

**Savannah River Remediation**

**X-WCP-H-00002**

**Revision: 17**

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

ISSUED: September 2019

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UNCLASSIFIED

No classification review required



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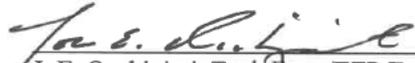
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### Revision Summary

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 <sub>eff</sub> 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.
Revision 10 (9/09)	Revised applicable sections impacted due to new Saltstone Facility organic limits adopted in Ref. 11; Removed reference to JCO-WSRC-TR-2003-00083, Section 5.02, as this has been incorporated into Ref. 13; Incorporated various changes to align with References 1 and 11; Updated Attachment 2.
Revision 11 (5/10)	Update to Hydrogen Generation Rate and NO <sub>eff</sub> minimum to correlate with Rev 28 of the Tank Farm WAC, X-SD-G-00001.

- Revision 12 (4/11)            Section 6.8 modified to address Industrial Hygiene and Transfer Requirements sections of the Tank Farm WAC; Table 2-1 Updated to match Saltstone WAC Revision 10 changes.
- Revision 13 (6/12)            Section 1.0 revised to describe WCHT transfers. Attachment 2 revised to support Saltstone and Tank Farm WAC revisions. Section 6.2 was revised to include discussion on methyl and dimethyl mercury.  
Attachment 2 was revised to reflect new or changed limits in the Saltstone WAC.
- Revision 14 (11/14)            Section 1.0 revised to clarify Liquid Waste Engineering name and Generator responsibilities; Section 6.2 revised to capture pH limit of >12 for transfers to Tank Farms; Section 10.0 revised to update reference documents. References 3, 12, 16, & 23 from Revision 13 have been deleted. Reference numbers have been corrected in the reference section and within the body of the WCP. Attachment 2 revised to reflect new or changed limits in the Saltstone WAC.
- Revision 15 (9/15)            Updated Section 2.0 Process Description to better match current conditions (e.g. elimination of F Tank Farm evaporator discussion).  
Table 1, Mercury analysis moved to Prior to Every Transfer column.  
Deleted 'new' from a statement in Section 6.2 regarding an evaluation of ETP concentrate meeting Saltstone WAC limits for organics after the introduction of MCU processing to the Tank Farm.  
Update Section 6.2 Methyl and Dimethyl Mercury subsection.  
Revised compliance approach for methyl mercury to be based on confirming total mercury to be less than 70.2 mg/L.
- Revision 16 (3/16)            Section 6.2 revised to address change to Ammonia compliance to account for analytical uncertainty.  
Section 6.2 revised to address change to the elemental mercury limit change to the Saltstone WAC.
- Revision 17 (8/19)            Table 1 final column sample frequency revised from "quarterly" to "After WCHT Transfer." Added TOC to this column.  
Section 6.2 revised to explain that mercury speciation is bounded by total mercury measurements.  
Table 2-1 and Table 2-2 revised to reflect limits consistent with Saltstone WAC for SWPF integration.

Revised hydrogen generation rate to reference new calculation methodology and deviation for thermolytic hydrogen generation rate.

Added oxalate discussion/evaluation to section 6.7

Revised Waste Generator and LWGR responsibilities

Added notes to Table 2-1 describing chemical targets imposed to support composite limits (e.g. thermolytic HGR, SDU liner qualification, and SDU flammability)

Revised Section 6.9 to explain TOC deviation justification and reference to X-WDEV-H-00001

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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**
  - **DSA 6.5.2**

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## **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) or Waste Concentrate Hold Tank (WCHT) 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 vary depending on the vessel from which the volume is transferred. ETP still has the capability to transfer concentrated waste directly from the WCT's. Transfers from the WCT's will be approximately 1300-1800 gallons. Of this type, there could be 1-3 transfers per week. ETP also has the capability to store concentrated waste in the Waste Concentrate Hold Tank (WCHT), which has a 25,000 gallon working capacity. Transfers from this vessel could be up to 25,000 gallons. The frequency of these transfers could vary greatly depending on the volumes. However, there is no expectation that the volumetric rate will be greater than that of WCT transfers (one to three volumes of 1300 to 1800 gallons 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.

Tank Farm Facility Engineering (TF-FE) has established a Waste Acceptance Criteria (WAC)<sup>1</sup> 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 TF-FE 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 Tank Farm WAC designates the Waste Generator and Liquid Waste Generator Representative (LWGR) 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);
  - the waste stream definition and complete characterization;
  - the justification for any deviation from the WAC;
  - identification of “SB” controlled requirements;
  - 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 LWGR, for all communications with TF-FE 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 TF-FE a copy of all available waste characterization data in the Wisdom Workgroup WG08;
  
- ◆ Conducting a self-assessment program to ensure compliance with the WCP;
  
- ◆ Reporting a WAC non-compliance to TF-FE 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;
  
- ◆ Participating in quarterly reviews of the proposed waste transfers;

- ◆ Communicate with WCS PDD Owner, or DIRT Chairperson, on WG08 updates regarding significant changes to existing waste stream volume or any non-routine WG08 update;
- ◆ Verify that any procedure changes associated with a waste stream do not impact any WAC/WCP agreements; and
- ◆ Notify the TF-FE WAC Cognizant Engineer when a special transfer is terminated

**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 H Tank Farm evaporators. ETP waste receipts are controlled by the ETP WAC<sup>2</sup>, 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 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 existing ETP procedures that are currently used to sample the waste and document the results are given in References 3 and 4.

**TABLE 1**  
 Transfer Sampling Schedule

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

#### 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 12.<sup>1</sup> The pH is verified to exceed 12 prior to every transfer.<sup>4</sup> 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 ( $\text{OH}^-$ ) is verified by ETP Operations to be above the 1.1M limit prior to transfer to Tank 50.<sup>4</sup> 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  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . The 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 the concentrate is only sodium nitrate and using a reference table<sup>13</sup> 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 primary 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°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°C, well below the 70°C limit. The ETP Evaporator Operation and Chemistry manuals<sup>3,4</sup> 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 (40°C) prior to transfer.

### 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 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. Volatile organic content (VOC) of the ETP waste concentrate will be verified after every transfer (see Table 1). VOC results have historically been less than 0.25 mg/l.

An engineering evaluation<sup>24</sup> was performed demonstrating that ETP waste concentrate meets limits established by the Saltstone Facility for tributylphosphate (TBP), butanol, isopropanol, methanol, NORPAR 13 (n-paraffin solvent diluent used in the F and H Canyons), tetraphenylborate (TPB), and ISOPAR L (solvent used to remove cesium in SWPF)<sup>10</sup>. TPB and ISOPAR L are not present in ETP influent waste streams<sup>25</sup>. The remaining organic components are removed via the ETP Organic Removal Columns, stripped out in the ETP evaporators, and/or prohibited from being fed directly to the evaporators.

### **Hydrogen Generation Rate**

Revision 1 of the SS Salt Disposition Integration (SDI) WAC implemented a new method for radiolytic hydrogen generation rate (HGR), which updated the current radiolytic HGR calculation methodology and introduced a new limit, thermolytic HGR<sup>10</sup>. The TF HGR is demonstrated through a flammability evaluation for each salt batch that includes an assumed volume of ETP material in Tank 50. For radiolytic HGR, ETP is in compliance with a value of 5.98E-11 H<sub>2</sub>/hr/gal, well below the SS WAC limit of 1.41E-08 H<sub>2</sub>/hr/gal for transfers from Tank 50<sup>30</sup>. Thermolytic HGR was found not to be in compliance with respect to total organic carbon (TOC) concentration and a deviation was developed, see Section 6.9.

### **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 as applied to waste tank vapor spaces, respectively<sup>15</sup>. For influents to Tank 50 whose temperature limits are a more restrictive 40°C, the corresponding ammonia limit is 720 mg/l. A more restrictive limit of 200 mg/l is imposed by the Saltstone Facility<sup>10</sup>. ETP restricts their influent ammonia concentration to much less than this value via its WAC<sup>2</sup> to ensure the Tank 50 limit is protected. Ammonia content (NH<sub>3</sub>) of the ETP waste concentrate has historically been verified quarterly. The quarterly samples have 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.

A calculation<sup>23</sup> was issued to document the Tank 50 ammonia concentration limit involving temperature, level, and the addition of ISOPAR L to Tank 50 from MCU. Based on this calculation, the ETP waste concentrate ammonia concentration is limited to 720 mg/L<sup>1</sup>. The downstream Saltstone Facility limit is protected via blending in Tank 50. The ammonia level will be verified to be below 355 mg/L prior to initiating the transfer to Tank 50 per ETP procedures.<sup>3,4</sup> The verification of ammonia concentration to being  $\leq 355$  mg/L accounts for analytical uncertainty up to 40 % (2 sigma up to 20%) and a unit conversion of ammonia's nitrogen to ammonia (14g/mol NH<sub>3</sub>N per 17 g/mol). The Tank Farm WAC<sup>1</sup> requires the inclusion of uncertainty for sample analysis showing compliance with the organic contribution of CLFL limit.

### **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.<sup>1</sup> 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.<sup>7</sup>

### **Methyl and Dimethyl Mercury**

Limits for methyl and dimethyl mercury are set based on the Saltstone WAC<sup>10</sup>. When fed to Waste Water Collection, these organomercury compounds are expected to adsorb to the resin in the Mercury Removal Columns and the activated carbon in the Carbon Columns in the Organic Removal (OR) system. Due to their high vapor pressures, complete separation of feed containing methyl and dimethyl mercury unloaded to the evaporators is expected. The methyl and dimethyl mercury will flash to the overheads where it will be reintroduced to the process at the OR system (passing through Mercury Removal and Carbon Columns).

ETP has a characterization value for effluent total mercury of 70.2 mg/L. The Saltstone WAC limit for mercury concentration received from Tank 50 for total mercury is 325 mg/L, with each species, except for dimethyl mercury, having a limit greater than or equal to this value. In the case of dimethyl mercury, speciation of WCHT samples indicate the OR system prevents detectable concentrations of dimethyl mercury from leaving ETP.<sup>26</sup> As a result, ETP does not need to perform mercury speciation as a total mercury measurement bounds speciation due to the ETP self-imposed limit of 70.2 mg/L being less than the Saltstone WAC limits for each species.

### **6.3 Requirements for Radionuclide Content** **[\*A/C\* CST SAC 5.8.2.15 & 5.8.2.25]**

The Tank Farm inhalation dose potential (IDP) acceptance criterion for waste receipt/transfers into Tank 50 is set to 1.79E+05 rem/gal per Section 10.4.2 of the Tank Farm WAC. The criteria for other Tank Farm tanks are 1.0E+07 rem/gal for Type IV tanks and 2.0E+08 for “Low Rem” transfers. There is an additional criterion 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.<sup>5</sup> 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 10.5 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 172.63 mg/L, above the RCRA TCLP limit of 5.0 mg/L. Selenium has been measured up to 316.56 mg/L versus a RCRA TCLP limit of 1.0 mg/L. The arsenic and selenium concentrations are within the Saltstone WAC<sup>10</sup> limits of 197 mg/L and 375 mg/L respectively.

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 TF-FE 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 and DSA 6.5.2]**

The ETP Auditable Safety Analysis (ASA)<sup>5</sup> 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.<sup>9</sup> As documented in the ETP ASA<sup>5</sup>, the criticality potential for ETP is so low that additional controls or analyses 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 safe<sup>20</sup>. 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 ETP criticality analysis, the expected annual fissile mass is only 0.4 g/yr. Given that the maximum 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 Safety Basis**

This Waste Compliance Plan is being written to comply with the Tank Farm WAC which is part of the Tank Farm Documented Safety Analysis (DSA).<sup>11</sup> 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 3 and 4) 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 TF-FE 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 and as noted in Section 6.2. 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 1.98 wt % with a standard deviation of 3.72 wt%. Therefore, no deviation is required. The waste

characterization in Attachment 2 shows that this stream is within all other Saltstone WAC limits, with the exception of species mentioned in Section 6.9. The solids were characterized as part of the Tank 50 cleanout in 2002<sup>17</sup>. 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 After WCHT Transfer sample list to verify Saltstone WAC compliance.

Additions to Tank 50 have shown oxalate concentrations at a maximum of 4100 mg/L with an average of 1618 mg/L, higher than the SPF target of 880 mg/L but still below the limit of 27,200 mg/L. Using the same methodology as the TOC deviation for dilution, at the current baseline for oxalate, 460 mg/L, an addition of 30,000 gallons at the maximum concentration of 4100 mg/L to the minimum level of 76" in Tank 50 results in an oxalate concentration of 864 mg/L. This is assumed to be bounding as the higher concentrations of oxalate are associated with small transfers from the WCT (<2000 gal) and the larger transfers from the WCHT are more dilute. Additionally, these concentrations are historic to 2007 and Tank 50 has not exceeded the oxalate target per the quarterly sample.<sup>31</sup>

The Tank Farm requires that waste generators to Tank 50 comply a temperature requirement of 10-40°C. The 40°C limit is based on the maximum temperature for SPF influent.

## **6.8 Requirements for Waste Minimization and Process Improvements, Industrial Hygiene Concerns, and Transfer Requirements for Radioactive Waste into the Tank Farm**

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.

No new Industrial Hygiene Safety concerns are introduced as part of the ETP process. However, the ETP process can concentrate ammonia and dimethylmercury. When accessing piping and/or equipment along the transfer route from ETP to Tank 50, this should be accounted for. Otherwise normal IH protocols may be followed.

Transfers from ETP to Tank 50 have been evaluated against the facility WAC or Safety Basis restrictions. This waste stream has been shown to have a sufficiently low inhalation dose potential such that it could not

challenge the EGs and, therefore, need not be considered a Waste Transfer nor require transfer controls.<sup>12</sup> (Tank Farm DSA section 5.7.1)

## **6.9 Deviation from the WAC Requirements**

The ETP concentrate waste stream exceeds the SS WAC TOC target, resulting in a thermolytic HGR that exceeds the SS limit of 0.05%. Reference 31 shows that the TOC concentration of the ETP stream when mixed with sufficient volume in Tank 50 is less than the Saltstone WAC target of 750 mg/L. The TOC concentration will be tracked via the periodic Tank 50 Material Balance WAC compliance report currently used to show ETP compliance with the TOC Saltstone WAC limit in Tank 50.<sup>31</sup>

## **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 3, 4, 28, and 29) 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 TF-FE 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 TF-FE. ETP personnel will participate in the appropriate corrective actions and/or investigations.

## **10.0 References**

1. X-SD-G-00009, Rev. 1, "Waste Acceptance Criteria for Liquid Waste Transfers to the Tank Farms (U)."

2. X-SD-H-00009, *Latest Revision*, "F/H Effluent Treatment Facility Waste Acceptance Criteria."
3. SW22.2-IOP-2, "Evaporator Operation."
4. SW22.1-CHEM-1, "ETP Chemistry (U)", Section 4.9.1: Routine Evaporator System Samples, Attachment 7.10: Waste Concentrate Samples – Partial Analysis Sample Data , Attachment 7.11: Waste Concentrate Samples – Full Analysis Data, Attachment 7.12: Waste Concentrate Samples – 772-F Lab Analysis Data, Attachment 7.17: Waste Concentrate Samples – Quarterly Analysis
5. WSRC-TR-98-00379, *Latest Revision*, "Auditable Safety Analysis for the Effluent Treatment Facility."
6. WSRC-TR-94-0297, Rev. 2 "Characterization of Hazardous Constituents in HLW Supernate and Implications for Solid LLW Generation", G. K. Georgeton, September 2003.
7. WSRC-TR-94-0427, "Waste Characterization for the F/H Effluent Treatment Facility in Support of Waste Certification", D. F. Brown, October 17, 1994.
8. Code of Federal Regulations 40, Part 261.
9. WSRC-TR-91-58, "Effluent Treatment Facility- Preliminary Analysis of Potential Input and Accumulation of Fissile Isotopes", M. D. Boersma, January 31, 1991.
10. X-SD-Z-00004, Rev. 1, "Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility During Salt Disposition Integration (SDI) (U)."
11. WSRC-SA-2002-00007, *Latest Revision*, "Concentration, Storage, and Transfer Facilities Documented Safety Analysis."
12. WSRC-TR-97-00299, "Preliminary Evaluation of ETP Waste Acceptance Criteria (WAC) for Ammonia in Relation to Flammability Conditions", M. E. Jamison, September 19, 1997.
13. Handbook of Chemistry and Physics, 51<sup>st</sup> edition, page D-217, CRC Press, 1971.
14. WSRC-TR-97-0125, Rev. 4, "F/H Effluent Treatment Facility Evaporator Concentrate Special Waste Compliance Plan (U)," A. W. Wiggins, April 1998.

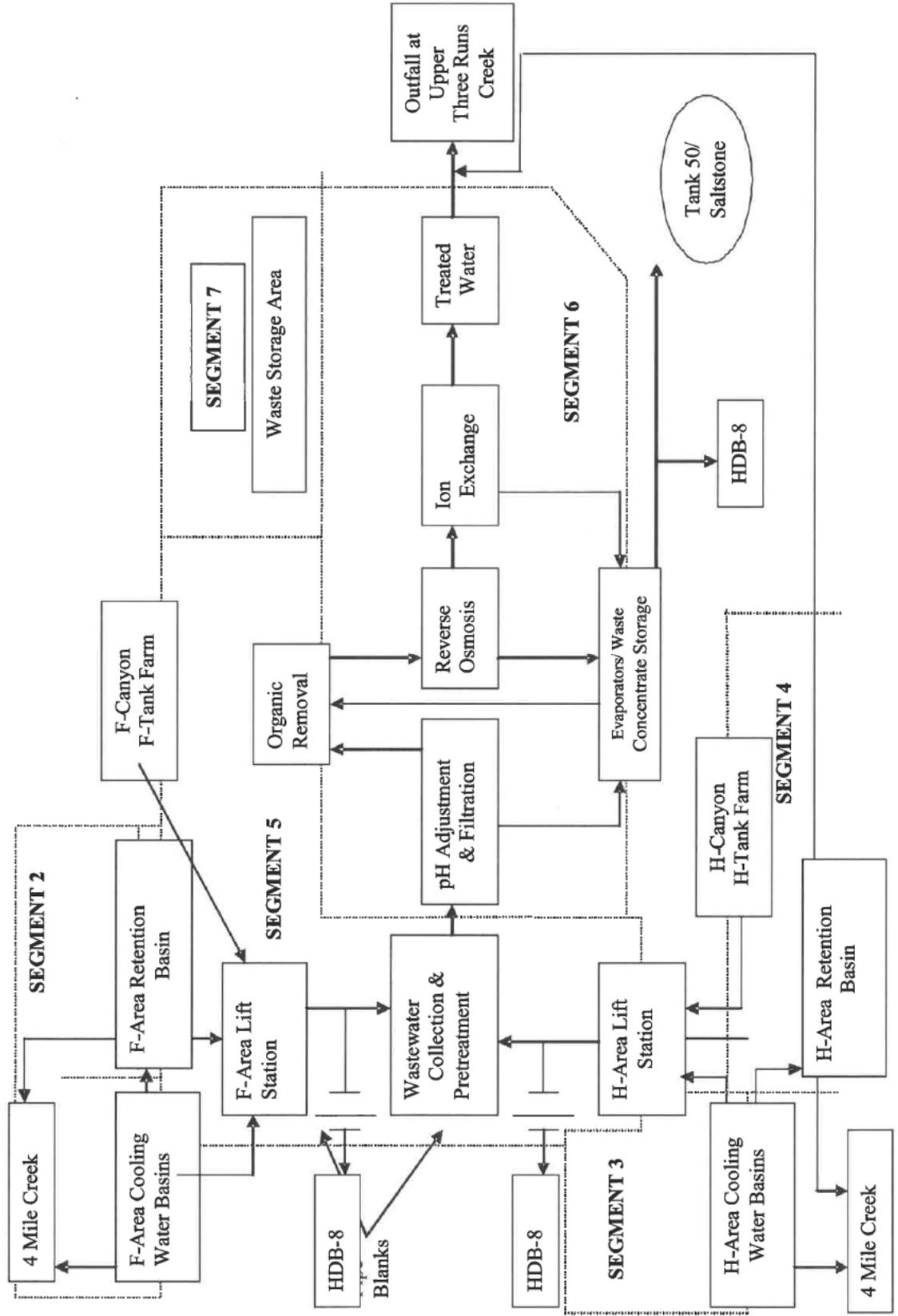
15. WSRC-TR-2002-00506, "Results of Sample Analysis from Solids Removed from Tank 50H", W. R. Wilmarth, October 31, 2002.
16. WSRC-TR-2000-00226, "Ammonia Henry's Law Constants in SRS High Level Waste Pump Tanks, R. F. Swingle et al, January 4, 2001.
17. WSRC-TR-99-00344, Compilation of Data on Radionuclide Data for Specific Activity, Specific Heat and Fission Product Yields, B. Boggs, et al., April 6, 2000.
18. X-WCP-H-00043, *Latest Revision*, "Tank 50 Waste Compliance Plan for Transfer to Saltstone."
19. S-EHA-H-00010 Rev. 1, "Emergency Planning Hazards Assessment for the Effluent Treatment Project", J.M. Wallace, November 2011.
20. N-NCS-H-00165, Rev. 1, "Nuclear Criticality Safety Evaluation: Tank 50 Solids", K. J. McCoid, Westinghouse Safety Management Solutions, Aiken, SC, May 2003.
21. N-NCS-H-00132, Rev. 0, "Nuclear Criticality Safety Evaluation: Tank 50 Valve Box Transfers", Murray, M. D., Westinghouse Safety Management Solutions, Aiken, SC, March 2002.
22. S-TSR-G-00001, *Latest Revision*, "Concentration, Storage and Transfer Facilities Technical Safety Requirements".
23. X-CLC-H-00581, Rev. 3, "Impact of CSSX Organic Carry-over on Tank Farm Operation", T. Britt, December, 2007.
24. X-ESR-H-00170, Rev. 0, "Evaluation of ETP Waste Concentrate Compliance to Revised Saltstone WAC Limits", A. W. Wiggins, Jr., January, 2009.
25. X-CLC-H-00867, Rev 0, "ETP Waste Concentrate Radiolytic Hydrogen Generation Rates for 0 to 130 Degrees Celsius", R.W. Dittmar, April, 2011.
26. SRNL-L3100-2015-00079, Rev. 1, "Results of Preliminary Hg Speciation Testing on Tank 22 and Waste Concentrate Hold Tank (WCHT) Material", C. J. Bannochie, March 2015.
27. SRNL-L3100-2016-00021, Rev. 0, "Results of Hg Speciation Testing on Tank 39 and 1Q16 Tank 50 Samples"
28. 241-H-ETF-200, "WASTE CONCENTRATE TANK(S) TRANSFER OPERATIONS"

29. 241-H-ETF-200A, "ETP TRANSFERS TO/FROM WCHT"
30. X-ESR-H-00956, Rev. 1, "Evaluation of Tank 50 Influent on Saltstone WAC Revision 18 Limits", L.A. Wooten, March 2019.
31. X-WDEV-H-00001, Rev. 0, "Deviation to the Tank Farm WAC Downstream Facility Thermolytic Hydrogen Generation Rate Limit at Saltstone for ETP Transfers to Tank 50, A.W. Wiggins, Jr., October 2018

## **11.0 Attachments**

1. ETP Process Flow Diagram
2. ETP Waste Concentrate Sample Data

**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
<b>Metals</b>			
	<u>mg/L</u>	<u>mg/L</u>	
Ag (Note 3)	30.7	6.19E+02	Pass
Al (Note 13)	2370	5.94E+03 (T)	Pass
As (Note 3) (Note 7)	35.7	1.97E+02	Pass
B	<16.2	7.43E+02 (T)	Pass
Ba (Note 3)	31.0 (115.6 max)	6.19E+02	Pass
Ca	<4.53	N/A	N/A
Cd (Note 7)	30	3.10E+02	Pass
Co	0.101	1.45E+02 (T)	Pass
Cr (Note 7)	30	1.50E+03	Pass
Cu	1.19	7.43E+02 (T)	Pass
Fe	3.12	4950 (T)	Pass
Total Hg (Note 3) (Note 7)	70.2 (92.16 max)	3.25E+02 (Elemental)	Pass
Li	0.965	7.43E+02 (T)	Pass
K (Note 14)	212	2.35E+03 (T)	Pass
Mn	<0.220	7.43E+02 (T)	Pass
Mo	3.52	7.43E+02 (T)	Pass
Ni (Note 9)	5.35	7.43E+02 (T)	Pass
Pb (Note 3) (Note 7)	33.4	7.50E+02	Pass
Se (Note 3) (Note 7)	35.8 (316 max)	3.75E+02	Pass
Si	17	1.07E+04 (T)	Pass
Na (Note 14)	121,000	57250 < Na < 155000(T)	Pass
Sr	<1.00	7.43E+02 (T)	Pass
Zn	49.2	8.03E+02 (T)	Pass
<b>Organics (Note 4)</b>			
	<u>mg/L</u>	<u>mg/L</u>	
Benzene (Note 4)	ND	3.10E+02 (T)	Pass
Butanol (Note 4) (Note 15)	ND	7.5E-01(T)	Pass
Formate (Note 10)	<100	6.38E+03 (T)	Pass
Propanol (Note 4) (Note 15)	ND	2.5E-01 (T)	Pass
Methanol (Note 4) (Note 15)	ND	5.00E-02(T)	Pass
TPB (Note 5)	ND	5.00	Pass
TBP (Note 5) (Note 15)	NA	1.00 (T)	Pass
Phenol (Note 4)	ND	750	Pass
EDTA	<200	3.10E+02 (T)	Pass
IsoPAR L (Note 5)	NA	8.75E+01	Pass
NORPAR 13 (Note 5) (Note 15)	NA	7.50E-01 (T)	Pass
Toluene (Note 4)	ND	3.10E+02 (T)	Pass
Total Organics (Note 6) (Note 13)	2924 (3090 max)	7.50E+02 (T)	Fail (See Section 6.9)

<b>Alkali Salts (Note 10)</b>	<b>mg/L</b>	<b>mg/L</b>	
Ammonia (Note 8)	147	2.00E+02	Pass
Carbonate (Note14)	<1200	1.20E+04(T)	Pass
Chloride (Note 3) (Note14)	549 (1530 max)	3.90E+03(T)	Pass
Fluoride	<100	4.07E+03	Pass
Hydroxide (Note14)	22623 (1.33M)	3.91E+04(T)	Pass
Nitrate (Note14)	344,000	1.46E+05(T)	Pass
Nitrite (Note14)	<100	4.14E+04(T)	Pass
Oxalate (Note14)	1618 (4100 max)	2.72E+04	Pass
		8.80E+02(T)	Fail
			(See Section 6.7)
Phosphate (Note 14)	<100	3.14 E+04(T)	Pass
Sulfate (Note 14)	<100 (1900 [Note 11])	4.75E+03 (T)	Pass
Insoluble Solids (TSS) (Note 3)	4000 - 70000	188000 (15 wt%)	Pass

**Note 1:** Saltstone limits based on X-SD-Z-00004, Acceptance Criteria for Aqueous Waste Sent to the Z-Area Saltstone Production Facility.

**Note 2:** ETP Waste Concentrate baseline sample results.

**Note 3:** 2003 – 2019 Waste Concentrate Tank Sample Results

**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). See section 6.2 for compliance basis.

**Note 5:** Not analyzed (NA) – value based on process knowledge (Ref. 30)

**Note 6:** Total Carbon (TIC + TOC) based ETP waste concentrate tank baseline sample results (SRNL ADS LIMS# 200056011, May 19, 2010).

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

**Note 8:** Ammonia limited to 355 mg/L – see section 6.2

**Note 9:** Note DELETED

**Note 10:** ETP waste concentrate tank baseline sample results (SRNL ADS LIMS# 200059737, March 7, 2011)

**Note 11:** ETP waste concentrate tank baseline sample results (SRNL ADS LIMS# 200056011, May 19, 2010)

**Note 12:** Organic Removal processes in ETP will prevent detectable concentrations of dimethyl mercury from leaving ETP (See Section 6.2). Methyl Mercury to be bounded by total mercury (Ref. 26).

**Note 13:** Constituent uses a more conservative Target to protect the Saltstone thermolytic HGR WAC Limit (Ref. 10).

**Note 14:** Constituent uses a more conservative Target based on qualification of the SDU 6 coating/liner system (Ref 10).

**Note 15:** Constituent uses a more conservative Target to protect SDU Flammability Limit (Ref 10).

**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	< 1.85E-01	< 8.33E-01	2.88E+03 (T)	Pass (Note 5)
Ni-59	<221	<100	1.13E+03 (T)	Pass
Ni-63	<122	<55	1.13E+05	Pass
Co-60	< 1.97E-01	< 8.87E-02	9.75E+02 (T)	Pass (Note 5)
Se-79	<13.3	<5.99	1.90E+04 (T)	Pass
Sr-90	1680	757	2.62E+06	Pass
Nb-94	< 1.47E-01	< 6.62E-02	1.53E+02 (T)	Pass (Note 5)
Tc-99	<6.09	<2.7	2.11E+05	Pass
Ru-106	< 2.04	< 9.19E-01	3.12E+05 (T)	Pass (Note 5)
Sn-126	<18.8	<8.5	1.80E+04 (T)	Pass
Sb-125	< 1.37	< 6.17E-01	7.99E+03 (T)	Pass (Note 5)
I-129	1.01	0.46	6.30E+01	Pass
Cs-134	11.7	5.27	5.93E+03 (T)	Pass
Cs-135	<59.5	<26.8	2.50E+02(T)	Pass
Cs-137	24100	10800	1.29E+06	Pass
Ce-144	< 1.51	< 6.80E-01	3.12E+04 (T)	Pass (Note 5)
Pm-147	<630	<284	1.57E+06 (T)	Pass
Sm-151	<925	<417	2.25E+04 (T)	Pass
Eu-154	< 4.25E-01	< 1.91E-01	1.62E+03 (T)	Pass (Note 5)
Ra-226	< 6.00	< 2.70	1.00E+03 (T)	Pass (Note 5)
Th-229	No Data	N/A	1.63E+05 (T)	Pass (Note 4)
Th-230	<202	<91.0	6.26E+03 (T)	Pass
Th-232	<1.07E-03	<4.8E-04	2.88E+03 (T)	Pass
U-232	No Data	N/A	2.27E+03 (T)	Pass (Note 4)
U-233	<94.5	<42.6	1.13E+04	Pass
U-234	<60.9	<27.4	3.12E+03 (T)	Pass
U-235	0.427	0.192	1.13E+02	Pass
U-236	<0.636	<0.286	3.12E+03 (T)	Pass
U-238	24.3	10.9	3.12E+03 (T)	Pass
Np-237	< 7.44E-01	< 3.35E-01	1.00E+04 (T)	Pass (Note 5)
Pu-238	<109	<49	6.67E+04 (T)	Pass
Pu-239	79.9	36	6.67E+04 (T)	Pass
Pu-240	79.9	36	6.67E+04 (T)	Pass
Pu-241	<208	<94	8.38E+05	Pass
Pu-242	<38.5	<17.3	6.67 E+04 (T)	Pass
Pu-244	No Data	N/A	7.02E+04 (T)	Pass (Note 4)
Am-241	3.59	1.62	6.67E+04 (T)	Pass (Note 5)
Am-242m	< 6.17E-02	< 2.78E-02	4.50E+05 (T)	Pass (Note 5)
Am-243	7.86	3.54	6.67E+04 (T)	Pass (Note 5)
Cm-242	< 5.10E-02	< 2.30E-02	1.13E+04 (T)	Pass (Note 5)
Cm-244	4.24E-01	1.91E-02	6.67E+04 (T)	Pass (Note 5)
Cm-245	< 1.28	< 5.77E-01	2.25E+05 (T)	Pass (Note 5)
Total Alpha	200.69	9.4	2.13E+05	Pass
Total Beta-Gamma	17480	7874	N/A	N/A

- Note 1:** Saltstone limits based on X-SD-Z-00004, 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.
- Note 5:** Updated data obtained from SRNL LIMS Submission ID 200052511, 7/20/09