The Effect of Tri-N-Butyl Phosphate on Tank 48 as a Result of Salt Solution Transfers within the In-Tank Precipitation Facility

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**THE EFFECT OF TRI-N-BUTYL PHOSPHATE ON TANK 48 AS A RESULT OF SALT
SOLUTION TRANSFERS WITHIN THE IN-TANK PRECIPITATION FACILITY (U)**

SUMMARY

The transfer of 12,000 gallons of In-Tank Precipitation (ITP) spent salt solution waste from the ITP Feed Tank to Tank 48H will not result in any flammability, compatibility, criticality, or combustibility problems. No impacts on downstream facilities or processes were identified. Addition of the solution to Tank 48H will not result in an increase in the rate of hydrogen production. Insoluble tri-n-butyl phosphate (TBP) will collect on the surface of the contents of Tank 48H. However, the quantity of TBP will be insufficient to form a layer thick enough to pose a credible combustibility hazard.

Flammability calculations were performed in regards to the transfer of the spent salt solution waste. Under the most conservative conditions, the composite Lower Flammable Limit (LFL) will not be reached in Tank 48H. These calculations were performed to support the Safety Evaluation (SE) addressing the transfer of the solution from the Feed Tank to Tank 48H. Flammability calculations and determinations conducted in this document address related vapor flammability concerns including those related to TBP.

INTRODUCTION

The transfer of 12,000 gallons of non-radioactive spent salt solution from the ITP Feed Tank to Tank 48H is being considered. The effect on flammability, compatibility, criticality, and combustibility in Tank 48H as a result of this transfer is the primary focus of this investigation. The 12,000 gallons of spent salt solution are from non-radioactive chemical testing of the ITP facility. One safety concern is that this transfer involves the potential formation of a combustible gas mixture in Tank 48H due to the presence of volatile organic compounds in the 12,000 gallons of spent salt solution. Four volatile organic compounds are contained in the waste from non-radioactive chemical testing of the ITP facility. These are benzene, methanol, isopropanol, and 1-butanol formed by the decomposition of TBP. A maximum TBP usage limit of 25 gallons was set by the Test Authorization document.¹ This volume is the equivalent of 2000 mg/L TBP in the 12,000 gallons of spent salt solution. The maximum concentrations of benzene, methanol, and isopropanol contained in the 12,000 gallons of waste salt solution transferred to Tank 48H are 20 mg/L, 400 mg/L, and 430 mg/L, respectively.^{1,2} The maximum benzene concentration is equivalent to 15 ppm assuming the salt solution density is 1.3 g/mL. This maximum concentration was determined previously for flammability controls for feed solution transfers to Tank 48H.² The 400 mg/L and 430 mg/L alcohol concentrations permit the addition of 230 gallons of sodium titanate cold feeds material (containing 3% alcohol by volume) into the 12,000 gallons of waste salt solution. For reference purposes, the LFLs,³ or vapor fractions, for the organic compounds, present in the waste solution, are listed in Table I along with their maximum concentration. No LFL data are available for TBP at 50°C due to its very low vapor pressure.⁴ However, the LFL for 1-butanol is listed since it is a volatile decomposition product of TBP. All flammability calculations assume TBP has instantly and completely decomposed to 1-butanol and phosphate, a grossly conservative assumption. Furthermore, TBP quantities (i.e., 25.8 L) previously added to Tank 48H^{5,6} were assumed to still be present, a grossly conservative assumption. This information is reflected as a separate TBP entry in Table I. Calculations documented herein were performed to evaluate the issue of flammability. Equations, data, and assumptions necessary to perform this investigation are listed in Appendix A - Flammability Equations, Calculations, and Assumptions.

Table I. A list of the organic compounds, their LFLs, and the maximum quantity of each that will be added to Tank 48H.

<u>Chemical</u>	<u>Maximum Quantity</u>	<u>LFL (vapor fraction)³</u>
Benzene	20 mg/L	0.012
Methanol	400 mg/L	0.060
Isopropanol	430 mg/L	0.020
TBP (from the proposed transfer)	25 gal	not available
1-Butanol	- -	0.014
TBP (from previous Tank 48H additions)	25.8 L	not available

DISCUSSION

The effect on flammability, compatibility, criticality, and combustibility in Tank 48H, as a result of the transfer of 12,000 gallons of ITP Feed Tank spent salt solution, was evaluated. To accomplish this task, several items were addressed. The flammability potential of waste salt solution in Tank 48H was determined under the most conservative assumptions. Impacts on downstream facilities or processes were investigated. The effect on the rate of hydrogen production in Tank 48H was calculated. The effect of TBP on fissile material behavior was examined. The accumulation and potential combustibility of insoluble TBP on the surface of the contents of Tank 48H was tested.

Flammability Potential In Tank 48H

The flammability potential in Tank 48H, of the volatile organic compounds transferred to Tank 48H, was calculated under the worst-case scenario. The worst-case scenario for Tank 48H would occur if the total amount of all TBP added to the Tank (both past and present) and the maximum concentrations of benzene, methanol, and isopropanol were added to Tank 50H in the absence of ventilation. Additionally, all TBP was assumed to instantly and completely decompose to phosphate and 1-butanol (3 times as many moles). The volume of the contents of Tank 48H was assumed to be same as the current volume (i.e., 282,000 gallons).⁷ Henry's Law data were available for benzene, methanol, isopropanol, and 1-butanol in salt solution^{8,9} and were used to determine the relative contribution of these four compounds to the vapor composition. The temperature of Tank 48H was assumed to be 50°C. This is well above the most recent tank temperature of 26°C¹⁰ and is grossly conservative.

The above scenario represents the most conservative case since the flammability calculations were conducted assuming that dilution of the vapor concentrations by ventilation was ignored. With this basis, the percentage of the LFL of each compound was calculated. From Le Chatelier's rule, the sum of the percentages of the LFLs for the individual compounds results in the percentage of composite LFL for the organic compounds. The individual percentage of the LFL for each compound under the worst-case scenario for Tank 48H is shown in Table II. In addition to the percentage of the LFL for each compound, data relevant to the calculations are also listed. For the ITP Feed Tank spent salt solution in Tank 48H, the data indicate that under the most conservative of assumptions, only 6.5% of the composite LFL could be obtained. The presence of these organics in Tank 48H, in the absence of ventilation, would shorten the current "Time to LFL" by 6 months (6.6 years to 6.1 years) if no material was lost. This value is based upon the

Table II. Tank 48H data for ITP decontaminated salt solution waste under the worst-case scenario.

<u>Chemical</u>	<u>Moles in Vapor</u>	<u>Gas Volume (L)</u>	<u>Vapor Fraction</u>	<u>% LFL</u>
Benzene	1.08 E+1	2.86 E+2	7.50 E-5	6.25 E-1
Methanol	2.90 E+0	7.67 E+1	2.02 E-5	3.36 E-2
Isopropanol	1.18 E+1	3.12 E+2	8.20 E-5	4.10 E-1
1-butanol	1.08 E+2	2.88 E+3	7.55 E-4	5.39 E+0
				$\Sigma = 6.46 \% \text{ of LFL}$

most recent benzene concentration and generation rates in Tank 48H.¹¹ Equations, data, and assumptions necessary to perform the "Time to LFL" calculations are contained in Appendix A - Flammability Equations, Calculations, and Assumptions.

Another flammability concern was the production of hydrogen gas from the radiolytic decomposition of TBP. The rate of hydrogen gas generated from the radiolysis of Tank 48H contents (in the absence of TBP) is expected to be 0.46 molecules of hydrogen gas per 100 eV.¹² This G-value is based upon radiolysis tests performed upon Tank 48H simulants (tetraphenylborate solutions) and is approximately the same as that for pure water.¹³ No data are available on the rate of hydrogen gas production from the radiolysis of TBP in caustic salt solutions and slurries (similar to those present in Tank 48). However, three different G-values (1.11, 1.59, and 1.73 molecules hydrogen gas per 100 eV) have been reported for the production of hydrogen gas from the radiolysis of pure TBP.^{14,15,16} Due to the relative expected concentrations of TBP and water in Tank 48H, radiolysis of the water in Tank 48H salt solutions will produce hydrogen at a substantially higher rate than will radiolysis of the TBP in the salt solutions (i.e., the rate of production of hydrogen will be comparable for Tank 48H salt solutions both with and without TBP).

The determination of the effect of concentration on hydrogen gas production was based upon the total number of electrons in the molecules interacting with the ionizing radiation within a given volume.¹⁷ Water has eight valence electrons. The concentration of water in salt solution is approximately 55 molar. Therefore, one liter of water would contain 2.6×10^{26} electrons. Tri-n-butyl phosphate has 104 valence electrons and, given the expected concentration in Tank 48H, will account for 2.5×10^{22} valence electrons in one liter of solution. Therefore, water in the salt solution will have greater than four orders of magnitude more electrons to interact with the ionizing radiation than will TBP. Even accounting for a G-value for pure TBP which is almost four times greater (assuming the largest G-value, 1.73 molecules hydrogen gas per 100 eV) than that of water in Tank 48H (0.46), the TBP contribution to hydrogen generation is insignificant. As an alternative reference point, a TBP concentration of 4000 mg/L would be necessary in Tank 48H to produce a 1.0 % increase in the rate of hydrogen gas formation. To achieve this concentration, 4400 L of pure TBP would have to be added to the current contents of Tank 48H. Calculations addressing the effect of TBP on hydrogen gas generation are shown in Appendix B - Calculation of the Effect of TBP on Hydrogen Generation.

Compatibility of Tank 48H Waste

The compatibility of the the ITP spent salt solution in Tank 48H and downstream facilities was investigated. A previous review⁵ concerning the addition of "Information Only" Salt Solution, which was similar in composition to the present ITP Feed Tank spent salt solution, to Tank 48H addressed the impact of TBP on the Tank Farm, Defense Waste Processing Facility (DWPF), and Saltstone. The only potential concern that was identified was the effect of phosphate concentration on DWPF. Phosphate is the ultimate decomposition product of TBP and is of concern as to its influence on the ability to make "good glass" in DWPF. The original phosphate concentration in Tank 48H was 950 mg/L (i.e., 0.01 molar).⁵ Addition of both the intended 12,000 gallons of TBP-containing ITP Feed Tank spent salt solution and previous TBP-containing spent salt solutions would not change the phosphate concentration in Tank 48H. The concentration would remain 950 mg/L and no effect on the DWPF process would be observed. Calculations addressing the effect of TBP on phosphate concentration in Tank 48H are shown in Appendix C - The Effect of TBP on Phosphate Concentration.

Criticality Potential In Tank 48H

Experimental studies¹⁸ have shown that the addition of TBP into the ITP process will not affect the chemical behavior of uranium and plutonium. Furthermore, there is not enough fissile material in Tank 48H to result in a criticality event.¹⁹ Given this information, no criticality concerns exist as a result of the addition of the TBP-containing spent salt solution to Tank 48H.

Combustibility Potential of TBP In Tank 48H

A potential combustibility concern related to insoluble TBP was identified. The solubility of TBP in Tank 48H is expected to be approximately 1 mg/L.²⁰ The TBP concentration in Tank 48H, as a result of the transfer, will be 84 mg/L. Therefore, insoluble TBP will collect on the surface of the contents of Tank 48H posing a potential combustibility concern. Laboratory tests indicate that there is a minimum thickness of TBP which is not combustible. The combustibility of isolated pools of insoluble TBP floating on Tank 48H simulated salt solutions has been tested.²¹ The pools could not be ignited with a butane flame when the bulk solution was heated to 70°C. This indicates that isolated pools of TBP are not sufficiently thick to be combustible. Ignition of laboratory-scale test samples are expected to be more easily achieved than a pool fire in a full-scale waste tank. Laboratory tests and solubility data indicate that at least 110 gallons of TBP are required to cover the entire surface of salt solution in Tank 48H.²¹ The volume (i.e., 25 gallons) of TBP added to Tank 48H will be insufficient to cover the entire surface of Tank 48H but will form isolated pools instead. Therefore, 25 gallons of TBP does not pose a credible combustibility hazard in Tank 48H.

The Effect of Future ITP Feed Tank Spent Salt Solution Additions

The effect of future ITP Feed Tank additions to Tank 48H was evaluated. To accomplish this task, all assumptions previously described were assumed to be valid. The volume of spent salt solution was doubled (24,000 gallons) and the total volume of TBP transferred with the 24,000 gallons of salt solution was assumed to remain constant (i.e., 25 gallons) since the value is restricted by the Test Authorization document.¹ This action results in only 7.3% of the composite LFL being obtained. The presence of these organics in Tank 48H, in the absence of ventilation, would shorten the current "Time to LFL" from 6.6 years to 6.0 years if no material was lost. The additional salt solution would decrease the phosphate concentration from 950 mg/L to 910 mg/L. No effect on the rate of hydrogen production would be observed.

CONCLUSION

In conclusion, no flammability, compatibility, criticality, or combustibility concerns for Tank 48H or its downstream facilities were identified in regards to the disposal of 12,000 gallons of TBP-containing ITP Feed Tank Salt Solution to Tank 48H. Calculations were performed to evaluate the flammability potential as a result of the transfer of the spent salt solution waste. Under the most conservative conditions, the data indicate that only 6.5% of the composite LFL could be obtained. The presence of these organics in Tank 48H, in the absence of ventilation, would shorten the current "Time to LFL" by 6 months (6.6 years to 6.1 years) if no material was lost. Addition of the solution to Tank 48H will not result in an increase in the

rate of hydrogen production. Insoluble TBP will collect on the surface of the contents of Tank 48H. However, the quantity of TBP will be insufficient to form a layer thick enough to pose a credible combustibility hazard.

Technical Reviewer :

D. D. Walker

Interim Waste Technology Section

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APPENDIX A - Flammability Equations, Calculations, and Assumptions

The following equations were used to calculate the data listed in Tables I and II. Data and assumptions used in performing the calculations precede the equations.

Tank 48H

Data

volume	=	1.3 E+6 gal	=	4.9 E+6 L
volume of current contents	=	2.82 E+5 gal	=	1.07 E+6 L
volume transferred to Tank 48H	=	1.2 E+4 gal	=	4.5 E+4 L
volume of vapor space after transfer	=	1.0 E+6 gal	=	3.8 E+6 L

Assumptions

- 1) For the Tank 48H worst-case scenario, 12,000 gallons of spent salt solution are transferred to Tank 48H from the ITP Feed Tank. The contents of Tank 48H are assumed to be at the current volume. The maximum concentration of benzene, methanol, and isopropanol transferred to Tank 48H are 20 mg/L, 400 mg/L, and 430 mg/L, respectively.
- 2) The total amount of TBP added to the Tank (both past, 25.8 L, and present, 25 gal) and the maximum concentrations of benzene, methanol, and isopropanol are assumed added to Tank 48H in the absence of ventilation.
- 3) All TBP was assumed to instantly and completely decompose to phosphate and 1-butanol (3 times as many moles). For this reason, 1-butanol is listed in place of TBP in Table II.
- 4) Henry's Law data for benzene, methanol, isopropanol, and 1-butanol in salt solution^{8,9} were used to determine the relative contribution of these four compounds to the vapor composition.
- 5) The temperature of the solution is 50°C (323 K). This is a conservative assumption since the most recently documented temperature of Tank 48H was 26°C.¹⁰

Flammability Equations

Composite LFL Calculations:

For benzene, isopropanol, and methanol in Tank 48H, the total number of moles of each compound that will be gaseous is determined assuming the maximum concentration (20 mg/L, 430 mg/L, and 400 mg/L, respectively) of each compound, the solution volume, and previously determined Henry's Law constants for each compound in salt solution. The Henry's Law constants are shown in the table below.

Compound	Henry's Law Constant <u>H</u>	Solution Conditions <u>at which the value was measured</u>
Benzene	5.6	High hydroxide, 5.0 molar Na ⁺ salt solution at 50°C
Methanol	0.0015	Average, 5.0 molar Na ⁺ salt solution at 50°C
Isopropanol	0.011	Average, 5.0 molar Na ⁺ salt solution at 50°C

For 1-butanol in Tank 48H, the total number of moles that will be gaseous is based upon the total amount of TBP added to the tank, TBP density, and previously determined Henry's Law constant (0.026) for the compound in 5.1 molar sodium salt solution at 50°C. A derivation of Henry's Law is used and shown below.

For benzene, isopropanol, and methanol

$$\text{total amount, g} = (\text{solution concentration, g/L})(\text{solution volume, L})$$

For 1-butanol (from TBP)

$$\text{total amount, g} = (\text{mol. wt. 1-butanol})(3)((25 \text{ gal})(3.785 \text{ L/gal}) + (25.8 \text{ L}))$$

$$X(1000 \text{ mL/L})(d, \text{ g/mL})/(\text{molecular weight of TBP})$$

$$\text{where } d = \text{density of TBP (0.979 g/mL)}$$

From Henry's Law

$$H = C_v/C_l$$

where H = Henry's Law Constant

C_v = equilibrium vapor concentration of a compound in g/L

C_l = equilibrium solution concentration in g/L

$$\text{total amount, g} = (C_v)(\text{Vapor Volume, L}) + (C_l)(\text{volume of contents, L})$$

substitute for C_l ($= C_v/H$) and rearrange to obtain

$$C_v = (\text{total amount, g})/((\text{Vapor Volume, L}) + (\text{volume of contents, L})/H)$$

$$\text{now, g compound that are gaseous} = (C_v)(\text{Vapor Volume, L})$$

$$\text{and, moles in vapor} = (\text{g compound that are gaseous})/(\text{molecular weight})$$

From this, the gas volume and the remainder of the data can be calculated using the Ideal Gas Law as shown on the next page.

$$\text{Gas Volume} = (\text{moles in vapor})(0.08205 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K})(\text{Temperature, K})/(1 \text{ atm})$$

$$\text{Vapor Fraction, P} = (\text{Gas Volume, L})/(\text{Vapor Volume, L})$$

$$\% \text{ LFL} = ((\text{Vapor Fraction, P})/(\text{LFL vapor fraction}))\times 100$$

The percentage of the composite Lower Flammability Limit (%LFL) can be obtained from the sum of all individual % LFL (derived from Le Chatelier's rule).

Time to LFL Calculations:

Rate of benzene production was 0.72 moles/day prior to salt solution transfer.¹¹

LFL for benzene is 1.2 percent (by volume).

So using the Ideal Gas Law, the Time to LFL is:

$$\frac{(0.012)(\text{Vapor Volume, L})(1 \text{ atm})}{(0.08205 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K})(\text{Temperature, K})} \\ (0.72 \text{ moles/day})$$

$$= 2400 \text{ days or } 6.6 \text{ years}$$

After transfer, the salt solution, will contribute 6.46% of the composite LFL, therefore residual benzene generation must account for 93.54% of the composite LFL. The residual rate of benzene production is assumed to be the same as prior to transfer (.72 moles/day)¹¹ and the LFL for benzene is 1.2% (by volume).

So using the Ideal Gas Law, the Time to LFL is:

$$\frac{(0.9354)(0.012)(\text{Vapor Volume, L})(1 \text{ atm})}{(0.08205 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K})(\text{Temp. K})} \\ (0.72 \text{ moles/day})$$

$$= 2200 \text{ days or } 6.1 \text{ years}$$

APPENDIX B - Calculation of the Effect of TBP on Hydrogen Generation

The information below was used to evaluate the effect of TBP on hydrogen gas generation.

Water :

$$(55 \text{ moles H}_2\text{O/L})(6.02 \text{ E}+23 \text{ molecules/mole})(8 \text{ e}^-/\text{molecule H}_2\text{O})$$

$$= 2.6 \text{ E}+26 \text{ e}^-/\text{L}$$

TBP :

$$\frac{(((25 \text{ gal})(3.785 \text{ L/gal})+(25.8 \text{ L}))(1000 \text{ mL/L})(d. \text{ g/mL})(6.02 \text{ E}+23)(104 \text{ e}^-))}{(\text{molecular weight of TBP})(\text{Tank 48H volume, L})}$$

where $d =$ density of TBP (0.979 g/mL)

$$= 2.5 \text{ E}+22 \text{ e}^-/\text{L}$$

Cumulative G-Value :

$$\text{GH}_2 \text{ (total)} = \frac{(2.6 \text{ E}+26 \text{ e}^-/\text{L})(0.46)}{(2.6 \text{ E}+26 \text{ e}^-/\text{L})+(2.5 \text{ E}+22 \text{ e}^-/\text{L})} + \frac{(2.5 \text{ E}+22 \text{ e}^-/\text{L})(1.73)}{(2.6 \text{ E}+26 \text{ e}^-/\text{L})+(2.5 \text{ E}+22 \text{ e}^-/\text{L})}$$

$$= 0.46 \text{ molecules H}_2 \text{ per } 100 \text{ eV}$$

1% Increase In G-Value :

$$(1.01)(0.46) = \frac{(2.6 \text{ E}+26 \text{ e}^-/\text{L})(0.46)}{(2.6 \text{ E}+26 \text{ e}^-/\text{L}) + (X)} + \frac{(X)(1.73)}{(2.6 \text{ E}+26 \text{ e}^-/\text{L}) + (X)}$$

$$X = 9.5 \text{ E}+23 \text{ e}^-/\text{L} \text{ (from TBP)}$$

now,

$$(9.5 \text{ E}+23 \text{ e}^-/\text{L})(1/104 \text{ e}^-)(1/6.02 \text{ E}+23)(266.3 \text{ g TBP/mole})(1000 \text{ mg/g})$$

$$= 4000 \text{ mg/L TBP}$$

APPENDIX C - The Effect of TBP on Phosphate Concentration

The following equations and data were used to evaluate the effect of TBP on the phosphate concentration in Tank 48H.

The phosphate concentration in Tank 48H prior to any TBP additions was 950 mg/L (0.01 molar).⁵

The total amount of TBP added to the Tank is 25.8 L (past) and 25 gal (present).

Therefore, the number of moles of phosphate is equivalent to the number of moles of TBP (443 moles). Based upon the volume currently in Tank 48H and the volume to be added, the phosphate concentration would remain 950 mg/L.