to exceed 9.5 prior to every transfer.⁵ ETP procedures require 115 gallons of 50 wt% sodium hydroxide will be added to meet the Tank Farm WAC corrosion prevention criteria. The pH is verified for every waste transfer to Tank 50, and has always been above 12. Thus, the minimum inhibitor requirements are satisfied.

The free hydroxide (OH⁻) is verified by ETP Operations to be above the 1.1M limit prior to transfer to Tank 50.⁵ If the sample result is below 1.1M, additional caustic is added until the limit is met.

The Tank Farm WAC also has limits for Cl⁻, F⁻, NO₃⁻, and SO₄⁻². Chloride is sampled for once a month. The other three anions are not routinely sampled but are included in the Tank 50 sample results shown in Attachment 2. None of the anions has exceeded the Tank Farm WAC. The ETP WAC, based in part on TF WAC requirements, protects these limits from being exceeded. For nitrates, the waste concentrate density can be used to show compliance. The concentrate is drawn off the evaporator at a maximum specific gravity of 1.23. Assuming that the concentrate is only sodium nitrate and using a reference table¹⁶ for sodium nitrate to compare density to molarity yields a maximum nitrate concentration of 4.33M, well below the Tank Farm WAC limit of 8.5M.

6.2 Requirements to Prevent Accumulation of Flammable/Explosive Species [*A/C* CST SAC 5.8.2.15 & 5.8.2.25]

The ETP waste stream main flammable constituent is ammonia with trace concentration of hydrogen from radiolytic hydrolysis reactions. However, ammonia will dominate the composite lower flammability limit because of the low radionuclide activity content in the ETP.

The Tank Farm WAC has criteria that all transfers are below 70 deg C for flammability concerns in pump tank vapor space. The ETP lab measures the temperature of the waste concentrate pH sample prior to each transfer. The highest value recorded is 54 deg C, well below the 70 deg C limit. The ETP Evaporator Operation and Chemistry manuals^{5,6} (refs. 5 and 6) have been revised to record the sample temperature and verify with the H Disposition Project (H Tank Farm) operator that it is within the limit prior to transfer. This temperature data will be recorded in the WG08 database.

Organic Evaluation

The main source of organics in ETP is residual organics from the F and H Canyons and Tank Farms that pass through the ETP process. ETP receives and processes waste from the Tank Farms and Canyons and transfers the evaporator bottoms (waste concentrate) to Tank 50. The organics in the waste are primarily the soluble residue of tri-butyl phosphate and n-paraffin used in the solvent extraction process in the canyons. These are relatively heavy organics, both of which have boiling points higher than water. Organics resulting from ion exchange resins (digested and undigested) were also received from the canyons. Smaller quantities of organic constituents from RBOF and DWPF are also received in the Tank Farms. The Tank Farms contain more inorganic resins than organic resins, but inorganic resins (e.g., zeolite) do not decompose and form flammable constituents. Therefore, inorganic resins do not have a flammability concern from thermal, chemical or radiolytic decomposition. Defoaming agents used in the evaporators are another source of organic material. The organic constituents that are present in the defoaming agents are not expected to contribute significantly to the composite lower flammability level due to the limited quantities and the significant dilution from the tank farm supernatant.

Another source of organics is liquid scintillation cocktail from the Tritium and ETP laboratories. This material is mainly naphthalenes and alkyl benzene compounds along with the scintillation chemicals. The quantity is very small due to the relatively small volume of these laboratory streams (<1% of total waste flow).

ETP waste streams are treated to remove organics in both the carbon beds and the evaporator. Thus, flammable and/or explosive organic vapors or organic liquids

will not be present in the ETP evaporator bottoms concentrate. Visual examination of the waste concentrate samples shows no floating layers, hence less than 0.5% O/A. Volatile organic content (VOC) of the ETP waste concentrate will be verified at least quarterly (see Table1). The recent sample was checked for Total Organic Carbon (TOC) and was well below the Saltstone WAC – 1550 mg/L vs. 5000 mg/L limit. Quarterly VOC results have been <10 mg/L.

Hydrogen Generation Rate

The hydrogen generation rate was calculated for the ETP waste concentrate stream based on composition limitations from the Saltstone WAC¹². See Attachment 3 for details of the calculation. The resulting hydrogen generation rate of 6.36E-09 ft³ H₂/hr/gal for the current Saltstone WAC limits is far below any of the criteria found in section 11.2.2 of the Tank Farm WAC¹.

The NO_{eff} is calculated using the equation found in the Tank Farm WAC¹:

$$[\text{NO}_{\text{eff}}] = [\text{NO}_3] + 0.5 * [\text{NO}_2]$$

For ETP waste concentrate:

$$[\text{NO}_3] = 220 \text{ g/L} / 62 \text{ g/gmol} = 3.5\text{M}$$

$$[\text{NO}_2] = 0.100 \text{ g/L} / 46 \text{ g/gmol} = 0.002\text{M}$$

Therefore:

$$[\text{NO}_{\text{eff}}] = 3.5\text{M}, \text{ which is greater than the required } 0.89\text{M} \text{ for Tank } 50.$$

Ammonia Evaluation

The Tank Farm WAC requires the ammonia concentration to be less than 5% of the LFL, which correlates to a 554 mg/L and 238 mg/L ammonia concentration at 70°C and 100°C in the solution under equilibrium conditions, respectively²⁰. The Special WCP in support of ETP transfer to Tank 43 during Tank 50 valve box installation showed waste concentrate ammonia sample results with an average and maximum concentration of 350 mg/L and 1,900 mg/L, respectively¹⁸. These sample results were considered potentially non-representative since the ammonia would probably evolve off prior to sampling or after the sample was taken.¹⁵ Recent sample results from ETP waste generators show ammonia levels of up to 205 mg/L for the 2F evaporator (March 2002) with most other streams around 10 mg/L or less. Weekly sample results of the filtrate from the ETP microfilters show ammonia levels less than 10 mg/L. In addition, raising the pH in the waste concentrate tanks prior to transfer to the tank farm would cause the ammonia to be driven from solution before the waste is transferred. Ammonia content (NH₃) of

the ETP waste concentrate has historically been verified quarterly. The quarterly samples have generally shown ammonia concentration of <100 mg/L, but two samples (10/13/05 and 4/13/06) have shown levels of 2230 mg/L and 1290 mg/L, respectively. For this reason, the ammonia sample frequency has been changed from quarterly to prior to every transfer, and recent relatively high values (up to 597 mg/L – December 2007) observed in these pre-transfer samples of the WCTs.

A calculation²⁹ was issued to document the Tank 50 ammonia concentration limit involving temperature, level, and the addition of Isopar to Tank 50 from MCU. Based on this calculation, the ETP waste concentrate ammonia concentration is limited to 720 mg/L. (This is an increase from the previous “unrestricted” limit of 238 mg/L but below the more recent limit of 1090 mg/L, which took into account a maximum level of 290” in Tank 50.) The ammonia level will be verified to be below 720 mg/L prior to initiating the transfer to the H tank farm per ETP procedures.^{5,6}

Shock Sensitive Compounds Evaluation

The Tank Farm WAC prohibits the introduction of wastes containing silver unless it is present in minimal quantity as a result of analytical or laboratory methods.¹ Silver has not been measured in this waste stream above the detection limit of 10 mg/L, and the actual concentration is expected to be many times below this detection value.⁹

6.3 Requirements for Radionuclide Content

[*A/C* CST SAC 5.8.2.15 & 5.8.2.25, JCO WSRC-TR-2003-00083, 5.0.2]

The Tank Farm inhalation dose potential (IDP) acceptance criterion for waste receipt/transfers into Tank 50 is set to 2.09E+5 rem/gallon per section 11.4.2 of the Tank Farm WAC. The criteria for other Tank Farm tanks is 1.0E+07 rem/gal for Type IV tanks and 2.0E+08 for “Low Rem” transfers. There is an additional criteria that any transfer that exceeds 9.8E+07 rem/gal be considered a “sludge slurry” transfer and requires transfer lines to be flushed after each transfer. ETP is a Radiological facility with significantly lower radionuclide limits than the Hazard Category 2 Tank Farm.⁷ By definition, a Radiological facility cannot have a dose rate during an accident causing greater than 10 Rem dose at 30 meters, much lower than the Tank Farm dose limit. The ETP waste concentrate stream is therefore classified as a “Low-Rem” waste stream and is acceptable for any Tank Farm tank.

6.4 Requirements for Regulatory Compliance

The ETP operates under the same type of permit as the CST Tank Farms, an Industrial Wastewater Treatment Facility Permit, and must also comply with the requirements of SRS' NPDES permit and Part 70 (Title V) Air Quality permit. No RCRA "listed wastes" are treated or permitted in the ETP without DHEC approval. Section 11.5 of the Tank Farm WAC lists the species that are allowed above the TCLP criteria. For the species not mentioned, sampling analyses have demonstrated they are at the detection limit (see Attachment 2) with the exceptions of arsenic and selenium. Arsenic has been measured in the waste concentrate stream at levels up to 55.52 mg/L, above the RCRA TCLP limit of 5.0 mg/L. Selenium has been measured up to 37.49 mg/L versus a RCRA TCLP limit of 1.0 mg/L. The arsenic and selenium are within the Saltstone WAC¹² limits of 750 mg/L and 450 mg/L. Other hazardous wastes listed in 40 CFR not included in the Tank Farm WAC or discussed above are not present in the ETP waste stream.⁴

In addition, this WCP identifies by chemical name and/or CAS number all potential criteria or air toxic pollutants (SDHEC R.61-62.5, Standard 2 and Standard 8 pollutants, respectively) contained in the material to be transferred. The LWGR shall provide additional information upon request to the LWDE as necessary to complete air emission estimates for each such regulated pollutant or for radiological NESHAP evaluations.

6.5 Requirements for Criticality Safety [*A/C* CST SAC 5.8.2.15]

The ETP Auditable Safety Analysis (ASA)⁷ documents the ETP as a Radiological facility. Thus, the radionuclide inventory is below the Category 3 threshold limits. The total curie content being processed within the ETP was found to be significantly below the Category 3 threshold values. Accumulation of a critical mass at any point in the ETP process is not credible based on process considerations.¹¹ As documented in WER-WMT-91-0107¹³, the criticality potential for ETP is so low that controls or analyses in addition to that in the letter are not required. The oxalate solids in Tank 50 that originate from the ETP process have also been evaluated and have been found to be critically safe²⁶. Therefore, ETP evaporator concentrate is inherently safe with respect to criticality in the uncontrolled geometry of a high level waste tank.

Transfers to Tank 50 will comply with the Tank Farm WAC requirement of less than 16.5 mg/L U-235 (equivalent to 78.4 d/m/ml) and 1.68 mg/L Pu-239 (equivalent to 2.29E+05 d/m/ml). Sample results show U-235 concentration at 0.427 d/m/ml and Pu-239/240 concentration at 79.9 d/m/ml, both far below the

Tank 50 criticality criteria. Based on the ETP criticality analysis¹³, the expected annual fissile mass is only 0.4 g/yr. Given that the input to the ETP is 20,000,000 gallons per year and the concentration factor is 175, the maximum fissile concentration in waste concentrate would be:

$$0.4 \text{ g/yr} / (20,000,000 \text{ gallons/yr} * 3.785 \text{ L/gal}) * 1000 \text{ mg/g} * 175 = 9.3\text{E-}04 \text{ mg/L}$$

This is well below any fissile concentration limits.

6.6 Requirements for Compatibility with the Tank Farm's Authorization Basis

This Waste Compliance Plan is being written to comply with the Tank Farm's WAC which is part of the Tank Farm's Documented Safety Analysis (DSA).¹⁴ The WCP and WAC are part of the implementation of the Technical Safety Requirements for the Tank Farm. The characterization as described in this WCP provides the basis for demonstrating compliance with the Tank Farm's DSA. Procedures (References 5 and 6) are used to both conduct the analyses of the evaporator concentrate waste and perform the transfer of the concentrate waste to the Tank Farm.

6.7 Requirements to Satisfy Downstream Facility Acceptance Criteria [*A/C* CST SAC 5.8.2.15]

This waste stream has been characterized sufficiently for LWDE to comply with all requirements for downstream facilities. The ETP evaporator bottoms chemical composition is expected to be very similar to the tank farm evaporator bottoms; therefore, no downstream processability impacts are expected. Sample results listed in Attachment 2 show the ETP waste concentrate meets all the Tank 50/Saltstone WAC limits and targets. In fact, most of the radionuclides are 2 to 3 orders of magnitude (100 to 1000X) below the WAC limits. Some are 6 orders of magnitude (a million times) lower than the limits. Therefore, there is no need for additional sampling of WCT beyond the analysis listed in Table 1.

Although sample results have indicated solids content of this stream has exceeded the Saltstone WAC limit of 15 wt % twice since 6/1/02, operating experience of the ETP has shown no line pluggage due to the solids content of the waste concentrate waste stream. Sample results since 5/30/03 have shown only one exceedance (16.94 wt %) and have generally been well below the Saltstone WAC, averaging only 2.20 wt % with a standard deviation of 2.75 wt%. Therefore, no deviation is required. The waste characterization in Attachment 2 shows that this stream is within all other Saltstone WAC limits. The solids were characterized as

part of the Tank 50 cleanout in 2002¹⁹. The analyses showed the solids to be mainly metal oxalates (sodium and iron), carbon (probably granular activated carbon) and aluminosilicates. This is consistent with the ETP process which uses oxalic acid for filter cleaning, carbon for organic removal, and aluminum nitrate as a filter aid. Saltstone operation in 2002/2003 showed this material was compatible with the Saltstone process. Oxalate has been added to the quarterly WCT sample list to verify Saltstone WAC compliance.

6.8 Requirements for Waste Minimization and Process Improvements

The ETP evaporator process is a waste minimization activity that significantly reduces the volume of waste requiring disposal/treatment through the Tank Farm or Z-Area. No further waste minimization is necessary.

6.9 Deviation from the WAC Requirements

No deviations are required at this time.

The previous deviation²⁵ is no longer needed since sample analyses have been obtained to fill in the missing characterization data.

7.0 Liquid Waste Generator Representative (LWGR)

The ETP Liquid Waste Generator Representative is the ETP Engineering Lead/Manager. The alternate will be the Waste Concentrate System engineer.

8.0 Documentation

Procedures (References 5 and 6) are used to both document the analyses of the evaporator concentrate waste and perform the transfer of the concentrate waste to the Tank Farm. These procedures will serve as documentation for compliance with the Tank Farm WAC and this WCP. Copies of the completed procedures will be made available for LWDE for review to verify WAC compliance. A database of transfer and characterization information will be created in the Wisdom Work Group (WG08) per the WAC to provide easy tracking. Information will be provided per the WAC requirements.-

9.0 Waste Characterization Self-Assessment and Non-Compliance

Self-assessment and non-compliance reporting will be handled procedurally through the procedures utilized to perform the waste transfers. Any non-compliance with this WCP will result in immediate notification of LWDE. ETP personnel will participate in the appropriate corrective actions and/or investigations.

10.0 References

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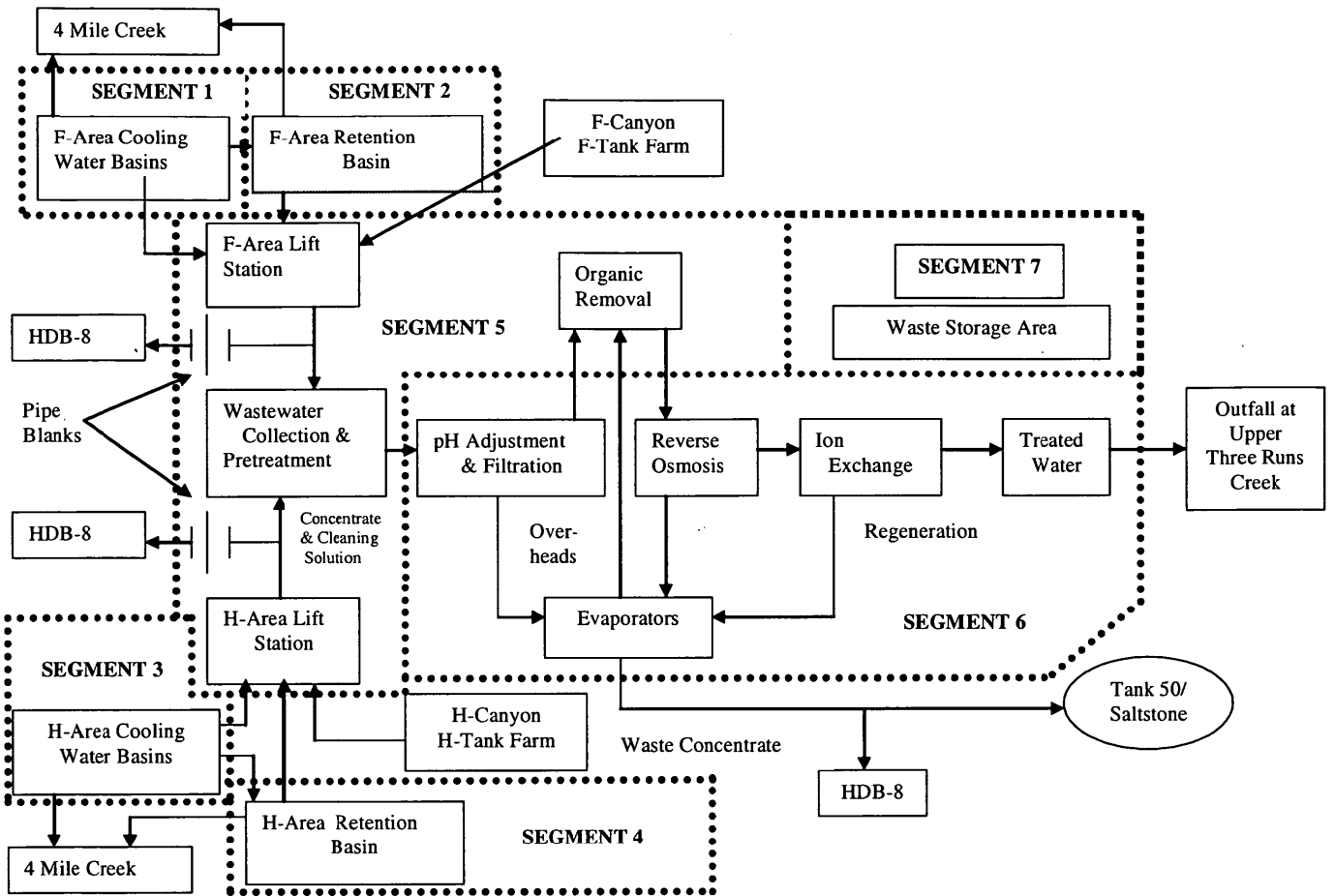
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11.0 Attachments

1. ETP Process Flow Diagram
2. ETP Waste Concentrate Sample Data
3. Hydrogen Generation Rate Calculation

Attachment 1: ETP Process Flow Diagram



Attachment 2: ETP Waste Concentrate Sample Data

The following tables compare the Saltstone WAC limits to the recent ETP waste concentrate tank (WCT) sample data.

Table 2-1: Comparison of ETP Waste Concentrate to Saltstone Limits - Chemicals

Constituent	ETP WCT (Note 2)	Saltstone WAC (T) = Targets	Pass/Fail
<u>Metals</u>			
	<u>mg/L</u>	<u>mg/L</u>	
Ag (Note 3)	<0.15 (43.70 max)	750	Pass
Al	2370	141,000	Pass
As (Note 3) (Note 7)	0.2101 (164.97 max)	750	Pass
B	<16.2	900 (T)	Pass
Ba (Note 3)	11.3 (115.56 max)	750	Pass
Ca	<4.53		N/A
Cd (Note 7)	<0.20	375	Pass
Co	0.101	900 (T)	Pass
Cr (Note 7)	2.44	1500	Pass
Cu	1.19	900 (T)	Pass
Fe	3.12	6000 (T)	Pass
Hg (Note 3) (Note 7)	70.2 (92.16 max)	325	Pass
Li	0.965	900 (T)	Pass
K	212	36,700 (T)	Pass
Mn	<0.220	900 (T)	Pass
Mo	3.52	900 (T)	Pass
Ni	5.35	900 (T)	Pass
Pb (Note 3) (Note 7)	<2.46 (93.20 max)	750	Pass
Se (Note 3) (Note 7)	<0.025 (190.99 max)	450	Pass
Si	17	12,900 (T)	Pass
Na	121,000		N/A
Sr	<1.00	900 (T)	Pass
Zn	49.2	975 (T)	Pass
<u>Organics (Note 4)</u>			
	<u>mg/L</u>	<u>mg/L</u>	
Benzene (Note 4)	ND	375 (T)	Pass
Butanol+Isobutanol (Note 4)	ND	2250	Pass
Isopropanol (Note 4)	ND	2250	Pass
Methanol (Note 4)	ND	225 (T)	Pass
TPB	<10	30	Pass
TBP (Note 5)	<100	300 (T)	Pass
Phenol (Note 4)	ND	750	Pass
EDTA	<200	375 (T)	Pass
Toluene (Note 4)	ND	375 (T)	Pass
Total Organics (Note 3) (Note 6)	1550 (3090 max)	5000	Pass
<u>Alkali Salts</u>			
	<u>mg/L</u>	<u>mg/L</u>	
Ammonia (Note 8)	<100 (859.5 max)	7130	Pass
Carbonate	<1200	145,000	Pass
Chloride (Note 3)	414 (1287 max)	9680	Pass
Fluoride	<20	4940	Pass

Hydroxide (Total Alkalinity)	19,380 (1.14M)	191,000	Pass
Nitrate	227,000	529,000	Pass
Nitrite	<100	259,000	Pass
Oxalate	339	3300	Pass
Phosphate	65	35,600	Pass
Sulfate	253	68,900	Pass
Insoluble Solids (TSS) (Note 3)	28730 avg (225000 Max)	188000 (15 wt%)	Fail (Max)

Note 1: Saltstone limits based on X-SD-Z-0001, Rev. 4, Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility.

Note 2: ETP waste concentrate tank baseline sample results.

Note 3: Average and maximum values from WCT transfer database in WG08.

Note 4: Organic results from quarterly VOC results (1Q06) - none detected (ND = <0.25 mg/L), Semi-volatile organics (SVOC) were <3.7 mg/L (2Q04).

Note 5: Tributyl phosphate not analyzed (NA) – value based on influent concentration less than 100 mg/L and 90+% removed prior to waste concentrate by activated carbon.

Note 6: Total Carbon (TIC + TOC) based on 4/2/04 sample.

Note 7: SCDHEC R.61-62-5, Section 2 or 8 toxic air pollutant.

Note 8: Ammonia limited to 1090 mg/L – see section 6.2

Table 2-2: Comparison of ETP Waste Concentrate to Saltstone Limits - Radionuclides

Isotope	ETP WCT	ETP WCT	Saltstone	Pass/Fail
	dpm/mL (Note 2)	pCi/mL	WAC pCi/mL (T) = Targets	
H-3 (Note 3)	8440	3800	5.63E+05	Pass
C-14	<25	<11	1.13E+05	Pass
Al-26	<1.84	<0.83		N/A
Ni-59	<221	<100	1.13E+05 (T)	Pass
Ni-63	<122	<55	1.13E+05	Pass
Co-60	<1.79	<0.81	1.13E+06 (T)	Pass
Se-79	<13.3	<5.99	1.90E+04 (T)	Pass
Sr-90	1680	757	2.87E+05	Pass
Nb-93m	No Data		2.85E+06 (T)	Pass (Note 4)
Nb-94	<1.52	<0.69	1.53E+04 (T)	Pass
Mo-93	No Data		1.18E+07 (T)	Pass (Note 4)
Tc-99	<6.09	<2.7	4.22E+05	Pass
Ru-106	<89.5	<40	1.13E+06 (T)	Pass
Sn-126	<18.8	<8.5	1.80E+04 (T)	Pass
Sb-125	<48.4	<22	2.25E+06 (T)	Pass
I-129	1.01	0.46	1.13E+03	Pass
Cs-134	11.7	5.27	1.13E+06 (T)	Pass
Cs-135	<59.5	<26.8	1.13E+06 (T)	Pass
Cs-137	24100	10800	1.40E+06	Pass
Ce-144	<46	<21	1.13E+05 (T)	Pass
Pm-147	<630	<284	5.63E+06 (T)	Pass
Sm-151	<925	<417	2.25E+04 (T)	Pass
Eu-154	<5.13	<2.3	2.25E+06 (T)	Pass
Eu-155	<21.6	<9.7	1.13E+04 (T)	Pass
Ra-226	<196	<88.3	7.97E+03 (T)	Pass
Th-229	No Data		1.63E+05 (T)	Pass (Note 4)
Th-230	<202	<91.0	1.62E+04 (T)	Pass
Th-232	<1.07E-03	<4.8E-04	2.88E+03 (T)	Pass
U-232	No Data		1.71E+05 (T)	Pass (Note 4)
U-233	<94.5	<42.6	1.13E+04	Pass
U-234	<60.9	<27.4	1.13E+04 (T)	Pass
U-235	0.427	0.192	1.13E+02	Pass
U-236	<0.636	<0.286	1.13E+04 (T)	Pass
U-238	24.3	10.9	1.13E+04 (T)	Pass
Np-237	<33	<15	2.50E+04 (T)	Pass
Pu-238	<109	<49	2.50E+04 (T)	Pass
Pu-239	79.9	36	2.50E+04 (T)	Pass
Pu-240	79.9	36	2.50E+04 (T)	Pass
Pu-241	<208	<94	8.38E+05	Pass
Pu-242	<38.5	<17.3	2.50E+04 (T)	Pass
Pu-244	No Data		2.50E+04 (T)	Pass (Note 4)
Am-241	143	64.41	2.50E+04 (T)	Pass
Am-242m	No Data		2.50E+04 (T)	Pass (Note 4)
Am-243	<1.61	<0.73	2.50E+04 (T)	Pass
Cm-242	<0.224	<0.10	1.13E+04 (T)	Pass

Cm-244	113	51	2.50E+04 (T)	Pass
Cm-245	No Data		2.50E+04 (T)	Pass (Note 4)
Total Alpha	<40	<18	2.50E+04	Pass
Total Beta-Gamma	30900	13900		N/A

Note 1: Saltstone limits based on X-SD-Z-0001, Rev. 4, Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility.

Note 2: ETP waste concentrate tank baseline sample results (SRNL ADS LIMS# 3-211264).

Note 3: Maximum tritium value based on ETP WAC is 120,000 dpm/mL (54,000 pCi/mL).

Note 4: Bounded by total alpha or total beta-gamma results.

Attachment 3: Hydrogen Generation Rate Calculation

The rate of hydrogen generation due to radiolysis is determined based on the amount of radionuclides in the waste and the level of nitrates/nitrite.

For ETP waste concentration, the hydrogen generation rate is bounded by the following assumptions:

1. Total alpha is all Pu-238 and is limited to 22,500 pCi/mL per the current Saltstone WAC (Ref. 12).
2. Total beta-gamma is made up of the following nuclides: Cs-137, Ba-137M, Sr-90, and Y-90 and are bounded by the current Saltstone WAC.
3. Ba-137M is in equilibrium with Cs-137 at a ratio of 0.935:1.
4. Sr-90 and Y-90 are at the same concentration.
5. No nitrate or nitrite present in the stream. (Conservative assumption since nitrate and nitrite inhibit hydrogen generation.)
6. No uncertainties are included in the calculation since the values are “bounding” values rather than actual analytical results.

To convert from pCi/mL to Ci/gal for waste concentrate:

$$1 \text{ pCi/mL} = 1000 \text{ mL/L} \times 3.785 \text{ L/gal} \times 1\text{E-}12 \text{ Ci/pCi}$$

$$1 \text{ pCi/mL} = 3.785\text{E-}09 \text{ Ci/gal}$$

Therefore, the radionuclide content of the ETP waste concentrate is:

	SS WAC	
<u>Nuclide</u>	<u>pCi/mL</u>	<u>Ci/gal</u>
Pu-238	22,500	8.52E-05
Cs-137	1,400,000	5.30E-03
Ba-137m	1,310,000	4.96E-03
Sr-90	287,000	1.09E-03
Y-90	287,000	1.09E-03

The decay heat (Q) for the nuclides is taken from Reference 21:

<u>Nuclide</u>	<u>Q</u> <u>Btu/hr/Ci</u>
Pu-238	0.110
Cs-137	0.003
Ba-137m	0.013
Sr-90	0.004
Y-90	0.019

The decay heat generated per gal of waste concentrate would be the decay heat per Ci multiplied by the Ci/gal:

<u>Nuclide</u>	<u>SS WAC</u> <u>Btu/hr/gal</u>
Pu-238	9.37E-06
Cs-137	1.59E-05
Ba-137m	6.45E-05
Sr-90	4.35E-06
Y-90	2.07E-05

To determine the hydrogen generation rate, the rates of hydrogen generation for alpha and beta-gamma nuclides from the Tank Farm WAC (Ref. 1) are used. The assumption that no nitrate or nitrite is present will bound the hydrogen rate calculated.

The rate for alpha particles is:

$$RA = 134.7 \text{ ft}^3 \text{ H}_2/10^6 \text{ Btu}$$

The rate for beta/gamma is:

$$RB/G = 48.36 \text{ ft}^3 \text{ H}_2/10^6 \text{ Btu}$$

Using the rates and the heat generation values gives the hydrogen generation for each nuclide:

<u>Nuclide</u>	<u>Decay Heat Btu/hr/gal</u>	<u>H₂ Rate ft³ H₂/10⁶ Btu</u>	<u>H₂ Generated ft³/hr/gal</u>
Pu-238	9.37E-06	134.7	1.26E-09
Cs-137	1.59E-05	48.36	7.69E-10
Ba-137m	6.45E-05	48.36	3.12E-09
Sr-90	4.35E-06	48.36	2.10E-10
Y-90	2.07E-05	48.36	1.00E-09
			Total 6.36E-09 ft ³ H ₂ /hr/gal

Adjusting this value to a temperature of 43° C (from 0° C) gives: 7.39E-09 ft³ H₂/hr/gal

The calculated hydrogen generation rate is far below the limits found in the Tank Farm WAC (Ref. 1) for influent sludge slurry waste streams (1.5E-5 ft³ H₂/hr/gal), type IV tanks (2.6E-06 ft³ H₂/hr/gal), evaporator feed tanks (9.6E-06 ft³ H₂/hr/gal), or Tank 50 (4.8E-08 ft³ H₂/hr/gal).

Calculation prepared by: A. C. W. J.
 Verified by: S. J. Kudo
 Verification method: Document Review
 Title: Coz Eng
 Date: 2/24/08