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Small Tank Catalyzed Peroxide Oxidation of Tank 48H Tetraphenylborate

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ABBREVIATIONS AND ACRONYMS

1PB	Phenylboronic acid
2PB	Diphenylborinic acid
3PB	Triphenylborane
AHP	Analytical Hierarchy Process
AOX	Absorbable Organically Bound Halogens
ARP	Actinide Removal Process
CCPO	Copper-Catalyzed Peroxide Oxidation
CPC	Chemical Processing Cell
CsTPB	Cesium Tetraphenylborate
CTE	Critical Technology Element
CLFL	Composite Lower Flammability Limit
DOE	United States Department of Energy
DSA	Documented Safety Analysis
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
FBSR	Fluidized Bed Steam Reforming
FC	Facility Control
FY	Fiscal Year
gpm	Gallons per Minute
HDB	H-Area Diversion Box
HLW	High-Level Waste
HPLC	High Performance Liquid Chromatography
IC	Initial Condition
IIT B52	A proprietary antifoam agent prepared by Illinois Institute of Technology
ITP	In-Tank Precipitation
KTPB	Potassium Tetraphenylborate
LFL	Lower Flammability Limit
LW	Liquid Waste
M	Manufacturing/Quality (with respect to TRL tables)
MCU	Modular Caustic Side Solvent Extraction Unit
MOC	Minimum Oxygen Control
MSDS	Material Safety Data Sheet
MST	Monosodium Titanate
NaTPB	Sodium Tetraphenylborate
NFPA	National Fire Protection Association
NPH	Natural Phenomena Hazard(s)
ORNL	Oak Ridge National Laboratory
P	Programmatic/Customer Focus/Documentation (with respect to TRL tables)
PC	Performance Category
PCHA	Preliminary Consolidated Hazard Analysis

ppm	Parts per Million
PVV	Process Vessel Ventilation
RAMI	Reliability, Availability, Maintainability, Inspectability
ROAR	Risk and Opportunities Report
ROM	Rough Order of Magnitude (Estimate)
SC	Safety Class
scfm	Standard Cubic Feet per Minute
SCIX	Small Column Ion Exchange
SDC	Seismic Design Criteria
SEE	Systems Engineering Evaluation
SME	Subject Matter Expert
SPC	Salt Processing Cell
SPF	Saltstone Production Facility
SRAT	Sludge Receipt and Adjustment Tank
SRS	Savannah River Site
SS	Safety Significant
SSC	Systems, Structures, and Components
SVOA	Semi-Volatile Organic Analysis
SWPF	Salt Waste Processing Facility
T	Technology/Technical (with respect to TRL tables)
TAML®	Tetra-amido-macrocyclic-ligand
TE	Technology Element
TF	Tank Farm
TMP	Technology Maturation Plan
TOC	Total Organic Carbon
TPB	Tetraphenylborate
TRA	Technology Readiness Assessment
TR&C	Task Requirements and Criteria
TRL	Technology Readiness Level
TSR	Technical Safety Requirements
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WAC	Waste Acceptance Criteria
WPS	Waste Processing Systems

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1 PURPOSE OF THE TECHNOLOGY MATURATION PLAN

Small tank copper-catalyzed peroxide oxidation (CCPO) is a potentially viable technology to facilitate the destruction of the tetraphenylborate (TPB) solids contained within the Tank 48H waste at the Savannah River Site (SRS). The primary functions of this technology maturation plan (TMP) with respect to the proposed technology are to:

i. Summarize the basic chemistry and historical application of catalyzed peroxide oxidation and its relevance to the treatment of TPB solids in the bulk Tank 48H waste.

ii. Establish the principal technology elements (TEs) for the proposed process, and subsequently assess each TE with respect to its potential designation as a critical technology element (CTE).

iii. Summarize fiscal year (FY) 2012 activities associated with technology maturation of the CCPO process.

iv. Determine the associated technology readiness levels (TRLs) for each CTE using the methodologies described in the United States Department of Energy (DOE) Technology Readiness Assessment (TRA) Guide [1].

v. Ascertain potential technology gaps that might hinder technology deployment, and document strategies for closing the gaps and maturing the technology to TRL 6.

This TMP is intended to be a dynamic document to enable content modifications as potential updates to the currently assessed maturity of the technology are disclosed.

2 INTRODUCTION

Tank 48H 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 [2] 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 48H vapor space sufficiently below the composite lower flammability limit (CLFL). In addition, the chemistry of the Tank 48H material poses a significant challenge to the salt processing and sludge processing facilities within the liquid waste system. Therefore, destruction of the organic constituents prior to permanent disposition is a key element for the liquid waste life-cycle completion. Numerous technology and systems engineering evaluations (SEEs) through 2006 [3-5] have been performed to identify technologies that could treat and/or disposition the waste in Tank 48H and potentially return the tank to Tank Farm (TF) service. The initial evaluations recommended aggregation through the Saltstone Production Facility (SPF) as the preferred technology. Subsequent analyses of non-aggregation technologies recommended Fluidized Bed Steam Reforming (FBSR). The most recent systems engineering analysis provided insight into other

technologies that were promising but required modifications to the liquid waste system. Many of these changes are in line with those that are now taking place within the liquid waste system. In a review of the alternatives that were presented as part of a SEE performed in 2006 [5], the most promising options revisited were: (1) direct vitrification and (2) chemical destruction.

Direct vitrification has become a viable option due to potential process enhancements in the Defense Waste Processing Facility (DWPF), such as the use of an alternate reductant (glycolic acid) to pretreat the sludge feed in the Chemical Processing Cell (CPC) while significantly reducing or eliminating the generation of hydrogen associated with the currently utilized reductant (formic acid). This modification, and the associated decrease in hydrogen, will increase the allowable proportions of other flammable components in the DWPF feed whilst maintaining the total flammables content sufficiently below the CLFL.

The chemical destruction option became viable when experimentation using a CCPO (modified Fenton's) process revealed near-complete destruction of TPB under alkaline conditions (pH ≈ 11) [6]. The more traditionally used iron-catalyzed Fenton's process typically requires acidic conditions (pH < 5) [7] to achieve high destruction efficiencies of TPB. Processing under an acidic environment has previously posed two significant issues:

A. Former emphasis was placed on in-situ treatment of the Tank 48H waste. Tank 48H is, however, constructed from carbon steel and at low pH the carbon steel corrodes rapidly. In alkaline solutions the formation of protective films greatly reduces the corrosion rate.

B. Tank 48H waste is maintained under alkali conditions via the addition of sodium hydroxide (NaOH) due to the aforementioned corrosion issues. As such acid processing would firstly require a reduction of the Tank 48H waste pH, followed by an increase in pH at processing completion so that the waste remains compatible with other TF operations. Both of these operations would ultimately increase the volume of waste to be dispositioned after organic treatment.

The availability of two stainless steel tanks located in 241-96H mitigate potential corrosion issues (Item A), and provide the ability to process smaller reaction volumes which can be more readily controlled; each tank has a liquid capacity of approximately 6000 gallons [8]. These tanks were considered unavailable in previous treatment evaluations due to their use for the Actinide Removal Process (ARP), as MST strike tanks. They are, however, expected to become available once ARP operations are discontinued, and the intent is to transfer batches of waste from Tank 48H to the 241-96H stainless steel tanks for organics treatment via the CCPO process.

Increased waste volume (Item B) after organics destruction treatment remains an issue if an acidic processing environment is used. However, the ability to process under an alkaline environment [6] provides a viable augmentation to the traditional iron-catalyzed Fenton's process, and has the potential to lessen waste volume increases associated with acidic processing.

A table-top engineering evaluation of both direct vitrification [9] and chemical destruction [10] options was conducted as a "zero-step" to further technology maturation, the recommendations of which proposed the chemical destruction option as the most viable alternative for successful technical and cost-effective maturation [11]. The CCPO is currently being developed within the framework of this TMP.

3 CATALYZED-PEROXIDE OXIDATION TECHNOLOGY BACKGROUND

Hydrogen peroxide (H_2O_2) is a strong oxidant with electrochemical oxidation potentials of 1.80 and 0.87 volts at pH 0 and 14, respectively [12]. In 1894 H.J.H. Fenton studied the oxidation of tartaric acid ($C_4H_6O_6$) 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 [13]. 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 [14]. Thenceforth the catalyzed peroxide oxidation process has been ubiquitously applied to organic destruction processes for industrial effluents including the treatment of textile wastewaters [15], reduction of polynuclear aromatic hydrocarbons in water [16], improvement in dewatering of activated sludge [17], removal of absorbable organically bound halogens (AOX) from pharmaceutical wastewater [18], treatment of brines [19], and treatment of paper pulp manufacturing effluents [20]. Catalyzed peroxide oxidation is also extensively used for in-situ remediation of contaminated soils [21] whereby the reagent is pumped directly into the soil. The advantage of the peroxide oxidation with respect to in-situ soil remediation is the fact that excess reagent decomposes to environmentally benign products, water and oxygen.

Iron-catalyzed peroxide oxidation of organic compounds at low pH is generally referred to as a "Fenton's process." The CCPO process in non-acidic environments and/or with a non-iron transition metal catalyst (under consideration in this TMP) is typically termed a "modified Fenton's process".

3.1 Basic Chemistry of Catalyzed Peroxide Oxidation

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 [22]. In general, however, reactions subsequent to hydroxyl radical formation (Reactions 3-4 and 3-5) 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 [6]. The more traditionally used iron-catalyzed Fenton's process typically requires acidic conditions (pH < 5) [7] to achieve high destruction efficiencies of TPB.

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

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

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 [7], and the ferrous ion remains in solution to continue formation of the hydroxyl radicals.

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

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

${}^{\bullet}OOH$ 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 3-3 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 3-4) or by oxygen addition (Reaction 3-5) both of which form organic radicals which are highly reactive and can be further oxidized [7].

$$RH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H_2O \qquad (3\text{-}4)$$

$$R{=}R + {}^{\bullet}OH \rightarrow {}^{\bullet}R\text{-}ROH \qquad (3\text{-}5)$$

3.2 Typical Reaction Products

Under optimized peroxide oxidation 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 [$HCOO^-$]). The general reaction for a stoichiometric ratio of hydrogen peroxide/TPB is shown below though the self-decomposition of hydrogen peroxide (discussed in the latter text) necessitates a greater than stoichiometric hydrogen peroxide/TPB ratio:

$$(C_6H_5)_4B^- + 60H_2O_2 \rightarrow 24CO_2 + 70H_2O + BO_2^- \qquad (3\text{-}6)$$

A significant number of oxidized organics will be formed as intermediates (or final products for incomplete reactions) during the conversion process due to the indiscriminate mode by which hydroxyl radicals oxidize organic compounds, and the subsequent number of potential reaction

pathways available. 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. Benzene, phenol (C_6H_5OH) and biphenyl ($[C_6H_5]_2$) are likely early intermediate breakdown products during peroxide oxidation of TPB. 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 [23].

An important distinction between copper- and iron-catalyzed reactions is that copper also promotes organics decomposition via hydrolysis reactions. Copper-catalyzed hydrolysis has been considered for the destruction of sodium tetraphenylborate (NaTPB) in Tank 49H (Reaction 3-7) [24], and KTPB in the DWPF Salt Processing Cell (SPC) prior to waste vitrification [25-26]. Copper-catalyzed hydrolysis has also 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 $C_6H_5B(OH)_2$) [27].

$$Na(C_6H_5)_4B + 2H_2O \rightarrow 4C_6H_6 + NaBO_2 \qquad (3\text{-}7)$$

However, unlike peroxide oxidation, the hydrolysis reaction does not fully decompose TPB to carbon dioxide and water. 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 [27]. The copper-catalyzed decomposition of TPB occurs by a combination of hydrolysis and hydroxyl radical oxidation reactions, and the extent to which each of these reactions occurs likely depends on pH, temperature, and other factors that directly affect hydroxyl radical formation.

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

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 \qquad (3\text{-}8)$$

The decomposition of hydrogen peroxide is thermodynamically favorable (heat of decomposition at 25 °C [50 wt% H_2O_2] = 95.4 kJ/mol [28]), and the proportion of peroxide that decomposes roughly doubles for each 10 °C increase above room temperature [29]. At higher pHs, the stability of hydrogen peroxide deteriorates very rapidly [29]. Since the Tank 48 waste has a nitrite (NO_2^-) molarity of approximately 0.5M [2] there is also the possibility of consuming hydrogen peroxide through nitrite oxidation per Reaction 3-9:

$$H_2O_2 + NO_2^- \rightarrow H_2O + NO_3^- \qquad (3\text{-}9)$$

3.3 Application of Peroxide Oxidation for the Treatment of Nuclear Waste

A number of investigations have been conducted to assess the applicability of catalyzed peroxide oxidation for the destruction of organics contained in nuclear waste. Data from laboratory- and bench-scale (10 liter reactor volume) tests utilizing an iron catalyst to treat both simulant and actual waste slurries (containing ion-exchange resins) from three underground storage tanks at the Oak Ridge National Laboratory (ORNL) has been reported [30]. The reaction with the resins required a dilute acidic solution (pH = 3-5) and temperatures (T = 60-100 °C). The ion-exchange resin was oxidized to carbon dioxide and inorganic salts. Small amounts (<3 vol%) of carbon monoxide (CO) were also generated in addition to trace quantities of VOCs from the bench-scale tests. Maximum VOC concentrations measured were 48 ppm diethylbenzene ($C_6H_4[C_2H_5]_2$), 40 ppm acetone ($[CH_3]_2CO$), and 21 ppm benzene, with a maximum total VOC concentration of 122 ppm. Treatment times of 10 hours or less were typically required to reduce the organics content below specified waste acceptance requirement limits.

With respect to investigations related specifically to the destruction of TPB, Table 1 provides a summary of test results from four relevant studies. The summary data includes reaction conditions, TPB destruction efficiencies, and by-product, and off-gas constituents. In particular, details included in the table relate to those process conditions that resulted in the highest TPB destruction efficiencies. Additional details regarding the supplementary scope and findings of each of the studies are provided in the subsequent text.

Table 1: Historical data for TPB destruction

Experimental Conditions	Results	Year / Document # / Reference

• Waste: T48 simulant (500 mL)
• Catalyst Type: Cu or 50/50 wt% Cu-Fe
• Catalyst conc.: 200 mg/L Cu or 200 mg/L Cu + 200 mg/L Fe
• Oxidant: 50 wt% H_2O_2
• Target pH:
1. Adjust to 7.5 after catalyst addition (using nitric acid (HNO_3))
2. Adjust to 3.5 after H_2O_2 addition (using HNO_3)
• Temperature: boiling
	• TPB destruction >98.5% (TPB < detection limit)
	• Decomposition Products:
	  • 2PB, 1PB and C_6H_5OH < detection limits
	• Off-gas:
	  • Approximately equal proportions of C_6H_6 and CO_2, C_6H_6, CO_2,
	  • C_6H_6 evolved during initial 2 hours of testing
	  • Other off-gas constituents ⇨ NO_x, O_2, $(C_6H_5)_2$
		• 2003
		• ORNL/TM-2003/262 [31]

• Waste: T48 simulant (100 mL) • Catalysts: Cu or 50/50 wt% Cu-Fe • Catalyst conc.: 200 mg/L Cu or 200 mg/L Cu + 200 mg/L Fe • Oxidant: 50 wt% H_2O_2 • Target pH: 1. Adjust to 7.5 after catalyst addition (using HNO_3) 2. Adjust to 3.5 after H_2O_2 addition (using HNO_3) • Temperature: boiling	• <1000 ppm total organic carbon (TOC) in product (TOC destruction >90%) • Decomposition product and off-gas analyses not performed	• 2004 • WSRC-RP-2004-00240 [23]
• Waste: T48 simulant (500 mL) • Catalyst type: Fe • Catalyst conc.: 500 mg/L • Oxidant: 50 wt% H_2O_2 • Target pH: 7 (using HNO_3) • Temperature: 45 °C	• TPB destruction >88% • Decomposition Products: • 2PB, 1PB and C_6H_5OH < detection limits • Off-gas analyses not performed	• 2003 • WSRC-TR-2003-00365 [32]

• Waste: T48 simulant (600 mL)
• Catalyst type: Cu
• Catalyst conc.: 500 mg/L
• Oxidant: 30 wt% H_2O_2
• Target pH: 11 (using HNO_3)
• Temperature: heated to 35, 45, 55, and 75 °C after catalyst addition
	• TPB destruction >99.8%
	• 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% lower flammability limit (LFL)
	  • Off-gas not analyzed for CO_2
		• 2004
		• WSRC-TR-2005-00114 [6]

Another ORNL study [31] investigated the use of the catalyzed peroxide oxidation reaction specifically for the treatment of TPB contained in SRS Tank 48H waste. Both mixed copper-iron and copper-only catalysts were tested. Tests were performed on a laboratory-scale in an acidic environment (pH 3.5) and with the simulant heated to boiling. The process exhibited >98.5% organics removal. It was, however, determined that approximately equal fractions of the TPB were converted to benzene and carbon dioxide with the majority of the benzene being detected during the initial stages of processing (0-2 hours). It is suspected that the benzene was generated by hydrolysis of the TPB which as previously discussed is known to occur in the presence of copper [24-27].

The use of copper and iron-based catalysts under acidic reaction conditions for peroxide oxidation of Tank 48H simulant has also been reported [23]. Experiments were conducted at laboratory-scale (with the simulant heated to boiling) and established the effects of catalyst type and reaction pH on post-reaction total organic carbon (TOC) compound levels. Various catalyst types including 50/50 wt% copper-iron, copper-only, and iron-only catalysts were tested. The effects of pH control after addition of the catalyst (and prior to hydrogen peroxide addition) were also assessed. Effects of the catalyst type were indeterminate, and TOC conversions of >90% were achieved whichever catalyst system was employed. In contrast, pH control was shown to be a significant process variable. The optimal control regime required an initial pH adjustment close to neutral conditions (pH ~ 7.5) after addition of the catalyst, a subsequent period of oxidation under these conditions, and then a second pH adjustment to around 3.5 for further oxidation. Adjustment to mild acid conditions is normal for the Fenton's reaction though it is apparent that extensive hydrolysis of the TPB to benzene and other products can occur if this adjustment is made immediately after catalyst addition. The intermediate neutralization phase serves to inhibit the hydrolysis reaction. For comparison TOC conversions for a 50/50 copper-iron catalyst with and without pH adjustment to 7.5 after catalyst addition were recorded at >90% and <50%, respectively.

Application of non-acidic environments to facilitate a Fenton's type reaction (at 45 °C) has also been investigated [32]. Two catalysts, iron and Tetra-Amido-Macrocyclic-Ligand (TAML®) were considered at pH 7 and pH 11, respectively. The highest TPB conversion of 88% was realized for the iron-catalyzed reaction (at pH 7) though significantly greater than stoichiometric proportions of hydrogen peroxide were required to achieve the indicated level of TPB decomposition. In contrast, the maximum TPB conversion exhibited for the TAML®-catalyzed reaction (at pH 11 and identical hydrogen peroxide proportions) was 68%.

The investigation which serves as the precursor to the technical maturation of the CCPO process utilized copper-only catalysts at non-acidic pH 11 and pH 14 [6]. For this study a temperature regime incorporating hold times at 35, 45, 55, and ultimately 75 °C was employed. The analyses also sought to identify intermediate and final decomposition products, and quantify the proportions of these products. The following summarizes the general results 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 organics treatment of the Tank 48H 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, including benzene. The benzene concentration in the vapor space or off-gas was measured at below 25% of the lower flammability limit (LFL) throughout testing.

As part of the FY2012 maturation strategy for the CCPO process, laboratory-scale investigations were performed [33] in order to (1) verify the results from the 2004 experiments [6], and (2) to consider processing optimization. A summary of the results from this study is provided in Section 6.

4 LIFE-CYCLE BENEFIT

The chemistry of the Tank 48H material poses a challenge to the salt and sludge processing facilities within the liquid waste system. Therefore, destruction of the organics prior to permanent disposition is fundamental to the liquid waste life-cycle completion.

There are a number of significant benefits with the planned approach for chemical destruction in the 241-96H strike tanks including [10]:

- The use of existing infrastructure with minimal modifications to support systems,
- The processing of Tank 48H waste can occur concurrently with salt processing which should negate or minimize potential extensions to the high-level waste (HLW) system life cycle,
- The chemical destruction process will utilize a safety strategy similar to that currently adopted for Tank 48H.

In addition, the chemical destruction technology maturation process in Building 241-96H will be able to leverage the significant development efforts associated with the FBSR project, which was intended to be deployed in 241-96H. Relevant information includes, for example: (1) waste characterization and Tank 48 infrastructure; (2) safety analyses; (3) permitting documentation; (4) shielding calculations; and (5) civil/structural evaluation of 241-96H. Several aspects of the design changes proposed for FBSR, such as design modifications to the 241-96H strike tanks, valve box modifications, and the Tank 48 transfer pump, are available for use with the chemical destruction option [34].

Other life-cycle benefits result from the planned technology maturation approach discussed in the subsequent sections of this report. Methodical evaluation of all systems in the peroxide oxidation process ensures that:

- Overall project costs are minimized by resolving technology maturity issues and avoiding engineering re-work and potential delays in peroxide oxidation commissioning,
- The peroxide oxidation process design will achieve program mission operating requirements by the assessment of technology readiness and the completion of required technology maturation activities.

Technology maturation costs are typically small in comparison to impacts from design re-work and potential delays in the operating schedule of the peroxide oxidation process. The TRA process is also designed to ensure that future performance issues associated with the technology systems are identified and resolved before operations commence.

5 IDENTIFICATION OF CRITICAL TECHNOLOGY ELEMENTS

A TE is deemed critical if the system being developed depends on this TE to meet operational requirements **AND** if the TE (or its application) is either new or novel. The peroxide oxidation process for treatment of the TPB (from Tank 48H waste) in the 241-96H strike tanks has been divided into five TEs (or process sub-systems) which are depicted in the process diagram of Figure 1.

DOE TRA Guide [1] provides a series of questions for determining whether a TE should be designated a CTE. These questions are presented in Table 2. For a technology to be critical, the answer to one of the questions in **BOTH** sets of criteria should be answered “yes”. Of the five TEs only the reaction process (including the reaction vessel) has been determined to be a CTE. Rationale for a CTE or non-CTE designation for each TE is presented in subsequent text.

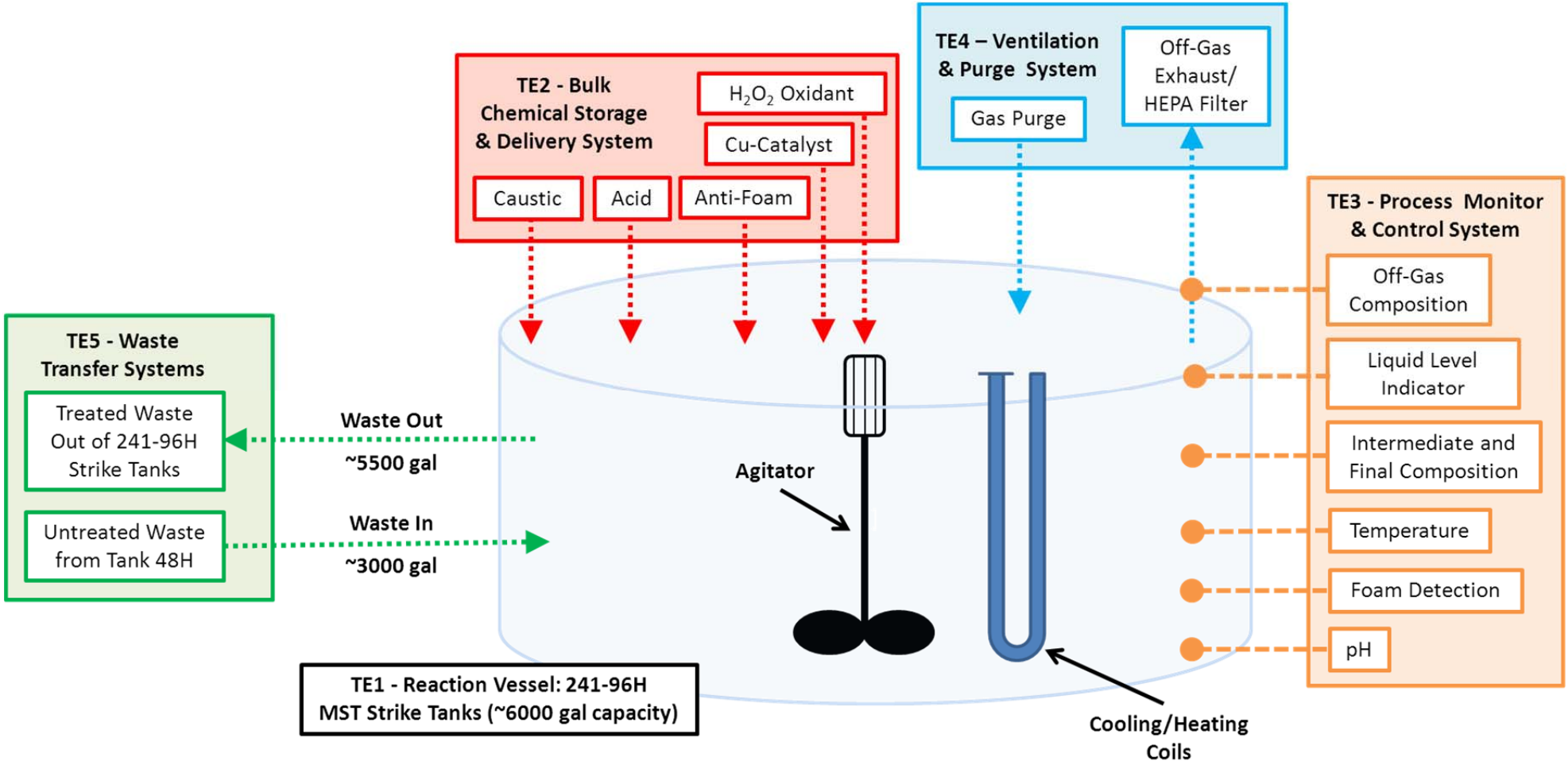

Figure 1: CCPO process schematic

Table 2: Identification of CTEs

Questions to Determine CTE Designation	Reaction Process /Vessel	Bulk Chemical Storage & Delivery System	Reaction Monitoring & Control Systems	Ventilation & Purge Systems	Waste Transfer System
CRITERIA – SET 1					
Does the technology directly impact a functional requirement of the process or facility?	Y	Y	Y	Y	Y
Do limitations in the understanding of the technology result in a potential schedule risk; i.e., the technology may not be ready for insertion when required?	Y	N	N	N	N
Do limitations in the understanding of the technology result in a potential cost risk; i.e., the technology may cause significant cost overruns?	Y	N	N	N	N
Do limitations in the understanding of the technology impact the safety of the design?	Y	N	N	N	N
Are there uncertainties in the definition of the end state requirements for this technology?	Y	N	N	N	N
CRITERIA – SET 2					
Is the technology new or novel?	N	N	N	N	N
Is the technology modified?	Y	N	N	N	N
Have the potential hazards of the technology been assessed? † (see note)	Y	N	N	N	N
Has the technology been repackaged so a new relevant environment is realized?	Y	N	N	N	N
Is the technology expected to operate in an environment and / or achieve performance beyond its original design intention or demonstrated capability?	Y	N	N	N	N
CTE DESIGNATION	**CTE**	**Non-CTE**	**Non-CTE**	**Non-CTE**	**Non-CTE**

† - This question has been interpreted as "Are there potential hazards that have not been assessed and are not well understood?"

5.1 TE1 – Reaction Process and Vessel

The reaction process comprises both the chemical reaction and the reaction containment vessel (including the currently available waste mixing and cooling capabilities for the vessel). The safe, consistent and effective application of CCPO reaction is essential to realize successful demonstration and potential implementation of the proposed TPB chemical destruction technology. The viability of the CCPO process has been recently assessed on a laboratory-scale with waste simulant [33] to both verify the results from the 2004 study [6] and to optimize the CCPO process. The available results from these investigations support the viability of the process with respect to TPB destruction and are discussed in detail in Section 6. Subsequent (near-term) maturation activities should include confirmation of the simulant results using real waste, and demonstration of the CCPO process at an engineering-scale in terms of performance, consistency, and safety. The reaction process is designated a CTE given the obvious impact that it has on the overall viability of the chemical destruction process.

The stainless steel tanks in 241-96H, currently used as the MST strike tanks for ARP, will operate as reaction vessels for the CCPO process. The tanks are constructed from 304L stainless steel which exhibits excellent corrosion resistance in both acidic and caustic environments [35]. 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. Modeling analysis [36] has been performed for a proposed impeller design for the tanks, and demonstrated that the impeller provides sufficient high velocity zones to mix a tank containing solids similar to sludge particles. However, the modeling was performed to specifically assess the mixing of salt waste and MST to facilitate the adsorption process between the MST and any actinides in the salt waste. Potential differences in the rheological, physical, and chemical properties for the salt/MST waste mixture and the Tank 48 waste may necessitate remodeling of the mixing characteristics of the agitator. Additionally, engineering-scale testing will be required to optimize mixing speed to facilitate efficient organic destruction whilst also ensuring the insoluble solids remain in suspension.

An optimized mixing strategy may be required to limit the formation of foam during waste slurry mixing. Foam formation is due to TPB precipitates and their propensity to envelope gas bubbles in the waste slurry subsequently rising to the surface of the slurry. This phenomenon results in reduced TPB participation in the reaction process, and thus potentially reduced TPB conversion efficiencies. Studies have highlighted the successful use of IIT B52 anti-foam (a proprietary anti-foam agent prepared by Illinois Institute of Technology) to suppress foam formation in laboratory-scale studies with simulated KTPB slurries [37-38]. The use of anti-foaming agents are considered the “first line of defense” in negating the formation of foam, and it is currently envisaged that existing mixing equipment in the MST strike tanks will be utilized with no required modifications other than mode of operation. However, the degree of associated foam formation with the peroxide oxidation of real waste is unknown, and both the use of anti-foam and an optimized mixing strategy (including optimizing impeller design) may be required.

It is probable that the contents of CCPO reaction vessels will require heat input to optimize the chemical destruction reactions. For the FY2012 investigations [33] processing temperatures of 35, 50, and 65 °C were considered. Preliminary data suggests that a temperature of 50 °C will likely be required to achieve the desired levels of organic destruction in a time frame that would not adversely impact the Liquid Waste System Plan. It has not been established if the currently installed cooling coils could also be utilized for heating the contents of the reaction vessel to the 50 °C temperature. A thermal analysis will be required to determine the maximum achievable temperature in the reaction vessel by passing a heated medium through the cooling coils (while also accounting for reaction enthalpies in the vessel), and to subsequently establish if additional heating capabilities are required (for example, immersion heater, external heating jacket etc.).

5.2 TE2 – Bulk Chemical Storage and Delivery System

The peroxide oxidation of TPB will be directly impacted by the ability to feed reactants to the process, but the bulk chemical storage and delivery systems required are ubiquitously used in commercial applications, and neither new or novel. As such the bulk chemical storage and delivery system is designated non-CTE.

The TPB chemical oxidation process will likely utilize the following 5 chemicals:

i. 50 wt% nitric acid for pH control
ii. Copper catalyst (copper nitrate – $Cu(NO_3)_2$)
iii. 50 wt% hydrogen peroxide
iv. Sodium hydroxide caustic (if necessary for pH control prior to transfer from CCPO reaction vessels to downstream facilities or tanks)
v. IIT B52 anti-foaming agent (if necessary).

Note that in the 2004 investigations [6] the copper catalyst was added in the form of copper sulfate though comparative testing between copper sulfate and nitrate, with respect to reaction kinetics and organics decomposition, has indicated no discernible differences [33]. Since sulfate has the potential to impact the quality of the vitrified glass [39] copper nitrate is the preferred form for the copper catalyst. However, the use of copper nitrate introduces complex handling requirements. The storage and handling of copper nitrate will necessitate engineering and administrative protocols that prevent contact with combustible materials, due to its potential ignitability and flammability impacts. Storage and handling requirements are specified by the Material Safety Data Sheet (MSDS) for copper nitrate [40].

Hydrogen peroxide also has specific handling requirements. The following list highlights some of the potential hazards of hydrogen peroxide if not stored and handled properly [28-29]:

- Decomposition of hydrogen peroxide generates heat and gas which can result in rapid pressure build-up leading to pressure bursts of inadequately vented containers.
- Decomposition of hydrogen peroxide can generate sufficient heat and oxygen to initiate combustion of ignitable materials.

- Oxygen enrichment of hydrocarbon vapors resulting from the decomposition of hydrogen peroxide can result in vapor phase explosions.
- Hydrogen peroxide can form explosive mixtures with some organic substances.

While hydrogen peroxide has not been utilized at SRS in bulk quantities its safe storage and handling is standard practice, and subject to standard safety protocols and analyses within the chemical industry [29].

Bulk storage and handling/delivery of caustic and acidic components are routine operations at SRS. A storage volume estimate [41] has been developed for the CCPO process chemicals based on simultaneous 3100 gallon transfers of Tank 48 waste to each CCPO reaction vessel. The minimum chemical storage volumes are provided in Table 3.

Table 3: Minimum CCPO process chemical storage capacity

Process Additive (Solution)	Minimum Vessel Capacity (gallons)
50 wt. % Nitric Acid	1725
Copper Nitrate	10
50 wt. % Hydrogen Peroxide	4000
50 wt.% Sodium Hydroxide	1000

5.3 TE3 – Reaction Monitoring and Control Systems

Reaction and monitoring control is an essential sub-system of the chemical destruction process, Monitoring and control systems are ubiquitously utilized for SRS waste processing operations to control reaction rate, efficiency and safety, and are therefore designated as non-CTEs. Monitoring equipment will likely encompass off-gas analyzers, temperature sensors, pH sensors, and foam indicators that will provide feedback with respect to reaction status and reaction anomalies. Laboratory-scale testing is being performed to determine which process conditions can be readily measured and subsequently utilized to provide feedback on reaction status. For example, detection of higher than atmospheric baseline concentrations of carbon dioxide in the off-gas is evidence of progression of the oxidation reaction; in contrast a decline in carbon dioxide concentration and concurrent increase in oxygen concentration might be indicative that the reaction is nearing its end-point since the hydrogen peroxide is undergoing auto-decomposition rather than oxidizing the organic components of the waste. Monitoring of key process parameters, like off-gas composition, may ultimately be used to ensure the reaction progresses in a safe, predictable, and efficient manner. Specific off-gas data available from the laboratory-scale tests [33] is discussed in Section 6, and additionally in Section 5.4 with specific reference to potential flammability concerns.

5.4 TE4 – Ventilation and Inerting Systems

The ability to vent, and potentially inert, the vapor space in the 241-96H strike tanks are essential system features required to ensure the safe operation of the chemical destruction process. Technology related to radioactive waste tank ventilation and inerting systems are extensively utilized at SRS. As such the design and operation of such systems is expected to be consistent with currently utilized SRS technologies. Consequently, these systems are designated non-CTE.

The MST strike tanks in 241-96H currently incorporate Process Vessel Ventilation (PVV) systems that provide continuous negative ventilation to remove flammable vapors and assist in minimizing contamination. The vessels do not, however, incorporate an inerting system, and a design modification of the 241-96H strike tanks may be required to enable the introduction of an inert gas into the tanks to facilitate minimum oxygen content (MOC) control to prevent flammability [42].

Preliminary off-gas data from the FY2012 laboratory-scale testing indicates significant benzene generation (in addition to carbon dioxide) associated with pH adjustment which occurs in the first 24 hours of processing. The off-gas data is discussed in Section 6.1 and illustrated in Figure 4. It is acknowledged that the production of substantial amounts of benzene can adversely impact the safe operation of the CCPO process. However, it is envisaged that further process optimization will prevent or significantly reduce both the peak and cumulative production of benzene. Proposed experimentation to reduce benzene generation is discussed in Section 6.1.3.

Whilst the ultimate goal is to prevent or minimize benzene production, a preliminary (draft) calculation [43] based on the FY2012 off-gas data [33] indicates that the cumulative release of benzene during the first 24 hours could potentially necessitate a flow rate of approximately 315 scfm through the reaction vessel head space to ensure the benzene generated remains at < 25% LFL. This is the combustible concentration limit (not requiring automatic instrumentation with safety locks) specified by National Fire Protection Association (NFPA) 69 [44]. The currently installed PVV system is controlled to provide a total flow rate of 100 scfm per vessel [45]. As such, fans with higher flow capacities may be required to provide the indicated flow rate of 315 scfm per vessel.

NFPA also stipulates that the concentration of combustible gases could potentially be increased to 60% LFL if automatic instrumentation with safety locks is provided. Alternatively, MOC control utilizing, for example, a nitrogen inerting gas may be employed to negate issues of flammability in the reaction vessel head space.

5.5 TE5 – Waste Transfer System

Waste transfers in and out of the waste tanks are an integral part of SRS operations [46] and both Tank 48H and the strike tanks in 241-96H currently incorporate systems that will be utilized for the blending and transfer of the waste. Potential upgrades may be required for these

systems. Design modifications to 241-96H strike tank cell piping and and valve box re-piping were previously considered for waste transfers from Tank 48H to the 241-96H strike tanks prior to treatment via FBSR [34], and the proposed changes would be equally applicable to proposed chemical destruction technology route.

The treatment of waste will be via a batch process, and prior to transfer of the untreated waste from Tank 48H it will be agitated using up to four currently installed dual-nozzle slurry pumps to ensure a relatively homogeneous discharge stream. A well-mixed Tank 48H waste stream contains approximately 3.26 wt% insoluble solids [47]. A recent study [48] demonstrated operation of 3 or 4 slurry pumps satisfies solid suspension requirements with less than 30% variation in solids concentration between the main tank volume and the transfer pump inlet. However, the study did not assess the impact of cooling coils in Tank 48H on slurry pump operation. Another mixing study [49] for Tank 50H assessed the effects of coiling coils on blending the tank contents, and concluded that the inclusion of coiling coils effectively doubled the waste blending time. An extension of the analysis performed in the Tank 48H mixing simulation [48] will be required to determine the effects of the coiling coils on blending the material in Tank 48H. Such a study would, however, be related to the operation of the existing pumps in terms of velocity and time, and no slurry mixing pump development, upgrades, or replacements are likely.

Once mixed, the waste in Tank 48H will be pumped to the tanks in 241-96-H through a combination of existing [50], and newly installed, transfer lines. Solids may still settle during actual transfer through the piping system. However, empirical data [51] indicates that inconsequential settling of the insoluble solids in Tank 48H waste is observed during the first hour of stagnation. In addition, testing has demonstrated that it takes between 2 hours to one day for the largest particles, KTPB solid, in a stagnant tank fluid to be settled down to the tank floor [52]. The settling time during transfer will likely be longer than the 2 hour stagnant settling time due to waste motion. However, it is imperative to assess the transfer line for potential areas of stagnation or non-turbulent flow to prevent solids settling and cumulative long-term build-up.

The impact of benzene concentration in the transfer piping was also considered. While potential benzene release in Tank 48H during slurry mixing, and the subsequent concentration of benzene in the tank vapor space, can be managed using gas ventilation and purging systems to prevent benzene levels exceeding the LFL, this is not the case for the transfer pipes. Consequently concerns exist with respect to benzene levels potentially exceeding LFL concentrations in the transfer lines. However, empirical data indicates that the benzene concentration in the Tank 48H vapor space will remain below 5% of its LFL while operating the slurry pumps for waste transfers out of Tank 48H without the need for tank inerting operations [53]. As such the concentrations of benzene would not be expected to exceed the LFL in the transfer line piping.

Once treated, the waste will be transferred from the strike tanks in 241-96-H through H-Area Diversion Box (HDB) 7 to a designated receipt tank. Of particular significance with respect to the treated waste are the potential impacts it will have on downstream transfer lines, tanks, facilities,

and processes. Downstream impacts have received preliminary consideration as part of a flow-sheet options analysis for the CCPO-processed waste [54]. The findings from this study are discussed in Section 6. A more rigorous assessment of downstream impacts is anticipated in Phase 2 of the maturation strategy (see Section 8 and Figure 4).

There is the potential that more significant development activities may be required for these (and other yet to be determined) systems, and that a current designation of non-CTE will be modified to CTE. Changes to non-CTE designations will be updated in future revisions of this TMP as deemed appropriate.

6 FY2012 TECHNOLOGY MATURATION ACTIVITIES

TEs that are designated as CTEs (i.e., the CCPO process) are subject to a rigorous development process (as detailed in Reference 1) which is used to establish the current level of maturity of a given CTE and subsequently determine the developmental requirements to progress the technology to a higher level of maturity. This process is detailed in Sections 7 and 8.

A number of critical activities [55] were identified for completion in FY2012 with the intent of utilizing the combined results from these activities to assess the viability of the CCPO process, and to subsequently determine if the technology warranted further development. The following activities detailed in the section have been completed, or their findings sufficiently developed to warrant inclusion in this report.

6.1 Laboratory-Scale Simulant Testing

A study was initiated in FY2012 to verify the results from the 2004 experiments [6], and to further optimize the process in terms of the following process attributes:

i. *Complete (or Near-Complete) Organic Destruction* – the required level of organic destruction is dictated by the destination of the treated waste and the organic limits imposed on a particular transfer destination. A flow-sheet options report has been developed [54] to assess various transfer options for the CCPO-processed waste, and to determine whether the treated waste meets feed composition requirements with respect to allowable levels of chemical (including organic species) and radioactive constituents.

ii. *Repeatable and Predictable Levels of Organic Destruction* – it is necessary to develop a process with a sufficiently robust operating envelope that provides both repeatable and predictable levels of organic destruction.

iii. *Enhanced Reaction Kinetics* – improving the reaction kinetics (while maintaining safe operation) will enable completion of the Tank 48 clean up within the currently devised Liquid Waste System Plan [56].

iv. *Minimized Chemical Addition* – the CCPO process involves the addition of nitric acid, copper catalyst, hydrogen peroxide, and potentially both anti-foam and sodium hydroxide. It is desirable to limit the proportion of chemicals added to the waste to minimize potential downstream impacts. For example, there is a limit on the amount of copper that can be incorporated into vitrified glass, and thus the goal would be to minimize the proportion of catalyst required without significantly impacting the reaction kinetics or level of organic destruction.

v. *Minimized Waste Volume* – the 2004 study indicated a volume increase of 183% [6] due to the addition of the various reactants and catalysts. It is advantageous with respect to both processing life-cycle and cost to minimize the volume of waste that must subsequently be dispositioned as Saltstone grout or vitrified glass.

vi. *Minimized VOCs* – VOCs, most notably benzene, derived from degradation of the TPB, can volatilize to produce a flammable mixture in the vapor space of the reaction vessel. Minimizing the formation of the benzene will reduce both the risks associated with its flammability and the control requirements to manage the vapor space.

vii. *Minimized Reaction Temperature* – the 2004 study [6] ultimately utilized a temperature of 75 °C to achieve a TPB destruction >99.8%. However, it is recognized that lower process temperatures yield benefits in terms of reducing system complexity, operation costs, and safety. Thus the goal is to promote the reaction at the lowest achievable temperature while maintaining the required reaction kinetics and level of organic destruction. The CCPO reaction vessels (MST strike tanks) do not have a dedicated heating capability and the current intent is to utilize the coiling coils for heating also. A thermal calculation will be required to determine the maximum achievable temperature in the reaction vessel by passing a heated medium through the cooling coils.

viii. *Minimized Hazardous Emissions* – with respect to environmental emission compliance it is desirable to minimize the proportion of hazardous emissions, such as benzene and mercury. It may be possible to affect the off-gas composition by, for example, optimizing conditions for the peroxide oxidation reaction (at higher pH) as opposed to the hydrolysis reaction (at lower pH). It is believed that the latter results in higher benzene concentrations in the off-gas [24].

ix. *Minimized MST Decomposition* – a concern exists with the respect to degradation of the MST during CCPO-processing resulting in desorption and potential dissolution of the adsorbed fissile actinides. The preferred dispositioning route for fissile isotopes is through DWPF for incorporation into vitrified glass. This is achieved by filtering the MST from the waste stream and transferring to DWPF. If, however, the actinides are desorbed, and subsequently dissolved during the CCPO process, they will move forward as part of the liquid waste stream for processing at either the Salt Waste Processing Facility (SWPF) or SPF. If the filtrate is sent to SWPF it would be subjected to another MST strike and re-adsorption of the actinides would occur. If, however, the filtrate is sent

directly to SPF the fissile actinides would be dispositioned in grout and may potentially challenge or exceed the Saltstone Waste Acceptance Criteria (WAC) [57]. However, preliminary assessment has indicated that the fissile actinide components of the CCPO-processed waste would be an order of magnitude lower than the WAC specified limits [54].

x. *Minimized Production of Fouling By-Products* – biphenyl and terphenyl compounds are decomposition products for TPB [32] and have the potential to foul equipment both in and downstream of the reaction vessel. Minimizing the formation of these compounds will reduce inspection and maintenance activities that would otherwise be required to assess and resolve potential fouling issues.

6.1.1 2004 CCPO Process Verification

The first FY2102 test essentially utilized the same processing conditions as the 2004 investigations but was unable to repeat the high TPB destruction efficiencies demonstrated in the 2004 tests. The FY2012 test indicated a TPB destruction level of approximately 85% compared to >99.8% in 2004. Potential factors associated with the reduced destruction efficiencies for the verification test have not been identified although the 2004 test did include an initial several day hold at room temperature that was not incorporated into the FY2012 test due to the perceived slow reaction kinetics at this temperature. Results with respect to major organic species identified for each test are shown in Table 4.

Table 4: Major organic constituents detected in 2004 CCPO test and 2012 verification test

Test	TPB Destruction (%)	Determined by HPLC (mg/L)	Determined by VOA (mg/L)	Determined by SVOA (mg/L)
2012 (DEMO 1)	84.2	TPB: 2420 3PB: <10 2PB: <10 1PB: <10 Phenol: 10	Benzene: 0.2	Biphenyl: 760 p-Terphenyl: 240 o-Terphenyl: 3 m-Terphenyl: 3
2004	>99.8	TPB: <10 3PB: <10 2PB: <10 1PB: <10 Phenol: 10	Benzene: <0.05	p-Terphenyl: 11

Note: HPLC = High Performance Liquid Chromatography
VOA = Volatile Organic Analysis
SVOA = Semi-Volatile Organic Analysis

Consequently process optimization testing was initiated and demonstrated the viability of the CCPO process with respect to high TPB destruction efficiencies (>99.9%). Details of these optimization tests are provided in the following sections.

6.1.2 FY2012 CCPO Process Optimization

The following discussion summarizes major findings from the CCPO process optimization studies with respect to temperature, pH, copper catalyst loading, and hydrogen peroxide addition [33]. Appendix A also provides a tabulated summary of the experimental conditions for each test and pertinent results. Note that with respect to Appendix A (and the subsequent discussion) the time for 100% boron dissolution is utilized as a tentative indication of the reaction time to achieve 100% TPB degradation.

i. *Temperature* – at 65 °C (and pH 11) >99.9% TPB destruction was achieved in less than 24 hours compared to approximately 370 hours at 50 °C. Processing at 35 °C for 500 hours achieved <51% TPB destruction. Higher processing temperatures also resulted in reduced amounts of VOCs, namely benzene, and semi-volatile organic compounds, such as biphenyl and terphenyl. Low benzene generation rates are advantageous with respect to minimizing impacts on environmental emissions and reaction vessel vapor space flammability. Minimizing the semi-volatile organic species (in particular biphenyl and terphenyl) should reduce the propensity of fouling in, or downstream of, the reaction vessel. Even though processing at 65 °C significantly decreases processing time and results in fewer residual organics there are a number of potential issues with processing at this temperature:

- It has not been established if the 65 °C temperature can be achieved in the reaction vessel utilizing the currently installed cooling coils as a means of heating. This is equally true for the 50 °C temperature, but in general lowering the process temperature will reduce both the complexity of the system and the degree of system modifications required.

- Based on a TPB destruction time of <24 hours (at 65 °C) it is probable that the TPB was degraded by acid hydrolysis as opposed to peroxide oxidation since the 24 hour reaction period corresponds to significantly less than the stoichiometric requirement of hydrogen peroxide. Since benzene is the ultimate product of acid hydrolysis, processing at higher temperatures will likely yield greater proportions of benzene in the off-gas.

- At higher temperatures the vapor pressure of both benzene and biphenyl increases.

Given the issues highlighted above with respect to higher temperature processing, subsequent testing was limited to 50 °C since >99.9% TPB destruction could still be achieved at this temperature in a reasonable batch cycle time (370 hours).

ii. *pH* – lowering the reaction pH below 11 (at 50 °C) was found to play a significant role with respect to CCPO destruction efficiencies and kinetics. The aforementioned reaction time of 370 hours at 50 °C was decreased to approximately 120 hours and <24 hours by lowering the pH from 11 to 9 and 7, respectively. Once again the <24 hour processing time at pH 7 implies that the acid hydrolysis mechanism (and subsequent benzene formation) predominates. As such subsequent tests were limited to pH 9 (and 50 °C). In addition, processing at pH 9 resulted in the lowest proportion of residual organics, such as benzene and biphenyl (see Appendix A).

iii. *Copper Catalyst Loading* – tests referred to in (i) and (ii) utilized 500 mg/L copper catalyst (added as a hydrated copper nitrate). One aim of the process optimization studies was to reduce the proportion of additive chemicals to minimize adverse impacts to downstream processing facilities. As such tests were conducted with 0, 100, and 500 mg/L of copper at 50 °C and pH 9. With zero copper added approximately 81% TPB degradation was achieved in approximately 480 hours; this is in comparison to 98.5% (in approximately 400 hours) and >99.9% (in approximately 120 hours) for 100 and 500 mg/L of copper, respectively. Clearly 100 mg/L is insufficient to produce the same level of TPB destruction in the same time-frame as the 500 mg/L loading. At the time of writing additional experiments were being conducted with intermediate copper loadings between 100 and 500 mg/L.

iv. *Hydrogen Peroxide Addition Rate* – tests were conducted to establish if adding hydrogen peroxide at faster rates enhanced reaction kinetics. 0.2, 0.4, and 1.0 mL/h addition rates (at 50 °C, pH 9, 500 mg/L copper) were considered. These rates are equivalent to 1, 2, and 5 gpm, respectively, for the full-scale process. Increasing the peroxide addition rate provided only marginal enhancement of reaction rate. However, two noticeable effects associated with increased peroxide addition rate were observed. Firstly, the proportion of residual organic compounds was reduced by at least an order of magnitude for the 1.0 mL/h addition rate in comparison to the slower addition rates. At the highest peroxide addition rate the concentration of semi-volatile organic compounds was measured at 8 mg/L compared to 192 mg/L for the slowest addition rate. While low proportions of residual organic compounds are desirable the higher peroxide addition results in increased waste volume without significantly enhanced reaction rate or TPB destruction. Secondly, the highest peroxide addition rate (1.0 mL/h) resulted in higher concentrations of soluble titanium (60 mg/L is equivalent to approximately 10% of the available titanium as MST) which implies degradation of the MST and potential desorption of the fissile actinides. In contrast the concentration of soluble titanium at 0.2 and 0.4 mL/h peroxide addition rates were 10 and 20 mg/L, respectively.

Based on initial tests, the following parameters were considered to provide optimum processing with respect to TPB destruction, residual organic content, processing time, waste volume increase, and MST degradation:

- Temperature: 50 °C
- pH: 9
- Copper catalyst loading: 500 mg/L
- Hydrogen peroxide addition rate: 0.4 mL/h (for 500 mL simulant).

Another important aspect of the laboratory-scale tests was to establish process consistency. At the time of writing, a number of duplicate tests were being performed utilizing the parameter set indicated above. Preliminary indications are that the process is capable of consistently attaining >99.9% TPB destruction though the reaction time may vary marginally.

The off-gas was also analyzed for selected experiments. Figure 2 (including inset figure of the initial 30 hours of processing) illustrates off-gas data for an experiment (DEMO 2 in Appendix A) utilizing the optimized set of parameters indicated previously. The data has been adjusted for a waste batch of 3100 gallons (from the 500 mL laboratory-scale waste volume) [43]. Pertinent details of the data include the following:

a. During acid addition (at room temperature) carbon dioxide is released. The initial formation of carbon dioxide spikes in the first 10 hours and its presence is assumed to be due to the reaction of the nitric acid with carbonate anions contained in the Tank 48 waste.

b. After heating to the reaction temperature of 50 °C, with almost concurrent initiation of the hydrogen peroxide/catalyst addition, significant benzene release occurs for approximately 24 hours. The current assumption is that the benzene is formed during acidification (as anticipated via an acid hydrolysis reaction), but remains in the waste slurry solution either as a liquid or entrapped gas. Upon heating to 50 °C the benzene liquid volatilizes and the entrapped benzene gas is released. The relevance of benzene in the off-gas with respect to vapor space flammability was previously discussed in Section 5.4.

c. The concentration of benzene in the off-gas essentially falls to zero after 30 hours of processing.

d. Following the initial carbon dioxide spike, the rate of evolution of carbon dioxide gradually increases up to approximately 100 hours of processing after which a slow decline in generation rate is apparent. Carbon dioxide formed after the initial spike (associated with acidification) is assumed to be the result of gradual destruction of TPB and its decomposition products.

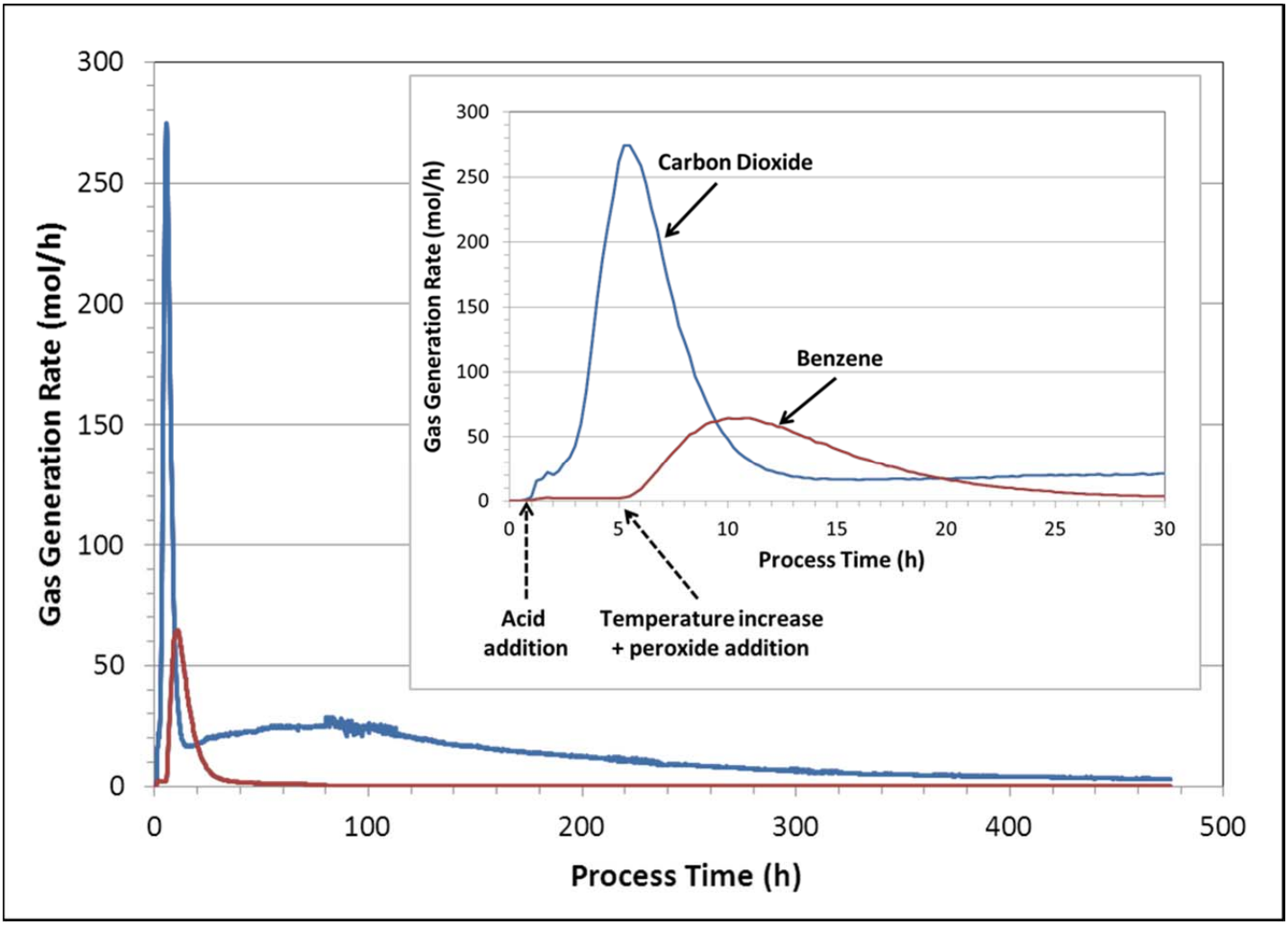

Figure 2: Off-gas data for CCPO process (SRNL data adjusted to 3100 gallon waste batch)

6.1.3 Proposed Near-Term Experimentation

Whilst the CCPO tests utilizing simulated Tank 48H waste have indicated excellent TPB destruction efficiencies and low levels of residual organics, such as biphenyl and terphenyl, a near-term requirement is validation of the process with real waste. In addition, the simulant tests have indicated significant generation of benzene due to the acid hydrolysis reaction that occurs during pH adjustment. It is not known if the indicated level of benzene formation will also occur with real waste since the dispersion of the TPB compounds is significantly different between the real and simulated wastes. In the simulant, the slurry maintains a mat of floating material which is subject to immediate contact with the nitric acid as it drops into the reaction vessel; in contrast the TPB solids are submerged in the real waste [33]. In the event that real waste testing confirms the formation of benzene, alternative processing methods would be explored to prevent or minimize benzene formation. For example, performing an intermediate acidification step whereby the system is held at a higher pH for a specified time prior to lowering to the final

pH has been shown to decrease the generation of benzene [23]. Other potential process modifications include the addition of the nitric acid over a longer time period to ensure the benzene generation rate remains below a specified level that is determined to be safe, or adjusting the pH with weaker acids. Acids, such as formic and phosphoric, are weaker than nitric acid, and while their addition will provide the necessary pH adjustment they do not readily promote acid hydrolysis.

6.2 Flow-Sheet Options for CCPO-Processed Waste

The primary intent of the flow-sheet options assessment [54] was to identify available flow-sheets 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. It should be noted, however, that opportunities to blend the CCPO-processed waste prior to processing in a downstream facility will potentially reduce the required level of organic destruction. The flow-sheet options considered were:

Option 1 – transfer to a TF tank and blend with tank contents for future disposition at SPF or DWPF

Option 2 – transfer (via Tank 50) for processing at SPF

Option 3 – filter in the 512-S cross-flow filter and subsequent transfer of filtrate for processing at DWPF, and insoluble solids (via Tank 50) for processing at SPF

Option 4 – transfer for processing in the SWPF (via Tanks 21/24 or 49), and subsequent transfer of insoluble solids and cesium strip effluent for processing at DWPF, and decontaminated salt solution (DSS) (via Tank 50) for processing at SPF

Option 5 – recycle to Tank 48 with periodic decants to Tank 50

Option 6 – transfer (via Tanks 42/51 or 40) for processing at DWPF.

The flow-sheet options assessment considered those requirements related to the physical, chemical, and radiological limits that must be met in order to transfer the CCPO-processed waste via a particular flow-sheet. A comparative assessment was made between the predicted composition of the CCPO-processed waste, and regulating documents, such as the Documented Safety Analysis (DSA), Technical Safety Requirements (TSR), and WAC, to determine if any specified limits were either exceeded or challenged for each of the proposed flow-sheets.

The residual organics in the CCPO-processed waste was a primary content assessed for each of the options. The allowable organic level is designated (in the regulating document) as a

contribution to the hydrogen LFL in a receipt or blending tank for each of the options. Some organic-related concentration limits are also specified as allowable proportions of TPB and other organic components. Table 5 provides the specified organic limits for transfer to the TF, to DWPF, to SPF, and via SWPF and reference to the relevant regulating documents.

Table 5: Organic limits applicable to flow-sheet options for CCPO waste

Requirement	TF [Ref. 58]	SPF [Ref. 57]	DWPF [Ref. 59]	SWPF [Ref. 60]
Contribution to Flammability	Flammability contribution of organics is bounded by 5% H_2 LFL without reliance on temperature controls	Volatiles other than Isopar L, benzene (from TPB), NH_3, and H_2 < 10% to the CLFL	Organic material in the sludge feed transferred to DWPF shall contribute < 0.1% H_2 LFL	Organic material present in the feed shall contribute < 0.1% H_2 LFL in the DWPF Sludge Receipt and Adjustment Tank (SRAT)
Specific Organic Compound Concentration Limits (mg/L)	Not defined	TPB < 5.00E+00 Phenol < 7.50E+02	Not defined	TPB < 1.00E+01 Benzene < 4.50E+02 Phenol < 7.50E+02

All of the flow-sheet options considered restrict either the contribution of organics in the CCPO-processed waste to downstream flammability, or to TPB concentration limits. With respect to the former the intention is to conduct flammability contribution calculations based on the FY2012 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. Regarding the latter criteria, the following indicates the TPB destruction levels that would be required to transfer the CCPO-processed waste to SPF or SWPF (taking no account of blending in receipt tanks).

Pre-process TPB mass concentration = 12,240 mg/L [54]. Therefore, to achieve a CCPO-processed TPB content of:

5 mg/L (SPF WAC [57]) requires 99.96% TPB destruction

10 mg/L (SWPF WAC [60]) requires 99.92% TPB destruction

Per the data from FY2012 laboratory-scale experiments the final TPB concentration was <4 mg/L [33]. As such this result satisfies TPB acceptance criteria specified in both the SPF and SWPF WACs though equivalent levels of TPB destruction must be verified with real-waste and in larger scale systems.

It is apparent that all of the flow-sheets considered require high organic destruction efficiencies for the CCPO-processed waste. These requirements are designated by the various regulating

documents and typically based on concerns of flammability in downstream tanks or facilities. These limits will need to be reassessed unless testing can demonstrate that the CCPO process can consistently achieve organic destruction levels that do not exceed the designated limits.

Other specified limits that are either exceeded or challenged by the currently envisaged composition of the CCPO-processed waste are related to the proportions of radionuclides, in particular Cs-137, Pu-238, and U-235 (for DWPF) [54]. Where they exceed a specified limit for a tank or facility, the Cs-137 and Pu-238 concentrations are less than an order of magnitude greater than the designated limit. It is thus conceivable that the CCPO-processed waste could be blended in receipt and preparation tanks to reduce the radionuclide concentrations below the specified limits. With respect to criticality for processing in DWPF, the U-235 fissile loading of the CCPO-processed waste (12.3 wt%) is over an order of magnitude greater than the DWPF WAC requirement (0.93 wt%) [59]. As such the CCPO-processed waste would require blending in the sludge preparation tanks to meet criticality prevention requirements, and may also require the addition of neutron poisons.

6.3 Flow-Sheet Options Alternative Evaluation

An alternative analysis [61] of the flow-sheet options (detailed in Section 6.2) was performed by an independent team consisting of relevant subject matter experts (SMEs) utilizing an Analytical Hierarchy Process (AHP). The evaluation included a pair-wise comparison of the six flow-sheet options with respect to the following criteria:

Table 6: Scoring criteria for flow-sheet options alternatives analysis

Primary Criteria	Sub-Criteria
System Plan Risk	Downstream Impacts
	Interference
	Life-Cycle Duration
Complexity	Process Safety Controls
	Operations/Maintenance/Sampling
	Design
	Installation
	Environmental
Radionuclide Fate	N/A

System Plan Risk

System plan risk relates to the potential of each flow-sheet option to cause delay/interruption to other Liquid Waste (LW) System Plan objectives. A concept that has no identifiable risk for interrupting other LW processes would be rated higher than a concept that would inherently require interruption to or is shown to have potential for delay to other processes.

Complexity

Simple solutions are typically easier to design, install and operate and therefore more desirable. The sub-criteria indicated in Table 6 were judged to provide a good measure of a concepts complexity.

Radionuclide Fate

It is preferential to SRS stakeholders to send radionuclides (curies) to DWPF rather than SPF. A concept that sends more radionuclides to DWPF would be rated higher than one that sends more radionuclides to SPF.

The evaluation has shown that Options 1, 4, and 6 obtained similar scores based on the AHP evaluation results, a sensitivity analysis, and a cost/benefit review; Option 4 (feed to SWPF) possessed the best overall score.

> Option 1 – transfer to a TF tank and blend with tank contents for future disposition at SPF or DWPF
>
> Option 4 – transfer for processing in the SWPF (via Tanks 21/24 or 49), and subsequent transfer of insoluble solids and cesium strip effluent for processing at DWPF, and DSS (via Tank 50) for processing at SPF
>
> Option 6 – transfer (via Tanks 42/51 or 40) for processing at DWPF.

The evaluation concluded that any of the top three options could be utilized to successfully disposition the CCPO effluent stream based on the information available at the time of the evaluation. In addition, the following recommendations were made:

- Continued development of the top three scoring options after the effluent composition from the CCPO process is more clearly defined.
- Application of newly derived process information to the alternatives evaluation to determine if one of the three options presents a greater advantage over the other two.

6.4 Preliminary Consolidated Hazards Analysis

The Preliminary Consolidated Hazards Analysis (PCHA) [62] identifies and evaluates accident conditions and events that have the potential to cause or contribute to the uncontrolled release of hazardous material from operation of the CCPO process that might affect the safety of the off-site public and on-site workers. In addition, it identifies those events that have the potential to cause a loss of production or damage to a facility. Table 7 provides descriptions of the accident event scenarios that were postulated as part of the PCHA, and Table 8 summarizes the safety controls and their safety function and designation, Safety Class (SC), Safety Significant (SS), and Facility Control (FC), with respect to consequence prevention/mitigation. At this point, however, it is understood that the CCPO process has not been sufficiently matured and additional accident conditions and events may be determined applicable as development of the technology progresses.

In Table 7 the following nomenclature is sometimes used to additionally define a functional classification.

Performance Categorization (PC) – a category defined in DOE-STD-1021-93 [63], assigned through the safety analysis process, which determines the level of Natural Phenomena Hazards (NPH) input. Consult the indicated DOE standard for details regarding the specific PCs indicated in Table 8.

Seismic Design Category (SDC) – a classification based on a graded approach used to establish the seismic NPH design and evaluation requirements for structures, systems, and components (SSCs) in accordance with ANSI/ANS 2.26 [64]. Consult the indicated ANSI/ANS standard for details regarding the specific SDCs indicated in Table 8.

Table 7: CCPO accident event descriptions

Event No.	Event Description
TK48ALT-1-001	Decomposition of hydrogen peroxide in storage tank results in over-pressurizing the storage tank releasing oxygen which results in a fire.
TK48ALT-1-002	Fire in the 241-96H process cell causes tank failure which results in spill to the process cell
TK48ALT-2-001	Explosion in the 241-96H reaction vessel due to ignition of flammable vapors
TK48ALT-2-002	Explosion in the 241-96H process cell due to ignition of flammable vapors
TK48ALT-2-003	Transfer of material from the 241-96H reaction vessel back to Tank 48 which leads to a benzene release and subsequently resulting in an explosion
TK48ALT-3-001	Transfer of material from Tank 48 to the 241-96H reaction vessel results in a spill inside the process cell in Building 241-96H
TK48ALT-3-002	Component failure results in a spill from reaction vessel
TK48ALT-3-003	Overheating of material in reaction vessel results in boiling of the material which results in a release
TK48ALT-3-004	Spill of cold chemicals in chemical storage area
TK48ALT-4-001	Shielding is removed (e.g., during maintenance activities) resulting in increased exposure to direct radiation
TK48ALT-7-001	Fire in the 241-96H process cell causes tank failure which results in spill to the process cell
TK48ALT-7-002	Seismic event causes failure of reaction vessel with loss of cell ventilation resulting in a cell explosion which ruptures transfer line and subsequent spill of contents of second reaction vessel
TK48ALT-7-003	Explosion in the 241-96H reaction vessel due to ignition of flammable vapors
TK48ALT-7-004	Tornado causes loss of PVV, which leads to reaction vessel explosion resulting in subsequent spill into process cell and process cell explosion
TK48ALT-8-001	Transfer of out of spec. material in the 241-96H reaction vessel (i.e., organics not fully destructed, process chemicals not neutralized) results in unacceptable downstream consequences
TK48ALT-8-002	Addition/mixing of incompatible chemicals within storage tanks results in an energetic reaction
TK48ALT-8-003	Reaction vessel product out of spec.

Table 8: Summary of CCPO safety/facility controls

Safety Designation	Safety Control	Safety Function	Event No.
IC/SC	Product Validation Program	Protect the CSTF DSA assumption regarding organic concentration in a waste tank	TK48ALT-8-001
SS	Severe Weather Response Program	Stop transfer	TK48ALT-7-003
SS	Chemical Control Program	Prevent the production of a flammable vapor space in reaction tank/process cell (from benzene)	TK48ALT-2-001
SS	Transfer Control Program	Prevent inadvertent transfer	TK48ALT-2-003
SS	CLFL Monitoring	Monitor flammable limit	TK48ALT-2-003
SS/SDC=3	Diesel Generator	Provide back-up power	TK48ALT-2-001
SS	Process Vessel Ventilation (PVV)	Maintain flow to prevent flammable vapor space	TK48ALT-2-001
SS/SDC-3	PVV	Maintain flow to prevent flammable vapor space	TK48ALT-7-002
SS/PC-2	PVV	Maintain flow to prevent flammable vapor space	TK48ALT-7-003
SS/PC-3	PVV	Maintain flow to prevent flammable vapor space	TK48ALT-7-004
SS/SDC-3	Process Cell Ventilation	Maintain flow to prevent flammable vapor space	TK48ALT-2-002 TK48ALT-7-002
SS	Process Cell	Maintain integrity to mitigate consequences / Support cell ventilation	TK48ALT-2-001 TK48ALT-2-002
SS/SDC-3	Process Cell	Maintain integrity to mitigate consequences / Support cell ventilation	TK48ALT-7-002
SS/PC-2	Process Cell	Maintain integrity to mitigate consequences	TK48ALT-7-003
SS/PC-3	Process Cell	Maintain integrity to mitigate consequences	TK48ALT-7-004
SS	Process Vessel	Maintain integrity to prevent release	TK48ALT-2-002
SS/SDC-3	Process Vessel	Maintain integrity to prevent release	TK48ALT-7-002
SS	Temperature Monitoring with Alarm and interlock	Maintain temperature below analyzed limits	TK48ALT-2-001
SS	Cell Conductivity Probes	Detect leak into process cell	TK48ALT-2-002
SS	Tank 48 Ventilation	Maintain flow to prevent flammable vapor space	TK48ALT-2-003
FC	Process Vessel	Maintain integrity to prevent release	TK48ALT-1-002 TK48ALT-3-002
FC	Process Cell Leak Detection	Notify personnel of material in sump of process cell	TK48ALT-1-002
FC	Combustible Loading Program	Limit combustible material inside process cell to prevent release	TK48ALT-1-002
FC	Process Cell Sump with Conductivity Probe	Contain release of material in the process cell to mitigate consequences	TK48ALT-3-001 TK48ALT-3-002
FC	Tank Level Indication with Interlock	Stop addition of material into reaction vessel	TK48ALT-2-002 TK48ALT-3-001
FC	Temperature Monitoring	Maintain temperature below analyzed limits to prevent overheating	TK48ALT-3-003
FC	Chilled Water System	Control temperature to prevent overheating	TK48ALT-3-003
FC	Radiological Protection Program	Protect the worker during maintenance while shielding is removed	TK48ALT-4-001

IC = Initial Condition

6.5 Task Requirements and Criteria

The Task Requirements and Criteria (TR&C) document [65] relates to the design, construction and operation of the CCPO process (to be located in Building 241-96H), and the necessary modifications to the utilities, infrastructure, and Waste Transfer Systems to support installation, operation, and feed transfer from Tank 48 to the CCPO reaction vessels. At this point the CCPO process has not been sufficiently matured, and the information contained in the TR&C document is considered preliminary and thus on HOLD.

6.6 Risk and Opportunity Analysis Report

The Risk and Opportunity Analysis Report (ROAR) [66] identifies risks, opportunities and handling strategies that will be used to tailor an integrated risk management strategy for the Tank 48 CCPO Project. A total of 59 risks were validated. These 59 risks were comprised of 12 high risks, 22 moderate risks, 3 low risks, 5 risks which, if realized would require the project to be rebaselined through an appropriate change control process, and 17 operational vulnerabilities. High risks were related to qualification of existing SSCs for use in CCPO processing, redesign of current systems such as the PVV (dependent on assessment of vapor flammability), the need for incorporation of additional systems, such as vessel heating and vessel inerting, and potential scale-up issues from the laboratory-scale process. As process maturation continues new risks may be identified which will be assessed, and risk handling strategies developed and implemented.

7 TRL DETERMINATION

Figure 3 and Table 9 provide the progression of technology maturation stages as defined by the DOE TRA Guide [1]. The TRL scale adopted by DOE is used for conducting TRAs. A TRL indicates the maturity level of a given technology. The TRL scale ranges from 1 (basic principle observed) through 9 (total system used successfully in operations).

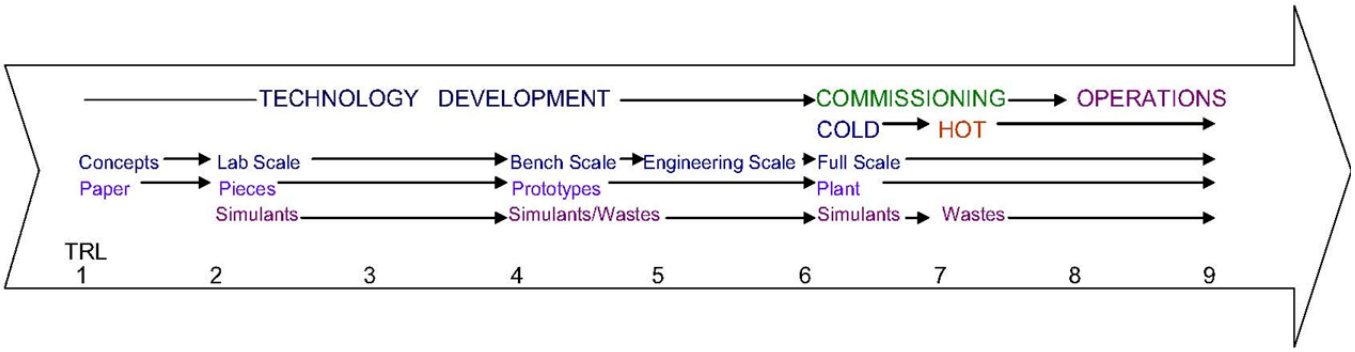

Figure 3: Schematic of DOE technology readiness levels

Table 9: DOE technology readiness level scale

Relative Level of Technology Development	Technology Readiness Level	TRL Definition	Description
System Operations	TRL 9	Actual system operated over the full range of expected conditions	Actual operation of the technology in its final form, under the full range of operating conditions. Examples include using the actual system with the full range of wastes.
System Commissioning	TRL 8	Actual system completed and qualified through test and demonstration	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental testing and evaluation of the system with real waste in hot commissioning.
	TRL 7	Full-scale, similar (prototypical) system demonstrated in a relevant environment	Prototype full scale system. Represents a major step up from TRL 6, requiring demonstration of an actual system prototype in a relevant environment. Examples include testing the prototype in the field with a range of simulants and / or real waste and cold commissioning.
Technology Demonstration	TRL 6	Engineering / pilot scale, similar (prototypical) system validation in a relevant environment	Representative engineering scale model or prototype system, which is well beyond the lab scale tested in TRL 5, is tested in a relevant environment. Represents a major step up in a technology's demonstrated readiness. Examples include testing a prototype with real waste and a range of simulants.
Technology Development	TRL 5	Laboratory scale, similar system validation in relevant environment	The basic technological components are integrated so that the system configuration is similar to (matches) the final application in almost all respects. Examples include testing a high-fidelity system in a simulated environment and / or with a range of real waste and simulants.
	TRL 4	Component and / or system validation in laboratory environment	Basic technological components are integrated to establish that the pieces will work together. This is relatively "low fidelity" compared with the eventual system. Examples include integration of "ad hoc" hardware in a laboratory and testing with a range of simulants.
Research to Prove Feasibility	TRL 3	Analytical and experimental critical function and / or characteristic proof of concept	Active research and development is initiated. This includes analytical studies and laboratory scale studies to physically validate the analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative. Components may be tested with simulants.
	TRL 2	Technology concept and / or application formulated	Invention begins. Once basic principles are observed, practical applications can be invented. Applications are speculative, and there may be no proof or detailed analysis to support the assumptions. Examples are still limited to analytical studies.
Basic Technology Research	TRL 1	Basic principles observed and reported	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development (R&D). Examples might include paper studies of a technology's basic properties.

Table 10 provides the TRL requirements and definitions regarding testing scale, system fidelity, and environment. Testing should be performed in the proper environment and the technology tested should be of an appropriate scale and fidelity.

Table 10: DOE relationship of testing recommendations to the TRL

TRL	Scale of Testing[1]	Fidelity[2]	Environment[3]
9	Full	Identical	Operational (Full Range)
8	Full	Identical	Operational (Limited Range)
7	Full	Similar	Relevant
6	Engineering / Pilot	Similar	Relevant
5	Lab / Bench	Similar	Relevant
4	Lab	Pieces	Simulated
3	Lab	Pieces	Simulated
2		Paper	
1		Paper	

1. Full Scale = Full plant scale that matches final application
1/10 Full Scale < Engineering / Pilot Scale < Full Scale (Typical)
Lab Scale < 1/10 Full Scale (Typical)

2. Identical System – configuration matches the final application in all respects
Similar System – configuration matches the final application in almost all respects
Pieces System – matches a piece or pieces of the final application
Paper System – exists on paper (no hardware)

3 Operational (Full Range) – full range of actual waste
Operational (Limited Range) – limited range of actual waste
Relevant – range of simulants + limited range of actual waste
Simulated – range of simulants

7.1 TRL Determination for Each CTE

The TRL calculator is a tool provided in the DOE TRA Guide [1] for applying TRLs for technology development programs. First, a set of top-level questions is used to determine the anticipated TRL (see Appendix B, Table B1). The anticipated TRL is determined from the question with the first "yes" answer. Second, evaluation of the detailed questions is started one level below the anticipated TRL. To attain a specific TRL, the CTE should receive a "yes" response to all questions at the TRL level from which the questions are found. If it is determined from the detailed questions that the technology has not attained the maturity of the starting level, then the next levels down are evaluated in turn until all of the questions for a specific TRL are answered "yes". The TRL is defined by the level from which all questions are answered affirmatively. The TRL tables contain questions associated with Technology/Technical (T), Manufacturing/Quality (M), and Programmatic/Customer Focus/Documentation (P) aspects.

Each of these areas (i.e., T, M, and P) was assessed separately and assigned a TRL for the sole reaction process CTE. Per this assessment Technology aspects have been determined to be at a TRL of three (3), Programmatic aspects at a TRL of two (2), and Manufacturing/Quality aspects at a TRL of three (3). As such the chemical destruction process has been assessed at an overall TRL 2. Detailed technology development requirements are detailed in Section 8. Complete TRL assessment tables can be found in Appendix B.

Gaps to achieve a higher TRL were determined from "no" answers in the TRL tables. Actions to close the gaps were documented in the tables. This process allowed the program to assess which activities need to be completed in order to bring each aspect of the CTE to a TRL of six (6). These actions are shown in red in Tables B2 to B17 in Appendix B, and also summarized in Section 8.

8 TECHNOLOGY DEVELOPMENT REQUIREMENTS

The schematic in Figure 4 provides a general depiction of the TRL development process as it applies to maturing the peroxide oxidation reaction process from a TRL 2 to TRL 6 (and thereafter to hot operations TRL 9), and the subsequent text documents the specific developmental requirements associated with the maturation of the CCPO process.

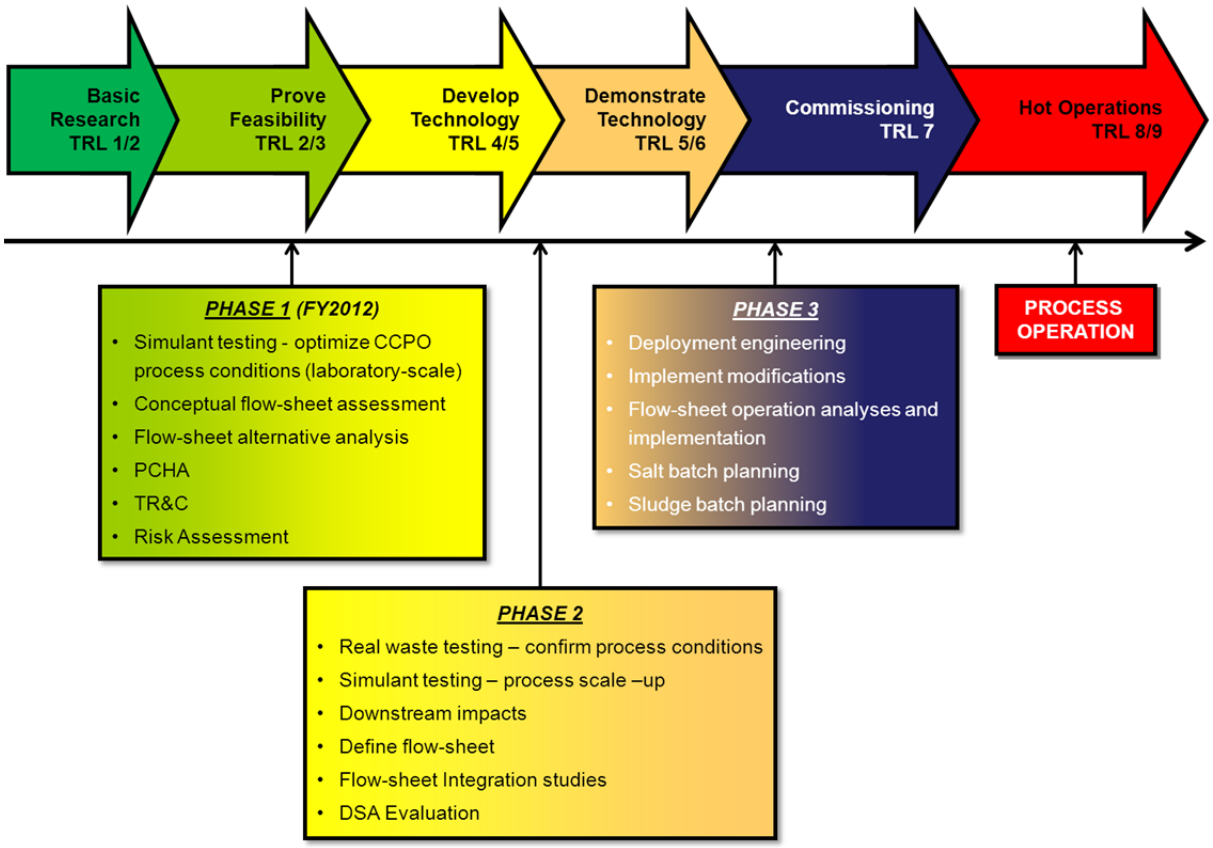

Figure 4: Schematic depicting general TRL development for CCPO process

The following text provides comprehensive detail regarding the work required to be completed in order to bring the CCPO process to a TRL 6. For each requirement the TRL type (T, M, P) and level (3-6) to be satisfied are identified.

- Laboratory-scale real waste testing to verify simulant test data and determine the extent of benzene formation due to acid hydrolysis. **(4T, 5T)**
- Laboratory-scale simulant testing to determine process changes that would prevent or minimize the formation of benzene. **(4T, 5T)**
- Laboratory-scale testing utilizing a range of simulants. **(4T, 5T)**
- Detailed design and testing of an engineering-scale system will be performed. The engineering-scale tests are intended to determine:
    i. Scalability and feasibility of the CCPO process with respect to TPB conversion efficiencies for the range of simulant Tank 48H wastes. **(3P, 4M, 4P, 5M, 5P, 5T, 6T)**
    ii. Scalability, testing, and validation of the process safety functions. **(4M, 5M, 5T, 6M, 6T)**
    iii. Integration of the engineering-scale TEs identified in Section 5. **(4M, 4T, 5M, 5T, 6M, 6T)**
    iv. Operating limits for key system components and safety controls. **(5P, 6T)**
    v. Technical issues related to full-scale up. **(6T)**
    vi. Off-normal operating responses. **(6P)**
- Reliability, availability, maintainability, inspectability (RAMI) levels to be determined. **(5M, 6M)**
- A science and technology exit criteria to be developed. **(4P)**
- A conceptual design including system description, process flow diagrams, general arrangement diagrams, three-dimensional drawings, process and instrumentation diagrams, material balance and functional process description to be developed. **(4P)**
- Interface control document to be developed. **(6P)**
- Additional development activities will include:
    — Downstream impacts and materials compatibility testing to determine if the physical, chemical, and radiological characteristics of the CCPO product (per simulant testing) adversely affect downstream processes or facilities.
    — Continued TR&C and PCHA development as the maturity of the CCPO technology progresses.
    — Continued development of process risks and handling strategies.
    — Reaction vessel heating calculation to determine if currently installed cooling coils can also be utilized for heating the vessel contents.

- Reaction vessel mixing calculation to ensure that a batch from Tank 48 can be adequately mixed in the reaction vessel to facilitate efficient and complete TPB destruction and suspend solids.
- Environmental compliance assessment to determine if off-gas release from CCPO is compliant with regulatory requirements.
- Assessment of potential changes that might be required to current DSA/WACs in order to implement the CCPO process.
- Consideration of Waste Processing System (WPS) requirements with respect to processing, disposal, and pertinent interfaces. TRL tables related to the WPS requirements are provided for reference in Appendix C but will not be developed prior to review of the laboratory-scale validation and optimization data discussed in Section 6.

9 DEVELOPMENTAL COST ESTIMATES

For some of the development activities listed in Section 8 a rough order of magnitude (ROM) cost estimate has been developed (see Table 11). It is anticipated that these activities could be initiated and completed in FY2013. These estimates are based on the cost of similar scope of previous projects.

Table 11: ROM cost estimates for CCPO maturation activities

Development Scope	Cost ($)
SRNL Real Waste Hydrolysis Demonstrations	600,000
SRNL ARP/MCU Impact Analysis	350,000
SRNL SCIX Impact Analysis	250,000
SRNL DWPF CPC Impact Analysis	400,000
ARP Materials Compatibility	100,000
Hydraulically-Scaled Demonstration of Process (> 1/10 Scale)	1,200,000
DSA Development	370,000
Design Services (Limited to Conceptual Design)	1,750,000
Total	**5,020,000**

MCU = Modular Caustic Side Solvent Extraction Unit
SCIX = Small Column Ion Exchange

10 CONCLUSION

This TMP has determined the CCPO reaction process (and the associated reaction vessel) to currently be the sole CTE, and documents the current TRL and the path to maturation. It is acknowledged, however, that as the proposed maturation activities progress developmental issues may be revealed that warrant CTE designations for other TEs. Technology aspects of the CCPO process have been determined to be at a TRL of three (3), Programmatic aspects at a TRL of two (2), and Manufacturing/Quality aspects at a TRL of three (3). The overall TRL is subsequently two (2).

11 REFERENCES

1. United States Department of Energy, *"Technology Readiness Assessment Guide,"* DOE G 413.3-4A (2011).
2. S.C. Shah, *Estimated Radiological and Chemical Characterization of Tank 48,* X-ESR-H-00239, Rev. 1 (2010).
3. B. Dean, *CBU, LWDP, Salt Processing Projects, Tank 48 Disposition Project, WSRC In-House Treatment Option Evaluation*, G-ADS-H-00007, Rev. 0 (2004).
4. D. Maxwell, *Re-Evaluation of Tank 48H Disposition Alternatives*, CBU-PIT-2005-00147, Rev. 0 (2005).
5. G.C. Winship, *Liquid Waste Disposition Projects: Tank 48H Return to Service Systems Engineering Evaluation (SEE) Results Report,* G-ADS-H-00011, Rev. 0 (2006).
6. 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).
7. C. Walling, *Fenton's Reagent Revisited*, Accounts of Chemical Research, **8** (1975) 125.
8. E.E. Seufert, 241-96H Actinide Removal Process – Capacity Enhancement, P-CLC-H-00011, Rev. 2 (2008).
9. J. E. Occhipinti, *Direct Vitrification Option in DWPF for Tank 48 – Tank 48 Alternative Technology Table Top Engineering Evaluation*, SRR-STI-2011-00317, (2011).
10. W.B. Van-Pelt, and S.D. Fink, *Tank 48 Tetraphenylborate Chemical Destruction*, SRR-STI-2011-00318 (2011).
11. L.D. Olson, and K.H. Subramanian, *SRS Tank 48 Waste Treatment EM-1 Briefing* SRR-CES-2011-00083 (2011).
12. E. Neyens, and J. Baeyens, *A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique*, Journal of Hazardous Materials, **B98** (2003) 33.
13. H.J.H. Fenton, *Oxidation of Tartaric Acid in Presence of Iron*, Journal of the Chemical Society, **65** (1894) 899.
14. 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.
15. M. Pérez, F. Torrades, X. Doménech, and J. Peral, *Fenton and Photo-Fenton Oxidation of Textile Effluents*, Water Res., **36** (2002) 2703.
16. F.J. Beltrán, M. González, F.J. Rivas, and P. Alvarez, *Fenton Reagent Advanced Oxidation of Polynuclear Aromatic Hydrocarbons in Water*, Water Air Soil Pollut. **105** (1998) 685.
17. M.C. Lu, C.J. Lin, C.H. Liao, W.P. Ting, and R.Y. Huang, *Influence of pH on the*

Dewatering of Activated Sludge by Fenton's Reagent, Water Sci. Technol. **44** (2001) 327.

18. C. Hölf, S. Sigl, O. Specht, I. Wurdack, and D. Wabner, *Oxidative degradation of AOX and COD by Different Advanced Oxidation Processes: A Comparative Study with Two Samples of a Pharmaceutical Wastewater*, Water Sci. Technol. **35** (1997) 257.
19. F.J. Rivas, F.J. Beltrán, O. Gimeno, and P. Alvarez, *Treatment of Brines by Combined Fenton's Reagent-Aerobic Biodegradation. II. Process Modelling*, J. Hazard. Mater. **96** (2003) 259.
20. M. Pérez, F. Torrades, J.A. Garc´ıa-Hortal, X. Doménech, J. Peral, *Removal of Organic Contaminants in Paper Pulp Treatment Effluents Under Fenton and Photo-Fenton Conditions*, Appl. Catal. B: Environ. **36** (2002) 63.
21. United States Environmental Protection Agency (EPA), *In Situ Treatment Technologies for Contaminated Soil*, EPA 542/F-06/13 (2006).
22. S.P. Simner, *The Role of Copper in the Hydrogen Peroxide Oxidation of Organic Compounds*, SRR-CES-2012-00002, Rev. 0 (2012).
23. J. Wilks, and C. Mitchell, *Chemical Oxidation of Tank 48 Simulant*, WSRC-RP-2004-00240 (2004).
24. T.B. Peters, *Phenylborate Decomposition Using 3.2 mg/L Copper in Tank 49H Solution*, WSRC-TR-2001-00060 (2001).
25. 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.
26. R.E. Eibling, *Processing of Tetraphenylborate Precipitates in the Savannah River Site Defense Waste Processing Facility,* WSRC-MS-90-162 (1990).
27. 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).
28. US Peroxide, LLC, *Fenton's Reagent General Chemistry*," http://h2o2.com/pages.aspx?pid=143&name=General-Chemistry-of-Fenton-s-Reagent.
29. Solvay Chemicals Publication HH-2323, *Hydrogen Peroxide: Safety and Handling Technical Data Sheet*, Solvay Chemicals, Inc. (2005).
30. 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).
31. P.A. Taylor, *Treatment of SRS Tank 48H Simulants Using Fenton's Reagent*, ORNL/TM-2003/262 (2003).
32. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, *Process Development for*

Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365, Rev. 0 (2003).

33. T.B. Peters, J.M. Pareizs, J.D. Newell, F.F. Fondeur, C.A. Nash, T.L. White, and S.D. Fink, *Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants,* SRNL-STI-2012-00342, Rev. 0 (2012).
34. *Tank 48 Treatment Process Project Restart Report*, SRR-SPT-2011-00091, Rev. 0 (2011).
35. 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*.
36. G. Taylor, *ARP Mixing Tank*, SRNL-ITB-2004-00026 (2004).
37. M.A. Baich, D.P. Lambert, and P.R. Monson, *Laboratory Scale Antifoam Studies for the STTPB Process*, WSRC-TR-2000-00261, Rev. 0 (2000).
38. T.B. Calloway, M.A. Baich, and D.P. Lambert, *Fate of IIT B52 Antifoam Agent Across the Small Tank Tetraphenylborate Process*, WSRC-TR-2001-00102, Rev. 0 (2001).
39. C.I. Aponte, *Tank 48 Catalytic Peroxide Oxidation Process Assessment of Potential Copper and Sulfate Downstream Processing Impacts*, SRR-CES-2012-00015, Rev. 0 (2012).
40. Copper Nitrate Material Safety Data Sheet (CAS Number: 3251-23-8).
41. C.I. Aponte, *Inputs for the Development of the Tank 48 Chemical Destruction Sim Suite™ Plant Model Input*, X-ESR-H-00372, Rev. 1 (2012).
42. W.A. Condon, *Interoffice Memorandum: Initial Safety Screen of Treatment of Tank 48 Bulk Waste in 241-96H Strike Tanks with Copper Catalyzed Peroxide Destruction*, SRR-LWP-2011-00044, Rev. 0 (2011).
43. T.E. Britt, *Impact of CCPO Operation on the Flammability of the 241-96H Strike Tanks*, X-CLC-H-00933, Rev. 0 (2012) **(In Draft)**.
44. NFPA® 69 (2008 Edition), *Standard on Explosion Prevention Systems* (2008).
45. R. Stone, *241-96H MST Strike Tanks PVV System Equipment Sizing*, M-CLC-H-02601, Rev. 2 (2006).
46. N. Rao Pasala, *Tank Farm Transfer Control Program & Pump Tank Transfer Jet Control Program*, WSRC-TR-2002-00403, Rev. 17 (2002).
47. S.C. Shah, *Tank 48 Feed Chemical and Radionuclide Compositions*, X-CLC-H-00046, Rev. 4 (2010).
48. S.Y. Li, and S. Hyun, *Tank 48 CFD Modeling Analysis*, SRNL-STI-2011-00244 (2011).
49. R.A. Leishear, M.R. Poirier, and M.D. Fowley, *SDI Blend and Feed Blending Study Tank 50H Scale Modeling for Blending Pump Design Phase 1*, SRNL-STI-2010-00054,

Rev. 0 (2010).

50. G.L. Cauthen, *Path Forward: Use of Existing Transfer Lines from Tank 48 to Building 241-96H in support of the Tank 48 Treatment (T48TP) Project*, LWO-SPT-2009-00098 (2009).

51. E. Hansen, and G. Daniel, *Summary of SRNL Tank Farm Data*, SRNL-PSE-2008-00341, Rev. 0 (2008).

52. S.Y. Lee, and S. Hyun, *Jet Mixing Analysis for SRS High-Level Waste Recovery*, SRNL-STI-2011-00397 (2011).

53. J. Urbanik Coughlin, *Tank 48H Benzene Concentration During Slurry Pump Operations*, X-CLC-H-00781 (2009).

54. S.P. Simner, *Tank 48 Chemical Destruction – Flow-Sheet Options Report*, SRR-CES-2012-00018, Rev. 0 (2012).

55. K.H. Subramanian, *Tank 48 Alternative Studies Technology Maturation Strategy and Near Term Plan*, SRR-CES-2011-00085 (2011).

56. D.P. Chew, and B.A. Hamm, *Liquid Waste System Plan Revision 17*, SRR-LWP-2009-00001, Rev. 17 (2012).

57. C.K. Chiu, *Waste Acceptance Criteria for Aqueous Waste Sent to Z-Area Saltstone Production Facility*, X-SD-Z-00001, Rev. 10 (2011).

58. *Concentration, Storage, and Transfer Facilities Documented Safety Analysis*, WSRC-SA-2002-00007, Rev. 12 (2002).

59. 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).

60. M. Norton, *Recommended SWPF Feed Waste Acceptance Criteria*, X-ESR-J-00001, Rev. 1 (2009).

61. M. Augeri, *Copper-Catalyzed Peroxide Oxidation (CCPO) – Alternative Evaluation*, G-ADS-H-00019, Rev. 0 (2012).

62. S.P. Graham, *Tank 48 CCPO Preliminary Consolidated Hazard Analysis,* S-CHA-H-00018, Rev. A (2012).

63. DOE Standard, *Natural Phenomena Hazards Performance Categorization Guidelines for Structures, Systems, and Components*, DOE-STD-1021-93 (Reaffirmed with Errata April 2002).

64. ANSI/ANS Standard, *Categorization of Nuclear Facility Structures, Systems, and Components for Seismic Design*, ANSI/ANS-2.26-2004 (Reaffirmed 2010).

65. C.I. Aponte, *Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate*, G-TC-H-00051, Rev. 1 (2012).

66. G. Winship, Tank 48 Copper-Catalyzed Peroxide Oxidation (CCPO): Risk and Opportunity Analysis Report, G-RAR-H-00015, Rev. 0 (2012).

67. M.J. Barnes, *Decomposition of Tetraphenylborate in Tank 48H*, WSRC-TR-96-0113, Rev. 0 (1996).

68. Letter: L. David Olson to Dr. David C. Moody, Subject: *Contract DE-AC09-09SR2205-Tank 48H Treatment Execution Strategy Recommendation*, May 17, 2011 (Document No. SRR-2011-00012).

69. Letter: Angela S. Morton to Kathryn Burnau, *Subject: Tank 48H Treatment Analysis Alternative*, August 29, 2011 (Contract No. DE-AC09-09SR22505).

70. SLA-SRNL-00061, *T48 Chemical Destruction R&D Planning* (2011).

71. Letter: Kathryn B. Burnau to Angela S. Morton, *Subject: Contract DE-AC09-09SR22505 – Request for Authorized Unpriced Work – Tank 48H Treatment Alternate Technology*, June 17, 2011 (Document No. SRR-CAA-2011-00288).

72. SRNL 2009 Strategic Plan (http://shrine.srs.gov/html/srnl/srnl_resources/srnlstratplan09.pdf).

APPENDIX A: FY2012 SRNL Experimental Data

	TEST PARAMETERS							TEST DATA					
									Residual Organics (mg/L)				
Test Designation	Simulant Vol. (mL)	pH	Temp. (°C)	Cu (mg/L)	H_2O_2 Add. Rate (mL/h)	Test Time (h)	Total H_2O_2 (mL)	% TPB Decomp.	HPLC	VOA (Benzene)	SVOA	Time for 100% B in Soln. (h)	Max. Ti Conc. (% of Total Ti as MST)
Thermal 35 °C	500	11	35	500	0.2	372	74.4	50.8	TPB: 7460 3PB: <100 2PB: <100 1PB: <100 Phenol: <100	0.77	Total: 1957 (Biphenyl: 1650)	N/A	3.9
Thermal 50 °C	500	11	50	500	0.2	372	74.4	99.9	TPB: 16 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	0.12	Total: 991 (Biphenyl: 940)	370	6.2
Thermal 65°C	500	11	65	500	0.2	372	74.4	>99.9	TPB: <10 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	<0.05	Total: 344 (Biphenyl: 92)	<24	3.9
DEMO 1	500	11	35-75	500	0.2	497	99.4	84.2	TPB: 2420 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	0.2	Total: 898 (Biphenyl: 760)	N/A	<1
Test 1a	500	9	50	500	0.2	404	80.8	>99.9	TPB: <10 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	<0.05	Total: 192 (Biphenyl: 29)	120	1.5
Test 1b	500	7	50	500	0.2	404	80.8	>99.9	TPB: <10 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	<0.05	Total: 511 (Biphenyl: 195)	<24	3.1
DEMO 2	500	9	50	500	0.4	480	192	>99.9	TPB: <4 3PB: <4 2PB: <4 1PB: <4 Phenol: <4	<0.05	Total: 82 (Biphenyl: 16)	160	3.1
Test 2a	500	9	50	500	1	480	480	>99.9	TPB: <4 3PB: <4 2PB: <4 1PB: <10 Phenol: <4	<0.05	Total: 8 (Biphenyl: 2)	100	9.3
Test 2b	500	9	50	100	0.2	480	96	98.5	TPB: 245 3PB: <10 2PB: <10 1PB: <10 Phenol: <10	0.1	Total: 81 (Biphenyl: 51)	400	2.3
Test 2c	500	9	50	0	0.2	480	96	80.7	TPB: 2585 3PB: 12 2PB: <10 1PB: <10 Phenol: 33	0.2	Total: 380 (Biphenyl: 301)	NA	4.6

	Effect of Temperature (pH 11; 500mg/L Cu; 1xH_2O_2)
	Effect of pH (50 °C; 500mg/L Cu; 1xH_2O_2)
	Effect of Cu Catalyst Addition (pH 9; 50 °C; 1xH_2O_2)
	Effect of H_2O_2 Addition Rate (pH 9; 50 °C; 500 mg/L Cu)

NOTES:

1. Tests are identified by the same name designation as the SRNL simulant report [33].

2. The colors in the above legend indicate those tests that can be compared to establish the effects of changes in a single process variable. For example, red cells indicate tests conducted at varied process temperatures but with constant pH, Cu concentration, and hydrogen peroxide addition rate.

APPENDIX B: TRL Tables for CCPO Process CTE

Table B1: Top level questions for determining anticipated TRL for the CCPO Process CTE 1

Top-Level Questions		Yes / No	If Yes, then Basis and Supporting Documentation
TRL 9	Has the actual equipment / process successfully operated in the full operational environment (hot operations)?	N	N/A
TRL 8	Has the actual equipment / process successfully operated in a limited operational environment (hot commissioning)?	N	N/A
TRL 7	Has the actual equipment / process successfully operated in the relevant operational environment (cold commissioning)?	N	N/A
TRL 6	Has prototypical engineering scale equipment / process testing been demonstrated in a relevant environment; to include testing of the safety function?	N	N/A
TRL 5	Has bench-scale equipment / process testing been demonstrated in a relevant environment?	N	N/A
TRL 4	Has laboratory-scale testing of similar equipment systems been completed in a simulated environment?	Y	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
TRL 3	Has equipment and process analysis and proof of concept been demonstrated in a simulated environment?	Y	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [6].
TRL 2	Has an equipment and process concept been formulated?	Y	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. D.P. Lambert, T.B. Peters, and S.D.

Top-Level Questions		Yes / No	If Yes, then Basis and Supporting Documentation
			Fink, In-Tank Peroxide Oxidation Process for the Decomposition of Tetraphenylborate in Tank 48H, WSRC-TR-2005-00114, Rev. 0 (2005) [6]. W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10]. L.D. Olson, and K.H. Subramanian, SRS Tank 48 Waste Treatment EM-1 Briefing, SRR-CES-2011-00083 (2011) [11].
TRL 1	Have the basic process technology process principles been observed and reported?	Y	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. H.J.H. Fenton, Oxidation of Tartaric Acid in the Presence of Iron, J. Chem. Soc., 65 (1894) 899 [13]. E. Neyens, and J. Baeyens, A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique, J. Hard. Mater., B98 (2003) 33 [12]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].

Technology/Technical Aspects TRL Determination

Table B2: TRL1 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. "Back of envelope" environment	H.J.H. Fenton, Oxidation of Tartaric Acid in the Presence of Iron, J. Chem. Soc., **65** (1894) 899 [13]. C. Walling, Fenton's Reagent Revisted, Accounts Chem. Res., **8** (1975) 125 [7].
Y	2. Physical laws and assumptions used in new technologies defined	E. Neyens, and J. Baeyens, A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique, J. Hard. Mater., **B98** (2003) 33 [12].
Y	3. Paper studies to confirm basic principles	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. C. Walling, Fenton's Reagent Revisted, Accounts Chem. Res., **8** (1975) 125 [7]. E. Neyens, and J. Baeyens, A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique, J. Hard. Mater., **B98** (2003) 33 [12]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	4. Basic scientific principles observed and understood	
Y	5. Research hypothesis formulated	
Y	6. Basic characterization data exists	

Table B3: TRL2 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Potential system or components have been identified	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. 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) [6]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31].
Y	2. Paper studies show that application is feasible; to include compliance with DOE STD 1189-2008, *Integration of Safety into the Design Process*	S.P. Graham, Tank 48 CCPO Preliminary Consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62]. W.A. Condon, Interoffice Memorandum: Initial Safety Screen of Treatment of Tank 48 Bulk Waste in 241-96H Strike Tanks with Copper Catalyzed Peroxide Destruction, SRR-LWP-2011-00044, Rev. 0 (2011) [42].
Y	3. An apparent theoretical or empirical design solution identified	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10].
Y	4. Basic elements of technology have been identified	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. 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) [6]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31].
Y	5. Desktop environment (paper studies)	

Y / N	Criteria	Basis and Supporting Documentation
Y	6. Components of technology have been partially characterized	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [6]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23].
Y	7. Performance predictions made for each element	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [6].
Y	8. Initial analysis shows what major functions need to be done	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10].
N/A	9. Modeling & Simulation only used to verify physical principles	Physical characteristics of the reaction process will be determined empirically.
Y	10. Rigorous analytical studies confirm basic principles	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	11. Individual parts of the technology work (No real attempt at integration)	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10].

Y / N	Criteria	Basis and Supporting Documentation
Y	12. Know what output devices are available	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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 (2005) [6].
Y	13. The scope and scale of the waste problem has been determined	S.C. Shah, Estimated Radiological and Chemical Characterization of Tank 48H, X-ESR-H-00239, Rev. 1 [2].
Y	14. Know what experiments are required (research approach)	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].

Table B4: TRL3 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Academic (basic science) environment	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	2. Predictions of elements of technology capability validated by analytical studies	
Y	3. Science known to extent that mathematical and / or computer models and simulations are possible	M.J. Barnes, Decomposition of Tetraphenylborate in Tank 48H, WSRC-TR-96-0113, Rev. 0 (1996) [67].
N/A	4. Predictions of elements of technology capability validated by Modeling and Simulation (M&S)	Physical characteristics of the reaction process will be determined empirically.
Y	5. Laboratory experiments verify feasibility of application	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32].
Y	6. Predictions of elements of technology capability validated by laboratory experiments	

Y / N	Criteria	Basis and Supporting Documentation
		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 (2005) [6].
Y	7. Key process parameters / variables and associated hazards have begun to be identified; to include compliance with DOE STD 1189-2008, *Integration of Safety into the Design Process*	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62]. W.A. Condon, Interoffice Memorandum: Initial Safety Screen of Treatment of Tank 48 Bulk Waste in 241-96H Strike Tanks with Copper Catalyzed Peroxide Destruction, SRR-LWP-2011-00044, Rev. 0 (2011) [42]. W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10].
Y	8. Paper studies indicate that system components ought to work together	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. 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 (2005) [6].
Y	9. Performance metrics for the system are established (what it must do)	S.P. Simner, Tank 48 Chemical Destruction – Flow-Sheet Options Report, SRR-CES-2012-00018, Rev. 0 (2012) [54].
Y	10. Scientific feasibility fully demonstrated	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of

Y / N	Criteria	Basis and Supporting Documentation
		Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	11. Analysis of present state of the art shows that technology fills a need	D.P. Chew, and B.A. Hamm, Liquid Waste System Plan Revision 17, SRR-LWP-2009-00001, Rev. 17 (2012) [56].
Y	12. Key physical and chemical properties have been characterized for a number of waste samples	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H, WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	13. A simulant has been developed that approximates key waste properties	
Y	14. Laboratory scale tests on a simulant have been completed	
Y	15. Specific waste(s) and waste site(s) has (have) been identified	Letter: L. David Olson to Dr. David C. Moody, Subject: Contract DE-AC09-09SR2205-Tank 48H Treatment Execution Strategy Recommendation, May 17, 2011 (Document No. SRR-2011-00012) [68].
Y	16. The individual system components have been tested at the laboratory scale	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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 (2005) [6]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23].

Table B5: TRL4 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Key process variables / parameters have been fully identified and preliminary hazard evaluations have been completed and documented; to include compliance with DOE-STD 1189-2008, *Integration of Safety into the Design Process*	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62].
Y	2. Individual components tested in laboratory or by supplier	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
Y	3. Subsystems composed of multiple components tested at lab scale using simulants	
Y	4. Modeling & Simulation used to simulate some components and interfaces between components	S.Y. Li, and S. Hyun, Tank 48 CFD Modeling Analysis, SRNL-STI-2011-00244 (2011) [48]. R.A. Leishear, M.R. Poirier, and M.D. Fowley, SDI Blend and Feed Blending Study Tank 50H Scale Modeling for Blending Pump Design Phase 1, SRNL-STI-2010-00054, Rev. 0 (2010) [49]. S.Y. Lee, and S. Hyun, Jet Mixing Analysis for SRS High-Level Waste Recovery, SRNL-STI-2011-00397 (2011) [52].
N	5. Overall system requirements for end user's application are documented	Preliminary technical requirements are documented in: C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
Y	6. Laboratory experiments with available components show that they work together	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
Y	7. Analysis completed to establish component compatibility (do components work together)	
Y	8. Technology demonstrates basic functionality in simulated environment; to include test and validation of safety functions	
Y	9. Controlled laboratory environment used in testing	
Y	10. Low fidelity technology "system" integration and engineering completed in a lab environment	

Y / N	Criteria	Basis and Supporting Documentation
Y	11. Key physical and chemical properties have been characterized for a range of wastes	S.C. Shah, Estimated Radiological and Chemical Characterization of Tank 48, X-ESR-H-00239, Rev. 1 (2010) [2].
N	12. A limited number of simulants have been developed that approximate the range of waste properties	To date testing has been conducted on a single simulant composition based on a well-mixed Tank 48 slurry (see reference below). Future laboratory-scale testing should consider higher and lower loadings of TPB. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	13. Laboratory-scale tests on a limited range of simulants and real waste have been completed	To date testing has been conducted on a single simulant composition based on a well-mixed Tank 48 slurry (see reference below). Future laboratory-scale testing should consider higher and lower loadings of TPB. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. Laboratory-scale real waste tests should be conducted to verify the data obtained with simulant.
Y	14. Process / parameter limits and safety control strategies are being explored	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62]. W.A. Condon, Interoffice Memorandum: Initial Safety Screen of Treatment of Tank 48 Bulk Waste in 241-96H Strike Tanks with Copper Catalyzed Peroxide Destruction, SRR-LWP-2011-00044, Rev. 0 (2011) [42].
Y	15. Test plan documents for prototypical lab-scale tests completed	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].

Table B6: TRL5 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. The relationships between major system and sub-system parameters are understood on a laboratory scale	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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 (2005) [6].
N	2. Plant size components available for testing	Reuse of currently installed tanks (and relevant sub-systems) and waste transfer systems between tanks. However, there is potentially a need for: 1. vent/purge system modifications 2. new off-gas monitoring equipment 3. new chemical storage and supply equipment 4. 241-96H strike tank mixing equipment demonstration and possible impeller redesign.
Y	3. System interface requirements known (How would system be integrated into the plant)	Reuse of currently installed tanks (and relevant sub-systems) and waste transfer systems between tanks.
N	4. Requirements for technology verification established; to include testing and validation of safety functions	Preliminary technical requirements are documented in: C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
N	5. Interfaces between components / subsystems in testing are realistic (bench top with realistic interfaces)	To date only laboratory-scale with <1 liter reactor volume have been conducted (see reference below): T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
Y	6. High fidelity lab integration of system completed, ready for test in relevant environments; to include testing and validation of safety functions	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	7. Lab-scale, similar system tested with range of simulants	To date testing has been conducted on a single simulant composition based on a well-mixed Tank 48 slurry (see reference below). Future laboratory-scale testing should consider higher and lower loadings of TPB. T.B. Peters et al., Results of Copper-Catalyzed

Y / N	Criteria	Basis and Supporting Documentation
		Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	8. Fidelity of system mock-up improves from laboratory to bench-top scale	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	9. Laboratory environment for testing modified to approximate operational environment; to include testing and validation of safety functions	
N	10. Component integration issues and requirements identified	Preliminary technical requirements are documented in: C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
N	11. Requirements definition with performance thresholds and objectives established for final plant design	
N	12. Integration of modules / functions demonstrated in a laboratory / bench-scale environment	To date only laboratory-scale with <1 liter reactor volume have been conducted (see reference below): T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	13. Formal control of all components to be used in final prototypical test system	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	14. The range of all relevant physical and chemical properties has been determined (to the extent possible)	To date testing has been conducted on a single simulant composition based on a well-mixed Tank 48 slurry (see reference below). Future laboratory-scale testing should consider higher and lower loadings of TPB. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	15. Simulants have been developed that cover the full range of waste properties	To date testing has been conducted on a single simulant composition based on a well-mixed Tank 48 slurry (see reference below). Future laboratory-scale testing should consider higher and lower loadings of TPB. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. Laboratory-scale real waste tests should be conducted to verify the data obtained processing simulant.
N	16. Testing has verified that the properties / performance of the simulants match the properties / performance of the actual wastes	
N	17. Laboratory-scale tests on the full range of simulants using a prototypical system have been completed	
N	18. Laboratory-scale tests on a limited range of real wastes using a prototypical system have	

Y / N	Criteria	Basis and Supporting Documentation
	been completed	
N	19. Test results for simulants and real waste are consistent	
N	20. Laboratory to engineering scale scale-up issues are understood and resolved; to include testing and validation of safety functions	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
Y	21. Limits for all process variables / parameters and safety controls are being refined	S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62]. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].

Table B7: TRL6 questions for CCPO process CTE: technology/technical aspects

Y / N	Criteria	Basis and Supporting Documentation
N	1. The relationships between system and sub-system parameters are understood at engineering scale allowing process / design variations and tradeoffs to be evaluated	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	2. Operating environment for final system known	
N	3. Operating limits for components determined (from design, safety and environmental compliance)	
N	4. System technical interfaces defined	Preliminary technical requirements are documented in: C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
N	5. Component integration demonstrated at an engineering scale	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	6. Engineering feasibility fully demonstrated (e.g. would it work)	
N	7. Engineering-scale system is high-fidelity functional prototype of operational system	
N	8. Engineering-scale tests on the full range of simulants have been completed	
N	9. Engineering to full-scale scale-up issues are understood and resolved	
N	10. Laboratory and engineering-scale experiments are consistent	
N	11. Limits for all process variables / parameters and safety controls are defined	
N	12. Plan for engineering-scale testing executed – results validate design	

Programmatic / Customer Focus / Documentation Aspects TRL Determination

Table B8: TRL1 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Initial scientific observations reported in journals / conference proceedings / technical reports	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H,WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	2. Know who cares about the technology, e.g., sponsor, funding source, safety and hazardous materials handling (DOE STD 1189-2008 compliance), etc.	Letter: Angela S. Morton to Kathryn Burnau, Subject: Tank 48H Treatment Analysis Alternative, August 29, 2011 (Contract No. DE-AC09-09SR22505) [69].
Y	3. Know who would perform research and where it would be done	SLA-SRNL-00061, T48 Chemical Destruction R&D Planning (2011) [70].

Table B9: TRL2 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Customer identified	Letter: Kathryn B. Burnau to Angela S. Morton, Subject: Contract DE-AC09-09SR22505 – Request for Authorized Unpriced Work – Tank 48H Treatment Alternate Technology, June 17, 2011 (Document No. SRR-CAA-2011-00288) [71].
Y	2. Know what program the technology would support	
Y	3. Customer expresses interest in the application	Letter: Angela S. Morton to Kathryn B. Burnau, Subject: Tank 48H Treatment Analysis Alternative, August 29, 2011 (Contract No. DE-AC09-09SR22505) [69].
Y	4. System architecture defined in terms of major functions to be performed	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10]. L.D. Olson, and K.H. Subramanian, SRS Tank 48 Waste Treatment EM-1 Briefing, SRR-CES-2011-00083 (2011) [11].
Y	5. Analytical studies reported in scientific journals / conference proceedings / technical reports	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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) [30]. J. Wilks, and C. Mitchell, Chemical Oxidation of Tank 48H Simulant, WSRC-RP-2004-00240 (2004) [23]. P.A. Taylor, Treatment of SRS Tank 48H Simulants Using Fenton's Reagent, ORNL/TM-2003/262 (2003) [31]. D.P. Lambert, T.B. Peters, M.E. Stallings, and S.D. Fink, Process Development for Destruction of Tetraphenylborate in SRS Tank 48H,WSRC-TR-2003-00365 (2003) [32]. 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 (2005) [6].
Y	6. Preliminary strategy to obtain TRL Level 6 developed (e.g. scope, schedule, costs); to include compliance with DOE STD 1189-2008, *Integration of Safety into the Design Process*	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10]. L.D. Olson, and K.H. Subramanian, SRS Tank 48 Waste Treatment EM-1 Briefing, SRR-CES-2011-

Y / N	Criteria	Basis and Supporting Documentation
		00083 (2011) [11].
Y	7. Know capabilities and limitations of researchers and research facilities	SRNL 2009 Strategic Plan (http://shrine.srs.gov/html/srnl/srnl_resources/srnlstratplan09.pdf) [72].
Y	8. Qualitative idea of risk areas (cost, schedule, performance)	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10]. L.D. Olson, and K.H. Subramanian, SRS Tank 48 Waste Treatment EM-1 Briefing, SRR-CES-2011-00083 (2011) [11].

Table B10: TRL3 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. Some key process and safety requirements are identified; to include compliance with DOE STD 1189-2008, *Integration of Safety into the Design Process*	S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62].
Y	2. The basic science has been validated at the laboratory scale	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. 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 (2005) [6].
Y	3. Preliminary system performance characteristics and measures have been identified and estimated	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
Y	4. Customer representative identified to work with development team	Customer representative will review TR&C document prior to issue (see reference below). C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
Y	5. Customer participates in requirements generation	
N/A	6. Requirements Tracking system defined to manage requirements creep	In-line with research and development requirements.
Y	7. Customer identifies technology need date	D.P. Chew, and B.A. Hamm, Liquid Waste System Plan Revision 17, SRR-LWP-2009-00001, Rev. 17 (2012) [56].
N	8. Scaling studies have been started	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
Y	9. Risk areas identified in general terms	W.B. Van-Pelt, and S.D. Fink, Tank 48 Tetraphenylborate Chemical Destruction, SRR-STI-2011-00318 (2011) [10]. L.D. Olson, and K.H. Subramanian, SRS Tank 48 Waste Treatment EM-1 Briefing, SRR-CES-2011-00083 (2011) [11]. M. Augeri, Copper-Catalyzed Peroxide Oxidation (CCPO) – Alternative Evaluation, G-ADS-H-00019, Rev. 0 (2012) [61]. G. Winship, Tank 48 Copper-Catalyzed Peroxide Oxidation (CCPO): Risk and Opportunity Analysis

Y / N	Criteria	Basis and Supporting Documentation
		Report, G-RAR-H-00015, Rev. 0 (2012) [66].
N	10. Risk mitigation strategies identified	Preliminary risks mitigation strategies have been identified in: G. Winship, Tank 48 Copper-Catalyzed Peroxide Oxidation (CCPO): Risk and Opportunity Analysis Report, G-RAR-H-00015, Rev. 0 (2012) [66].
N	11. Rudimentary best value analysis performed for operations	Rudimentary operations analysis to be developed.

Table B11: TRL4 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
N	1. Overall system requirements for end user's application are known	The following preliminary studies have assessed system requirements and performance metrics: S.P. Simner, Tank 48 Chemical Destruction – Flow-Sheet Options Report, SRR-CES-2012-00018, Rev. 0 (2012) [54]. C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
N	2. System performance metrics measuring requirements have been established	
Y	3. Laboratory testing requirements derived from system requirements are established	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N	4. Science and Technology Demonstration exit criteria established (S&T targets understood, documented, and agreed to by sponsor)	Exit criteria to be developed. Preliminary flow-sheet assessment studies have been completed (see references below): S.P. Simner, Tank 48 Chemical Destruction – Flow-Sheet Options Report, SRR-CES-2012-00018, Rev. 0 (2012) [54]. M. Augeri, Copper-Catalyzed Peroxide Oxidation (CCPO) – Alternative Evaluation, G-ADS-H-00019, Rev. 0 (2012) [61].
N	5. The conceptual design has been documented (system description, process flow diagrams, general arrangement drawings, and material balance)	Conceptual design package to be developed. Preliminary TR&C has been developed (see reference below): C.I. Aponte, Task Requirements and Criteria: Tank 48 Disposition by Small Tank Catalyzed Peroxide Oxidation of Tank 48 Tetraphenylborate, G-TC-H-00051, Rev. 1 (2012) [65].
Y	6. Initial cost drivers identified	D.P. Chew, and B.A. Hamm, Liquid Waste System Plan Revision 17, SRR-LWP-2009-00001, Rev. 17 (2012) [56].
Y	7. Formal risk management program initiated	G. Winship, Tank 48 Copper-Catalyzed Peroxide Oxidation (CCPO): Risk and Opportunity Analysis Report, G-RAR-H-00015, Rev. 0 (2012) [66].
N	8. Scaling documents and designs of technology have been completed	Scaling documents and designs to be developed.
N	9. Functional process description developed (systems / subsystems identified)	Functional process description to be developed.

Y / N	Criteria	Basis and Supporting Documentation
Y	10. Technology availability dates established	D.P. Chew, and B.A. Hamm, Liquid Waste System Plan Revision 17, SRR-LWP-2009-00001, Rev. 17 (2012) [56].

Table B12: TRL5 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
N	1. Preliminary design engineering begins	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	2. Three dimensional drawings and P&IDs for the prototypical engineering-scale test facility have been prepared	
N	3. Detailed design drawings have been completed to support specification of engineering-scale testing system	
N	4. Preliminary technology feasibility engineering report completed; to include compliance with DOE-STD 1189-2008, *Integration of Safety into the Design Process*	
N	5. Configuration management plan in place	Configuration management plan to be developed.
N	6. Test plan for prototypical lab-scale tests executed – results validate design; to include testing and validation of safety functions	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	7. Test plan documents for prototypical engineering-scale test completed	
N	8. Finalization of hazardous material forms and inventories, completion of process hazard analysis, and identification of system / components level safety controls at the appropriate preliminary design phase	Preliminary hazards analysis is complete (see reference below): S.P. Graham, Tank 48 CCPO Preliminary consolidated Hazard Analysis, S-CHA-H-00018, Rev. A (2012) [62].
N	9. Risk management plan documented; to include compliance with DOE-STD 1189-2008, *Integration of Safety into the Design Process*	Preliminary risks and management strategies have been identified in: G. Winship, Tank 48 Copper-Catalyzed Peroxide Oxidation (CCPO): Risk and Opportunity Analysis Report, G-RAR-H-00015, Rev. 0 (2012) [66].

Table B13: TRL6 questions for CCPO process CTE: programmatic/customer focus/documentation aspects

Y / N	Criteria	Basis and Supporting Documentation
N	1. Preliminary design drawings for final plant system are complete; to include compliance with DOE-STD 1189-2008, *Integration of Safety into the Design Process*	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	2. Collection of actual maintainability, reliability, and supportability data has been started.	
N	3. Performance Baseline (including total project cost, schedule, and scope) has been completed	
N	4. Operational requirements document available; to include compliance with DOE-STD 1189-2008, *Integration of Safety into the Design Process*	
N	5. Off-normal operating responses determined for engineering scale system	
N	6. Scaling issues that remain are identified and understood. Supporting analysis is complete.	
N	7. Analysis of project timing ensures technology will be available when required	
N	8. Have established an interface control process	Interface control process document to be developed.
N	9. Acquisition program milestones established for start of final design (CD-2)	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	10. Technology "system" design specification complete and ready for detailed design	
N	11. Formal configuration management program defined to control change process	
N	12. Final Technical Report on Technology completed; to include compliance with DOE-STD 1189-2008, *Integration of Safety into Design Process*	
N	13. Finalization of hazardous material forms and inventories; completion of process hazard analysis, identification of system / components level safety controls at the appropriate preliminary / final design phase	

Manufacturing / Quality Aspects TRL Determination

Table B14: TRL3 questions for CCPO process CTE: manufacturing/quality aspects

Y / N	Criteria	Basis and Supporting Documentation
Y	1. No system components, just basic laboratory research equipment to verify physical principles	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].
N/A	2. Design techniques have been identified / developed	Equipment reuse - there are no critical manufacturing processes. Currently installed tanks and transfer pipes to be utilized
N/A	3. Current manufacturability concepts assessed	
Y	4. Sources of key components for laboratory testing identified	T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33].

Table B15: TRL 4 questions for CCPO process CTE: manufacturing/quality aspects

Y / N	Criteria	Basis and Supporting Documentation
N/A	1. Laboratory components tested are surrogates for system components	Equipment reuse - there are no critical manufacturing processes. Currently installed tanks and transfer pipes to be utilized
Y	2. Available components assembled into laboratory scale system	Equipment to be used is already in place. T.B. Peters et al., Results of Copper-Catalyzed Peroxide Oxidation (CCPO) of Tank 48H Simulants, SRNL-STI-2012-00342, Rev. 0 (2012) [33]. Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
Y	3. Scalable technology prototypes have been produced (Can components be made bigger than lab scale)	
Y	4. Equipment scale-up relationships are understood / accounted for in technology development program	
N	5. Integration studies have been started	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	6. Key manufacturing processes for equipment systems identified	
N	7. Key manufacturing processes assessed in laboratory	
N/A	8. Mitigation strategies identified to address manufacturability / producibility shortfalls	Equipment to be used is already in place. Currently installed tanks and transfer pipes to be utilized.

Table B16: TRL 5 questions for CCPO process CTE: manufacturing/quality aspects

Y / N	Criteria	Basis and Supporting Documentation
N/A	1. Prototypes of equipment system components have been created (know how to make equipment)	Equipment to be used is already in place. Currently installed tanks and transfer pipes to be utilized.
N/A	2. Tooling and machines demonstrated in lab for new manufacturing processes to make component	
N/A	3. Manufacturing techniques have been defined to the point where largest problems defined	
N	4. Availability and reliability (RAMI) target levels identified	RAMI levels to be determined.
N	5. Some special purpose components combined with available laboratory components for testing	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.

Table B17: TRL 6 questions for CCPO process CTE: manufacturing/quality aspects

Y / N	Criteria	Basis and Supporting Documentation
N	1. Availability and reliability (RAMI) levels established	RAMI levels to be determined.
N/A	2. Critical manufacturing processes prototyped	Equipment reuse - there are no critical manufacturing processes. Currently installed tanks and transfer pipes to be utilized.
N/A	3. Most pre-production hardware is available to support fabrication of the system	
N	4. Materials, process, design, and integration methods have been employed (e.g. can design be produced)	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.
N	5. Components are functionally compatible with operational system	
N	6. Integration demonstrations have been completed (e.g. construction of testing system); to include testing and validation of safety functions	
N/A	7. Process and tooling are mature to support fabrication of components / system	Equipment reuse - there are no critical manufacturing processes. Currently installed tanks and transfer pipes to be utilized
N	8. Production demonstrations are complete (at least one time)	Engineering-scale tests to be conducted subsequent to laboratory-scale tests.

APPENDIX C: TRL Tables Related to Waste Processing Systems (WPS)

Table C1: TRL development questions related to WPS

TRL 4 Questions for the WPS			
WPS:			
	Y/N	**Questions**	**Basis & Supporting Documents**
Processing		1. Is the WPS, as it appears in the conceptual design, intended to accept the full range of wastes to be processed?	
		2. Is the WPS capable of meeting targets for startup and completion of waste processing?	
		3. Have the target operational and performance requirements for the WPS been determined?	
		4. Have all TEs that require an increase or change in capability been identified as CTEs?	
		5. Has WPS process flow been modeled?	
		6. Have WPS single point failures been identified?	
		7. Can TEs be sized to meet WPS throughput requirements?	
		8. Have all new or novel operating modes of the WPS been modeled and/or tested at lab scale?	
		9. Have all recycle streams been identified and included in the conceptual design process flow models?	
		10. Have the key safety aspects of the WPS related to processing been identified?	
		11. Are appropriate measures in place to ensure safe operation of the processing activities?	
Disposal		12. Will the WPS produce a product or products that can be dispositioned?	
		13. Are all WPS waste streams identified and characterized to the extent necessary for conceptual design?	
		14. Can all WPS waste streams, including, process liquids, off gases, and solids identified in the conceptual design be treated and disposed?	
		15. Will the waste streams meet the waste acceptance criteria of the proposed disposition facilities/sites?	
		16. Have the disposition facilities/site been contacted to ensure that the waste forms are compatible with facility/site operations, procedures, and regulations?	
		17. Have the key safety aspects of the WPS related to disposal been identified?	
		18. Are appropriate measures in place to ensure safe operation of the disposal activities?	
Interfaces		19. New or novel interfaces among WPS systems have been identified as CTEs?	
		20. Are all WPS technology interfaces and dependencies determined and understood at the conceptual level?	
		21. Can all WPS components be successfully mated?	
		22. Are the processing modes of the TEs (e.g., batch, continuous) compatible?	

TRL 6 Questions for the WPS			
WPS:			
	Y/N	**Questions**	**Basis & Supporting Documents**
Processing		1. Have all TEs that require an increase or change in capability been identified as CTEs?	
		2. Can the WPS accept the full range of wastes to be processed?	
		3. Is the WPS capable of meeting targets for startup and completion of waste processing?	
		4. Have the target operational and performance requirements for the WPS been determined?	
		5. Have major sections of the WPS and their interfaces been modeled and/or piloted?	
		6. Has WPS data collection and data flow been modeled/tested?	
		7. Has WPS process flow and process control been modeled/tested?	
		8. Have WPS single point failures been identified?	
		9. Can TEs be sized to meet WPS throughput requirements?	
		10. Have all new or novel operating modes of the WPS been modeled and/or piloted?	
		11. Are all recycle streams fully characterized?	
		12. Are all WPS recycle streams included in process models?	
		13. Have the key safety aspects of the WPS related to processing been identified?	
		14. Are appropriate measures in place to ensure safe operation of the processing activities?	
		15. Is the appropriate documentation in place that adequately describes the safety features related to processing, and their functions in the overall integrated WPS?	
Disposal		16. Will the WPS produce a product or products that can be dispositioned?	
		17. Are all WPS waste streams identified?	
		18. Have the waste streams produced by the WPS been fully characterized?	
		19. Has a disposition path been determined for each waste stream, including, process liquids, off gases, and solids?	
		20. Will the waste forms meet the waste acceptance criteria of the proposed disposition facilities?	
		21. Have the disposition facilities/sites been contacted to ensure that the waste streams are compatible with disposal facility/site operations, procedures, and regulations?	
		22. Have the key safety aspects of the WPS related to disposal been identified?	
		23. Are appropriate measures in place to ensure safe operation of the disposal activities?	
		24. Is the appropriate documentation in place that adequately describes the safety features related to disposal, and their functions in the overall integrated WPS?	
Interfaces		25. Are all WPS technology interfaces and dependencies determined and understood?	
		26. New or novel interfaces among WPS systems have been identified as CTEs?	
		27. Have all WPS TE interfaces been modeled or piloted?	
		28. Are the processing modes of the TEs (e.g., batch, continuous) compatible?	