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Assessment of the Impact of TOA Partitioning on DWPF Melter Off-Gas Flammability

W. E. Daniel

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REVIEWS AND APPROVALS

AUTHORS:

W. E. Daniel, Engineering Process Development Date

TECHNICAL REVIEW:

F. G. Smith, III, Process Modeling & Computational Chemistry, Reviewed per E7 2.60 Date

APPROVAL:

D. R. Click, Manager Date
Process Technology Programs

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

E. J. Freed, Manager Date
SRR Engineering

EXECUTIVE SUMMARY

An assessment has been made to evaluate the impact on the DWPF melter off-gas flammability of increasing the amount of TOA in the current solvent used in the Modular Caustic-Side Solvent Extraction Process Unit (MCU) process. The results of this study showed that the concentrations of nonvolatile carbon of the current solvent limit (150 ppm) in the Slurry Mix Evaporator (SME) product would be about 7% higher and the nonvolatile hydrogen would be 2% higher than the actual current solvent (126 ppm) with an addition of up to 3 ppm of TOA when the concentration of Isopar® L in the effluent transfer is controlled below 87 ppm and the volume of MCU effluent transfer to DWPF is limited to 15,000 gallons per Sludge Receipt and Adjustment Tank (SRAT)/SME cycle. Therefore, the DWPF melter off-gas flammability assessment is conservative for up to an additional 3 ppm of TOA in the effluent based on these assumptions. This report documents the calculations performed to reach this conclusion.

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LIST OF ABBREVIATIONS

BOBCalixC6	calix[4]arene-bis(tert-octyl benzo-crown-6
Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol
DWPF	Defense Waste Processing Facility
MCU	Modular Caustic Side Solvent Extraction Unit
MW	Molecular Weight
SB7b	Sludge Batch 7b
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TGA	Thermogravimetric Analysis
TOA	tri-n-octylamine
TOC	Total Organic Carbon

1.0 Introduction

The strip effluent fed to the DWPF Sludge Receipt and Adjustment Tank (SRAT) contains entrained solvent from the Modular Caustic Side Solvent Extraction Unit (MCU) cesium extraction process. The current solvent consists of the diluent Isopar® L with[1] the following additives:

- 0.007 M BOBCalixC6, calix[4]arene-bis(tert-octyl benzo-crown-6)
- 0.75 M Cs-7SB, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol
- 0.003 M TOA, tri-n-octylamine

BOBCalixC6 is the cesium extractant, Cs-7SB is the modifier used to increase the solubility of BOBCalixC6, and TOA is used as a suppressor of impurity effects and the ion-pair dissociation as well as to improve stripping. Due to the high volatility (0.5 mm Hg vapor pressure at 20°C) of the diluent Isopar® L, it is assumed to be completely removed during the SRAT processing. Therefore the concentration of Isopar® L remaining in the SME product is considered to be zero. Only the three nonvolatile components of the solvent listed above remain to carry carbon into the melter and impact melter off-gas flammability.

There are other mechanisms other than mechanical carryover (which is currently accounted for in the MOG flammability evaluation) by which TOA can end up in the Strip Effluent.

This report assesses the carbon/hydrogen contribution of additional TOA in the strip effluent due to these other mechanisms with respect to the current assumptions/limits in the DWPF Off-gas flammability evaluation.

2.0 Results and Discussion

2.1 Solvent Composition and Decomposition

Table 2-1 lists the chemical composition of the current solvent including the chemical formula, molecular weight, and weight percent (wt%) of the components of the solvents. The wt% distribution given in Table 2-1 for the current solvent was obtained from the TTQAP for this task[2] and is based on the nominal compositions listed in the introduction. The nonvolatile constituents of the solvent are italicized in Table 2-1. These nonvolatile constituents for the solvent were blended into a hypothetical "nonvolatile solvent" using the mole percent listed in Table 2-1. The equivalent stoichiometric formulations for this hypothetical "nonvolatile solvent" are shown on the left hand side of Eq. (1). Using these equivalent stoichiometric formulations, an equivalent nonvolatile molecular weight can be calculated for the solvent which is shown in Table 2-1. Equation (1) represents the stoichiometric decomposition of the hypothetical "nonvolatile solvents" to form the most flammable gas mixtures. The high oxygen demand by the solvent carbon is evident from the CH_4 and C decomposition products shown, which are both heavy oxygen consumers and make up nearly 80% of all carbons in the nonvolatile portion of the current MCU solvent.

Table 2-1. Carbon Sources in Entrained Solvent in Strip Effluent.

Solvent	Component	Chemical Formula	MW	Wt%	Mol% Nonvolatile	Nonvolatile Equiv. MW
Current	*BOBCalixC6*	$C_{72}H_{92}O_{12}$	1149.64	0.94	0.92	345.877
	Cs-7SB	$C_{16}H_{22}F_4O_3$	338.34	29.78	98.68	
	TOA	$C_{24}H_{51}N$	353.68	0.12	0.39	
	Isopar® L	C_{11}-C_{13}	163	69.15	N/A	

Current Solvent "Nonvolatiles" Decomposition:

$$C_{16.547}H_{22.759}O_{3.071}F_{3.947}N_{0.004} \rightarrow 5.690\ CH_4 + 6.800\ C + 3.071\ CO + 0.987\ CF_4 + 0.002\ N_2 \qquad (1)$$

2.2 Flammability Assessment

In order to examine the flammability impact of the MCU solvents, several assumptions have to be made. The assumptions used in this flammability assessment are:

1. The concentration limit of the current solvent in the strip effluent fed to DWPF was assumed to be 150 ppm. This solvent concentration will be referred to as the current solvent limit and was used in the current DWPF flammability calculations.[3] This current solvent limit will be compared with the new values in this report.
2. The actual concentration of the current solvent in the strip effluent was calculated based on the maximum Isopar® L concentration of 87 ppm[4] as follows:

$$\frac{87\ ppm\ Isopar}{\frac{69.15\ wt\%\ Current}{100}} = 126\ ppm\ current\ solvent\ actual \qquad (2)$$

3. 15,000 gallons of strip effluent (specific gravity = 1.002) are fed to the SRAT per CPC cycle and all of the nonvolatile solvent constituents are transferred to the SME.
4. The SME batch is 5,678 gallons with a specific gravity of 1.3994[3].

Using the assumptions above, the amount of additional TOA (tri-n-octylamine) that can be added to the 15,000 gallon effluent to simulate TOA Partitioning will be found that stays below the flammability limits for the current solvent limit.

From assumptions 1, 2, and 3, the mass of solvents added to each SRAT Batch is calculated by:

$$\frac{15{,}000\ gal\ solvent}{SRAT\ Batch} \times \frac{3.7854\ L}{gal} \times \frac{1.002\ kg}{L} \times \frac{150\ kg\ current\ solvent\ limit}{10^6\ kg} = 8.534\ \frac{kg\ current\ solvent\ limit}{SRAT\ Batch} \qquad (3)$$

$$\frac{15{,}000\ gal\ solvent}{SRAT\ Batch} \times \frac{3.7854\ L}{gal} \times \frac{1.002\ kg}{L} \times \frac{126\ kg\ current\ solvent\ actual}{10^6\ kg} = 7.158\ \frac{kg\ current\ solvent\ actual}{SRAT\ Batch} \qquad (4)$$

Based on the information above and the calculations outlined below, the ppm of TOA added to the 15,000 gallons of strip effluent with the actual current solvent concentration (126 ppm) was incremented by 1 ppm starting at 1 ppm to find the maximum value where the flammability limits of the current solvent limit would still be bounding. The maximum value found was 3 ppm of additional TOA added to the 15,000 gallons of strip effluent with the actual current solvent concentration (126 ppm). The rest of the calculations use this maximum 3 ppm value and then compare the actual current solvent concentration with the additional TOA to the current solvent limit in terms of flammability potential. The new solvent mass per SRAT Batch for the maximum 3 ppm addition of TOA is calculated by:

$$7.158\,\frac{kg\ current\ solvent\ actual}{SRAT\ Batch} + \frac{15{,}000\ gal\ solvent}{SRAT\ Batch} \times \frac{3.7854\ L}{gal} \times \frac{1.002\ kg}{L} \times \frac{\frac{3}{10^6}}{1-\frac{3}{10^6}}\,\frac{kg\ TOA}{SRAT\ Batch} = 7.329\,\frac{kg\ current\ solvent\ with\ TOA\ addn}{SRAT\ Batch} \qquad (5)$$

Using the new solvent mass from Equation (5), the carbon source concentrations can be recalculated taking into account the original solvent mass from Equation (4) and the original concentrations from Table 2-1. For example, the weight percent of TOA in the actual current solvent concentration (126 ppm) with the maximum 3 ppm addition of TOA to the strip effluent is calculated by:

$$\frac{\left[7.158\frac{kg\ current\ solvent\ actual}{SRAT\ Batch}\times\frac{0.13\ \text{wt\% TOA}}{100}+\frac{15{,}000\ gal\ solvent}{SRAT\ Batch}\times\frac{3.7854\ L}{gal}\times\frac{1.002\ kg}{L}\times\frac{\frac{3}{10^6}}{1-\frac{3}{10^6}}\frac{kg\ TOA}{SRAT\ Batch}\right]}{7.329\frac{kg\ current\ solvent\ with\ TOA\ addn}{SRAT\ Batch}} * 100 = 2.45\ \text{wt\%} \qquad (6)$$

The revised weight percent for TOA is significantly higher since the 3 ppm addition of TOA occurs for the entire 15,000 gallons of effluent and does not add any Isopar® L. Using the logic described above, Table 2-2 lists the chemical composition of the proposed current solvent with 3 ppm TOA addition to the strip effluent including the chemical formula, molecular weight, and weight percent (wt%) of the components of the solvents.

Table 2-2. Carbon Sources in Entrained Solvent in Strip Effluent with Additional 3 ppm TOA.

Solvent	Component	Chemical Formula	MW	Wt%	Mol% Nonvolatile	Nonvolatile Equiv. MW
Current w/ TOA Partitioning	*BOBCalixC6*	$C_{72}H_{92}O_{12}$	1149.64	0.92	0.86	346.425
	Cs-7SB	$C_{16}H_{22}F_4O_3$	338.34	29.09	91.75	
	TOA	$C_{24}H_{51}N$	353.68	2.45	7.39	
	Isopar® L	C_{11}-C_{13}	163	67.54	N/A	

Based on the compositions in Table 2-2, the equivalent stoichiometric formulations for this hypothetical "nonvolatile solvent" and its decomposition to flammable gases are shown in Equation (7) below:

Current Solvent with 3 ppm additional TOA "Nonvolatiles" Decomposition:

$$C_{17.071}H_{24.744}O_{2.855}F_{3.670}N_{0.074} \rightarrow 6.186\ CH_4 + 7.112\ C + 2.855\ CO + 0.917\ CF_4 + 0.037\ N_2 \qquad (7)$$

From assumption 4, the mass of a SME batch is calculated by:

$$\frac{5{,}678\ gal}{SME\ Batch} \times \frac{3.7854\ L}{gal} \times \frac{1.3994\ kg}{L} = 30{,}078.1\ \frac{kg}{SME\ Batch} \tag{8}$$

Based on the wt% Isopar® L compositions in Table 2-1 and the kg of solvent per SRAT Batch found above, the kg of nonvolatiles from the solvents per SME Batch is calculated by:

$$8.534\ \frac{kg\ current\ solvent\ limit}{SRAT\ Batch} \times \frac{SRAT\ Batch}{SME\ Batch} \times (1 - wt\%\ Isopar) = \frac{kg\ current\ nonvolatile}{SME\ Batch} \tag{9}$$

Based on the compositions in Table 2-2 and the kg of solvent per SRAT Batch with 3 ppm of TOA added to the strip effluent, the kg of nonvolatiles from the solvents per SME Batch is calculated by:

$$7.329\ \frac{kg\ current\ solvent\ with\ TOA\ addn}{SRAT\ Batch} \times \frac{SRAT\ Batch}{SME\ Batch} \times (1 - wt\%\ Isopar) = \frac{kg\ current\ solvent\ with\ TOA\ addn\ nonvolatile}{SME\ Batch} \tag{10}$$

The calculated mass of the nonvolatile components of the solvents in each SME Batch are shown in Table 2-3. The amount of carbon from the nonvolatile components of the solvents in each SME Batch are calculated by:

$$\frac{kg\ nonvolatile}{SME\ Batch} \times \frac{1}{Nonvolatile\ Equiv.\ MW} \times \frac{kgmol\ nonvolatile}{kg\ nonvolatile} \times \frac{kgmol\ C}{kgmol\ nonvolatile} \times \frac{12.01\ kg\ C}{kgmol\ C} \times \frac{1}{30{,}078.1 kg\ SME\ Batch} \times \frac{1.0E06\ ppm\ C}{\frac{kg\ C}{kg\ SME\ Batch}} = \frac{ppm\ C}{SME\ Batch} \tag{11}$$

Where the nonvolatile equivalent molecular weight for each solvent is defined in Table 2-1 and Table 2-2 and the kilograms of nonvolatile are defined from Equation (10). The $\frac{kgmol\ C}{kgmol\ nonvolatile}$ term is defined as 16.547 for the current solvent and 17.071 for the current solvent with 3 ppm additional TOA based on the stoichiometric equations (1) and (7). The calculated mass of carbon from the solvents per SME Batch is shown in Table 2-3.

The moles of hydrogen per mole of carbon (Moles H/Moles C) for the nonvolatiles in the solvents are shown in Table 2-3. These molar ratios are calculated using the moles defined in the equivalent stoichiometric formulations for the solvent shown in Equation (1) and (7).

To calculate the moles of oxygen used for the decomposition of the nonvolatile carbon sources from the solvents, the following decomposition reactions are used:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{12}$$

$$C + O_2 \rightarrow CO_2 \tag{13}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{14}$$

Note that the CF_4 and CCl_4 compounds are considered noncombustible or do not use up oxygen. So for each mole of CH_4 decomposed, 2 moles of O_2 are used. For each mole of C decomposed, 1 mole of O_2 is used. For each mole of CO decomposed, 0.5 mole of O_2 is used. Using the stoichiometric equations (1) and (7), and the decomposition reactions (12) through (14), the moles of O_2 used per mole of C in the nonvolatile of the solvents can be calculated. For example, for the current solvent:

$$\frac{\left[\frac{5.690\ mol\ CH_4}{mol\ current\ nonvol}\times\frac{2\ mol\ O_2}{mol\ CH_4}+\frac{6.800\ mol\ C}{mol\ current\ nonvol}\times\frac{1\ mol\ O_2}{mol\ C}+\frac{3.071\ mol\ CO}{mol\ current\ nonvol}\times\frac{0.5\ mol\ O_2}{mol\ CO}\right]}{\left[\frac{5.690\ mol\ CH_4}{mol\ current\ nonvol}\times\frac{1\ mol\ C}{mol\ CH_4}+\frac{6.800\ mol\ C}{mol\ current\ nonvol}\times\frac{1\ mol\ C}{mol\ C}+\frac{3.071\ mol\ CO}{mol\ current\ nonvol}\times\frac{1\ mol\ C}{mol\ CO}+\frac{0.987\ mol\ CF_4}{mol\ current\ nonvol}\times\frac{1\ mol\ C}{mol\ CF_4}\right]} =$$

$$\frac{19.713\ mol\ O_2}{16.546\ mol\ C} = 1.191\frac{mol\ O_2}{mol\ C} \tag{15}$$

The calculated O_2 demand moles per mole of C for the solvents are shown in Table 2-3.

The next value calculated for the solvents is the total O_2 demand per SME Batch. In order to calculate these values, the total moles of C per SME batch needs to be found using the following equation:

$$\frac{ppm\ C}{SME\ Batch}\times\frac{\frac{1\ kg\ C}{1.0E06\ kg\ SME\ Batch}}{ppm\ C}\times 30{,}078.1\ kg\ SME\ Batch\times\frac{1000g\ C}{kg\ C}\times\frac{gmol\ C}{12.01\ g\ C}=\frac{total\ gmol\ C}{SME\ Batch} \tag{16}$$

Using Equation (16), the total gmole of C per SME Batch for the current solvent limit is 126.0 and for the actual current solvent concentration (126 ppm) with 3 ppm additional TOA is 117.2. With these values the total O_2 demand per Batch are calculated by:

$$\frac{total\ gmol\ C}{SME\ Batch}\times\frac{gmol\ O_2\ demand}{gmol\ C}=\frac{Total\ gmol\ O_2\ demand}{SME\ Batch} \tag{17}$$

The calculated total O_2 gmole demand per SME Batch for each solvent is shown in Table 2-3.

Table 2-3. Comparison of Nonvolatile Components of Current Solvent with and without TOA Partitioning

Nonvolatile Solvent in SME Batch	Current Solvent Limit	Actual Current Solvent plus 3 ppm TOA
Mass, kg	2.63	2.38
Carbon, ppm	50.3	46.8
Total Moles C	126.0	117.2
Moles H/Moles C	1.375	1.449
Total Moles H	173.3	169.9
O_2 demand Moles/Mole C	1.191	1.225
Total O_2 demand Moles/Batch	150	144

The key results from Table 2-3 are:

1. The concentration of nonvolatile carbon from the solvent in the SME product is about 7% lower for the actual current solvent concentration with 3 ppm of additional TOA than that of the current solvent limit without TOA partitioning.

2. The total moles of H are about 2% lower for the actual current solvent concentration with 3 ppm of additional TOA than that of the current solvent limit without TOA partitioning.

3. The total oxygen demand is about 4% lower for the actual current solvent concentration with 3 ppm of additional TOA than that of the current solvent limit without TOA partitioning.

4. The H/C molar ratios are about 5% higher for the actual current solvent concentration with 3 ppm of additional TOA than that of the current solvent limit without TOA partitioning.

Considering these results, the maximum 3 ppm addition of TOA to the effluent for the actual current solvent concentration should not increase the melter off-gas flammability potential compared to the current solvent limit without TOA partitioning.

The impact to the overall flammability potential due to additional TOA to the current solvent should be relatively small, since the contribution by the entire solvent to the total organic carbon (TOC) fed to the melter is small, less than 1% for the baseline Sludge Batch 8 (SB8) composition used in the latest flammability calculations[3].

3.0 Conclusions

From the results shown in Table 2-3 and the assumptions in the current L1 flammability calculation, it is concluded that the actual current solvent concentration with 3 ppm of additional TOA added would produce slightly less flammable conditions in the melter off-gas than the current solvent limit without TOA partitioning. As shown in Table 2-3, the total moles of carbon and hydrogen from the actual current solvent concentration for up to 3 ppm of TOA addition to the strip effluent are less than those of the current solvent limit. As a result, the total oxygen demand for the actual current solvent concentration for up to 3 ppm of TOA addition to the strip effluent is also shown to be lower than that of the current solvent limit. Therefore, the existing flammability calculations for Sludge Batch 8[3] based on the current solvent composition and concentration are bounding if the assumptions used to make this determination remain valid.

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