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Literature and Data Review for Evaluating the Production of Dimethyl Mercury in the Defense Waste Processing Facility

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LIST OF ACRONYMS

ARP	Actinide Removal Process
CPC	Chemical Process Cell
°C	Degree Celsius
DWPF	Defense Waste Processing Facility
DMM	Dimethyl Mercury
DOE	Department of Energy
DSS	Decontaminated Salt Solution
DWTT	Decontamination Waste Treatment Tank
E_a	Activation Energy
ETF	Effluent Treatment Facility
FAVC	Formic Acid Vent Condenser
FTIR	Fourier Transform InfraRed
GC	Gas Chromatograph
k	rate constant (1/s)
kJ	kilojoule
KW	Kilowatt
L	liter
LDR	Land Disposal Restrictions
LFL	Lower Flammability Limit
LPPP	Low Point Pump Pit
LPPP-RPT	Low Point Pump Pit – Recycle Pump Tank
LWO	Liquid Waste Organization
mg	milligram
MCU	Modular Caustic Side Solvent Extraction Unit
MFT	Melter Feed Tank
mol	mole
MS	Mass Spectrometer
MST	Monosodium Titanate
MSDS	Material Safety Data Sheet
MWWT	Mercury Water Wash Tank
ODM	Operational Decision Making
OGCT	Off Gas Condensate Tank
PRFT	Precipitate Reactor Feed Tank
RCT	Recycle Collection Tank
RPM	Revolutions Per Minute
SB	Sludge Batch
SCFM	Standard Cubic Feet per Minute
SDS	Safety Data Sheet
SE	Strip Effluent
SEFT	Strip Effluent Feed Tank
SHT	Solvent Hold Tank
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TCLP	Toxicity Characteristic Leaching Procedure
W	Watts
WCS	Waste Characterization System
wt.%	Weight Percent

1.0 EXECUTIVE SUMMARY

As part of an ongoing effort to better understand the behavior of mercury in the Liquid Waste flowsheet, Savannah River Remediation (SRR) has recently conducted liquid sampling of Tank 50-H, Tank 21-H, Tank 22-H, Solvent Hold Tank (SHT), and Waste Collection Hold Tank. Some of the sample results indicated the presence organic mercury compounds. One of the organic mercury compounds identified was dimethyl mercury. Dimethyl mercury is volatile and can contribute to the flammability of a vessel's vapor space. The impact of the presence of dimethyl mercury in the vapor space of the DWPF vessels has been reviewed. Based on available literature surveys, the properties of dimethyl mercury, calculations, and available laboratory data, the following can be concluded:

- The quantities of dimethyl mercury sent in the sludge and salt streams to Defense Waste Processing Facility (DWPF) are very low due to the high volatility (due to mixing and temperature) of dimethyl mercury from the liquid phase to the vapor phase and currently do not impact Chemical Process Cell (CPC) vessel flammability.
- Based on the available data, CPC processing does not generate dimethyl mercury in the quantities necessary to impact CPC vessel flammability based on its volatility (due to mixing and temperature) from the liquid phase to the vapor phase and the reducing nature of the process chemistry.
- Based on available sample data and laboratory testing, no measurable dimethyl mercury is expected to be present in the recycle streams at DWPF.

Based on the assessment of available data for dimethyl mercury, transfers and processing at DWPF can be resumed.

2.0 BACKGROUND

A mercury program team was established in February 2015[1]. The mercury program team was established to investigate the following items:

- Mercury inventory and speciation in the liquid waste system,
- Holdup and chemical processing behavior of mercury,
- Impact identification, including worker safety and equipment degradation, and
- Mercury removal and disposal options.

In conjunction with the establishment of the mercury program team, Savannah River Remediation (SRR) received results that a sample of grout prepared from a Tank 50-H sample exceeded the Land Disposal Restrictions (LDR) regulatory requirement in the Toxicity Characteristic Leaching Procedure (TCLP) for mercury in the extraction fluid. Several parallel paths have been established to determine the root cause of why the extraction fluid exceeded the LDR mercury requirement. One of these paths, involved sending salt solution samples from Tank 50-H (4th Quarter 2014 Tank 50-H and 1st Quarter 2015 Tank 50-H) and a 14 day Savannah River National Laboratory (SRNL) TCLP extraction fluid to Eurofins Laboratory for mercury speciation. Results obtained from Eurofins Laboratory indicated the presence of elemental mercury, ionic mercury (Hg(I) and Hg(II)), and methyl mercury in the salt samples from Tank 50-H and the 14 day SRNL TCLP extraction fluid[2]. Dimethyl mercury was found in one (1st Quarter 2015 Tank 50-H) of the two Tank 50-H samples and 14 day SRNL TCLP extraction fluid[2]. Since then, several samples have been taken or are in the process of being taken to gain insight to the formation of dimethyl mercury and methyl mercury based on the different unit operations conducted within the Liquid Waste system.

On April 21, 2015, SRNL issued the Eurofins Laboratory results for the Solvent Hold Tank (SHT) from the Modular Caustic Side Solvent Extraction Unit (MCU) and Tank 21-H[3]. Tank 21-H currently contains the salt solution that will make up Salt Batch 8. Results obtained from Eurofins Laboratory indicated the presence of ionic mercury (Hg(I) and Hg(II)) and methyl mercury in both samples. The SHT contained elemental mercury and was indeterminate for dimethyl mercury based on the organic content of the solvent[3]. The Tank 21-H sample contained no detectable elemental mercury, but contained detectable dimethyl mercury[3]. Based on these recent results and the fact that DWPF receives a Strip Effluent (SE) stream that could contain a small amount solvent, an Operational Decision Making (ODM) process[4] per Manual S4, procedure ADM.56 was invoked to discuss the restart of DWPF operation with SE. During the ODM process, the production and receipt of streams containing dimethyl mercury at DWPF was discussed. If dimethyl mercury is produced during sludge-only and/or coupled operations at DWPF, depending on concentration, it could pose a flammability concern in the vapor space of the DWPF vessels that must be considered.

3.0 REVIEW OF AVAILABLE DATA FOR DIMETHYL MERCURY IN THE DWPF OFF GAS

This section will discuss available data relative to the incoming streams to DWPF, the potential formation of dimethyl mercury within the DWPF process, and the potential presence of dimethyl mercury in the condensate streams of DWPF. Specifically, this evaluation will look at the following:

- Dimethyl mercury impact of the sludge slurry stream addition from H-Tank Farm, the addition of Precipitate Reactor Feed Tank (PRFT) containing batch washing material containing Monosodium Titanate (MST), trace sludge solids, and neutralized oxalic acid cleaning solution, and the SE stream,
- Discuss the potential for dimethyl mercury formation during CPC processing (Sludge Receipt Adjustment Tank (SRAT), Slurry Mix Evaporator (SME), and Melter Feed Tank (MFT), and
- Discuss the potential for dimethyl mercury presence in DWPF Recycle (MWWT, SMECT, and RCT).

3.1 Incoming Streams Potentially Containing Dimethyl Mercury

DWPF receives three streams from the Tank Farm. The first is a sludge slurry stream and the other two streams are a result of Salt Processing. The streams from salt processing include a strip acid stream containing Cs-137 called SE and a MST-sludge solids stream called the Actinide Removal Process (ARP) stream. DWPF has the option of either performing a sludge-only operation in which no salt streams are added or a coupled operation in which salt stream(s) are added. Options for the coupled operation in DWPF include; processing sludge and ARP together, or processing sludge and SE together, or processing sludge, ARP, and SE together.

3.1.1 Potential Contribution of Dimethyl Mercury from Sludge Slurry Contained in Tank 40-H

Dimethyl mercury from sludge slurry transferred from Tank 40-H is considered negligible based upon 1) the insignificant quantities of dimethyl mercury identified in waste tanks (in general) to date, and 2) the nature of the process (periodically requiring mixing), which ensures any dimethyl mercury generated within the liquid phase, however insignificant, is removed into the vapor phase prior to transfer to the facility. Each of these is discussed in more detail in the sections that follow.

3.1.1.1 Literature Review of Dimethyl Mercury in LWO Waste Tanks

In a review of site literature for the presence of dimethyl mercury in the Liquid Waste System, no substantial quantities of dimethyl mercury have been identified in any waste tank to date. A report was found that documented vapor sample results of dimethyl mercury and total mercury for various tanks in the Tank Farm analyzed by Frontier Geosciences (which is now Eurofins Laboratory)[5]. This report was generated as a part of the Mercury Management Program established in 2001 due to the detection of mercury vapor found near the 3H evaporator overheads tanks[5]. The results of the vapor analysis indicate that dimethyl mercury was present in the vapor space of 31 tanks sampled in the Tank Farm, including Tank 51-H and Tank 40-H. Also, recent liquid samples from second quarter 2015 Tank 50-H and Tank 21-H confirm the presence of dimethyl mercury, methyl mercury and ethyl mercury[6]. However, there are no direct liquid measurements of dimethyl mercury applicable to the Tank 40-H slurry. Based on the results of the previous studies and the recent confirmation of dimethyl mercury presence, the potential concentrations of dimethyl mercury in the sludge and salt streams received by DWPF must be considered.

3.1.1.2 Review of Tank 40-H Processing

An additional approach to understanding the potential for the presence of dimethyl mercury in the Tank 40-H liquid is to evaluate the likelihood of formation and retention based on a Tank 40-H processing review. To perform the evaluation, one has to understand its rate of formation, rate of degradation, and vapor–liquid equilibrium in the Liquid Waste System. Very little data exists in literature that is applicable to the conditions in the Tank Farm and DWPF. However, as a part of the Mercury Management Team initiatives, some degradation tests and formation tests were performed for dimethyl mercury by SRNL and Frontier Geosciences[7]. For the degradation studies, three different simulants and temperatures were used. The simulants represented tank waste, the evaporator overheads, and acidified Effluent Treatment Facility (ETF). Samples were injected with an initial 1.6 µg/L of dimethyl mercury (no dimethyl mercury was added to the blanks) at time zero and testing was completed at 39 °C, 65 °C, and 83 °C. In order to discern the actual

degradation from other mechanisms that can cause the loss of dimethyl mercury such as diffusion, photolytic decomposition, loss to the head space, amalgamation with metallic components, etc., bottles were filled ~99% with salt solution, sealed, and kept in the dark. For the formation testing, one simulant was made representing a salt supernate applicable to Tank Farm evaporator feeds. Simulant samples contained a starting soluble mercury concentration of 10 mg/L and were then either left un-amended (no organics), spiked with 1,600 mg/L acetate, or with a mixture of acetate plus 6 other potentially methylating (dodecane, Alconox detergent, Sodium EDTA, digested resin solution, Trimethylamine, and Antifoam H-10) organics. Sludge solids were also introduced to the test matrix to determine if there was a catalytic term being introduced from the sludge solids. Testing was completed at 39 °C, 60 °C, and 81 °C. Again, samples were filled ~99% full, sealed, and exposure to light was minimized. From the degradation and formation testing, rate constants and activation energies were determined[7]. It was also determined that the presence of sludge solids did not have a catalytic impact on the production of dimethyl mercury. The use of the rate constants and activation energies in Reference 7 were limited to qualitative analysis only due to the limited data sets and the fact that the experiments did not reach equilibrium. Although it is recommended that this be used for qualitative analysis, this is the only existing literature data applicable to formation in waste streams generated in the Tank Farm. Thus, it provides the best information available for predicting the formation and degradation of dimethyl mercury in the Tank Farm and thus caustic conditions below 80 ˚C at DWPF.

Since DWPF can reach temperatures greater than 80˚C under caustic conditions, the data reported in Reference 7 was revisited. In Reference 7, the rate constants determined used all data from the Frontier dimethyl mercury formation report. Because of competing reactions, the previous rate constants may not be conservative for short reaction times. Therefore, the data was re-evaluated using the "Acetate plus All Organics" case to formulate more conservative first order rate constants for DWPF based on the simple reaction mechanism of Equation 1[7]. The reactants term in Equation (1) is the sum of the concentration of soluble mercury compounds that could contribute to dimethyl mercury formation, including inorganic mercury ions and monomethyl ions. This evaluation can be found in Appendix A. The new first rate constants for formation are provided below in Table 1.

$$\text{Reactants} \xrightarrow{k_{formation}} (CH_3)_2Hg\ (aq) \qquad \text{Equation (1)}$$

Table 1– First Order Rate Constants (k formation) and Activation Energy for "Acetate Plus All Other Organics" for Caustic Conditions

Temperature	First Order Rate Constant - k (1/s)
39˚C	7.660E-10
60˚C	5.487E-09
81˚C	1.168E-08
E_a(kJ/mole)	-60.246

Based on the new first order rate constants and activation energy, rate constants for specific temperatures can be estimated via interpolation and extrapolation of the data. The first order rate constants were estimated for 30˚C to 90˚C in increments of 5˚C and 90˚C to 105˚C in increments in 1˚C are also presented in Appendix A for use in this report. As noted, the rate constants for the formation of dimethyl mercury, even when conservatively estimated, are extremely small.

As mentioned previously, the dimethyl mercury experiments were performed to isolate formation as a function of temperature and did not need to account for volatility from the solution due to the minimization of the headspace above the liquid. A report has been recently issued documenting the physical properties for dimethyl mercury[8]. Based on Reference 8, dimethyl mercury is defined as volatile based its relatively high air/water distribution constant (K_H), approximately 0.3 and Henry's Law relationship involving the ratio of vapor pressure to water solubility, and it has a calculated vapor pressure of 62.37 mmHg at 25 ˚C. The boiling point for dimethyl mercury ranges from 93˚C to 94˚C[8]. Thus, it is appropriate to consider volatility of dimethyl mercury generated in the liquid phase.

Another study in literature was found that addressed the transport and distribution of dimethyl mercury in relationship to aqueous ecosystems on a laboratory scale[9]. This study looked at the volatilization of dimethyl mercury as a function of mixing (0 revolutions per minute (RPM), 20 RPM, 40RPM and 60RPM) and temperature (10˚C, 20˚C and 30˚C) with a starting concentration of 0.4mg/L of dimethyl mercury (isotope Hg-203)[9]. The set of experiments was conducted in 600 mL beakers (open to the atmosphere) containing ~500 mL of a pH neutral solution of New Algal Assay Medium containing no mercury outside of the mercury added at the start of the experiment. The temperature of the beaker was controlled via the use of a water bath and the beaker was equipped with a paddle style stirrer equipped with a gauge to indicate speed and vinyl baffle to suppress a vortex from forming. Although not all combinations of interest for DWPF and Tank Farm processing conditions were studied, the results of the experiments provide key findings that are applicable to Tank Farm and DWPF operations. For a temperature of 20˚C, where the solution was not being mixed, the experimental results indicate that approximately 46% of the liquid phase dimethyl mercury was lost to the vapor space within 9 hours. For the experiments where agitation is performed at 20 RPM, 40 RPM, and 60 RPM at 20˚C, approximately 80%, 90%, and 95% was partitioned to the vapor phase within 4 hours, respectively. Another set of experiments addressed the volatility of dimethyl mercury as a function of temperature at a fixed agitator speed of 40 RPM. These experiments were performed at 10˚C, 20˚C, and 30˚C. Within 4 hours, approximately 85%, 92%, and 96% of the dimethyl mercury partitioned to the vapor phase from the 10˚C, 20˚C, and 30˚C experiments, respectively. These results support the volatility of dimethyl mercury and indicate that mixing and temperature expedite the removal of dimethyl mercury from aqueous solutions in approximately half the time of the non-agitated test. Based on this literature data[9], the same criteria should apply to Tank Farm and DWPF operations where mixing and ventilation are provided. To evaluate this, the recent Tk50-H 2Q15 sample results from Eurofins Laboratory were reviewed. Based on the review of the data, it appears dimethyl mercury is being readily released from Tank 50-H during the slurry pump operation. The dimethyl mercury concentration present in the sample appears to be largely from the rate of formation under a minimal headspace. This assumes that reactants are available in the solution to produce dimethyl mercury and that the refrigeration of the samples slowed the reaction kinetics in regards to the rate of formation. Thus, for tanks that are continuously mixed and ventilated, it can be assumed that the dimethyl mercury is released to the vapor phase at the same approximate rate as it is formed. In other words, there is near-instantaneous volatilization. The evaluation of the Tank 50-H sample data provided by Eurofins Laboratory can be found in Appendix B.

For Tank 40-H, the gas release mode has been adjusted for a three slurry pump run operation[10]. This is due to a slurry pump that is currently leaking and contributing inhibited water to the tank. In order to minimize the contribution of water to the tank, three out of the four slurry pumps are operated. However, DWPF requires that for every three transfers of sludge slurry made from Tank 40-H, that the fourth transfer be completed operating all four slurry pumps. Based on the gas release mode, Tank 40-H can sit quiescent for 22 days prior to the slurry pump operation for the release of radiolytic hydrogen from the sludge slurry. Tank 40-H is equipped with ventilation to allow the removal of radiolytic hydrogen during quiescent time and during slurry pump operation. The minimum exhaust flow is 175 cubic feet per minute (cfm) as noted in calculation S-CLC-H-00714[11]. The minimum time constant for vapor space hydrogen depletion, in a quadrant of the tank, was calculated as 5.7 hours[11]. As mentioned previously, the dimethyl mercury has been noted in Reference 9 to volatilize from the liquid under quiescent conditions at 20˚C (~45% loss in 9 hours). It was also confirmed in Reference 9 that dimethyl mercury acts as a sparingly soluble gas in aqueous solutions like oxygen and carbon dioxide which means that the rate of volatility increases with agitation. The average temperature for Tank 40-H during Sludge Batch 8 operation is plotted in Appendix C. Prior to the receipt of sludge slurry into DWPF, the sludge slurry is mixed for approximately eight hours in Tank 40-H[12]. This mixing would release much of the dimethyl mercury from the slurry to the vapor space of Tank 40-H. After this initial release and with continuous mixing and ventilation, it is assumed that the dimethyl mercury rate of formation in the liquid (at a specified temperature) would be released near-instantaneously to the vapor space in Tank-40H.

The same argument of volatility due to mixing and temperature applied to Tank 40-H apply to 511-S Low Point Pump Pit (LPPP). Upon receipt of sludge slurry into 511-S, the transfer line is flushed with water to remove sludge solids and the agitator is operated to suspend solids so that a uniform slurry is transferred to the SRAT vessel located in the 221-S building[12]. All of the tanks in 511-S are of similar design and build. The agitator power has been measured for the LPPP-Precipitate Pump Tank at a volume of 4,500 gallons[13]. From this data, a specific power value can be calculated by dividing the power by the volume in liters (9400W/(4500

gallons*3.785L/gallon) = 0.552W/L). The specific power exceeds the power requirement for the data reported in Reference 9 for 60 RPM, which was reported as 4.68E-08 watts/L at 20˚C. Based on the mixing in tank and the specific power exceeding the value reported in Reference 9, it is assumed that the dimethyl mercury rate of formation in the liquid (at a specified temperature) would be released near-instantaneously to the vapor space. The rate of formation values are small based on the temperature provided in Appendix A.

3.1.2 Potential Contribution of Dimethyl Mercury from SE and ARP[14]

The contribution of dimethyl mercury from SE and ARP is considered negligible based upon the nature of the process (inherent mixing). As an additional measure, the amount of mercury required in the feed to produce sufficient dimethyl mercury (to impact purge rates in the SEFT and PRFT) is shown to be orders of magnitude in excess of mercury concentrations denoted in the Tank Farm. The transfer line is also evaluated as part of this section due to the potentially stagnant nature of the liquid.

3.1.2.1 Review of MCU Processing

In an attempt to address a bounding value for the potential concentration of dimethyl mercury in the SE produced from Modular Caustic Side Solvent Extraction Unit (MCU), SRNL issued memo number SRNL-L3100-2015-00083[15] on May 7, 2015. At that time, the estimate did not account for any potential volatilization of dimethyl mercury due to mixing or the temperature of the process. However a formation rate for dimethyl mercury was calculated as 4.97E-08 mg/L/s[15]. Prior to receipt of clarified salt solution from 512-S, the salt solution passes through many unit operations that involve mixing, filtering, and pumping providing several opportunities to release the dimethyl mercury. The remaining unreleased dimethyl mercury, present in the clarified salt solution, would be sent to the extraction contactor bank. In the extraction bank, the clarified salt solution is mixed with solvent at a high rate of speed to remove the Cs. Because dimethyl mercury is miscible in most hydrocarbons[16], it is expected that there will be partitioning of dimethyl mercury from the aqueous feed into the hydrocarbon-based solvent. The Cs removal step is accomplished by processing the clarified salt solution and solvent through seven CINC model V10 contactors equipped with rotors that have vanes. The rotors are operated at a minimum of ~1200 RPM with a maximum power requirement of 7.5 KW for a volume of ~4.84 gallons or 18.3 liters. An average power requirement has been estimated to be 1.8KW to 3.2KW based on the voltage supply. Based on the lowest average power requirement for the rotor and the volume of the contactor, a specific power for one contactor can be calculated. The specific power is 1800 watts/18.3 L providing a value of 98.4 watts/L. This specific power far exceeds the power requirement for the data reported in Reference 9 for 60 RPM, which was reported as 4.68E-08 watts/L at 20˚C. As noted previously, the salt solution passes through 7 contactors prior to leaving the extraction bank. Using the results of the study in Reference 9, a large fraction of the dimethyl mercury will volatilize from the salt solution during mixing in the extraction bank and any remaining dimethyl will be associated with the solvent phase. Thus, the release of dimethyl mercury from the Decontaminated Salt Solution (DSS) will be reduced to the level of its formation rate (assumes that reactants are available to generate dimethyl mercury). The DSS generated from the extraction bank is then sent through a coalescer and decanter and stored in the DSS hold tank prior to being sent to Tank 50-H.

The solvent stream from the extraction contactors is sent to the scrub contactor bank and then sent to the strip contactor bank. The scrub contactor bank has two CINC V05 contactors and the strip contactor bank has seven CINC V05 contactors. The scrub and strip rotors are operated at a minimum of ~1800 RPM. The volume of the V05 contactor is 0.86 gallons or 3.25 liters. The maximum power requirement for the V05 is 1.75 KW and has an average power requirement that was estimated to be 740W to 810W based on the voltage supply. Based on the lowest average power requirement for the rotor and the volume of the contactor, a specific power for one contactor can be calculated. The specific power is 740 watts/3.25L providing a value of 227.7 watts/L. The calculated specific power far exceeds the power requirement for the data reported in Reference 9 for 60 RPM. Again, a large fraction of the dimethyl mercury will volatilize during mixing in the scrub and strip contactor banks and any remaining dimethyl mercury will be associated with the solvent phase.

Thus, the release of dimethyl mercury from the strip effluent will be reduced to its formation rate (assumes that reactants are available to generate dimethyl mercury).

3.1.2.2 Evaluation of SEFT and PRFT

Although no dimethyl mercury is anticipated from the ARP/MCU process based upon the inherent mixing that occurs, the SEFT and PRFT were evaluated to determine what quantity of mercury would be required to impact the current purge volumes. The SEFT and PRFT are currently being purged to remove Isopar L and radiolytic hydrogen from the vapor space. In these calculations, there is margin that would allow another flammable component to be added to the vapor space. The question is how much dimethyl mercury could be in the vapor space of the SEFT or PRFT that might cause an issue in regards to flammability. Appendix D contains a calculation to estimate the maximum concentration in liquid that if instantaneously released would pose an issue in the SEFT. This has been calculated as 0.227 mg/L of dimethyl mercury in the SE. Based on the discussions above and using the dimethyl mercury concentration (for liquid), a calculation can be performed to determine what the mercury concentration has to be present in the SE to pose an issue. The calculation is found below:

Calculation for Total Soluble Mercury Needed to Obtain Instantaneous Release Concentration

Inputs to Calculation:

SE Dimethyl Mercury Concentration (see Appendix D) Assumed Instantaneously Released per Second	= 0.227mg/L/s
k constant at 105˚C (see Appendix A)	= 5.111E-08 1/s

Rate of formation of Dimethyl Mercury = k constant @temperature *Soluble Mercury Concentration in mg/L

Re-arranging equation to solve for Soluble Mercury:

Soluble Mercury in mg/L = Rate of formation of Dimethyl Mercury/ K constant @temperature

Soluble Mercury = $\frac{\frac{0.227mg}{L*s}}{5.111E-08\ 1/s} = 4.44E06\ mg/L$

For comparison, the reported mercury concentration in for Tank 21-H was 101 mg/L[3], nearly four orders of magnitude less than that required to be present to generate enough dimethyl mercury to impact the purge calculations for the SEFT and PRFT. Comparing this to the value calculated from the rate constant would indicate that there is not enough mercury present to achieve the instantaneous release of 0.227mg/L/s from the liquid to the vapor space. The same methodology can be applied to the PRFT using the rate constant at 105˚C and the assumed instantaneously released per second of 0.217 mg/L/s found in Appendix D. The total mercury required to achieve an instantaneous rate for the PRFT is 4.25E06 ($= \frac{\frac{0.217mg}{L*s}}{5.111E-08\ 1/s}$). Again, there is not enough mercury present to achieve the instantaneous release of 0.217mg/l/s from the liquid to the vapor space.

3.1.2.3 Evaluation of Transfer Line for SE

Normal SE processing in MCU and DWPF results in transfers into the SEFT approximately every 18 hours. The Transfer Line between MCU and the SEFT has a volume of 1689 gallons, approximately 3 MCU batches, and does not drain between transfers. As discussed above, the volatilization rate of dimethyl mercury into the vapor space of the SEFT and upstream vessels is expected to be equal to its generation rate. However, the Transfer Line is full, stagnant between transfers, and is not vented. Therefore, any dimethyl mercury generated within the Transfer Line is expected to remain in solution until transferred into the SEFT.

During normal operations, the residence time in the transfer line is short and per the discussions above would not present a flammability concern in the SEFT. However, it is possible that an appreciable volume of dimethyl mercury could accumulate during an extended processing outage.

Appendix F calculated a maximum allowable concentration in the Transfer Line following an extended processing outage. Using conservative assumptions an allowable concentration was calculated to be 2.37 mg/L. The length of time required to generate this concentration of dimethyl mercury can be calculated based on the concentration of soluble mercury in the Strip Effluent and the temperature.

Data on the temperature of the Strip Effluent entering the Transfer Line is not available, thus the data from the receiving tank will be used. Note that the SEFT temperature tends to decrease upon receipt of Strip Effluent and increase due to the use of high speed agitation. It is therefore believed to be conservative to use the maximum temperature as documented in Appendix G (30°C).

Inputs to Calculation:

SE Mercury Concentration (Reference 15)	= 83 mg/L or 4.138E-04g mole/L
k constant at 30˚C (see Appendix A)	= 4.445E-10 1/s
Allowable Dimethyl Mercury Concentration in Transfer Line (See Appendix F)	= 2.37 mg/L or 1.027E-05 g mole/L

The time required to generate the allowable dimethyl mercury concentration in the Transfer Line is calculated by dividing the allowable dimethyl mercury concentration by the rate of formation of dimethyl mercury and converting to days.

(Appendix A, Equation A-9) = $t = -ln\frac{A_t}{A_0} * 1/k$

$$t = -\ln\left(\frac{(4.138E-04-1.027E-05)\frac{gmole}{L*s}}{4.138E-04\frac{gmole}{L*s}}\right) \times \frac{sec}{4.445E-10} \times \frac{1min}{60sec} \times \frac{1hr}{60min} \times \frac{1day}{24hr} \times \frac{1\,year}{365\,days} = 1.79\ years$$

It would take ~1.79 years to reach a dimethyl mercury concentration that could not be accommodated by the SEFT purge. This is far longer than any operational outages experienced to this date. Given the mercury sample data to date and the lengthy time required to generate dimethyl mercury, there are no impacts on SEFT flammability.

3.2 Potential Dimethyl Mercury Formation During CPC (SRAT/SME/MFT) Processing

Though no influents into the DWPF process are expected to contain any appreciable quantities of dimethyl mercury, this section evaluates the potential for the formation of dimethyl mercury during the CPC process. Dimethyl mercury formation is not anticipated during the process in any significant quantity based upon 1) review of results from simulant studies, and 2) consideration of process chemistry as well as the incoming feed.

3.2.1 Literature Review of Formation of Dimethyl Mercury During the SRAT/SME Cycle

Dimethyl mercury formation in DWPF has been evaluated previously and determined to be unlikely based upon the processing conditions experienced[17]. As evidenced in Waste Characterization System (WCS), the Liquid Waste System contains a preponderance of mercury based upon historical canyon processing. DWPF was specifically designed to reduce and remove of mercury from the liquid waste system by adding a reducing acid (90 wt.% formic acid). DWPF has also historically added antifoam (organic surfactant) to the process during heat-up and periods of boiling to control foaming. Additionally, there are trace amounts of organics likely

contained within the feed to DWPF. Previous studies conducted for the evaporator system have indicated that the most favorable conditions for dimethyl mercury formation were high temperature and a high pH[7 and 18]. Other changes to the DWPF process flowsheet include caustic boiling to disposition caustic salt waste streams, and boiling for longer periods of time after neutralization reactions to steam strip the mercury and to accommodate the SE stream from MCU. These longer boil times have resulted in higher pH regimes in the SRAT and SME.

To evaluate the potential for dimethyl mercury formation during high pH regimes in the CPC, results from nonradioactive simulant testing were evaluated. Though there is limited simulant data available to directly evaluate the dimethyl mercury formation during CPC processing, there is indirect evidence that even during high pH processing in the CPC, dimethyl mercury does not form. In 2013, simulant testing was performed on an alternate DWPF flowsheet in which formic acid was replaced with glycolic acid as the reducing acid[19]. Testing evaluated the flowsheet chemistry under typical processing scenarios, including caustic boiling (via addition of ARP material prior to acid addition) and re-processing of heel material (via back-to-back SRAT and SME runs). These runs also included the addition of antifoam. Specific to the scaled SRAT test, the setup included off gas monitoring during the entirety of the SRAT process using both a FTIR and MS. The report concluded that no dimethyl mercury was formed during any portion (caustic or acidic) of the scaled SRAT cycle based on the results of the off gas. Though this testing consisted of the addition of a reducing acid different than that currently used (glycolic acid versus formic acid), the two flowsheets are expected to be comparable in terms of mercury chemistry (reduction and subsequent steam stripping) during the SRAT and SME process.

To more directly evaluate the potential for dimethyl mercury formation during SRAT processing with the current flowsheet (formic acid as the reducing acid), FTIR spectra from recent scaled simulant runs was evaluated[20]. Though the aim of the test was to evaluate the impact of different strip effluent (salt waste stream) volumes on SRAT and SME off-gassing (namely hydrogen, carbon dioxide, nitrous oxide), the FTIR spectrum was retained and re-evaluated to determine if the spectrum had signatures consistent with the presence of dimethyl mercury. The testing was similar to the glycolic acid testing discussed previously in that the pH range during monitoring included regimes of caustic (high pH) boiling with antifoam present. As discussed in Appendix H, the FTIR spectrum do not definitively show the presence of dimethyl mercury during CPC processing. However, it should be noted that the analysis cannot preclude the potential for trace amounts of dimethyl mercury that may be masked by the presence of other (known) species that are in higher concentrations with shared spectral peaks.

Based upon the review of the available off-gas data from the simulant testing, there is no evidence of the formation of dimethyl mercury during any part of the SRAT process. The SRAT cycles covered processing conditions of high and low pH at high and low temperatures over several days. These processing conditions (pH and temperature) provide ample opportunity to create dimethyl mercury and are applicable to the processing conditions seen during the SME and MFT. Thus, it is assumed that no dimethyl mercury would be formed in the SME or MFT. The next two sections discuss the chemistry in both high pH conditions in more detail.

3.2.2 Caustic Conditions in the SRAT Prior to Acid Additions

The temperatures in the SRAT, while caustic, range from 20˚C to 101˚C. These conditions are conducive to produce dimethyl mercury due to the fact that the feed streams contain mercury, organics, and high temperatures. When the SRAT is in the operation mode, the air purge to the vessel accounts for Isopar L, radiolytic hydrogen, and catalytic hydrogen as if they are always present in the vapor space. Catalytic hydrogen makes up the majority of the required purge. During caustic boiling operations in the SRAT, only Isopar L (if PRFT addition is made) and radiolytic hydrogen are being produced. Catalytic hydrogen is not produced during this portion of the SRAT cycle, because no acid has been added yet and the concentration of nitrite is above 500 mg/kg slurry[21]. This holds true even if the caustic heel contains residual formate. The amount of nitrite in the sludge slurry is the key to effectively deactivate the noble metal catalysts that produce hydrogen[21]. The nitrite concentration of the Sludge Batch 8 sludge slurry has been reported by SRNL to be 11,300 mg/kg[22]. This is ~22 times the minimum required nitrite value, based on Reference 21. The calculation performed to determine the amount of purge for the SRAT, allowed some margin that would allow another flammable component to be added to the vapor space in addition to Isopar L, radiolytic and catalytic hydrogen. The question is how much dimethyl mercury could be in the vapor space of the SRAT during caustic conditions that might cause an issue in regards to flammability. Appendix E contains a calculation to estimate the maximum concentration in liquid that if instantaneously released to the

vapor space would pose an issue in the SRAT. This has been calculated as 0.417 mg/L of dimethyl mercury assuming the presence of catalytic hydrogen. As shown above, the nitrite concentration for SB8 exceeds the nitrite requirement for poisoning the catalytic hydrogen production during caustic boiling, thus the allowable concentration of dimethyl mercury in the liquid could be much larger.

Based on the specific power discussion below, a calculation can be performed to determine what the mercury concentration would have to be in the liquid to achieve a formation rate equal to the 0.417 mg/L/s which would be instantaneously released into the vapor space of the vessel. Since the first order rate constant is a function of temperature, a temperature of 105˚C was selected to in order to bound the expected temperature during boiling in the SRAT. The corresponding rate at 105˚C is 5.111E-08 s^{-1} times the soluble mercury concentration.

Calculation for Total Soluble Mercury Needed to Obtain Instantaneous Release Concentration

Inputs to Calculation:

SRAT Dimethyl Mercury Concentration (see Appendix E) Assumed Instantaneously Released per Second	= 0.417 mg/L/s
k constant at 105˚C (see Appendix A)	= 5.111E-08 1/s

Rate of formation of Dimethyl Mercury = K constant @temperature *Mercury Concentration in mg/L

Re-arranging equation to solve for Mercury = Rate of formation of Dimethyl Mercury/ K constant @temperature

Re-arranging equation to solve for Mercury = $\frac{\frac{0.417mg}{L*s}}{5.111E-08\ 1/s} = 8.16E06\frac{mg}{L}$

The total available mercury in Tank 40-H was determined as 1.86 wt.% mercury on a dried solids basis[22]. Using the density and weight percent dried solids for the Tank 40-H sample, the mg/L value for mercury can be determined. The mg/L in Tank 40-H is:

$$\frac{1.86gHg}{100gdried\ solids} * \frac{17.26gdried\ solids}{100gslurry} * \frac{1.16g\ slurry}{mL\ slurry} * \frac{1000mL}{1L} * \frac{1000mg}{1g} = \frac{3.724E03mg}{L}$$

Comparing this to the value calculated from the rate constant would indicate that there is not enough mercury present to achieve the instantaneous release of 0.417mg/L/s from the liquid to the vapor space.

3.2.3 Caustic Conditions in the SRAT Following Acid Additions

The other high pH condition experienced during the CPC is following extensive time at boiling following acid addition. As noted previously, soluble mercury is needed for the reaction to occur. The likely reason for the absence of dimethyl mercury in the simulant runs discussed earlier is due to the addition of concentrated formic acid (90wt. %) during the SRAT cycle. This addition reduces the mercury species present in the sludge slurry to its elemental state. Thus, it would alter the mercury form needed to produce dimethyl mercury.

3.2.3.1 Specific Power Calculation for the SRAT, SME, MFT, SEFT, and RCT

The SEFT, SRAT, SME, MFT, and RCT are of similar design and build. Data for the agitator power has been collected previously for the SEFT and RCT and is documented in Reference 13. The specific power for the vessels can be calculated using the RCT or SEFT data. The specific power for the vessels is calculated to be 0.261W/L (7400W / (7500gallon*3.785L/gallon)) which is well above the power requirement for the data reported in Reference 9 for 60 RPM showing the vessels are well mixed. Therefore, if dimethyl mercury is present in the vessels, the dimethyl mercury concentration in the sludge slurry can be assumed to equal its rate of formation at a given temperature if the vessel is readily mixed and ventilated.

3.3 Dimethyl Mercury Formation in DWPF Recycle

The recycle stream at DWPF is comprised of several streams that eventually end up in the RCT. From the RCT, the material is transferred to the LPPP-Recycle Pump Tank (RPT) and then to the Tank Farm. Tank 22-H is currently receiving the DWPF recycle stream via the LPPP-RPT. The major contributors to the recycle stream are the condensate (dilute nitric acid) from the SMECT, condensate (dilute nitric acid) from the OGCT, laboratory sample returns, and the Decontamination Waste Treatment Tank (DWTT). From a historical perspective, the SMECT, OGCT, and laboratory waste streams have had very low solids content. However, occasionally DWPF has introduced sludge slurry that has been processed in DWPF from unplanned carryover events and decontamination of process equipment in the DWTT. In regards to sample analysis of the recycle stream for dimethyl mercury, there is available data confirming the absence of detectable dimethyl mercury albeit limited data. The first data point is a sample pulled from Tank 22-H on March 22, 2015. This sample was sent to SRNL, once at SRNL the sample was prepared and then shipped to Eurofins Laboratory for mercury speciation. The second data point includes sample results of the SRAT and SME condensate streams generated from simulant runs (MWWT, condenser, and FAVC) performed as part of the flowsheet development for incorporation of the streams from MCU[23]. The samples were analyzed by a Gas Chromatography/Mass Spectrometry (GC/MS). No detection limit of the instrument was provided, only that dimethyl mercury was not found. However, the condensate data did indicate the presence of methyl mercury compounds. Methyl mercury was also detected in the Tank 22-H analysis performed by Eurofins Laboratory. These sample data are in agreement. Based on these limited data sets, it can be assumed that no dimethyl mercury is currently present in the recycle streams at DWPF. However, it should be noted that samples were retrieved from the RCT and OGCT during the processing of DWPF Batch 735. These samples have been sent to SRNL. SRNL has prepared and shipped the samples to Eurofins Laboratory for mercury speciation. The sample results from Eurofins Laboratory have not been received yet.

4.0 CONCLUSIONS

Based on the information found in this evaluation, the following conclusions can be made:

- First order rate constants for dimethyl mercury formation were reformulated using the “Acetate plus All Organics” data reported in SRNL-WHM-2004-00009, Rev. 0. The reformulation was performed to add conservatism necessary for the extrapolation of the data above the maximum temperature where the experiments were performed at 81˚C. DWPF processing conditions can exceed 81˚C. The revision of the first order rate constants was also necessary to provide a conservatively high formation rate for short reaction times. These more conservative rates are still very low and do not pose a concern in DWPF. The derivation of the first order rate constants can be found in Appendix A.
- Based on current purges, the maximum acceptable dimethyl mercury liquid concentrations have been calculated for the PRFT, the SEFT, and the SRAT that would pose a flammability concern if instantaneously released to the vapor space. These are estimated as 0.217 mg/L, 0.227 mg/L, and 0.417 mg/L, respectively. Given the rate of formation of dimethyl mercury, the soluble mercury concentration required to pose a flammability concern is orders of magnitude greater than any sample results. This report also shows that these concentrations are not reached in DWPF operations.
- Based on available literature data for dimethyl mercury, the incoming sludge and salt streams were evaluated for their flammability impact on the DWPF process. At this time, no flammability impacts to the processing of these streams have been identified.
- Based upon the review of the available off-gas data from the simulant testing and reducing chemistry of the SRAT cycle (which is not favorable to dimethyl mercury formation), there is no evidence of the formation of dimethyl mercury during any part of the SRAT process. However, no sludge slurry samples were analyzed to confirm whether or not dimethyl mercury was present.
- Based on available data sets, it can be assumed that no measurable dimethyl mercury is currently present in the recycle streams at DWPF.

- The conclusions drawn in this report for the fate of dimethyl mercury in DWPF are based on the simulant studies and available data sets. Due to the number of data sets, it should be noted that the collection of more data could change the conclusions drawn in this report.

5.0 RECOMMENDATIONS

- Sampling of key DWPF process streams should be completed as currently planned for mercury speciation at Eurofins Laboratory.

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Appendix A

Dimethyl Mercury (DMHG) Rate for use in SRAT Calculations at High pH (based on Frontier DMHg formation rate in caustic solution)

First order reactions are defined generically by:

$$A \xrightarrow{yields} B \qquad \text{Equation (A-1)}$$

First Order Rate constant is defined in Equation (A-1).

$$-r_A = kA_A \qquad \text{Equation (A-2)}^{a}$$

Where:

$-r_A$ = rate of reaction for disappearance of reactant A per unit time (seconds) or $-\frac{dA}{dt}$

k = reaction rate or rate constant (1/s) for the forward reaction

A_A = Reactant concentration

Equation A-1 can then be re-arranged and integrated on both sides to produce the final integrated rate equation. The following steps below demonstrate this.

$$\frac{-dA}{dt} = kA \qquad \text{Equation (A-3)}$$

$$\frac{dA}{A} = -kdt \qquad \text{Equation (A-4)}$$

$$\int_{A_0}^{A_t} \frac{dA}{A} = \int_0^t -kdt \qquad \text{Equation (A-5)}$$

$$lnA_t - \ln A_0 = -k(t-0) \qquad \text{Equation (A-6)}$$

$$ln\frac{A_t}{A_0} = -kt \qquad \text{Equation (A-7)}$$

$$-ln\frac{A_t}{A_0} = kt \qquad \text{Equation (A-8)}$$

$$k = -ln\frac{A_t}{A_0} * 1/t \qquad \text{Equation (A-8)}$$

If solving for time,

$$t = -ln\frac{A_t}{A_0} * 1/k \qquad \text{Equation (A-9)}$$

The data used in the Excel Spreadsheet in Figure A- 1 are presented in g mole/L of dimethyl mercury. These data are converted to the molar concentration of reactant at time t (A_t). The highest rate of generation data was selected from the raw data presented in Reference 7.

[a] R.H. Perry and C.H. Chilton, "Chemical Engineering Handbook, 5th Edition", Section 4, Pages 4-3 to 4-5, Copyright 1973.

DMHg rate for use in SRAT calculations at high pH (based on Frontier DMHg formation rate in caustic solution)

In SRNL-WHM-2004-00006, rate constants used all data in Frontier DMHg formation report.
Because of competing reactions, the previous rate constants may not be conservative for short reaction times.
Here, I used the All Organics case and formed more conservative first order rate constants
Created conservative rate constants based on the most extreme (large) single points in the formation data.
Used data points that gave the largest rates at each temperature.

M.W. Of Hg =	200.59	g/gmole
M.W. of DMHg =	230.66	g/gmole
1g =	1000	mg
1ug =	1000	mg

	initial soluble mercury:		[A]o =	10 mg/L=	4.985E-05	g mol/L

T (deg C)	time (hr)	time (s)	[DMHg] (μg/L)	[DMHg] (g mol/L)	[A] (g mol/L)	-ln(A/Ao)	k (1/s)
39.1	600	2160000	19.01	8.24E-08	4.98E-05	1.65E-03	7.660E-10
60	144	518400	32.66	1.42E-07	4.97E-05	2.84E-03	5.487E-09
81	144	518400	69.41	3.01E-07	4.96E-05	6.05E-03	1.168E-08

T (deg C)	T (K)	1/T (1/K)	1/RT (mol/kJ)	k (1/s)	ln(k)
39.1	312.25	0.003203	0.385181654	7.66E-10	-20.9898
60	333.15	0.003002	0.361017474	5.49E-09	-19.0209
81	354.15	0.002824	0.339610254	1.17E-08	-18.2655

Ea = -60.246 kJ/mol

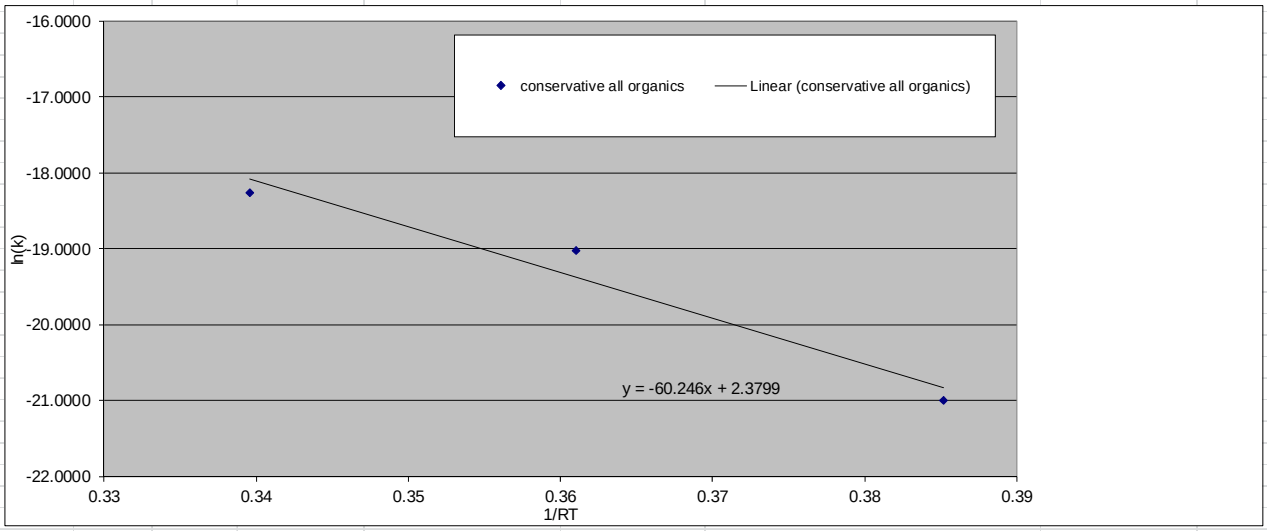

Figure A- 1 – Copy of Excel Spreadsheet Used to Calculate New First Order Rate Constants

Once the first order rate constants are determined, the Arrhenius equation[a] can be applied to determine the temperature dependence of reaction rates via plotting LN(k) versus (1/RT). Equation A-9 provides the Arrhenius equation.

$$k = A * e^{-E_a/RT} \qquad \text{Equation (A-10)}$$

Where:
k = rate constant (1/s)
A= Frequency factor (1/s)
E_a = Activation Energy (kJ/g mole)
R = Gas Constant = 0.0083144 (kJ/(K*g mole))
T = Temperature in Kelvin

Taking the *LN*:

$LN(k) = LN(A)+(-E_a/RT)$

The plot provided in Figure A- 1 shows the fit of the new and old data, which mathematically can be represented by y=b+ax, where, y is equal to the rate constant, b is equal to the intercept (*A)*, a is equal to the slope of the line (E_a) and x is equal to (*1/RT*). The fit of the new data produces a new equation of LN(*k*)= -60.246*(*1/RT*)+2.3799 in Figure A- 1. This was then used to generate the table below. An example for 25˚C is provided below.

LN(k)= -60.246(1/(0.0083144*(25+273)))+2.3799*
LN(k) = -2.194E+01
k = 2.976E-10 *1/s*

The production of dimethyl mercury is a function of starting mercury concentration, thus it must be multiplied by the mercury concentration in mg/L.

Table A- 1 - Table of Rate Constants as a Function Of Temperature - Formation

T (deg C)	T (K)	1/T (1/K)	1/RT (mol/kJ)	ln(k)	k (1/s)
25	298	3.356E-03	4.036E-01	-2.194E+01	2.976E-10
28*	301	3.322E-03	3.996E-01	-2.169E+01	3.792E-10
30	303	3.300E-03	3.969E-01	-2.153E+01	4.445E-10
35	308	3.247E-03	3.905E-01	-2.115E+01	6.553E-10
40	313	3.195E-03	3.843E-01	-2.077E+01	9.542E-10
45	318	3.145E-03	3.782E-01	-2.041E+01	1.373E-09
50	323	3.096E-03	3.724E-01	-2.005E+01	1.954E-09
55	328	3.049E-03	3.667E-01	-1.971E+01	2.751E-09
60	333	3.003E-03	3.612E-01	-1.938E+01	3.832E-09
65	338	2.959E-03	3.558E-01	-1.906E+01	5.288E-09
70	343	2.915E-03	3.507E-01	-1.875E+01	7.228E-09
75	348	2.874E-03	3.456E-01	-1.844E+01	9.791E-09
80	353	2.833E-03	3.407E-01	-1.815E+01	1.315E-08
85	358	2.793E-03	3.360E-01	-1.786E+01	1.751E-08
90	363	2.755E-03	3.313E-01	-1.758E+01	2.315E-08
91	364	2.747E-03	3.304E-01	-1.753E+01	2.445E-08
92	365	2.740E-03	3.295E-01	-1.747E+01	2.582E-08
93	366	2.732E-03	3.286E-01	-1.742E+01	2.726E-08
94	367	2.725E-03	3.277E-01	-1.736E+01	2.877E-08
95	368	2.717E-03	3.268E-01	-1.731E+01	3.036E-08
96	369	2.710E-03	3.259E-01	-1.726E+01	3.202E-08
97	370	2.703E-03	3.251E-01	-1.720E+01	3.377E-08
98	371	2.695E-03	3.242E-01	-1.715E+01	3.560E-08
99	372	2.688E-03	3.233E-01	-1.710E+01	3.752E-08
100	373	2.681E-03	3.224E-01	-1.705E+01	3.953E-08
101	374	2.674E-03	3.216E-01	-1.699E+01	4.163E-08
102	375	2.667E-03	3.207E-01	-1.694E+01	4.384E-08
103	376	2.660E-03	3.199E-01	-1.689E+01	4.615E-08
104	377	2.653E-03	3.190E-01	-1.684E+01	4.857E-08
105	378	2.646E-03	3.182E-01	-1.679E+01	5.111E-08

*Added for Tank 50-H Calculation

Appendix B

Evaluation of Sample Results Reported by Eurofins Laboratory for Tk50-H 2Q15

Table B- 1 contains the results of recent measurements of the dimethyl mercury content in Tanks 50-H, 21-H, and 22-H. Thus far, the highest dimethyl mercury measurement in the SRS tank farm supernate has been 0.0235 mg/L in the Tank 50 2Q15 sample. These data along with the total mercury found in the supernate for Tanks 50-H, 21-H, and 22-H are also presented below in Table B- 1.

Table B- 1- Summary of Mercury and Dimethyl Mercury Measurements in SRS Tank Farm Supernate Samples (References 2, 3, and 6)

Sample	Total Hg (mg/L)	% Relative Standard Deviation of Dimethyl Mercury	Dimethyl Hg (mg/L)	% Relative Standard Deviation of Dimethyl Mercury
Tk21-H	120*	±5.4	0.0156	±5.6
Tk22-H	119	±2.9	ND	N/A
Tk50-H 4Q14	78.7	±2.1	ND	N/A
Tk50-H 1Q15	126	±10	0.00219	±12
Tk50-H 2Q15	97.7	±5.0	0.0235	±13

* Used soluble mercury for Tank 21-H, because it was larger than total mercury, ND - non detect

In order to understand the time element and if dimethyl mercury is being released as published in Reference 9, the sample data for Tk50-H 2Q15 was reviewed. Prior to pulling samples from Tank 50-H, it is required that the slurry pump(s) be run for a set period of time. Per sample request CST-2015-00033, the slurry pump was to be run for a minimum of 4.4 hours. Per the control room log on 4/7/2015, the E-1 slurry pump was run for approximately 8 hours prior to the sample pull on 4/7/2015. Although no power calculation has been completed, slurry pumps typically operate at 1300 RPM to 2200 RPM and have a set time requirement to ensure the tank is uniformly mixed based on how many pumps are operated[b]. Since one pump was operated, the minimum time for operation is 4.5 hours[b]. The sample pull was completed within one hour of shutting down the slurry pump. The sample was pulled and the headspace above the sample was minimized. The sample was received at SRNL on 4/7/2015. The samples were then prepared and then refrigerated prior to final dilution. The samples were diluted and then shipped on 4/15/2015 and received by Eurofins on 4/17/2015. In order to use the adjusted rate constants to calculate total time, the temperature of the sample must be considered. The temperature of Tank 50-H was plotted in PI Process Book to look at the temperature of the tank during the sampling activity. Several thermocouples are installed at different levels in the tank and they can be seen in Figure B- 1. The highest temperature observed is ~28˚C. Using the new first order rate constants in Appendix A and the reported mercury concentration, a rate of formation can be calculated for dimethyl mercury as a function of time. The total time can then be calculated using this rate and the reported sample value for Tk50-H 2Q15 in Table B- 1 from Eurofins Laboratory. The time element can provide insight into the volatilization of dimethyl mercury from liquid in Tank 50-H which should support the observations in Reference 9. Using the inputs below, the total time has been calculated.

[b]R. Young, "Prestart Operations" Manual SW11.1-WTS(50-Z)-1, Procedure 4.1, Rev. 16 October 21, 2014

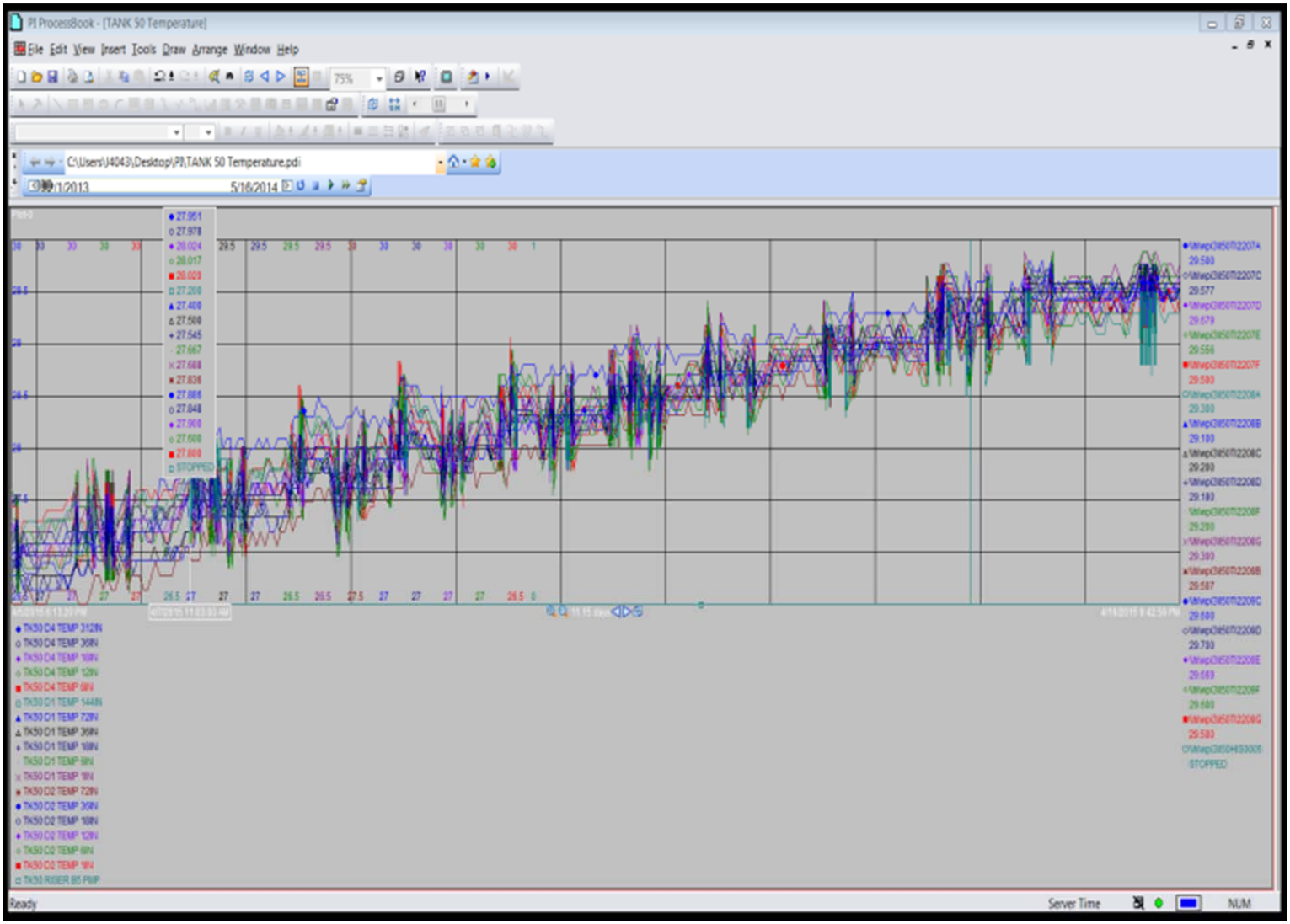

Figure B- 1 – Temperature Profile During Sample Pull from Tank 50-H

Calculation for Total Time of Dimethyl Mercury Production Based on Rate Constants

<u>Inputs to Calculation:</u>

Adjusted Tk50-H 2Q15 Dimethyl Mercury Concentration	= 0.0235mg/L or 1.019E-07 g mole/L (Reference 6)
k constant at 28˚C (see Appendix A)	= 3.792E-10 1/s
Tank 50-H Soluble Hg Concentration(includes 2 standard deviations)	= 97.7 +97.7*2*5/100 = 107.5 mg/L or 5.359E-04 gmole/L

(Appendix A, Equation A-9) = $t = -ln\frac{A_t}{A_0} * 1/k$

$$t = -\ln\left(\frac{(5.359E-04-1.019E-07)\frac{gmole}{L*s}}{5.359E-04\,\frac{gmole}{L*s}}\right) \times \frac{sec}{3.792E-10} \times \frac{1min}{60sec} \times \frac{1hr}{60min} \times \frac{1day}{24hr} = 5.80\ days$$

Approximately 10 days passed from the time the sample was pulled from Tank 50-H to the sample shipment to Eurofins Laboratory[6]. This time is longer than the calculated 5.8 days. The reasons for this could be the use of adjusted rates provided in Appendix A and/or limiting the exposure of the samples to room temperatures and light by refrigerating (2˚C to 4˚C) the samples in the dark the majority of the time. The refrigeration of the samples slows the kinetics related to formation down, but by how much is currently unknown. It should also be noted that the calculated gram moles per liter per second for dimethyl mercury is a very small number and when subtracted from the initial mercury concentration introduces uncertainty to the calculation. Despite these uncertainties, the projected dimethyl mercury concentration [3.52E-02 mg/L (3.792E-10 $\frac{1}{s} * \frac{60s}{1min} * \frac{60min}{1hr} * \frac{24hr}{1day} * 10\ days * 107.5\ mg/L = \frac{0.0352mg}{L}$)]of the sample held at 28˚C for 10 days compares well with the Eurofins Laboratory result. Based on the sample data and assumptions made in this report, it indicates that essentially all of the dimethyl mercury was released upon the ~8 hours of agitation in Tank 50-H. This qualitative data analysis supports the literature study findings in Reference 9 and supports the argument that tanks that are agitated and ventilated release dimethyl mercury readily to the vapor space. However, it should be assumed that the rate of formation would continue as long as reactants are available. Based on this, it should be assumed that the rate of formation is the rate released to the vapor space for agitated vessels.

Appendix C

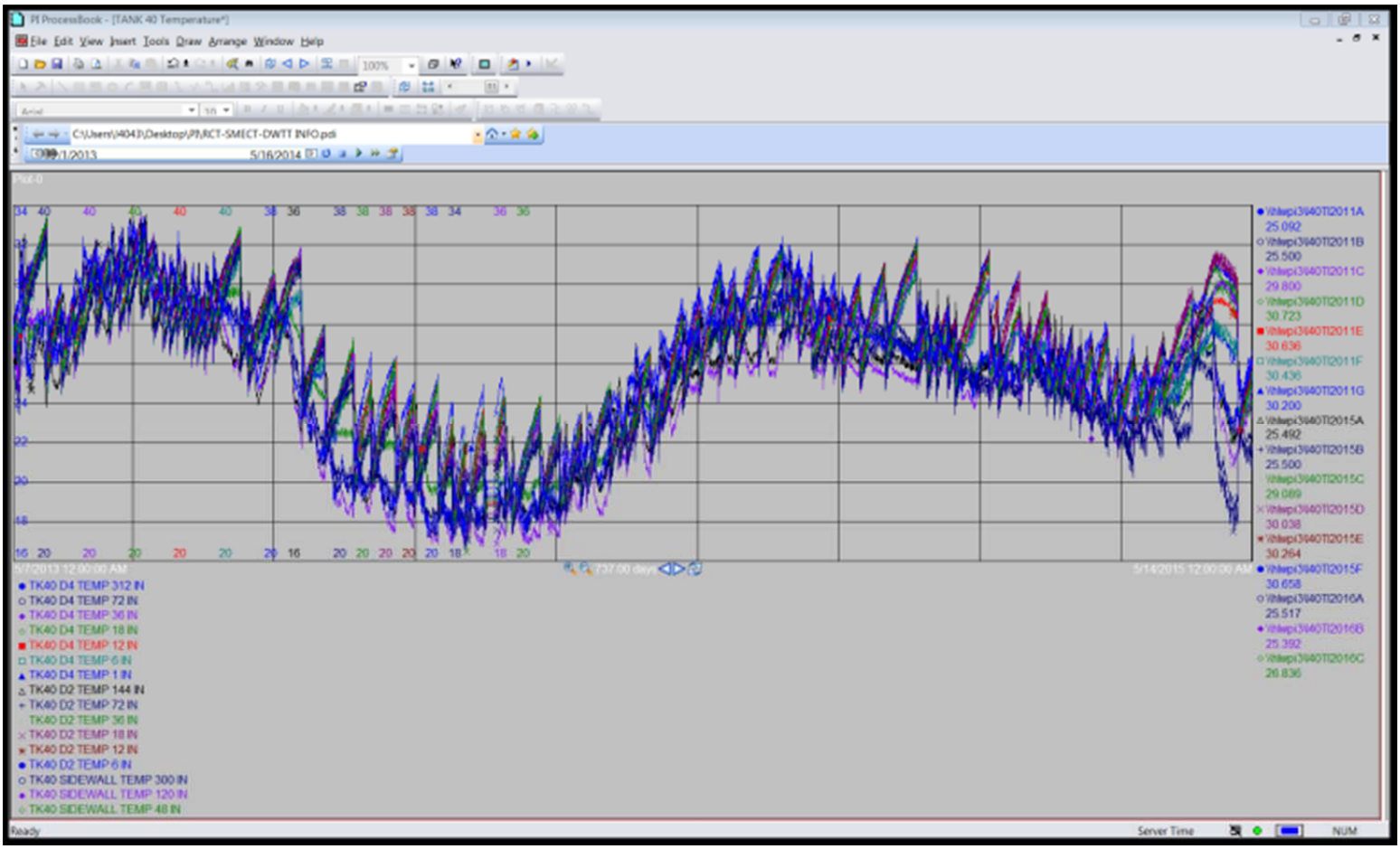

Figure C - 1- Tank 40-H Temperature at Different Elevations in the Tank from 5/07/2013 to 5/14/2015

Appendix D

Reviews and Approvals

Prepared by:

Helen Boyd

H. P. Boyd, DWPF Process and Regulatory Engineering

Date: 5/28/15

Technical review by:

A. T. Clare, DWPF Process and Regulatory Engineering

Date: 5/28/15

Verification Method: Document Review

Purpose

This appendix calculates the maximum concentration of dimethyl mercury in the liquid that the SEFT and PRFT purges can accommodate upon instantaneous release. It should be noted that references for this Appendix are contained within the Appendix.

Inputs

Dimethyl Mercury LFL at 25°C	2.5	vol%	Ref. 1
Methane Heat of Combustion	212.79	kcal/mol	Ref. 2
Maximum SEFT and PRFT Temperature (At and Above RTDs)	42.4	°C	Ref. 3 and 4
Maximum SEFT and PRFT Temperature (Below RTDs)	105	°C	Ref. 3 and 4
Minimum SEFT and PRFT Pressure	0.9263	atm	Ref. 3 and 4
SEFT Purge Flow Rate at 21.1°C	1.1	scfm	Ref. 5
PRFT Purge Flow Rate at 21.1°C	1.6	scfm	Ref. 5
Purge Temp	21.1	°C	Ref. 3 and 4
Purge Pressure	1	atm	Ref. 3 and 4
SEFT Hydrogen Generation at 42.4°C	0.00512	cfm	Ref. 3
PRFT Hydrogen Generation at 42.4°C	0.00722	cfm	Ref. 4
SEFT Isopar L Contribution to CLFL	0.488	N/A	Ref. 3
PRFT Isopar L Contribution to CLFL	0.488	N/A	Ref. 4
LFL Hydrogen at 105°C	3.648	vol%	Ref. 3
LFL of Hydrogen at 42.4°C	3.923	vol%	Ref. 3
SEFT Vapor Space	1343	gal	Ref. 3
PRFT Vapor Space	690	gal	Ref. 4
Molecular Weight of Dimethyl Mercury	230.66	g/mol	Ref. 1
Maximum SEFT Liquid Volume	10657	gal	Ref. 3
Maximum PRFT Liquid Volume	8310	gal	Ref. 4
SEFT RTD Liquid Level	1800	gal	Ref. 3
PRFT RTD Liquid Level	600	gal	Ref. 4

Assumptions

1. Assumption: Flammable gases (i.e., hydrogen, Isopar L, and dimethyl mercury) are well mixed in the bulk vapor space.

   Basis for Why this Assumption is Valid: Hydrogen is a gas that diffuses rapidly. There are no pockets in the SEFT or PRFT that can trap a significant amount of hydrogen. Based on engineering judgment, hydrogen is well mixed in the SEFT and PRFT vapor space.

   The convective flux analysis shows that even a 0.1°C difference in temperature between the liquid surface and the vapor space, thermal convection will sufficiently mix the vapor space and prevent the formation of a flammable layer of Isopar L (Shown in Reference 3 and 4).

   Given that such a small difference in temperature (0.1°C) is adequate to provide mixing of the Isopar L, the dimethyl mercury is similarly assumed to be sufficiently mixed by thermal convection.

   Sensitivity to this Assumption: The calculation is sensitive to this assumption. If flammables did not diffuse rapidly, a local concentration above LFL could be reached.

Additional Text: None.

2. Assumption: The release rate of hydrogen from liquid is equal to its generation rate.

   Basis for Why this Assumption is Valid: Excluding the possibility of trapped hydrogen (see Assumption 5), this is the conservative assumption. This assumption maximizes the rate of release of hydrogen into the vapor space and, therefore, leads to maximum purge rates.
   Sensitivity to this Assumption: A reduction in the release rate would produce more favorable results.
   Additional Text: None.

3. Assumption: The gases in the vessel behave ideally.

   Basis for Why this Assumption is Valid: The pressure in the vessel is near atmospheric and temperature is significantly higher than the critical temperature of air (-140˚C). Therefore air behaves ideally at vessel conditions. The concentration of hydrogen, Isopar L, and dimethyl mercury is small therefore they also behave ideally at vessel conditions.
   Sensitivity to this Assumption: A non-ideal behavior by gases would require use of non-ideal equation of state for calculations.
   Additional Text: None.

4. Assumption: The ventilation factor (K) is 1.0 for hydrogen at all liquid levels when the purge is equal to or less than 194 scfm in the SEFT and equal to or less than 153 scfm in the PRFT.

   Basis for Why this Assumption is Valid: The K value is the fraction of the flow at the outlet that can be attributed to the bulk composition. This factor indicates the presence or not of a "short circuit" in the design of the ventilation system by which ventilation flow may enter and exit the vessel without mixing with the atmosphere of the vessel. The evaluation to determine the maximum allowed purge flow in the SEFT or PRFT while maintaining K equal to 1 is included in Appendix D of References 3 and 4.

   Sensitivity to this Assumption: If the purge rate exceeds 194 scfm for the SEFT or 153 for the PRFT, then K would be reduced. The minimum required purge rate calculation assumes a K=1; since the minimum required purge rate is below 194 scfm for the SEFT and 153 for the PRFT, it is a valid assumption. Purge rates are inversely proportional to the value of K and are therefore very sensitive to this assumption.

   Additional Text: None.

5. Assumption: The SEFT and PRFT contain insufficient solids to retain a significant volume of hydrogen and therefore a release of retained hydrogen is not considered.

   Basis for Why this Assumption is Valid: Reference 6 determined the maximum volume of hydrogen retaining solids allowed in the SEFT to be 434.4 gal and 289.6 gal in the PRFT. This was compared to the expected volume of 115 gal (SEFT) and 214 gal (PRFT) and it was concluded that the SEFT and PRFT contain insufficient solids to retain a significant volume of hydrogen. The presence of dimethyl mercury would slightly reduce the allowed solids. However; the significant difference between the expected volume and the allowed volume would easily accommodate this reduction.

   Sensitivity to this Assumption: If excessive solids accumulated in the SEFT or PRFT, enough hydrogen could be retained to cause the vapor space to reach LFL once released.

   Additional Text: None

6. Assumption: The Heat of Combustion for Methane is appropriate to use in the temperature adjustment of the dimethyl mercury LFL.

Basis for Why this Assumption is Valid: Reference 1 utilizes the LFL of methane to conservatively calculate an LFL for dimethyl mercury. Therefore, adjusting the LFL by using the methane heat of combustion is appropriate.

Sensitivity to this Assumption: If the heat of combustion for dimethyl mercury were lower, the temperature adjusted LFL would be lower.

Additional Text: None

7. Assumption: This analysis assumes the hydrogen generation rate in the SEFT is based upon a blend of MST/Sludge Solids and Strip Effluent. A maximum MST/Sludge Solid volume of 4000 gallons is assumed to exist in the SEFT with the remainder of the waste up to the overflow volume (10657 gallons) being Strip Effluent.

   Basis for Why this Assumption is Valid: There is the potential for inadvertent transfers through a three way valve that would result in MST/Sludge Solids in the SEFT. Due to the slow rate of MST/Sludge Solid transfers to the Sludge Receipt and Adjustment Tank (SRAT) (normally less than 10 gpm) and the ability to compare tank levels between the SRAT, SEFT, and Precipitate Reactor Feed Tank (PRFT) during transfers, it is expected that an inadvertent transfer from the PRFT to the SEFT would be quickly detected and terminated. Thus 4000 gallons is believed to be an extremely conservative assumption of the maximum possible volume of MST/Sludge in the SEFT.
   Sensitivity to this Assumption: If there are more than 4000 gallons of MST/Sludge Solids in the SEFT, the hydrogen generation rate in the SEFT will be higher.
   Additional Text: This assumption is provided in Reference 3. At waste volumes greater than 4000 gallons in the SEFT, it is conservative to assume that there are 4000 gallons of MST/Sludge Solids in the tank since the waste stream has a higher radiolytic hydrogen generation rate than the Strip Effluent stream. At waste volumes less than or equal to 4000 gallons in the tank, the entire waste volume is conservatively assumed to be MST/Sludge Solids (4.87E-05 ft^3/hr/gal at 45°C) for hydrogen generation contributions while also conservatively assuming Isopar L and dimethyl mercury are present in the tank.

8. Assumption: Isopar L is present in the PRFT but the hydrogen generated is based only on the MST/Sludge Solids waste stream.

   Basis for Why this Assumption is Valid: Isopar L can be present in the PRFT due to leakage of Strip Effluent through the 3-way valve from the Strip Effluent Feed Tank (SEFT). However, since a majority of the waste in the PRFT is MST/Sludge Solids, which has a higher hydrogen generation rate, it is conservative to assume the hydrogen is generated from the waste volume only consisting of MST/Sludge Solids.
   Sensitivity to this Assumption: If Isopar L is not present in the PRFT, the purge flow rate would be lower.
   Additional Text: None.

Analytical Methods and Computations

SEFT Purge Calculations
The minimum required purges for the SEFT were calculated in Reference 5. This purge flow rate is used to back calculate the fraction of the CLFL from the hydrogen generation rates using the equations in Reference 3. The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen concentration from the allowable flammable contribution to the CLFL. This is converted into a vapor concentration using the minimum vapor space volume. Finally the vapor concentration is converted to a liquid concentration.

Because liquid levels in the SEFT less than the RTDs are possible, a sensitivity analysis calculating the maximum waste volume to remain less than 95% CLFL with purge is also included.

Dimethyl Mercury Temperature Corrected LFL

The dimethyl mercury LFL is 2.5 vol% at 25°C. The flammability of dimethyl mercury is dependent on temperature. The LFL decreases as the temperature increases. The impact can be determined by the Burgess Wheeler Equation (Ref. 7):

$$(1) \qquad LFL_T = LFL_{25°C} \times \left(1 - A(T - 25)\right)$$

where, LFL_T = LFL at temperature T, volume %

T = Temperature in Tank in °C

A = empirical coefficient.

The LFL can be corrected by the Burgess Wheeler Law by determining the necessary coefficient. The coefficient can be calculated from the heat of combustion of dimethyl mercury. However, because methane was used to determine the LFL, the methane heat of combustion is used to adjust the LFL (See Assumption 6). The equation for the empirical coefficient is (Ref. 7)

$$(2) \qquad A = \left[\!\left[\frac{0.75}{H_C \times LFL_{25°C}}\right]\!\right]$$

Where:

H_C = Heat of combustion of methane = 212.79 kcal/mol

Such that:

$$\left[\!\left[\frac{0.75}{212.79 \times 2.5}\right]\!\right] = 1.41E - 03$$

The dimethyl mercury LFL at various temperatures (e.g., 42.4°C and 105°C) is calculated using Equation 1 and the result from Equation 2:

$$LFL_{42.4°C} = 2.5 \times \left(1 - 1.41\text{E-}03 \times (42.4 - 25)\right) = 2.439\ vol\%$$

$$LFL_{105°C} = 2.5 \times \left(1 - 1.41\text{E-}03 \times (105 - 25)\right) = 2.218\ vol\%$$

Allowable Dimethyl Mercury Contribution to CLFL

The purge flow rate give in Reference 5 is given for a temperature of 21.1°C and a pressure of 1 atm. The flow rate is temperature and pressure corrected for SEFT conditions as follows:

$$(3) \qquad Q_{purge} = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

Where:

Q_{purge}= Volumetric flow rate at T_2 and P_2

Q_1= Volumetric flow rate at T_1 and P_1 = 1.1 scfm

P_1 = 1 atm

P_2 = 0.9263 atm

T_1 = 21.1 °C = 294.25 K

T_2 = 42.4 °C = 315.55 K

Such that:

$$Q_{purge} = 1.1 \times \frac{1}{0.9263} \times \frac{315.55}{294.25} = 1.27\ cfm$$

The total flow through the SEFT vapor space is then calculated by adding the purge flow to the flammable flow.

$$(4) \qquad Q_{vent} = Q_{purge} + Q_H$$

Where:

Q_{vent}= Total volumetric flow in the SEFT vapor space

Q_H= Hydrogen generation rate = 0.00512 cfm

Such that:

$$Q_{vent} = 1.27 + 0.00512 = 1.275\ cfm$$

The contribution of hydrogen to the CLFL is the calculated by taking the ratio of the hydrogen generation rate divided by its LFL and the total flow rate.

$$(5) \qquad CLFL_H = \frac{\frac{Q_H}{LFL}}{Q_{vent}}$$

Where:
$CLFL_H$= Contribution of hydrogen to the CLFL
LFL= LFL of hydrogen in the SEFT = 0.03923 ft^3 flammables/ft^3 vapor space
Such that:

$$CLFL_H = \frac{\frac{0.00512}{0.03923}}{1.275} = 0.103$$

The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen and Isopar L contribution to the CLFL from the maximum allowable combustible concentration. Because the SEFT has safety interlocks, NFPA 69 allows for the maximum combustible concentration in the tank vapor space to be limited to 60% of the CLFL of the mixture. Therefore the allowable dimethyl mercury contribution to the CLFL is calculated as follows:

$$(6) \qquad CLFL_{DMHg} = 0.6 - CLFL_H - CLFL_I$$

Where:
$CLFL_{DMHg}$ = Contribution of dimethyl mercury to the CLFL
$CLFL_I$= Contribution of Isopar L to the CLFL = 0.488
Such that:

$$CLFL_{DMHg} = 0.6 - 0.103 - 0.488 = 0.009$$

<u>Allowable Dimethyl Mercury Concentration in the SEFT Liquid</u>
The allowable dimethyl mercury contribution to the CLFL is equal to the ratio of the dimethyl mercury concentration to its LFL. Therefore the allowable dimethyl mercury concentration is calculated as follows:

$$(7) \qquad C_{v\ DMHg} = CLFL_{DMHg} \times LFL_{42.4}$$

Where:
$C_{v\ DMHg}$ = Allowable concentration of dimethyl mercury in the vapor space
Such that:

$$C_{v\ DMHg} = \frac{2.439}{100} \times 0.009 = 0.000219 ft^3 DMHg/ft^3\ vapor\ space$$

Using the volume of the SEFT vapor space the allowable volume of dimethyl mercury is calculated as:

$$(8) \qquad V_{v\ DMHg} = V_v \times C_{v\ DMHg}$$

Where:
$V_{v\ DMHg}$= Allowable volume of dimethyl mercury in the vapor space
V_v = SEFT Vapor Space = 1343 gal
Such that:

$$V_{v\ DMHg} = 1343 \times \frac{3.785L}{gal} \times 0.000219 = 1.11L$$

The molar volume of a gas at 0 °C and 1 atm is 22.414 L/mol. This is temperature and pressure corrected for SEFT conditions as follows:

$$(9) \qquad \frac{V_2}{n} = \frac{V_{STP}}{n} \times \frac{P_{STP}}{P_2} \times \frac{T_2}{T_{STP}}$$

Where:
$\frac{V_2}{n}$= Molar volume at T_2 and P_2
$\frac{V_{STP}}{n}$= Molar volume at T_{STP} and P_{STP} = 22.414 L/mol
P_{STP} = 1 atm
T_{STP} = 0 °C = 273.15 K
Such that:

$$\frac{V_2}{n} = 22.414 \times \frac{1}{0.9263} \times \frac{315.55}{273.15} = 27.95 L/mol$$

The gaseous volume can then be converted to a liquid mass by:

$$(10) \qquad m_{l\,DMHg} = V_{v\,DMHg} \times \frac{V_2}{n} \times MW$$

Where:
$m_{l\,DMHg}$= Mass of dimethyl mercury in the liquid
MW = Molecular weight of dimethyl mercury = 230.66 g/mol
Such that:

$$m_{l\,DMHg} = 1.11 \times \frac{1}{27.95} \times 230.66 = 9.16g$$

To convert to a liquid concentration the mass of dimethyl mercury is divided by the maximum liquid volume in the SEFT.

$$(11) \qquad C_{l\,DMHg} = \frac{m_{l\,DMHg}}{V_l}$$

Where:
$C_{l\,DMHg}$= Maximum allowable concentration of dimethyl mercury in the SEFT
V_l = Maximum SEFT liquid volume = 10657 gal
Such that:

$$C_{l\,DMHg} = \frac{9.16}{10657} \times \frac{1000mg}{g} \times \frac{gal}{3.785l} = 0.227mg/L$$

<u>Sensitivity Analysis</u>
Additional scope is to evaluate the volume of waste in the SEFT at which the vapor space is less than 95% CLFL, i.e., vessel flammability is not credible, at the maximum temperature of 105°C with purge operating. This is done by calculating the volume at which the following is true:

$$0.95 = \frac{X_H}{LFL_H} + \frac{X_I}{LFL_I} + \frac{X_D}{LFL_D}$$

Where:
X_H = the hydrogen equilibrium concentration in vapor space
X_I = the Isopar L concentration in vapor space
X_D = the dimethyl mercury concentration in vapor space
LFL_H = the LFL of hydrogen at 105°C = 3.648 vol%
LFL_I = the LFL of Isopar L at 105°C = 0.623 vol%
LFL_D = the LFL of dimethyl mercury at 105°C = 2.218 vol%

The first step is to determine the equilibrium hydrogen concentration using the purge rate of 1.1 scfm. The purge rate and the hydrogen generation rate in scfm are temperature corrected to 105°C and used in the following equation to calculate the hydrogen equilibrium concentration in the SEFT vapor space.

$$X_H^0 = \frac{Q_t}{K(Q_t + Q_p)}$$

where, K = the ventilation efficiency factor, 1 (Assumption 4)

Q_t = total hydrogen generation rate at tank temperature and pressure, cfm

Q_p = purge flow rate at tank temperature and pressure, cfm.

The hydrogen generation rate is based on the radiolytic generation rate from MST/Sludge Solids, 4.87E-05 ft^3/hr/gal at 45°C per Assumption 7. Therefore this rate is similarly adjusted for actual tank conditions and multiplied by the waste volume to obtain the hydrogen generation rate for the total waste in the tank.

For the Isopar L and dimethyl mercury contributions, the concentration in the vapor space is determined by:

$$X = \frac{c \times V_w}{V_{vs}}$$

Where:

X = the gaseous concentration of the species in the vapor space

c = the aqueous concentration of the species in the waste

V_w = the volume of the waste in the tank

V_{vs} = the volume of vapor space in the tank

This method conservatively assumes all of the dimethyl mercury and Isopar L in the waste evolves to the vapor space.

The CLFL at various waste volumes can then be calculated until the CLFL approached 95%. The volume at which the CLFL remains below 95% at equilibrium conditions in the SEFT is approximately 2830 gallons. Since the RTDs can read a minimum volume of 1800 gallons, it is not credible for the vessel to become flammable at waste volumes below the RTDs while the purge system is operating.

PRFT Analysis

The allowable dimethyl mercury concentration in the PRFT liquid and the volume at which the CLFL remains below 95% at equilibrium conditions in the SEFT were calculated using the same methodology as for the SEFT. The allowable dimethyl mercury concentration was calculated to be 0.217 mg/L. The volume at which the CLFL remains below 95% at equilibrium conditions in the SEFT is approximately 2160 gallons. Since the RTDs can read a minimum volume of 600 gallons, it is not credible for the vessel to become flammable at waste volumes below the RTDs while the purge system is operating.

Summary of Conclusions

The purge flow rates on the SEFT are such that dimethyl mercury could be present in concentrations up to 0.227 mg/L without presenting a flammability concern. The RTDs at 1800 gallons would remain adequate to protect the temperature of the vessel.

The purge flow rates on the PRFT are such that dimethyl mercury could be present in concentrations up to 0.217 mg/L without presenting a flammability concern. The RTDs at 600 gallons would remain adequate to protect the temperature of the vessel.

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Appendix E

Reviews and Approvals

Prepared by:

Helen Boyd
H. P. Boyd, DWPF Process and Regulatory Engineering

Date: 5/28/15

Technical review by:

A. T. Clare, DWPF Process and Regulatory Engineering
Verification Method: Document Review

Date: 5/28/15

Purpose

This appendix calculates the maximum concentration of dimethyl mercury in the liquid that the SRAT purge can accommodate upon instantaneous release. It should be noted that references for this Appendix are contained within the Appendix.

Inputs

Dimethyl Mercury LFL at 25°C	2.5	vol%	Ref. 1
Methane Heat of Combustion	212.79	kcal/mol	Ref. 2
Maximum SRAT Temperature	105	°C	Ref. 3
Minimum SRAT Pressure	0.9263	atm	Ref. 3
SRAT Purge Flow Rate at 21.1°C	186	scfm	Ref. 4
Purge Temp	21.1	°C	Ref. 3
Purge Pressure	1	atm	Ref. 3
SRAT Hydrogen Generation at 105°C	317.8	cfh	Ref. 3
SRAT Isopar L Generation at 105°C	2.01	cfh	Ref. 3
LFL Hydrogen at 105°C	3.648	vol%	Ref. 3
LFL of Isopar L at 105°C	0.623	vol%	Ref. 3
CLFL of Hydrogen and Isopar L in the SRAT	0.0354	ft^3/ft^3 vapor space	Ref. 3
SRAT Vapor Space	143.3	ft^3	Ref. 3
Molecular Weight of Dimethyl Mercury	230.66	g/mol	Ref. 1
Maximum SRAT Liquid Volume	10928	gal	Ref. 3

Assumptions

1. Assumption: Flammable gases (i.e., hydrogen, Isopar L, and dimethyl mercury) are well mixed in the bulk vapor space.

   Basis for Why this Assumption is Valid: Hydrogen is a gas that diffuses rapidly. There are no pockets in the SRAT that can trap a significant amount of hydrogen. Based on engineering judgment, hydrogen is well mixed in the SRAT vapor space.

   The convective flux analysis shows that even a 0.1°C difference in temperature between the liquid surface and the vapor space, thermal convection will sufficiently mix the vapor space and prevent the formation of a flammable layer of Isopar L (Shown in Reference 3).

   Given that such a small difference in temperature (0.1°C) is adequate to provide mixing of the Isopar L, the dimethyl mercury is similarly assumed to be sufficiently mixed by thermal convection.

   Sensitivity to this Assumption: The calculation is sensitive to this assumption. If flammables did not diffuse rapidly, a local concentration above LFL could be reached.

   Additional Text: None.

2. Assumption: The release rate of hydrogen from liquid is equal to its generation rate.

   Basis for Why this Assumption is Valid: Excluding the possibility of trapped hydrogen (see Assumption 5), this is the conservative assumption. This assumption maximizes the rate of release of hydrogen into the vapor space and, therefore, leads to maximum purge rates.

   Sensitivity to this Assumption: A reduction in the release rate would produce more favorable results.

   Additional Text: None.

3. Assumption: The gases in the vessel behave ideally.

   Basis for Why this Assumption is Valid: The pressure in the vessel is near atmospheric and temperature is significantly higher than the critical temperature of air (-140˚C). Therefore air behaves ideally at vessel conditions. The concentration of hydrogen, Isopar L, and dimethyl mercury is small therefore they also behave ideally at vessel conditions.
   Sensitivity to this Assumption: A non-ideal behavior by gases would require use of non-ideal equation of state for calculations.
   Additional Text: None.

4. Assumption: The ventilation factor (K) is 1.0 for hydrogen at all liquid levels when the purge is equal to or less than 320 scfm.

   Basis for Why this Assumption is Valid: The K value is the fraction of the flow at the outlet that can be attributed to the bulk composition. This factor indicates the presence or not of a "short circuit" in the design of the ventilation system by which ventilation flow may enter and exit the vessel without mixing with the atmosphere of the vessel. The evaluation to determine the maximum allowed purge flow in the SRAT while maintaining K equal to 1 is included in Appendix D of Reference 3.

   Sensitivity to this Assumption: If the purge rate exceeds 320 scfm, then K would be reduced. The minimum required purge rate calculation assumes a K=1; since the minimum required purge rate is below 320 scfm, it is a valid assumption. Purge rates are inversely proportional to the value of K and are therefore very sensitive to this assumption.

   Additional Text: None.

5. Assumption: Retained hydrogen is not addressed in this calculation.

   Basis for Why this Assumption is Valid: Retained hydrogen is not currently addressed in the DWPF Safety Analysis. A PISA (Reference 5) was issued to address this issue within CPC vessels, including the SRAT. The compensatory measures include prohibition of starting a stopped agitator without performing an engineering evaluation to determine that the release of retained gas will not exceed 95% CLFL. Because the evaluation is performed on a case by case basis, trapped hydrogen is not evaluated here. Additionally, data from Reference 6 suggests accumulation of hydrogen in the SRAT liquid is a very slow process. During normal operations agitators are not stopped for significant periods of time.

   Sensitivity to this Assumption: The compensatory measures are in place to ensure the flammable concentration in the vapor space remains less than 95% CLFL following agitator restart.

   Additional Text: None.

6. Assumption: The Heat of Combustion for Methane is appropriate to use in the temperature adjustment of the dimethyl mercury LFL.

   Basis for Why this Assumption is Valid: Reference 1 utilizes the LFL of methane to conservatively calculate an LFL for dimethyl mercury. Therefore, adjusting the LFL by using the methane heat of combustion is appropriate.

   Sensitivity to this Assumption: If the heat of combustion for dimethyl mercury were lower, the temperature adjusted LFL would be lower.

   Additional Text: None

Analytical Methods and Computations

Purge Calculations

The minimum required purges for the SRAT were calculated in Reference 4. This purge flow rate is used to back calculate the hydrogen and Isopar L contribution to the CLFL using the equations in Reference 3. The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen concentration from the allowable flammable contribution to the CLFL. This is converted into a vapor concentration using the minimum vapor space volume. Finally the vapor concentration is converted to a liquid concentration.

Dimethyl Mercury Temperature Corrected LFL

The dimethyl mercury LFL is 2.5 vol% at 25°C. The flammability of dimethyl mercury is dependent on temperature, the LFL decreases as the temperature increases. The impact can be determined by the Burgess Wheeler Equation (Ref 7):

$$(1) \qquad LFL_T = LFL_{25°C} \times \left(1 - A(T - 25)\right)$$

Where:

LFL_T = LFL at temperature T, volume %

T = Temperature in Tank in °C

A = empirical coefficient.

The LFL can be corrected by the Burgess Wheeler Law by determining the necessary coefficient. The coefficient can be calculated from the heat of combustion of dimethyl mercury. However, because methane was used to determine the LFL, the methane heat of combustion is used to adjust the LFL (See Assumption 6). The equation for the empirical coefficient is (Ref. 7):

$$(2) \qquad A = \left[\!\left[\frac{0.75}{H_C \times LFL_{25°C}}\right]\!\right]$$

Where:

H_C = Heat of combustion of methane = 212.79 kcal/mol

Such that:

$$\left[\!\left[\frac{0.75}{212.79 \times 2.5}\right]\!\right] = 1.41E - 03$$

The dimethyl mercury LFL at various temperatures (e.g., 105°C) is calculated using Equation 1 and the result from Equation 2:

$$LFL_{105°C} = 2.5 \times \left(1 - 1.41\text{E-}03 \times (105 - 25)\right) = 2.218\ vol\%$$

Allowable Dimethyl Mercury Contribution to CLFL

The purge flow rate give in Reference 4 is given for a temperature of 21.1°C and a pressure of 1 atm. The flow rate is temperature and pressure corrected for SRAT conditions as follows:

$$(3) \qquad Q_{purge} = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

Where:

Q_{purge}= Volumetric flow rate at T_2 and P_2

Q_1= Volumetric flow rate at T_1 and P_1 = 186 scfm

P_1 = 1 atm

P_2 = 0.9263 atm

T_1 = 21.1 °C = 294.25 K

T_2 = 105 °C = 378.15 K

Such that:

$$Q_{purge} = 186 \times \frac{1}{0.9263} \times \frac{378.15}{294.25} = 258.05\ cfm$$

The total flow through the SRAT vapor space is then calculated by adding the purge flow to the flammable flow.

(4) $$Q_{vent} = Q_{purge} + Q_H + Q_{Iso}$$

Where:
Q_{vent}= Total volumetric flow in the SRAT vapor space
Q_H= Hydrogen generation rate = 317.8 cfh = 5.30 cfm
Q_{Iso}= Isopar L generation rate = 2.01 cfh = 0.0335 cfm
Such that:

$$Q_{vent} = 258.05 + 5.30 + 0.0335 = 263.38\ cfm$$

The contribution of these flammables to the CLFL is the calculated by taking the ratio of the flammable flow rate divided by the CLFL and the total flow rate.

(5) $$CLFL_F = \frac{\frac{Q_H + Q_{Iso}}{CLFL}}{Q_{vent}}$$

Where:
$CLFL_F$= Contribution of Isopar L and Hydrogen to the CLFL
CLFL= CLFL of hydrogen and Isopar L in the SRAT = 0.0354 ft^3 flammables/ft^3 vapor space
Such that:

$$CLFL_F = \frac{\frac{5.30 + 0.0335}{0.0354}}{263.38} = 0.572$$

The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen and Isopar L contribution to the CLFL from the maximum allowable combustible concentration. Because the SRAT has Gas Chromatographs (GCs) and safety interlocks, NFPA 69 allows for the maximum combustible concentration in the tank vapor space to be limited to 60% of the CLFL of the mixture. Therefore the allowable dimethyl mercury contribution to the CLFL is calculated as follows:

(6) $$CLFL_{DMHg} = 0.6 - CLFL_F$$

Where:
$CLFL_{DMHg}$= Contribution of dimethyl mercury to the CLFL
Such that:

$$CLFL_{DMHg} = 0.6 - 0.572 = 0.028$$

<u>Allowable Dimethyl Mercury Concentration in the SRAT Liquid</u>
The allowable dimethyl mercury contribution to the CLFL is equal to the ratio of the dimethyl mercury concentration to its LFL. Therefore the allowable dimethyl mercury concentration is calculated as follows:

(7) $$C_{v\,DMHg} = CLFL_{DMHg} \times LFL_{105}$$

Where:
$C_{v\,DMHg}$= Allowable concentration of dimethyl mercury in the vapor space
Such that:

$$C_{v\,DMHg} = \frac{2.218}{100} \times 0.028 = 0.00062 ft^3 DMHg/ft^3 air$$

Using the volume of the SRAT vapor space the allowable volume of dimethyl mercury is calculated as:

(8) $$V_{v\,DMHg} = V_v \times C_{v\,DMHg}$$

Where:
$V_{v\,DMHg}$= Allowable volume of dimethyl mercury in the vapor space
V_v = SRAT Vapor Space = 143.3 ft^3
Such that:

$$V_{v\,DMHg} = 143.3 \times \frac{28.317L}{ft^3} \times 0.00062 = 2.51L$$

The molar volume of a gas at 0 °C and 1 atm is 22.414 L/mol. This is temperature and pressure corrected for SEFT conditions as follows:

$$\frac{V_2}{n} = \frac{V_{STP}}{n} \times \frac{P_{STP}}{P_2} \times \frac{T_2}{T_{STP}} \quad (9)$$

Where:
$\frac{V_2}{n}$= Molar volume at T_2 and P_2
$\frac{V_{STP}}{n}$= Molar volume at T_{STP} and P_{STP} = 22.414 L/mol
P_{STP} = 1 atm
T_{STP} = 0 °C = 273.15 K
Such that:

$$\frac{V_2}{n} = 22.414 \times \frac{1}{0.9263} \times \frac{378.15}{273.15} = 33.5L/mol$$

The gaseous volume can then be converted to a liquid mass by:

$$m_{l\,DMHg} = V_{v\,DMHg} \times \frac{V_2}{n} \times MW \quad (10)$$

Where:
$m_{l\,DMHg}$= Mass of dimethyl mercury in the liquid
MW = Molecular weight of dimethyl mercury = 230.66 g/mol
Such that:

$$m_{l\,DMHg} = 2.51 \times \frac{1}{33.5} \times 230.66 = 17.28g$$

To convert to a liquid concentration the mass of dimethyl mercury is divided by the maximum liquid volume in the SRAT.

$$C_{l\,DMHg} = \frac{m_{l\,DMHg}}{V_l} \quad (11)$$

Where:
$C_{l\,DMHg}$= Maximum allowable concentration of dimethyl mercury in the SRAT
V_l = Maximum SRAT liquid volume = 10928 gal
Such that:

$$C_{l\,DMHg} = \frac{17.28}{10928} \times \frac{1000mg}{g} \times \frac{gal}{3.785l} = 0.417mg/L$$

Summary of Conclusions
The purge flow rates on the SRAT are such that dimethyl mercury could be present in concentrations up to 0.417 mg/L without presenting a flammability concern.

References
1. Meraw, H. J. *Volatilization and Flammability Characteristics of Elemental and Organic Mercury*, X-ESR-S-00048, Rev. 1.
2. Domalski, E. S. *Selected Values of Heats of Combustion and Heats of Formation of Organic Compounds Containing the Elements C, H, N, O, P, and S*, Journal of Physical and Chemical Reference Data Vol. 1, No. 2, 1972.
3. Riddick, E. F. *Purge Requirements for the Sludge Receipt and Adjustment Tank*, X-CLC-S-00308, Rev. 1.

4. Riddick, E. M. *Determination of TSR Setpoints for CPC Nitrogen System*, M-CLC-S-00818. Rev. 3.

5. *Retained Hydrogen in DWPF Vessels*, PI-2014-0013.

6. Boyd, H. P. *Quiescent Times for Vessels in the Chemical Process Cell*, X-ESR-S-00247, Rev. 0.

7. Kuchta, J. M. *Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel Related Industries-A Manual*, Bureau of Mines Bulletin 680, U.S. Department of the Interior, Bureau of Mines, Washington DC, 1985.

Appendix F

Reviews and Approvals

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Verification Method: Document Review

Purpose

This appendix calculates the maximum concentration of dimethyl mercury in the Transfer Line that the SEFT purge can accommodate upon instantaneous release. It should be noted that references for this Appendix are contained within the Appendix.

Inputs

Dimethyl Mercury LFL at 25°C	2.5	vol%	Ref. 1
Methane Heat of Combustion	212.79	kcal/mol	Ref. 2
Maximum SEFT Temperature (At and Above RTDs)	42.4	°C	Ref. 3
Minimum SEFT Pressure	0.9263	atm	Ref. 3
SEFT Purge Flow Rate at 21.1°C	1.1	scfm	Ref. 4
Purge Temp	21.1	°C	Ref. 3
Purge Pressure	1	atm	Ref. 3
SEFT Hydrogen Generation at 42.4°C	0.00512	cfm	Ref. 3
SEFT Isopar L Contribution to CLFL	0.488	N/A	Ref. 3
LFL of Hydrogen at 42.4°C	3.923	vol%	Ref. 3
SEFT Vapor Space	1343	gal	Ref. 3
Molecular Weight of Dimethyl Mercury	230.66	g/mol	Ref. 1
SEFT Volume	12000	gal	Ref. 3
SEFT High Level Alarm	9600	gal	Ref. 5
MST Hydrogen Generation Rate at 45°C	4.87E-05	ft^3/hr/gal	Ref. 3
SE Hydrogen Generation Rate at 45°C	1.38E-05	ft^3/hr/gal	Ref. 3
Transfer Line Volume	1689	gal	Ref. 9

Assumptions

1. Assumption: Flammable gases (i.e., hydrogen, Isopar L, and dimethyl mercury) are well mixed in the bulk vapor space.

   Basis for Why this Assumption is Valid: Hydrogen is a gas that diffuses rapidly. There are no pockets in the SEFT that can trap a significant amount of hydrogen. Based on engineering judgment, hydrogen is well mixed in the SEFT vapor space.

   The convective flux analysis shows that even a 0.1°C difference in temperature between the liquid surface and the vapor space, thermal convection will sufficiently mix the vapor space and prevent the formation of a flammable layer of Isopar L (Shown in Reference 3).

   Given that such a small difference in temperature (0.1°C) is adequate to provide mixing of the Isopar L, the dimethyl mercury is similarly assumed to be sufficiently mixed by thermal convection.

   Sensitivity to this Assumption: The calculation is sensitive to this assumption. If flammables did not diffuse rapidly, a local concentration above LFL could be reached.

   Additional Text: None.

2. Assumption: The release rate of hydrogen from liquid is equal to its generation rate.

   Basis for Why this Assumption is Valid: Excluding the possibility of trapped hydrogen (see Assumption 5), this is the conservative assumption. This assumption maximizes the rate of release of hydrogen into the vapor space and, therefore, leads to maximum purge rates.

Sensitivity to this Assumption: A reduction in the release rate would produce more favorable results.
Additional Text: None.

3. Assumption: The gases in the vessel behave ideally.

   Basis for Why this Assumption is Valid: The pressure in the vessel is near atmospheric and temperature is significantly higher than the critical temperature of air (-140˚C). Therefore air behaves ideally at vessel conditions. The concentration of hydrogen, Isopar L, and dimethyl mercury is small therefore they also behave ideally at vessel conditions.
   Sensitivity to this Assumption: A non-ideal behavior by gases would require use of non-ideal equation of state for calculations.
   Additional Text: None.

4. Assumption: The ventilation factor (K) is 1.0 for hydrogen at all liquid levels when the purge is equal to or less than 194 scfm in the SEFT.

   Basis for Why this Assumption is Valid: The K value is the fraction of the flow at the outlet that can be attributed to the bulk composition. This factor indicates the presence or not of a "short circuit" in the design of the ventilation system by which ventilation flow may enter and exit the vessel without mixing with the atmosphere of the vessel. The evaluation to determine the maximum allowed purge flow in the SEFT while maintaining K equal to 1 is included in Appendix D of References 3.

   Sensitivity to this Assumption: If the purge rate exceeds 194 scfm for the SEFT, then K would be reduced. The minimum required purge rate calculation assumes a K=1; since the minimum required purge rate is below 194 scfm for the SEFT, it is a valid assumption. Purge rates are inversely proportional to the value of K and are therefore very sensitive to this assumption.

   Additional Text: None.

5. Assumption: The SEFT contains insufficient solids to retain a significant volume of hydrogen and therefore a release of retained hydrogen is not considered.

   Basis for Why this Assumption is Valid: Reference 6 determined the maximum volume of hydrogen retaining solids allowed in the SEFT to be 434.4 gal. This was compared to the expected volume of 115 gal and it was concluded that the SEFT contains insufficient solids to retain a significant volume of hydrogen. The presence of dimethyl mercury would slightly reduce the allowed solids. However; the significant difference between the expected volume and the allowed volume would easily accommodate this reduction.

   Sensitivity to this Assumption: If excessive solids accumulated in the SEFT, enough hydrogen could be retained to cause the vapor space to reach LFL once released.

   Additional Text: None

6. Assumption: The Heat of Combustion for Methane is appropriate to use in the temperature adjustment of the dimethyl mercury LFL.

   Basis for Why this Assumption is Valid: Reference 1 utilizes the LFL of methane to conservatively calculate an LFL for dimethyl mercury. Therefore, adjusting the LFL by using the methane heat of combustion is appropriate.

   Sensitivity to this Assumption: If the heat of combustion for dimethyl mercury were lower, the temperature adjusted LFL would be lower.

   Additional Text: None

7. Assumption: This analysis assumes the hydrogen generation rate in the SEFT is based upon a blend of MST/Sludge Solids and Strip Effluent. A maximum MST/Sludge Solid volume of 4000 gallons is assumed to exist in the SEFT with the remainder of the waste up to the overflow volume (10657 gallons) being Strip Effluent.

   Basis for Why this Assumption is Valid: There is the potential for inadvertent transfers through a three way valve that would result in MST/Sludge Solids in the SEFT. Due to the slow rate of MST/Sludge Solid transfers to the SRAT (normally less than 10 gpm) and the ability to compare tank levels between the SRAT, SEFT, and Precipitate Reactor Feed Tank (PRFT) during transfers, it is expected that an inadvertent transfer from the PRFT to the SEFT would be quickly detected and terminated. Thus 4000 gallons is believed to be an extremely conservative assumption of the maximum possible volume of MST/Sludge Solids in the SEFT.
   Sensitivity to this Assumption: If there are more than 4000 gallons of MST/Sludge Solids in the SEFT, the hydrogen generation rate in the SEFT will be higher.
   Additional Text: None.

8. Assumption: The initial dimethyl mercury concentration in the SEFT is 55% of the allowable concentration.

   Basis for Why this Assumption is Valid: As part of this evaluation a maximum allowable dimethyl mercury concentration in the SEFT liquid is calculated. Per Reference 7, 45% of the dimethyl mercury volatilized within nine hours. This experiment was performed with a vessel open to the environment. It is expected that a greater amount of dimethyl mercury would volatilize when exposed to a vapor space with a forced purge, as would be the case in the SEFT. Additionally, transfers from MCU to the SEFT occur approximately once every eighteen hours. During outages, such as those being evaluated, the time between transfers into the SEFT is weeks to months. Therefore this is an extremely conservative assumption.
   Sensitivity to this Assumption: If the dimethyl mercury concentration in the SEFT decreased, the allowable concentration in the Transfer Line would increase.
   Additional Text: None.

Analytical Methods and Computations

Purge Calculations
The minimum required purges for the SEFT were calculated in Reference 4. This purge flow rate is used to back calculate the fraction of the CLFL from the hydrogen generation rates using the equations in Reference 3. The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen concentration from the allowable flammable contribution to the CLFL. This is converted into a vapor concentration using the minimum vapor space volume. The vapor concentration is converted to a liquid concentration.

Dimethyl Mercury Temperature Corrected LFL
The dimethyl mercury LFL is 2.5 vol% at 25°C. The flammability of dimethyl mercury is dependent on temperature. The LFL decreases as the temperature increases. The impact can be determined by the Burgess Wheeler Equation (Ref. 8):

$$(1) \qquad LFL_T = LFL_{25°C} \times \left(1 - A(T - 25)\right)$$

Where:
LFL_T = LFL at temperature T, volume %
T = Temperature in Tank in °C
A = empirical coefficient.
The LFL can be corrected by the Burgess Wheeler Law by determining the necessary coefficient. The coefficient can be calculated from the heat of combustion of dimethyl mercury. However, because methane

was used to determine the LFL, the methane heat of combustion is used to adjust the LFL (See Assumption 6). The equation for the empirical coefficient is (Ref. 8)

(2) $A = \left[\!\left[\frac{0.75}{H_C \times LFL_{25°C}}\right]\!\right]$

Where:
H_C = Heat of combustion of methane = 212.79 kcal/mol
Such that:

$$\left[\!\left[\frac{0.75}{212.79 \times 2.5}\right]\!\right] = 1.41E-03$$

The dimethyl mercury LFL at various temperatures (e.g., 42.4°C and 105°C) is calculated using Equation 1 and the result from Equation 2:

$$LFL_{42.4°C} = 2.5 \times \left(1 - 1.41\text{E-}03 \times (42.4 - 25)\right) = 2.439\ vol\%$$

Hydrogen Generation

The hydrogen generation rate in the SEFT is equal to the generation rate of the MST/Sludge Solids plus the hydrogen generation rate of the Strip Effluent. Per Assumption 7 the volume of MST/Sludge Solids is 4000 gallons. The hydrogen generation rate of the MST/Sludge Solids is calculated as:

(3) $Q_{MST} = R_{MST} \times V_{MST}$

Where:
Q_{MST}= Hydrogen generation rate from MST/Sludge Solids, ft^3/hr
R_{MST}= Hydrogen generation rate from MST/Sludge Solids = 4.87E-05 ft^3/hr/gal
V_{MST}= Volume of MST/Sludge Solids = 4000 gal
Such that:

$$Q_H = 4.87E-05 \times 4000 = 0.195\ cfh$$

The remaining liquid in the SEFT is Strip Effluent and is calculated as:

(4) $V_{SE} = V_{High} - V_{MST}$

Where:
V_{SE} = Volume of Strip Effluent
V_{High} = SEFT high level alarm = 9600 gal
Such that:

$$V_{SE} = 9600 - 4000 = 5600 gal$$

The hydrogen generation rate of the Strip Effluent is then calculated as:

(5) $Q_{SE} = R_{SE} \times V_{SE}$

Where:
Q_{SE}= Hydrogen generation rate from MST/Sludge Solids, cfh
R_{SE}= Hydrogen generation rate from MST/Sludge Solids = 1.38E-05 ft^3/hr/gal
V_{SE}= Volume of MST/Sludge Solids = 5600 gal
Such that:

$$Q_{SE} = 1.38E-05 \times 5600 = 0.077\ cfh$$

The total hydrogen generation rate is then calculated by adding the hydrogen generation rate from MST/Sludge Solids to the Strip Effluent.

(6) $Q_{H\,45} = Q_{MST} + Q_{SE}$

Where:
$Q_{H\,45}$= Total hydrogen generation rate at 45°C, cfm

Such that:

$$Q_{H\,45} = (0.077 + 0.195) \times \frac{hr}{60min} = 0.0045cfm$$

The hydrogen generation rate is given for a temperature of 45°C and a pressure of 1 atm. The generation rate is temperature and pressure corrected for SEFT conditions as follows:

(7) $$Q_H = Q_{H\,45} \times \frac{P_{45}}{P_2} \times \frac{T_2}{T_{45}}$$

Where:
Q_H= Hydrogen generation rate
P_{45} = 1 atm
P_2 = 0.9263 atm
T_{45} = 45 °C = 318.15 K
T_2 = 42.4 °C = 315.55 K
Such that:

$$Q_H = 0.0045 \times \frac{1}{0.9263} \times \frac{315.55}{318.15} = 0.0048\ cfm$$

<u>Allowable Dimethyl Mercury Contribution to CLFL</u>

The purge flow rate give in Reference 4 is given for a temperature of 21.1°C and a pressure of 1 atm. The flow rate is temperature and pressure corrected for SEFT conditions as follows:

(8) $$Q_{purge} = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

Where:
Q_{purge}= Volumetric flow rate at T_2 and P_2
Q_1= Volumetric flow rate at T_1 and P_1 = 1.1 scfm
P_1 = 1 atm
T_1 = 21.1 °C = 294.25 K
Such that:

$$Q_{purge} = 1.1 \times \frac{1}{0.9263} \times \frac{315.55}{294.25} = 1.273\ cfm$$

The total flow through the SEFT vapor space is then calculated by adding the purge flow to the flammable flow.

(9) $$Q_{vent} = Q_{purge} + Q_H$$

Where:
Q_{vent}= Total volumetric flow in the SEFT vapor space
Q_H= Hydrogen generation rate = 0.0048 cfm
Such that:

$$Q_{vent} = 1.273 + 0.0048 = 1.278\ cfm$$

The contribution of hydrogen to the CLFL is the calculated by taking the ratio of the hydrogen generation rate divided by its LFL and the total flow rate.

(10) $$CLFL_H = \frac{\frac{Q_H}{LFL}}{Q_{vent}}$$

Where:

$CLFL_H$= Contribution of hydrogen to the CLFL
LFL= LFL of hydrogen in the SEFT = 0.03923 ft^3 flammables/ft^3 vapor space
Such that:

$$CLFL_H = \frac{\frac{0.0048}{0.03923}}{1.278} = 0.097$$

The allowable contribution of dimethyl mercury to the CLFL is then calculated by subtracting the hydrogen and Isopar L contribution to the CLFL from the maximum allowable combustible concentration. Because the SEFT has safety interlocks, NFPA 69 allows for the maximum combustible concentration in the tank vapor space to be limited to 60% of the CLFL of the mixture. Therefore the allowable dimethyl mercury contribution to the CLFL is calculated as follows:

(11) $$CLFL_{DMHg} = 0.6 - CLFL_H - CLFL_I$$

Where:
$CLFL_{DMHg}$ = Contribution of dimethyl mercury to the CLFL
$CLFL_I$= Contribution of Isopar L to the CLFL = 0.488
Such that:

$$CLFL_{DMHg} = 0.6 - 0.097 - 0.488 = 0.015$$

<u>Allowable Dimethyl Mercury Concentration in the SEFT Liquid</u>
The allowable dimethyl mercury contribution to the CLFL is equal to the ratio of the dimethyl mercury concentration to its LFL. Therefore the allowable dimethyl mercury concentration is calculated as follows:

(12) $$C_{v\,DMHg} = CLFL_{DMHg} \times LFL_{42.4}$$

Where:
$C_{v\,DMHg}$= Allowable concentration of dimethyl mercury in the vapor space
Such that:

$$C_{v\,DMHg} = \frac{2.439}{100} \times 0.015 = 0.00037 ft^3 DMHg/ft^3\ vapor\ space$$

Using the volume of the SEFT vapor space the allowable volume of dimethyl mercury is calculated as:

(13) $$V_{v\,DMHg} = V_v \times C_{v\,DMHg}$$

Where:
$V_{v\,DMHg}$ = Allowable volume of dimethyl mercury in the vapor space
V_v = SEFT Vapor Space
The vapor space in the SEFT is equal to the SEFT volume (12000) minus the SEFT level alarm (9600), 2400 gallons. Thus:

$$V_{v\,DMHg} = 2400 \times \frac{3.785L}{gal} \times 0.00037 = 3.36L$$

The molar volume of a gas at 0 °C and 1 atm is 22.414 L/mol. This is temperature and pressure corrected for SEFT conditions as follows:

(14) $$\frac{V_2}{n} = \frac{V_{STP}}{n} \times \frac{P_{STP}}{P_2} \times \frac{T_2}{T_{STP}}$$

Where:
$\frac{V_2}{n}$= Molar volume at T_2 and P_2
$\frac{V_{STP}}{n}$= Molar volume at T_{STP} and P_{STP} = 22.414 L/mol
P_{STP} = 1 atm
T_{STP} = 0 °C = 273.15 K
Such that:

$$\frac{V_2}{n} = 22.414 \times \frac{1}{0.9263} \times \frac{315.55}{273.15} = 27.95 L/mol$$

The gaseous volume can then be converted to a liquid mass by:

(15) $m_{l\,DMHg} = V_{v\,DMHg} \times \frac{V_2}{n} \times MW$

Where:
$m_{l\,DMHg}$= Mass of dimethyl mercury in the liquid
MW = Molecular weight of dimethyl mercury = 230.66 g/mol
Such that:

$$m_{l\,DMHg} = 3.36 \times \frac{1}{27.95} \times 230.66 = 27.75 g$$

To convert to a liquid concentration the mass of dimethyl mercury is divided by the maximum liquid volume in the SEFT.

(16) $C_{l\,DMHg} = \frac{m_{l\,DMHg}}{V_l}$

Where:
$C_{l\,DMHg}$= Maximum allowable concentration of dimethyl mercury in the SEFT
V_l = SEFT high level alarm = 9600 gal
Such that:

$$C_{l\,DMHg} = \frac{27.75}{9600} \times \frac{1000 mg}{g} \times \frac{gal}{3.785 l} = 0.764\, mg/L$$

<u>Allowable Dimethyl Mercury Concentration in the Transfer Line</u>
Per Assumption 8, the initial SEFT concentration is equal to 55% of the allowable dimethyl mercury concentration in the SEFT liquid as calculated above. Thus:

(17) $C_{SEFT\,i} = 0.55 \times C_{l\,DMHg}$

Where:
$C_{SEFT\,i}$= initial SEFT concentration
Such that:

$$C_{SEFT\,i} = 0.55 \times 0.764 = 0.42\, mg/L$$

Given the SEFT initial concentration and the SEFT final concentration, the allowable dimethyl mercury concentration in the transfer line can be calculated as follows:

(18) $C_{TL} = \frac{V_{high} \times C_{l\,DMHg} - V_{SEFT\,i} \times C_{SEFT\,i}}{V_{TL}}$

Where:
C_{TL}= allowable dimethyl mercury concentration in the transfer line
V_{TL}= initial SEFT volume, 1689 gal
$V_{SEFT\,i}$= initial SEFT volume
The initial SEFT volume is equal to the SEFT high level alarm (9600 gal) minus the Transfer Line volume (1689 gal), 7911 gallons. Thus:

$$C_{TL} = \frac{9600 \times 0.764 - 7911 \times 0.42}{1689} = 2.37 mg/L$$

Summary of Conclusions
The purge flow rates on the SEFT are such that dimethyl mercury could be present in the Transfer Line in concentrations up to 2.37 mg/L without presenting a flammability concern.

References

1. Meraw, H. J. *Volatilization and Flammability Characteristics of Elemental and Organic Mercury*, X-ESR-G-00048, Rev. 1.

2. Domalski, E. S. *Selected Values of Heats of Combustion and Heats of Formation of Organic Compounds Containing the Elements C, H, N, O, P, and S*, Journal of Physical and Chemical Reference Data Vol. 1, No. 2, 1972.

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7. L.P. Kolb, D.B. Porcella, and E.J. Middlebrooks, *Ecological Implications of Dimethyl Mercury in an Aquatic Food Chain*, Reports Paper 267, January 1973. (Web address http://digitalcommons.usu.edu/cgi/viewcontent.cgi?article=1266&context=water_rep/267).

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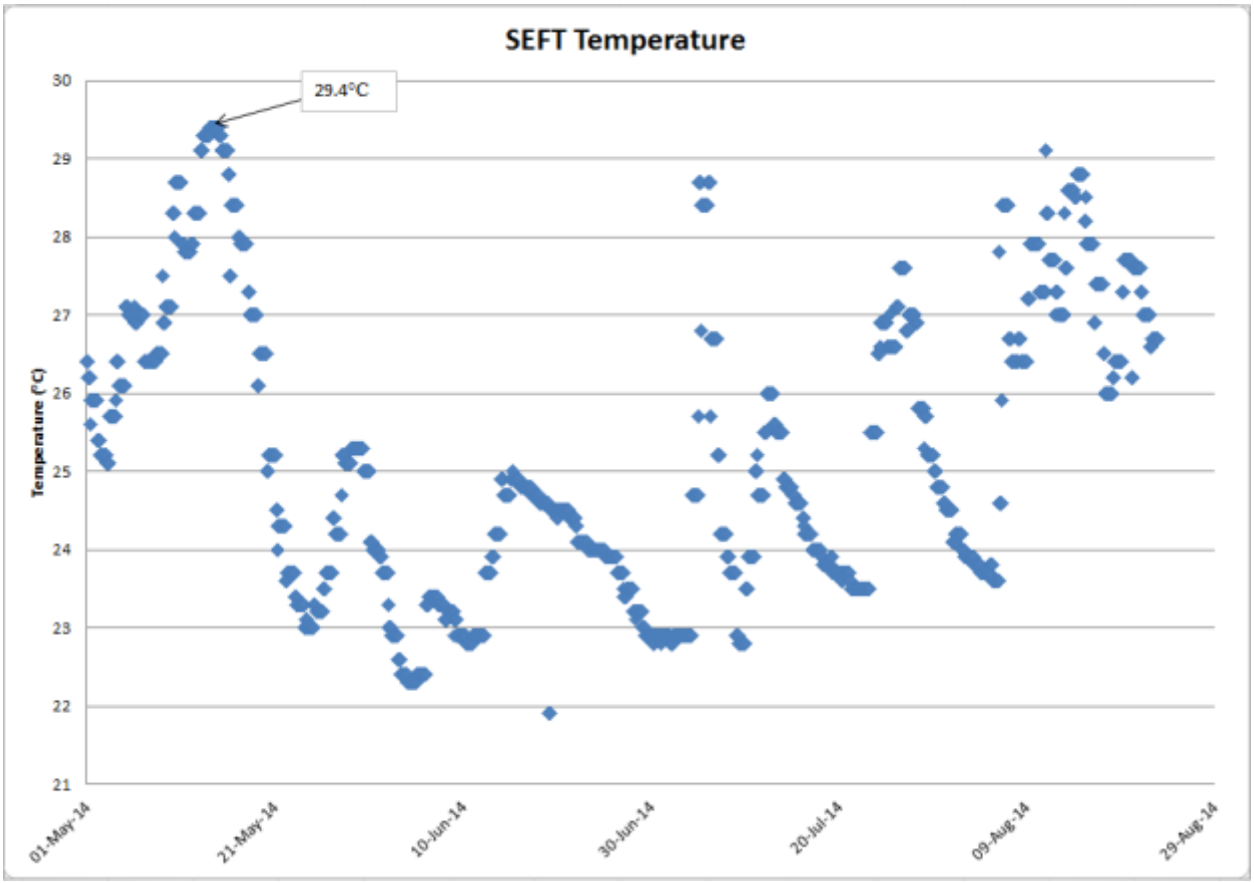
Appendix G

The SEFT temperature from May 1st, 2014 until August 23rd, 2014 is documented below. The SEFT cooling coils were not used during this time frame. Increases in temperature are typically associated with the high speed agitation that is required prior to transferring to the SRAT. Decreases in temperature are typically associated with incoming transfers from MCU.

The highest temperature seen during this time period was 29.4°C.

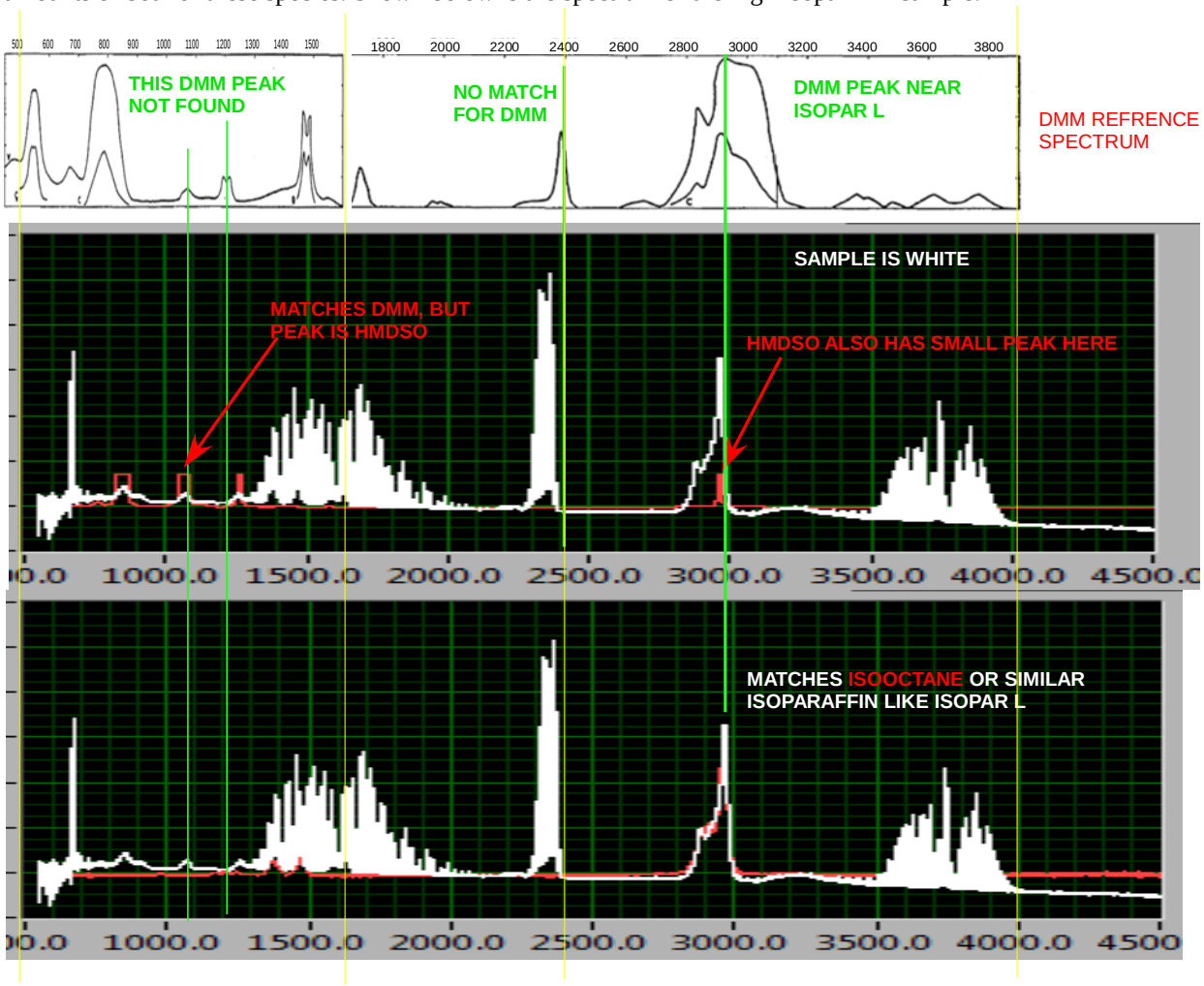


Appendix H

Three FTIR spectra from the SB8-D6 SEFT to SME run are compared to a tabulated spectrum of dimethyl mercury (DMM). The spectra are compared to the two organic species known to be present during these runs: hexamethyldisiloxane (HMDSO) and Isopar™ L. Isopar™ L is actually compared to either isooctane (C_8H_{18}) or 2,6-dimethyl-4-heptanone ($C_9H_{18}O$) which have similar spectra. The FTIR database does not contain any C_9-C_{12} isoparaffins.

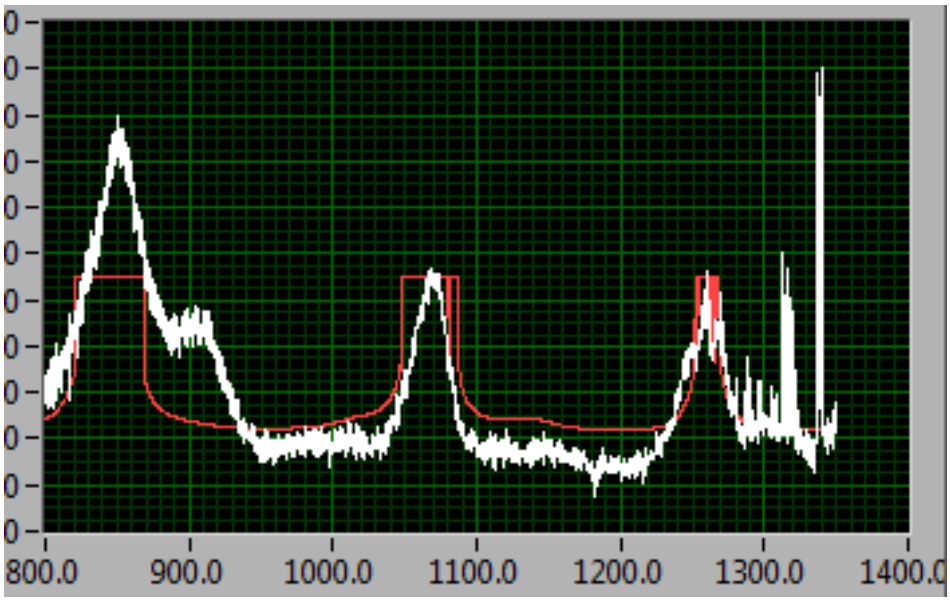
The DMM spectrum used for comparison is that of a liquid sample on KBr windows (H.S. Gutowsky, J. Chem. Phys., **17**, 128 (1949)).

The three spectra compared are one with high Isopar™ L, one with high HMDSO, and one with low amounts of both of these species. Shown below is the spectrum of the high Isopar™ L sample.

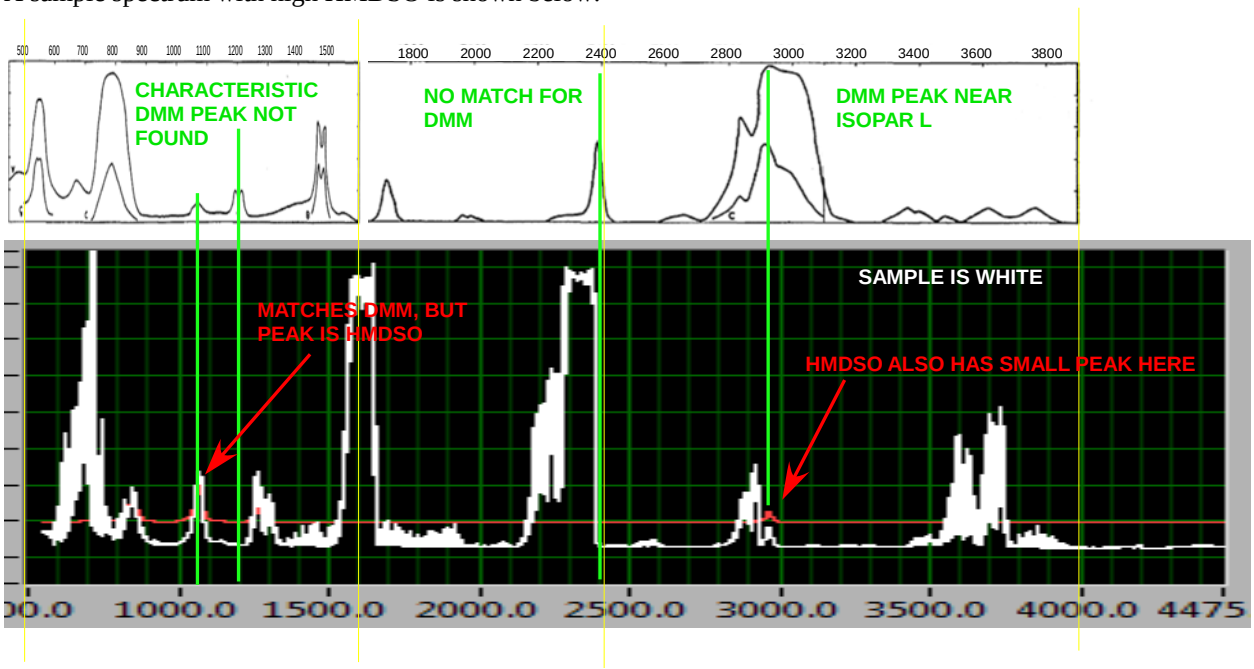


The sample spectrum does not match the DMM peaks at about 1200 wavenumber or at 2400; the peak at around 2900 is covered by the Isopar™ L peak that matches isooctane very well. The peak at about 1080 is offset from the sample peak that matches HMDSO well. Therefore, this sample spectrum shows no evidence of DMM, although trace amounts could still be present that would be obliterated by the species actually present.

The match between the sample and HMDSO in the region from 800-1350 is shown below. The small peak at about 900 is likely trimethylsilanol (TMS) which is half of HMDSO with a hydrogen in place of the other TMS group.

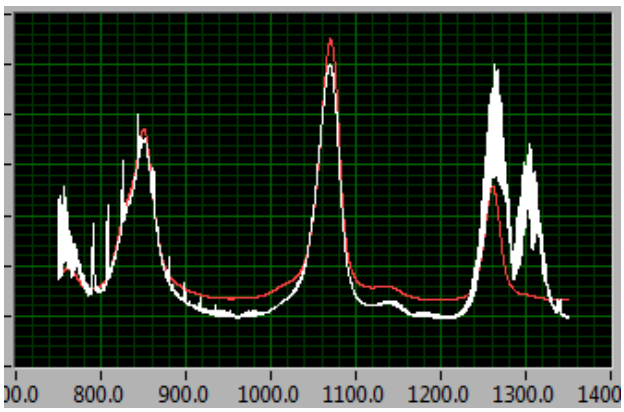


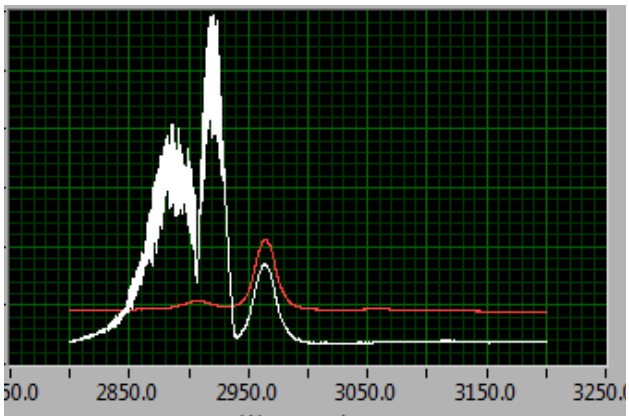
A sample spectrum with high HMDSO is shown below.



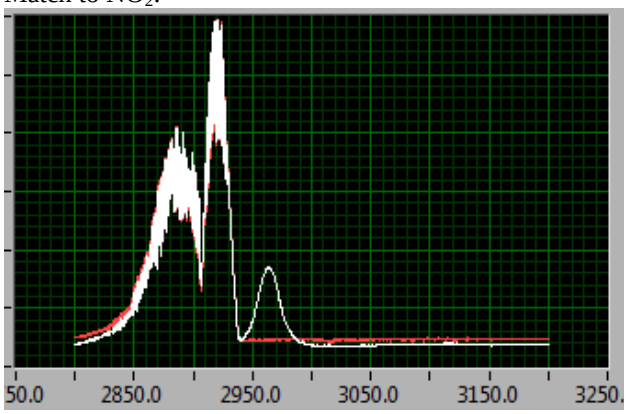
Again, several of the peaks for DMM do not match the sample spectrum. The match of HMDSO to the spectrum is shown in two regions below. The peaks at about 2890 and 2920 match NO_2 perfectly.

Matches to HMDSO:

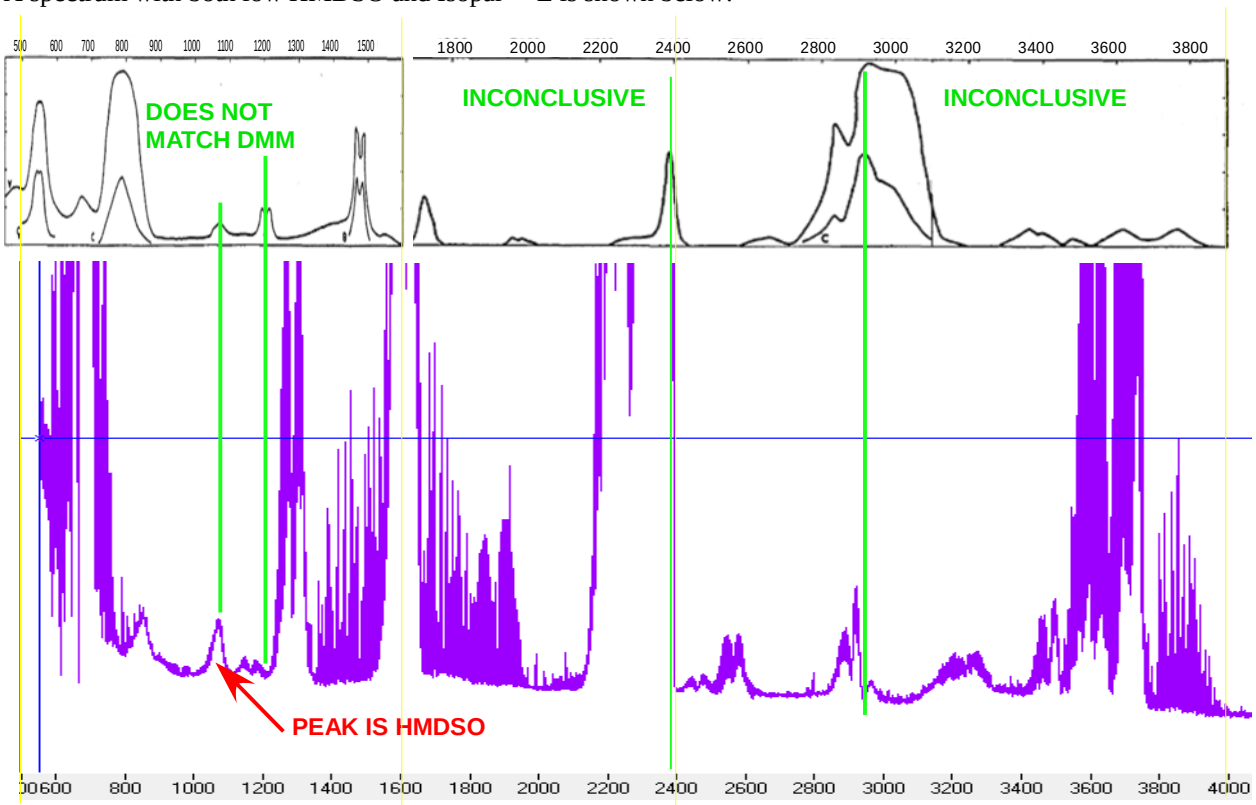




Match to NO_2:



A spectrum with both low HMDSO and Isopar™ L is shown below:



This comparison is more inconclusive because there are small peaks near where DMM has peaks. However, the two small peaks next to the on identified as HMDSO are also from HMDSO and are offset from the DMM peak, so it appears that DMM is not present. Similarly, the DMM peak at about 2900 is not present; it would be a broad, smoother peak that the small peak seen just to the right of the green line, so again it does not appear that significant DMM is present.

Overall, the FTIR spectra do not definitively show the presence of DMM, but very small amounts could still be present that would not have a strong enough spectrum to be seen in the presence of the other species actually known to be in the sample.

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DESIGN VERIFICATION SHEETS

ENGINEERING TECHNICAL REPORT CHECKLIST / VERIFICATION BY DOCUMENT REVIEW

S4-ENG.51 Form

Report Number: X-ESR-S-00258 Revision: 0

Report Title: Literature and Data Review for Evaluating the Production of

The following checklist is used to ensure technical reports are complete and in compliance with Manual E7. Add any notes or comments to the end of the checklist with the item number.

Item No.	Item	Yes / No N/A*	Comments Use continuation page at end of form if more space is needed
	Version / Format		
1	If revising an existing report, are you starting with the latest, approved version of the report obtained from DCR?	N/A	
2	Are all of the pages properly labeled with Report Number, Revision Number, and Sequential Page Number?	Yes	
3	Are the Subject and Purpose clearly stated and do they meet the end users needs?	Yes	
	References		
4	Are all References properly documented within the report and can they be easily verified within Document Control, on-line, or within the library, etc.? If reference documents are not readily available, are they attached?	Yes	
5	Have the correct design bases documents been identified (e.g., Codes, Standards, DOE Orders, SRR Requirements, Regulatory Requirements)?	Yes	
	Open Items / Input		
6	Is there a reference/source for each input?	Yes	
7	Do the identified references/sources fully support the inputs?	Yes	
8	Are all assumptions used to support the report individually listed?	Yes	
9	Is there a justification written for each assumption that includes a technical basis?	Yes	

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ENGINEERING TECHNICAL REPORT CHECKLIST / VERIFICATION BY DOCUMENT REVIEW

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Item No.	Item	Yes / No N/A*	Comments Use continuation page at end of form if more space is needed
	Open Items / Input - continued		
10	Do the justifications adequately support the assumptions?	Yes	
11	If the report has open items, is there a method identified to track them?	N/A	
	Results / Conclusions		
12	Are the results of the report consistent with the input and assumptions?	Yes	
13	Do the results of the report affect any other technical documents?	No	
14	Do the results substantiate the conclusion?	Yes	
	Approvals		
15	Does the document identify the method of verification, if applicable, and does it have a signature block for the verifier/checker?	Yes	
Items 16-28 are only to be completed when Verificaiton by Document Review is being performed. The verifier assures the technical accuracy of the document by performing administrative and mathematical checks as appropriate, and by evaluating the modification against the following questions:			
16	Were the inputs correctly selected and identified?	Yes	
17	Are the assumptions made in the performance of the design or analytical activity adequately described and reasonable?	Yes	
18	When necessary, are the assumptions identified for subsequent re-verification when the detailed design activities are completed?	N/A	
19	Were appropriate design or analytical methods and computer programs used?	Yes	
20	Were the design or analytical inputs correctly incorporated into the design, analysis or evaluation?	Yes	
21	Have engineering actions required to support risk handling strategies been verified?	N/A	
22	Is the design output reasonable compared to the design or analytical inputs?	N/A	

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Item No.	Item	Yes / No N/A*	Comments Use continuation page at end of form if more space is needed
23	Are the necessary design inputs for interfacing organizations specified in the design documents or in supporting procedures or instructions?	N/A	
24	Have suitable materials, parts, processes, and inspection and testing criteria been specified?	N/A	
25	Have existing and potential workplace hazards been identified, evaluated, and controls incorporated for the risk to worker injury or illness?	N/A	
26	Was a review conducted to confirm that there are no interferences with other ongoing or planned modifications?	N/A	
27	Have engineering judgments been identified, technically justified, and supported?	Yes	
28	Have design optimization strategies been considered/met (e.g., appropriate tailoring of requirements, design attributes, and operating strategies)?	N/A	

Item No. Cont.	Comments Continuation

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Document Number: X-ESR-S-00258 Revision: 0

Document Title: Literature and Data Review for Evaluating the Production of Dimethyl Mercury in the DWPF Appendix F

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Item No.	Item	Yes / No N/A*
1	Were the inputs correctly selected and identified?	Yes
2	Are the assumptions made in the performance of the design or analytical activity adequately described and reasonable?	Yes
3	When necessary, are the assumptions identified for subsequent re-verification when the detailed design activities are completed?	N/A
4	Were appropriate design or analytical methods and computer programs used?	Yes
5	Were the design or analytical inputs correctly incorporated into the design, analysis or evaluation?	Yes
6	Have engineering actions, required to support risk handling strategies, been verified?	N/A
7	Is the design output reasonable compared to the design or analytical inputs?	Yes
8	Are the necessary design inputs for interfacing organizations specified in the design documents or in supporting procedures or instructions?	N/A
9	Have suitable materials, parts, processes, and inspection and testing criteria been specified?	N/A
10	Have existing and potential workplace hazards been identified, evaluated, and controls incorporated for the risk to worker injury or illness?	N/A
11	Was a review conducted to confirm that there are no interferences with other ongoing or planned modifications?	N/A
12	Have engineering judgments been identified, technically justified, and supported?	N/A
13	Have design optimization strategies been considered/met (e.g., appropriate tailoring of requirements, design attributes, and operating strategies)?	N/A

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Document Title: Literature and Data Review for Evaluating the Production of Dimethyl Mercury in the DWPF Appendix E

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1	Were the inputs correctly selected and identified?	Yes
2	Are the assumptions made in the performance of the design or analytical activity adequately described and reasonable?	Yes
3	When necessary, are the assumptions identified for subsequent re-verification when the detailed design activities are completed?	N/A
4	Were appropriate design or analytical methods and computer programs used?	Yes
5	Were the design or analytical inputs correctly incorporated into the design, analysis or evaluation?	Yes
6	Have engineering actions, required to support risk handling strategies, been verified?	N/A
7	Is the design output reasonable compared to the design or analytical inputs?	Yes
8	Are the necessary design inputs for interfacing organizations specified in the design documents or in supporting procedures or instructions?	N/A
9	Have suitable materials, parts, processes, and inspection and testing criteria been specified?	N/A
10	Have existing and potential workplace hazards been identified, evaluated, and controls incorporated for the risk to worker injury or illness?	N/A
11	Was a review conducted to confirm that there are no interferences with other ongoing or planned modifications?	N/A
12	Have engineering judgments been identified, technically justified, and supported?	N/A
13	Have design optimization strategies been considered/met (e.g., appropriate tailoring of requirements, design attributes, and operating strategies)?	N/A

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Document Title: Literature and Data Review for Evaluating the Production of Dimethyl Mercury in the DWPF, Appendix D

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Item No.	Item	Yes / No N/A*
1	Were the inputs correctly selected and identified?	Yes
2	Are the assumptions made in the performance of the design or analytical activity adequately described and reasonable?	Yes
3	When necessary, are the assumptions identified for subsequent re-verification when the detailed design activities are completed?	N/A
4	Were appropriate design or analytical methods and computer programs used?	Yes
5	Were the design or analytical inputs correctly incorporated into the design, analysis or evaluation?	Yes
6	Have engineering actions, required to support risk handling strategies, been verified?	N/A
7	Is the design output reasonable compared to the design or analytical inputs?	Yes
8	Are the necessary design inputs for interfacing organizations specified in the design documents or in supporting procedures or instructions?	N/A
9	Have suitable materials, parts, processes, and inspection and testing criteria been specified?	N/A
10	Have existing and potential workplace hazards been identified, evaluated, and controls incorporated for the risk to worker injury or illness?	N/A
11	Was a review conducted to confirm that there are no interferences with other ongoing or planned modifications?	N/A
12	Have engineering judgments been identified, technically justified, and supported?	N/A
13	Have design optimization strategies been considered/met (e.g., appropriate tailoring of requirements, design attributes, and operating strategies)?	N/A

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Location of report and supplemental information: E-mail sent containing report. E-mail sent containing calculations and reference location. Verbal request made for items checked below. This serves as documentation of the verbal request.

☑ Analytical/Experimental Approach	Instruction:	Ensure literature and R&D data supports approach
☑ Mathematical Check	Instruction:	Ensure no transcription errors & equations used in the report are correct. Exceptions are Appendix D through G; another reviewer will review.
☐ Inputs	Instruction:	N/A SRB 6/1/2015
☑ Assumptions	Instruction:	Ensure literature and R&D data supports assumptions
☑ Output	Instruction:	Ensure output of equations in body of report is correct & conclusions
☑ Transcription	Instruction:	Ensure no transcription errors are made in body of report and Appendix A and B.

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