# Tank 48 Chemical Destruction – 13237

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## ABSTRACT

Small tank copper-catalyzed peroxide oxidation (CCPO) is a potentially viable technology to facilitate the destruction of tetraphenylborate (TPB) organic solids contained within the Tank 48H waste at the Savannah River Site (SRS). A maturation strategy was created that identified a number of near-term development activities required to determine the viability of the CCPO process, and subsequent disposition of the CCPO effluent. Critical activities included laboratory-scale validation of the process and identification of forward transfer paths for the CCPO effluent. The technical documentation and the successful application of the CCPO process on simulated Tank 48 waste confirm that the CCPO process is a viable process for the disposition of the Tank 48 contents.

## INTRODUCTION

Tank 48 is a large 4.9 million liter (1.3 million gallon) Type IIIA liquid waste tank located at SRS, which currently holds approximately 910,000 liters (240,000 gallons) of radioactive legacy liquid waste material from the operation of the In-Tank Precipitation process. The tank contains approximately 26,000 kg of organic TPB compounds, predominantly insoluble potassium tetraphenylborate along with smaller quantities of cesium tetraphenylborate. The TPB poses a significant challenge (in particular with respect to the generation of flammable gas) to the salt processing and sludge processing facilities within the SRS Liquid Waste System. Therefore, destruction of the organic constituents prior to permanent disposition is a key element for the liquid waste life-cycle completion.

Fluidized bed steam reforming (FBSR) was designated as the baseline technology to treat the organic materials in Tank 48. However, recent advances to the liquid waste system have enabled the reconsideration of a cost-effective Fenton's-type chemical destruction process, which utilizes hydrogen peroxide and a copper catalyst to break-down the TPB and its organic decomposition products. In addition, the future availability of two 22,700 liter (6000 gallon) reaction vessels in Building 241-96H, currently utilized in the Actinide Removal Process as monosodium titanate strike tanks, will enable the Tank 48 waste to be treated via a small volume batch-type process as opposed to the previously envisioned large volume in-tank process. In addition to the use of existing infrastructure, the chemical destruction technology maturation process for CCPO in 241-96H will be able to leverage the significant development efforts associated with the FBSR project, which was also 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 also available for use with the chemical destruction option.

The viability of the CCPO process was assessed within the framework of a technology maturation plan. The program has completed a series of experiments on simulant waste, preliminary consolidated hazards analysis and risk analysis, and has also identified alternative disposition routes for the CCPO-treated effluent.

## BASIC CHEMISTRY

The chemical destruction process relies on the production of hydroxyl radicals ($^{\bullet}OH$) which are powerful oxidants with a high propensity to degrade organic materials [1]. Iron-catalyzed peroxide oxidation of organic compounds at low pH is generally referred to as a “Fenton’s process.” The CCPO process utilizing non-acidic environments with a non-iron transition metal catalyst is termed a “modified Fenton’s process”.

The basic chemistry for the formation of hydroxyl radicals and their destruction of organics is illustrated in the subsequent text with specific reference to the more ubiquitously studied Fenton’s reagent chemistry (and the use of a ferrous ion catalyst). The corresponding chemistry utilizing a copper catalyst is less well understood, particularly in terms of the initial mechanism for hydroxyl radical formation. The primary advantage of the copper catalyst in comparison to iron is its ability to promote the decomposition of TPB in alkaline environments.

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

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

The hydroxyl radicals subsequently oxidize organic compounds by hydrogen abstraction (Equation 2) or by oxygen addition (Equation 3) both of which form organic radicals which are highly reactive and can be further oxidized [2].

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

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

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 necessitates a greater than stoichiometric hydrogen peroxide/TPB ratio:

$$(C_6H_5)_4B^- + 60H_2O_2 \rightarrow 24CO_2 + 70H_2O + BO_2^- \qquad \text{(Eq. 4)}$$

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, 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.

An important distinction between copper- and iron-catalyzed reactions is that copper also promotes organic decomposition via hydrolysis. Copper-catalyzed hydrolysis has been considered for the destruction of sodium tetraphenylborate in Tank 49H (Equation 5) [3].

$$Na(C_6H_5)_4B + 2H_2O \rightarrow 4C_6H_6 + NaBO_2 \qquad \text{(Eq. 5)}$$

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. The copper-catalyzed decomposition of TPB is expected to occur by a combination of hydrolysis and hydroxyl radical oxidation reactions.

## TECHOLOGY MATURATION

Process maturation was performed utilizing the methodologies described in the United States Department of Energy (DOE) Technology Readiness Assessment (TRA) Guide [4], which outlines three primary steps:

i. 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).
ii. Determine the associated technology readiness levels (TRLs) for each CTE.
iii. Ascertain potential technology gaps that might hinder technology deployment and document strategies for closing the gaps, and maturing the technology.

## 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 in the 241-96H strike tanks has been divided into five TEs (or process sub-systems) which are depicted in Fig. 1. 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.

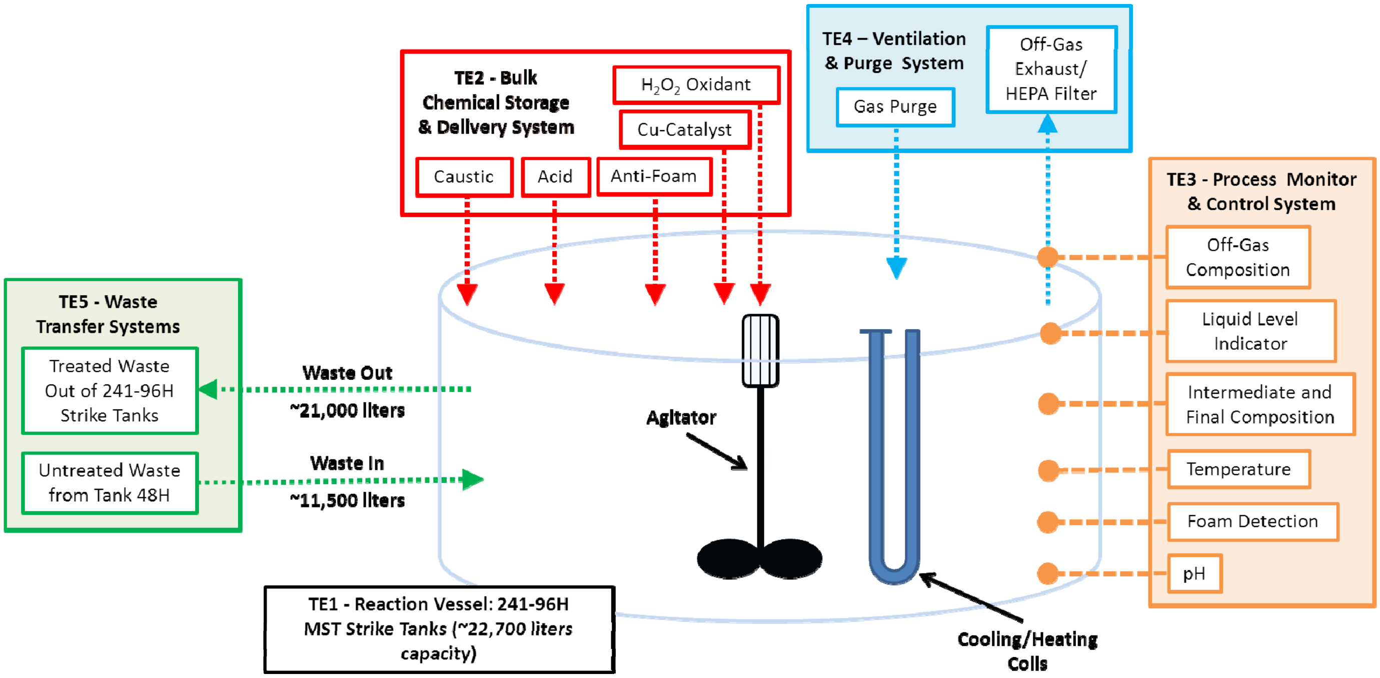

**Fig. 1.** CCPO technology elements

## TE1 – Reaction Process and Vessel

The reaction process comprises both the chemical reaction and the reaction containment vessel (including the currently available waste mixing capabilities for the vessel). The reaction must initially be assessed on a laboratory-scale with waste simulant, and the laboratory data then confirmed with real waste. Subsequent to the laboratory tests, the process must be demonstrated 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, and the fact that the copper-catalyzed reaction is a modification of the more ubiquitously studied (and commercially utilized) Fenton's process. In addition, data for copper-based catalysis in a neutral or alkali environment, even on a laboratory-scale, is limited to the few exploratory studies.

## 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. Anti-foaming agent (if necessary).

Bulk storage and handling/delivery of caustic and acidic components are routine operations at SRS. 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 for copper nitrate [5]. The safe storage and handling of hydrogen peroxide is standard practice, and subject to standard safety protocols and analyses within the chemical industry [6].

### 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 potential reaction anomalies.

### 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.

### TE5 – Waste Transfer Systems

Waste transfers in and out of the waste tanks are an integral part of SRS operations, 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. Consequently, the waste transfer systems are designated non-CTE.

## TRL DETERMINATION

Fig. 2 indicates the progression of technology maturation stages as defined by the DOE TRA Guide [4]. 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). A TRL calculator is a tool provided in the DOE TRA Guide [4] for applying TRLs for technology development programs. Via this process the CCPO process has been assessed at a TRL 2 predominantly because (1) the process has not been demonstrated with radioactive waste, and (2) process investigations have been restricted to the laboratory-scale.

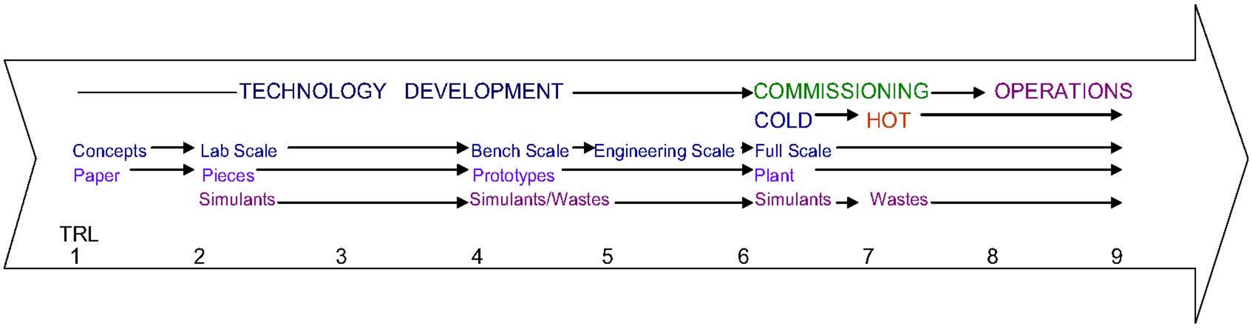

**Fig. 2**: Schematic depicting DOE TRLs

## TECHNOLOGY GAPS AND MATURATION ACTIVITIES

Having (currently) identified the reaction process/vessel as the sole CTE, and determined the CCPO process to be a TRL 2, the third step in the development process is to identify potential technology gaps that might hinder technology deployment and document strategies for closing the gaps. The schematic in Fig. 3 provides a general depiction of the TRL development process as it applies to maturing the CCPO process from a TRL 2 to TRL 6 (and thereafter to hot operations TRL 9).

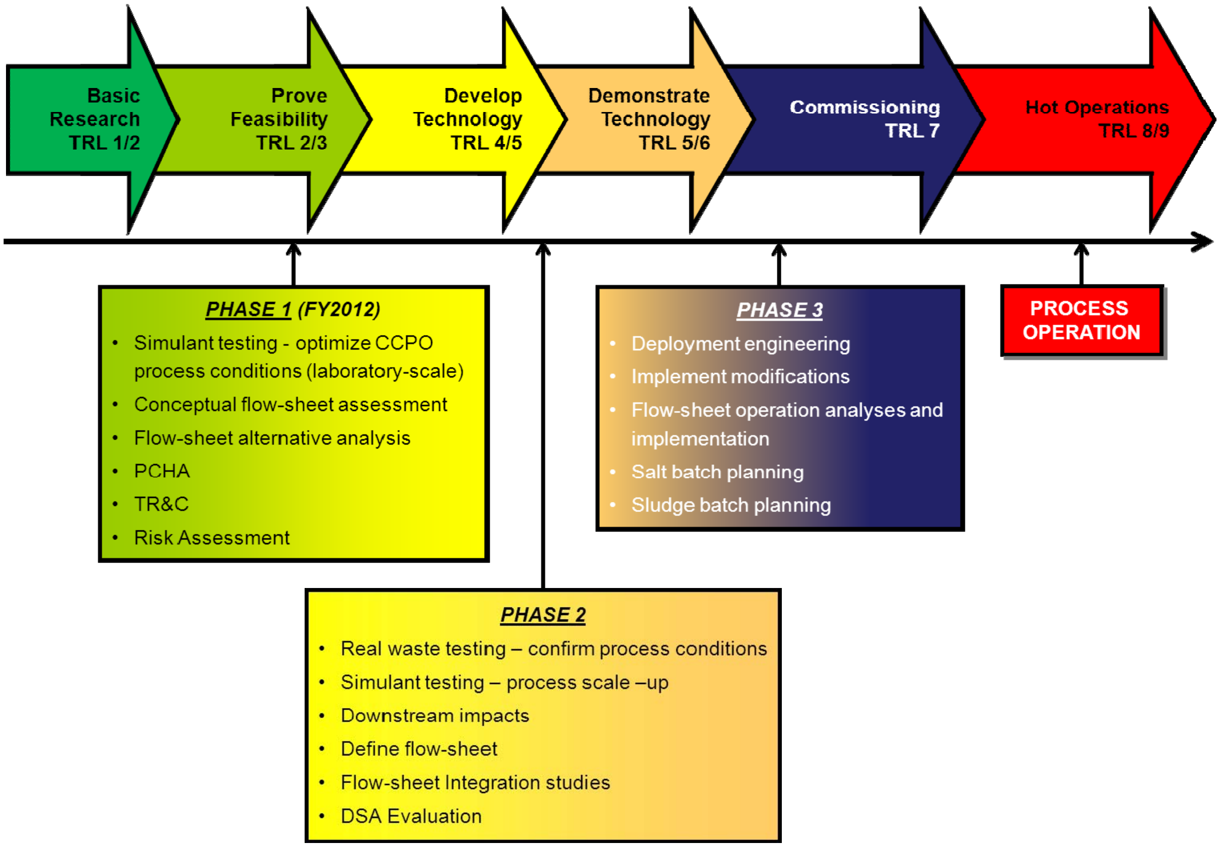

**Fig. 3**: Schematic depicting general TRL development for CCPO process

For Phase 1 (FY2012) development a number of activities were identified, though two in particular were considered critical to establish the viability of the CCPO process, and to subsequently determine if the technology warranted further development. These were:

(1) To assess the process further on a laboratory-scale since data for copper-based catalysis in a neutral or alkali environment, even on a laboratory-scale, is limited to a very few exploratory scoping studies.

(2) Determining if the CCPO-processed effluent could be transferred to other SRS tanks or facilities based on current waste acceptance criteria.

## Laboratory-Scale Simulant Testing

Preliminary laboratory-scale investigations (utilizing simulated Tank 48 waste) have been directed at optimizing the CCPO processing parameters, in particular pH and temperature, to achieve the following process attributes:

- Complete (and repeatable) organic destruction
- Enhanced reaction kinetics

- Minimized reaction temperature
- Processing in alkaline environments
- Minimized benzene gas generation
- Minimized formation of fouling by-products (such as biphenyl and terphenyl).

At 50 °C and pH 9 TPB destruction levels exceeding 99.9% (< 4 mg/L TPB) were consistently achieved in processing times of less than 150 hours [7]. In addition, increasing the rate of hydrogen peroxide addition was shown to decrease the proportions of residual biphenyl and terphenyl products.

Another important aspect of the laboratory-scale tests was to monitor the off-gas composition throughout the CCPO process. Fig. 4 (including inset figure of the initial 30 hours of processing) illustrates off-gas data for an experiment utilizing the optimized set of parameters indicated previously. The data has been adjusted for a waste batch of 11,700 liters (3100 gallons) (from the 500 mL laboratory-scale waste volume).

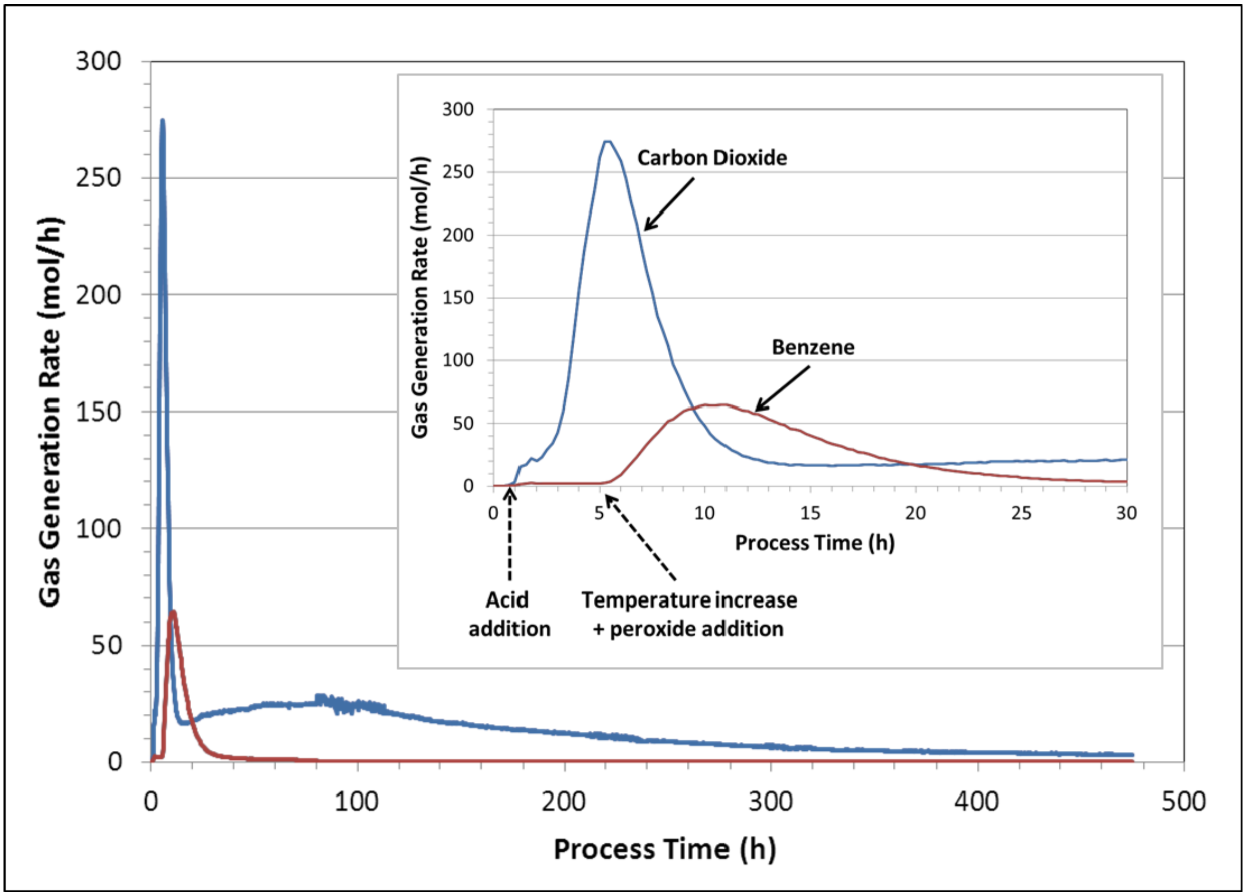

**Fig. 4**: Off-gas data for CCPO process; SRNL data adjusted to 11,700 liters (3100 gallons) waste batch

The preliminary off-gas data from the FY2012 laboratory-scale testing indicates significant benzene generation (in addition to carbon dioxide) associated with pH adjustment (and hydrolysis) which occurs in the first 24 hours of processing. It is acknowledged that the production of substantial amounts of benzene can adversely impact the safe operation of the CCPO process. Preliminary calculation indicates that the cumulative release of benzene during the first 24 hours of processing could potentially necessitate a flow rate of > 510 SCMH (300 SCFM) through the reaction vessel head space to ensure the benzene generated remains at < 25% lower flammability limit (LFL). This is the combustible concentration limit (not requiring automatic instrumentation with safety locks) specified by National Fire Protection Association (NFPA) 69 [8]. The currently installed process vessel ventilation system is controlled to provide a total flow rate of 170 SCMH (100 SCFM) per vessel. As such, fans with higher flow capacities would likely be required to provide the calculated flow rates. 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, minimum oxygen concentration control utilizing, for example, a nitrogen inerting gas may be employed to negate issues of flammability in the reaction vessel head space.

## Options for CCPO Effluent Transfer

The choice of a particular transfer option is primarily influenced by the level of organic destruction achieved by the CCPO process since both the tank farm (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. Table I provides the specified organic limits for transfer to the TF [9], to the Saltstone Production Facility (SPF) [10], to the Defense Waste Processing Facility (DWPF) [11], and via the Salt Waste Processing Facility (SWPF) [12]. 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 I**: Organic limits applicable to flow-sheet options for CCPO waste

| Requirement | TF [9] | SPF [10] | DWPF [11] | SWPF [12] |
|---|---|---|---|---|
| **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<br>< 5.00E+00<br>Phenol<br>< 7.50E+02 | Not defined | TPB<br>< 1.00E+01<br>Benzene<br>< 4.50E+02<br>Phenol<br>< 7.50E+02 |

All of the transfer 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.

Per the data from FY2012 laboratory-scale experiments the final TPB concentration was <4 mg/L [7]. As such this result satisfies TPB acceptance criteria specified for SPF [10] and SWPF [12] though equivalent levels of TPB destruction must be verified with real-waste and in larger scale systems.

## CONCLUSION

Initial maturation activities have demonstrated that CCPO is a viable process for removing the TPB from Tank 48H waste, and identified potential transfer paths for the CCPO effluent. 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. In the event that real waste testing confirms the formation of benzene, alternative processing methods would be explored to prevent or minimize benzene formation. A potential process modification includes 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.

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