Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Assessment of Methane Generation from the Thermolysis of Organics in Caustic Waste

S. C. Hunter
W. H. Woodham
July 2020
SRNL-STI-2020-00270, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2020-00270
Revision 0

Keywords: *Methane, Thermolysis*

Retention: *Permanent*

Assessment of Methane Generation from the Thermolysis of Organics in Caustic Waste

S. C. Hunter
W. H. Woodham

July 2020

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory®

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

S. C. Hunter, Chemical Flowsheet Development Date

W. H. Woodham, Chemical Flowsheet Development Date

TECHNICAL REVIEW:

C. L. Crawford, Separation Sciences and Engineering, Reviewed per E7 2.60 Date

APPROVAL:

G. A. Morgan, Jr., Manager Date
Chemical Flowsheet Development

S. D. Fink, Director Date
Chemical Processing Sciences

J. E. Occhipinti, Manager Date
Tank Farm Facility Engineering

EXECUTIVE SUMMARY

Methane generation has been detected during thermolytic Hydrogen Generation Rate (HGR) testing of SRS tank waste and in simulant samples. Simulant testing has shown methane generation in the presence of trimethylsilanol (TMS) and radioactive sample testing has shown methane generation in presence of methylmercury, both of which are found within SRS waste tanks. The 2019 report *Evaluation of the Current State of Knowledge for Thermolysis of Organics within SRS Waste Forming Volatile Organic Compounds (VOCs)* reviewed historical data and assessed literature pertaining to thermolytic methane generation. That review recommended undertaking thermolysis studies on simulated waste to detect and quantify VOCs. The purpose of this assessment is to review chemistry and current knowledge of organics in SRS waste to recommend which organics in SRS waste tanks, if any, should be tested for thermolytic methane generation. An evaluation of observed methane generation rates has been performed to assess the implication for current CSTF controls. Based on the inputs used in this report, it was concluded that no methane generation data observed to date has challenged the existing 5% organic contribution to the Composite Lower Flammability Limit (CLFL) assumption in the CSTF tank farm at temperatures below 100 °C.

Evidence shows that thermolytic pathways to methane generation become significant at temperatures >100 °C in caustic waste. Currently, the influences of thermolytic methane production on the flammability of vessels at >100 °C (e.g., evaporators) is unclear. It is recommended that testing should be undertaken using the HGR experimental approach for methane generation. The initial simulant testing should obtain quantitative methane generation rates at elevated temperatures for methylated siloxanes/silanes and methylmercury with the goal of determining the current mechanism for thermolytic methane generation seen in SRS tank waste. The results of this testing should then be compiled and analyzed to ascertain the risk of challenging the current projected organic contribution of 5% to the CLFL at elevated temperatures. Following this testing, an evaluation of possible flammable gas generation in the 2H and 3H Evaporators should be performed to assess the risk of methane generation at the high temperatures employed by the evaporators.

TABLE OF CONTENTS

LIST OF TABLES vii
LIST OF FIGURES vii
LIST OF ABBREVIATIONS viii
1.0 Introduction 1
2.0 Thermolytic Methane Generation 1
  2.1 Organic Mechanistic Studies on Hanford Site Waste 1
  2.2 Methane Generation in the Bayer Process 2
  2.3 Antifoam Degradation Compounds 3
  2.4 Organo-Mercury Compounds 4
  2.5 Organics found in CSTF 7
3.0 Evaluation of Methane Generation Rates Observed at SRS 8
4.0 Conclusions 10
5.0 Recommendations, Path Forward or Future Work 11
6.0 References 12

LIST OF TABLES

Table 2-1. CSSX and NG-CSSX Solvent Components 8

Table 3-1. Observed Methane Generation Rates in Previous HGR Testing with Waste Samples. 8

Table 3-2. Time to 5% Methane LFL Calculated Using WCS Data 10

LIST OF FIGURES

Figure 2-1. Principal Reaction Pathways for Oxidation of Organic Compounds. 2

Figure 2-2. Proposed Mechanism for the Reaction of Lactate in 6 *m* NaOH at 180 °C. 3

Figure 2-3. Proposed Mechanism for the Methane Generation in TMS HGR Testing. 4

Figure 2-4. (Top) Concentration of Hydrogen and Methane in HBP Testing. (Bottom) Concentration of Hydrogen and Methane in Tank 38 Testing. 6

LIST OF ABBREVIATIONS

CLFL	Composite Lower Flammability Limit
CSSX	Caustic Side Solvent Extraction
CSTF	Concentration, Storage and Transfer Facility
DBP	di-butyl phosphate
DWPF	Defense Waste Processing Facility
EDTA	ethylenediaminetetraacetate ion
HBP	high boiling point
HEDTA	(2-hydroxyethyl)ethylenediaminetriacetate ion
HGR	Hydrogen Generation Rate
HMDSO	hexamethyldisiloxane
HMW	high molecular weight
LMW	low molecular weight
MBP	mono-butyl phosphate
MGR	Methane Generation Rate
NG-CSSX	Next Generation Caustic Side Solvent Extraction
PUREX	Plutonium Uranium Redox Extraction
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TBP	tri-n-butyl phosphate
TMS	trimethylsilanol
TOC	Total Organic Content
VOC	Volatile Organic Compounds

1.0 Introduction

Methane was detected during hydrogen generation rate (HGR) testing of Savannah River Site (SRS) waste samples from Tanks 28, 38, and 44.[1-4] Methane was also detected in further thermolytic HGR testing, specifically with simulants containing trimethylsilanol (TMS).[1,5] This evidence of thermolytic methane generation prompted the authoring of the report, *Evaluation of the Current State of Knowledge for Thermolysis of Organics within SRS Waste Forming Volatile Organic Compounds (VOCs)*.[6] That review assessed the current knowledge of VOCs from thermolysis in organics in SRS caustic tank waste, recommending further experiments to measure the methane generation rate. This report is an extension of the discussion found within the previously mentioned assessment, as well as what is found in Section 4 (Thermolysis Releasing Other Flammable Compounds) and Section 9 (Volatile Organic Compounds) of X-ESR-G-00062.[7] The following areas of inquiry were pursued in this evaluation:

- Reexamination of previous studies of organics in nuclear waste to assess the current knowledge on thermolytic reaction pathways that lead to VOC formation,
- Understanding of the mechanistic pathways of organic compounds responsible for methane generation in the Bayer Process,
- Literature search on silanol and siloxane chemistry to help propose a mechanism for the methane generation seen in the TMS experiment,
- Review of the current knowledge on organomercury chemistry in SRS waste,
- Review of known organics found in SRS waste as they relate to methane generation, and
- Evaluation of methane generation rates observed at SRS.

2.0 Thermolytic Methane Generation

2.1 Organic Mechanistic Studies on Hanford Site Waste

There has been a substantial amount of prior work to understand the radiolytic and thermolytic pathways to flammable gas generation within nuclear waste. For thermolysis, most mechanistic studies have been done on Hanford site waste which, in comparison to SRS, has its own unique profile of organics in its waste stream.[8-12]

The oxidation pathways of organics in waste that leads to VOC generation is based principally on either radiolytic or thermal processes as described by Stock in Figure 2-1.[11] Typically, these pathways involve the formation of reactive free radicals, by either radiolytic or certain thermal processes, that react with the organics in the waste stream. These pathways form organic free radicals which can then react with other organics, and these cascading reactions can eventually lead to the formation of VOCs. VOC generation from other processes that do not involve reactive free radicals are also taking place simultaneously. These processes typically involve the reaction of organics with ionic reagents within the waste stream to form more reactive species that are quickly oxidized, potentially producing VOCs in the process.

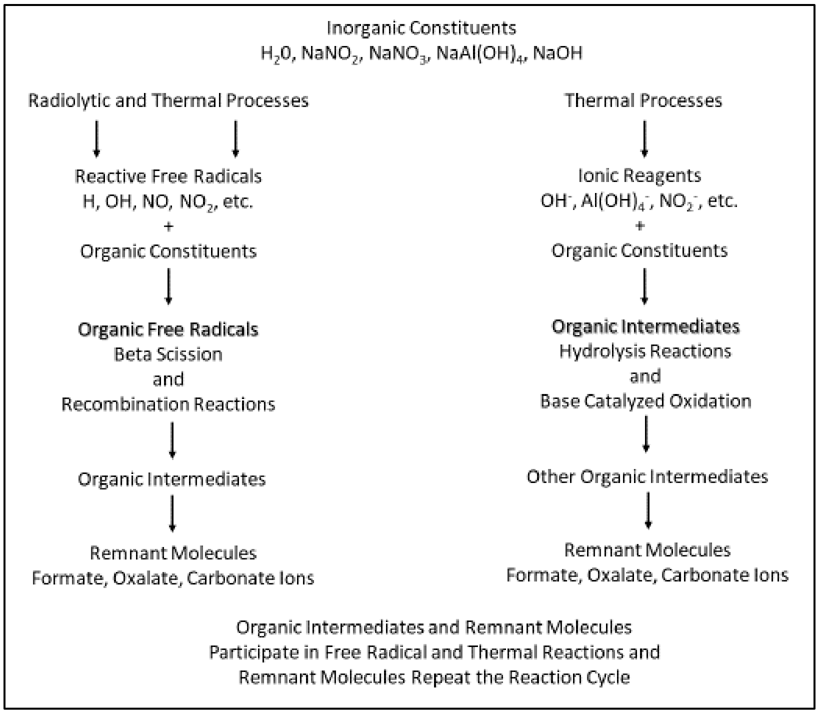


Figure 2-1. Principal Reaction Pathways for Oxidation of Organic Compounds.

A majority of the previous mechanistic studies were done on metal complexants such as glycolate, citrate, ethylenediaminetetraacetate ion (EDTA), and (hydroxyethyl)ethylenediaminetriacetate ion (HEDTA), which are either not currently found in SRS waste, or are found in only trace amounts.[7] This work has been previously summarized.[12] For example: citrate degrades to acetate and oxalate by hydroxide ions with little gas produced in a “reverse Claisen” reaction, glycolate and HEDTA degradation pathways involve an aluminum-catalyzed reaction in the presence of nitrite ions that is not fully understood, and EDTA is relatively inert under the conditions studied.[8] These reaction pathways lead to aldehyde intermediates which can undergo hydroxide-ion catalyzed “Cannizzaro reactions” to produce flammable hydrogen gas. These complexants do not contain methyl groups, but methane generation was observed during degradation studies. This methane is potentially produced from methyl-containing intermediates in certain reaction pathways. For example, acetate is produced during the decomposition of citrate and could be a source for methane gas. The methane-to-hydrogen ratio in this testing was found to increase with temperature, going from <0.05 at 60 °C, to approaching values between 0.5-1 at 120 °C.[6]

2.2 Methane Generation in the Bayer Process

The Bayer process, the predominant industrial process in the production of alumina, has similar caustic aqueous conditions to storage and processing of SRS waste. Section 2.6 (Thermolysis Reactions in Caustic Solution Related to The Bayer Industrial Process) in SRNL-STI-2018-000163, covered the work done by Costine and co-workers on the thermolytic degradation of organic compounds present in the Bayer process.[6] In summary, they found that thermolysis tends to show a hydrogen-to-methane molar ratio of ≥75.

Laird et al. took a further look at the underlying substances responsible for the VOCs seen in the Bayer process.[13] They looked at volatile products formed from the degradation of organics, both low and high molecular weight (LMW and HMW), in a synthetic Bayer liquor (6 m (mol kg^{-1}) NaOH at 180 °C). In their study, both methane and hydrogen gases, along with some other VOCs, were detected in the thermal decomposition of all three HMW substances (humic acids, cellulose, and lignin). Of the nine LMW organics studied, hydrogen gas was detected in the headspace analysis of six of them. Methane gas was also detected in the headspace analysis of lactate, the only LMW compound studied that contains a methyl group. As shown in Figure 2-2, two reaction pathways, based on a base catalyzed oxidation by water, were proposed that would involve the deprotonation of the aliphatic hydroxyl group, followed by the formation of an O-C double bond and the elimination of a methyl group carbanion. The methyl carbanion could then abstract a proton from water to generate methane. With respect to methane generation in SRS waste, a study of organic compounds that contain methyl groups found in SRS should be considered. As in the Hanford complexant testing, degradation pathways of organic compounds that lead to the formation of reactive species containing methyl groups may also be potential sources for methane generation.

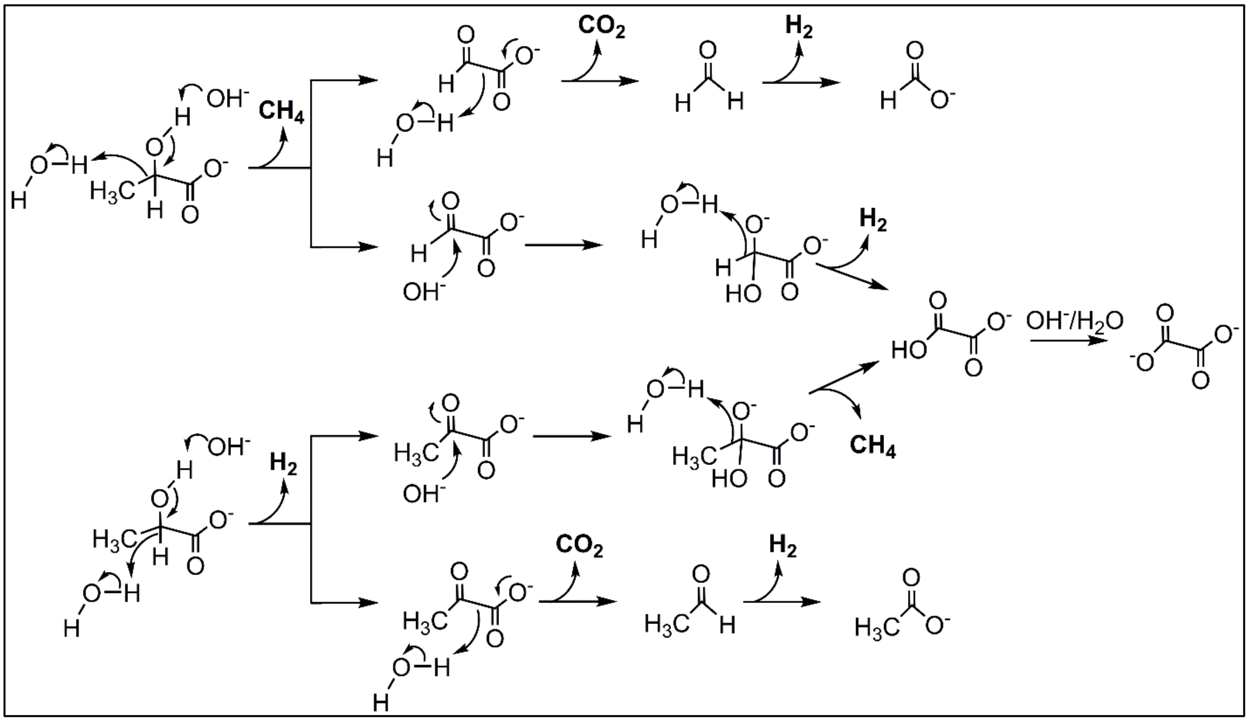


Figure 2-2. Proposed Mechanism for the Reaction of Lactate in 6 *m* NaOH at 180 °C.[10]

2.3 Antifoam Degradation Compounds

In HGR radioactive waste testing, methane was detected in samples at elevated temperatures for Tanks 28, 38, and 44.[1-4] Volatile organic analysis (VOA) of the Tank 44 samples found 0.9 mg/L of octamethylcyclotetrasiloxane.[4] Octamethylcyclotetrasiloxane is possibly a degradation product or impurity of antifoam H-10, a polydimethylsiloxane-based antifoam that was formerly used in Concentration, Storage and Transfer Facility (CSTF) evaporators. All three of these tanks are current or former evaporator drop tanks that contain saltcake and the polydimethylsiloxanes might be the source of the methane generation. VOA samples were taken for each tank, but only Tank 44 material was shown to have measurable concentrations of OMCTS.

As previously reported in *Antifoam Degradation Testing* SRNL-STI-2015-00352, Antifoam 747, used in the Defense Waste Processing Facility (DWPF), decomposes to form the flammable organic products hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), and propanal.[14] In limited testing, TMS has been detected in CSTF Tank 22 at 2.7 mg/L and in DWPF processing samples at 11 mg/L.[15,16] HMDSO and propanal were not detected in the Tank 22 sample and were near or below detection limits in DWPF samples. In recent HGR simulant testing with TMS (added at 256 mg/L), methane was observed in the offgas at

100 °C along with HMDSO.[5] Silanol chemistry was investigated further to understand the mechanism for this methane generation.

In the TMS simulant test, HMDSO was the major gas detected in the headspace analysis. This well-known condensation/hydrolysis equilibrium between TMS and HMDSO has been previously studied.[17,18]

$$\mathrm{Me_3Si{-}OH + HO{-}SiMe_3 \rightleftharpoons Me_3Si{-}O{-}SiMe_3 + H_2O}$$

The Si–C bond (69 kcal/mol) is significantly weaker than the Si–O bond (112 kcal/mol). However, the Si-O bond is much more polar, and the low-lying d orbitals on Si make it easily attacked by nucleophiles. As such, silanols can be fully deprotonated in aqueous solutions, forming silanolates.[18,19]

$$\mathrm{Me_3Si{-}OH + OH^- \rightleftharpoons Me_3SiO^- + H_2O}$$

It can be assumed that the above two equilibrium processes are taking place simultaneously in caustic solutions. The cleavage of Si–C bonds is much more rare; examples include by concentrated sulfuric acid, pyrolysis, photocatalysis, and free radicals.[20] Mercury is known to cleave Si–C bonds, and TMS as well as polydimethylsiloxanes are potentially a major source for the dimethylmercury found in the High Level Waste stream.[21] A previous study by Tatlock and Rochow found that the Si–C bond in HMDSO can be cleaved, generating methane gas when HMDSO is treated with a strong base at elevated temperatures (>100 °C).[22] In the presence of water, the methane generation was found to be much faster, possibly showing that this reaction involves a base-catalyzed oxidation by water (Figure 2-2), similar to the lactate example mentioned in Section 2-2.

Recent HGR testing identified methane formation from a variety of waste tank conditions (Tank 28, Tank 38, and Tank 44 material) and noted an absence of methane at other conditions (e.g., Tank 22 material). The concentrations and speciation of Si–C bonds in these samples is largely unknown. Due to the nature of silanols in solution, the unknown reactivity of doubly- versus triply-methylated silicon, and the varied matrices in tested samples, an exact pathway to methane generation observed in the recent HGR testing cannot be conclusively ascertained, and further studies are recommended.

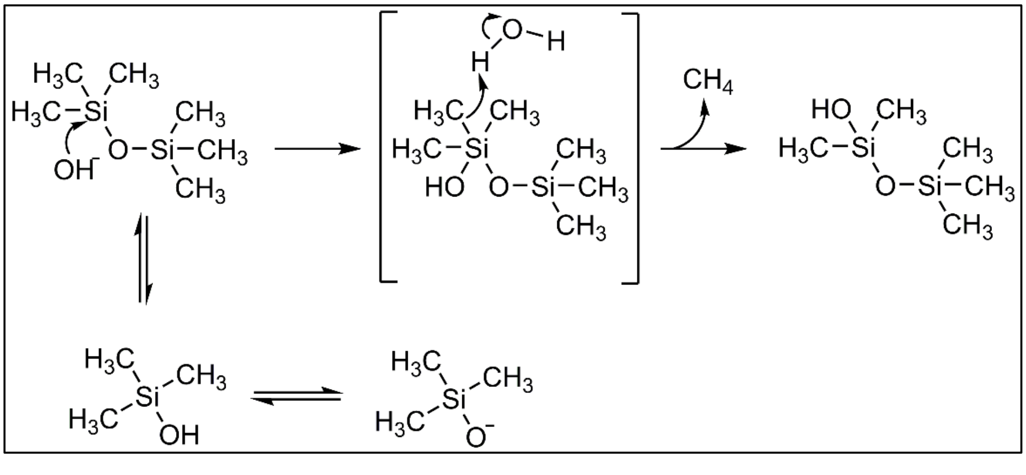


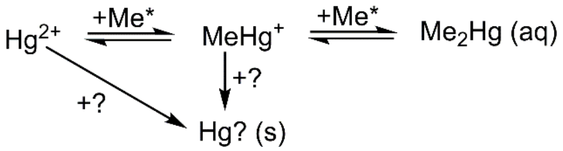
Figure 2-3. Proposed Mechanism for the Methane Generation in TMS HGR Testing.

2.4 Organo-Mercury Compounds

Organo-mercury compounds are present in the SRS CSTF tanks.[23] Dimethylmercury concentrations are typically below 1 mg/L, while methylmercury ($MeHg^+$) concentrations have been found up to 200 mg/L.[3]

It is suspected that CH_3HgOH is the predominate form of methylmercury in caustic tank waste.[24] The large concentrations of methylmercury found in tank waste is primarily due to its solubility and low vapor pressure. With over 60 MT of mercury in SRS tanks, one would anticipate methylmercury concentrations to continually increase over time.[25]

Simulant waste studies at three temperatures (39 °C, 65 °C, and 83 °C) found that in the presence of organics, Hg(II) is rapidly methylated to methylmercury; however, a rate for the methylation could not be determined due to the nature of the study.[26,27] In comparison, the rate of formation for dimethylmercury is relatively slow, but increases with increasing temperature. An unidentified solid was the major product at the highest tested temperature (83 °C), and the following reaction mechanism was proposed:



where Me* is an organic methyl donor. The demethylation process is slow in comparison due to the stability of the Hg-C bond. Typically, demethylation occurs by either a photochemical or a biological process. Photolysis and biological generation of flammable gases were discussed in X-ESR-G-00062 and were not considered to be an appreciable source of flammable gases found at CSTF.[4] Mercury is known to be both thiophilic and selenophilic.[28,29] For example, through a proton-transfer reaction, selenoneine cleaves the Hg-C bond of methylmercury halides, generating methane.[30] This was recently demonstrated by SRNL with Tank 50 waste simulant spiked with methylmercury in the presence of excess sulfide.[31]

Methane generation was detected during HGR testing on Tank 38 waste and a high boiling point (HBP) simulant, as shown by the red dots in Figure 2-4.[1] Due to experimental limitations during the HBP simulant test, a methane generation rate could not be determined quantitatively from this study. From previous speciation testing of mercury in Tank 38, the concentrations of methylmercury and dimethylmercury were 160-200 mg/L and 0.0525-0.148 mg/L respectively.[32] The HBP simulant had 450 mg/L of $Hg(NO_3)_2$, and as mentioned above, Hg(II) is rapidly methylated in the presence of organics. It is possible that a methylated mercury species is partially accountable for the methane generated. It should be noted that the HBP simulant also contained TMS and more testing is needed to determine if the methane generated was from TMS, a methylated mercury species, a combination of the two, or another organic species entirely.

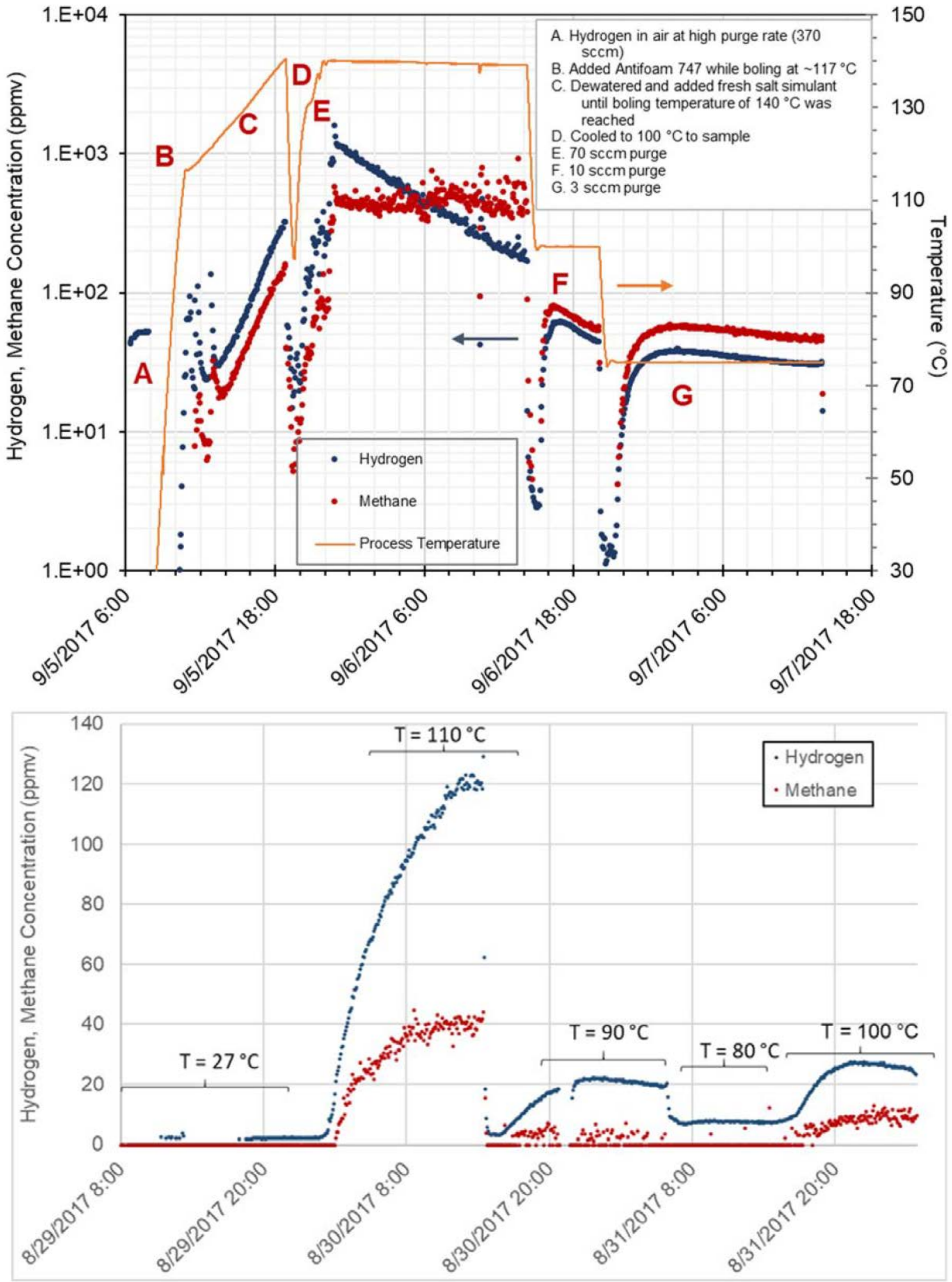
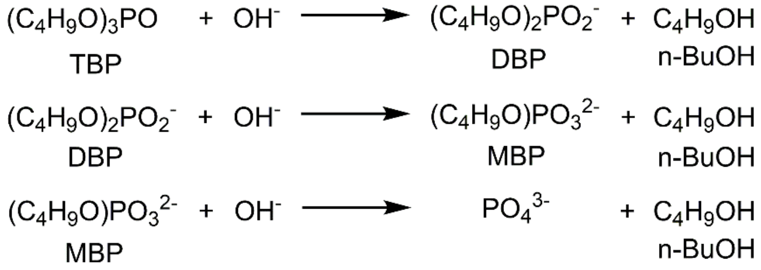


Figure 2-4. (Top) Concentration of Hydrogen and Methane in HBP Testing. (Bottom) Concentration of Hydrogen and Methane in Tank 38 Testing.[1]

Based on current knowledge, Crawford et al. proposed the following Methane Generation Rates (MGR) for dimethylmercury and methylmercury.[6] Using 1 mg/L, the maximum known concentration of dimethylmercury in tank waste, and degradation data for dimethylmercury, an estimated methane generation rate of 9.1E-09 to 2.0E-06 ft^3/gal-hr in the temperature range of 39 to 170 °C was postulated.[6] Methylmercury is the predominate organo-mercury found in SRS waste, but there is a lack of data on methylmercury in caustic solutions. For comparison, using the maximum concentration found for methylmercury in CSTF of 200 mg/L, a methane generation rate of 2.2E-07 to 4.5E-02 ft^3/gal-hr in the temperature range of 26 to 170 °C in reagent water was estimated.[6]

2.5 Organics found in CSTF

A large assortment of organic compounds has been discharged into the tank farm throughout the history of the site.[33] Most of these are present in such dilute amounts that they are considered to be an insignificant source of thermolytic methane. Others such as oxalate and formate, processing chemicals used in DWPF, are stable in the aqueous waste and are not considered a source of methane. N-paraffin and tri-n-butyl phosphate (TBP) make up the solvent for the Plutonium Uranium Redox Extraction (PUREX) separation process. Most of the n-paraffin is volatilized in canyon evaporators before reaching the tank farms. It is estimated that approximately 1,520 MT of tri-n-butyl phosphate has been sent to the tank farm.[34] The decomposition of TBP in the tank farm has been extensively studied, and has been shown to follow the reaction sequence shown below:



$$\underset{\text{TBP}}{(C_4H_9O)_3PO} + OH^- \longrightarrow \underset{\text{DBP}}{(C_4H_9O)_2PO_2^-} + \underset{\text{n-BuOH}}{C_4H_9OH}$$

$$\underset{\text{DBP}}{(C_4H_9O)_2PO_2^-} + OH^- \longrightarrow \underset{\text{MBP}}{(C_4H_9O)PO_3^{2-}} + \underset{\text{n-BuOH}}{C_4H_9OH}$$

$$\underset{\text{MBP}}{(C_4H_9O)PO_3^{2-}} + OH^- \longrightarrow PO_4^{3-} + \underset{\text{n-BuOH}}{C_4H_9OH}$$

TBP is hydrolyzed in the caustic waste, forming di-butyl phosphate (DBP) and butanol. DBP also can undergo hydrolysis, forming monobutyl phosphate (MBP) and butanol.[33] Methane and other VOCs are produced from radiolysis of TBP.[35] In thermolytic simulant testing of TBP, no evidence was found of methane generation from TBP or its degradation products.

The Caustic Side Solvent Extraction (CSSX) solvent for cesium removal can get entrained in the aqueous waste stream and transferred to the tank farm.[7] The historical composition of the solvent over time is listed in Table 2.1. The CSSX diluent Isopar® L would have similar behavior to N-paraffin from the PUREX solvent in CSTF; as such, it is not considered a contributor to thermolytic generation of methane. Previous thermal studies on the CSSX solvent were performed at temperatures ≤ 61 °C, temperatures that thermolytic pathways to methane would most likely not predominate. However, organic products in the degradation pathways for certain CSSX solvent components (suppressor and modifier) have methyl ligands that could be a source for thermolytic methane generation. It should also be noted that thermolysis of CSSX solvent was investigated in Tank 38 simulant and shown to be relatively inert at concentrations expected in Tank 50 (only tank in which CSSX solvent is expected).

An estimated 56.4 MT of spent ion exchange resins have been transferred to the tank farm, with two-thirds of it digested in alkaline permanganate prior to transfer.[4] The resins have a polymeric backbone made of polystyrene or a styrene-divinylbenzene copolymer. Fragmentation of the resin from the permanganate digestion leaves short-chain alcohol and carboxylic acid groups.[33] The anion resins typically contain a quaternary amine functional group, which upon radiolytic degradation forms amines such as methylamine, dimethylamine, and trimethylamine. Trimethylamine is thermally stable up to 350 °C and has been found to form dimethylamine and formaldehyde when oxidized.[36,37] The authors found no evidence for thermolytic methane generation from methylamines in caustic waste. As previously proposed, most of the methane is generated by reactive organic intermediates in both radiolytic and thermolytic pathways. Except for methylmercury and TMS, where thermolytic methane generation rates can be obtained, the organic chemical variability within SRS tanks, coupled with the short life span of these intermediates, makes it difficult to ascertain direct methane generation pathways.

Table 2-1. CSSX and NG-CSSX Solvent Components.[4]

Component	**Function**	**Original (CSSX) Solvent Concentration (wt %)**	**Next-Generation (NG-CSSX) Solvent Concentration (wt %)**
MaxCalix 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy) calix[4]arenebenzocrown-6	Extractant	0	2.40
BoBCalixC6 Calix[4]arene-bis(*t*-octylbenzo-crown 6)	Extractant	0.94	0
Cs-7SB 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol	Modifier	29.67	20.73
DCiTG* *N*,*N'*-Dicyclohexyl-*N"*-isotridecylguanidine	Suppressor	0	0.23
TOA Tri-n-octylamine	Suppressor	0.12	0
Isopar® L C_{12}-isoparaffinic hydrocarbon	Diluent	69.26	76.72

3.0 Evaluation of Methane Generation Rates Observed at SRS

To date, methane has been observed in several HGR experiments performed by SRNL, including testing with samples from Tanks 28, 38, and 44. The observed methane rates and conditions of each experiment are listed in Table **3-1**.

Table 3-1. Observed Methane Generation Rates in Previous HGR Testing with Waste Samples.

Material (Tank No.)	**Temperature (°C)**	**Sodium (M)**	**Hydroxide (M)**	**Observed MGR (ft^3 h^{-1} gal^{-1})**
28	124.8	13.0	8.23	≤5.7E-07
38	111.5	7.79	2.85	5E-07
44	106.7	6.28	<0.01	1.8E-06
44	100	6.28	<0.01	5.4E-07

Table **3-1** shows the majority of tests with appreciable methane formation were performed at temperatures higher than 100 °C. A notable exception to this observation is the measurement of methane generated from Tank 44 material at 100 °C.

The Tank 44 test described in Table **3-1** was performed by dissolving saltcake samples from Tank 44 and heating the combined dissolved salt solution. The analysis of this material revealed a concentration of 0.9 mg/L octamethylcyclotetrasiloxane and no detectable levels of organomercury. The presence of octamethylcyclotetrasiloxane is possibly indicative of organic material related to the historic additions of Dow H-10 (chemically identical to Xiameter AFE-1010, a polydimethylsiloxane-based antifoam agent).

The presence of residual antifoam compounds in saltcake is not surprising given the prior addition of antifoam to evaporator pots during waste evaporation and minimization campaigns.

The relatively high reactivity of methane production in Tank 44 (relative to rates observed in Tank 28 and Tank 38 testing) merits additional discussion. A few possible explanations may be put forward. First, it should be noted that the 0.9 mg/L of octamethylcyclotetrasiloxane measured in Tank 44 dissolved salt solution was determined by SRNL's volatile organic analysis/semivolatile organic analysis (VOA/SVOA) techniques, which employ a gas chromatograph/mass spectrometer to ascertain organic concentrations. While octamethylcyclotetrasiloxane is sufficiently volatile to be measured by GC/MS, it is uncertain if heavier oligomers of polydimethylsiloxane were present in the Tank 44 dissolved salt solution. Octamethylcyclotetrasiloxane is known to exist in equilibrium with other polydimethylsiloxane species, so it is reasonable to assume that other methylsilicone species were possibly present in solution that could not be analyzed. Additionally, the Tank 44 HGR experiment was conducted at a reduced hydroxide and sodium concentration (relative to Tanks 28 and 38). Polydimethylsiloxane and its derivatives are known to be hydrophobic. It is possible that increased concentrations of methylsiloxanes were available in Tank 44 dissolved salt supernatant solution due to the reduced ionic strength in the solution relative to that of the interstitial liquid in a saltcake remaining after dissolution. The hypothetical increased concentration would, in this case, be a contributor to the relatively high reactivity.

While it seems that the increased reactivity observed in Tank 44 methane generation is possibly linked to dissolved salt solutions previously exposed to H-10 antifoam, it is beneficial to evaluate the implication of similar rates across the CSTF in the event of transfer of dissolved salt solution to additional tanks for storage. This evaluation may be made by first determining a temperature dependence of the MGR observed in Tank 44 testing. This is accomplished by assuming Arrhenius behavior, as is shown in the following equation:

$$MGR = ke^{-E/RT}$$

$$\ln MGR = \ln k - \frac{E}{RT}$$

A temperature-dependent expression for Tank 44 methane generation may be derived by determining the slope and intercept of the line fit to Tank 44 data when plotted as ln(MGR) (where MGR is the methane generation rate in ft^3 h^{-1} gal^{-1}) vs. inverse temperature (as K^{-1}). The resulting equation from this fit is given below:

$$MGR = 1.13 \times 10^{25} e^{-223{,}700/RT}$$

This expression may be incorporated into existing flammability calculations in cases where direct observation of MGR is unknown to determine the time required to reach 5% of the LFL of methane in the headspace of a given tank. The results of these calculations are reported in Table **3-2**. The calculations were performed using inputs for temperature, free supernatant volume, and headspace volume from WCS obtained on April 16, 2020.

Table 3-2. Time to 5% Methane LFL Calculated Using WCS Data.

Tank[†]	Temperature Limit (°C)	Time to 5% CH_4 LFL (days)	%CH_4 LFL at 7 days (Equivalent to %CLFL)
28[††]	60	∞	$<3.2\times10^{-5*}$
30	90	16.0	2.2
32	100	11.0	3.2
36	100	13.9	2.6
37	95	23.7	1.5
38[††]	95	116.1	0.4
43[††]	95	75.4	0.6
44[††]	60	∞	$5.0\times10^{-4*}$
47	95	19.1	1.9

[†] Only Tanks 30, 32, 36, 37, 38, 43, and 47 were considered for this evaluation. All other tanks were incapable of producing an equilibrium headspace with 5% of the methane LFL when considering atmospheric breathing. Tanks 28 and 44 are included for reference to actual measurements of MGR.

[††] Tanks 28, 38, 43, and 44 are evaluated using observed MGRs from testing with radioactive waste material and temperature-corrected using the activation energy observed from Tank 44 testing.

[*] Tanks 28 and 44 are currently defined as slow generation tanks and are therefore evaluated at 28 days rather than 7 days.

All the tanks evaluated in Table **3-2** have high assumed temperature limits (≥90 °C). Further, most of these tanks (30, 32, 37, 38, and 43) are evaporator system tanks and fall under unique control programs. As can be seen in Table **3-2**, none of the times to 5% methane LFL fall below 7 days, which is the response time required for rapid generation rate tanks. It may be stated then that current controls in place in the CSTF appear sufficient for managing the methane generation reactivity observed in Tank 44 testing.

In summary, the apparent reactivity of methane generation in Tank 44 HGR testing is not identified as a threat to existing flammability controls in the CSTF for the following reasons:

- Most observed methane rates during HGR testing suggest that methane generation phenomena are largely restricted to temperatures higher than 100 °C,
- No quantified observation of thermolytic methane has been made at temperatures lower than 100 °C in CSTF testing,
- The relatively high reactivity of methane production in Tank 44 material at 100 °C is probably due to the presence of residual methylsiloxanes added as antifoam in CSTF evaporators, and is therefore likely unique to saltcake- and concentrated supernatant-containing tanks,
- Transfer of material from saltcake-containing tanks will inherently dilute any reactive material,
- Re-evaporation (i.e., temperatures higher than 100 °C) is less likely to be performed for dissolved saltcake material, and
- Based on the inputs used in this report, times to LFL for rapid generating tanks appear sufficient to control the conservative calculation of methane generation to below 5% of the methane LFL.

It is recommended that testing be performed with methylsilicones, methylsilanes, and methylmercury species to better understand the behavior of these organics in caustic waste.

4.0 Conclusions

Methane generation has been detected during thermolysis testing from SRS Tank waste and in simulants. Simulant testing has shown methane generation in the presence of TMS, an antifoam degradation product, as well as methylmercury, both of which are found within SRS waste tanks. The 2019 report *Evaluation of the Current State of Knowledge for Thermolysis of Organics within SRS Waste Forming Volatile Organic Compounds (VOCs)* reviewed historical data and assessed literature pertaining to thermolytic methane generation. That report recommended performing thermolysis studies on simulated waste to detect and quantify VOCs.

Evidence shows that thermolytic pathways to methane generation become significant at temperatures >100 °C in caustic waste. It is recommended that testing should be undertaken using the HGR experimental approach for methane generation. The initial simulant testing should obtain quantitative methane generation rates at elevated temperatures for methylated siloxanes/silanes and methylmercury with the goals of determining the current mechanism for thermolytic methane generation seen in SRS tank waste. The results of this testing should then be compiled and analyzed to ascertain the risk of challenging the current projected organic contribution of 5% to the CLFL.

An evaluation of observed methane generation rates has been performed to assess the implication for current CSTF controls. Based on the inputs used in this report, it was concluded that no methane generation data observed to date has challenged the existing 5% organic contribution to the CLFL assumption in the CSTF tank farm.

5.0 Recommendations, Path Forward or Future Work

The following recommendations should be considered:

- Simulant testing should be undertaken on methylated siloxanes/silanes and methylmercury to measure quantitative methane generation rates. Testing involving methylmercury should also measure HGR for comparison to previous work involving HGR as a function of Total Organic Carbon (TOC).
- Testing should be conducted to determine the role silanes and other organics play in the methylation of mercury in SRS waste, and how this affects thermolytic methane generation.
- Data from the testing described above (as well as literature data) should be leveraged to assess the generation of methane and other flammable gases in the 2H and 3H evaporators, where temperatures higher than 100 °C are expected.

6.0 References

1. Martino, C. J.; Newell, J. D.; Woodham, W. H.; Pareizs, J. M.; Edwards, T. B.; Lambert, D. P.; Howe, A. M. *Investigation of Thermolytic Hydrogen Generation Rate of Tank Farm Simulated and Actual Waste*; SRNL-STI-2017-00611, Rev. 1; Savannah River National Laboratory: **2019**.

2. Martino, C. J.; Newell, J. D.; Pareizs, J. M.; Duignan, M.; Restivo, M. L. *Investigation of Thermolysis Hydrogen Generation Rate in Tank 38 and Tank 50 Waste Samples with Sodium Glycolate*; SRNL-STI-2018-00559, Rev. 0; Savannah River National Laboratory: **2019**.

3. Martino, C.J.; Pareizs, J. M..; Woodham, W. H. *Investigation of Thermolytic Hydrogen Generation Rate in Tank 28 and Tank 39 Samples*; SRNL-STI-2019-00411, Rev. 0; Savannah River National Laboratory: **2019**.

4. Martino, C.J.; Pareizs, J. M.; Woodham, W. H. *Investigation of Thermolytic Hydrogen Generation Rate in Tank 44 Dissolved Saltcake Samples*; SRNL-STI-2019-00730, Rev. 0; Savannah River National Laboratory: **2020**.

5. Woodham, W. H.; Martino, C. J. *Evaluation of Thermolytic Production of Hydrogen from Glycolate and Common Tank Farm Organics in Simulated Waste*; SRNL-STI-2019-00605, Rev. 1; Savannah River National Laboratory: **2020**.

6. Crawford, C. L.; Fink, S. D.; Nash, C. A.; Pareizs, J. M. *Evaluation of the Current State of Knowledge for Thermolysis of Organics within SRS Waste Forming Volatile Organic Compounds (VOCs)*; SRNL-STI-2018-00163, Rev. 1; Savannah River National Laboratory: **2019**.

7. Keilers, C. H., Jr; Altman, S. N.; Crawford, C. L.; Fink, S. D.; Henley, D.; Mills, J.; Wiersma, B. J. *Flammable Gas Generation Mechanisms for High Level Liquid Waste Facilities*; X-ESR-G-00062, Rev. 1; **2017**.

8. Ashby, E. C.; Annis, A.; Barefield, E. K.; Boatright, D.; Doctorovich, F.; Liotta, C. L.; Neumann, H. M.; Konda, A.; Yao, C. F.; Zhang, K.; McDuffie, N. G. *Synthetic Waste Chemical Mechanism Studies*; WHC-EP-0823; Westinghouse Hanford Company: **1994**.

9. Barefield, E. K.; Boatright, D.; Desphande, A.; Doctorovich, R.; Liotta, C. L.; Neumann, H. M.; Seymore, S. *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1995 Progress Report*; PNL-I 1247, Pacific Northwest Laboratory: **1996**.

10. Camaioni, D. M.; Samuels, W. D.; Lenihan, J. C.; Sharma, A. K.; Autrey, S. T.; Lilga, M. A.; Hogan, M. O.; Clauss, S. A.; Wahl, K. L.; Campbell, J. A. *Organic Tanks Safety Program Waste Aging Studies Final Report*, PNNL-11909, Pacific Northwest National Laboratory: **1998**.

11. Stock, L. M. The Chemistry of Flammable Gas Generation; RPP-6664, Rev. 0; **2000**.

12. Stock, L. M. Occurrence and Chemistry of Organic Compounds in Hanford Site Waste Tanks; RPP-21854, Rev. 0; **2004**.

13. Laird, D. W.; Rowen, C. C.; Machold, T.; May, P. M.; Hefter G. Volatile Products from the Degradation of Organics in a Synthetic Bayer Liquor. *Ind. Eng. Chem. Res.* **2013**, *52*, 3613-3617.

14. Lambert, D. P.; Zamecnik, J. R.; Newell, J. D.; Williams, M. S. *Antifoam Degradation Testing*; SRNL-STI-2015-00352, Rev. 0; **2015**.

15. Martino, C. J.; Crawford, C. L. *Results of Antifoam Degradation Product Analysis of Tank 22H*; SRNL-L3100-2015-00146, Rev. 0; **2015**.

16. Hay, M. S.; Martino, C. J. *Analysis of Condensate Samples in Support of the Antifoam Degradation Study;* SRNL-STI-2015-00698, Rev. 1; **2016**.

17. Grubb, W. T. A Rate Study of the Silanol Condensation Reaction at 25° in Alcoholic Solvents. *J. Am. Chem. Soc.* **1954**, *76*, 3408-3414.

18. Šefčík, J.; Rankin, S. E.; Kirchner, S. J.; McCormick, A. V. Esterification, condensation, and deprotonation equilibria of trimethylsilanol. *J. Non-Cryst. Solids* **1999**, *258*, 187-197.

19. Sommer, L. H.; Pietrusza, E. W.; Whitmore, F. C. Properties of the Silicon-Hydroxyl Bond in Trialkylsilanols. *J. Am. Chem. Soc.* **1946**, *68,* 2282-2284.

20. Rücker, C.; Kümmerer Environmental Chemistry of Organosiloxanes. *Chem. Rev.* **2015**, *115,* 466-524.

21. Wilmarth, W. R.; Rosencrance, S. W.; Duffey, C. E. *Studies of Mercury in High Level Waste Systems*; WSRC-TR-2003-00238, Rev. 1; **2004**.

22. Tatlock, W. S.; Rochow, E. G. The Action of Strong Base on Hexamethyldisiloxane. *J. Am. Chem. Soc.* **1950**, *72*, 528-530.

23. Bannochie, C. J. Results of Hg Speciation Testing on the 3Q17 Tank 50 Sample; SRNL-L3300-2017-00037, Rev. 1; **2018**.

24. Martino, C. J. Organic Mercury in the Modular Caustic-Side Solvent Extraction Unit (MCU); WSRC-RP-2004-00707, Rev. 0; **2004**.

25. V. Jain, H. Shah, J. E. Occhipinti, W. R. Wilmarth, and R. E. Edwards, Evaluation of Mercury in Liquid Waste Processing Facilities Phase I Report; SRR-CES-2015-00012, Rev. 1; **2015**.

26. Wilmarth, W. R. *Results of Dimethylmercury Degradation Experiments at Frontier Geosciences*; SRT-LWP-2004-00018; **2004**.

27. Martino, C. J. *Kinetic Treatment of Dimethyl Mercury Degradation and Formation Studies*; SRNL-WHM-2004-00006, Rev. 0; **2004**.

28. Melnick, J. G.; Yukerwich, K.; Parkin, G. On the Chalcogenophilicity of Mercury: Evidence for a Strong Hg-Se Bond in [Tm$^{Bu^t}$]HgSePh and Its Relevance to the Toxicity of Mercury. *J. Am. Chem. Soc.* **2010**, *132*, 647-655.

29. Karri, R.; Chalana, A.; Kumar, B.; Jayadev, S. K.; Roy, G. Exploiting the κ^2-Fashioned Coordination of [Se_2]-Donor Ligand L_3Se for Facile Hg-C Bond Cleavage of Mercury Alkyls and Cytoprotection against Methylmercury-Induced Toxicity. *Chem. Eur. J.* **2019**, *25*, 12810-12819.

30. Palmer, J. H.; Parkin, G. Protolytic Cleavage of Hg-C Bonds Induced by 1-Methyl-1,3-dihydro-2H-benzimidazole-2-selone: Synthesis and Structural Characterization of Mercury Complexes. *J. Am. Chem. Soc.* **2015**, *137*, 4503-4516.

31. Duignan, M. R.; Crawford, C. L.; Restivo, M. L.; Alexander, M. R.; Hill, K. A.; Pareizs, J. M. *Methane Generation Rates from Tank 50 Simulant with Methylmercury Containing Saltstone Grout Solids* SRNL-STI-2020-00013, Rev. 0; **2020**.

32. Bannochie, C. J.; Fellinger, T. L.; Garcia-Strickland, P.; Shah, H. B.; Jain, V.; Wilmarth, W. R. Mercury in Aqueous tank waste at the Savannah River Site: Facts, forms, and impacts. *Sep. Sci. Technol.* **2018**, *53*, 1935-1947.

33. Walker, D. D. *Organic Compounds in Savannah River Site High-Level Waste*; WSRC-TR-2002-00391, Rev. 0; Savannah River Technology Center: **2002**.

34. Boley, C.S. “Estimation of Canyon Historical Solvent Losses to Tank Farms”, HLW-STE-98-0318, **1998**.

35. Davis, W. Jr. Ch. 7, “Radiolytic Behavior,” in Science and Technology of Tributyl Phosphate, W. W. Schultz, and J. D. Navratil, ed., Vol. 1, CRC Press, Boca Raton, Florida, **1984**.

36. Jones, P. W.; Gesser, H. D. Formation of Hydrogen from Amine Oxidation and Pyrolysis. *Combust. Flame* **1972**, 19, 134.

37. Lewis, F. D.; Ho T.-I.; Simpson, J. T. Photochemical addition of tertiary amines to stilbene. Stereoelectronic control of tertiary amine oxidation. *J. Org. Chem.* **1981**, *46*, 1077-1082.

Distribution:

cj.bannochie@srnl.doe.gov
alex.cozzi@srnl.doe.gov
brady.lee@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
brenda.garcia-diaz@srnl.doe.gov
connie.herman@srnl.doe.gov
dennis.jackson@srnl.doe.gov
joseph.manna@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
gregg.morgan@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
amy.ramsey@srnl.doe.gov
william.ramsey@srnl.doe.gov
eric.skidmore@srnl.doe.gov
michael.stone@srnl.doe.gov
boyd.wiedenman@srnl.doe.gov
Records Administration (EDWS)

bill.clark@srs.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
curtis.gardner@srs.gov
pauline.hang@srs.gov
anna.murphy@srs.gov
tony.polk@srs.gov
anthony.robinson@srs.gov
mark-a.smith@srs.gov
patricia.suggs@srs.gov
thomas.temple@srs.gov

celia.aponte@srs.gov
timothy.baughman@srs.gov
earl.brass@srs.gov
azikiwe.hooker@srs.gov
lauryn.jamison@srs.gov
ryan.mcnew@srs.gov
phillip.norris@srs.gov
christine.ridgeway@srs.gov
azadeh.samadi-dezfouli@srs.gov
arthur.wiggins@srs.gov
seth.hunter@srnl.doe.gov
charles.crawford@srnl.doe.gov
wesley.woodham@srnl.doe.gov