SRR-CES-2012-00018
Revision 0
May 2012

Keywords:

Tank 48
Tetraphenylborate
Peroxide Oxidation
Flow-sheet

Tank 48 Chemical Destruction – Flow-Sheet Options Report

Prepared by:

Steven P. Simner

May 2012

Savannah River Remediation
Aiken, SC 29808

Prepared for U. S. Department of Energy

APPROVALS

Prepared by:

S.P. Simner — 5/17/2012

Steven P. Simner — Date

SRR Engineer, Technology Implementation

Approved by:

Celia I. Aponte — 5/17/2012

Celia I. Aponte — Date

SRR Technical Reviewer, Technology Implementation

E.A. Brass — 5/17/2012

Earl A. Brass — Date

SRR Design Authority, Tank 48 Chemical Destruction

E.A. Brass for K. Subramanian — 5/17/2012

Karthik H. Subramanian — Date

SRR Chief Technology Officer

TABLE OF CONTENTS

ABBREVIATIONS AND ACRONYMS 4

TABLES 6

FIGURES 6

1 PURPOSE 7

2 BACKGROUND 8

3 TANK 48 WASTE COMPOSITION 18

4 REQUIREMENTS DOCUMENTS 29

5 FLOW-SHEET OPTION ASSESSMENT 31

6 CONCLUSION 54

7 REFERENCES 55

ATTACHMENT 1: Flow-Sheet Criteria Tables 58

ABBREVIATIONS AND ACRONYMS

1PB	phenylboronic acid
2PB	diphenylborinic acid
3PB	triphenylborane
ARM	area radiation monitor
ARP	Actinide Removal Process
CCPO	copper-catalyzed peroxide oxidation
CFR	Code of Federal Regulations
CLFL	composite lower flammability limit
CsTPB	cesium tetraphenylborate
CSTF	Concentration, Storage, and Transfer Facilities
CSSX	Caustic Side Solvent Extraction
CTE	critical technology element
DCF	dose conversion factor
DF	decontamination factor
DOE	U.S. Department of Energy
DOE-SR	U.S. Department of Energy Savannah River
DSA	Documented Safety Analysis
DSS	decontaminated salt solution
DWPF	Defense Waste Processing Facility
ETAF	Engineering Transfer Approval Form
FY	fiscal year
HDB	H-Diversion Box
HEPA	high-efficiency particulate air
HGR	hydrogen generation rate
HPLC	high performance liquid chromatography
IDP	inhalation dose potential
IPI	installed process instrumentation
ITP	In-Tank Precipitation
KTPB	potassium tetraphenylborate
LFL	lower flammability limit
LOC	loss of confinement
LPPP	Low Point Pump Pit
LWHT	Late Wash Hold Tank
LWPT	Late Wash Precipitate Tank
M	Molarity
M&TE	measuring and testing equipment
MCU	Modular Caustic Side Solvent Extraction Unit
MST	monosodium titanate
NaTPB	sodium tetraphenylborate
NCSE	Nuclear Criticality Safety Evaluation
NESHAP	National Emission Standards for Hazardous Air Pollutants
NGS	Next Generation Solvent
NPH	natural phenomena hazards

ORNL	Oak Ridge National Laboratory
PCHA	Preliminary Consolidated Hazard Analysis
PDD	Program Description Document
Pu-239(eq)	Pu-239 (equivalent mass)
QA	Quality Assurance
ROAR	Risk and Opportunity Analysis Report
SAC	Specific Administrative Control
SCDHEC	South Carolina Department of Health and Environmental Control
SCIX	Small Column Ion Exchange
SPC	Salt Processing Cell
SPF	Saltstone Production Facility
SR	surveillance requirement
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation, LLC
SS	stainless steel
SSCs	Structures, Systems, and Components
SWPF	Salt Waste Processing Facility
TCLP	toxicity characteristic leaching procedure
TE	technology element
TF	Tank Farm
TMP	technology maturation plan
TOC	total organic carbon
TPB	tetraphenylborate
TR&C	Task Requirements and Criteria
TRL	technology readiness level
TSR	Technical Safety Requirements
TTQAP	Task Technical and Quality Assurance Plan
U-235(eq_{SLU})	U-235 (equivalent mass in sludge)
VOC	volatile organic compound
WAC	Waste Acceptance Criteria
WCP	Waste Compliance Plan
WCS	Waste Characterization System
wt%	weight percentage
WS	Waste Solidification
WSMS	Washington Safety Management Solutions, LLC

TABLES Page

Table 1: Summary of data from the 2005 SRNL CCPO study 14

Table 2: Tank 48 chemical and radionuclide composition (including acceptance criteria for waste transfer to downstream facilities) 21

Table 3: IDPs for Tank 48, Tank 48 supernate, and CCPO-processed waste 27

Table 4: Team members for developing criteria applicable to CCPO-processed waste 29

Table 5: Relevant CCPO process off-gas emissions and SCDHEC limits 31

Table 6: Components contained in Tank 48 waste but not identified in SPF WAC 41

Table 7: Mass concentrations of uranium and plutonium in the CCPO-processed waste 53

FIGURES

Figure 1: CCPO process schematic 15

Figure 2: Maturation strategy for CCPO process 16

Figure 3: FY12 CCPO process development and associated tasks 17

Figure 4: CCPO process schematic detailing chemical and physical changes to the Tank 48 waste 28

Figure 5: Flow-sheet schematic illustrating requirements documents for transfer of waste from Tank 48 and subsequent CCPO treatment 34

Figure 6: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to an TF storage tank 37

Figure 7: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to SPF (via Tank 50) 39

Figure 8: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste through the 512-S cross-flow filter 42

Figure 9: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed to SWPF 46

Figure 10: Flow-sheet schematic illustrating requirements documents for recycle of the CCPO-processed waste to Tank 48 and associated Tank 50 decant 49

Figure 11: Flow-sheet schematic illustrating requirements documents for transfer of CCPO-processed waste to DWPF 51

1 PURPOSE

A copper-catalyzed peroxide oxidation (CCPO) process is currently being evaluated to determine its potential for destroying organic compounds (predominantly tetraphenylborate (TPB)) contained in Tank 48 and for meeting the associated technology maturation requirements [1-2]. Previous data has indicated that TPB destruction levels > 99.8% are achievable (for Tank 48 simulant) via this process at pH 11 [3]. However, it has not been established if this level of organic destruction is repeatable (or can potentially be enhanced), and whether the residual organics in the treated waste (≤ 0.2% per the 2005 data [3]) are low enough to enable transfer and storage in the Tank Farm (TF); or processing at the Saltstone Production Facility (SPF), Defense Waste Processing Facility (DWPF), or the Salt Waste Processing Facility (SWPF) with ultimate disposition as vitrified glass and/or Saltstone grout. In addition to the organic compounds, Tank 48 also contains other components, including radionuclides such as Cs-137 and Pu-238, which must be assessed for their potential to exceed or challenge currently specified limits with respect to the TF and the aforementioned disposition processes.

The primary intent of this report is to identify available flow-sheet options for permanent disposition of the CCPO-processed Tank 48 waste, and to subsequently determine the viability of each flow-sheet based on a comparative analysis between compositional limits of a given flow-sheet and the predicted CCPO-processed composition. For example, the choice of a particular flow-sheet is influenced by the level of organic destruction achieved by the CCPO process since both the TF and downstream processing facilities impose limits on volatile organics in the waste stream to protect flammability limits. Establishing the required level of organic destruction will also determine whether subsequent optimization of the process is necessary.

Each flow-sheet identifies the tanks and the processing facilities through which the treated waste will pass for eventual disposition as vitrified glass or Saltstone grout. The proposed flow-sheets will be assessed with respect to the current chemical, radiological, and physical requirements that will be imposed on the CCPO-processed feed when transferring to the TF or to any of the downstream processing facilities. Criteria to be considered for each flow-sheet option includes those specified in documents such as Technical Safety Requirements (TSR), Documented Safety Analysis (DSA), Waste Acceptance Criteria (WAC), and environmental

regulations. For a criterion that is specified in more than one of the requirements documents, the more conservative criterion is to be applied.

In concert with flow-sheet development, a number of additional activities are being performed in order to establish the potential for successful maturation of the CCPO technology. These include optimization of the CCPO process via laboratory-scale experiments on simulant waste, identification of accident conditions and events, and the potential project risks associated with maturing and implementing the CCPO technology. The findings from all of the aforementioned activities will be utilized to establish if the CCPO process warrants further development.

It is important to recognize that this document assesses each flow-sheet option based on the chemical, physical, and radiological characteristics of the CCPO-processed waste, and how the waste composition potentially exceeds or challenges criteria specified in the aforementioned governing documents. It is not the intent of this report to assess the viability of each flow-sheet based on implementation cost and complexity, interference with other site operations, and potential impacts on the life-cycle duration for waste dispositioning. These aspects will be considered as part of an alternatives analysis that will be issued as a separate document.

2 BACKGROUND

Tank 48 currently holds approximately 240,000 gallons of radioactive legacy liquid waste material from the operation of the In-Tank Precipitation (ITP) process. The tank contains approximately 26,000 kg [4] of organic TPB compounds, predominantly insoluble potassium tetraphenylborate (KTPB) along with smaller quantities of cesium tetraphenylborate (CsTPB). Other insoluble solid constituents include monosodium titanate (MST) and sludge solids. The TPB has the potential to decompose to benzene (C_6H_6), which has required the use of controls to maintain the concentrations of flammable components in the Tank 48 vapor space below 5% of the composite lower flammability limit (CLFL). In addition, the organic content and the associated flammability issues pose a challenge to the salt processing and sludge processing facilities within the liquid waste system. One option to destroy the organics in Tank 48 is the CCPO process, which was determined to be the most viable technology for successful technical and cost-effective maturation by a table-top engineering evaluation in comparison with direct vitrification of the material [5].

Former emphasis with respect to the CCPO process was placed on in-situ treatment of the Tank 48 waste. Tank 48 is, however, constructed from carbon steel and at low pH the evolution of hydrogen inhibits protective film formation and the carbon steel corrodes rapidly. In alkaline solutions the formation of protective films greatly reduces the corrosion rate, and thus the successful application of the CCPO process at pH 11 [3] was considered compatible with processing in-situ in Tank 48. In contrast the current application of the CCPO process is intended to take place in two stainless steel (SS) tanks located in 241-96H with each tank having a liquid capacity of approximately 6200 gallons. These tanks were considered unavailable in previous treatment evaluations due to their use for the Actinide Removal Process (ARP), as MST strike tanks. They will, however, become available once processing operations commence in SWPF, and ARP operations are discontinued [6]; the intent is to transfer batches of waste from Tank 48 to the 241-96H SS tanks for organic treatment via the CCPO process.

A. Basic Chemistry of Catalyzed Peroxide Oxidation

Hydrogen peroxide (H_2O_2) is a strong oxidant with electrochemical oxidation potentials of 1.80 and 0.87V at pH 0 and 14, respectively [7]. In 1894 H.J.H. Fenton studied the oxidation of tartaric acid by hydrogen peroxide and noted that its oxidation rate increased dramatically when ferrous ion (Fe^{2+}) (in the form of a soluble ferrous salt) was added in conjunction with the hydrogen peroxide [8]. It was not until 1934, however, that the role of the ferrous ion in catalyzing the reaction via the formation of hydroxyl radicals ($^{\bullet}OH$) (powerful oxidants with a high propensity to degrade organic materials) was first realized [9]. Iron-catalyzed peroxide oxidation of organic compounds at low pH is generally referred to as a “Fenton’s process.” The CCPO in non-acidic environments (utilized for the CCPO process) is typically termed a “modified Fenton’s process”.

The basic chemistry for the formation of hydroxyl radicals and their destruction of organics is illustrated in the subsequent text with specific reference to the more ubiquitously studied Fenton’s reagent chemistry (and the use of a ferrous ion catalyst). The corresponding chemistry utilizing a copper catalyst is less well understood, particularly in terms of the initial mechanism for hydroxyl radical formation, though potential roles of copper in enhancing the Fenton’s type reaction are discussed elsewhere [10]. In general, however, reactions subsequent to hydroxyl radical formation (Reactions 2-4 and 2-5) are considered applicable to peroxide oxidation processes utilizing catalysts other than iron. The primary advantage of the copper catalyst in comparison to iron is its ability to promote the decomposition of TPB in alkaline environments

[3]. The more traditionally used iron-catalyzed Fenton's process typically requires acidic conditions (pH < 5) [11] to achieve high destruction efficiencies of TPB.

The reaction scheme for hydroxyl radical formation via hydrogen peroxide catalysis is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2\text{-}1)$$

During hydroxyl radical creation, the soluble Fe^{2+} is oxidized to insoluble ferric ion (Fe^{3+}), which may precipitate as iron hydroxide ($Fe(OH)_3$), and thereafter provides no subsequent benefit to the reaction. If, however, the pH is less than 5, the ferric ion can be reconverted to the ferrous ion, per the reactions shown below [11], and the ferrous ion remains in solution to continue formation of the hydroxyl radicals.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OOH \qquad (2\text{-}2)$$

$$Fe^{3+} + {}^{\bullet}OOH \rightarrow Fe^{2+} + H^+ + O_2 \qquad (2\text{-}3)$$

${}^{\bullet}OOH$ is termed the perhydroxyl (or hydroperoxyl) radical and is a weaker oxidizer than un-catalyzed hydrogen peroxide. As such this component does not directly aid the destruction of organics, but per Reaction 2-3 it can react to regenerate ferrous ions which in turn stimulate further reaction with hydrogen peroxide to produce more hydroxyl radicals.

The hydroxyl radicals subsequently oxidize organic compounds by hydrogen abstraction (Reaction 2-4) or by oxygen addition (Reaction 2-5) both of which form organic radicals which are highly reactive and can be further oxidized [11].

$$RH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H_2O \qquad (2\text{-}4)$$

$$R{=}R + {}^{\bullet}OH \rightarrow {}^{\bullet}R\text{-}ROH \qquad (2\text{-}5)$$

B. Typical Reaction Products

Under optimized processing conditions (pH, temperature, and sufficient catalyst and hydrogen peroxide to facilitate reaction completion) the organics can be predominantly converted to carbon dioxide (CO_2), water (H_2O), and other potential small chained carbon anions (such as oxalate [$C_2O_4^{2-}$] and formate [$HCOO^-$]) via the catalyzed peroxide oxidation reaction. For a stoichiometric ratio of hydrogen peroxide / TPB the general reaction is shown below though the

self-decomposition of hydrogen peroxide (discussed in the latter text) necessitates a greater than stoichiometric hydrogen peroxide / TPB ratio:

$$(C_6H_5)_4B^- + 60H_2O_2 \rightarrow 24CO_2 + 70H_2O + BO_2^- \qquad (2\text{-}6)$$

However, given the indiscriminate mode by which hydroxyl radicals oxidize organic compounds, and the subsequent number of potential reaction pathways available, a number of oxidized organics may be formed as intermediates (or final products for incomplete reactions) during the conversion process. Some of these compounds may be undesirable as is the case with the formation of volatile organic compounds (VOCs), like benzene, which can evaporate into the vapor space of the processing tank causing flammability concerns. Flammability concerns are further compounded due to the potentially simultaneous evolution of benzene and self-decomposition of hydrogen peroxide into oxygen. Intermediate breakdown products of peroxide oxidation of TPB are likely to include benzene, phenol (C_6H_5OH), and biphenyl ($[C_6H_5]_2$). Further oxidation of the organic intermediates will lead to production of oxidized species, such as alcohols (R-OH), carbonyl (C=O) compounds, carboxylic acids (R-COOH), and organic peroxides (ROOR′), with many of the intermediates likely to contain multiple functional groups [12].

An important distinction between copper- and iron-catalyzed reactions is that copper also promotes organic decomposition via hydrolysis reactions. Copper-catalyzed hydrolysis was utilized for the destruction of sodium tetraphenylborate (NaTPB) in Tank 49 (Reaction 2-7) [13], and was proposed for decomposing KTPB in the DWPF Salt Processing Cell (SPC) prior to waste vitrification [14-15] in the original ITP flow-sheet. In addition, copper-catalyzed hydrolysis has been utilized in the destruction of TPB decomposition products including triphenylborane (3PB or $(C_6H_5)_3B$), diphenylborinic acid (2PB or $(C_6H_5)_2BOH$), and phenylboronic acid (1PB or $C_6H_5B(OH)_2$) [16].

$$Na(C_6H_5)_4B + 2H_2O \rightarrow 4C_6H_6 + NaBO_2 \qquad (2\text{-}7)$$

However, unlike peroxide oxidation, the hydrolysis reaction does not fully decompose TPB to carbon dioxide and water. Indeed the intermediates listed previously for the peroxide oxidation reaction, such as benzene, phenol, and biphenyl, tend to constitute the final reaction products for copper-catalyzed hydrolysis [16]. In reality the copper-catalyzed decomposition of TPB will occur by a combination of hydrolysis and hydroxyl radical oxidation reactions, and the extent to

which each of these reactions occurs will likely be dependent on pH, temperature, and factors affecting hydroxyl radical formation. It is conceivable that the hydrolysis reaction could be initially promoted to remove the phenyl groups from the TPB to form benzene, phenol, and biphenyl which could then be further decomposed to carbon dioxide and water via the peroxide oxidation reaction.

Additional reaction products of peroxide oxidation include oxygen and water due to the self-decomposition of hydrogen peroxide per the reaction below:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 \qquad (2\text{-}8)$$

The self-decomposition process is thermodynamically favorable (heat of decomposition at 25 °C [50 wt% H_2O_2] = 95.4 kJ/mol [17]), and enhanced by increases in temperature and pH [17]. With respect to temperature the rate of decomposition is roughly doubled for each 10 °C increase above room temperature. At higher pH, the stability of hydrogen peroxide deteriorates very rapidly [18]. Since the Tank 48 waste also contains significant nitrite (NO_2^-) (see Table 2) there is also the possibility of consuming hydrogen peroxide through nitrite oxidation per Reaction 2-9:

$$H_2O_2 + NO_2^- \rightarrow H_2O + NO_3^- \qquad (2\text{-}9)$$

C. Experimental Results to Date

The success of a CCPO process for destroying TPB in Tank 48 simulant was demonstrated in 2005 [3]. This study considered the use of copper-only catalysts at non-acidic conditions (pH 11 and pH 14). The analyses also sought to identify intermediate (including process off-gases) and final decomposition products, and quantify the proportions of these products. The following text and Table 1 summarizes the data for the two alkaline environments analyzed:

pH 14 – these experiments resulted in a slow TPB decomposition rate (approximately 15% decomposition in 9 weeks), and as such peroxide oxidation at pH 14 is not considered a viable option for organic treatment of the Tank 48 waste.

pH 11 – these experiments led to near-complete (i.e., > 99.8%) TPB decomposition in approximately 3 weeks while providing complete oxidation of TPB decomposition by-products. The benzene concentration in the vapor space was measured at below 25% of the lower flammability limit (LFL) throughout testing. After an initial hold at room temperature the

simulant was heated to 35, 45, 55, and ultimately 75 °C to achieve > 99.8% destruction efficiency.

It is the near-complete decomposition of TPB at pH 11 that represents the precursor to the proposed development of a mature CCPO process that can be effectively carried out in alkaline environments. One point of note with respect to the level of organic destruction observed in the 2005 studies: the CCPO-processed slurry was analyzed for TPB and more than ten of its decomposition products using high performance liquid chromatography (HPLC). The detection limit for each compound had previously been limited to 10 mg/L, and neither TPB, nor its decomposition products, were detected via HPLC analysis of the final product from the 2005 test at pH 11. However, the assumption was made that each compound could theoretically be present at slightly less than the detection limit. Since analysis of the final product from the 2005 testing sought to detect approximately fifteen organic compounds the assumption is made that each is present at close to the detection limit of the analysis technique (i.e., 10 mg/L). Thus with respect to calculating the efficiency of the process approximately 150 mg/L of residual organics was assumed. As such, the process efficiency was calculated as less than 100%. For the planned fiscal year (FY) 12 testing it is envisaged that the HPLC detection limits will be enhanced to between 1 to 2 mg/L for TPB and some of its common decomposition products, such as phenol, biphenyl, 3PB, 2PB, and 1PB [2]. In addition, other methods for determining the level of VOCs in the CCPO-processed slurry are being considered.

Table 1: Summary of data from the 2005 SRNL CCPO study [3].

Experimental Conditions	Results

• Waste: Tank 48 simulant (600 mL)
• Catalyst type: Cu (as $CuSO_4$)
• Oxidant: 30 wt% H_2O_2
• Target pH: adjusted to pH 11 (using HNO_3) prior to catalyst addition
• Temperature: heated to 35, 45, 55, and 75 °C after catalyst addition
	• TPB destruction >99.8%
	• Detectable decomposition products:
	  • $(C_6H_5)_2(C_6H_4)$, $(C_6H_5)_2(C_6H_4)_2$, $(C_6H_5OH)N(CH_3)$, $HCOO^-$, and $C_2O_4^{2-}$
	• Off-gas:
	  • C_6H_6 <25% LFL
	  • Off-gas not analyzed for CO_2

D. CCPO Technology Maturation Strategy

A technology maturation plan (TMP) [1] has been developed to establish the principal technology elements (TEs) for the proposed CCPO process, and to subsequently assess each TE with respect to its potential designation as a critical technology element (CTE) (as defined in Reference 19). Figure 1 is a schematic of the process and indicates the currently determined TEs. The reaction process (TE1) (including the reaction vessel and mixer) was determined to presently be the sole CTE. The TMP is being used to guide a phased approach to the technical maturation of the CCPO process. The phased approach allows for interim decisions along the technology maturation pathway. The decisions will be made in a partnering effort along with the U.S. Department of Energy (DOE) to minimize project costs while ensuring that Tank 48 waste disposition is successful within regulatory requirements. The CCPO process will be matured in a phased approach as illustrated in Figure 2.

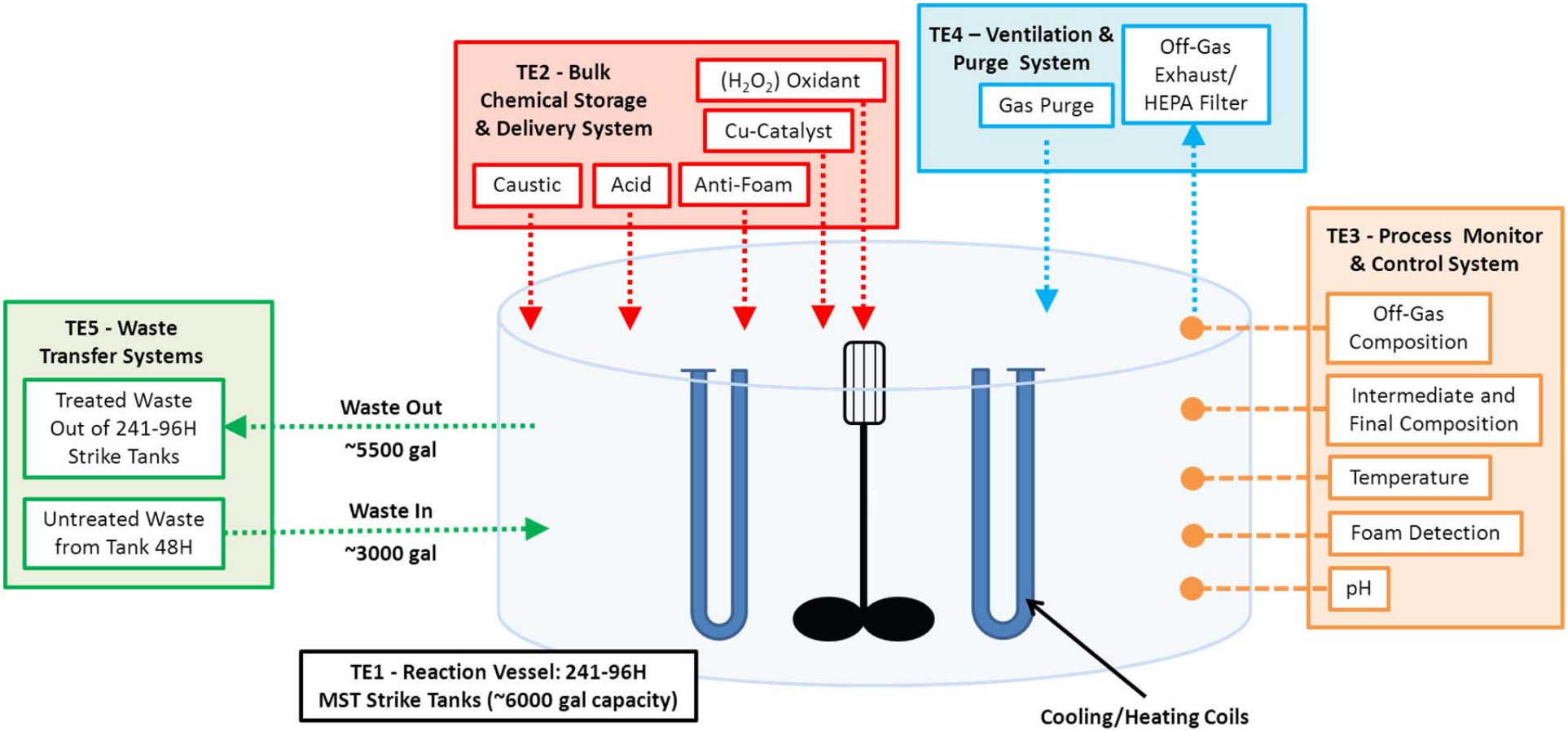

Figure 1: CCPO process schematic.

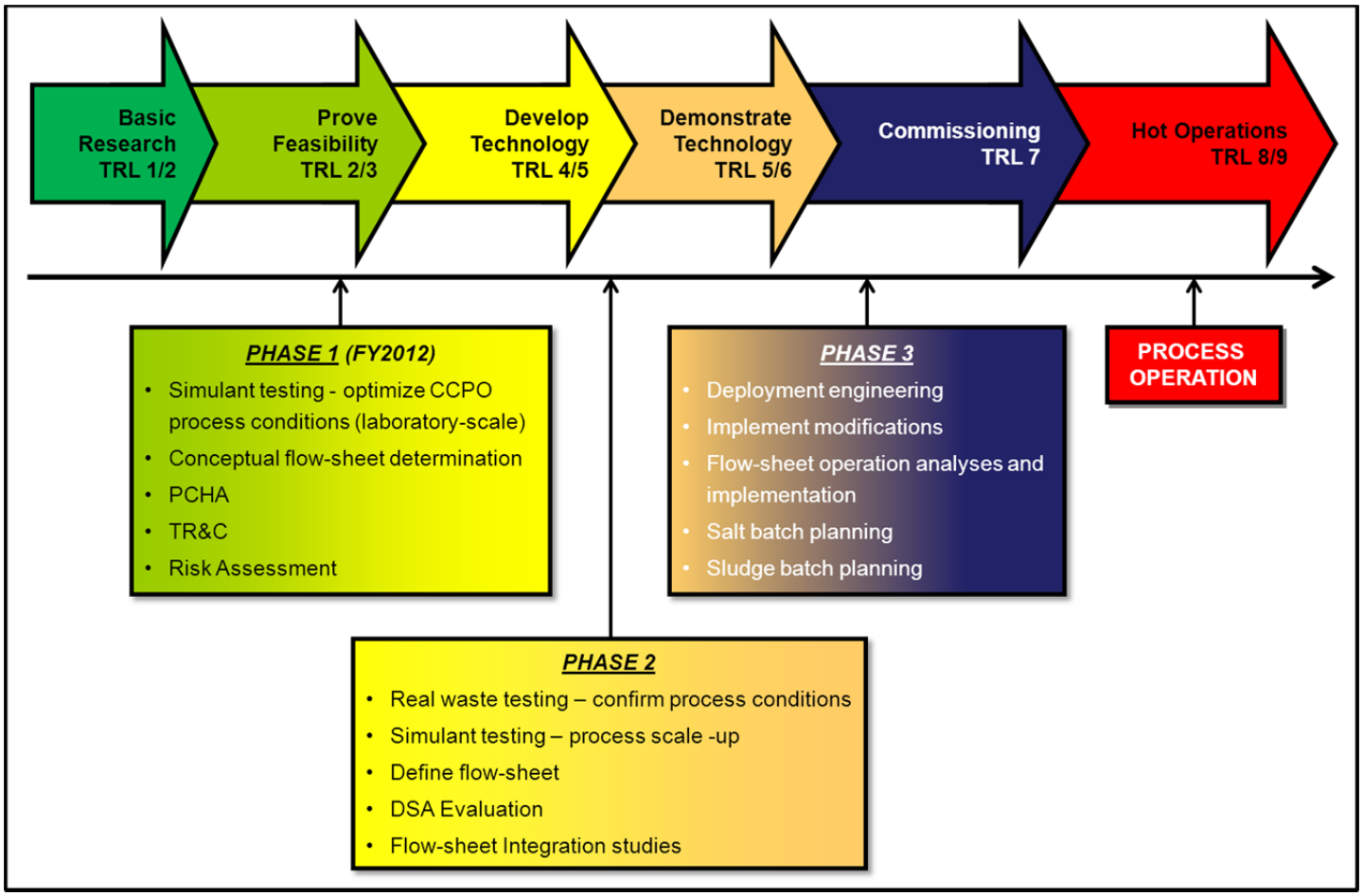

Figure 2: Maturation strategy for CCPO process (TRL = technology readiness level [19]).

Phase 1 of the technology maturation strategy consists of feasibility and demonstration testing on waste simulant [2]. As indicated in Figure 2 the determination of flow-sheet options (per this report) is assessed in concert with the experimental investigations of Phase 1. Finally, Phase 1 incorporates development a Preliminary Consolidated Hazards Analysis (PCHA), a Task Requirements and Criteria (TR&C) document, and Risk and Opportunity Analysis Report (ROAR) consistent with the development process. At the completion of Phase 1, the intent is to evaluate the experimental data with respect to each notional flow-sheet (and the implementation requirements for each) to identify whether an optimum flow-sheet exists. That data review will provide the basis for moving on to Phase 2 of technology maturation.

Phase 2 of technology maturation will consist of real waste demonstration testing. Phase 2 will include testing within a defined flow-sheet and initiate the necessary flow-sheet integration

studies. In addition, Phase 2 of the testing will incorporate CCPO scale-up (using simulant), safety basis evaluation and planning for deployment engineering.

Phase 3 of the technology maturation will consist of the necessary optimal flow-sheet integration studies that will define the necessary modifications. In addition, the effort will be integrated into operations and system planning activities, such as salt batch and sludge batch planning.

The FY12 maturation plan and associated tasks are summarized in Figure 3.

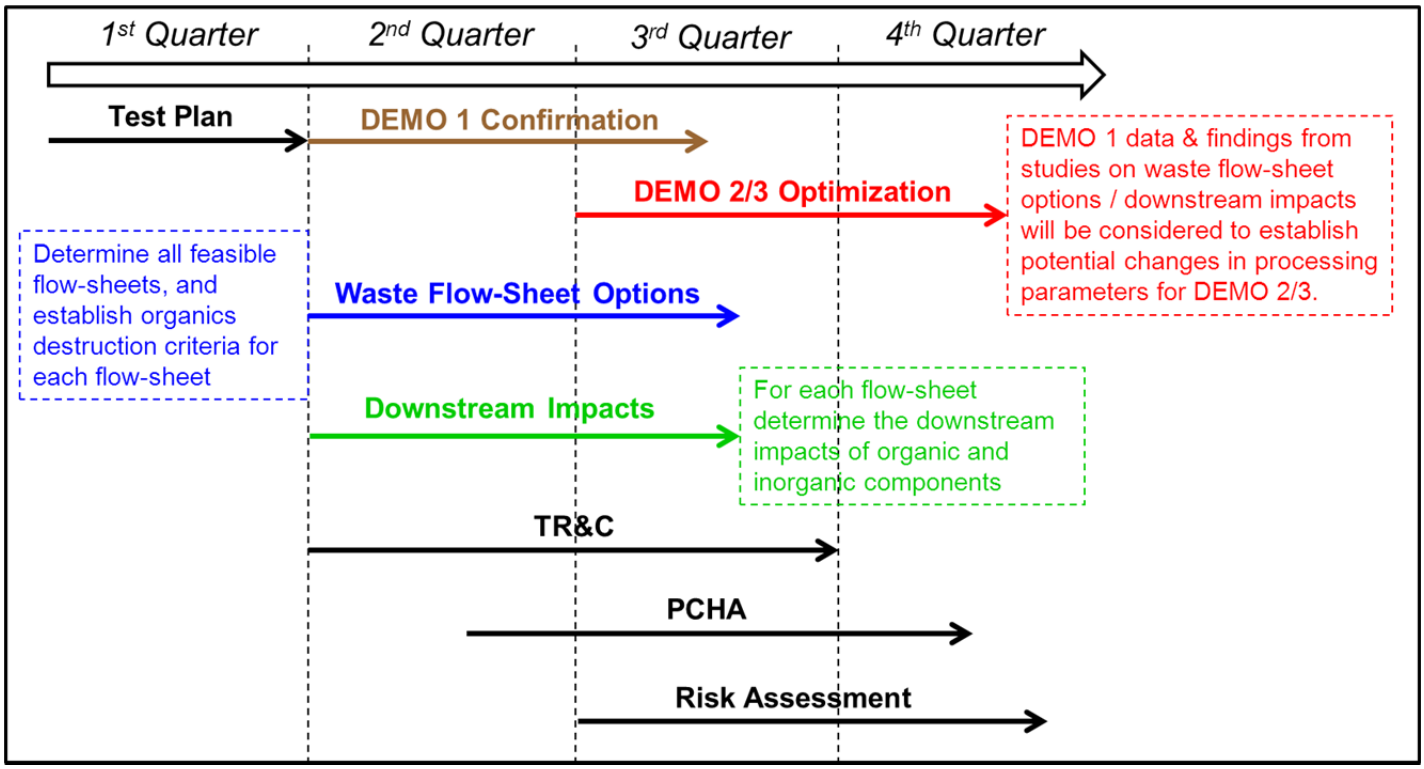

Figure 3: FY12 CCPO process development and associated tasks (Phase 1).

Demonstration 1 of the FY12 testing scope reassesses the feasibility of the technology by repeating the successful experimental results on waste simulant (i.e., process parameters identical to those used in the original 2005 experiment [3]), and perform scoping testing within the framework of a parametric test matrix [2]. Experimentation occurs concurrently with the development of notional flow-sheets per this document. These development activities determine the "success criteria" against which the experimental results will be measured to decide whether further technology maturation is warranted.

The parameters for Demonstration 2 have been established utilizing Demonstration 1 test results and flow-sheet analyses. Variations to the following experimental parameters are being considered in scoping tests for the second demonstration experiment: pH, temperature, catalyst type and quantity, and reactant addition rate. Demonstration 3 (if necessary) will consist of simulant waste testing in the optimum simulant conditions within the framework of the optimal flow-sheet. Upon completion, all of the data from real waste and simulant demonstrations will be utilized to decide whether deployment of the CCPO technology is warranted.

3 TANK 48 WASTE COMPOSITION

Table 2 indicates the chemical composition for the typical Tank 48 (well-mixed) feed with 3.26 wt% solids [20]. The table also indicates the composition of the Tank 48 supernate (equivalent to the low solids feed in Reference 20), and the CCPO-processed feed that will be transferred to the TF storage tanks or for disposition by other processes. The estimated composition of the CCPO-processed feed is based on the following inputs:

i. Well-mixed feed transfer from Tank 48 [20].
ii. 99.8% organic destruction [3] (also see subsequent paragraph).
iii. A dilution factor of 1.83 [3]; note that the dilution factor will be updated based on FY12 testing [2].
iv. Radionuclide activities based on decay per Reference 20.
v. The addition of approximately 500 mg/L copper (added as copper sulfate) [3].
vi. Anion concentrations are based on the empirical data from Reference 3; note that a dilution factor is already incorporated into these empirically measured values.

With respect to the CCPO-processed organic composition, as previously noted for the 2005 studies [3], TPB and its decomposition products were not detected in the final slurry product. However, the organic species detection limit utilizing HPLC analysis was 10 mg/L, and thus for conservatism it is assumed that the CCPO-processed waste contains 10 mg/L of TPB and each of its potential decomposition products. It is envisaged, however, that enhanced sample preparation for HPLC analysis will enable a detection limit of 1 mg/L for TPB, and 2 mg/L (or potentially lower) for its decomposition products [2]. The FY12 studies will also consider process optimization of the CCPO process to reduce the degree of dilution, and to utilize copper nitrate

in lieu of copper sulfate as the source for the copper catalyst since DWPF has limits on the sulfate content based on its solubility limits in the vitrified glass. This document will be updated to include data obtained during the FY12 studies but for this revision the post-CCPO composition provided in Table 2 is assumed.

There are also some incidental changes in the physical and chemical characteristics of the Tank 48 waste that will occur during the CCPO process. Changes that occur to the waste during the CCPO process are either intended, as is the case for TPB destruction, or incidental in the case of nitrite oxidation, for example. These are highlighted in Figure 4 and discussed in the subsequent text.

Potassium and Cesium – as a consequence of TPB decomposition potassium and Cs-137 are released into the slurry where they can react with nitrates, for example, and subsequently dissolve into solution. As such the CCPO process results in the conversion of K and Cs-137 from insoluble to soluble components which will ultimately affect disposition options for the Cs-137 radionuclide.

Nitrate and Nitrite Concentrations – the oxidizing processes occurring during the CCPO process can also result in oxidation of nitrite to nitrate. In addition, nitric acid is added to the waste prior to CCPO treatment to reduce the pH from 14 to $\leq$ 11. The exact proportion of nitric acid required to achieve the required pH reduction will be established during FY12 experimentation, and subsequently updated in a future revision of this report.

Hydroxide Concentration – caustic may be added after treatment of the waste (and prior to transfer from the reaction vessel) to increase the pH as needed from the reaction pH to a pH that is compatible with downstream storage or processes.

Carbonate, Oxalate, and Formate – in the 2005 tests [3] increases in carbonate, oxalate, and formate species were observed between the pre- and post-treated simulants.

Monosodium Titanate - MST ($NaTi_2O_5H$) is an irregularly-shaped, amorphous, porous solid that was added to Tank 48 to adsorb strontium (Sr-90) and actinides. There is the potential for MST reaction during the CCPO process, which may subsequently result in desorption phenomena. As such the Sr-90 and actinides would potentially be transferred from the insoluble MST solids to the supernate portion of the waste which may ultimately influence available

disposition flow-sheets. As part of the planned FY12 experimental analysis [2] the potential reactivity of MST and the fate of the adsorbed strontium and actinides will be determined.

Potential Off-Gas Components – in addition to those components remaining in the CCPO-processed waste, the CCPO reaction will evolve gaseous species that will exit the process in the off-gas. Figure 4 indicates components that might be contained in the process off-gas. Oxygen evolution results from the self-decomposition of hydrogen peroxide. Carbon dioxide is the desired product of the CCPO decomposition process. Carbon monoxide has been detected in previous experiments utilizing a Fenton's-type process to treat both simulant and actual waste slurries (containing ion-exchange resins) from three underground storage tanks at the Oak Ridge National Laboratory (ORNL) [21]. Nitrogen oxide (NO_x) gases may result from the reaction of nitric acid which is added to lower the processing pH. Benzene and biphenyl are decomposition products of TPB and are expected to volatilize or sublime (in the case of biphenyl) at the relatively high processing temperatures (≤ 75 °C). It is currently unknown if elemental mercury or organomercurial compounds will be present in the off-gas since in previous studies mercury measurements were not conducted for the off-gas [3]. With specific reference to organomercurial compounds a recent literature review [22] concludes that in the event that organomercurials did exist in the Tank 48 waste, their reaction with hydrogen peroxide could potentially convert them to mercury (II) compounds or elemental mercury. For the planned Savannah River National Laboratory (SRNL) testing [2] the presence of mercury in the pre- and post-treated slurries, and in the off-gas is being analyzed as part of the CCPO technology maturation.

Table 2: Tank 48 chemical and radionuclide composition (including acceptance criteria for waste transfer to downstream facilities).

Component	Well-Mixed Tank 48 Feed [Ref. 20]	CCPO-Processed Feed [1]	Tank 48 Supernate [Ref. 21]	TF (DSA) [Ref. 24]	SPF (WAC) [Ref. 25]	512-S (WAC) [Ref. 26]	DWPF (WAC) [Ref. 26]	SWPF (WAC) [Ref. 27]
Solids (wt%)								
Total Solids (wt%)	2.052E+01	9.92E+00	1.75E+01	*Not Applicable (NA)*	*Not Defined (ND)*	*ND*	1.20–1.90E+01	*ND*
Insoluble Solids (wt%)	3.26E+00	5.00E-01 [2]	0.00E+00	*NA*	1.50E+01	*ND*	*ND*	~1.00E+00 [3, 4, 5] (< 1200 mg/L)
KTPB (wt%)	2.35E+00	0.00E+00 [6]	7.73E-03	*NA*	*ND*	*ND*	*ND*	*ND*
MST solids (wt%)	1.74E-01	1.00E-01	2.29E-03	*NA*	*ND*	*ND*	*ND*	*ND*
Organic Species (mg/L)								
TPB	2.24E+04	< 1.00E+01 [6]	9.77E+00	Flammability [7] contribution of organics is bounded by 5% H_2 LFL without reliance on temperature controls	TPB < 5.00E+00 Phenol < 7.50E+02 Volatiles other than Isopar L, benzene (from TPB), NH_3, and H_2 < 10% to the CLFL	Organic material in the MST/sludge transferred to 512-S shall contribute < 0.1% H_2 LFL	Organic material in the sludge feed transferred to DWPF shall contribute < 0.1% H_2 LFL	TPB < 1.00E+01 [5] Benzene < 4.50E+02 [4, 8] Phenol < 7.50E+02 [4, 8] Organic material present in the feed shall contribute < 0.1% H_2 LFL in the DWPF SRAT [9]
Phenol	1.25E+03	< 1.00E+01 [6]	9.16E+02					
Biphenyl	8.09E+02	< 1.00E+01 [6]	9.77E+00					
Triphenylborate (3PB)	2.24E+02	< 1.00E+01 [6]	9.77E+00					
Biphenylborate (2PB)	1.76E+02	< 1.00E+01 [6]	9.77E+00					
Phenylborate (1PB)	1.62E+02	< 1.00E+01 [6]	9.77E+00					
Benzene	7.68E+01	< 1.00E+01 [6]	0.00E+00					
Nitrobenzene	3.81E+02	< 1.00E+01 [6]	9.65E+00					
Nitrosobenzene	3.53E+01	< 1.00E+01 [6]	9.65E+00					
4-Phenylphenol	9.65E+00	< 1.00E+01 [6]	9.65E+00					
2-Phenylphenol	9.65E+00	< 1.00E+01 [6]	9.65E+00					
Diphenylamine	9.65E+00	< 1.00E+01 [6]	9.65E+00					
o-terphenyl	9.65E+00	< 1.00E+01 [6]	9.65E+00					
m-terphenyl	9.65E+00	< 1.00E+01 [6]	9.65E+00					
p-terphenyl	1.78E+02	< 1.00E+01 [6]	9.65E+00					

Component	Well-Mixed Tank 48 Feed [Ref. 20]	CCPO-Processed Feed [1]	Tank 48 Supernate [Ref. 21]	TF (DSA) [Ref. 24]	SPF (WAC) [Ref. 25]	512-S (WAC) [Ref. 26]	DWPF (WAC) [Ref. 26]	SWPF (WAC) [Ref. 27]
Anion Species (mg/L)								
F^-	1.93E+01	< 13 [6]	1.93E+01	*NA*	4.94E+03	*ND*	1 wt% NaF in glass [10]	5.93E+03 [4, 8]
Br^-	9.65E+01	< 100 [6]	9.65E+01	*NA*	*ND*	*ND*	*ND*	*ND*
CO_3^{2-}	2.86E+04	1.56E+04	2.86E+04	*NA*	1.45E+05	*ND*	*ND*	1.74E+05 [4, 8]
NO_3^-	1.82E+04	7.28E+04 [6] (1.17M)	1.82E+04	$[NO_3^-] \geq 1.0M$ [11] Actual = 1.17M	5.29E+05	*ND*	*ND*	$NO_{eff} = [NO_3^-] + ½[NO_2^-] \geq 1.0M$ [4, 5, 12]
NO_2^-	3.01E+04	8.60E+03 [6] (0.19M)	3.01E+04	$[OH^-] + [NO_2^-] \geq 0.4[NO_3^-]$ [11]	2.59E+05	*ND*	*ND*	
OH^-	4.64E+04	2.54E+04 (1.49M)	4.64E+04	$[OH^-] \geq 0.1[NO_3^-]$ [11]	1.91E+05	*ND*	*ND*	> 3.40E+04 [4, 5]
SO_4^{2-}	9.14E+02	1.15E+03 [6]	9.14E+02	*NA*	6.89E+04	*ND*	0.6 wt% in glass [10]	8.27E+04 [4, 8]
Cl-	7.10E+02	9.40E+01 [6]	7.10E+02	*NA*	9.68E+03	*ND*	1 wt% NaCl in glass [10]	1.16E+04 [4, 8]
$COOH^-$	1.48E+03	4.24E+02 [6]	1.48E+03	*NA*	*ND*	*ND*	*ND*	*ND*
PO_4^{3-}	1.31E+03	3.91E+02 [6]	1.31E+03	*NA*	3.56E+04	*ND*	3 wt% in glass [10]	4.27E+04 [4, 8]
$C_2O_4^{2-}$	1.78E+03	2.58E+03 [6]	1.78E+03	*NA*	3.30E+04	*ND*	*ND*	3.96E+04 [4, 8]
Metal and Cation Species (mg/L)								
Al	2.36E+03	1.29E+03	2.36E+03	*NA*	1.41E+05	*ND*	*ND*	6.74E+03 [4, 5]
As	4.50E+00	2.46E+00	0.00E+00	*NA*	7.50E+02	*ND*	*ND*	9.00E+02 [4, 8]
B	9.97E+02	5.45E+02	4.68E+02	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
Ba	5.86E+00	3.20E+00	5.86E+00	*NA*	7.50E+02	*ND*	*ND*	9.00E+02 [4, 8]
Ca	1.34E+02	7.32E+01	7.64E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Ce	9.77E-01	5.34E-01	9.77E-01	*NA*	*ND*	*ND*	*ND*	*ND*

Component	Well-Mixed Tank 48 Feed [Ref. 20]	CCPO-Processed Feed [1]	Tank 48 Supernate [Ref. 21]	TF (DSA) [Ref. 24]	SPF (WAC) [Ref. 25]	512-S (WAC) [Ref. 26]	DWPF (WAC) [Ref. 26]	SWPF (WAC) [Ref. 27]
Cd	3.42E+01	1.87E+01	3.42E+01	*NA*	3.75E+02	*ND*	*ND*	4.50E+02 [4, 8]
Cr	7.82E+01	4.27E+01	4.70E+01	*NA*	1.50E+03	*ND*	0.3 wt% Cr_2O_3 in glass [10]	1.80E+03 [4, 8]
Cs	1.64E+01	8.98E+00	3.91E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Cu	3.91E+00	1.24E+02	2.93E+00	*NA*	9.00E+02	*ND*	0.5 wt% in glass [10]	1.08E+03 [4, 8]
Fe	2.22E+02	1.21E+02	2.93E+00	*NA*	6.00E+03	*ND*	Wt. Ratio Fe/Pu-239 ≥ 160 Acutal = 2600 [17]	7.20E+03 [4, 8]
Gd	3.91E+00	2.14E+00	3.91E+00	*NA*	*ND*	*ND*	*ND*	*ND*
Hg	2.13E+01	1.17E+01	0.00E+00	*NA*	3.25E+02	*ND*	2.10E+04	3.90E+02 [4, 8]
K	2.92E+03	1.60E+03	3.51E+02	*NA*	3.67E+04	*ND*	3.8846 wt% K_2O in glass [13]	1.63E+03 mg/L [5, 14]
La	1.27E+01	6.95E+00	1.27E+01	*NA*	*ND*	*ND*	*ND*	*ND*
Li	1.17E+01	6.41E+00	1.17E+01	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
Mg	2.64E+01	1.44E+01	9.77E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Mn	8.05E+00	4.40E+00	9.77E-01	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
Mo	1.30E+01	7.09E+00	1.05E+01	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
Na	9.17E+04	5.01E+04	9.17E+04	*NA*	2.5 – 7.0M ⇨ 5.75E+04 – 1.61E+05 mg/L [15]	*ND*	*ND*	1.29–1.61E+05 [5]
Ni	1.47E-02	8.01E-03	0.00E+00	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
P	2.36E+02	1.29E+02	2.36E+02	*NA*	*ND*	*ND*	*ND*	*ND*
Pb	1.92E+02	1.05E+02	1.92E+02	*NA*	7.50E+02	*ND*	*ND*	9.00E+02 [4, 8]
S	5.45E+02	2.98E+02	3.13E+02	*NA*	*ND*	*ND*	*ND*	*ND*
Sb	1.14E+01	6.23E+00	7.45E+00	*NA*	*ND*	*ND*	*ND*	*ND*
Se	4.69E+00	2.56E+00	0.00E+00	*NA*	4.52E+02	*ND*	*ND*	5.40E+02 [4, 8]
Si	1.38E+02	7.53E+01	1.22E+02	*NA*	1.29E+04	*ND*	*ND*	8.42E+02 [4, 5]
Sn	7.53E+01	4.11E+01	7.53E+01	*NA*	*ND*	*ND*	*ND*	*ND*

Component	Well-Mixed Tank 48 Feed [Ref. 20]	CCPO-Processed Feed [1]	Tank 48 Supernate [Ref. 21]	TF (DSA) [Ref. 24]	SPF (WAC) [Ref. 25]	512-S (WAC) [Ref. 26]	DWPF (WAC) [Ref. 26]	SWPF (WAC) [Ref. 27]
Sr	2.64E+01	1.44E+01	3.00E-01	*NA*	9.00E+02	*ND*	*ND*	1.08E+03 [4, 8]
Ti	8.35E+02	4.56E+02	9.77E-01	*NA*	*ND*	*ND*	2 wt% TiO_2 in glass [10]	*ND*
V	9.00E-01	4.92E-01	9.00E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Zn	1.17E+01	6.41E+00	6.69E+00	*NA*	9.75E+02	*ND*	*ND*	1.17E+03 [4, 8]
Zr	1.96E+00	1.07E+00	1.96E+00	*NA*	*ND*	*ND*	*ND*	*ND*
Noble Metal Species (mg/L)								
Ag	2.93E+00	1.60E+00	2.93E+00	*NA*	7.50E+02	*ND*	*ND*	9.00E+02 [4, 8]
Pd	1.03E-01	5.61E-02	7.36E-02	*NA*	*ND*	*ND*	*ND*	*ND*
Rh	6.84E-01	3.74E-01	1.14E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Ru	1.13E+00	6.20E-01	2.86E-01	*NA*	*ND*	*ND*	*ND*	*ND*
Radionuclides (Ci/gal)								
Cs-137	1.30E+00 [16]	7.10E-01	6.33E-02	*NA*	1.80E-01	1.11E+00	1.34E+00 sludge 1.65E+01 Cs strip	5.25E+00 [4, 5]
Sr-90	2.41E-04	1.32E-04	5.58E-06	*NA*	8.52E-02	3.05E-01	*ND*	5.21E-03 (soluble) 3.56E-02 (insoluble) [4, 5]
Tc-99	1.80E-04	9.84E-05	1.80E-04	*NA*	1.60E-03	*ND*	*ND*	1.92E-02 [4, 8]
Th-232	7.92E-12	4.33E-12	7.92E-12	*NA*	1.09E-05	*ND*	*ND*	1.31E-05 [4, 8]
U-233	3.91E-06	2.14E-06	3.71E-07	*NA*	4.28E-05	*ND*	U-235 ÷ U-Total < 0.93 wt% Actual = 12.3 [17]	8.74E-05 [4, 8]
U-234	1.28E-05	6.99E-06	1.76E-06	*NA*	4.28E-05	*ND*		8.74E-05 [4, 8]
U-235	8.55E-09	4.67E-09	1.19E-09	*NA*	4.28E-07	*ND*		8.74E-07 [4, 8]
U-236	3.57E-07	1.95E-07	7.76E-09	*NA*	4.28E-05	*ND*		8.74E-05 [4, 8]
U-238	8.38E-09	4.58E-09	1.096E-09	*NA*	4.28E-05	*ND*		8.74E-05 [4, 8]
Np-237	9.95E-07	5.44E-07	5.30E-08	*NA*	9.46E-04	*ND*	*ND*	2.73E-04 [4, 8]
Pu-238	7.01E-03	3.83E-03	3.41E-06	*NA*	9.46E-04	9.76E-03	1.29E+00	2.08E-03 [4, 8]

Component	Well-Mixed Tank 48 Feed [Ref. 20]	CCPO-Processed Feed [1]	Tank 48 Supernate [Ref. 21]	TF (DSA) [Ref. 24]	SPF (WAC) [Ref. 25]	512-S (WAC) [Ref. 26]	DWPF (WAC) [Ref. 26]	SWPF (WAC) [Ref. 27]
Pu-239	1.96E-05	1.07E-05	1.15E-05	*NA*	9.46E-04	1.46E-04	Wt. Ratio Fe/Pu-239 ≥ 160 Acutal = 2600 [17] Pu-239 ≤ 0.59 g/gal Actual = 1.76E-04 g/gal [17]	2.08E-03 [4, 8]
Pu-240	8.89E-06	4.86E-06	4.120E-07	*NA*	9.46E-04	7.06E-05	[Pu-240] > [Pu-241] [17]	2.08E-03 [4, 8]
Pu-241	2.95E-04	3.99E-04	0.00E+00	*NA*	3.17E-03	1.12E-02		6.97E-03 [4, 8]
IDP (rem/gal)								
Inhalation dose Potential (IDP)	1.22E+06 [18, 19]	6.69E+05 [19]	4.13+03 [19]	1.5E+09	2.09E+05 rem/gal Sr-90≤8.51E-02 Cs-137≤4.50E-01 Eu-154≤8.51E-03 Pu-241≤3.17E-03 Total α≤ 9.49E-04	3.00E+06 rem/gal Cs-137 ≤ 1.11E+00 Soluble Pu-238 ≤ 3.0E-03 Ci/gal	2.47E+08 rem/gal Cs-137 ≤ 1.34E+00 (sludge stream) Cs-137 ≤ 1.65E+01 (strip effluent)	Solids [4, 5] 1.33E+05 rem/gal Solution [4, 5] 4.40E+05 rem/gal

Table Notes: See pg. 26

Table Notes:

1 Values for CCPO-processed feed composition are based on applying a dilution factor of 1.83 [3] to the well-mixed Tank 48 feed [20] (unless indicated otherwise). Note that the Tank 48 composition data from Reference 20 is based on Tank 48 samples retrieved in 2003, 2004, and 2005.

2 Total insoluble solids for CCPO-processed feed are based on complete decomposition and dissolution of KTPB, no decomposition of MST, and 1.83 dilution factor.

3 Assuming density of approximately 1 g/mL for feed solution.

4 Value based on a nominal feed of 6.44M Na.

5 Value based on acceptance criteria for waste feed to SWPF.

6 Value based on empirical data from 2005 study (Reference 3). Note that the Tank 48 simulant used in 2005 study is based on Tank 48 composition data from 2003.

7 Criteria in RED text are exceeded by the composition of the predicted CCPO-processed waste.

8 Value based on acceptance criteria for waste feed from SWPF to Saltstone.

9 Value based on acceptance criteria for waste feed from SWPF to DWPF.

10 Value based on limits for vitrified glass; wt% contribution of CCPO-processed feed with and without blending will be determined during DWPF batch preparation.

11 Concentration, Storage, and Transfer Facilities (CSTF) Corrosion Control Program [28] states that for 1.0M ≤ $[NO_3^-]$ ≤ 2.75M;

$[OH^-] \geq 0.1[NO_3^-]$

$[OH^-] + [NO_2^-] \geq 0.4[NO_3^-]$

Molar quantities in CCPO-processed waste:

$[NO_3^-]$ = (72.8 g/L ÷ 62.0 g/mol) = 1.17M

$[NO_2^-]$ = (8.6 g/L ÷ 46.01 g/mol) = 0.19M

$[OH^-]$ = (25.4 g/L ÷ 17.01 g/mol) = 1.49M

Molar quantities in CCPO-processed waste:

($[OH^-]$: **1.49M**) ≥ (0.1$[NO_3^-]$: **0.12M**)

($[OH^-]$: 1.49M) + ($[NO_2^-]$: 0.19M) = **1.68M** ≥ (0.4$[NO_3^-]$: **0.47M**)

12 $NO_{eff} = [NO_3^-] + ½[NO_2^-] \geq 1.0M$

$[NO_3^-] + ½[NO_2^-]$ = 1.17M + ½(0.19M) = **1.27M**

13 See Reference 28.

14 Value based on feed of 5.6M Na (Target).

15 M_w Na = 2.30E+04 mg/mol; 1.0M Na (aq.) ⇨ 2.30E+04 mg/L

2.5M Na (aq.) ⇨ ⇨ 5.75E+04 mg/L; 7.0M Na (aq.) ⇨ ⇨ 1.61E+05 mg/L

16 All Tank 48 radionuclide concentrations account for decay to Aug-14-2014 [20]. Per Reference 6 it is anticipated that processing of Tank 48 waste will not commence until 2023. Hence, the data utilized for determining IDP is considered conservative.

17 See Table 7 and related text in Section 5 for Option 6

18 See Reference 29.

19 See Table 3.

Table 3: IDPs for Tank 48, Tank 48 supernate, and CCPO-processed waste.

Radionuclide	T48 (Ci/gal)	CCPO (Ci/gal)	Supernate (Ci/gal)	DCF [1] (rem/Ci) [Ref. 30]	T48 (rem/gal)	% Contribution to IDP	CCPO (rem/gal)	% Contribution to IDP	Supernate (rem/gal)	% Contribution to IDP
Cs-137	1.30E+00	7.10E-01	6.33E-02	1.90E+04	2.47E+04	2.02	1.35E+04	2.02	1.20E+03	29.13
Sr-90	2.41E-04	1.32E-04	5.58E-06	8.90E+04	2.14E+01	< 0.01	1.17E+01	< 0.01	4.97E-01	0.01
Tc-99	1.80E-04	9.84E-05	1.80E-04	1.50E+04	2.70E+00	< 0.01	1.48E+00	< 0.01	2.70E+00	0.07
Th-232	7.92E-12	4.33E-12	7.92E-12	1.70E+08	1.35E-03	< 0.01	7.36E-04	< 0.01	1.35E-03	< 0.01
U-233	3.91E-06	2.14E-06	3.71E-07	3.60E+07	1.41E+02	0.01	7.70E+01	0.01	1.34E+01	0.32
U-234	1.28E-05	6.99E-06	1.76E-06	3.50E+07	4.48E+02	0.03	2.45E+02	0.03	6.16E+01	1.49
U-235	8.55E-09	4.67E-09	1.19E-09	3.10E+07	2.65E-01	< 0.01	1.45E-01	< 0.01	3.69E-02	< 0.01
U-236	3.57E-07	1.95E-07	7.76E-09	3.20E+07	1.14E+01	< 0.01	6.24E+00	< 0.01	2.48E-01	< 0.01
U-238	8.38E-09	4.58E-09	1.10E-09	3.00E+07	2.51E-01	< 0.01	1.37E-01	< 0.01	3.29E-02	< 0.01
Np-237	9.95E-07	5.44E-07	5.30E-08	8.50E+07	8.46E+01	< 0.01	4.62E+01	< 0.01	4.51E+00	0.11
Pu-238	7.01E-03	3.83E-03	3.41E-06	1.70E+08	1.19E+06	97.29	6.51E+05	97.29	5.80E+02	14.04
Pu-239	1.96E-05	1.07E-05	1.15E-05	1.90E+08	3.72E+03	0.30	2.03E+03	0.30	2.19E+03	52.92
Pu-240	8.89E-06	4.86E-06	4.12E-07	1.90E+08	1.69E+03	0.14	9.23E+02	0.14	7.83E+01	1.90
Pu-241	2.95E-04	3.99E-04	0.00E+00	3.30E+06	9.74E+02	0.20	1.32E+03	0.20	0.00E+00	< 0.01
Total IDP	-	-	-	-	**1.22E+06**	-	**6.69E+05**	-	**4.13E+03**	

[1] DCF = dose conversion factor

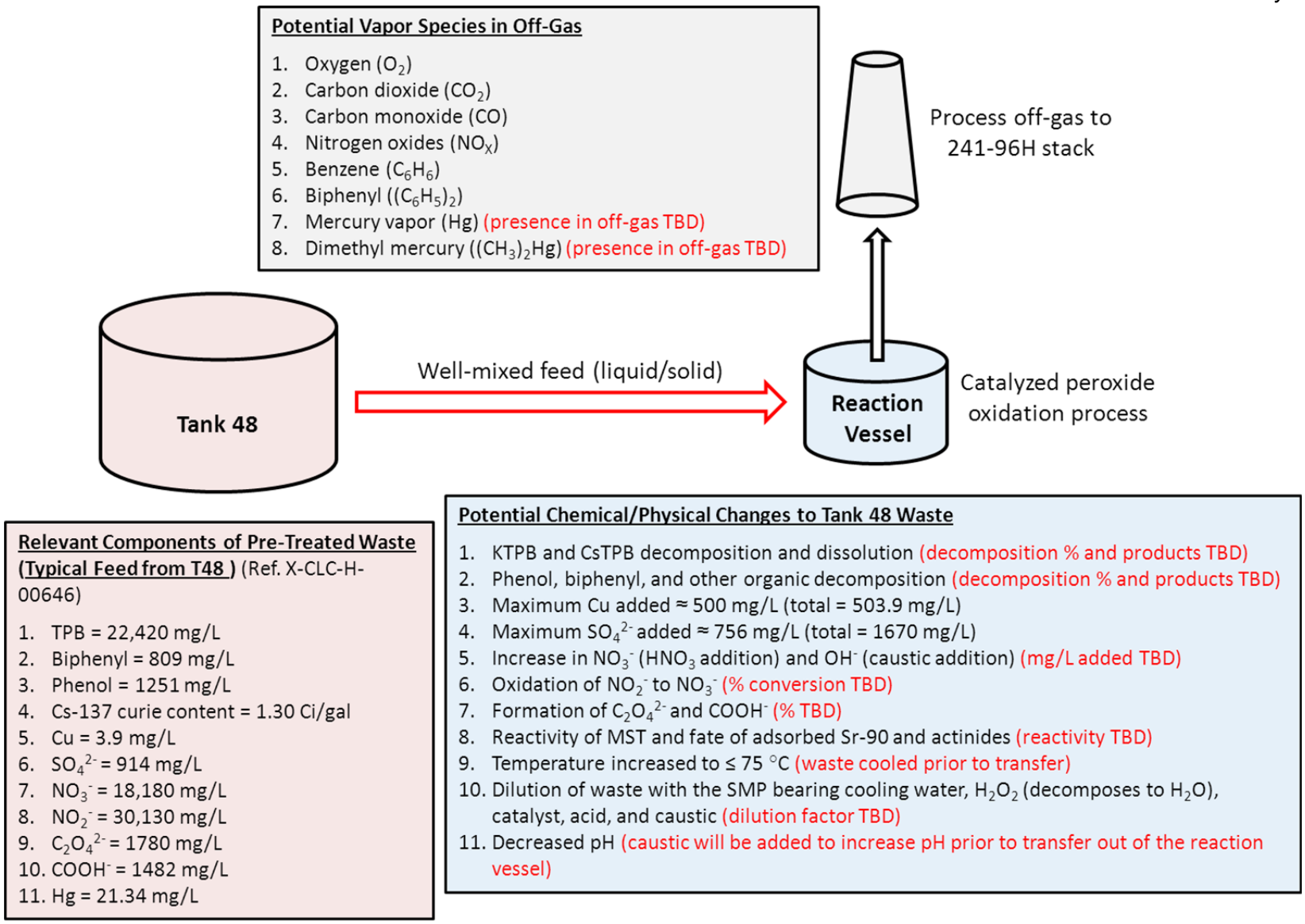

Figure 4: CCPO process schematic detailing chemical and physical changes to the Tank 48 waste.

4 REQUIREMENTS DOCUMENTS

A total of six flow-sheet options were developed. An assessment team (shown in Table 4) was subsequently chartered to identify criteria applicable to transferring the treated Tank 48 waste via each of the flow-sheet options.

Table 4: Team members for developing criteria applicable to CCPO-processed waste.

Team Member	Affiliation
Earl Brass	Savannah River Remediation, LLC (SRR) – Technology Development
Karthik Subramanian	SRR – Technology Development
Steven Simner	SRR – Technology Development
Celia Aponte	SRR – Technology Development
Maria Rios-Armstrong	SRR – Technology Integration
Huong Colleran	SRR – Technology Integration
Thomas Britt	SRR – Technology Integration
Hasmukh Shah	SRR – Project Integration and Planning
Ronald Campbell	SRR – Environmental Compliance
Aaron Condon	Washington Safety Management Solutions, LLC (WSMS)
Samuel Fink	Savannah River National Laboratory (SRNL)
Thomas Peters	SRNL
Jeffrey Bentley	U.S. Department of Energy Savannah River (DOE-SR)
Patricia Suggs	DOE-SR
William (Joe) Copeland	DOE-SR

Attachment 1 lists the documents [23-27, 30-32] that were identified and reviewed for each flow-sheet. Attachment 1 also provides criteria deemed pertinent to realization of a particular flow-sheet. Much of the information included in Attachment 1 does not directly influence flow-sheet assessment with respect to physical, chemical, and radiological requirements. In these instances a criterion is indicated as generally applicable, and will require further consideration as the CCPO technology is matured and implemented. The subsequent text provides a brief description of the document-types reviewed.

Technical Safety Requirements

The TSR [31] contains operating limits, surveillance requirements (SRs), and administrative controls necessary to protect the health and safety of the public and to minimize the potential consequences to workers from the uncontrolled release of radioactive or other hazardous

materials. It should be noted that the WAC ensures that any TSR requirement with respect to the waste composition and its physical and chemical properties is met. As such waste generator's compliance with the WAC ensures compliance with the TSR for a respective facility.

Documented Safety Analysis

The DSA [23] provides an assessment of hazards associated with normal, abnormal, and accident conditions. The assessment also includes natural phenomena hazards (NPH) and man-made external events, including the identification of energy sources or processes that might contribute to the generation of uncontrolled release of radioactive and other hazardous materials. The hazard and accident analyses are the central elements of this process. The results of the hazard analysis form the basis for grading the level of detail necessary to ensure an acceptable DSA. The hazard analysis specifically identifies safety-significant structures, systems, and components (SSCs) and specific administrative controls (SACs) for defense in depth and worker safety, and TSR controls. The hazardous events evaluated include fires, explosions, loss of confinement (LOC), and external/NPH events and criticality, for example. It should be noted that the WAC ensures that any DSA requirement with respect to the waste composition and its physical and chemical properties is met. As such waste generator's compliance with the WAC ensures compliance with the DSA for a respective facility.

Waste Acceptance Criteria

The WAC Programs ensure that the composition of a waste stream received into a particular facility is within analyzed limits. WACs are applicable to transfers out of the TF into SPF [24], 512-S [25], DWPF [25], and SWPF [26], and into the TF from any of the aforementioned facilities (except transfers within the TF). In general the WAC addresses such items as inhalation dose potential (IDP), fissile material, heat generation rate, hydrogen generation rate (HGR), organic concentration, flammability, and environmental compliance.

Air Emissions (Environmental Regulations)

The CCPO process must be compliant with environmental regulations with respect to off-gas emissions. Air emissions are primarily regulated by the South Carolina Department of Health and Environmental Control (SCDHEC) [32]. Regulation 61-62.5, Air Pollution Control Standards No. 2 (Ambient Air Quality) and No. 8 (Toxic Air Pollutants) specifically detail the air emission limits for various chemical pollutants. The criteria relevant to likely emissions from the CCPO process (per 2005 data [3]) are listed in Table 4.

Table 5: Relevant CCPO process off-gas emissions and SCDHEC limits [32].

Emission Component	Limit ($\mu g/m^3$ – unless stated otherwise)
Standard No. 2	
Carbon Monoxide (CO)	40 mg/m^3
Nitrogen dioxide (NO_2)	100
Standard No. 8	
Benzene (C_6H_6)	150.00
Biphenyl ($(C_6H_5)_2$)	6.00
Mercury (Hg) (including mercury compounds)	0.25
Nitrobenzene ($C_6H_5NO_2$)	25.00
Phenol (C_6H_5OH)	190.00

With respect to the potential radionuclide air emissions a preliminary radiological National Emission Standards for Hazardous Air Pollutants (NESHAP) evaluation under Code of Federal Regulations (CFR) Title 40, Part 61, Subpart H [33] will be performed to estimate the radiological/airborne emissions and the associated dose from CCPO process. The chemical and radiological air emissions evaluations may require approval by SCDHEC.

Off-gas data with respect to all relevant emission species has not been previously collected though this is within the intended scope of the planned FY12 experimental investigations [2]. Some of the compounds identified in Table 5 may not volatilize or sublime at the reaction temperature and thus will not be contained within the off-gas. Results from the experimental program will determine compliance of the off-gas composition with the corresponding emission limits.

Wastewater Treatment (Environmental Regulations)

Prior to any modifications to the existing tank farm facilities to implement the CCPO process, an industrial wastewater treatment facility construction permit issued by SCDHEC will be required. The application for this permit should address the change in use of equipment in 241-96H, any new wastewater treatment equipment required to be installed in support of the CCPO process, and any required approvals needed by the down-stream facilities to accept the treated waste streams resulting from the Tank 48 CCPO process.

5 FLOW-SHEET OPTION ASSESSMENT

The subsequent text provides a description of flow-sheet options designated 0 through 6, and also discusses those criteria that must be met in order to transfer the waste out of the reaction

vessel, and that are potentially challenged by the CCPO-processed feed composition (or Tank 48 supernate in the case of Option 5). It is important to note that the CCPO-processed waste will be transferred in batches of approximately 5500 gallons (11,000 gallons for both reaction vessels) every 1-3 weeks (depending on optimization of process kinetics). This is important for those options in which a batch is added to the contents of a storage, blend, or feed tank prior to final disposition. For example, the SPF WAC applies to the composition of Tank 50 subsequent to addition of the CCPO-processed waste rather than the composition of the CCPO-processed waste itself. As such while the CCPO-processed feed to Tank 50 may exceed specific WAC criteria it is the composition of the CCPO-processed waste blended with the contents already contained in Tank 50 that must meet the SPF WAC.

Table 2 provides the chemical, radiological, and physical limits currently imposed on the CCPO-processed waste (and the Tank 48 supernate for Option 5) by the WACs for SPF, 512-S, DWPF, and SWPF and by the DSA for the TF. The components of concern are those in the CCPO-processed waste that currently challenge the relevant WAC or DSA criteria; these components are highlighted in red in Table 2. Comparisons between the feed compositions and the designated criteria take no account of blending with the contents of other tanks, which was discussed in the previous paragraph though where relevant the potential benefits of blending will be subsequently discussed for each flow-sheet option.

One important note relates to comparison of the residual organics in the treated waste and the relevant limiting criteria. Determining the allowable residual organics in the treated waste for a particular flow-sheet is a key component of this report since it enables the success criteria of organic destruction efficiency to be established for the CCPO FY12 investigations [2]. However, for each option the allowable organic content of the treated waste is expressed as an allowable percentage contribution to the LFL of hydrogen for TF, 512-S, DWPF, and SWPF, and as percentage contribution to the CLFL for SPF (Tank 50). For TF, 512-S, and DWPF the limits on residual organics are 5%, 0.1%, and 0.1% of the hydrogen LFL, respectively, and no limits are specified for TPB. For SWPF the limit is < 0.1% based on the allowable contribution to the hydrogen LFL in the downstream DWPF Sludge Receipt and Adjustment Tank (SRAT) and for SPF the limit is 5% CLFL in Tank 50. Both the SPF and SWPF WACs do, however, specify a maximum TPB concentration of 5 and 10 mg/L, respectively, though this is merely based on the presumed TPB detection limit for the HPLC analysis method. A future intention is to conduct flammability contribution calculations based on the FY12 CCPO post-treated product, and

establish if the product challenges the specified LFL or CLFL limits. The findings from these calculations will be included in a subsequent revision of this document.

***OPTION 0* – TRANSFER FROM TANK 48 AND CCPO PROCESS**

Option 0 encompasses transfer of the untreated waste from Tank 48 to the CCPO reaction vessel, and subsequent CCPO processing of the waste. As such it is not strictly considered a flow-sheet option, but it is, however, necessary to assess those criteria that might potentially affect the proposed maturation and execution of the waste transfer and the CCPO process. First and foremost it should be noted that per Section 5.8.2.49 of the Concentration, Storage and Transfer Facilities (CSTF) TSR [31], transfers to or from Tank 48 are prohibited. This criterion will obviously require amendment prior to future treatment of the waste in Tank 48.

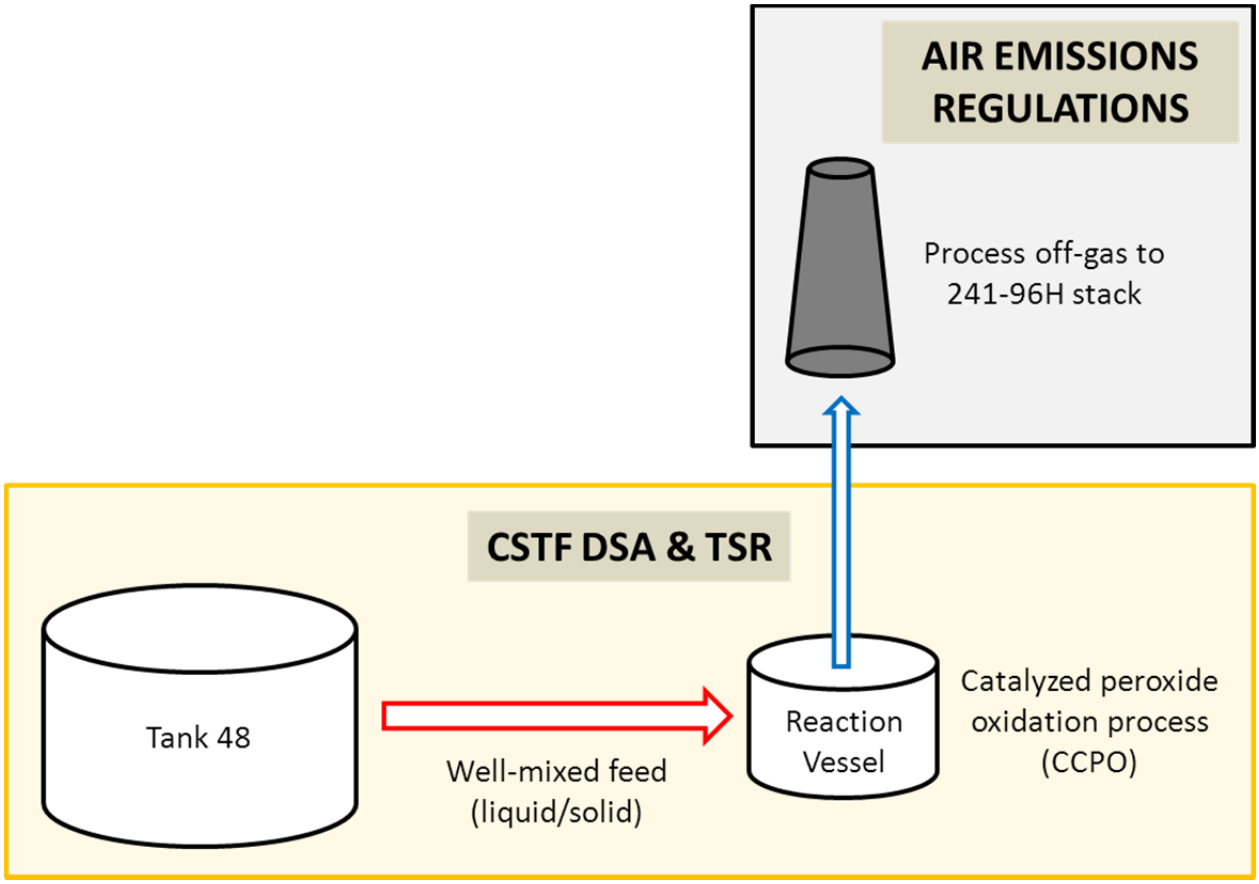

Figure 5: Flow-sheet schematic illustrating requirements documents for transfer of waste from Tank 48 and subsequent CCPO treatment.

The treatment of the Tank 48 waste via CCPO will be a batch process in which approximately 3000 gallons of Tank 48 waste are pumped into the CCPO reaction vessel. Prior to transfer of the untreated waste from Tank 48, the waste will be agitated using four currently installed low-shear slurry pumps to ensure a relatively homogeneous discharge stream, in particular with

respect to the suspension of insoluble solids. The release of entrapped benzene in the Tank 48 sludge solids during slurry pump operation has historically been a concern though recent measurement data indicates that the benzene concentration in the Tank 48 vapor space will remain below 5% of its LFL while operating the slurry pumps for waste transfers out of Tank 48 without the need for tank inerting operations [34].

Once the waste in Tank 48 is mixed it will then be pumped to the CCPO reaction vessels in 241-96H through a combination of existing transfer lines [35] and newly installed jumpers. The ARP MST strike tanks in 241-96H will operate as reaction vessels for the CCPO reaction. These tanks are constructed from 304L SS and are expected to exhibit excellent corrosion resistance in both acidic and caustic environments [36]. With respect to shielding the ventilation inlet ducts on the process cells are currently designed for a maximum of 1.1 Ci/gal Cs-137 [37], and based on the Cs-137 decayed curie content of the typical (well-mixed) Tank 48 feed (1.30 Ci/gal – Table 2) these ducts will require additional shielding. Agitation in the tanks will be required to (1) provide adequate mixing to optimize interaction of the reactants and provide uniform heat transfer in the solution, and (2) maintain insoluble solids suspension to ensure the post-reaction transfer of the sludge particles out of the tanks. With respect to the latter, modeling analysis [38] has been performed for the current MST strike tank impeller design, and demonstrates that the impeller provides sufficient high velocity zones to mix a tank containing solids similar to sludge particles.

The CCPO reaction process essentially incorporates the following basic steps:

1. Agitation of waste in the reaction vessel.
2. Addition of acid to lower the pH to the target pH (acid concentration and target pH to be determined by planned FY12 studies).
3. Adjustment to target reaction temperature (to be determined by planned FY12 studies).
4. Addition of copper catalyst (copper compound and amount added to be determined by planned FY12 studies).
5. Addition of hydrogen peroxide (concentration and addition rate to be determined by planned FY12 studies).
6. Sampling to determine point at which desired destruction efficiency has been achieved.
7. Cooling, pH adjustment (caustic addition), and agitation prior to transfer.

As indicated in the above list many of the process parameters will be determined in planned FY12 studies; details of these studies are provided in the Task Technical and Quality Assurance Plan (TTQAP) [2]. It is envisaged that experimentation will provide a well-defined operating envelope with respect to chemical addition rate and sequence, pH, temperature, inerting requirements, the formation of intermediate compounds and off-gas constituents, and the minimization of foam formation (via the use of anti-foam and an appropriate mixing strategy).

Of particular significance with respect to the CCPO process is the off-gas produced during the peroxide oxidation reaction. For an ideal process (in terms of air emissions) the off-gas would be limited to oxygen (from the self-decomposition of hydrogen peroxide) and carbon dioxide (from the destruction of the TPB). However, previous experimentation has indicated that other compounds such as nitrogen oxides and benzene may be present. Figure 4 details potential off-gas compounds, and in addition to the aforementioned vapor species also indicates carbon monoxide, biphenyl, mercury, and dimethyl mercury. Biphenyl is an intermediate product of the TPB destruction process and may sublime; in previous experiments, however, the biphenyl has subsequently condensed on the cooler surfaces of the reaction vessel [3]. Mercury and organomercurials were not analyzed in previous testing though the presence of mercury in the Tank 48 waste (see Table 2) and the relatively high processing temperatures (≤ 75 °C) prompt the need to confirm that mercury is not being emitted into the atmosphere at levels that would exceed the regulatory limits per Standard 8 of the SCDHEC [32] (see Table 5). With specific reference to organomercurial compounds a recent literature review [22] concluded that in the event that organomercurials did exist in the Tank 48 waste, their reaction with hydrogen peroxide could potentially convert them to mercury (II) or elemental mercury. Ultimately off-gas measurement data from the planned FY12 will be compared to the SCDHEC and other pertinent regulations to establish those off-gases that exceed or challenge the established regulatory limits.

***OPTION 1* – TRANSFER TO TF**

This option involves transfer of the treated waste to a storage or preparation tank in the TF where it will be mixed with feeds from other tanks prior to transfer to one of the four process routes indicated in Figure 6 below. For the discussion of this particular option it is assumed that acceptance of the CCPO-processed waste from Tank 48 into a TF storage or preparation tank affirms its acceptability for further disposition utilizing any of the indicated processes. As such criteria designated in the CSTF DSA and TSR are applicable to this option.

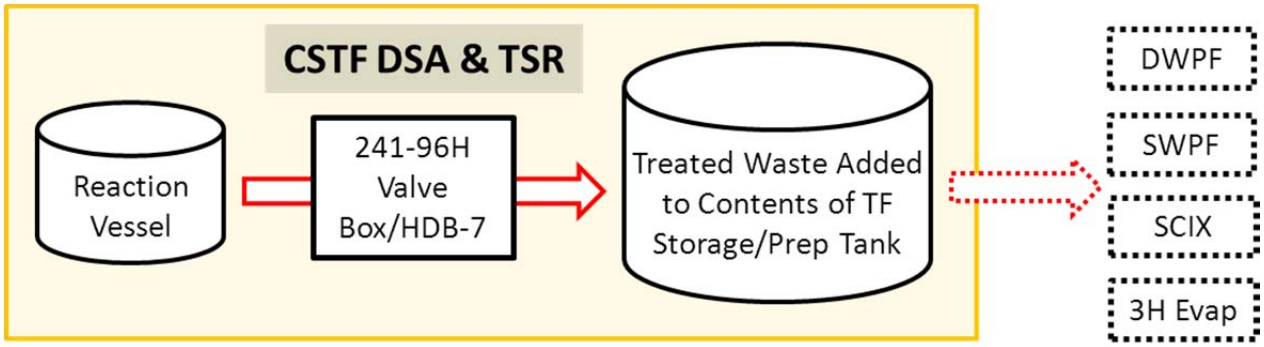

Figure 6: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to a TF storage tank (SCIX = Small Column Ion Exchange).

One of the primary criteria for acceptance of the treated Tank 48 waste into a TF tank is that the flammability contribution of organics shall not exceed 5% of the hydrogen LFL. As discussed in Section 3 it has not yet been determined how this LFL contribution limit translates to an allowable concentration of residual organics in the CCPO-processed waste though the near-term intent is to calculate this value and update it in a later revision of this document. Ultimately, acceptance of the post-treated CCPO waste into a specific tank will be dependent on the composition of the contents already in the tank and its subsequent disposition route.

All TF tanks are subject to requirements specified in the CSTF Corrosion Control Program [27]. For waste feeds with nitrate molarity ≥ 1.0M the following requirements are specified:

i. $[OH^-] \geq 0.1[NO_3^-]$

ii. $[OH^-] + [NO_2^-] \geq 0.4[NO_3^-]$

Both of these requirements are satisfied based on the compositional values indicated in Table 2. It is important to note that with respect to corrosion control the aforementioned requirements are specified for the contents of a specific receipt tank after transfer of a given waste stream as

opposed to the composition of an individual incoming waste stream to the receipt tank. Ultimately, the CCPO-processed waste will be assessed with respect to corrosion control prior to transfer from the CCPO reaction, and adjustments made to ensure compliance with the CSTF Corrosion Control Program [27].

***OPTION 2* – TRANSFER TO SPF (VIA TANK 50)**

Option 2 involves transfer of the treated waste via the 241-96H Valve Box and H-Diversion Box (HDB) 7 to Tank 50 for eventual disposition at the SPF, as depicted in Figure 7.

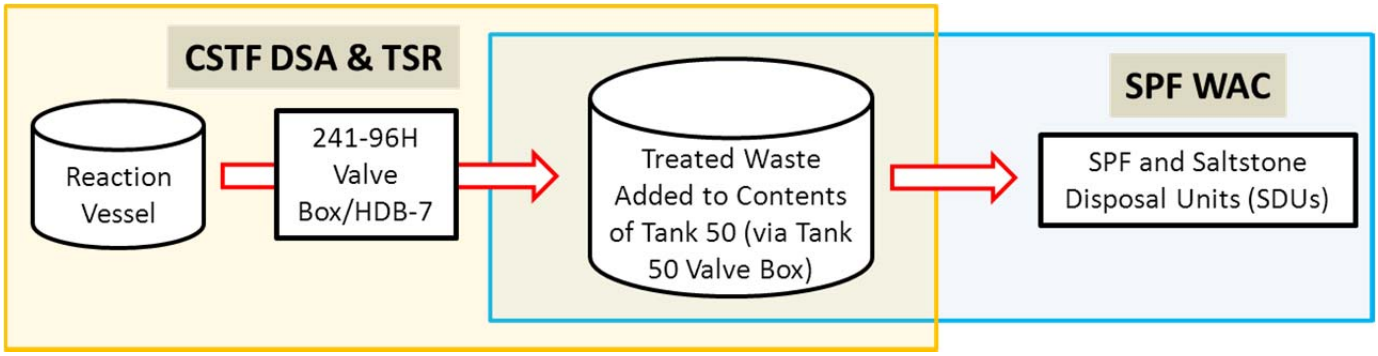

Figure 7: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to SPF (via Tank 50).

Tank 50 is the regulatory point of compliance for the SPF and is thus subject to limitations set forth in the CSTF DSA and SPF WAC. With specific regard to TPB, the SPF WAC sets a maximum TPB concentration limit of 5 mg/L (lower than the presumed TPB detection limit of 10 mg/L). For a well-mixed Tank 48 waste stream the following destruction level would be required to achieve a TPB concentration of 5 mg/L.

> *For a well-mixed Tank 48 waste stream:*
>
> TPB = 22,400 mg/L [20]; adjusted TPB (per 1.83 dilution factor [3]) = 12,240 mg/L
>
> Therefore, to achieve a CCPO-processed TPB content of 5 mg/L requires 99.96% TPB destruction.

The required TPB destruction efficiency of 99.96% does not take into account the potential dilution of the CCPO-processed feed in Tank 50. A dilution factor of, for example, 10 in Tank 50 would effectively increase the TPB limit in the feed to 50 mg/L which would require a 99.59% TPB destruction. The potentially beneficial role of mixing the CCPO-processed feed with other tank contents, and the subsequent reduction in the TPB destruction efficiency required of the CCPO process, are ultimately dependent on a number of factors which include the CCPO-processed batch size, the batch transfer frequency, the composition of the tank to which the batch is to be transferred, and how frequently the waste from the receipt tank is dispositioned.

The current proportion of phenol in the untreated waste also exceeds the SPF WAC though it is anticipated that phenol will be readily oxidized during the CCPO process. The proportions of all organics remaining in the treated slurry will be established during the planned FY12 CCPO process verification and optimization tests [2].

The SPF WAC specifies a sodium molarity range of 2.5 – 7.0M which is equivalent to 5.75E+04 to 1.61E+05 mg/L. The CCPO-processed feed is less than this at 5.01E+04 mg/L though this value does not account for the potential of adding caustic (sodium hydroxide) to the CCPO-processed waste prior to transfer from the reaction vessels in 241-96H. In addition, the CCPO-processed waste will be mixed with other waste streams in Tank 50 which have potentially higher sodium concentration.

With respect to radionuclides the concentrations of Cs-137 and Pu-238 in the CCPO-processed feed are approximately 4-5 times higher than the Tank 50 SPF WAC limits of 1.80E-01 and 9.46E-04 Ci/gal, respectively. In addition, transfers with IDP > 2.09E+05 rem/gal are prohibited through the Tank 50 Valve Box and the transfer lines into Tank 50. The Tank 48 IDP is 1.22E+06 rem/gal [29], which converts to 6.69E+05 rem/gal after CCPO process dilution; this exceeds the designated WAC limit by more than a factor of 3. Since Pu-238 is the major contributor to alpha emission, the CCPO-processed waste (Pu-238 = 3.83E-03 Ci/gal) also exceeds the alpha limit specified in the WAC (2.50E+05 pCi/mL equivalent to 9.49E-04 Ci/gal). It is, however, conceivable that components of the CCPO-processed feed, like Cs-137 and Pu-238, which exceed SPF WAC criteria by less than an order of magnitude, will be blended with other influents upon addition to Tank 50 such that they no longer challenge the WAC criteria.

Two additional requirements of the SPF WAC are not related to specific constituents. Firstly, any constituent with a molarity ≥ 0.5M shall not be transferred to SPF without formal review and authorization by Waste Solidification (WS) Engineering. Table 6 highlights those components present in the Tank 48 waste that are not specifically addressed in the WAC and provides the respective concentrations, none of which approach the 0.5M limit. Secondly, any radionuclide not identified in the WAC having an activity concentration greater than or equal to 1.25E+04 pCi/mL (4.73E-05 Ci/gal) shall not be transferred to SPF without formal review and authorization by WS Engineering. However, with reference to Table 2, the SPF WAC currently provides specific limits for all radionuclides contained in the Tank 48 waste.

Table 6: Components contained in Tank 48 waste but not identified in SPF WAC.

Constituent	Concentration in CCPO-processed Waste (mg/L) [1]	Molecular Weight (E+03 mg/mol)	Molarity (M)
Br-	5.27E+01	79.90	6.60E-04
COOH-	8.10E+02	45.02	1.80E-02
Ca	7.32E+01	40.08	1.83E-03
Ce	5.34E-01	140.12	3.81E-06
Cs	8.89E+00	132.91	6.69E-05
Gd	2.14E+00	157.25	1.36E-05
La	6.95E+00	138.91	5.00E-05
Mg	1.44E+01	24.31	5.92E-04
P	1.29E+02	30.97	4.17E-03
S	2.98E+02	32.07	9.29E-03
Sb	6.23E+00	121.76	5.12E-05
Sn	4.11E+01	118.71	3.46E-04
Ti	4.56E+02	47.87	9.53E-03
V	4.92E-01	50.94	9.66E-06
Zr	1.07E+00	91.22	1.17E-05
Pd	5.61E-02	106.42	5.27E-07
Rh	3.74E-01	102.91	3.63E-06
Ru	6.20E-01	101.07	6.13E-06

[1] CCPO-processed chemical species concentrations from Table 2.

***OPTION 3* – FILTER IN 512-S**

Current use of 512-S involves pumping ARP feed through a sub-micron SS cross-flow filter to separate MST/sludge solids from salt solution. When sufficient MST/sludge solids have been accumulated in the Late Wash Precipitate Tank (LWPT) they are transferred to DWPF, and the filtrate is collected in the Late Wash Hold Tank (LWHT) and transferred to Tank 50 after processing in the Modular Caustic Side Solvent Unit (MCU). In contrast, following separation by the cross-flow filter, Option 3 (Figure 8) would involve transfer of the insoluble solids (with low CsTPB insoluble solid content) to SPF (via Tank 50), and the liquid portion (with high soluble Cs content) to DWPF. The CSTF DSA and TSR, the 512-S/DWPF WAC, and the SPF WAC must be considered in evaluating Option 3.

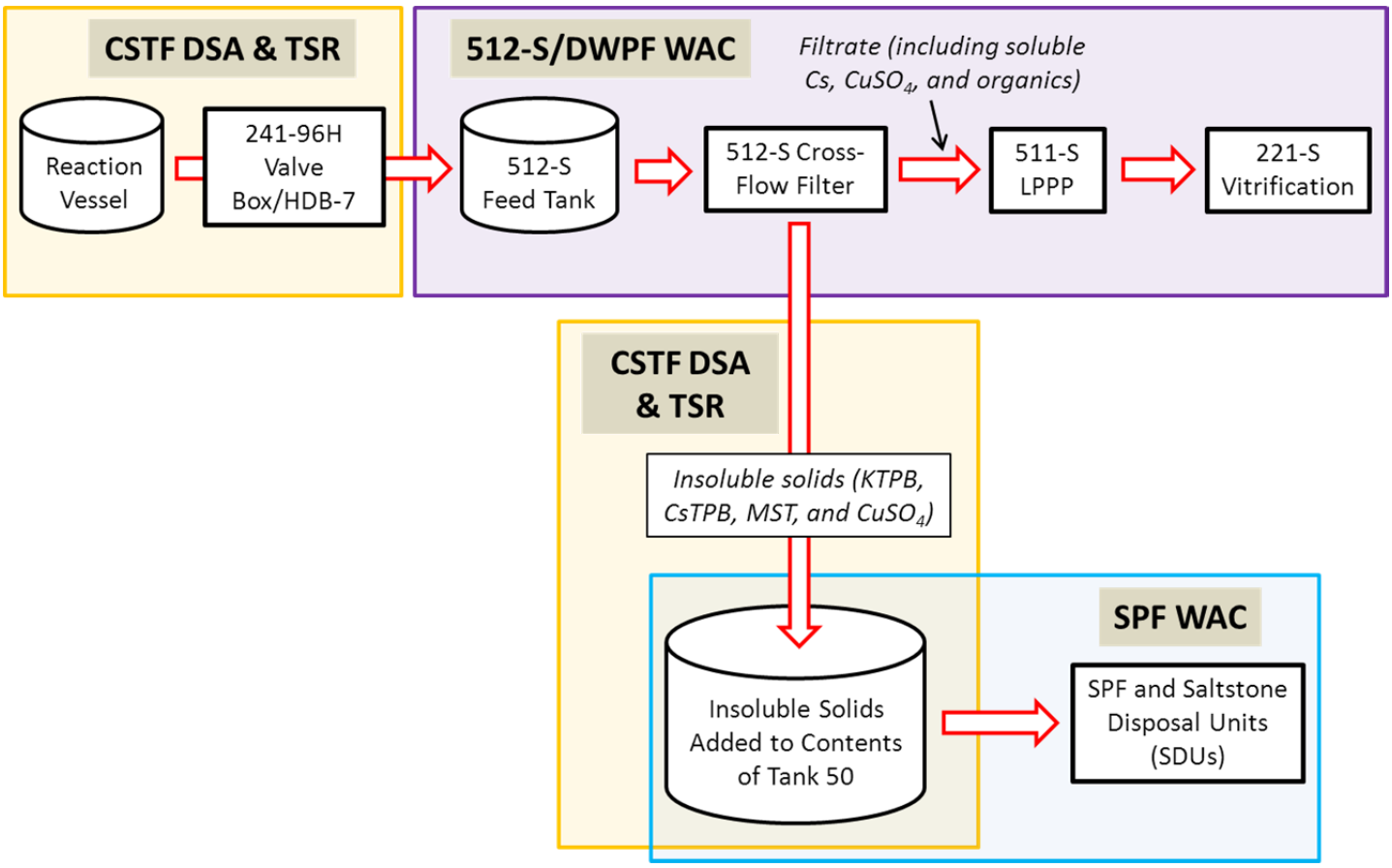

Figure 8: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste through the 512-S cross-flow filter (LPPP = Low Point Pump Pit).

With respect to 512-S many of the constituents listed for the Tank 48 waste concentration limits (Table 2) are not defined in the respective WAC. Of those constituents that are defined it is the

organic and the Cs-137 concentrations that will likely either exceed or challenge the WAC. Particularly restrictive is the requirement that the waste feed not contribute more than 0.1% of the hydrogen LFL in the 512-S feed tank. As previously discussed a flammability calculation will be ultimately required to determine what this limit represents with respect to allowable concentrations of TPB and TPB decomposition products. The findings from this calculation will be included in a later revision of this document.

The allowable 512-S curie concentration for Cs-137 is 1.11 Ci/gal to maintain a dose rate of < 0.5 rem/hr. Per the currently assumed level of dilution (1.83 [3]) for the Tank 48 waste the decayed curie concentration of Cs-137 in the CCPO-processed waste would be < 1 Ci/gal. However, as part of the FY12 studies process optimization will be assessed with respect to reducing the volume dilution that occurs during processing. As such the 1.11 Ci/gal Cs-137 limit may be exceeded potentially requiring additional shielding.

The WAC for 512-S also imposes an IDP limit of 3.00E+06 rem/gal. Based on the bounding IDP calculated for Tank 48 (1.22E+06 rem/gal [29]), and subsequent dilution during CCPO processing, the IDP for the waste transferred from the CCPO reaction vessel to 512-S is approximately 6.69E+05 rem/gal which may potentially challenge the 512-S IDP limit of 3.00E+06 rem/gal. Indeed if process optimization [3] yields less process dilution then this limit could likely be exceeded. An associated criterion of the IDP limit is that the soluble Pu-238 concentration should be $\leq$ 3.0E-03 Ci/gal. Currently, for Tank 48 it is assumed that the actinides, including Pu-238, are adsorbed onto MST and thus associated with the solid portion of the waste. However, as part of the FY12 study scope [2] the potential reactivity of MST and subsequent actinide desorption is being investigated. Assuming 100% desorption the soluble Pu-238 would equal 3.83E-03 Ci/gal which exceeds the WAC specified limitation.

For transfer of the filtered solids to Tank 50, requirements designated by the CSTF DSA/TSR and SPF WAC are applicable. During the proposed CCPO process both KTPB and CsTPB (Cs-137) are decomposed and their respective cations dissolved. As such the majority of Cs-137 is contained within the supernate of the waste and filtering will result in separation of the higher activity liquid and the lower activity insoluble solids. Thus, with a significantly reduced Cs-137 concentration in the solid portion of the waste (dependent on TPB destruction efficiency and any volume concentration factor that occurs from separating the liquids) the insoluble portion of the waste may be transferred to Tank 50 without challenging the SPF WAC limitation of 0.18 Ci/gal

for Cs-137. In contrast, when the liquid portion of the waste is removed from the transferred waste, the solid portion will effectively be contained in a significantly smaller volume. Prior to separation in 512-S the Pu-238 constituent (adsorbed onto the MST solids) is dispersed within the entire liquid waste volume and has a curie content of 3.83E-3 Ci/gal in CCPO-processed waste (Table 2); note also that the proportion of MST solids is approximately 0.1 wt% in the CCPO-processed feed (Table 2). After removal of the majority of the liquid, the same 3.83E-03 Ci (for Pu-238), previously contained within one gallon of waste, will now be contained (assuming actinide absorption is not affected by peroxide reactivity) within in a smaller volume (equivalent to a higher MST solids loading), and thus the number of radionuclides per unit volume is increased. This would likely impact the transfer of the high solids portion of the waste to Tank 50 which has a maximum Pu-238 concentration limit of 9.46E-04 Ci/gal. In addition, the SPF WAC specifies a 15 wt% limit for insoluble solids in the waste feed to Tank 50 which will have to be considered with respect to the degree of solids concentration through 512-S.

The filtrate from 512-S will be transferred to DWPF. The DWPF WAC also imposes the restrictive requirement that the waste feed not contribute more than 0.1% of hydrogen LFL. However, it can be assumed that if the waste satisfied this same criterion for transfer through 512-S then it will also be satisfied for direct transfer to DWPF. To ensure the successful operation of the DWPF melter by preventing the formation of a secondary glass phase or a salt layer, the DWPF WAC establishes limits for different elements (as indicated in Table 2). Copper sulfate, which is the current catalyst of choice for the CCPO process, DWPF has a limit of 0.50 wt% copper and 0.60 wt% and sulfate in the vitrified glass (note: the indicated sulfate limit is applicable for current sludge batches transferred to DWPF but will need to be re-evaluated for each future sludge batch). The potential impact of the copper sulfate on the DWPF glass was assessed in a recent report [39] which concluded that the proportion of copper sulfate present in the CCPO-processed waste might impact the respective glass solubility limits, and that blending of the waste stream may be required in a sludge feed qualification tank. It is important to note, however, that copper sulfate likely exhibits only partial solubility in the CCPO-processed waste, and thus the proportions of copper and sulfate ions transferred to DWPF as part of the filtrate may be lower than the values indicated in Table 2. The actual proportions of soluble and non-soluble copper sulfate will be established in the FY12 testing [2], and the required catalyst addition subsequently adjusted to reduce the proportion of insoluble copper sulfate which is presumed not to contribute to catalysis of the CCPO reaction. In addition, the FY12 studies [2]

are considering the use of copper nitrate in lieu of copper sulfate which would negate potential issues with respect to sulfate solubility limits.

***OPTION 4* – DIRECT TRANSFER TO SWPF**

This option involves transfer of the waste via the 241-96H Valve Box/HDB-7 to the SWPF. SWPF will separate key high-activity radionuclides from the low-activity salt waste, using proven separation technologies of filtration and centrifugal contactors, similar to those currently utilized within the ARP/MCU facilities but on a larger scale. After separation, the high-activity salt waste will be transferred to DWPF for vitrification, and the remaining high volume/low-activity salt waste will be transferred to Tank 50 for ultimate disposition in SPF grout.

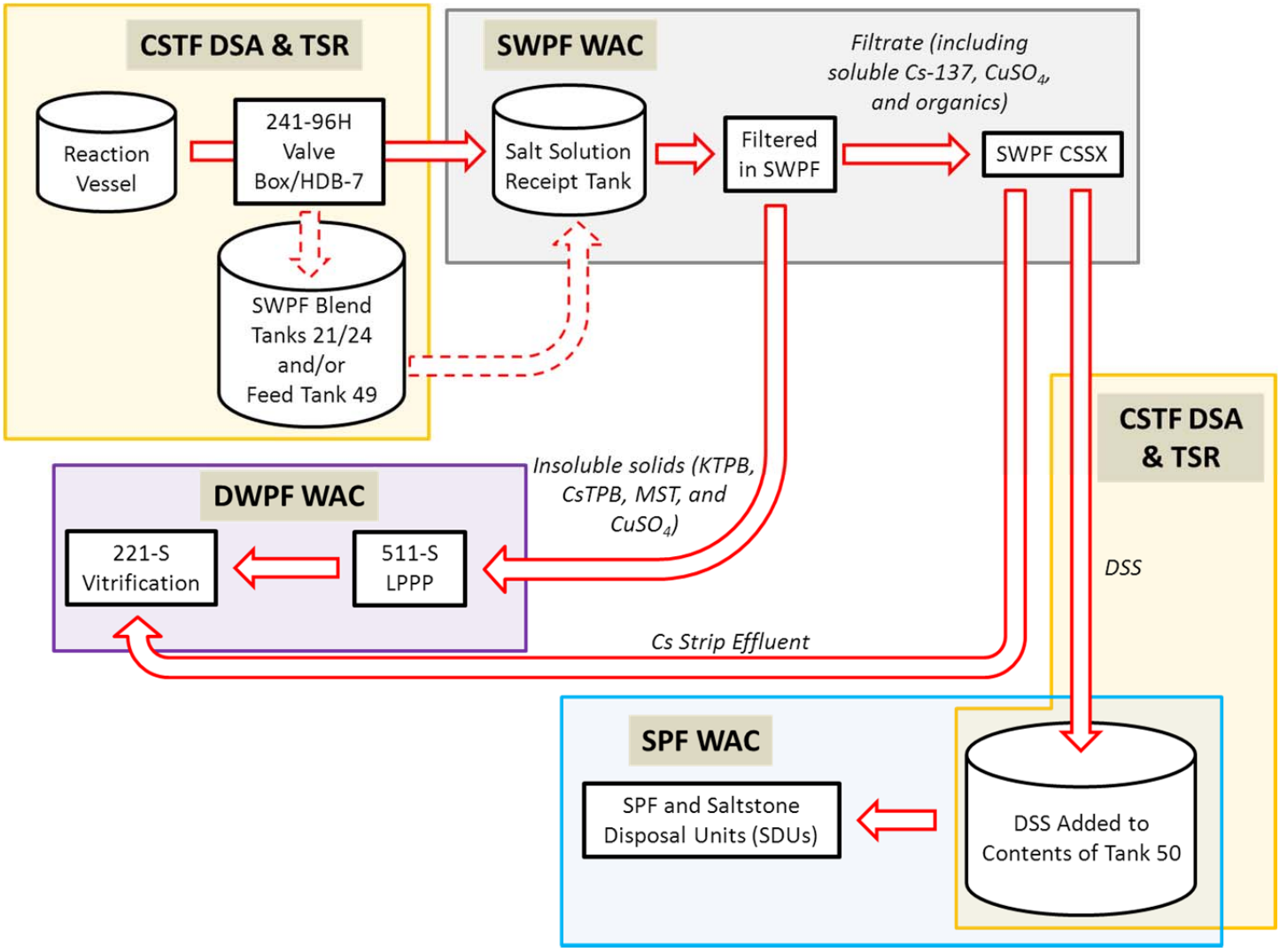

Figure 9: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to SWPF.

Table 2 provides SWPF WAC prescribed limits for waste being transferred into SWPF for a number of components. Those components or properties contained in the CCPO-processed waste that challenge the designated limits include solids content, organic concentration, nitrite and nitrate concentrations, potassium concentration, Pu-238 curie content, and IDP.

Figure 9 depicts a direct transfer route from the CCPO reaction vessel to SWPF in addition to an alternative route that includes the SWPF blending and/or feed tanks, Tanks 21/24 and 49, respectively. This provides the opportunity to blend the CCPO-processed waste to ensure it meets the SWPF WAC specifications. There are two chemical components of the CCPO-processed waste that may ultimately negate a direct transfer of the waste to SWPF, namely sodium and free hydroxide. For sodium the SWPF WAC specifies an acceptable sodium concentration range of 5.6 to 7.0M which is equivalent to approximately 129-1.61E+05 mg/L. This range is specified to protect the decontamination factor (DF) for Cs-137. The CCPO-processed waste indicates a sodium content of 5.01E+04 mg/L. With respect to free hydroxide the SWPF WAC specifies a minimum content of 3.40E+04 mg/L whereas the CCPO-processed waste is calculated to be 2.54E+04 mg/L. It is important to note, however, that caustic (sodium hydroxide) may be added to the CCPO-processed waste in the reaction vessel to increase the pH prior to transfer out of 241-96H.

Limits on organic components are specified by the requirement that the organic material present in the feed from SWPF shall contribute < 0.1 % of the hydrogen LFL downstream in the DWPF SRAT. In regards to TPB and some of its potential decomposition products, concentration limits are set at 10 mg/L for TPB, 450 mg/L for benzene, and 750 mg/L for phenol. To date no analytical work has been performed to demonstrate the effect that residual TPB may have on the ability of the solvent to extract or strip Cs-137. To achieve 10 mg/L TPB from a Tank 48 waste stream containing 22,400 mg/L would require a TPB destruction efficiency of 99.96%.

The following requirement is used to determine if the concentration of nitrite and nitrate in the feed material to SWPF are compliant with the SWPF WAC:

$$NO_{eff} > 1.0M, \text{ where } NO_{eff} = [NO_3^-] + \tfrac{1}{2}[NO_2^-]$$

The presence of nitrate and nitrate anions are important due to their ability to scavenge hydrogen. For the nitrite and nitrate anion concentrations listed in Table 2 for the CCPO-

processed waste, NO_{eff} = 1.27M which is significantly larger than the minimum 1.0M requirement.

Performance of the Caustic Side Solvent Extraction (CSSX) process is adversely impacted by elevated potassium content in the feed. The potassium concentration limit is 1.63E+03 mg/L, which is slightly above the 1.60E+03 mg/L for the diluted CCPO-processed waste, though as mentioned previously optimization of the process to minimize waste volume increase would potentially result in challenge to the SWPF WAC potassium limit. High potassium levels > 0.05 M (~ 2 g/L) have also been shown to promote the separation of a second solvent phase at or below 13 °C [40]. Of significant note is the fact that SWPF may potentially utilize a different solvent to that currently utilized for the MCU process. Termed the Next Generation Solvent (NGS) the material has significantly improved compatibility with potassium. [41]. As such the concentration of potassium in the CCPO-processed feed will potentially no longer be an issue for SWPF.

The decontaminated salt solution (DSS) and the Cs strip effluent exiting the CSSX process will be transferred to SPF (via Tank 50) and DWPF, respectively. As such DSS will be subject to the requirements of CSTF DSA and the SPF WAC; the Cs-effluent will be subject to the limitations designated in the DWPF WAC. Insoluble solids filtered in SWPF are likely to include unreacted KTPB and CsTPB, MST (assuming the MST is not broken down during the peroxide oxidation reaction), and any other insoluble or precipitated solids such as the copper sulfate catalyst; this feed will be required to meet those criteria defined in the DWPF WAC. It is assumed that if the CCPO-processed feed was acceptable for transfer to SWPF then the post-SWPF processed products should have been previously determined as acceptable for transfer to the respective downstream facilities.

***OPTION 5* – TANK 48 RECYCLE**

This option involves processing a batch of the Tank 48 waste via the CCPO process and recycling the treated waste back to Tank 48 as indicated in Figure 10. For transfers between Tank 48 and the CCPO reaction vessel, the waste does not exit the TF and thus only criteria specified in the CSTF DSA and TSR are applicable. However, this option will also incorporate an initial decant of the Tank 48 supernate to Tank 50, in addition to subsequent decants (to maintain the Tank 48 waste below the tank fill limit) due to waste volume increases associated with the CCPO process. After the TPB destruction is complete the other post-treatment flow-sheet options indicated in this document can be employed for further waste dispositioning.

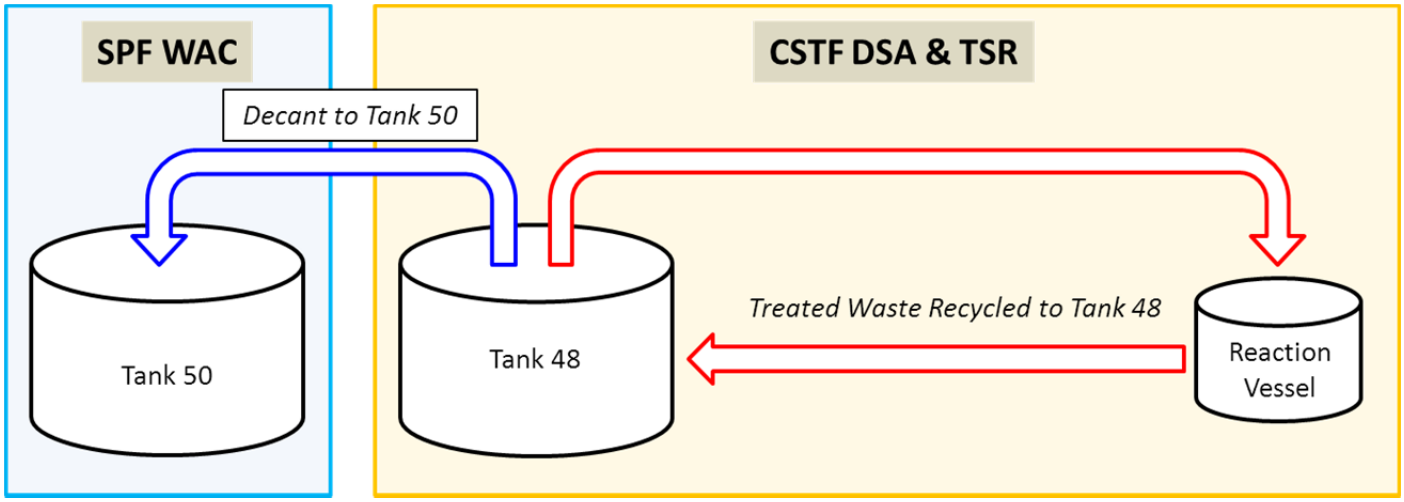

Figure 10: Flow-sheet schematic illustrating requirements documents for recycle of the CCPO-processed waste to Tank 48 and associated Tank 50 decant.

Each supernate decant from Tank 48 is subject to criteria limits designated by the SPF WAC. The composition of the Tank 48 supernate is included in Table 2 [20]. With respect to the initial decant, prior to the first transfer of the waste to CCPO reaction vessels, it is the level of organics in the supernate that are likely to challenge the WAC. For TPB and its decomposition products the indicated concentrations in the supernate are < 10 mg/L (presumed analysis detection limit). The SPF WAC currently specifies a limit of 5 mg/L. For phenol the WAC limit is 750 mg/L (75% DSA) while the supernate contains > 900 mg/L. For subsequent decants (after CCPO processing has commenced) the supernate will contain increased levels of Cs-137 due to the destruction of CsTPB and subsequent cesium dissolution. In addition, the potential reactivity of the MST during the peroxide oxidation may yield soluble actinides that might challenge the SPF

WAC limits. The actual proportions of Cs-137 and actinides in the recycled Tank 48 supernate will be dependent on the level of CsTPB and MST decomposition occurring during the CCPO process both of which will be established during FY12 testing [2].

One potential concern with Option 5 relates to the addition of copper catalyst into Tank 48 during each recycle of the CCPO-processed waste. The presence of copper in Tank 48 has the potential to decompose TPB into benzene [13]. The CSTF DSA (Section 18.4.10) [23] refers to SAC 5.8.2.48.K; one of the safety functions of this SAC is to prevent inadvertent addition of chemicals which could cause an abnormal benzene release. After the TPB destruction is complete the other post-treatment flow-sheet options indicated in this document can be employed for further waste dispositioning.

***OPTION 6* – DIRECT TRANSFER TO DWPF**

This option involves transfer of the waste via the 241-96H Valve Box/HDB-7 to the DWPF as depicted in Figure 11. A tentative proposal for this option is to transfer the CCPO-processed waste directly to DWPF without blending in Tanks 42/51 and 40 though the feasibility of this proposal will require a rigorous assessment of potential impacts to DWPF throughput. If blending is deemed necessary prior to DWPF transfer this capability is available in the aforementioned sludge preparation and feed tanks.

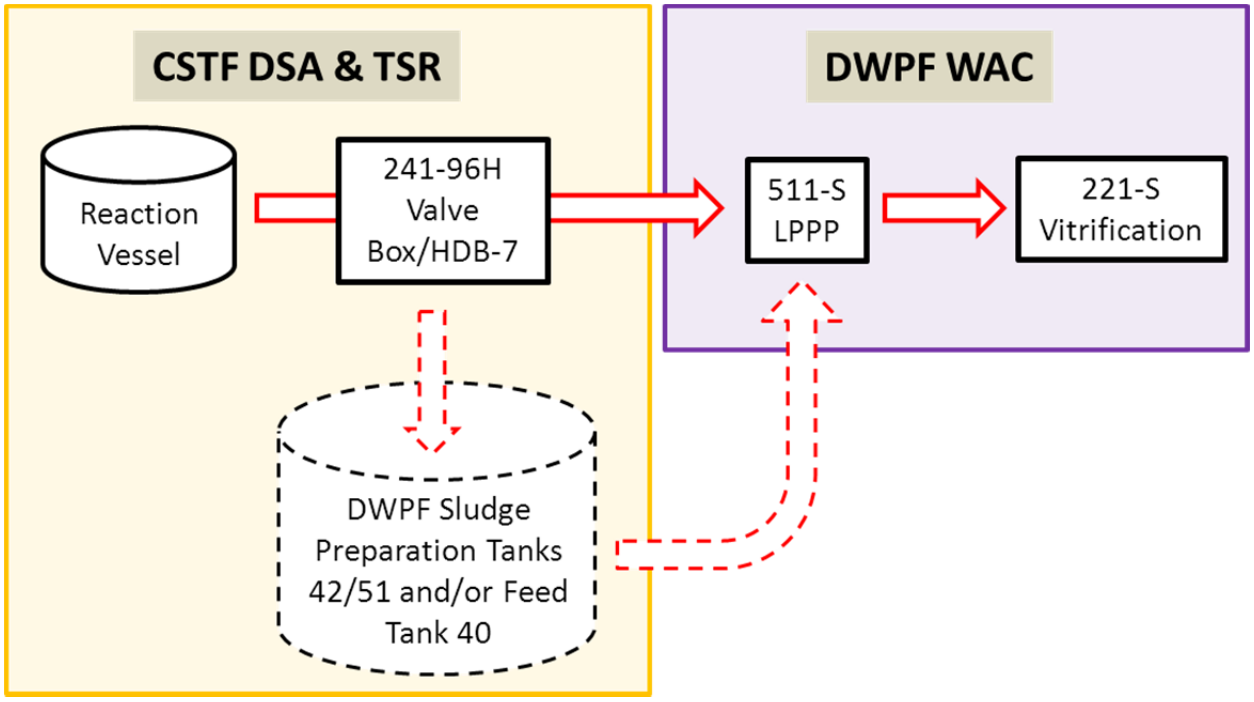

Figure 11: Flow-sheet schematic illustrating requirements documents for transfer of the CCPO-processed waste to DWPF.

With respect to organic concentration the DWPF WAC states that organic material in the sludge feed transferred to DWPF shall contribute < 0.1% of the hydrogen LFL. Since the direct feed option by-passes the DWPF preparation and feed tanks there is no opportunity to blend the feed with other TF waste prior to transfer to DWPF. However, as indicated in the above schematic it is possible that the CCPO-processed waste could be diverted to the DWPF preparation and feed tanks prior to transfer to DWPF.

To ensure the successful operation of the DWPF melter by preventing the formation of a secondary glass phase or a salt layer, the DWPF WAC establishes limits for different elements.

For copper sulfate, which is the current catalyst of choice for the CCPO process, DWPF has a limit of 0.50 wt% copper and 0.60 wt% and sulfate in the vitrified glass. The potential impact of the copper sulfate on the DWPF glass was assessed in a recent report [39] which concluded that the proportion of copper sulfate present in the CCPO-processed waste might impact the respective glass solubility limits, and that blending of the waste stream may be required in a sludge feed qualification tank. As previously noted FY12 studies will consider the use of copper nitrate in lieu of copper sulfate which would negate potential issues with respect to sulfate solubility limits.

With respect to nuclear criticality there are four pertinent criteria specified in the DWPF WAC which include (see Table 7 for relevant radionuclide concentrations):

i. *Pu-240 concentration > Pu-241 concentration*
   5.63E-03 mg/L (Pu-240) > 1.02E-03 (Pu-241)

ii. *Fe/Pu-239(eq) weight ratio ≥ 160*
   1.21E+02 mg/L (Fe) ÷ 4.65E-02 mg/L (Pu-239(eq)) = 2600

iii. *Pu-239(eq) concentration ≤ 0.59 g/gal*
   4.65E-02 mg/L ⇨ 1.76E-04 g/gal Pu-239(eq) ≤ 0.59 g/gal

iv. *The U-235(eq_{SLU}) enrichment in sludge shall be n 0.93 wt%*
   (U-235(eq_{SLU}) ÷ U_{Total}) x 100% = (6.53E-01 ÷ 5.32E+00) x 100% = 12.3%

Where: Pu-239(eq) = Pu-239 + Pu-241 + Cm-244 + 15(Cm-245) + 35(Am-242m)
U-235(eq_{SLU}) = U-235 + 1.4(U-233)

The only limit of concern is related to the U-235(eq_{SLU}) fissile loading which is over an order of magnitude greater than the DWPF WAC requirement. As such there is the potential that the CCPO-processed waste would likely require blending with depleted uranium for direct transfer to DWPF to meet the specified limit of 0.93 wt%. It is more likely, however, that the CCPO-processed waste would be blended in the sludge preparation tanks to meet criticality requirements.

Table 7: Mass concentrations of uranium and plutonium in the CCPO-processed waste.

Radionuclide	Specific Activity (Ci/g) [Ref. 42]	CCPO-Processed Feed (Ci/gal)	CCPO-Processed Feed (mg/L)
U-233	9.68E-03	2.14E-06	5.84E-02
U-234	6.25E-03	6.99E-06	2.95E-01
U-235	2.16E-06	4.67E-09	5.71E-01
U-236	6.47E-05	1.95E-07	7.96E-01
U-238	3.36E-07	4.58E-09	3.60E+00
U_{Total}	⇨ U-233 + U-234 + U-235 + U-236 + U-238		5.32E+00
U-235(eq_{SLU})	⇨ U-235 + 1.4(U-233)		6.53E-01
Pu-238	1.71E+01	3.83E-03	5.92E-02
Pu-239	6.22E-02	1.07E-05	4.54E-02
Pu-240	2.28E-01	4.86E-06	5.63E-03
Pu-241	1.03E+02	3.99E-04	1.02E-03
Pu-239(eq)	⇨ Pu-239 + Pu-241		4.65E-02
Fe	⇨ See Table 2		1.21E+02

An additional concern with direct transfer of the CCPO-processed to DWPF relates to the total solids content. The DWPF WAC indicates a solids range of 12-19 wt% whereas the CCPO-processed waste may contain < 10 wt%. Sending low solids directly to DWPF will potentially result in DWPF cycle time impacts since additional time may be required to boil off liquid from the waste stream to satisfy the range specified by the DWPF WAC.

6 CONCLUSION

The initial intent of this document was to determine the feasibility of a number of flow-sheet options with respect to transferring the CCPO-processed Tank 48 waste, and to subsequently establish success criteria (with respect to organic destruction) that could be applied to FY12 CCPO laboratory-scale experiments [2]. However, all options considered have extremely restrictive requirements with respect to either TPB concentration limits or the contribution that organics in the CCPO-processed waste can make to the downstream LFL criteria. In addition, while the original 2005 data implied complete organic destruction this cannot be verified due to detection limits of the various analyses used. Hence two (potentially combined) pathways must be evaluated to enable downstream processing of the CCPO treated waste. The first is relaxation of the TPB concentration and flammability contribution limits. This topic is currently beyond the scope of this document though once the FY12 experimental data is available, and the potential for technology maturation is considered positive enough to move forward, implementation of these changes to the allowable TPB (and total organic) concentration will become part of the technology maturation and deployment process. The second is to enhance the detection limits of the organic analysis techniques such that the waste can be shown to comply with the current organic limits. This path is being considered as part of the FY12 testing strategy [2]. In addition to organics, the concentrations of Cs-137 and Pu-238 are exceeded or challenged for some of the options though dilution during the CCPO process (and potential blending with the contents of other tanks) alleviates these issues for many of the flow-sheet options.

7 REFERENCES

1. S.P. Simner, *Technology Maturation Plan: Small Tank Catalyzed Peroxide Oxidation of Tank 48H Tetraphenylborate*, SRR-CES-2011-00066, Rev. 0 (2011).
2. T.B. Peters, D.P. Lambert, R.A. Pierce, and S.D. Fink, *Task Technical and Quality Assurance Plan for Process Optimization for Cu-Catalyzed Peroxide Oxidation of Tank 48H Tetraphenylborate*, SRNL-RP-2011-01525, Rev. 1 (2012).
3. D.P. Lambert, T.B. Peters, and S.D. Fink, *In-Tank Peroxide Oxidation Process for the Decomposition of Tetraphenylborate in Tank 48H*, WSRC-TR-2005-00114, Rev. 0 (2005).
4. S.C. Shah, *Estimated Radiological and Chemical Characterization of Tank 48,* X-ESR-H-00239, Rev. 1 (2010).
5. L.D. Olson, and K.H. Subramanian, *SRS Tank 48 Waste Treatment EM-1 Briefing* SRR-CES-2011-00083 (2011).
6. D.P. Chew, and B.A. Hamm, *Liquid Waste System Plan Revision 17*, SRR-LWP-2009-00001, Rev. 17 (2012).
7. E. Neyens, and J. Baeyens, *A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique*, Journal of Hazardous Materials, B98 (2003) 33.
8. H.J.H. Fenton, *Oxidation of Tartaric Acid in Presence of Iron*, Journal of the Chemical Society, **65** (1894) 899.
9. F. Haber, and J.J. Weiss, *The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts*, Proceedings of the Royal Society of London, Series A, **147** (1934) 332.
10. S.P. Simner, *The Role of Copper in the Hydrogen Peroxide Oxidation of Organic Compounds*, SRR-CES-2012-00002, Rev. 0 (2012).
11. C. Walling, *Fenton's Reagent Revisited*, Accounts of Chemical Research, **8** (1975) 125.
12. R.C. Fowler, *Chemical Oxidation of Tank 48 Simulant*, WSRC-RP-2004-00240 (2004).
13. T.B. Peters, *Phenylborate Decomposition Using 3.2 mg/L Copper in Tank 49H Solution*, WSRC-TR-2001-00060 (2001).
14. C.L. Crawford, M.J. Barnes, R.A. Peterson, W.R. Wilmarth, and M.L. Hyder, *Copper-Catalyzed Sodium Tetraphenylborate, Triphenylborane, Diphenylborinic Acid and Phenylboronic Acid Decomposition Kinetic Studies in Aqueous Alkaline Solutions*, Journal of Organometallic Chemistry, **581** (1999) 194.
15. R.E. Eibling, *Processing of Tetraphenylborate Precipitates in the Savannah River Site Defense Waste Processing Facility,* WSRC-MS-90-162 (1990).
16. C.J. Bannochie, J.C. Marek, R.E. Eibling, and M.A. Baich, *Factors Affecting the Rate of Hydrolysis of Phenylboronic Acid in Lab-Scale Precipitate Reactor Studies*, WSRC-MS-92-324 (1992).

17. US Peroxide, LLC, *Fenton's Reagent General Chemistry*," http://h2o2.com/pages.aspx?pid=143&name=General-Chemistry-of-Fenton-s-Reagent.
18. Solvay Chemicals Publication HH-2323, *Hydrogen Peroxide: Safety and Handling Technical Data Sheet*, Solvay Chemicals, Inc. (2005).
19. United States Department of Energy, *"Technology Readiness Assessment Guide,"* DOE G 413.3-4A (2011).
20. S.C. Shah, *Tank 48 Feed Chemical and Radionuclide Compositions*, X-CLC-H-00646, Rev. 4 (2010).
21. P.A. Taylor, *Destruction of Ion-Exchange Resin in Waste from the HFIR, T1, and T2 Tanks Using Fenton's Reagent*, ORNL/TM-2002/197 (2002).
22. J.D. Newell, *Fate of Organomercurials when Reacted With Chemical Oxidants*, SRNL-L3100-2012-00027 (2012).
23. *Concentration, Storage, and Transfer Facilities Documented Safety Analysis*, WSRC-SA-2002-00007, Rev. 12 (2002).
24. C.K. Chiu, *Waste Acceptance Criteria for Aqueous Waste Sent to Z-Area Saltstone Production Facility*, X-SD-Z-00001, Rev. 10 (2011).
25. A.R. Shafer, *Waste Acceptance Criteria for Sludge, ARP, and MCU Process Transfers to 512-S and DWPF*, X-SD-G-00008, Rev. 8 (2011).
26. M. Norton, *Recommended SWPF Feed Waste Acceptance Criteria*, X-ESR-J-00001, Rev. 1 (2009).
27. C.M. Cole, *CSTF Corrosion Control Program*, WSRC-TR-2002-00327, Rev. 4 (2007).
28. K.G. Brown, C.M. Jantzen, and G. Ritzhaupt, *Relating Liquidus Temperature to Composition for Defense Waste Processing Facility (DWPF) Process Control*, WSRC-TR-2001-00520, Rev. 0 (2001).
29. G.N. Eide, *Fluidized Bed Steam Reformer (FBSR) Waste Feed Inhalation Dose Potential*, U-CLC-H-00098, Rev. 0 (2011).
30. J.M. East, *S-CLC-G-00268, Rev. 0, Dose Potential Inhalation Dose Conversion Factors*, WSMS-SAE-02-0015 (2002).
31. *Technical Safety Requirements: Concentration, Storage, and Transfer Facilities*, S-TSR-G-00001, Rev. 26 (2010).
32. South Carolina Department of Health and Environmental Control (SCDHEC): Air Pollution Control Regulations and Standards: Regulation 61-62.5 Air Pollution Control Standards (2011).
33. Code of Federal Regulations (CFR) Title 40, Part 61, Subpart H: *National Emission Standards for Hazardous air Pollutants* (2012).
34. J. Urbanik Coughlin, *Tank 48H Benzene Concentration During Slurry Pump Operations*,

X-CLC-H-00781 (2009).

35. G.L. Cauthen, *Path Forward: Use of Existing Transfer Lines from Tank 48 to Building 241-96H in support of the Tank 48 Treatment (Tank 48TP) Project*, LWO-SPT-2009-00098 (2009).
36. Outo Kumpu Publication 1197EN-GB:3, *Type 304, Type 304L UNS S30400, UNS S30403: The Basic Austenitic Stainless Steel, A Versatile Corrosion Resistant Material for General Purpose Applications*.
37. R.L. Reed, *Dose Rate Estimations for Building 241-96H During ARP Operations*, N-CLC-H-00595, Rev. 0 (2005).
38. G. Taylor, *ARP Mixing Tank*, SRNL-ITB-2004-00026 (2004).
39. C. Aponte, *Tank 48 Catalytic Peroxide Oxidation Process Assessment of Potential Copper and Sulfate Downstream Processing Impacts*, SRR-CES-2012-00015, Rev. 0 (2012).
40. *MCU Solvent Storage Temperature Limit (Inter-Office Memorandum),* SRNL-WPT-2005-00146 (2005).
41. T.B. Peters, A.L. Washington, II, and S.D. Fink, *Results of Cesium Mass Transfer Testing for Next Generation Solvent with Hanford Waste Simulant AP-101*, SRNL-STI-2011-00559, Rev. 0 (2011).
42. US DOE, Integrated Data Base Report-1996: U. S. Spent Nuclear Fuel and Radioactive Waste Inventories, Projections, and Characteristics, Appendix B Characteristics of Important Radionuclides, DOE/RW-006, Rev. 13, December 1997 (DOE database).
43. R.L. Reed, *Dose Rate Estimations for the 241-96H Valve Box*, N-CLC-H-00581, Rev. 0 (2005).
44. K.H. Rosenberger, *Tank 50 Valve Box and Transfer Line Shielding Evaluation*, S-CLC-H-00795, Rev. 0 (2001).

ATTACHMENT 1: Flow-Sheet Criteria Tables

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
Process Controls							
1. CSTF TSR Admin Controls							
5.8.2.1 Radiological Protection Program	*Applicable* Comments: Ventilation ducts to CCPO reaction vessels are designed for 1.11 Ci/gal Cs-137 and may require additional shielding for 1.30 Ci/gal Cs-137 from Tank 48 [37]. No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].	*Not Applicable* Comments: No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].	*Applicable.* Comments: Tank 50 curie limit is 0.18 Ci/gal Cs-137 based on Tank 50 gamma shielding; treated Tank 48 waste will require proper batch planning and blending. No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43]. No changes to Tank 50 Valve Box shielding max 30 Ci/Gal Cs-137 [44].	*Applicable* Comments: 512-S is designed for 1.11 Ci/gal Cs-137 to maintain dose rate < 0.5 mrem/hr and may require additional shielding for 1.30 Ci/gal Cs-137 from Tank 48. **Note**: Process dilution may result in product < 1.1 Ci/gal Cs-137. No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].	*Not Applicable* Comments: No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].	*Applicable* Comments: Decant of Tank 48 supernate results in > 1.30 Ci/gal feed to CCPO reaction vessels. Ventilation ducts to CCPO reaction vessels are designed for 1.11 Ci/gal Cs-137 and may require additional shielding [38]. Decant of Tank 48 supernate does not challenge Tank 50 curie limit of 0.18 Ci/gal Cs. No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].	*Not Applicable* Comments: No changes to DWPF shielding required (max 46 Ci/gal Cs-137). No changes to 241-96H Valve Box shielding required (max 30 Ci/gal Cs-137) [43].
5.8.2.2 Emergency Response Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.3 Environmental Compliance Program	*Applicable* Comments: See Regulatory Compliance Section 6 of this table.						
5.8.2.4 Industrial Hygiene Program	*Applicable* Comments: H_2O_2 is not a standard chemical used at SRS and must be assessed for IH impacts.	*Applicable* Comments: Generic requirements independent of flow-sheet. Employee protection from untoward exposures to chemical, physical, and biological hazards is universally applicable to this option.					
5.8.2.5 Critical Lift Program	*Applicable* Comments: Generic requirements independent of flow-sheet. Applicable during design implementation.						
5.8.2.6 Fire Protection Program	*Applicable* Comments: H_2O_2 strong oxidizer - evaluate for use in process area.	*Applicable* Comments: Generic requirements independent of flow-sheet.					
5.8.2.7 Installed Process Instrumentation (IPI), Measuring and Testing Equipment (M&TE), and Other TSR Measuring Devices	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.8 Configuration Management Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.9 Preventive Maintenance Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.10 Nuclear Criticality Safety Program	*Applicable* Comments: Nuclear Criticality Safety Evaluation (NCSE) is required: Tank 48 has a critical mass of 1.	*Applicable* Comments: NCSE is required.					*Applicable* Comments: NCSE is required. DWPF has a limit of 0.93 wt% equivalent U-235 enrichment and glass fissile limit of 879 g/m^3.
5.8.2.11 Quality Assurance (QA) Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.12 Structural Integrity Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.13 Corrosion Control Program	*Applicable* Comments: Dilution to Tank 48 waste will occur during operation of the slurry mixer pumps.	*Applicable* Comments: Effects of CCPO-processed waste on corrosion will need to be determined.				*Applicable* Comments: Dilution to Tank 48 waste will occur during operation of the slurry mixer pumps.	*Applicable* Comments: Effects of CCPO-processed waste on corrosion will need to be determined.
5.8.2.14 Traffic Control Program	*Applicable* Comments: There is nothing unique in the transfers of the Tank 48 destruction product stream to 241-96H.	*Applicable* Comments: This is applicable to all tanks (and associated transfer routes) within the TF.	*Applicable* Comments: This is applicable to all tanks (and associated transfer routes) within the TF.	*Applicable* Comments: This is applicable to all tanks (and associated transfer routes) within the TF. At 512-S512-S512-S and DWPF, their controls will take precedence.	*Applicable* Comments: The TF Program is limited to the portions of the route within the TF; beyond the TF, SWPF controls, WAC, will take precedence.	*Applicable* Comments: This is applicable to all tanks (and associated transfer routes) within the TF.	*Applicable.* Comments: The TF Program is limited to the portions of the route within the TF; beyond the TF, DWPF controls, WAC, will take precedence.
5.8.2.15 WAC Program	*Not Applicable* Comments: This is a transfer within the TF. WACs apply to transfers between facilities.	*Not Applicable* Comments: This is a transfer within the TF. WACs apply to transfers between facilities.	*Not Applicable* Comments: A transfer to Tank 50 from 241-96H is a transfer within the TF, so the TF WAC does not apply; however, subsequent transfer of the waste to SPF means that the SPF WAC will apply.	*Not Applicable* Comments: Not a transfer within the TF, so the TF WAC does not apply; however, subsequent transfer to 512-S and DWPF will require compliance with the appropriate DWPF controls, WAC, etc.	*Not Applicable* Comments: Not a transfer within the TF, so the TF WAC does not apply; however, the material must comply with the SWPF WAC, so a Waste Compliance Plan (WCP) will be required; note also, that separate WACs have been recommended for transfers from SWPF to DWPF and SWPF to Saltstone; compliance likely will impact the Tank 48 product stream; a tight DWPF requirement is that the organic content must not generate more than 0.1 % of the hydrogen LFL.	*Not Applicable* Comments: This is a transfer within the TF. WACs apply to transfers between facilities.	*Not Applicable* Comments: For the transfers within the TF, i.e., routes involving the cited tanks and lines, the program applies; however, DWPF controls will be applicable upon entering that facility.

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.16 Connector Installation Program	*Applicable*	*Applicable* Comments: Relevant to HDB-7 jumper connector and 241-96H Valve Box.	*Applicable* Comments: Relevant to HDB-7 jumper connector, 241-96H Valve box, and Tank 50 valve box.	*Applicable* Comments: Relevant to 241-96H Valve Box.	*Applicable* Comments: Relevant to 241-96H Valve Box and Tank 49 Valve Box.	*Applicable* Comments: Relevant to HDB-7 jumper connector, 241-96H Valve box, and Tank 50 valve box.	*Applicable* Comments: Relevant to HDB-7 jumper connector, 241-96H Valve Box, and Tanks 40, 42, and 51 Valve Boxes.
5.8.2.17 Chemical Inventory Control Program	*Applicable* Comments: New chemicals/materials brought into the TF fall under this program; CCPO process chemicals fall under this program; storage location will be in the vicinity of 241-96H.	*Not Applicable* Comments: The process chemicals used to destroy TPB are stored in the vicinity of 241-96H; the features of the program will be applied per Option 0.					
5.8.2.18 High-Efficiency Particulate Air (HEPA) Filter Program	*Applicable* Comments: Mercury and peroxide vapors may affect HEPA integrity.						
5.8.2.19 Sludge Carryover Minimization Program	*Not Applicable* Comments: This requirement applies to supernate transfers.					*Applicable* Comments: This requirement will apply to supernate transfers from Tank 48 to Tank 50.	*Not Applicable* Comments: This requirement applies to supernate transfers.
5.8.2.20 Software Control Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.21 Transfer Control Program	*Applicable* Comments: The constraints of concern are unchanged by the transfer of this material: material balances, vent requirements, siphons, water hammers, overpressurizations, flushes, etc.	*Applicable* Comments: The constraints of concern are unchanged by the transfer of this material: material balances, vent requirements, siphons, water hammers, overpressurizations, flushes, etc. However, since this will involve frequent transfers similar to the recycle transfers by DWPF, allowances may be possible as is the case with DWPF Recycles (see WCP/WAC) and evaporator recycles; generic Engineering Transfer Approval Forms (ETAFs)).	*Applicable* Comments: The concerns associated with a transfer remain applicable: material balances, vent requirements, siphons, water hammers, overpressurizations, flushes, etc.				

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.22 Flammable Vapor Sampling Program	*Applicable* Comments: The first criteria is not applicable since the IDP of waste transferred to the 241-96H must all be less than or equal to 1.4E+06 rem/gal (DSA). The second criteria, prior to the start of the transfer and following the transfer, sampling will be required.	*Applicable* Comments: Either or both of the criteria may be applicable depending on the tank chosen to receive the Tank 48 Chemical Destruction waste stream.	*Applicable* Comments: The specific aspects applied to Tank 50 are applicable. Upon leaving Tank 50, the SPF WAC will control.	*Applicable* Comments: The specific aspects applied to Tank 50 and possibly Tank 49, are applicable. Upon crossing the demarcation between the TF and DWPF, DWPF WAC will control.	*Applicable* Comments: The program requires hydrogen sampling of transfer lines and jackets and encasements.	*Applicable* Comments: The program requires hydrogen sampling of transfer lines and jackets and encasements.	*Applicable* Comments: The program requires hydrogen sampling of transfer lines and jackets and encasements. DWPF establishes controls within their facility.
5.8.2.23 Transfers from Waste Tank Annuli	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.24 Severe Weather Response	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.25 Evaporator Feed Qualification Program	*Not Applicable* Comments: Evaporators not used in this flow-sheet.	*Applicable* Comments: Waste must be within DSA limits for Si, Na-Al-Si-O, OH-.	*Not Applicable* Comments: Evaporators not used in this flow-sheet.				
5.8.2.26 242-16H Evaporator Scale Evaluation	*Not Applicable* Comments: Evaporators not used in this flow-sheet.	*Applicable* Comments: Related to evaporator evaluation as opposed to feed composition.	*Not Applicable* Comments: Evaporators not used in this flow-sheet.				
5.8.2.27 Flammability Control Program	*Applicable* Comments: Though the strike vessels in 241-96H are not included in the Program Description Document (PDD), the transfer of Tank 48 waste will raise, at a minimum, hydrogen flammability issues that will require addressing.	*Applicable* Comments: All the tanks in the TF will fall under this control.	*Applicable* Comments: The specific Tank 50 controls will apply; however, upon moving to Saltstone, the SPF WAC will control.	*Applicable* Comments: The specific aspects applied to Tank 50 and possibly Tank 49 are applicable. Upon crossing the demarcation between the TF and DWPD, DWPF WAC will control.	*Not Applicable* Comments: This program applies to waste tanks only. However, there are proposed controls (WAC) for SWPF receipts. In addition, there are proposed WACs for transfers from SWPF to DWPF and Saltstone. Of these, DWPF restricts the organic content such that no more than 0.1% of the hydrogen LFL may be generated by resident organics.	*Applicable* Comments: The specific aspects applied to Tank 50 and possibly Tank 48 are applicable. Applicability to 241-96H should be considered.	*Applicable.* Comments: The specific aspects applied to the aforementioned tanks and associated lines, etc. Upon crossing the demarcation between the TF and DWPF, DWPF WAC will control.
5.8.2.28 Waste Tank Quiescent Time Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						
5.8.2.29 Pump Run Program	*Applicable* Comments: Generic requirements independent of flow-sheet.						

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.30 Salt Dissolution/Interstitial Liquid Removal Program	*Not Applicable* Comments: Salt dissolution/interstitial liquid removal processed not utilized.						
5.8.2.31 HGR Control	*Applicable* Comments: Though 241-96H is not specifically addressed in this Program, all waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses.	*Applicable* Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses.	*Applicable* Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses. Upon transfer to Saltstone, the SPF WAC will control. Tank 50 further limits hydrogen generation by maintaining a specific distribution of radionuclides (as a result of the MCU process) and the application of a specific NO_{eff} to scavenge. The addition of the Tank 48 chemical destruction product stream must not jeopardize the HGR.	*Applicable* Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses. Upon crossing the demarcation between the TF and DWPF, the DWPF WAC will control. (241-96H is not specifically addressed). The Tank 50H controls on hydrogen generation remain applicable.	*Applicable* Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses. Upon crossing the demarcation between the TF and SWPF, the SWPF WAC will control.	Applicable Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses. (241-96H is not specifically addressed). Tank 50 further limits hydrogen generation by maintaining a specific distribution of radionuclides (as a result of the MCU process) and the application of a specific NO_{eff} to scavenge hydrogen. The addition of the Tank 48 chemical destruction product stream must not jeopardize the HGR.	*Applicable* Comments: Waste in the TF must fall below the bounding HGRs used in the DSA for various safety analyses. Upon crossing the demarcation between the TF and DWPF, the DWPF WAC will control.
5.8.2.32 Waste Characterization System (WCS) Control Program	*Applicable* Comments: Though 241-96H is not included in the WCS system, data acquisition, etc. will be needed as is performed for the waste tanks.	*Applicable* Comments: This is applicable to all the waste tanks involved in the proposed transfer flow-sheet.					
5.8.2.33 Tank Top/Secondary Containment Loading Program	*Applicable* Comments: Apply to temporary and new installation of loads on tank tops and secondary containments. Does not directly impact chemical destruction process efficiency or the resulting product.						
5.8.2.35 Waste Tank Mixing Device Operation	*Applicable* Comments: Control of waste tank mixing device to prevent aerosolization. Applies to this option since Tank 48 requires mixing to move solids forward. Does not directly impact chemical destruction process efficiency or the resulting product.	*Applicable* Comments: Does not directly impact chemical destruction process efficiency or the resulting product.	*Applicable* Comments: Applies to Tank 50, but not directly to Saltstone. Does not directly impact chemical destruction process efficiency or the resulting product.	*Not Applicable* Comments: Only applies to control of waste tank mixing device to prevent aerosolization.	*Not Applicable* Comments: Only applies to control of waste tank mixing device to prevent aerosolization.	*Applicable* Comments: Applies to this option since Tank 48 requires mixing to move solids forward. Impact to chemical destruction process efficiency or the resulting product needs to be evaluated.	*Applicable* Comments: Applies to this option. Does not directly impact chemical destruction process efficiency or the resulting product.
5.8.2.36 Pump Tank Transfer Jet Control	*Not Applicable* Comments: Related to isolation of steam and air in pump tank transfers jets when not in use. Does not apply to this option (no pump tanks involved).	*Applicable* Comments: Related to isolation of steam and air in PT transfers jets when not in use. This will apply if product is sent to an F-area receipt tank (HDB-8 pump tank).	*Not Applicable* Comments: Related to isolation of steam and air in pump tank transfers jets when not in use. Does not apply to this option (no pump tanks involved).				

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.37 Pump Tank Backup Ventilation Systems Program	*Not Applicable* Comments: Related backup portable ventilation for transfers greater than 1200 gallons. Does not apply to this option (no pump tanks involved).	*Applicable* Comments: Related to backup portable ventilation for transfers greater than 1200 gallons. This will apply if product is sent to an F-area receipt tank (HDB-8 pump tank).	*Not Applicable* Comments: Related backup portable ventilation for transfers greater than 1200 gallons. Does not apply to this option (no pump tanks involved).				
5.8.2.39 Event Response Program	*Applicable* Comments: Related to actions for placing the facility in a safe condition. General requirement. Does not directly impact chemical destruction process efficiency or the resulting product.						
5.8.2.40 Liquid Addition Program	*Not applicable* Comments: Only applicable to Tank 15.						
5.8.2.41 Area Radiation Monitor (ARM) Location Program	*Not Applicable* Comments: Related to placement of ARMs for high-rem waste transfers for above-ground lines, slurry mixer pump operation. Not applicable to this option (no above-ground transfer line or slurry mixer pumps).						
5.8.2.42 299-H Inventory Control Program	*Not Applicable* Comments: 299-H inventory less than Haz Cat 3. Will apply to failed equipment needing decontamination prior to repair. Does not directly impact chemical destruction process efficiency or the resulting product.						
5.8.2.43 Prohibited Operations	*Applicable* Comments: No waste transfers allowed through HI-241-948-WTS-L-1151A and 241-948-WTS-L-1151B [5.8.2.43.b]	*Applicable* Comments: No waste transfers allowed through FDB-1, FDB-5, FDB-6, HDB-1, HDB-3, HPP-1, Tank 16, F-Area Catch Tank, 242-F Evaporator, 242-H Evaporator, and F and H-Area CTS [5.8.2.43.a]. No waste transfers allowed through FL-241-917-WTS-L-7, FL-241-920-WTS-L-8, FL-241-933-WTS-L-3260, FL-641-000-WTS-L-107-DB2, FM-241-926-WTS-L-960, FM-241-927-WTS-L-1013, FM-241-927-WTS-L-1054, HL-241-913-WTS-L-451, HL-241-914-WTS-L-103, HL-241-916-WTS-L-20E [5.8.2.43.b].	*Applicable* Comments: Transfers through the Tk50 valve box and lines into Tk50 with IDP > 2.09E+05 rem/gal are prohibited (Tk48 IDP is 1.22E+06 rem/gal) [5.8.2.43.u].	*Not Applicable*	*Not Applicable*	*Applicable* Comments: No waste transfers allowed through HI-241-948-WTS-L-1151A and 241-948-WTS-L-1151B [5.8.2.43.b]; Transfers through the Tk50 valve box and lines into Tk50 with IDP > 2.09E+05 rem/gal are prohibited (Tk48 IDP is 1.22E+06 rem/gal) [5.8.2.43.u].	*Not Applicable*
5.8.2.44 Tank Fill Limits	*Applicable* Comments: Applicable to all tanks in TF.						
5.8.2.45 Oil Control Program	*Applicable* Comments: Evaluate applicability based on new equipment to be installed.						

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
5.8.2.46 Waste Box Control Program	*Applicable* Comments: Applies to waste generated and put into a transportation box.						
5.8.2.47 Transfers to DWPF and Saltstone	*Not Applicable*		*Applicable* Comments: Changes to receipt facility WACs may drive changes to TSR.		*Not Applicable*		*Applicable* Comments: Changes to receipt facility WACs may drive changes to TSR.
5.8.2.48 Tank 48 Administrative Controls	*Applicable*	*Not Applicable* Comments: Only applies to Tank 48.				*Applicable*	*Not Applicable* Comments: Only applies to Tank 48.
5.8.2.49 Tank 48 Unauthorized Operations	*Applicable* Comments: Waste additions/transfers to or from Tank 48 are not permitted [5.8.2.49.e].	*Not Applicable* Comments: Only applies to Tank 48.				*Applicable* Comments: Waste additions/transfers to or from Tank 48 are not permitted [5.8.2.49.e].	*Not Applicable* Comments: Only applies to Tank 48.
5.8.2.50 Ventilation System Performance monitoring	*Applicable* Comments: Relates to operating waste tank mixing devices in a Type I, II, III, IIIA, or IV waste tank.	*Applicable* Comments: Depends on which tank is receiving waste. Operating waste tank mixing devices in a Type I, II, III, IIIA, or IV waste tank. Authorization agreement currently limits possible receipt tanks: "Waste transfers into Type I or II tanks are prohibited unless used to retrieve waste from Type I, II, or IV tanks".	*Applicable* Comments: Relates to operating waste tank mixing devices in a Type I, II, III, IIIA, or IV waste tank.	*Not Applicable* Comments: No gas evolution applies that would require monitoring.		*Applicable* Comments: Relates to operating waste tank mixing devices in a Type I, II, III, IIIA, or IV waste tank.	
5.8.2.51 Inhalation Dose Potential Control	*Applicable* Comments: Controls must ensure that IDP remains within DSA limits.						
5.8.2.52 242-16H Evaporator Chemical Cleaning	*Not Applicable* Comments: Not chemical cleaning 242-16H Evaporator.						
5.8.2.53 Chemical Cleaning Pump Tank Receipt Program	*Not Applicable* Comments: This control is for F-Area Type I Waste Tank chemical cleaning operations.						

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
2. WAC - DWPF	*Not Applicable* Comments: The DWPF WAC does not apply to this transfer. 241-96H ensures that feed sent to 512-S meets DWPF and TF WAC requirements.	*Not Applicable* Comments: The DWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The DWPF WAC does not apply to this transfer.	*Applicable* Comments: • Cs <1.11 Ci/gal (shielding). • IDP ≤3E+06 rem/gal. • Pu soluble ≤3E-03 Ci/gal & ≤0.1 mg/L, • U soluble ≤ 50 mg/L, U-235 (eq-sol) ≤3.0 wt% (15.25%), • HGR < 1.64E-6 ft^3/hr/gal, • Organic contribution to H_2 LFL < 0.1%, • Temperature ≤45°C, • Copper & sulfate (need to be evaluated if soluble).	*Not Applicable* Comments: The DWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The DWPF WAC does not apply to this transfer.	*Applicable* Comments: • U-235 (eq-sludge) ≤0.93 wt%. • Copper and sulfate (need to be evaluated). • Sulfate in washed sludge<0.058M. • Organic contribution ≤ 0.1% H_2 LFL. • 12-19 wt% dry total solids in sludge. • No additions to qualified sludge batch unless evaluated. • Pu 240 conc. > Pu 241 • Cs-137 IDP = 1.34 Ci/gal • H_2 generation < 8.95E-05 ft^3/hr/gal at 25 °C. • Temp <= 45 °C. • Max. particle size 80 mesh sieve. • 897 g/m^3 glass fissile limit (U-233, U-235, Pu-239, Pu-240).

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
3. WAC - SPF	*Not Applicable* Comments: The SPF WAC does not apply to this transfer.	*Not Applicable* Comments: The SPF WAC does not apply to this transfer.	*Applicable* Comments: • Receipt of Tank 48 material is prohibited; Tank 48 is considered a new waste stream. • Vault classification, toxicity characteristic leaching procedure (TCLP), and grout formulation may be required. • Saltstone has IDP limit of 2.09E+05 rem/gal; Tank 48 IDP is 1.22E+06 rem/gal). • Addition of any TPB into Tank 50 is prohibited; Tank 48 contains 2.3E+04 kg TPB; current WAC limit is set at TPB detection limit of 5 mg/L. • Tank 48 supernate TPB and generated benzene do not meet the WAC. • Slurry and supernate phenol do not meet the WAC. • HGR limit of 5.6E-08 ft^3/hr/gal: destruction process results in dilution and affect the NO_{eff} in H_2 generation calculation. Tank 48 rate is 1 order higher. • Any constituent not in WAC with 0.5M must be evaluated. • Prohibit any species would be capable of generating toxic gases vapors, or fumes • pH >10; product stream must be adjusted to meet this requirement. • Temperature limit of 40 °C: destruction process at 75 °C. • Tank 48 slurry does not meet limits for total organic carbon (TOC). • Cs-137, Pu-238, and alpha do not meet WAC.	*Applicable* Comments: • Receipt of Tank 48 material is prohibited; Tank 48 is considered a new waste stream. • Vault classification, TCLP, and grout formulation may be required. • Saltstone has IDP limit of 2.09E+05 rem/gal; Tank 48 IDP is 1.22E+06 rem/gal). • Addition of any TPB into Tank 50 is prohibited; Tank 48 contains 2.3E+04 kg TPB; current WAC limit is set at TPB detection limit of 5 mg/L. • Tank 48 supernate TPB and generated benzene do not meet the WAC. • Slurry and supernate phenol do not meet the WAC. • HGR limit of 5.6E-08 ft^3/hr/gal: destruction process results in dilution and affect the NO_{eff} in H_2 generation calculation. Tank 48 rate is 1 order higher. • Any constituent not in WAC with 0.5M must be evaluated. • Prohibit any species would be capable of generating toxic gases vapors, or fumes • pH >10; product stream must be adjusted to meet this requirement. • Temperature limit of 40 °C: destruction process at 75 °C. • Tank 48 slurry does not meet limits for TOC. • Cs-137, Pu-238, and alpha do not meet WAC.	*Not Applicable* Comments: The SPF WAC does not apply to this transfer.	*Applicable* Comments: • Receipt of Tank 48 material is prohibited; Tank 48 is considered a new waste stream. • Vault classification, TCLP, and grout formulation may be required. • Saltstone has IDP limit of 2.09E+05 rem/gal; Tank 48 IDP is 1.22E+06 rem/gal). • Addition of any TPB into Tank 50 is prohibited; Tank 48 contains 2.3E+04 kg TPB; current WAC limit is set at TPB detection limit of 5 mg/L. • Tank 48 supernate TPB and generated benzene do not meet the WAC. • Slurry and supernate phenol do not meet the WAC. • HGR limit of 5.6E-08 ft^3/hr/gal: destruction process results in dilution and affect the NO_{eff} in H_2 generation calculation. Tank 48 rate is 1 order higher. • Any constituent not in WAC with 0.5M must be evaluated. • Prohibit any species would be capable of generating toxic gases vapors, or fumes • pH >10; product stream must be adjusted to meet this requirement. • Temperature limit of 40 °C: destruction process at 75 °C. • Tank 48 slurry does not meet limits for TOC. • Cs-137, Pu-238, and alpha do not meet WAC.	*Not Applicable* Comments: The SPF WAC does not apply to this transfer.

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
4. WAC - SWPF	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.	*Applicable* Comments: • <5.25 Ci/gal at 6.44M Na (limit). • Na content 5.6 - 7.0M limit. • K content <0.05M at 5.6M Na (CSSX adversely affected by K). • Al <6.74E+03 mg/L at 6.44M Na (to limit aluminum precipitates in CSSX). • Si < 8.42E+02 mg/L at 6.44M Na (to limit precipitate formation in CSSX). • OH- >3.40E+04 mg/L at 6.44M Na (to limit precipitate formation in CSSX). • solids content <100 mg/L. • Sr-90 solids < 3.56E-02 Ci/gal; Sr-90 (soluble) <5.21E-03 Ci/gal. • NO_3^- + NO_2^- > 1.0M at 6.44M Na (required to scavenge hydrogen). • TPB < 10 ppm (minimum detection limit).	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.	*Not Applicable* Comments: The SWPF WAC does not apply to this transfer.
5. Foreign Material Exclusion - TPB Solvent Contamination	*Not Applicable* Comments: This program does not apply to the product stream but rather to maintenance activities on the processing equipment.						N/A
6. Vapor Space Corrosion Effects	Corrosion in the vapor space of Tank 48 has not been found to be an unusually aggressive phenomenon and the current chemistry control program has been sufficient to prevent vapor space and liquid/air interfacial corrosion in the Type III/IIIA tanks.	*Not Applicable*	*Not Applicable*	*Not Applicable*	*Not Applicable*	Corrosion in the vapor space of Tank 48 has not been found to be an unusually aggressive phenomenon and the current chemistry control program has been sufficient to prevent vapor space and liquid/air interfacial corrosion in the Type III/IIIA tanks.	*Not Applicable*
Safety Controls							

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
1. TSR - CSTF (Applicable sections indicated)	▪ Tank 48 Modes ▪ 5.8.2.48 Tank 48 Admin Controls • 5.8.2.49 Tank 48 Unauthorized Operations • B3.2.1 Tank 48 Waste Inerting System • B3.2.2 Tank 48 Emergency Purge Ventilation Equipment • B3.2.7 Tank 48 Fill Limit &tank Level Instrumentation • B3.2.10 Tank 48 Purge Exhaust Ventilation System • B3.2.11 Tank 48 Nitrogen Supply System • B3.3.1 Tank 48 Flammable Vapor Monitoring Requirements • B3.3.4 Tank 48 Oxygen Monitoring Requirements	• 3/4.8 Waste Storage Tanks (excluding Tank 48) • B3.8.1 Waste Tank Purge Ventilation System • B3.8.9 Waste Tank Purge Ventilation System 48)		*Not Applicable*	*Not Applicable*	▪ Tank 48 Modes ▪ 5.8.2.48 Tank 48 Admin Controls • 5.8.2.49 Tank 48 Unauthorized Operations • B3.2.1 Tank 48 Waste Inerting System • B3.2.2 Tank 48 Emergency Purge Ventilation Equipment • B3.2.7 Tank 48 Fill Limit &tank Level Instrumentation • B3.2.10 Tank 48 Purge Exhaust Ventilation System • B3.2.11 Tank 48 Nitrogen Supply System • B3.3.1 Tank 48 Flammable Vapor Monitoring Requirements • B3.3.4 Tank 48 Oxygen Monitoring Requirements	*Not Applicable*

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
2. DSA - CSTF (Applicable sections indicated)	• 2.3-1 Facility Overview • 2.4.5 Actinide Removal Process Facility • 3.3.3.3 Hazard Evaluation • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3.10 Type I, II, III, IIIA Waste Tanks • 4.3.11 Type I, II, III, IIIA Waste Tank High Liquid Level Conductivity Probes and Alarms (Excluding Tank 50) • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.3.6 ARP/MCU • 6.4.5 Critical Control Philosophy – Al Dissolution • 6.5.3 Criticality Controls – application of Incredibility Argument • Ch.18 Tank Accident Analysis	• 2.3-1 Facility Overview • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3.10 Type I, II, III, IIIA Waste Tanks • 4.3.11 Type I, II, III, IIIA Waste Tank High Liquid Level Conductivity Probes and Alarms (Excluding Tank 50) • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.4.5 Critical Control Philosophy – Al Dissolution • Ch.18 Tank Accident Analysis	• 2.3-1 Facility Overview • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3 Safety Class SSCs • 4.4 Safety significant SSCs • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.4.5 Critical Control Philosophy – Al Dissolution • 6.5.3 Criticality Controls – application of Incredibility Argument • Ch.18 Tank Accident Analysis	• 2.3-1 Facility Overview • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3.10 Type I, II, III, IIIA Waste Tanks • 4.3.11 Type I, II, III, IIIA Waste Tank High Liquid Level Conductivity Probes and Alarms (Excluding Tank 50) • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.4.5 Critical Control Philosophy – Al Dissolution • Ch.18 Tank Accident Analysis		• 2.3-1 Facility Overview • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3 Safety Class SSCs • 4.4 Safety significant SSCs • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.4.5 Critical Control Philosophy – Al Dissolution • 6.5.3 Criticality Controls – application of Incredibility Argument • Ch.18 Tank Accident Analysis	• 2.3-1 Facility Overview • 3.4.1 Accident Analysis Methodology • 3.4.2, Design Basis Accidents • 4.1 SSCs • 4.3.10 Type I, II, III, IIIA Waste Tanks • 4.3.11 Type I, II, III, IIIA Waste Tank High Liquid Level Conductivity Probes and Alarms (Excluding Tank 50) • 5.1.2 Derivation of Technical Safety Requirements - Scope • 5.5.2.4 Waste Storage Tank Level (Limiting Condition for Operation 3.8.4) • 5.5.2.13 Waste Tank Purge Portable Ventilation Equipment (Limiting Condition for Operation 3.8.13) • 5.5.5 Minimum Shift Crew • 6.3.1 Criticality Concerns – Waste Storage • 6.4.5 Critical Control Philosophy – Al Dissolution • Ch.18 Tank Accident Analysis
3. DSA - DWPF	*Not Applicable*			*Applicable* Comments: Criteria set by DWPF WAC.	*Applicable* Comments: Criteria set by DWPF WAC.	*Not Applicable*	*Applicable* Comments: Criteria set by DWPF WAC.
4. DSA - SPF	*Not Applicable*		*Applicable* Comments: Criteria set by Saltstone WAC.	*Applicable* Comments: Criteria set by Saltstone WAC.	*Applicable* Comments: Criteria set by Saltstone WAC.	*Applicable* Comments: Criteria set by Saltstone WAC.	*Not Applicable*
Regulatory Compliance							
1. NEPA/EEC[1]	*Applicable*						
2. Air Emissions Evaluations	*Applicable*						

Flow-Sheet Option #	**0**	**1**	**2**	**3**	**4**	**5**	**6**
Flow-Sheet Option	**Move Material from Tank 48 to 241-96H (Include Processing in 241-96H)**	**TF Interim Storage (Non-organic Tank)[6]**	**Direct Feed to Saltstone (via Tank 50)**	**512-S Filter Option[5]**	**Direct Feed to SWPF**	**Decant Tank 48 to Tank 50 and then Recycle to Tank 48[6]**	**Product to DWPF (Direct, via Tank 40, or via Tank 42 and Tank 51)**
a. Radiological NESHAP Evaluation	*Applicable*						
b. Chemical Air Emissions Evaluation[2]	*Applicable*						
3. Industrial Wastewater Treatment Facility documentation[3]	*Applicable*						
4. Federal Facility Agreement Assessment Report[4]	*Applicable*						
5. UDQE	*Applicable*						
Standard Communication Plan - NRC & DNFSB	*Applicable*						

Table Notes:
1 Update of existing document
2 SCDHEC Standard 2 (Criteria pollutants), Standard 8 (Air Toxic pollutants), Hg Emissions
3 Letter or application as necessary
4 If Necessary
5 SWPF will utilize transfer routes PCP341 (241-96H to 512-S) & PCP4 (LWPT to 511-S PT)
6 Would require further Salt/Sludge Processing