



CSTF Corrosion Control Program

Program Description Document

PREPARED BY:

Keisha Martin, Tank Farm Process Safety and Regulatory Engineering / Signature

12/15/15

Date

REVIEWED BY:

Bruce Wiersma, (Verification by Document Review) / Signature

12/16/15

Date

Drew Morgan, Nuclear Safety Engineer / Signature

12/15/15

Date

APPROVED BY:

Carol Sherburne, Tank Farm Process Safety and Regulatory Engineering Manager / Signature

12/15/15

Date

Thomas Hunt, Program Review Committee Chairman / Signature

12-15-15

Date

Elester Patten, Tank Farm & ETP Facility Manager / Signature

10/14/15

Date

John Contardi, Tank Farm Facility Engineering Manager / Signature

12/15/15

Date

SUMMARY OF REVISIONS

Revision	Date	Description
9	12/15	Deleted references to Mechanical Cleaning Mode consistent with DSA 2015 Annual update. Added requirements for Tank 48. Added sample frequency for Sludge and Salt Feed Tanks to Table 8. Clarified requirements for tanks that are noncompliant for chemistry. Added DSA statement regarding analytical uncertainty.
8	2/28/14	Revised to comply with Manual S4 Procedure ENG.36 and corrected document references. Added requirements for salt dissolution processing, high hydroxide temperature limits, out of service evaporator tube bundles, noncompliant ventilation requirements, structural integrity requirements for tanks out of chemistry compliance, and video inspections for dry salt tanks. Added equation to calculate dilute chemistry temperature limit below 40 °C. Removed Slurried Waste Tank designation requirements. Added annulus conductivity probe level requirements.
7	2/13	Incorporated changes to Closure Mode and deleted references to Removed From Service Mode, consistent with DSA Change Request HLW-CRF-12012, Rev. 0, Type I/II/IV Waste Tank Grouting. Added clarification for Acidic Chemical Cleaning that concentrations of acid between 4 wt% and 8 wt% are subject to the requirements of 8 wt%.
6	8/12	Established requirements for Chemical Cleaning of Type I and II Waste Tanks in H and F Tank Farms (excluding Tank 1, 5, and 6) consistent with DSA Revision 14. Updated the Vapor Space Corrosion section based on assessments and experimental testing performed by SRNL. Defined vapor space corrosion control requirements for Type III/IIIA tanks.
5	2/12	Defined the Corrosion Program Life Cycle Stages and associated DSA Waste Storage Tank Mode designation, Closure and Removed-from-Service Mode and established corrosion controls. Established minimum wall temperature limits for Operations,

		Gas Release, Closure, and Removed from Service Modes. Clarified the requirements for functional thermocouple for tanks undergoing the closure process.
4	12/10/07	Corrected constants in equations to calculate NO ₂ inhibition requirements for dilute nitrate solutions. Clarified how the steel wall thermocouples are verified to be within 3 feet of the bottom knuckle weld. Deleted the words, "If available and to extent practical," to clarify Section 3. Requirement frequencies were changed to days vice months and years. The PDD was clarified that components other than waste transfer lines (e.g., waste tanks) were looked at for MIC concerns. The PDD was revised to identify the available margins and sample accuracy based upon technical report, X-ESR-G-00010. Corrected Table 6 and Table 6 notes. Program direction for tanks declared as closure waste tanks. Reordered References
3	11/17/04	Addition to allow 30 day grace period for sample frequency and time allowance for sample analysis and results incorporation into WCS; Addition of sample analysis tracking in the ERD.
2	5/7/03	Addition of wording to allow engineering evaluations to extend the 45 day limit on restoring chemistry in a waste tank. Change to Table 6 to better clarify meaning; Rewording of sentences describing temperature monitoring to show that evaporator drop tank's supernate phase temperature monitoring has been excluded.
1	3/5/03	Addition of "Sampling Methodology" reference [75]; new wording regarding output documents.
0	2/14/03	Initial Issue

GLOSSARY OF TERMS

Active Waste Tank – a tank that has received a waste transfer within the past 365 days, is available to receive a waste transfer at any time, or is being slurried.

Bulk Waste Removal Tank (BWR)- a tank undergoing mixing processes designed for the ultimate removal of sludge from the tank inventory.

Caustic Stress Corrosion Cracking (SCC) – cracking due to sodium hydroxide concentration, stress and temperature.

Cleaning Activities Life Cycle – A tank (Type I, II and Type IV Waste Storage Tanks) preparing for operational closure. A tank enters the Cleaning Activity Life Cycle Stage when it is undergoing the final phases of waste removal including bulk sludge removal, bulk salt dissolution, chemical cleaning, cooling coil flushing, and annulus cleaning. When a tank is declared to be in the Cleaning Activity Life Cycle Stage, chemistry limits and sampling requirements specified in this Program Description Document are suspended or modified for a specified length of time.

Closed Waste Tank – A tank that has been grouted and support systems removed.

Dry Waste Tank – a tank that contains salt and/or sludge, but has an inadequate amount of free supernate to allow sampling for analysis

ERD – Emergency Response Datasheet (N-ESR-G-00001)

Final Stabilization Preparation Life Cycle – A tank going through the regulatory approval process for final stabilization. Active corrosion protection for waste storage tanks in the final stabilization preparation stage is not required and the tank is removed from the Corrosion Control Program. Tanks in this life cycle are Closure mode tanks as defined by the DSA. Administrative controls require the tank be stabilized within 10 years; any return to service shall be authorized only by engineering evaluation(s) ensuring the integrity of the tank is sufficient to meet the intended return to service DSA mode designation.

Inactive Waste Tank – a tank that has not received or sent a waste transfer within the past 365 days, nor is in the process of being mixed.

Nil-Ductility Transition Temperature (NDTT) a temperature below which a metal loses ductility and becomes brittle and may be subject to failure due to brittle fracture.

Nitrate SCC – cracking due to sodium nitrate concentration, stress and temperature.

Normal Operation Life Cycle – Corrosion protection for waste storage tanks in normal operation is optimized to minimize the risk of a leak site or loss of structural integrity for the time frame that the tanks remain in this life cycle.

Normal operation activities include storage, sludge/salt preparation, bulk sludge removal, and bulk salt dissolution.

Pitting – an extremely localized intense form of corrosion that may result in perforation with only a small amount of general wall thinning of the structure. Failures often occur suddenly.

Receiver Waste Tank – an active tank that is not slurried, undergoing salt processing, nor is an evaporator feed or drop tank.

Salt Feed Tank – a tank in which the chemistry has been qualified for salt waste processing. No additional waste transfers in are allowed until the next qualified batch.

Salt Processing Tank – a tank undergoing processes designed for the ultimate removal of salt from the tank inventory (eg., salt dissolution, interstitial liquid removal, etc.)

Stress Corrosion Cracking (SCC) – cracking caused by the simultaneous presence of tensile stress, a specific corrosive medium, and sufficiently high temperature

Sludge Feed Tank - a tank in which the chemistry has been qualified for sludge batch processing. No additional waste transfers in are allowed until the next qualified batch.

WCS – Waste Characterization System

Vapor-Space Corrosion – Vapor-Space corrosion is general or localized corrosion that may occur in the vapor space due to conditions created by relative humidity and the behavior of aggressive species to adsorb humidity, potentially forming localized aggressive solutions.

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1.0 Scope

The scope of the Concentration, Storage, and Transfer Facilities (CSTF) Corrosion Control Program Description Document (PDD) is to provide guidance to Engineering personnel for implementing corrosion related controls for waste tanks, cooling coils, evaporator tube bundles and waste transfer systems.

2.0 Purpose

The purpose of the Corrosion Control Program is to ensure that corrosion of safety related equipment in the tank farms is managed for general corrosion, stress corrosion and pitting corrosion, so as to preserve the integrity of each component for its service life as mandated by the Documented Safety Analysis (DSA). This Program Description Document shall conform to the requirements of S4 Manual Procedure ENG.36.

3.0 Background

3.1 *Safety Function*

The safety function of the CSTF Corrosion Control Program is to ensure that the waste tanks, evaporator tube bundles, waste transfer systems and cooling coils are managed for all applicable corrosion mechanisms to preserve the integrity of each component for its service life. Most of the controls listed in this document deal solely with the condition of a waste tank; however, since this program controls the chemistry and temperature of all waste in the tank farms, it protects all safety-related equipment in the tank farms' transfer paths from corrosion. In addition, controls are listed which protect the evaporator tube bundle in the event the tube bundle is not covered by waste.

This program does not apply to "Closed" tanks

3.2 *Key Attributes*

In order to protect the safety-related equipment, there are several attributes of this program that are necessary for tanks that are not designated as Closure Mode tanks as defined by the DSA; they are as follows:

1. **Temperature**

The corrosion control program sets temperature limits, to ensure that the risk of corrosion degradation is minimized.

- Based on tank chemistry
- Specific for each tank constituent (i.e., sludge/salt, supernate, and steel wall)

-
- Temperature is periodically checked using representative thermocouples placed in various places in each waste phase within the waste tanks

2. Chemistry

The corrosion control program requires minimum concentrations of inhibitor to be present for corresponding amounts of corrosive species in waste to prevent corrosion.

- Actual tank chemistry is obtained through periodic sampling – sampling schedule based on tank chemistry / use of tank is specified by the program
- Tank-to-tank transfers are evaluated to ensure chemistry is kept within limits
- Water Additions to Waste Tanks – the corrosion control program sets limits on how much water can be added to a waste tank over certain time intervals based on the concentration of the inhibitor in the tank
- Microbiologically Induced Corrosion (MIC) – this program addresses the potential for and lists mitigating actions to preclude MIC.
- Evaporator Tube Bundles – this program ensures that the evaporator tube bundles are kept from conditions that would lead to corrosion.
- Chromate Cooling Water – this program outlines the method to minimize the failure of cooling coils due to corrosion from the interior of the coil.

3. Humidity

The corrosion control program requires the operation of annulus ventilation in order to keep the annulus dry unless the tank is in the Cleaning Activities or Final Stabilization Preparation Life Cycle [1].

- Steam is supplied to the pre-heater so that dry air is circulated through the annulus.
- A conductivity probe, or an acceptable alternate (e.g., dip tube), in each annulus alerts operations if any liquid is detected in the annulus
- **Annulus ventilation is a credited control imposed by the Flammability Control Program.**

The parameters defining the Corrosion Control Program for Closure Mode Waste Storage Tanks are documented in Chapter 5 of the DSA.

3.3 Evaluations

The output documents generated by this PDD shall ensure independent verification or validation of results and conclusions. Output documents include, but are not limited to, calculations, procedures and technical reports.

Grace periods are allowed for operational flexibility. Good operating practice would dictate that grace periods are not to be relied upon as routine extensions of the specified interval.

Calculations issued as output documents shall be confirmed Type I calculations in accordance with the requirements of the E7 Manual, Procedure 2.31A. Technical Reports issued as output documents shall comply with the requirements of E7 Manual, Procedures 3.60 and 2.60. Additionally, the output documents will be assessed in accordance with Manual 11Q, Procedure 1.05 as applicable.

Proposed deviations from compensatory actions and monitoring requirements as described in this PDD shall conform to the requirements of S4 Manual Procedure ENG.36.

3.4 *Bases for Criteria*

The Corrosion Control Program is included in a list of general controls in Section 3.4.1.5.6 of the DSA. The initial Corrosion Control Program, established in G-TRT-G-00003, Appendix 6 [2], has been preserved in this document, although the means of implementation have been changed slightly.

The time limits given for the completion of a compensatory action or the monitoring frequency are all based on the desire to stop the initiation of corrosive reactions when possible and retard corrosion if it is initiated, while at the same time realizing the time needed to perform various corrective actions. Since the end results of corrosion are grave, the corrective actions to remove an environment conducive to corrosion from the CSTF must be pursued with speed and diligence. With this philosophy in mind, the time limits were established, based on the estimated time that various actions could reasonably be performed.

Corrosion is a comparatively slow phenomenon and limits are based on general chemistry regimes without distinctive thresholds between them. Thus, use of nominal values is acceptable and does not need to include analytical uncertainty.

4.0 Program Description

The Corrosion Program consist of three life cycle stages: (1) Normal Operation, (2) Cleaning Activities, and (3) Final Stabilization Preparation. Corrosion controls and the applicable DSA waste storage tank mode of operation are defined for each life cycle stage below. The change from one Life Cycle to the next is initiated by a request from the Project Manager in support of Tank Closure activities. The Life Cycle initiation and expiration dates will be tracked in the ERD.

Table 1- Corrosion Program Life Cycles and Controls.

Corrosion Life Cycles	Process Activities	DSA Waste Tank Modes	Temp Min	Temp Max	Chemistry	Annulus Ventilation	Sampling	Time Limits
Normal Operation	1. Storage 2. Sludge/Salt Preparation 3. BSR 4. BSD	1. Gas Release 2. Operations	Yes	Yes	Yes	Yes	Yes	No
Cleaning Activities	1. BSR 2. BSD 3. Chemical Cleaning 4. Waste Tank Annulus Cleaning	1. Gas Release 2. Operations	Yes	Yes	No	No*	No	Yes
		3. Acidic Chemical Cleaning 4. Non-Acidic Chemical Cleaning	No	Yes	No	No*	No	Yes
Final Stabilization Preparation	1. Regulatory Approval Process 2. Tank Grouting	1. Closure	No	No	No	No	No	Yes

Notes:

1. BSD = Bulk Salt Dissolution
 2. BSR = Bulk Sludge Removal
 3. Temperature Minimums are related to Nil Ductility Transition Temperature
- *Annulus ventilation is a credited control imposed by the Flammability Control Program**

4.1 Normal Operations Life Cycle

Corrosion protection for waste storage tanks in Normal Operation is optimized to minimize the risk of a leak site or loss of structural integrity for the time frame that the tanks remain in this life cycle. Normal operation activities include storage, sludge/salt preparation, bulk sludge removal, and bulk salt dissolution. Applicable DSA designations include Gas Release and Operation Modes.

Any activity carried out in a waste tank or other equipment that is not designated for operational closure is considered normal operations. The integrity of these structures, systems, and components (SSC) must be maintained to support the mission of the CSTF; therefore the most restrictive corrosion controls are implemented to protect the service life of these SSCs.

4.1.1 TEMPERATURE

Temperature limits were established to ensure that the risk of corrosion degradation is minimized based on tank chemistry. Temperature is periodically checked using representative thermocouples placed in various places in each waste phase within the waste tanks.

Maximum temperature limits were established for each specific waste phase (supernate and sludge/salt) and tank steel wall. The uncertainty in the limit and temperature measurement is addressed by lowering; (1) the high operating limit 4 °C less than the ERD temperature requirements when the ERD limit is greater than 55 °C and (2) lowering the high operating temperature limit 3 °C less than the ERD temperature requirement when the ERD limit is less than 55 °C [76]. The supernate temperature limits were established to prevent the initiation of stress corrosion cracking and pitting of the tank walls and cooling coils and to minimize the propagation of existing cracks. The maximum salt/sludge and steel wall temperature limits were established to maintain a liquid phase, which contains sufficient corrosion inhibitors, in continuous contact with the tank wall. The temperature limits dictated by this program are more restrictive than those required to maintain the structural and leak integrity of the tank [3], although other factors may necessitate even lower temperature limits.

The basis for the temperature limits is discussed in-depth in Reference 4. In order to ensure temperature monitoring is available, the Corrosion Control Program requires that there be at least one functional thermocouple (TC) to monitor each applicable waste phase and the steel wall for waste tanks, **with the exception of the supernate phase in evaporator drop tanks**. For Normal Operations, the TC monitoring the steel wall temperature for Type I, II, and III tanks must be within three feet of the bottom knuckle weld (this requirement is not applicable to Type IIIA or IV tanks).

Minimum tank wall temperature limits were established to minimize the risk of low temperature embrittlement of the carbon steel tank wall by maintaining the temperature above the nil ductility transition temperature (NDTT). Brittle fracture is not an issue for Type IV tanks because these tanks are not free-standing, but built into a concrete support structure with no annulus. Thus, no potential for rapid change of the steel temperature due to contact with cold outside air exists. Minimum tank wall temperatures limits are shown in Table 2.

Introducing a New Supernate Phase

When a new supernate phase is established in a sludge or salt tank, the requirement to have at least one functional TC for the new supernate phase shall be met within 5 days after sufficient liquid has been added to the tank to cover the lowest available thermocouple. The determination that sufficient liquid has been added to cover the lowest available thermocouple (and therefore the 5-day period to perform the monitoring has started) may be made by direct measurement of tank liquid level or by evaluation of liquid volumes added to the tank (e.g., from tanker trucks, IW tank, waste transfer).

There is no requirement to stop liquid additions at the point where the lowest thermocouple is just under the liquid surface in order to perform applicable monitoring. It is preferable to continue liquid additions until a process-related stable stopping point is reached. Filling the tank with several hundred thousand gallons (as part of the initial addition or a subsequent addition) prior to performing the applicable thermocouple monitoring is acceptable as long as temperature of the liquid added is below the supernate temperature limit expected to exist after the additions.

Supernate Temperature Limits for Concentrated Supernate ($NO_3 \geq 1 M$)

The recommended supernate temperature limits in Table 3 are for concentrated wastes (i.e., nitrate concentration greater than 1 molar) and are dependent on the molar concentration ratio (R) of the inhibitor species (e.g., nitrite and hydroxide) to the corrosive species (e.g., nitrate). For concentrated wastes, the ratio (R) of the hydroxide and nitrite concentrations to the nitrate concentration was observed to be an indicator of waste corrosivity [5]. Stress corrosion cracking is the primary degradation mechanism for this case. From Table 3 it is shown that the two limits are 70°C when R is less than 2.0 (except when the nitrate concentration is between 2.75 M and 5.5 M, then the lowest boiling point temperature in that range is the limit) and the boiling point when R is greater than or equal to 2.0. These limits are based on extensive laboratory testing and analysis of process history [6]. Due to the various waste tank compositions, the boiling point temperature differs from tank to tank. However, over a significant concentration range the boiling point differs by only a few degrees. An equation was developed to calculate the boiling point given the total molarity of the waste [6].

$$T_{bp} (^{\circ}C) = 100 + (\text{total molarity}) * 1.03^{\circ}C\text{-liter/mole} \quad (1)$$

For cases where R was greater than 2.0, the equation was utilized to determine the average boiling point for the nitrate concentration ranges 1 to 2.75 molar and 2.75 to 5.5 molar. The 5.5 to 8.5 molar nitrate concentration range was not considered due to solubility limitations. The boiling point was calculated in the following manner. It was assumed that since the primary components of the waste were nitrate, nitrite, and hydroxide, that the sum of these three molar concentrations could be utilized to determine the total molarity. The boiling point temperature was first determined at the lower end of the concentration range assuming that R was 2. For example, if the nitrate concentration is 1 molar, the sum of the hydroxide and nitrite concentrations would be 2 molar, and thus the total molarity would be 3 molar. Substituting this value into Equation 1 gives a calculated boiling point of 103°C. Performing a similar calculation using a nitrate concentration of 2.75 M, an estimated boiling point of 108°C is obtained. The average of these two temperatures is 105°C. A temperature of 105°C was determined to be an acceptable limit for wastes within this supernate

concentration range. The same assumptions and calculations were made for the nitrate concentration between 2.75 to 5.5 M. In this case the average estimated boiling point was 112°C.

Supernate Temperature Limits for Concentrated Supernate ($OH \geq 8M$)

During the evaporation process, the sodium hydroxide, sodium nitrate, sodium nitrite and other non-volatile constituent concentrations are increased. Sodium nitrate and sodium nitrite saturation is reached and crystallizes as saltcake in the evaporator drop tanks. The evaporator systems' feed is usually high in hydroxide, and therefore as the evaporation/recycle process continues the concentration of hydroxide in the system increases. It is not unusual to observe hydroxide concentrations in the evaporator systems above 8 molar and sometimes as high as 12 molar.

Testing was performed to establish significant independent variables affecting the corrosion process with different chemical, atmospheric and temperature regimes modeling the Tank Farm evaporator system. The test results indicated that the most important factors affecting corrosion of the steel are the solution temperature and hydroxide concentration [Ref. 75]. No evidence of caustic SCC or general corrosion in the laboratory specimens indicate that Type III/IIIA nuclear waste tanks are not susceptible to corrosion in highly caustic solutions up to 12 M hydroxide at 125°C when there is sufficient sodium nitrite (≥ 0.3 M) inhibitor present and the T-ratio ($[OH]/([NO_3.] + [NO_2.])$) is less than or equal to 10, therefore limiting the temperature limit to 115 °C is conservative (See Table 3).

Sludge/Salt/Steel Wall Limits ($NO_3 \geq 1 M$)

The temperature limits (see Table 4) for the salt and sludge phases (T_{ss}) and the steel wall (T_w) are based on maintaining a liquid phase, containing inhibitors, at the tank wall. The composition of the interstitial liquid in the salt and/or sludge, and hence the liquid which is in contact with the bottom and wall of the primary, is not completely known. However, laboratory tests and analysis of actual interstitial liquid have shown that for saltcake the R ratio is much greater than 2 [7]. The interstitial liquid present in sludge has also been characterized [8]. In general, the nitrate concentration in the supernate above the sludge was greater than that observed in the sludge interstitial liquid. It is likely that the nitrate concentration decreased due to ionizing radiation that converts the nitrate to the inhibitor species nitrite. Thus as the sludge ages, the R factor of the interstitial liquid increases indicating a decrease in the corrosivity of the liquid. For these reasons the temperature limits for the salt/sludge and the steel wall is the boiling point for a particular waste concentration.

The tank steel wall temperature limits apply to Type I, II, III and IIIA tanks. If the waste temperature were greater than the solution boiling point, it would be possible to produce nitrate-rich salt deposits on the tank wall [9]. As the waste ages and cools, there could be gradual intrusion of water vapor or supernate into the deposit. The resulting solution may have high local concentrations of nitrate ion. The effects of this condition on either nitrate or hydroxide stress corrosion

cracking cannot be predicted or simulated because of its complexity. Maintaining solution temperatures below the calculated maximum temperature limits prevent the occurrence of this phenomenon.

The static head of the waste above the location of the thermocouples that measure T_{ss} and T_w elevates the boiling point temperature above the atmospheric supernate boiling point temperature [10]. The boiling point temperature elevation is calculated on the basis of the volume and the specific gravity of the waste in each tank [11]. The Clausius-Clapeyron equation relates the boiling point elevation to the static head pressure due to the liquid depth. In general, most of the concentrated wastes (nitrate > 1 molar) have a specific gravity greater than 1.25. If a tank contains 120 inches of free supernate, the total pressure at a level 120 inches below the top of the supernate due to the liquid head, assuming a specific gravity of 1.25, is 20.1 psia. Substituting this pressure into the Clausius-Clapeyron equation, a boiling point elevation of 10°C is calculated. Therefore, it is recommended that the temperature limit for T_{ss} and T_w be determined not only by the supernate boiling point temperature but also the depth of free supernate. If the depth of free supernate is greater than 120 inches, the temperature, T_{ss} and T_w , limits shall be 10°C greater than the boiling point of the supernate. Depending on the composition of the supernate, these temperatures would be either 115°C or 122°C. If the depth of free supernate is less than 120 inches, T_{ss} and T_w limits shall remain the same as the boiling point of the supernate. In many cases, this is a conservative approach (i.e., the boiling point is actually higher) as the amount of free supernate in a tank is much greater than 120 inches. If the temperatures measured by the thermocouples rise to near these boiling point values, a more rigorous calculation should be performed. This calculation would involve determining the exact position of the thermocouple relative to the waste level. The boiling point elevation can be determined accurately from the Clausius-Clapeyron equation. The simplified approach to be implemented eliminates the difficulty of determining the elevation difference between the top of the supernate and the thermocouple that is being utilized to measure the temperature.

Supernate and Sludge/Salt/Steel Wall Temperature Limits for Supernate with Low Nitrate Concentrations ($NO_3 < 1 M$)

At nitrate concentrations less than 1 molar the predominant corrosion mechanism is pitting. There are two regions of the tank where pitting is a concern. The first region occurs at the vapor/liquid interface. Here a thin wetted film forms on the tank wall above the liquid level [12]. This film absorbs carbon dioxide that reacts with the hydroxide to form carbonate and bicarbonate. Unless there is sufficient hydroxide or nitrite in the bulk waste to replenish this film with inhibitors by diffusion processes, this layer becomes uninhibited and pitting results.

The second area is in the walls in contact with the bulk liquid. Depletion of hydroxide is slower in the bulk liquid than for the thin film, however, given enough time it will occur here also. Tanks that have a small volume of waste or

low hydroxide concentration are most susceptible to inhibitor depletion [13]. The temperature limits are summarized in Table 5.

There are two schemes for inhibiting nitrate induced pitting: 1) sodium hydroxide addition alone, or 2) the addition of sodium nitrite with a minimum hydroxide level. If the hydroxide concentration is greater than 1 molar the sodium hydroxide scheme has been selected. Laboratory tests have shown that no pitting is observed in simulated dilute waste that contains greater than 1 molar hydroxide [14, 15]. A theoretical model also demonstrated that a minimum hydroxide concentration of 1 M is sufficient to maintain a minimum pH of 12 in the wetted film region [12].

At high hydroxide concentrations stress corrosion cracking may become a concern. In hot caustic solutions carbon steel may become susceptible to caustic stress corrosion cracking. Laboratory testing was performed in simulated wastes that contained between 1 to 8 molar sodium hydroxide, 0.02 to 1.0 molar sodium nitrate, and at temperatures between 50 to 100°C [16, 17]. The results of the tests demonstrated that the presence of a small amount of nitrate was enough to prevent caustic cracking within these environmental conditions. If less than 0.02 molar nitrate is present there is a potential for caustic cracking at high temperatures. Therefore, for nitrate concentrations less than or equal to 0.02 molar the temperature limits were set at 60°C. If the hydroxide concentration exceeds 8 molar, the carbon steel may again become susceptible to caustic stress corrosion cracking. Therefore, for this case, the temperature limits are also 60°C. Otherwise a temperature of 100°C may be utilized for the temperature limits. The temperature limits for tanks that meet these hydroxide concentration conditions were based on the criteria that the liquid would always have sufficient inhibitor to prevent attack at temperatures less than 40°C. The establishment of these corrosion inhibitor concentration criteria determines when inhibitor additions shall be performed.

The 40°C temperature is sufficiently above the normal operating temperature (i.e., 18 to 32°C) of the tanks which contain dilute waste, while at the same time not resulting in the addition of excess inhibitor. It is recognized that the chemistry in a waste tank may change (become more dilute) based on the processing activities (e.g., sludge/salt preparation, bulk sludge removal, bulk salt dissolution) occurring in the waste tank and/or storage requirements for the waste tank. For dilute waste streams ($\text{NO}_3 < 1\text{M}$), the maximum supernate temperature can be revised based on the inhibitor ratio models [4, 19] below to ensure sufficient temperature controls are applied for the waste composition to ensure that it protects all safety-related equipment in the tank farms' transfer paths from corrosion. Revising the supernate temperature limit ensures the safety function of the program is met for managing corrosion and is within the bounds of the DSA.

$$\text{Temperature Limit} = \text{Log}([\text{NO}_2]/[\text{NO}_3]/0.038)/0.041 \quad (2)$$

The primary aggressive species in dilute solutions is the nitrate anion [18], although at very dilute nitrate concentrations, the chloride or sulfate ion may

become the aggressive species [19]. There are four possible conditions in the dilute waste: 1) the waste has nitrate concentrations less than 0.02 molar, 2) nitrate is the aggressive species, 3) chloride is the aggressive species, and 4) sulfate is the aggressive species. From these equations the minimum ratio of the nitrite to aggressive species can be calculated for a waste at 40°C. These ratios and the constant values for each condition, MIN, are shown below for all Tanks excluding Tank 48.

$$\text{NO}_3 < 0.02 \text{ M: } [\text{NO}_2] = 0.033 \quad (3)$$

$$\text{Nitrate: } [\text{NO}_2]/[\text{NO}_3] = 1.66 \quad (4)$$

$$\text{Chloride: } [\text{NO}_2]/[\text{Cl}]^{1.34} = 267 \quad (5)$$

$$\text{Sulfate: } [\text{NO}_2]/[\text{SO}_4^{2-}]^{0.84} = 1.75 \quad (6)$$

Tank 48 MIN concentrations are as following [78]:

$$\text{Nitrite: } [\text{NO}_2]/[\text{NO}_3]^{0.79} = 0.91 \quad (7)$$

$$\text{Chloride: } [\text{NO}_2]/[\text{Cl}]^{1.03} = 32 \quad (8)$$

$$\text{Sulfate: } [\text{NO}_2]/[\text{SO}_4]^{0.61} = 0.90 \quad (9)$$

A review of these equations showed that if any one of these requirements is violated, then inhibitor shall be added to the waste or the maximum supernate temperature limit must be adjusted if applicable. The maximum value obtained from these equations determines the minimum nitrite. The amount of nitrite added to the waste shall correspond to the value from the equation in which the requirement was violated, or if more than one requirement was violated, the value from the equation which calculates the largest nitrite concentration.

For tanks with dilute waste that contains sludge the sludge/salt temperature limit is 75°C. The concern is that areas of localized high temperature will develop and result in regions that are uninhibited against pitting. Laboratory tests have shown that as long as the temperature in the lower region of the tank is less than 75°C and the bulk supernate concentration of the aggressive anion is greater than 0.01 M no pitting occurs [20].

Bulk Waste Removal Temperature Limits

Table 6 applies to waste tanks undergoing bulk waste removal, however it can be applied to slurried waste tanks for a defined duration based on an engineering evaluation. The bases for the temperature limits in Table 6 are primarily the same as the bases for Table 5. The only difference between the two tables is the supernate temperature limit when the hydroxide concentration is less than or equal to 1 molar.

Waste removal operations have significant impact on the chemistry and temperature of the supernate. During these operations an inhibited solution, either inhibited water or dilute supernate from another waste tank, is added to the tank undergoing waste removal. This mixture is then agitated with single or multiple

mixing pumps. The supernate chemistry will be impacted as sludge particles are suspended, salts are dissolved, and interstitial liquid from the sludge is mixed with the inhibited solution. The temperature of the supernate will also gradually rise as mechanical energy from the pump is dissipated in the waste tank. The temperature limit for the bulk supernate during slurry pump operation shall be 75°C for supernate with a nitrate concentration less than 1 molar and a hydroxide concentration less than or equal to 1 molar. Laboratory tests showed that if the bulk solution is inhibited with greater than 0.01 molar sodium hydroxide, pitting does not occur below this temperature [20]. The agitation also prevents the occurrence of inhibitor depletion in the thin film above the liquid vapor interface [12]. The supernate in a waste tank is considered to be adequately mixed for the application of these higher temperature limits after at least one slurry pump is operated at or above its normal minimum speed for at least 3 continuous hours. The 3-hour operating time period is based on past operational experience, which indicates that the surface of the liquid is sufficiently agitated within the first 3 hours of pump operation (seen on videotapes of slurry pump operation as well as past experience with Tank 8). Once the pump operations have ceased, the temperature limit for the supernate shall remain at 75°C for no longer than 30 days. However, after 30 days the tank shall be considered to have returned to a “non-slurried” condition. Temperature limits will then be governed by the chemistry of the waste per Tables 3 through 5 of this control program as appropriate [21].

Over the years, the supernate in several waste tanks has been allowed to evaporate, leaving either a saltcake or sludge layer phase. Although there is no supernate above, these phases may contain interstitial liquid that may cause a corrosion concern. Due to the various mechanisms of concentration and depletion that can occur in the interstitial liquid, the composition of the interstitial liquid is difficult to predict. A conservative estimate of the interstitial liquid concentration is that it has the same composition as the supernate that was above the sludge or salt layer prior to the time when the tank became “dry”. The actual hydroxide concentration of the interstitial liquid is probably higher due to evaporation of the water from the interstitial liquid. Therefore, the composition results from the most recent sample that was obtained will be utilized to estimate the composition of the interstitial liquid, and hence to determine the temperature limits. Based on these compositions, Table 4 shall be utilized to determine the sludge/salt phase and steel wall temperature limits in dry waste tanks utilizing the salt/sludge levels. If the tanks are re-wetted, an engineering evaluation shall be performed to determine the new temperature limits.

The temperature at the tank exterior surface will be held at least 5°C below the boiling point of the solution. This temperature differential accounts for the maximum temperature drop across the steel wall of < 1°C [22]. This applies only to Types I, II, III and IIIA waste tanks since the Type IV tanks do not have steel wall thermocouples. The waste in Type IV tanks are low heat and therefore do not present a credible potential to boil waste; controls placed by the DSA on the

waste entering Type IV tanks will ensure that this remains true. In addition, other required thermocouples in Type IV waste tanks will be monitored to ensure that waste does not reach its boiling point.

4.1.2 CHEMISTRY

The corrosion inhibitor limits (hydroxide and nitrite) in Table 7 were established to minimize or prevent the corrosion of waste tank walls and cooling coils. The limits are based on experimental data developed at Savannah River Site (SRS). Samples of the waste are taken periodically to determine whether or not the tank is within the corrosion inhibitor limits (see Table 7 and Table 8). The bases for determining the sampling frequency is discussed as well as the requirements for sampling after a waste transfer.

The application of these corrosion inhibitor limits have successfully stabilized and minimized the stress corrosion cracking (SCC) of waste tank carbon steel walls experienced in the early days of SRS and pitting identified in laboratory tests somewhat later. These are the two major corrosion failure modes expected in SRS waste tanks and cooling coils. Since controlled inhibitor addition began in the mid-1970's, there have been no reports of SCC or evidence of it in the stress-relieved Type III and IIIA tanks. The frequency of cooling coil failures has also been minimized (although it is possible that not all cooling coil failures are related to the waste chemistry).

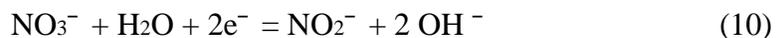
Compliance with these limits may not totally eliminate the potential for cracking of a waste tank. Cracking may occur below the specified temperature as result of concentrations of NO_3^- , NO_2^- and OH^- within the specified limits because of flaws in the metal, stress concentrations, or crevice formations. Cracking may also occur as a result of other corrosion mechanisms involving unknown contaminants that could conceivably be in a waste stream.

The chemistry controls ensure that SCC and pitting of the waste tank walls and cooling coils are mitigated. Corrosion control by addition of chemical inhibitors is the primary means of corrosion mitigation and also the result of continuously diligent and effective research over approximately 40 years. Table 7 summarizes the corrosion inhibitor limits. The primary corrosion inhibitors that are utilized are sodium hydroxide and sodium nitrite, while the primary aggressive species is the nitrate anion. The next sections describe the bases for each of the limits. Temperature limits associated with the various waste chemistries are described in the temperature control section of this document.

Limits 1 to 3 (Table 7):

Carbon steel exposed to alkaline solutions has a low general corrosion rate [26]. However, the presence of the nitrate anion may induce various forms of localized attack (i.e., SCC, pitting, etc.) even in these environments. It has been postulated that cracks are initiated at carbon present in the solid solution or Fe_3C at the grain boundary [27]. Cracks propagate along the grain boundaries of a material as the tensile stress maintains a crevice where the solution remains aggressive towards

the metal. The corrosion rate is influenced by the nitrate reduction kinetics as shown in the equation below [28].



Nitrate is more easily reduced as the solution becomes more acidic. Work at the Naval Research Laboratory has shown that during cracking the solution at the crack tip is approximately pH 3 [29], which is significantly different from the bulk pH. Equation 1 shows that adding hydroxide and/or nitrite anions will reverse the equilibrium of the reduction reaction. Therefore, these anions are useful corrosion inhibitors. Laboratory tests on carbon steel were performed to determine the appropriate combination of inhibitors that would prevent the initiation of new cracks and mitigate the propagation of the current cracks [5, 30 and 31]. Limits 1 to 3 are based on these tests.

As the NO_3^- concentration increases from 1 to 2.75 M, the susceptibility to nitrate SCC increases, and higher concentrations of inhibitors are required [5]. The inhibitor concentration is directly proportional to the nitrate concentration. The presence of 0.3 M OH^- and 1.1 M of $\text{OH}^- + \text{NO}_2^-$ will inhibit nitrate cracking in wastes containing 2.75 to 5.5 M NO_3^- . From 5.5 to 8.5 M NO_3^- , inhibitors at 0.6 M OH^- and 1.1 M of $\text{OH}^- + \text{NO}_2^-$ will be sufficient to prevent nitrate SCC.

Limits 4 and 5 (Table 7):

The nitrite and hydroxide minima are specified to minimize the potential for pitting corrosion of the carbon steel tank walls and cooling coils. The inhibitor concentration limits are based on either hydroxide alone or nitrite with a minimum pH level to inhibit pitting [5 and 31-36]. The discontinuity between the 3 and 4 hydroxide limits is due to a change in corrosion mode from SCC to pitting corrosion, and to the conservative approach taken for 4 and 5 to account for the limitations in the available data on which the standard can be based.

Pitting has not been a problem at hydroxide concentrations greater than 1 molar in over 40 years of experience in the tanks. No pitting is observed at 1 molar hydroxide ion for any of the diluted waste solutions tested [15, 35]. A theoretical model indicates that a hydroxide minimum of 1.0 M is sufficient to maintain a minimum pH of 12 in most of the aqueous film [12]. Lower hydroxide concentrations in the film are probably sufficient to protect the steel, especially when nitrite is present. However, there are not sufficient data available to specify a lower hydroxide ion concentration in the bulk solution that will provide adequate protection throughout the film.

The nitrite minimum is based on the concentration required to inhibit pitting of the tank wall or cooling coils in an aqueous film which has reached a steady state pH [35, 15, and 36]. The nitrite requirements include a 50% uncertainty to

account for both the increased requirements when processing worst-case (most corrosive) salt solution, for local variations in waste composition and for differences between actual waste and the laboratory simulants.

The inhibitor levels specified in limits 4 and 5 are based on the aqueous phase reaching steady-state with respect to the absorption of atmospheric carbon dioxide. Alkaline solutions absorb and react with carbon dioxide to produce bicarbonate and carbonate [13]. The steady state pH depends on the initial hydroxide and carbonate levels in the waste and carbon dioxide concentration in the air. The lowest steady-state pH which has been tested is pH = 10.3 [15, 37] and is the minimum specified for all nitrate concentrations below 1 molar. At nitrate concentrations between 0.02 to 1.0 molar, the nitrite concentrations specified by in 4b are sufficient to inhibit corrosion only if the solution pH does not fall below the steady state value of 10.3 [18]. A pH less than 10.3 could put the tank in a regime where adequate protection against pitting is not provided by the nitrite level specified in 4b and 5b [18].

The inhibitor requirements specified in limits 4 and 5 are based on a supernate temperature of 40°C (see background of temperature control). Pitting of carbon steel is worse at temperatures greater than the maximum allowable and greater concentrations of inhibitors would be required for prevention.

In general, the nitrate anion is the aggressive species that causes pitting. However, in very dilute solutions, sulfate or chloride, may become the species that is aggressive [19]. Minimum nitrite concentrations as a function of chloride or sulfate concentration in the supernate are represented by limits 4c and 4d, respectively. A review of limits 4b-d demonstrated that the solution is always inhibited if it contains the maximum value of nitrite calculated from the three equations [19]. For example, if the nitrite concentrations calculated from each equation are 0.5, 0.01, and 0.04 molar for nitrate, chloride and sulfate, respectively, the minimum nitrite required for the supernate would be 0.5 molar.

Therefore, the maximum value obtained from limits 4b, 4c, or 4d shall be utilized to determine the minimum nitrite concentration required to inhibit a dilute solution. Similarly, if the nitrate concentration is less than 0.02 molar, the maximum value obtained from limits 5b if the concentrations of the nitrate, chloride, and sulfate anions are not known, or 5c, 5d or 5e shall be utilized to determine the minimum nitrite concentration required if the concentrations of these constituents are known.

pH limit (Table 7):

This limit ensures that waste from other areas on site, that would rapidly corrode a carbon steel tank or cooling coils if not thoroughly mixed with waste already in the tank, is not routinely added to the waste tanks [38]. Waste that is acidic (pH < 7), could cause severe corrosion damage to parts of the waste tank or cooling coils when it comes in contact before being mixed with alkaline tank contents. The waste acceptance plan has specified pH 9.5 to allow a safety factor above pH 7 to

account for field measurements, which although accurate, may not be precise. The limit does not apply to well water (pH 4 to 5) used for line flushing.

Water Additions

Small volumes of uninhibited water and aqueous solutions are occasionally added to the waste tanks. This program allows the addition of up to 3,000 gallons of water (e.g., flush water, uninhibited water, spring water, well water, and all other forms of water available to the tank farm) to a tank within a rolling 30 day window without any corrective action. This is based on the fact that in the waste tanks, an addition of 3,000 gallons or less of water does not significantly change the inhibitor concentration of that tank's supernate, and within the given time, the inhibitor concentration from the supernate in the tank will diffuse into the water that has been added. In order to ensure this limit is not exceeded, the levels of each inactive tank will be evaluated every 30 days to ensure no unplanned addition of more than 3,000 gallons occurred.

In order for water to be considered inhibited, it must be verified to contain greater than 0.01 M hydroxide and 0.011 M nitrite. All other water additions are considered uninhibited.

Small volumes of uninhibited water and aqueous solutions are occasionally added to the waste tanks. Sources of these additions include rainwater, sump solutions, transfer line flush water, and decontamination solutions. These additions generally do not significantly alter the bulk chemistry of the waste already present in the tank. However, these additions increase the risk of corrosion near the vapor liquid interface. The difference between the densities of water and high level waste results in inadequate mixing of these solutions. Water additions to the tank are likely to separate and form a thin layer on top of the more dense bulk waste. During this time, solute concentrations in this layer are assumed to increase by diffusion only from the bulk waste. Because the water additions are likely to have pHs in the near-neutral range, the potential for corrosion does exist for a period of time before the concentration of inhibitors such as hydroxide and nitrite reach protective values in this added layer. Near-neutral pHs are well below the pH of 10 required to inhibit against pitting corrosion in pure water and the pH of 14 required for solutions containing corrosive anions, such as nitrate, sulfate, or chloride [41]. Water additions will remain corrosive until the required inhibitor concentrations are satisfied by diffusion from the bulk supernate into the addition layer. The inhibitor requirements for this layer were established as either 1M sodium hydroxide or a combination of 0.01M sodium hydroxide and 0.011 M sodium nitrite. These levels of inhibitor have been shown to prevent pitting attack in dilute wastes [41]. Although pit initiation and growth rates for carbon steel in alkaline solutions are not well established, the experience of cooling coil failures during sludge removal operations in the 1960s suggests that pit growth rates may be as high as 0.15 in/month [43]. Some period of time is required to initiate pits, and some pits may repassivate upon the establishment of inhibiting conditions. Diffusion calculations were performed to determine the largest water addition for

which the required inhibitor concentrations are achieved at the top of the layer in a reasonable time frame [77].

If this limit (3,000 gallons) is exceeded or it is anticipated that it will be exceeded, an engineering evaluation for directions or remedial actions shall be performed as soon as practical [41]. The engineering evaluation will consider variables such as the bulk concentration of the waste in the tank, the source of the uninhibited water, and recent additions of uninhibited water to the tank in its recommendation.

Vapor Space Corrosion

General or localized corrosion may occur in the vapor space due to conditions created by relative humidity and the ability of deposited aggressive species on the tank wall to adsorb humidity to form localized aggressive solutions [69]. Several mechanisms were proposed for the deposition of aggressive species on the tank wall within the vapor space to include: 1) salt residue on the steel tank left by evaporation or supernate transfers 2) species may have been deposited on the tank wall by evaporation from the supernate transport as an aerosol followed by condensation on the tank wall. In sufficiently humid conditions, the residue can adsorb atmospheric moisture and dissolve, forming a corrosive electrolyte. Testing indicated that supernate transfers and the consequent residual species on the tank wall is the predominant source of surface chemistry on the tank wall. As such the extent to which the initial solution is inhibited prior to transferring of the solution plays a key role in the corrosion in the vapor space. At the boundary conditions for Chemistry Limits 1 through 3 of the Corrosion Control Program minor and isolated pitting is possible within crevices in the vapor space of the tanks that contain stagnant dilute solution for an extended period of time, specifically when residues are left on the tank wall during supernate transfers.

Table 10 provides supernate chemistry control limits for a tank that is inactive for more than six months [70]. If the tank becomes active during the six month period, the limits in Table 7 remain applicable. These limits apply only to Type III/IIIA tanks. Compliance with these limits will be accomplished by quarterly engineering evaluations to identify any tanks that may not be compliant with the vapor space criteria.

Sampling Frequencies (Table 8 and Table 9)

The sample frequencies in Table 8 are set based on a statistical analysis of the historical corrosion chemistry sample data of the tanks in each category [39] and on an understanding of mechanisms that may change the concentrations of either aggressive or inhibitor species (e.g., hydroxide depletion) [13]. The frequencies in Table 8 may be used for any tank. Tanks that have a sample history of at least 15 samples since the last inter-tank transfer OR since waste was last slurried in the tank, may qualify for further extension of sampling frequency as specified in Table 9.

A 30 day grace period is permitted in the sample frequency specified in Table 8 and Table 9. Sampling results shall be incorporated into the Waste Characterization System (WCS) within 90 days of the date the sample was taken. A 30 day grace period is permitted in the time allowance for sample result incorporation into WCS. A sampling methodology has been documented that describes the types and locations of various samples needed to comply with this and other PDDs [40].

A. Active Tanks

A.1. Evaporator Feed and Drop Tanks

The sample frequency for active evaporator feed and drop tanks shall not exceed 180 days. The relatively frequent transfers into these tanks from several different sources (canyons, DWPF, etc.) may result in significant changes in the corrosion chemistry that need to be trended. Models for hydroxide depletion indicate that for dilute solutions (i.e., nitrate concentration is less than 1 molar) the hydroxide concentration can deplete to the steady state pH level of 9.5-10.3 within 3 to 180 days [13]. Therefore tanks with these composition ranges shall be sampled every 90 days. Models for hydroxide depletion in tanks with concentrated wastes (nitrate greater than 1 molar and hydroxide greater than or equal to 2.35 molar) indicate that at high hydroxide concentrations will take more than 5 years to attain the steady state pH level [13]. Therefore a 180-day sample frequency that will monitor changes in the chemistry due to waste transfers will be sufficient for the more concentrated wastes.

A.2. Fresh Canyon Waste Receiver with Nitrate Concentration Greater Than or Equal to 1 Molar

Fresh canyon waste receivers were separated out as a special case waste receiver. Previous service history show that these tanks, in addition to having relatively lower inhibitor concentrations compared to other waste receivers, also historically have higher temperatures. The higher temperatures result in a greater susceptibility to corrosion degradation mechanisms. Therefore, the sample frequency shall not exceed 365 Days. If the hydroxide concentration is less than 3 M, or the total inhibitor concentration is less than 4 M, the tanks will be sampled on a 180-day frequency.

A.3. Receivers with Nitrate Concentration Less Than 1 Molar

The ratio of the concentration of nitrate to nitrite typically determines whether dilute wastes are within corrosion chemistry limits. The statistical analysis of the historical sample data was utilized to establish the frequencies shown in Table 9. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models indicate that the steady state pH may be attained within a year [13]. Therefore the 90 and 180-day frequencies are justified. On the other hand, if the hydroxide concentration was greater than 2.35 M, it will take more than 5 years to attain the steady state pH. Therefore, the 365-day frequency is justified.

Dilute wastes may also be inhibited with 1 molar sodium hydroxide per Table 7. Models for hydroxide depletion predict that solutions with high hydroxide concentrations (greater than or equal to 2.35 molar) will take more than 5 years to attain the steady state pH [13]. An exception to these frequencies may occur at very dilute solutions (i.e., nitrate concentrations on the order of 0.01 M). If the chloride or sulfate species becomes the aggressive species rather than the nitrate, the sample frequency will be 90 days. Which species is aggressive can be determined by calculating the minimum nitrite level for each of these species and then determining which species requires the maximum amount of nitrite. The equations for the minimum nitrite calculations are shown in Table 7. The nitrate will be the most aggressive species except in some rare cases of dilute waste.

A.4. Receivers with Nitrate Concentration Greater Than or Equal to 1 Molar

Inhibition of concentrated wastes (nitrate greater than or equal to 1 molar) is achieved with a minimum hydroxide concentration and the combination of hydroxide and nitrite concentrations (see Table 7). Statistical analysis of the sample data was utilized to determine the frequencies based on the risk of being outside the corrosion chemistry controls [39]. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models suggest that the steady state pH may be attained within a year. Therefore 180 days is an adequate sample frequency. For hydroxide concentrations greater than or equal to 2.35 M, the steady state pH level will not be attained for more than 5 years [13]. Therefore these tanks may be sampled on a 365 day or 730 day basis as determined by Table 9.

A.5. Bulk Waste Removal Tanks

Due to the potential for changing the concentration during slurring operations, samples shall be taken once every 30 days to verify that the waste remains within corrosion chemistry, unless an engineering evaluation shows that a longer frequency is acceptable to coincide with slurry batch campaigns.

A.6. Salt Processing Tanks

The study of conditions present in tanks containing salt was instrumental in forming the basis for this program. Therefore, all limits listed in this program apply to salt processing tanks as if they were any other active tank. Salt processes are those operations taken to prepare for and perform salt disposition and may include, but are not limited to, salt dissolution and interstitial liquid removal.

During salt dissolution processing, it has been shown that the concentration of inhibitor species (NO_2^- and OH^-) are depleted and the concentration of the aggressive (NO_3^-) species is greatly increased [Ref. 71]. It is anticipated that as the salt dissolution process progresses that the tank chemistry will at some point fail to be in strict compliance with the requirements of Table 7, thus introducing the risk of nitrate induced stress corrosion cracking and pitting of the primary tank wall at the liquid air interface.

Water additions will most likely float on top of the salt cake due to differences in the specific gravity of the interstitial liquid and the dissolution water. Dissolution of the salt is controlled by diffusion from salt cake into the layer of dissolution water. This process is relatively slow, and thus the region at the liquid air interface may remain at essentially the same composition as the initial dissolution water for some time.

If inhibited water is utilized the concern for pitting at the liquid air interface is minimized initially. However, if this layer is allowed to remain stagnant the hydroxide inhibitor present at the liquid air interface will begin to deplete due to a reaction with carbon dioxide [Ref. 13].

A corrosion control plan [Ref. 71] was prepared to mitigate these risks and to allow the salt dissolution to move forward without the addition of inhibitors. The controls include lowering temperature limits and stagnant liquid air interface time limits with specific action items to protect both the tank where salt dissolution is performed and the tank that receives and stores the dissolved salt solution.

B. Inactive Tanks

B.1. Receivers with Nitrate Concentration Less Than 1 Molar

Inactive tanks have not received any transfers for over 365 days. Thus any change in the supernate chemistry would be due to hydroxide depletion. The ratio of the concentration of nitrate to nitrite typically determines whether dilute wastes are within corrosion chemistry limits. The statistical analysis of the historical sample data was utilized to establish the frequencies shown in Table 8 [39]. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models indicate that the steady state pH may be attained within a year [13]. Given that there are no transfers into the tank within a year, the 180 and 365-day frequencies are justified. On the other hand, if the hydroxide concentration was greater than 2.35 M, it will take more than 5 years to attain the steady state pH. Therefore, the 730-day frequency is justified. Dilute wastes may also be inhibited with 1 molar sodium hydroxide per Table 7. Models for hydroxide depletion predict that solutions with high hydroxide concentrations (greater than or equal to 2.35 molar) will take more than 5 years to attain the steady state pH [13]. An exception to these frequencies may occur at very dilute solutions (i.e., nitrate concentrations on the order of 0.01 M). If the chloride or sulfate species becomes the aggressive species rather than the nitrate, the sample frequency will be 90 days. Which species is aggressive can be determined by calculating the minimum nitrite level for each of these species and then determining which species requires the maximum amount of nitrite. The equations for the minimum nitrite calculations are shown in Table 7. The nitrate will be the most aggressive species except in some rare cases of dilute waste.

B.2. Receivers with Nitrate Concentration Greater Than or Equal to 1 Molar

Inactive tanks have not received any transfers for over 365 days. Thus any change in the supernate chemistry would be due to hydroxide depletion. Inhibition of concentrated wastes (nitrate greater than or equal to 1 molar) is achieved with a minimum hydroxide concentration and the combination of hydroxide and nitrite concentrations (see Table 7).

Statistical analysis of the sample data was utilized to determine the frequencies based on the risk of being outside the corrosion chemistry controls [39]. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models suggest that the steady state pH may be attained within a year. Given that there have not been any transfers into this tank for over a year, 365 Days is an adequate sample frequency. For hydroxide concentrations greater than or equal to 2.35 M the steady state pH level will not be attained for over 5 years [13]. Therefore these tanks may be sampled on a 730 or 1460-day basis depending on the results of the statistical analysis and/or the guidelines established in Table 8.

C. Exceptions to the Sample Frequency Rules

If a waste tank has been sampled 15 times since the last inter-tank transfer or since waste was slurried in the tank AND the statistical capability of the tank to meet minimum corrosion inhibitor limits (Sigma Level) can be established [39], the sample frequency for that tank may be determined using Table 9. If the frequency is extended using this provision, the extension will be documented in the ERD [42].

Evaporators

In order to prevent corrosion of the evaporator tube bundles, it is required that they either be submerged in waste or in inhibited water (unless the tube bundle is deemed Out of Service (OOS)). The basis document for the corrosion control program recommends that the tube bundle not be left uncovered for more than 30 days [54]. During the period of time when the evaporator is not operating, the pot shall have a pH greater than 12, as calculated by the following formula. During normal operation, the tube bundles are covered with waste that is sufficiently inhibited to prevent corrosion.

The amount of inhibitor needed to raise the pH in the evaporator pot to above 12 is very minimal. The 2F and 2H evaporators require approximately 11 gallons of 50 wt% caustic to raise the pH to 13; in the 3H, it takes approximately 53 gallons. The following equation yields the volume of 50 wt% caustic that is necessary to be added to increase the pH of the pot contents to 13.

$$(0.1 * (\text{gallons in pot})) / 19 = x \text{ gallons caustic} \quad (11)$$

This equation determines the gallons of 50 wt% caustic that needs to be added by taking the product of the desired concentration of 0.1 M (pH 13) and the gallons in the pot and dividing this product by the concentration of the 50 wt% caustic (19 M).

Credit may be given for the waste left in the evaporator pot, if it is sufficient to bring the pH of the pot over the minimum of 12, and the lance is operating when the water addition to the waste is made. To calculate whether the waste is sufficient to inhibit, use the free hydroxide concentration of the evaporator feed tank, multiply it by the expected volume of the waste left in the pot; then, divide by the total volume of the liquid in the pot. This number is the actual free hydroxide concentration in the pot. If this value is above 0.01 M, the waste left in the cone is sufficient to inhibit the pot. If not, the addition of caustic as described above must be completed within 30 days.

The intent of this program is to ensure that the tube bundle in the evaporator pot is submerged in an inhibited solution very quickly after going into an extended shutdown. This minimizes the chances for the initiation of corrosion on the tube bundle. This basis document was written specifically for the 2H and 2F evaporators, but a later evaluation [55] confirmed that this control can be extended to the 3H evaporator as well.

The evaporator tube bundle must also be protected against failure due to MIC. However, the high temperatures of the steam in the tube bundle kill all the microbiological entities that could cause this form of corrosion, so no further controls need to be placed on the system.

Prevention of Microbiologically Induced Corrosion (MIC)

MIC has not been observed in any of the tank farm systems; however some conditions at SRS do cause concern over the possibility of MIC occurring. The conditions that cause MIC concerns are stagnant water, low pH (pH<10.5), temperatures less than 100°F, presence of organic matter, and the absence of a biocide [56]. On occasion, uninhibited water is used in the tank farm, primarily for flushing transfer lines after a transfer, which could produce conditions that would encourage MIC.

In order to prevent conditions that would be favorable to MIC, transfer lines shall be vented and drained after each transfer. If there are known “low” points in the transfer line (as identified in the Structural Integrity (SI) Program), and that line needs to be flushed, that line must be flushed with inhibited water (pH>12) unless another waste transfer is planned within the next 5 days. A five-day maximum on the time that uninhibited water can remain stagnant in a transfer line has a technical basis combined with engineering prudence [56].

Chromate Cooling Water Lines

The cooling coils in each of the waste tanks are protected against corrosion from the exterior by the inhibitor and temperature requirements required for each of the waste tanks in this program. The interior of the cooling coils is protected against corrosion by the chromate that is in the cooling water. Periodic testing (at least every 90 days) of the chromate cooling water for the appropriate levels of chromate (greater than 450 ppm) coupled with a required flush of all isolated chromate cooling coils every 90 days will ensure that the cooling coils are

sufficiently protected against internal corrosion. A chromate concentration of 450 ppm must be verified every 90 days, because in a period longer than 90 days it is possible for the chromate concentration to decay down to approximately 200 ppm, which is the minimum level, needed to prevent corrosion.

A decision to not protect a certain cooling coil by the Facility Manager shall exempt that cooling coil from the requirements of this program, provided the coil is out of service.

The supports for the cooling coils that are in a waste phase are also protected by the temperature and chemistry controls on the waste in each tank. The vapor space corrosion section of this program is applicable to the supports for the cooling coils that are in the vapor space of the tank.

During the closure process, there is a potential risk of through-wall pitting of the cooling coils [1].

4.1.3 HUMIDITY

Annulus ventilation is required to prevent corrosion of the external tank wall, the secondary pan, and the secondary wall of double wall tanks due to the potential formation of condensate on the walls. Preheating the annulus air is required if the tank wall is less than 40°C.

Based on a review of SRS meteorological data, obtained from the onsite weather services of the Atmospheric Technology Group, including the dew point temperatures in the tank farm over the time period from 2000 to 2002, it was concluded that if the lowest tank steel-wall temperature is above 40°C, steam is not required to protect the annulus. This review discovered that typically, the dew point does not go above 80°F. No recorded dew point over the past 730 days exceeded 100°F [Ref. 74]. Therefore, if the tank's lowest steel wall temperature is above 40°C (104°F) (excluding tanks in Acidic and Non-Acidic Chemical Cleaning Mode and Closure Mode), no condensation should occur in the annulus. However, if liquid is detected (from rainwater, etc.) in the annulus, steam shall be, if the steam supply is functional, supplied to the annulus until it is dried, regardless of the temperature of the tank wall.

For tanks with a low heat generation rate, continuous operation of the annulus ventilation system with steam on prevents condensation from forming on the exterior of the primary tank wall and the secondary pan or wall of double-walled tanks as well as evaporating any standing liquid from the annulus pan. Heat, provided by the steam, is utilized in the system to raise the temperature of the air, causing the relative humidity to decrease, and thus minimizes the potential for condensation. The presence of water in the annulus may cause significant corrosion of the tank walls. Occasionally the annulus ventilation system needs to be shut down for repairs to supporting systems such as low pressure steam. This program places limits on the time which the annulus ventilation system may be shutdown. Provisions have also been made to operate the fans if steam is not available. During continuous operation in this mode, there is a risk that there will

be periods of time when condensation and rainwater will accumulate and therefore over time the integrity of the tank will degrade due to corrosion. Long term operation in this mode is not recommended. The only limitation of utilizing the annulus fans with no steam is that the tank wall temperature must be greater than the nil-ductility transition temperature (NDTT) (see [3]). For tanks with a high heat generation rate, continuous operation of the annulus ventilation system (without steam on) removes excess heat from the tank. Due to the high temperatures near the bottom of these tanks, water typically would evaporate rapidly and be removed due to the circulation of the air.

The purpose of this requirement is to prevent corrosion degradation of the exterior primary wall, the secondary pan, and the secondary wall of the double wall tanks. The degradation may result in an inadvertent release of radioactive material to the surrounding environment. Operation of the annulus ventilation in high heat tanks lowers the temperature of the primary steel and thus minimizes the potential for corrosion degradation of the steel or thermal degradation of the concrete. The annulus conductivity probe, a safety-significant instrument detects standing liquid in the annulus. Operation of the annulus air with steam will evaporate the water and prevent corrosion of tank steel. After 30 to 40 years of operation with steam, insignificant degradation of the tank walls has occurred. Operation of the ventilation fans with no steam will evaporate some of the moisture and reduce the potential for production of nitric acid and is therefore better than not operating the fans at all. However, there is a risk that there will be periods of the year when condensation and rainwater will accumulate in the annulus, and therefore over time the integrity of the tank will degrade due to corrosion.

For tanks that have a low heat generation rate, continuous operation of the annulus ventilation system in the past has prevented excessive general corrosion of the primary or secondary tank walls. The intent of this program is to prevent shut-down of the tank annulus ventilation systems for extended time periods. The annulus ventilation system, operated with steam, provides warm air to the annulus that minimizes the accumulation of moisture. Moisture in the annulus causes four concerns for the annulus integrity, (i) for cracked tanks, the moisture will dissolve salt deposits covering the leaksites and allows for intrusion of waste into the tank annulus [48], (ii) for all tanks, radiolysis of the air produces NO_2 gas which reacts with the moisture to produce the highly corrosive nitric acid [45], (iii) for all tanks, microbiologically induced corrosion (MIC) may initiate [46], and (iv) for all tanks, corrosion products may hide defects and therefore prevent the detection of changes in the tank wall surface by tank inspection.

Several Type I tanks and all of the Type II tanks have leaked waste through cracks into the annulus. The warm air circulating through the annulus evaporated the water from the waste and formed salt deposits that plugged the cracks and prevented further leakage. Inspections have shown that when the annulus ventilation is turned off, these deposits begin to dissolve and leakage of waste into the annulus resumes [48]. The dissolution of the salt deposits is likely due to the formation of condensation on the tank walls as the air cools. Although the waste

should be inhibited when it enters the annulus, dilution due to rainwater intrusion or reaction with carbon dioxide may change the chemistry of the leaked waste significantly from that of the waste inside the tank. Thus a new corrosive condition may be created.

Moisture by itself will cause general corrosion. Accelerated general corrosion may occur due to air radiolysis. This mechanism is initiated by gamma rays that irradiate the annulus air to produce NO₂ gas [47]. A nitric acid solution will form wherever air containing NO₂ is in contact with moisture. The reaction producing the nitric acid is:



If it is assumed that the dose rate is 1000 R/hr (a representative value for the annulus air [48]), and the volume of air in the annulus is approximately 23,000 ft³, the production of NO₂ gas is 1.9 x 10⁻⁸ atm/hr. Assuming that equilibrium is instantaneously established, the pH of the standing water may reach 2.9 within 1 hour. At this pH, carbon steel corrodes at a rate of approximately 40-50 mils per year [49]. If these conditions were allowed to persist significant wall thinning may occur. This mechanism was observed to occur in the reactor process room at SRS [50]. Inspections of the annular space to date have not revealed indications of excessive general corrosion [51] even with occasional steam and blower outages. There are several possible explanations for the lack of observed general corrosion. First, the rate at which the nitric acid production reaction occurs in cold dilute solutions may be slow [52], and therefore, the reaction may not attain equilibrium rapidly. Second, the contents of the tank may have contributed sufficient heat to maintain the temperature of the annulus air above the ambient temperature. Condensate would not form under these conditions. Third, the above calculations assume that the air in the annulus is stagnant. A small air flow in the annulus may dilute the NO₂ concentration sufficiently. Fourth, in tanks that have salt deposits, the condensate or standing water may contain other dissolved salts. The presence of these dissolved salts would likely decrease the absorption of the NO₂ gas into the water and the formation of nitric acid.

A final consideration is the potential for MIC. MIC was observed in the annulus pan during construction of the Type III tanks [46]. Wet, stagnant conditions were ideal for initiating pits beneath the microbes. The solution to the problem was to run warm annulus air to remove the moisture that sustains the microbes and the corrosion reaction. Maintaining warm air in the annulus minimizes the potential that this mechanism will initiate new pits or reinitiate pits that are present.

Given that the Type I and II tanks are older and have experienced more degradation, the allowable time period for a ventilation outage is 30 days. Also should defects form (i.e., pits or cracks), the structure will be more susceptible to brittle fracture due to the high nil-ductility transition temperature of the steel used for these tanks. Moisture build-up in the Type III and IIIA tanks is also undesirable. However, the lack of any known leaksites and the superior materials

and fabrication procedures used for these tanks allows for a longer allowable outage period.

There are situations where steam is not available to heat the ambient air prior to entering the waste tanks. If steam is not available, the annulus fans may be turned on in order to evaporate moisture as long as the tank walls remain above the low operating temperature limit on the roundsheets. The minimum temperature limit on the roundsheets ensures that the tank wall temperature remains above the minimum NDTT value (excluding tanks in Acidic and Non-Acidic Chemical Cleaning Mode and Closure Mode) [3] by a sufficient margin. The temperature limit minimizes the potential for brittle fracture of the tank walls. Portable fans may also be utilized in this situation. Due to the convection of the air, some undetermined amount of moisture (which depends on the temperature and relative humidity of the ambient air and the heat generated by the tank) will be evaporated. Additionally the air flow will reduce the concentration of NO₂ in the annulus that was produced by radiolysis. Therefore, although corrosion would occur due to moisture, it would not be accelerated by nitric acid. However, there will be time periods during the year when condensation will accumulate in the annulus. This mode of operation is not ideal; however, it may be utilized on an interim basis.

In addition to moisture due to condensation, rainwater leaks into the annulus through risers and other penetrations such as transfer lines. Conductivity probes are set near the floor of the waste tank annulus to detect the presence of liquids. The probes should be located as near as practical to the annulus floor to minimize the accumulation of liquid. In some situations, debris or waste prevents the probe from being placed directly on the annulus floor. Two benefits are realized by minimizing the accumulation of liquid: 1) the potential for deflagration or the accumulation of flammable gases is reduced and 2) long-term corrosion degradation of the pan, annulus floor, annulus wall or primary tank is mitigated or prevented. The first benefit reduces the risk of releasing a radioactive dose to the public. Given that this is the more immediate concern of the two, the level that the probe is set above the annulus floor (in the presence of debris or accumulated waste) will be based on this consideration. The second benefit maintains the structural integrity of safety class structures over an extended period of time. The maximum probe height settings are described in the Technical Safety Requirements (TSRs).

Circulation of warm air will evaporate rainwater and prevent the possibility of corrosion. For example, a test was performed that showed that operating the annulus ventilation at 2200 CFM, with an inlet temperature of 96°C, would evaporate approximately 10 gallons of liquid per hour [53]. In the event that steam is not available to heat the ambient air, the ventilation fans or portable ventilation fans shall be operated to evaporate the water. Although the drying capacity of the air is significantly decreased during periods of time when the humidity is above 50%, blowing air across the accumulated water will evaporate

water as long as the ambient air is below 100% relative humidity. The tank steel wall temperature shall be monitored also to ensure that it does not go below the minimum value i.e., the NDTT (excluding tanks in Acidic and Non-Acidic Chemical Cleaning Mode and Closure Mode).

For tanks with a high heat generation rate, circulation of air that has not been pre-heated with steam has been utilized to cool the waste tank steel. Cooling the waste tank in this manner minimizes the potential for corrosion degradation of the steel (see Temperature Control) or thermal degradation of the concrete (see Structural Integrity Program). Typically, the heat from the high heat tanks in combination with air convection will evaporate water from the annulus in a relatively short period of time.

4.2 *Cleaning Activity Life Cycle*

Tanks in the Cleaning Activities life cycle are undergoing vigorous cleaning activities. These activities include bulk sludge removal, bulk salt dissolution, and chemical cleaning (applicable to Type I/II waste storage tanks, excluding Tank 1). During the Cleaning Activities Life Cycle, the program allows for the suspension of corrosion inhibitor concentration requirements, sampling frequencies (shown in Table 8), and maintaining annulus ventilation requirements for up to 1460 days for waste removal activities, which accounts for a bounding case of the tank being exposed to oxalic for 365 days (Feeding 4 to 8 wt% oxalic acid at 60 to 75°C with no mixing for ≤ 30 days and the remainder of time at ≤ 4 wt% oxalic acid at 60°C) for chemical cleaning activities. A more realistic case for chemical cleaning activities is approximately 6 months. Since the life cycle is short, the corrosion controls imposed are greatly diminished, but are adequate to ensure that sufficient tank integrity remains to complete the closure process.

Applicable DSA designations include Gas Release, Operation, Acidic Chemical Cleaning, and Non-Acidic Chemical Cleaning Modes. Once the tank is declared clean and no further aggressive cleaning is required, the tank will transition into the Final Stabilization Preparation Life Cycle Stage. This declaration stops the Cleaning Activities Life Cycle Stage time clock (1460 days).

4.2.1 TEMPERATURE

Maximum temperature limits are applicable for each waste phase and the tank steel wall as established for the Normal Operations Life Cycle Stage. More restrictive temperature limits are applied for tanks that are undergoing acidic chemical cleaning during acid addition and mixing evolutions.

In assessing the waste storage tanks, going through the cleaning activities life cycle stage, temperature was an important variable for estimation of the expected corrosion rates during waste removal activities [1]. Bounding temperatures for each of the activities were assumed for the analysis. The maximum temperature experienced during bulk sludge removal due to mechanical heat generated by mixing devices is expected to be 60°C. The maximum temperature for salt

dissolution is expected to be 50°C. The maximum temperature in tanks storing salt cake is approximately 50 °C [23]. Additionally, salt dissolution is an endothermic process, which lowers the temperature of the waste below 50 °C [24]. The target temperature for heel removal with oxalic acid is 50 °C [1]. However, the reaction between the oxalic acid and the sludge is exothermic and the mixer pumps will also add mechanical heat to the system [1]. Therefore a reasonable maximum temperature for the oxalic acid chemical cleaning process will be 60 °C.

These operations are very low-volume operations or involve mixing pumps at high volumes. The highest temperatures are likely during the slurring process, when the pumps are adding heat to the tank and may challenge temperature limits. Consequently, temperature shall be monitored every shift when the mixing pumps are operating. After the slurring process, the mixing devices are turned off and most of the heat-generating sludge-slurry mixture is transferred out of the tank. Therefore, it is expected that the temperatures will not challenge the limits during low-volume phase of the process.

During Chemical Cleaning of Type I/II waste tanks, the concrete vault and, in the case of the Type I tanks, the concrete columns are credited for structural integrity controls for normal operation and natural phenomena events. The steel tank wall is not credited and therefore embrittlement of the primary tank wall is not an issue. Type I/II Chemical Cleaning Waste Tanks are exempt from NDTT requirements [62].

4.2.2 CHEMISTRY

The engineering assessment of waste tanks in the Cleaning Activities Life Cycle assumed that well water, which is conservatively bounding for inhibited water and supernate in terms of corrosion inhibitors, would be utilized for bulk waste removal operations, and that up to nominally 8 wt. % oxalic acid would be the method for chemical cleaning[1]. The structural integrity of waste tanks going through the Cleaning Activities Life Cycle was shown to remain acceptable through the entire proposed cleaning process assuming a total of 1460 days of process activities which includes the waste tank being exposed to OA for 365 days (Feeding 4 to 8 wt% oxalic acid at 60 to 75°C with no mixing for ≤ 30 days and the remainder of time at ≤ 4 wt% oxalic acid at 60°C) for chemical cleaning activities [1]. The presence of corrosion inhibitors was not considered in the analysis. Therefore, if the tank has been declared a waste tank in the Cleaning Activities Life Cycle no minimum hydroxide or nitrite concentrations are required (Table 7).

Acidic Chemical Cleaning Impacts to Treatment Tanks

The goal of acidic chemical cleaning is to break-up and dissolve the residual sludge solids heel (< 10,000 gallons) that remains in the tank so that final closure activities (i.e., grouting of the tank) may proceed. The baseline process for chemical cleaning utilizes oxalic acid (OA) and the tank that is being cleaned is

referred to as the treatment tank. OA at a maximum concentration up to 8 wt% is added to a treatment tank followed by water to dilute the solution to ≤ 4 wt%. The evolution of adding acid to the treatment tank, diluting with water, operating the mixing pumps, and transferring the solution to a receipt tank will be completed in a short period.

Corrosion of carbon steel waste tanks and dissolution of iron oxides in oxalic acid can result in a build-up of ferrous ions and ferric oxalate complexes in an acidic environment. During the chemical cleaning process, the concentration of ferric species increases due to dissolution of iron oxides such as hematite, magnetite, and iron oxide corrosion products such as goethite or lepidocrocite that reside in the sludge solids and in a layer of mill scale or corrosion product on the tank wall. Ferric ions may also evolve as ferrous species which react with oxygen present in the solution. Ferric oxalate complexes are relatively stable and remain soluble in oxalic acid; however ferrous ions could also result in the deposition of ferrous oxalate at the metal surface. This ferrous oxalate can serve to passivate the surface and mitigate corrosion.

Laboratory test were conducted to [References 25 and 64] to correlate the impact of OA sludge dissolution of Purex and HM sludge on waste tank corrosion and the propensity for corrosion induced hydrogen generation. Tests were performed with a 20:1 volume ratio of OA to sludge for acid concentrations of 8 wt%, 4 wt%, and 2.5 wt% with and without agitation. The tests also varied temperatures between 25-75°C. From Reference 25, corrosion rates were observed during a simulated waste test of 8 wt% OA in contact with Purex sludge (Tank 5 simulated sludge). Testing used vertical coupons to simulate the primary tank wall. Corrosion rates increased with an increase in temperature and agitation. Localized forms of corrosion were not an issue. Laboratory tests were also performed on an HM simulant at four conditions representative of the anticipated maximum operating conditions that may occur during the acidic chemical cleaning process [64]. The tests were performed with a 20:1 volume ratio of OA and sludge in contact with 8 wt%, 4 wt%, and 2.5% wt% acid concentration with and without agitation at 60 and 75°C. Test included a series of carbon steel coupon immersions and in-situ electrochemical tests conducted concurrently. Polished ASTM A285 grade C carbon steel coupons were immersed in sludge simulant/OA mixtures and removed from the test solution according to a four week planned interval test program. The program allowed for the assessment of changes in solution corrosivity and/or metal corrodibility over an extended period of time. The coupons were analyzed by gravimetric techniques (i.e., weight loss) to determine time-averaged general corrosion rates and pit penetration depths for each environmental condition.

Test results from coupon immersion in 2.5 and 4 wt.% OA at 60 °C with mixing indicated that general corrosion was the dominant corrosion mechanism at these conditions. Time averaged general corrosion rates decreased over the test interval. The solution corrosivity decreased over the four week test and general corrosion rates indicated that the metal corrodibility increased. This indicates that the

ferrous oxalate became less effective at passivating the surface over the duration of the test.

At 8 wt% OA and 60 °C with mixing, tests results indicate that both general corrosion and pitting occur. The time averaged general corrosion rates increased with each time interval for the test at 60 °C with mixing. General corrosion rate and maximum penetration shows that the solution corrosivity increased over the four week test. The general corrosion rate indicated that the metal corrodibility decreased over the four week test. This result indicates that the ferrous oxalate became more effective at passivating the surface over the duration of the test. Maximum penetration on the other hand indicated that the metal corrodibility increased over the duration of the test. This indicated that the passive film was less protective against metal penetration.

At 8 wt% OA and 75 °C stagnant tests results indicate that both general corrosion and pitting occur. The time averaged general corrosion rates decreased with each time interval. This result indicated that the solution had become less aggressive and/or the ferrous oxalate film had become more protective as the test progressed. Maximum and average pit depths also increased for each of the time intervals through the 3 week test. Both general corrosion rate and maximum penetration shows that the solution corrosivity decreased over the four week test. General corrosion rate indicated that the metal corrodibility also decreased over the four week test. This result indicates that the ferrous oxalate became more effective at passivating the surface and that the ferric oxalate complex has depleted over the duration of the test.

The corrosion rate is directly proportional to the hydrogen generation rate at potentials where hydrogen evolution is the dominant cathodic reaction. Linear polarization resistance was utilized to determine instantaneous corrosion rates (ICR) during this period. The maximum observed corrosion rates during the period where hydrogen was both thermodynamically and kinetically favored was converted to hydrogen generation rates. The hydrogen generation rate determined in Reference 64 will be utilized as the safety analysis value (i.e., 4.3E-05 ft³/min-ft²) imposed by the Flammability Control Program Description Document.

Acidic Chemical Cleaning Impact to Waste Tank Transfer Facility

The Waste Tank Chemical Cleaning Program imposes controls to maintain transfers from Acidic Chemical Cleaning Tank at 60 °C or less at an OA concentration of 4 wt% or less [62]. Based on recent testing [64] at these conditions the highest general corrosion rate is 45 mpy.

Reference 67, which addresses the transfer times for spent chemical cleaning solution in the transfer facility from Tank 12 to HDB2 and allowable stresses based on wall thinning was revised to reflect recent DSA controls as a result of testing in Reference 64. The maximum time allowed for spent chemical cleaning solution in the transfer facility for existing 3" Sch. 40 carbon steel transfer line is 617 days without exceeding ASME B31.3 code allowable stresses.

Acidic Chemical Cleaning Corrosion Impact to Receipt Tank(s)

Applicable active receipt tank will be selected to receive dissolved sludge from the chemical cleaning process where it will be utilized to neutralize spent oxalic acid. Laboratory tests have demonstrated that if the waste in the chemical cleaning receipt tank is not agitated, the less dense oxalic acid solution will accumulate at the surface [25 and 68]. To diminish potential corrosion, mixing must be accomplished quickly to neutralize the less-dense-acidic oxalic layer. The same tests demonstrated that short periods of moderate energy mixing were sufficient to blend the liquid layers and raise the pH of the solution near the surface.

4.2.3 HUMIDITY

Annulus ventilation is not required for waste tanks in the Cleaning Activities Life Cycle stages because significant corrosion degradation due to intermittent condensation on the tank wall is not anticipated during the short-term closure process [1]. **However, annulus ventilation is a credited control imposed by the Flammability Control Program.**

4.3 Final Stabilization Life Cycle

Active corrosion protection for waste storage tanks in the Final Stabilization Preparation stage is not required and the tank is exempt from the Corrosion Control Program Description Documents controls. Final Stabilization Preparation Life Cycle applies to waste tanks in Closure Mode. The Closure Mode tank is physically and electrically isolated from support services (e.g. thermocouples, riser access, annulus ventilation, etc.) in preparation for final stabilization with grout. Final grouting is authorized via a stringent review and approval process. This approval process can result in a significant delay from the time the tank enters the Final Stabilization Preparation life cycle stage to the time the tank is finally grouted. Administrative controls require the tank be stabilized within 10 years and any return to service shall be authorized only by engineering evaluation(s) ensuring the integrity of the tank is sufficient to meet the intended return to service DSA mode designation.

A fracture assessment [63] demonstrated that the risk of brittle fracture of Type I and II tanks in Closure Mode is unlikely.

5.0 Program Controls

5.1 Normal Operations

5.1.1 TEMPERATURE CONTROLS

Thermocouples

A functional thermocouple is required in each waste phase (supernate, sludge, and salt) for all tanks except for the supernate phase in the evaporator drop tanks. Drop tanks do not require a functional supernate thermocouple while the evaporator is operating. However, a functioning supernate thermocouple is required within 7 days of cessation of evaporator operations.

A functional thermocouple is required to monitor the steel wall temperature on all Type I, II, III, and IIIA waste tanks. Tanks 1-15 and 29-34 also require a steel wall thermocouple within 3 feet of the bottom knuckle weld.

An instrument loop calibration must be completed annually for the thermocouples in each waste tank. This is to ensure that the thermocouples are functioning properly. In addition, the steel wall thermocouples for Tank 1-15 and 29-34 must be checked bi-annually by visual inspection (i.e., cameras) to ensure they are still attached to the tank wall within 3 feet of the bottom knuckle weld.

If a transfer into or out of a tank results in a waste phase containing no functional TC, the TC in the adjacent phase may be used if it is determined to be representative (similar to or hotter than). The only exception is for evaporator drop tanks during evaporator operations. During this time, the supernate temperature limits do not apply to these tanks. [Basis: The evaporator drop tanks are excluded from supernate temperature requirements during evaporator operation due to the fact that the liquid/air interface during this time is moving (not stagnant), the evaporator is actually concentrating caustic in the drop tank, the liquid that is dropping is not boiling, and past experience shows that evaporator bottoms have been used to actually stop corrosion (evaporator bottoms were transferred to Tank 11 in the late 1960s in order to mitigate cooling coil failures [43]). However, the temperature limits do apply when the tank is no longer functioning as a drop tank, but rather as a storage tank (7 days following the termination of evaporator operation).

Roundsheets, ticklers, or PassPort will be used to prompt and record the temperature readings. Loop calibrations will be prompted by PassPort. Loop calibrations for tanks in Acidic Chemical Cleaning mode will be prompted through the Surveillance Tracking Database.

Temperature Limits

Minimum Temperature Limits

Maintaining the tank temperature above the nil ductility transition temperature (NDTT) for carbon steel tanks during Normal Operations and Cleaning Activities Life Cycle (excluding tanks in Acidic and Non-Acidic Chemical Cleaning Mode) are intended to minimize the probability of failure due to brittle fracture. Table 2 provides the wall temperature limits necessary to reduce the risk of brittle fracture to acceptable levels. No wall temperature limit is required for Tank 38 through Tank 51 to maintain the NDTT due to the unlikely probability of achieving a tank wall temperature of -12 °C [1].

Table 2- Minimum Temperature Limits for Nuclear Waste Tanks

Tanks	Tank Type	Wall Temperature Limits (° C) for Normal Operation and Cleaning Activities Life Cycle ¹	Temperature Limits for Final Stabilization Preparation Life Cycle
1 -12	Type I	21	No Monitoring Required
13-15	Type II	21	No Monitoring Required
21-24	Type IV	N/A	N/A
29-34	Type III	21	No Monitoring Required
25-28, 35-37	Type IIIA	15	No Monitoring Required
38-51	Type IIIA	No Monitoring Required	No Monitoring Required

Note: (1) Minimum wall temperature limits are not applicable to Type I/II Chemical Cleaning Waste Tanks

Maximum Temperature Limits

Maximum temperature limits for the waste and tank wall are specified to minimize the risk of corrosion. The following tables provide temperature limits dependent upon the concentration of nitrate and inhibitors.

Table 3. Maximum Temperature Limits For Supernate (T_{sup}) With Nitrate Concentrations Greater Than Or Equal To 1 Molar (M) (See Note 1 and 3)

Nitrate (M)	R<2	R \geq 2
$1.0 \leq [NO_3^-] \leq 2.75$	70°C	105°C
$2.75 < [NO_3^-] \leq 5.5$	105°C	112°C
$5.5 < [NO_3^-] \leq 8.5$	70°C	See Note 2
Applicable for [OH] \geq 8 M		
Nitrite (M)	T \leq 10	
$[NO_2^-] \geq 0.3$	115°C	

T_{sup} = supernate temperature

$$R = ([NO_2^-] + [OH^-]) / [NO_3^-]$$

$$T = [OH^-] / ([NO_3^-] + [NO_2^-])$$

Note 1: For the most recent concentrations of nitrate, nitrite, and hydroxide in each tank, review the WCS.

Note 2: Due to the liquid solubility limitations, it is not possible to have these supernate compositions.

Note 3: Lower temperature limit of 50 °C applies during Salt Dissolution Processing

Table 4. Maximum Temperature Limits For The Sludge/Salt and Steel Wall (T_{ss} , T_w) With Nitrate Concentrations Greater Than Or Equal To 1 Molar (M) (See Note 1).

Supernate Concentration	R < 2		R \geq 2	
	Liquid Level < 120 inches	Liquid Level \geq 120 inches	Liquid Level < 120 inches	Liquid Level \geq 120 inches
$1.0 \leq [NO_3^-] \leq 2.75$	$T_{ss} = 105^\circ C$ $T_w = 100^\circ C$	$T_{ss} = 115^\circ C$ $T_w = 110^\circ C$	$T_{ss} = 105^\circ C$ $T_w = 100^\circ C$	$T_{ss} = 115^\circ C$ $T_w = 110^\circ C$
$2.75 < [NO_3^-] \leq 5.5$	$T_{ss} = 105^\circ C$ $T_w = 100^\circ C$	$T_{ss} = 115^\circ C$ $T_w = 110^\circ C$	$T_{ss} = 112^\circ C$ $T_w = 107^\circ C$	$T_{ss} = 122^\circ C$ $T_w = 117^\circ C$
$5.5 < [NO_3^-] \leq 8.5$	$T_{ss} = 105^\circ C$ $T_w = 100^\circ C$	$T_{ss} = 115^\circ C$ $T_w = 110^\circ C$	See Note 2	See Note 2

T_w = Waste tank steel wall temperature

T_{ss} = Temperature of the salt or sludge phase

Note 1: For the most recent concentrations of nitrate, nitrite, and hydroxide in each tank, review the WCS.

Note 2: Due to liquid solubility limitations it is not possible to have these supernate compositions.

Note 3: Applicable to sludge/salt temperatures and steel wall for "Dry" tanks.

Table 5. Maximum Temperature Limits For Waste Tanks With Nitrate Concentrations Less Than 1 Molar (M) (See Note 1).				
Supernate Concentration	T_{sup}		T_{ss}, T_w	
	$[NO_3^-] \leq 0.02 \text{ M}$	$0.02 \text{ M} < [NO_3^-] < 1 \text{ M}$	$[NO_3^-] \leq 0.02 \text{ M}$	$0.02 \text{ M} < [NO_3^-] < 1 \text{ M}$
$0.01 < [OH^-] \leq 1$	40°C	40°C	$T_{ss} = 75^\circ\text{C}$ $T_w = 70^\circ\text{C}$	$T_{ss} = 75^\circ\text{C}$ $T_w = 70^\circ\text{C}$
$1 < [OH^-] \leq 8$	60°C	100°C	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$	$T_{ss} = 100^\circ\text{C}$ $T_w = 95^\circ\text{C}$
$[OH^-] > 8$	60°C	60°C	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$

Note 1: For the most recent concentrations of nitrate, nitrite, and hydroxide in each tank, review WCS.

Table 6. Maximum Temperature Limits For Bulk Waste Removal Tanks (See Note 1) With Nitrate Concentrations Less Than 1 Molar (M) (See Note 2).				
Supernate Concentration	T_{sup}		T_{ss}, T_w	
	$[NO_3^-] \leq 0.02 \text{ M}$	$0.02 \text{ M} < [NO_3^-] < 1 \text{ M}$	$[NO_3^-] \leq 0.02 \text{ M}$	$0.02 \text{ M} < [NO_3^-] < 1 \text{ M}$
$0.01 < [OH^-] \leq 1$	75°C	75°C	$T_{ss} = 75^\circ\text{C}$ $T_w = 70^\circ\text{C}$	$T_{ss} = 75^\circ\text{C}$ $T_w = 70^\circ\text{C}$
$1 < [OH^-] \leq 8$	60°C	100°C	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$	$T_{ss} = 100^\circ\text{C}$ $T_w = 95^\circ\text{C}$
$[OH^-] > 8$	60°C	60°C	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$	$T_{ss} = 60^\circ\text{C}$ $T_w = 55^\circ\text{C}$

Note 1: Applicable to waste tanks being slurried for a period starting when one or more mixing pumps have operated at or above minimum speed for 3 hours or more. The temperature limit can be extended up to 30 days after the pumps/mixers are shutdown. Waste Tanks that are slurried with nitrate concentration greater than or equal to 1 M are subject to the limits in Tables 3 and 4.

Note 2: For the most recent concentrations of nitrate, nitrite and hydroxide in each tank, review WCS.

Compensatory Measures

The following required actions are designed to ensure that the time period over which a waste tank is susceptible to corrosion is minimized.

1. If the waste tank temperature does not meet the minimum requirements of Table 2 and/or exceeds the limits established in Tables 3, 4, 5, and 6, with the

-
- exception of the supernate temperature limits for evaporator drop tanks during evaporator operations, the following shall occur:
- A. CSTF Engineering (CSTFE) shall be notified by CSTF Operations (CSTFO) of the condition within 24 hours if Operations is unable to bring the temperature within limits before this time is expired.
 - B. CSTF Engineering shall provide, within 5 days of notification, an evaluation that includes suggested actions needed to bring the tank temperature into compliance with Tables 2, 3, 4, 5, and 6. The evaluation shall also include the expected time needed to perform necessary actions. If mixing pumps are in operation at the time the condition is recognized, Engineering shall assess whether they should continue operation. If the temperature is restored within the limits listed in Tables 2-6 before the 5 days have expired, engineering does not have to provide an evaluation.
2. If the thermocouple for the supernate, salt, and/or sludge phases is not functional, or if the thermocouple for the steel wall is not functional (or the magnetic thermocouple attached to the outside of the primary tank wall of Tanks 1-15 or 29-34 becomes detached), the following actions shall occur: (Only applies to Type I, II, III, and IIIA waste tanks, excluding evaporator drop tanks during evaporator operation)
- A. The thermocouple shall be restored to functionality, or an alternate (e.g., a representative one in an adjacent phase) thermocouple shall be used to monitor the temperature of the affected waste phase or steel wall within 7 days after the condition is noticed. The normal monitoring frequency shall continue with the alternate thermocouple if the thermocouple is not restored.
 - B. If mixing pumps are in operation at the time of the thermocouple's failure, CSTF Engineering shall be notified to provide guidance on whether operation of the mixing pumps should continue.
 - C. A functional wall temperature thermocouple shall be restored in the affected waste phase/tank steel wall within 45 days. If requirements cannot be met within the allotted time frame, a path forward shall be written for restoration and approved by the Facility Operations Safety Committee (FOSC).
3. If there are no functional or representative thermocouples available in a Type IV waste tank, the following actions shall occur:
- A. CSTF Engineering shall be notified if there are any mixing pumps in operation in the affected tank. Engineering shall provide guidance as to whether or not the mixing pumps should remain in operation.
 - B. A representative thermocouple shall be functional in the tank within 30 days.
4. The maximum supernate temperature limit during salt dissolution processing

is 50 °C. This is lower than the current corrosion control program requirement at the estimated nitrate concentration for dissolved salt solutions ($\text{NO}_3 > 1\text{M}$). This lower temperature will further reduce the risk of corrosion. Laboratory testing at the expected inhibitor concentrations has indicated that the risk of significant corrosion at temperatures less than or equal to 50 °C, for short term exposures (e.g., less than 100 days) is low in these high nitrate solutions [Ref. 73].

Monitoring Frequencies

1. A heat load of 0.10 Btu/hr/gal in a waste tank, conservatively assuming the waste has the properties of water with no external heat removal, can produce a 5°C rise in temperature in a month. Heat loading would normally drive the required monitoring frequencies however, during normal operations it is checked daily per the DSA. For all active and inactive Type I, II, III, IIIA, and IV tanks, verify that the tank waste temperatures (supernate, salt, sludge, and steel wall as applicable) are no greater than the maximum temperature limits as listed in Tables 3, 4, 5, and 6 and steel wall temperatures do not go lower than the minimum requirements in Table 2 (as applicable) daily or every shift during slurry pump operation, unless an engineering evaluation justifies a longer frequency.
2. Perform an instrument loop calibration of thermocouples for each tank every 365 days.
3. For the active Type I, II, III, and IIIA tanks and inactive Type I, II, III, and IIIA tanks with heat loads above 0.10 Btu/hr/gal, ensure that the thermocouples used for reporting temperatures in each waste phase are reading representative phase temperatures every 90 days.
4. For the inactive Type I, II, III, and IIIA tanks with heat loads below 0.10 Btu/hr/gal, ensure that the thermocouples used for reporting temperatures in each waste phase are reading representative phase temperatures every 365 days.
5. Inspect the steel wall TCs for Tanks 1-15 and 29-34 and verify that they are attached to the steel primary wall within 3 feet of the bottom knuckle weld every 730 days.
6. Prior to each waste transfer and prior to operating mixing pumps, which have changed height, verify that there will be a functional, or functional alternate, thermocouple for each resulting waste phase. Operating (WTS, WTE) procedures shall ensure the compliance with this requirement.

5.1.2 CHEMISTRY CONTROLS

Chemistry Limits

In order to prevent corrosion, the appropriate amount of inhibitor must be present in the tank to sufficiently balance the nitrate concentration. The following table, Table 7, shows the required concentration of either hydroxide or nitrite for the

corresponding amount of nitrate in the waste tanks. The analytical uncertainties associated with the constituents of concern for the corrosion control program are within the conservatism applied in the establishment of those limits [60].

Table 7. Minimum Corrosion Inhibitor Concentration Limits					
Applicability	Limit	Parameter	Minimum Needed	Units	
5.5M < [NO ₃ ⁻] ≤ 8.5M	1	[OH ⁻]	0.6	Molar	
		[OH ⁻] + [NO ₂ ⁻]	1.1	Molar	
2.75M < [NO ₃ ⁻] ≤ 5.5M	2	[OH ⁻]	0.3	Molar	
		[OH ⁻] + [NO ₂ ⁻]	1.1	Molar	
1.0M ≤ [NO ₃ ⁻] ≤ 2.75M	3	[OH ⁻]	0.1[NO ₃ ⁻]	Molar	
		[OH ⁻] + [NO ₂ ⁻]	0.4[NO ₃ ⁻]	Molar	
0.02M < [NO ₃ ⁻] < 1.0M AND [OH ⁻] < 1.0M (See Note 2)	4	4a [OH ⁻]	1.0	Molar	
		OR			
		4b [NO ₂ ⁻]	0.038·[NO ₃ ⁻]·10 ^{1.64}	Molar	
		4c AND [NO ₂ ⁻]	6.11·10 ^{[1.64+1.34*\log[Cl⁻]]}	Molar	
		4d AND [NO ₂ ⁻]	0.04·10 ^{[1.64+0.84*\log[SO₄⁻²]]}	Molar	
		4e AND pH	10.3	pH	
[NO ₃ ⁻] ≤ 0.02 M AND [OH ⁻] < 1.0 M (See Note 2)	5	5a [OH ⁻]	1.0	Molar	
		OR			
		5b [NO ₂ ⁻] (if [Cl ⁻] $\&$ [SO ₄ ⁻²] is not known)	0.033	Molar	
		OR			
		5c [NO ₂ ⁻]	0.038·[NO ₃ ⁻]·10 ^{1.64}	Molar	
		5d AND [NO ₂ ⁻]	6.11·10 ^{[1.64+1.34*\log[Cl⁻]]}	Molar	
		5e AND [NO ₂ ⁻]	0.04·10 ^{[1.64+0.84*\log[SO₄⁻²]]}	Molar	
5f AND pH	10.3	pH			
Applicable to Tank 48 ONLY [NO ₃ ⁻] ≤ 1.0M AND [OH ⁻] < 1.0M	6	6a [NO ₂ ⁻]	0.91[NO ₃ ⁻] ^{0.79}	Molar	
		6b AND [NO ₂ ⁻]	1.5·10 ^{[1.35+1.03*\log[Cl⁻]]}	Molar	
		6c AND [NO ₂ ⁻]	1.5·10 ^{[-0.22+0.61*\log[SO₄⁻²]]}	Molar	
Influents to waste tanks from other areas on site (See Note 1).		pH	9.5	pH	

Note 1: Waste Acceptance Criteria provides the means for controlling the pH of influents to the tank farm. These influents do not include rainwater, raw water flushes, etc.

Note 2: The inhibitor requirements in Limits 4 & 5 are based upon a supernate temperature of 40°C.

Note 3: Tanks designated as being in the Cleaning Activities Life Cycle are exempt from the inhibitor requirements shown in this table.

Sampling Schedule

In order to assure that the chemistry in each tank stays within the limits given in Table 7, every tank’s supernate must be sampled periodically. A 30 day grace period is permitted in meeting this frequency. Table 8 identifies the frequency with which a tank must be sampled, based on that tank’s status and last known chemistry. If a tank has been sampled 15 times since receiving waste in a waste tank to waste tank transfer and the statistical capability of the tank to meet the minimum corrosion inhibitor limits (Sigma Level) can be established, the sample frequency shall be determined from Table 9. In either case, the sample frequency for each tank shall be noted in the ERD. The PassPort system, or its equivalent, shall be utilized to ensure that the samples are taken to meet the requirements of this section.

Status	Category	Inhibitor Levels	Frequency
ACTIVE WASTE TANKS	Evaporator Feed And Drop Tanks	$[\text{NO}_3^-] < 1\text{M}$ or $[\text{OH}^-] < 2.35\text{M}$ or $[\text{S}] < 3\text{M}$	90 days
		$[\text{NO}_3^-] \geq 1\text{M}$ or $[\text{OH}^-] \geq 2.35\text{M}$ or $[\text{S}] \geq 3\text{M}$	180 days
	Fresh Canyon Waste Receiver with Nitrate Concentration Greater Than or Equal to 1M	$[\text{OH}^-] < 3\text{M}$ or $[\text{S}] < 4\text{M}$	180 days
		$[\text{OH}^-] \geq 3\text{M}$ or $[\text{S}] \geq 4\text{M}$	365 days
	Receiver with Nitrate Concentration Less Than 1M	$[\text{NO}_2^-]/[\text{NO}_3^-] < 3.4$ or $[\text{OH}^-] < 0.02\text{M}$	90 days
		$3.4 \leq [\text{NO}_2^-]/[\text{NO}_3^-] < 4.8$ and $0.02\text{M} \leq [\text{OH}^-] < 2.35\text{M}$	180 days
		$[\text{NO}_2^-]/[\text{NO}_3^-] \geq 4.8$ or $[\text{OH}^-] \geq 2.35\text{M}$	365 days
	Receiver with Nitrate Concentration Greater Than or Equal to 1M	$[\text{OH}^-] < 2.35\text{M}$ or $[\text{S}] < 3\text{M}$	180 days
		$2.35\text{M} \leq [\text{OH}^-] < 3\text{M}$ and $3\text{M} \leq [\text{S}] < 4\text{M}$	365 days
		$[\text{OH}^-] \geq 3\text{M}$ or $[\text{S}] \geq 4\text{M}$	730 days
	Bulk Waste Removal Tanks	N/A	30 days
Sludge and Salt Feed Tanks	NA	730 days	
INACTIVE WASTE TANKS	Nitrate Concentration Less Than 1M	$[\text{NO}_2^-]/[\text{NO}_3^-] < 3.4$ or $[\text{OH}^-] < 0.02\text{M}$	180 days
		$3.4 \leq [\text{NO}_2^-]/[\text{NO}_3^-] < 4.8$ and $0.02\text{M} \leq [\text{OH}^-] < 2.35\text{M}$	365 days
		$[\text{NO}_2^-]/[\text{NO}_3^-] \geq 4.8$ or $[\text{OH}^-] \geq 2.35\text{M}$	730 days
	Nitrate Concentration Greater Than or Equal to 1M	$[\text{OH}^-] < 2.35\text{M}$ or $[\text{S}] < 3\text{M}$	365 days
		$2.35\text{M} \leq [\text{OH}^-] < 3\text{M}$ and $3\text{M} \leq [\text{S}] < 4\text{M}$	730 days
		$[\text{OH}^-] \geq 3\text{M}$ or $[\text{S}] \geq 4\text{M}$	1460 days
Chemical Receipt Tank	Chemical Cleaning Activities	Compliant with Table 7	90 days

$$S = [\text{OH}^-] + [\text{NO}_2^-]$$

Table 9. Sample Frequency for Waste Tanks Based on Statistical Analysis	
<i>Inactive Tanks with Nitrate Concentrations Less Than or Equal to 1 Molar and Active Tanks</i>	
Sigma Level	Frequency
0 - 2.99	90 days
3.00 - 3.49	180 days
3.50 - 3.99	365 days
4.00 or greater	730 days
<i>Inactive Tanks with Nitrate Concentrations Greater Than 1 Molar</i>	
Sigma Level	Frequency
0 - 2.99	180 days
3.00 - 3.49	365 days
3.50 - 3.99	730 days
4.00 or greater	1460 days

If the sample frequency is increased such that the next required sample is past due, then the next sample should be scheduled within a grace period of 30 days from the date that the new sample frequency is noted in the ERD. The sampling frequency for a slurried BWR tank can be extended only by an engineering evaluation. This evaluation must discuss the possible risks of extending the frequency and must provide adequate justification of the risks. The Facility Manager's concurrence with this evaluation shall provide the necessary authority to extend that tank's sampling frequency.

An engineering evaluation may be performed to allow the exclusion of a tank undergoing waste removal activities from this sampling frequency schedule. Such an evaluation must demonstrate that the risk of corrosion in the tank is minimal and explain any actions needed to retain the integrity of the waste tank (i.e., inhibitor additions). This evaluation should estimate the amount of corrosion that would occur during the time period between its exit from the sampling schedule until it is closed. If the evaluation shows that the tank wall integrity will not be lost during the anticipated time frame, that tank can be exempted from the program. The evaluation should also discuss the need to increase annulus leak detection monitoring. The concurrence of the Facility Manager on such an evaluation will automatically exempt that tank from the sampling frequencies shown above. If any of the assumptions (i.e., timeframe, chemistry, etc.) change after the evaluation is written, the tank must be re-evaluated using the new conditions to determine whether it is still safe to remove the sampling frequency requirements.

The Extended Sludge Processing (ESP) (i.e., Tanks 40 and 51) tanks are well characterized and all incoming streams are known. These tanks are treated as “receiver” tanks rather than Bulk Waste Removal tanks.

Water Additions to Waste Tanks

During normal operations of the tank farms, water must be added occasionally to a waste tank as a result of some form of flushing. These water additions could potentially change the chemistry of the waste tank and present a possibility for the chemistry to fall outside the limits set in Table 7. If more than 3,000 gallons of water are to be added to a tank, a pre-evaluated transfer approval form (pre-ETAF) or an engineering evaluation shall be completed. This evaluation should discuss the ramifications of adding large amounts of water to the tank and should also provide any necessary compensatory measures such as sampling or chemical additions. If the receipt tank has a specific gravity higher than 1.20, the evaluation should also discuss the possibility of stratification, and provide guidance on restoring the chemistry within the established limits.

Compensatory Measures

The following actions are required in order to minimize the risk of corrosion in a waste tank.

1. If the hydroxide and/or nitrite concentrations are outside the corrosion inhibitor limits shown in Table 7 the following actions shall be taken:
 - A. CSTFE shall provide CSTFO guidance regarding the continuance of waste transfers and the continued operation of mixing pumps. This guidance shall be given within 24 hours.
 - B. The chemistry in the tank shall be restored and/or a sample pulled within 45 days to verify the chemistry is within the required limits, unless an extension is justified by an engineering evaluation. This action may require the addition of corrosion inhibitors and/or concentrated supernate.
 - If the chemistry is restored in a well-mixed tank (one mixing pump operating for a total of 8 hours) or Evaporator Drop Tank, compliance can be justified by a material balance evaluation.
 - If the chemistry is restored through diffusion or pump recycles, a sample is required to verify restoration. CSTFE shall provide direction concerning chemical additions and sample verification of the supernate.
2. If a Type III/IIIA tank waste chemistry is outside of the inhibitor or temperature requirements for more than 3 months a UT examination of a

single, random vertical strip and a previously inspected area shall be performed within one calendar year of the date the tank chemistry was determined to be noncompliant [Ref. 72]. For Type III/IIIA tanks that are undergoing Salt Dissolution, a UT examination is required if the tank chemistry is out of compliance and the liquid air interface is stagnant for more than 3 months.

3. If the liquid level in an inactive waste tank increases by greater than 3,000 gallons during the period of 30 days (checked once every 30 days), not related to transfers, Engineering shall provide an evaluation to determine the need for any remedial action within 5 days.
4. For additions of water greater than 3,000 gallons, a pre-ETAF or engineering evaluation shall be provided prior to issuing a data modification tracker (DMT) for the execution of the water addition.
5. Waste tank corrosion samples shall be pulled at the frequency specified in Tables 8 and 9 and tracked in the ERD. A 30 day grace period is applicable for this. This 30 day grace period is also applicable when an increase in sample frequency results in a sample which is overdue. If the 30 day grace period will not be met, Engineering shall specify remedial actions and required timing.
6. Completion of corrosion sample analysis is required within 90 days of the date that the sample was pulled and shall be tracked in the ERD. A 30 day grace period is applicable to this requirement. If the 30 day grace period will not be met engineering shall specify remedial actions and required timing.
7. Minimizing the time noncompliant chemistry is stagnant during salt dissolution will mitigate the risk for pitting at the liquid air interface in a salt dissolution tank and mitigate the risk for nitrate stress corrosion cracking in a dissolved salt solution receiver tank for a Type III/IIIA tank that has been stress relieved. Salt dissolution processing strategy shall be implemented and controlled through Operating Procedures.
 - A. The maximum allowable dissolution time is 4 weeks. Dissolution time being from the completion of the water addition into the tank to the start of the next water addition.
 - B. The maximum allowable stagnant time in a dissolved salt solution receiver tank is 4 weeks.
 - C. A transfer out or liquid addition of 6 inches or greater can reset the dissolution time or stagnant time.
 - D. If the dissolution or stagnant time goes beyond 4 weeks an action plan for inhibiting the free liquid above the salt cake shall be implemented and

completed within 45 days.

- E. A confirmation sample shall be taken to verify that the supernate chemistry at the liquid air interface is in compliance with Table 7.

For non-stress relieved Type I, II, or IV salt dissolution receiver tanks:

- F. Dissolved salt solution shall not be transferred into a Type I, II, or IV waste tank unless the chemistry of the dissolved salt solution has been determined by a sample and/or flowsheet evaluation.
- G. If the sample result shows that the waste is within the current inhibitor requirements, the dissolved salt solution may be transferred.
- H. If the sample result shows that the waste is not within the current inhibitor requirements, the dissolved salt solution receiver tank may be pre-conditioned prior to the transfer so that the final composition of the waste in the dissolved salt receiver tank meets the current inhibitor concentration requirements. An evaluation to determine the amount of inhibitor needed to pre-condition the tank will be necessary as well as any mixing requirements.

Monitoring Frequencies

The following monitoring activities are required to ensure that each tank complies with the chemistry limits established in Table 7 and is monitored in accordance with Tables 8 and 9.

1. Each tank that contains liquid waste shall be periodically sampled in accordance with Table 8 & Table 9. The sample frequency dictated by Table 8 & Table 9 shall be shown in the ERD. The ERD must be updated when these frequencies change.
2. All dry salt tanks shall receive an annual video inspection to ensure tank conditions have not changed. The video inspection frequency shall be tracked by tickler or in the Passport system or its equivalent to ensure requirements are being met.
3. Prior to each waste tank to waste tank transfer, verify that the corrosion inhibitors of the receiving tank will remain within the limits established in Table 7 after the transfer is completed or perform an engineering evaluation to provide a technical justification to authorize temporarily taking the tank out of strict compliance with Table 7.

Evaporator Tube Bundle Corrosion Control

The evaporator tube bundle shall be submerged in an inhibited solution, as defined in the background section of this program, within 30 days of the removal of waste from the

evaporator pot. A failed tube bundle that is deemed OOS with no intention for return to service is exempt from the corrosion protection requirements.

Compensatory Measures

If more than 30 days elapse before the tube bundle is submerged in an inhibited liquid (as defined in the background section of this program), hydrotesting of the tube bundle must be performed to verify the integrity of tube bundle within one week prior to restarting the evaporator.

Prevention of Microbiologically Influenced Corrosion (MIC) in Transfer Lines, Evaporator Systems and Waste Tanks

Waste Tanks are protected from MIC due to the typically high hydroxide levels, salt levels, radiation fields, and non-stagnate conditions. Transfer lines and evaporator systems must be protected from conditions that could lead to MIC. The following measures ensure that these conditions do not occur.

Compensatory Measures

1. If there is a known "low" point in a transfer line, as shown in the SI program, and a flush is required, use inhibited water (pH>12) to flush that transfer line, unless another waste transfer is planned through that line within the next 5 days. If a line is flushed with uninhibited well water because another transfer is anticipated and that anticipated transfer does not occur, the line shall be flushed with inhibited water before the 5 days have expired.

Cooling Coil Corrosion Control

Cooling coils must be protected, both from the interior and exterior, from corrosion. The exterior of the cooling coils is protected by the chemistry and temperature limits imposed on the waste in each waste tank. The following compensatory measures and monitoring activities are intended to reduce the failure of cooling coils due to internal corrosion. A cooling coil that has failed leak testing and is deemed OOS by the Facility Manager is exempt from the cooling coil protection requirements.

Compensatory Measures

1. All functional, isolated cooling coils shall be flushed with chromate cooling water every 90 days, if not designated as a waste tank in Closure Mode.

Monitoring Frequencies

1. Chromate cooling water shall be sampled every 90 days to ensure that the chromate level in the water is sufficient to inhibit corrosion (>450 ppm).

Vapor Space Corrosion Controls

Table 10 provides supernate chemistry control limits for a tank that is inactive for more than six months [70]. If the tank is active during the six month period, the limits in Table 7 remain applicable. These limits apply only to Type III/IIIA tanks. Compliance with these limits will be accomplished by quarterly engineering evaluations to identify any tanks that may not be compliant with the vapor space criteria.

Table 10 – Minimum Chemistry Requirements for Tanks That Have Been Inactive for More than Six Months

Applicability	Parameter	Minimum Needed (M)
1 < [NO ₃ ⁻] ≤ 8.5	[OH ⁻]	1
	AND [NO ₂ ⁻]	0.2
	OR	
	[OH ⁻]	0.6
	AND [NO ₂ ⁻]	0.6
	AND [NO ₂ ⁻]	$6.11 * 10^{(1.64+1.34 * \text{Log}([\text{Cl}^-])}$
	AND [NO ₂ ⁻]	$0.04 * 10^{[1.64+0.84 * \text{Log}([\text{SO}_4^-])}$

Compensatory Measures

1. If any Type III/IIIA tank is discovered not to be in compliance with the vapor space program during the development of the quarterly vapor space corrosion report, the following action shall be taken:
 - A. The quarterly vapor space corrosion report will recommend actions to bring the tank(s) back into compliance with the vapor space corrosion criteria provided in Table 10.

Tanks in the Cleaning Activities Life Cycle are exempt from these requirements.

5.1.3 HUMIDITY CONTROL*Steam Supply to Ventilation*

Steam shall be supplied to the annulus ventilation pre-heater in order to heat the air in the annulus. By heating the air in the annulus, the risk of corrosion due to condensation is eliminated. Every week (7 days) a check shall be made to ensure that each annulus ventilation system is receiving steam and that each annulus ventilation system is operating.

If the steel wall temperature of the tank is above 40°C (lowest steel wall temperature reading), there is no requirement for the operation of steam, unless liquid is detected in the annulus. Waste tanks are required to have an annulus conductivity probe ≤ 1 inch above the annulus floor (excluding Type IV waste tanks) unless existing waste is limiting placement, at which point the waste will serve as the floor level (Not to exceed TSR requirements). Tanks preparing to undergo waste removal are exempt from this requirement and may raise the annulus conductivity probe ≥ 1 inch above the annulus floor (Not to exceed TSR requirements). Level exemptions for waste removal shall be implemented and controlled through Operating Procedures. In the event liquid is detected, steam shall be used until the annulus is dried.

Tanks in the Final Stabilization Preparation Life Cycle designated as Closure Mode are exempt from these requirements.

Compensatory Measures

1. If the annulus ventilation is not in operation or steam is not supplied to the annulus pre-heater and the tank steel-wall temperature is below 40°C, these conditions shall be corrected within 30 days for the Type I and II tanks and within 90 days for the Type III and IIIA tanks. If no steam is available, the ventilation shall be operated continuously (as long as the tank wall temperature is above the low operating limit on the roundsheets). If requirements cannot be met within the allotted time frame, a path forward shall be written for restoration and approved by the FOOSC.
2. If liquid is detected in the annulus or if the annulus does not contain a functional conductivity probe, the following action shall be taken:
 - A. If liquid is verified to be in the annulus, the ventilation system shall be operated with steam supplied to the annulus pre-heater and Engineering shall be notified. This action shall be completed within 24 hours.
 - B. The liquid level shall be tracked until non-detectable. If the liquid level does not decrease within 48 hours of ventilation operation with steam to the pre-heater, continue to rise, and/or ventilation is not operable with steam, Engineering shall provide a path forward to address meeting structural integrity fill limits within 5 days.

Monitoring Frequencies

1. Annulus conductivity probe level shall be verified annually to ensure that the probes are ≤ 1 inch above the annulus floor or waste level in the annulus (not to exceed TSR limits). The verification frequency shall be tracked by tickler or in the Passport system or its equivalent to ensure requirements are being met.

5.2 Cleaning Activity Life Cycle

During the Cleaning Activities Life Cycle, the program allows for the suspension of corrosion inhibitor concentration requirements, sampling frequencies, and maintaining annulus ventilation requirements for up to 1460 days for waste removal activities. Since the life cycle is short, the corrosion controls imposed are greatly diminished, but are adequate to ensure that sufficient tank integrity remains to complete the closure process. Corrosion control compensatory measures and monitoring frequencies, as stated during Normal Operations for MIC and Cooling Coils still apply.

5.2.1 TEMPERATURE

Maximum Limits

In assessing the waste storage tanks, going through the cleaning activities life cycle stage, temperature was an important variable for estimation of the expected

corrosion rates during waste removal activities [1] therefore, maximum supernate temperature limits and the associated temperature compensatory measures and monitoring frequencies are applicable during the Cleaning Activities Life Cycle. Bounding temperatures for each of the activities were assumed for the analysis. The maximum temperature experienced during bulk sludge removal due to mechanical heat generated by mixing devices is expected to be 60°C. The maximum temperature for salt dissolution is expected to be 50°C. The maximum temperature in tanks storing salt cake is also approximately 50°C [23]. Additionally, salt dissolution is an endothermic process, which lowers the temperature of the waste below 50°C [24]. An engineering evaluation or an approved operating plan for a particular waste tank can exempt a tank from these temperature controls. The evaluation or operating plan must provide justification for the relaxation of controls and must be properly reviewed and approved. The maximum supernate temperature limit for oxalic acid addition during Acidic Chemical Cleaning is 75 °C. The target temperature for heel removal with oxalic acid is 50 °C [1]. However, the reaction between the oxalic acid and the sludge is exothermic and the mixer pumps will also add mechanical heat to the system [1]. Therefore a reasonable maximum temperature for the oxalic acid chemical cleaning process will be 60 °C. There are NO exemptions allowed for maximum supernate temperature limits during Acidic Chemical Cleaning.

Minimum Temperature Limits

During Chemical Cleaning of Type I/II waste tanks, the concrete vault and, in the case of the Type I tanks, the concrete columns are credited for structural integrity controls for normal operation and natural phenomena events. The steel tank wall is not credited and therefore embrittlement of the primary tank wall is not an issue. Type I/II Chemical Cleaning Waste Tanks are exempt from NDTT requirements in Table 2 [62].

Compensatory Measures

1. The initial supernate temperature for an Acidic Chemical Cleaning Treatment Tank prior to oxalic acid addition shall be < 60 °C. If the supernate temperature reaches 60 °C, valve in cooling coils to cool the supernate below 60 °C. If the supernate temperature during oxalic acid addition reaches 70 °C, stop acid addition to the treatment tank and notify CST Engineering for guidance. The effects of instrument uncertainty or accuracy shall be accounted for during comparison to these limits.
2. If the maximum supernate temperature limits for sludge removal (60°C) and salt dissolution (50°C) during the Cleaning Activities Life Cycle are exceeded, stop mixing devices and transfers out of the tank until the temperatures conform to the required limits. The effects of instrument uncertainty or accuracy shall also be accounted for during the comparison of the acidic chemical cleaning temperature limit.

Monitoring Frequencies

1. Acidic Cleaning are very low-volume operations or involve mixing pumps at high volumes. The highest temperatures are likely during the slurring process, when the pumps are adding heat to the tank and may challenge temperature limits. Consequently, temperature shall be monitored every shift when the mixing pumps are operating. After the slurring process, the mixing devices are turned off and most of the heat-generating sludge-slurry mixture is transferred out of the tank. Therefore, it is expected that the temperatures will not challenge the limits during low-volume phase of the process.

5.2.2 CHEMISTRY

For waste tanks designated in the Cleaning Activities Life Cycle stage, sampling of the waste for corrosion control purposes is suspended during waste removal activities. The limits in Tables 7, 8, 9, and 10 do not apply. The analysis [1] assumes a total of 1460 days of closure activities which includes 365 days of chemical cleaning (Feeding 4 to 8 wt% oxalic acid at 60 to 75°C with no mixing for ≤ 30 days and the remainder of time at ≤ 4 wt% oxalic acid at 60°C).

Acidic Chemical Cleaning Waste Tanks

Prior to acidic chemical cleaning, the sludge volume in the Treatment Tank shall be verified to be less than or equal to 10,000 gallons by an engineering evaluation. An evaluation shall be performed to verify a maximum of 20:1 volume ratio of 8 wt% oxalic acid to sludge utilizing mapping, historical data, and/or visual inspection. Acidic Chemical Cleaning is not allowed in Tank 1 [62].

Acidic Chemical Cleaning Transfer Path

Applicable pump tanks in the transfer path shall be pre-conditioned with supernate, sodium hydroxide or other inhibitor to neutralize the acidic waste being added to it. Implementation is controlled by the Waste Tank Chemical Cleaning Program [62]. Once a chemical cleaning transfer has occurred in a transfer line, the affected transfer line must be vented and drained. If a transfer line has received acidic chemical cleaning solution, flushing is required using inhibited water ($\text{pH} \geq 12$).

Chemical Cleaning Receipt Tanks

In addition to the chemistry limits provided in Table 7, chemical cleaning receipt tanks shall comply with the following requirements imposed by the Waste Tank Chemical Cleaning Program [62]:

1. The chemical receipt tank shall be pre-conditioned with supernate, sodium hydroxide or other inhibitor to neutralize the acidic waste being added to it; and,
2. At least one mixing device shall be operating prior to and during the addition of acidic waste to ensure neutralization of the acidic waste to protect corrosion of the receipt tank.
3. Addition of acidic waste shall enter the receipt tank via a flow path below the waste tank liquid level. However, vent and drain operations into Tank

51 are permitted to receive acidic waste above the liquid level due to limited volume.

Compensatory Measures

1. The treatment tank shall be exposed to 8 wt% oxalic acid at 75 °C for ≤ 30 days. If 8 wt% acid addition activities extend beyond a total of 30 days for acidic chemical cleaning activities:
 - A. Perform a risk assessment (e.g., engineering evaluation, utilizing process history, ultrasonic inspection, etc.) of the primary tank wall loss
 - B. The risk assessment can be used to extend the time 8 wt% acid is in the tank, if warranted.
 - C. The allowance for tanks being exposed to 8 wt% oxalic acid at 75 °C for 30 days for acid addition shall be tracked separately from the 365 day allowance for Chemical Cleaning activities in the Tank Farm Morning Report or LCO Tracking Database.

2. The Cleaning Activities Life Cycle allows for the suspension of corrosion inhibitor concentration requirements, sampling, and maintaining annulus ventilation requirement for up to 1460 days and shall be tracked in the ERD. The allowance for tanks being exposed to oxalic acid for 365 days (Feeding 4 to 8 wt% oxalic acid at 60 to 75°C with no mixing for ≤ 30 days and the remainder of time at ≤ 4 wt% oxalic acid at 60°C) and for acidic chemical cleaning activities shall be tracked separately in the Tank Farm Morning Report or LCO Tracking Database. If waste removal activities extend beyond a total of 1460 days or more than 365 days for acidic chemical cleaning activities:
 - A. Perform an ultrasonic inspection of the primary tank wall and an engineering evaluation within 180 days of exceeding the time limit. The extent and scope of the inspection shall be determined by the Liquid Waste In-Service Inspection Review Committee (ISIRC) [1].
 - B. The engineering evaluation can be used to extend the time, if warranted.

5.2.3 HUMIDITY

Annulus ventilation is not required for waste tanks in the Cleaning Activities and Final Stabilization Preparation Life Cycle because significant corrosion degradation due to intermittent condensation on the tank wall is not anticipated during the short-term closure process [1]. However, annulus ventilation is a credited control imposed by the Flammability Control Program.

5.3 *Final Stabilization Preparation Life Cycle*

Active corrosion protection for waste storage tanks in the Final Stabilization Preparation stage is not required and the tank is exempt from the Corrosion Control Program DD controls.

An assessment has determined that the seismic integrity of Type I Waste Tanks (Type II Waste Tanks are bounded by Type I Waste Tanks) in this phase is acceptable accounting for a 100,000 gallon well water fill limit and a 10 year delay in grouting which equates to an additional 100 mil wall thickness reduction [63]. Administrative controls require the tank be stabilized within 10 years. In the unlikely event that the tank is not grouted within 10 years of the Closure declaration, an engineering evaluation for structural and leak integrity shall be performed on the tank to ensure that the intended safety class function is met. The approach to the evaluation may be similar to that of the realistic scenario calculation provided in Reference 1. Actual exposure time, liquid levels, temperature, and corrosive environment should be considered.

A fracture assessment demonstrated that the risk of brittle fracture for Type I and II tanks in the Final Stabilization Preparation Life Cycle designated as Closure Mode is unlikely. Therefore, the thermocouple attached to the exterior of the tank wall, utilized to monitor the steel wall temperature maybe removed once a tank has been declared to be in Closure Mode. The conclusion that the brittle fracture was unlikely for non-stress relieved tanks with higher minimum operating temperatures can be naturally extended to conclude that Type III/IIIA tanks with lower minimum operating temperatures have even lower risk of brittle fracture during Closure mode.

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