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).

Disclaimer:

Keywords:
Mercury, CPC, Melter, Eurofins, and DWPF

Phase 2 Report-Mercury Behavior in the Defense Waste Processing Facility

Date: May 2016

Authors: T.L. Fellinger and C.J. Bannochie

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

ARP	Actinide Removal Process
BDR	Basic Data Report
CPC	Chemical Process Cell
°C	Degree Celsius
CV-Hg	Cold Vapor Mercury
DWPF	Defense Waste Processing Facility
DMHg	Dimethyl Mercury
DOE	Department of Energy
DSS	Decontaminated Salt Solution
DWTT	Decontamination Waste Treatment Tank
FAVC	Formic Acid Vent Condenser
FGS	Frontier Global Sciences
FTIR	Fourier Transform InfraRed
GC	Gas Chromatograph
HEME	High Efficiency Mist Eliminator
HEPA	High Efficiency Particulate Air
HM	H Modified Plutonium Uranium Extraction
kg	kilogram
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
MeHg	Methylmercury
MOG	Melter Off Gas
MPC	Mercury Purification Cell
MS	Mass Spectrometer
MST	Monosodium Titanate
MSDS	Material Safety Data Sheet
MWWT	Mercury Water Wash Tank
NGS	Next Generation Solvent
OGCT	Off Gas Condensate Tank
PCCS	Product Composition Control System
PISA	Potential Inadequacy in Safety Analysis
PRFT	Precipitate Reactor Feed Tank
PUREX	Plutonium Uranium Extraction
PVV	Process Vessel Vent
RCT	Recycle Collection Tank
REDOX	Reduction Oxidation
RPM	Revolutions Per Minute
SAS	Steam Atomized Scrubber
SB	Sludge Batch
SE	Strip Effluent
SEFT	Strip Effluent Feed Tank
SEM	Scanning Electron Microscopy
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

LIST OF ACROYNMS (Continued)

SRR	Savannah River Remediation
TK	Tank
WAC	Waste Acceptance Criteria
WAPS	Waste Acceptance Product Specifications
WL	Waste Loading
wt.%	Weight Percent
XRD	X-Ray Diffraction

1.0 EXECUTIVE SUMMARY

A mercury program team was established in February 2015[1] 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.

Based on the objectives listed above, a two phased approach was taken. The first phase was dedicated to a review of the liquid waste inventory and chemical processing behavior using a system by system review methodology approach[2]. The methodology included assessing current knowledge, identification of gaps/information needs, and identification and execution of selected near term action recommendations. The second phase took an integrated approach to re-assess the overall system knowledge, to rank and prioritize critical gaps/information, assess impacts of removal and disposal options, and document an action plan needed to resolve overall mercury management removal.

As a part of the first phase, a mercury overview for the Defense Waste Processing Facility (DWPF) was presented to the mercury program team[3]. As a part of this presentation, partial condensate sample analytical results obtained from the Slurry Mix Evaporator Tank (SMECT), Off Gas Condensate Tank (OGCT), and the Recycle Collection Tank (RCT) generated from the processing of Batch 735 were presented. Also presented were four topics in regards to the identification of gaps/information needs and eight recommendations. These are listed below:

Item Number	GAPS/ INFORMATION NEEDS
1.	The Precipitate Reactor Feed Tank (PRFT) sample analyzed by Savannah River National Laboratory (SRNL) indicated mercury was present. Analysis should be performed for the PRFT to determine if mercury is present
2.	Why mercury is present in the analytical results for the Strip Effluent Hold Tank (SEHT) samples
3.	The impact of antifoam and solvent degradation products on mercury speciation for DWPF recycle streams
4.	Sample and analyze the solids plugging the vessels in the Mercury Purification Cell
Item Number	**RECOMMENDATIONS**
1.	Obtain remaining data for Batch 735
2.	Removing mercury from the Mercury Water Wash Tank (MWWT)/SMECT to reduce the amount of mercury sent back to the Tank Farm in the recycle stream
3.	Due to the potential introduction of mercury from the PRFT and Strip Effluent Feed Tank (SEFT), the Sludge Receipt and Adjustment Tank (SRAT) product analysis should be resumed to ensure the desired mercury endpoint is achieved
4.	More data should be collected to confirm the mercury behavior of the SMECT, RCT, and OGCT results of Batch 735. SRAT and Slurry Mix Evaporator (SME) product data should also be obtained
5.	Clean/replace the scrubber baskets to reduce the high differential pressure observed for SME and RCT/Melter Feed Tank (MFT) scrubber
6.	Flushing/cleaning SRAT/SME condensers
7.	Spare mercury pumps should be made available
8.	Restore operation of the Mercury Purification Cell (MPC)

As a part of the second phase, the preliminary results of Batch 735 were finalized and significant progress was made to address the gaps/information needs and provide recommendations. These include:

- A sampling and mercury analysis campaign was completed for:
  - SRAT receipt and SRAT product (Batches 736-738, 743-747, respectively)
  - SME receipt and SME product (Batches 736 and 738)

  - SMECT condensate data (Batches 735, 736, and 738; includes speciation by Eurofins Frontier Global Sciences (FGS))
  - OGCT condensate data (Batches 735, 736, and 738; includes speciation by Eurofins FGS)
  - RCT condensate data (Batches 735, 736, and 738; includes speciation by Eurofins FGS)
- A Systems Engineering Evaluation (SEE) to re-establish the mercury removal capability within DWPF[4].
- A path forward to implement the SEE recommendations[5].

The purpose of this report is to provide a summary of the DWPF processing history in regards to mercury, document the mercury results obtained on the product and condensate samples and provide further recommendations based on the data obtained. A summary of the highlights are found below:

<u>Summary of Highlights:</u>

- Sludge slurry, PRFT (Monosodium Titanate (MST)/sludge solids) and Strip Effluent (SE) are three main streams that are received at DWPF for processing. Based on the total mercury analyses of the SE and PRFT, the total contribution of the mercury to the DWPF coupled operations is less than 1% during Actinide Removal Process (ARP)/Modular Caustic Side Solvent Extraction (MCU) operations. This percentage increases to around 4% during Salt Waste Processing Facility (SWPF) operations. Based on speciation analysis, SE is also a source of methylmercury (MeHg). The likely source of MeHg is the salt solution fed to ARP/MCU which contains a small fraction of DWPF recycle material.
- The majority of the reactions related to the mercury chemistry, outlined in the Basic Data Report (BDR), were consistent with the mercury analysis of the products and condensate streams. The exception to this was the reaction chemistry for the OGCT and the identification of methyl and ethyl mercury (via sample analysis) in the SMECT.
- No mercury speciation has been performed on a sample of sludge slurry. This is needed to confirm the forms of mercury assumed in the BDR are correct.
- Mercury speciation data was obtained for the SMECT, OGCT, and RCT. Mercury species present in all three process vessels include ionic, elemental, and particulate mercury.
- Ethyl mercury was found in one of the SMECT samples taken from Batch 736. It was also found in one sample taken from Batch 738. MeHg was found in all of the SMECT samples and appears to increase over the cycle time of the batch. Possible sources include:
  - Reaction of the degradation products of antifoam with ionic mercury species present in the condensate,
  - Steam stripping of MeHg produced/added (Strip Effluent) during SRAT and SME processing, and
  - The decomposition of dimethylmercury (DMHg) to MeHg under acidic conditions, if present. It should be noted that the DMHg was found in one sample from Batch 738 at a low concentration.
- Nitrous/nitric acid is produced as a by-product of the neutralization reactions in the SRAT and is collected in the MWWT and SMECT. Nitric acid additions are also made to the SMECT to maintain the pH acidic. These acids can react with the elemental mercury present in the tank's sump and trench forming mercurous nitrate and potentially mercuric nitrate.
- The mercury mass balances performed during SRAT and SME cycles indicate that a significant amount of elemental mercury potentially resides in the SMECT and is not removed via the MWWT.
- The concentration of mercury in the OGCT depends on mercury reduction/ strip efficiency of the Chemical Process Cell (CPC) [i.e. SRAT and SME processing]. Mercury not removed during the CPC process volatilizes in the melter and is condensed in the OGCT.
- The amount of mercury in the RCT is dependent on the mercury content of the SMECT and the OGCT. Thus, the mercury concentration is expected to vary batch to batch based on the CPC operation, the rate of formation for mercurous/mercuric nitrate and other mercury species, and melter off gas (MOG) operation. Based on the limited data sets, the SMECT appears to be the largest contributor of elemental mercury to the RCT.
- Mercury material balance closure is challenging due to the changing conditions (solubility and forms) of condensate streams. Based on the results of individual batches, it appears between 25% and 57% of the mercury is currently retained after feed preparation steps are complete. This is inconsistent with the BDR assumption that 75% would be retained/removed at DWPF during SRAT processing.
- SRAT Batch 736 indicates mercury is not consistently being removed from the SRAT as intended. Based on the results of the SME, it appears the mercury was reduced during the SRAT, but not steam stripped. The reason for this is unknown.
- The sequence of the caustic addition to the RCT has changed to be earlier in the process. The presence of elemental mercury in the RCT samples supports the assumption in the BDR that since mercury slowly oxidizes in caustic, the oxidation should occur during the long term storage in the Tank Farm.

- The analytical results obtained for the RCT samples did not include solids analysis (sample was decanted to remove solids). Thus, the BDR assumption in regards to elemental mercury adsorbing on to the RCT solids could not be evaluated.

<u>Recommendations and Future Recommendations:</u>

- Nitric acid additions should be tailored to minimize the amount of nitric acid added to the SMECT to minimize oxidation of elemental mercury present in the tank's sump and trench.
- Complete the path forward actions outlined in SRR-WSE-2015-00055.
- If possible, the SRAT Product mercury analysis should be continued, to ensure the type of behavior observed during Batch 736 was an anomaly.
- Based on the formation of ethyl mercury and MeHg during CPC operations and its potential impact to Saltstone grout, efforts should be made to investigate the following:
  - More stable antifoams for the pH conditions of the CPC,
  - Minimization of the antifoam amounts added during CPC processing, when possible,
  - The mechanism of ethyl mercury and MeHg production in the SMECT. Currently, literature surveys indicate no published data to address the reaction chemistry for the conditions that exist in the SMECT, and
  - Complete feasibility studies related to sludge speciation, conversion of organic mercury to elemental mercury, and grout formulations to retain higher organic mercury content as funded under Environmental Management Technology Development Program (Fiscal Year 2016).

2.0 INTRODUCTION

The introduction for this report has been divided into 3 sub-sections. The intent and assumptions made with regards to mercury, found in the BDR, for the design of DWPF is provided in the first section. The timeline of DWPF operation is presented in the second section, and an overview of the historical sample results for mercury is presented in the third section.

2.1 Mercury Basis for DWPF

The BDR for DWPF was written to provide a basis for the design and construction of DWPF. The BDR[6] has since been superseded by other technical baseline documents (System Design Descriptions (SDDs) and Piping and Instrumentation Diagrams (P&IDs) as a few examples) upon the commissioning and operation of the plant. However, revision 139 of the BDR serves as a record document for historical purposes and contains assumed reactions for the mercury chemistry.[6] The information provided in the BDR is also important from the perspective that it provides an opportunity to identify changes and an opportunity to understand if the flowsheet changes have influenced the behavior of the mercury in DWPF.

Provided below is the summary of mercury chemistry found in the BDR for sludge washing, CPC, mercury purification, vitrification, OGCT/quencher/ejector/scrubbers, Decontamination Waste Treatment Tank (DWTT), and DWPF recycle during interim storage.

<u>Mercury Reactions assumed for Sludge Washing:</u>

$HgO + NaOH \rightarrow Na[HgO(OH)]$ *(10% conversion)* Equation 1

……

<u>Mercury Reactions assumed for CPC:</u>

SRAT Soluble:

$Hg(NO_3)_2 + HCOOH \rightarrow Hg + 2HNO_3 + 2CO_2$ Equation 2

$Na[HgO(OH)] + 2HCOOH \rightarrow HgO + CO_2 + H_2O + NaCOOH$ Equation 3

SRAT Insoluble:

$HgO + HCOOH \rightarrow Hg + CO_2 + H_2O$ *(Target Endpoint – 0.45 wt.% Hg in final product*[a]*)* Equation 4

……

Mercury Reactions assumed for the Mercury Purification:

$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2H_2O + 2NO_2$ Equation 5

……

Mercury Reactions assumed for Vitrification (1150˚C):

$2HgO \rightarrow Hg(v) + O_2$ Equation 6

$Hg \rightarrow Hg\ (v)$ Equation 7

$I_2 + 2Hg \rightarrow Hg_2I_2$ *(99% conversion)* Equation 8

$4Hg + 4HCl + O_2 \rightarrow Hg_2Cl_2 + 2H_2O$ *(90% conversion)* Equation 9

$2Hg_2Cl_2 + 4HCl + O_2 \rightarrow 4HgCl_2 + 2H_2O$ Equation 10

……

Mercury Reactions assumed for OGCT, Quencher, Ejector, and Scrubbers:

$HgCl_2 + 2Na_2CO_3 + H_2O \rightarrow HgO + 2NaCl + 2NaHCO_3$ Equation 11

$Hg_2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow Hg + HgO + 2NaCl + 2NaHCO_3$ Equation 12

$Hg_2I_2 + 2\ Na_2CO_3 + H_2O \rightarrow Hg + HgO + 2\ NaI + 2\ NaHCO_3$ Equation 13

……

Mercury Reactions assumed for DWTT:
$Hg(NO_3)_2 + 2NaOH \rightarrow HgO + NaNO_3 + H_2O$ Equation 14

……

Mercury Reactions assumed for DWPF Recycle during Interim Storage:

$Hg + NaNO_3 \rightarrow HgO + NaNO_2$ *(a)* Equation 15

$HgCl_2 + 2\ NaOH \rightarrow HgO + 2NaCl + H_2O$ Equation 16

$Hg_2Cl_2 + 2NaOH \rightarrow Hg + HgO + 2NaCl + H_2O$ Equation 17

$Hg_2I_2 + 2NaOH \rightarrow Hg + HgO + 2NaI + H_2O$ Equation 18

The design basis for mercury recovery from sludge processing was estimated to be approximately 75%. The remaining 25% of the mercury would be sent back in recycle to the Tank Farm with a small percentage of this mercury lost in off gas emissions. Information regarding salt processing in the BDR was not included in the reaction chemistry above, due to the fact that the salt process described by the BDR was not deployed during radioactive operations at DWPF. The salt process at DWPF has been subsequently replaced with a new flowsheet and is described in Section 2.2.

Based on the reaction information above, the two main species present are mercuric oxide (HgO) in the insoluble solids of the sludge slurry and sodium mercurate [NaHgO(OH)][7] in the supernate. In the SRAT, the sodium mercurate and mercury oxide present in the sludge slurry are reduced to the elemental state via formic acid addition in the SRAT. The elemental mercury is then steam stripped from the sludge slurry during boiling steps of the SRAT. The vapor from the SRAT is passed through a condenser (cooled by process water) and the elemental mercury is then collected and subsequently removed from

---

[a] *The Hg endpoint has been increased to 0.8 wt.% during processing of Sludge Batch 6. This is documented in SRR-WSE-2010-00213.*

the Liquid Waste System via the Mercury Water Wash Tank (MWWT) through the MPC. Residual mercury not removed via the steam stripping process remains in the SRAT product [8] and has the following four potential fates:

- Sent to the melter (~1150˚C), volatilized and collected in the OGCT,
- Potentially collect in the mercury sumps of the process vessels,
- Potentially collect in the off gas systems downstream of the SRAT in the CPC and Melt Cell (MC), and/or
- Undergoes chemical reactions due to the acidic conditions present in the condensate collection vessels (MWWT, SMECT, and OGCT) and is sent back in recycle waste via the RCT to the Tank Farm.

In essence, all of the BDR reactions listed above appear to be reasonable and in line with the current process based on the constituents and acids added/generated during processing with the exception of the reaction chemistry (Equations 11 through 13) defined for the OGCT, quencher, ejector and scrubbers. The BDR contains an assumption that NaOH is added to the OGCT to reduce corrosion and improve NOx scrubbing efficiency. NaOH is not currently added to the OGCT and the OGCT is acidic based on a sample characterization performed in 2005.[9] The predominant anions in the OGCT are nitrate followed by fluoride, formate, and chloride. Based on this change, a further review of literature was performed. In 2009, a preliminary modeling effort was completed to evaluate the impact of elevated mercury in the melter feed on the melter off-gas system[10]. The model predictions represent a vapor pressure driven off-gas carryover excluding the physically-entrained solids (which typically account for much of the off-gas carryover). Based on this modeling effort, a low percentage of the mercury fed to the melter is expected to be oxidized to $HgCl$ and $HgCl_2$ (percentage depends on available chloride concentration in the feed and vapor temperature of the melter) and HgO. The majority of the mercury is assumed to be elemental mercury entering the melter off gas (MOG) system. It is also noted in the model study that the subsequent formation of submicron semi-volatile salts in the condensate liquid is considered to be unlikely. The products of the modeling output and solution chemistry in the OGCT appear to be consistent with the available data for the OGCT condensate. Thus, confirming the potential mercury reactions assumed in the BDR for vitrification and that the products of the vitrification become the reactants in the OGCT.

2.2 Timeline of Operation for DWPF

After an extensive design, construction, and cold run campaign effort, DWPF began radioactive operation in 1996 to process retrieved sludge slurry from F and H Tank Farms utilizing a sludge only flowsheet with nitric acid and formic (dilute form initially, then switched to 90 wt. %) acid. As a part of the process, sludge slurry is received from the Low Point Pump Pit (LPPP) in the 221-S canyon building, chemically adjusted with acids, and frit is added to the adjusted sludge slurry so that a durable borosilicate glass waste form can be produced when the feed is vitrified in the melter. As a result of the evaporation of water during the feed preparation and vitrification steps, a recycle waste stream is generated and sent back to the Tank Farm via the LPPP. The LPPP contains three tanks. One tank is dedicated to the receipt of sludge slurry, one tank is dedicated to receiving recycle waste stream and the last tank was to receive processed salt solution.

DWPF operated in a sludge only mode until June of 2008. During that time, an alternate salt processing flowsheet was commissioned. As a result of salt processing, two streams are sent to DWPF for incorporation into the final glass product. The streams from salt processing include a strip acid stream containing Cs-137 called strip effluent (SE) produced from a Modular Caustic Side Solvent Extraction Unit (MCU) and a monosodium titanate (MST)-sludge solids stream or sludge solids stream (if no MST strike is required) produced from the ARP. The ARP product is transferred to the Precipitate Reactor Feed Tank (PRFT) and SE is sent via piping through the LPPP to the Strip Effluent Feed Tank (SEFT) in the 221-S canyon building. The current flow path for the sludge slurry, salt streams (ARP and SE), and condensate streams for DWPF are presented in Figure 1. In Figure 1, the blue represents the sludge slurry flow path, the yellow indicates the flow path for the salt streams coming to DWPF and the green indicates the flow path of condensate/recycle back to the Tank Farm.

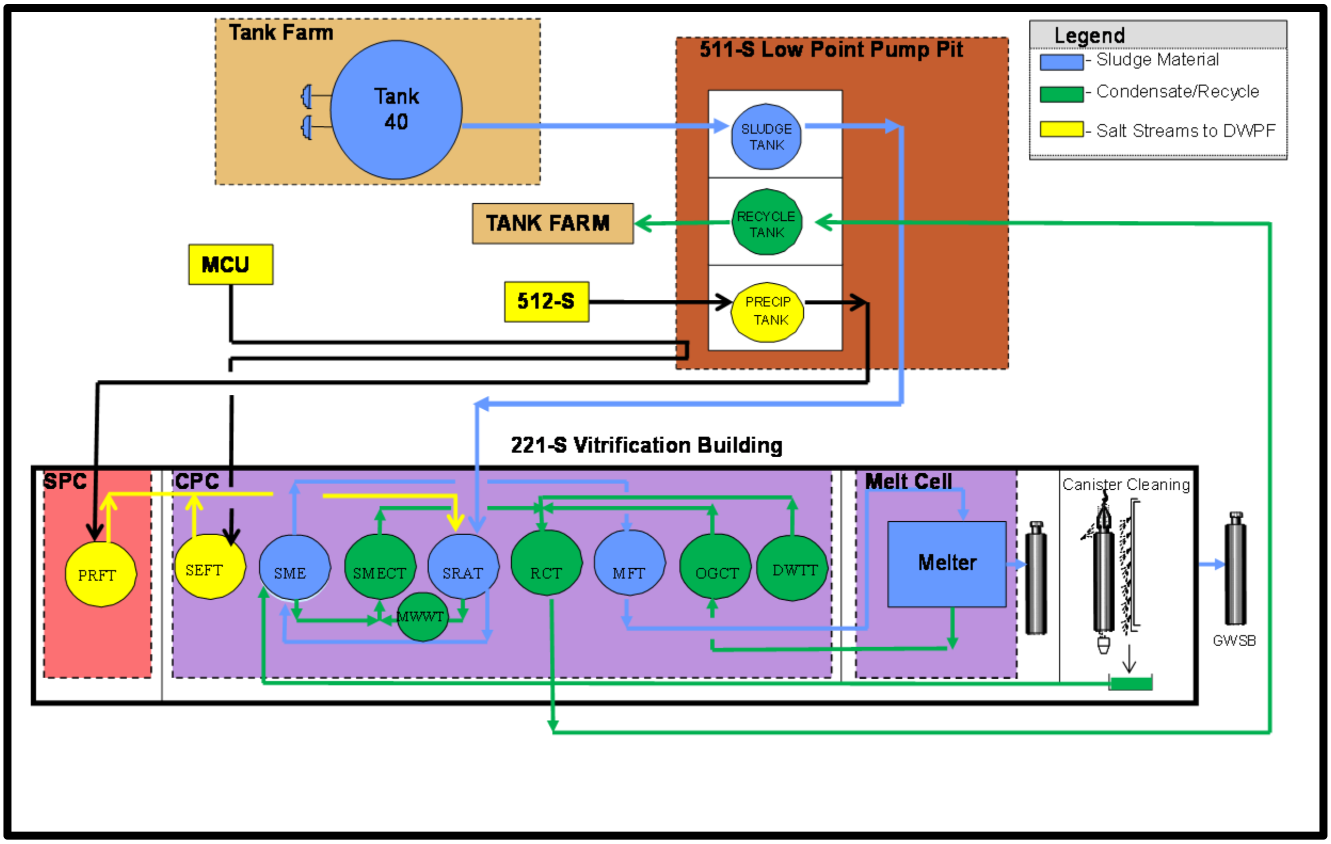


Figure 1 – DWPF Main Flow Paths for Sludge Slurry, Salt, and Condensate Streams

As can be seen in Figure 1, there are three tanks in the LPPP and the Chemical Process Cell (CPC) contains nine process vessels. Each vessel serves a purpose. Provided below is a brief description of each vessel's function.

LPPP – Contains three tanks called the LPPP –Sludge Tank, LPPP-Recycle Tank, and LPPP-Precipitate Tank. These tanks are mainly interim hold tanks for the process and contain material per the legend in Figure 1.

PRFT – Is located in the Salt Process Cell (SPC) and is currently the only tank in service in this cell. The PRFT receives the ARP product from 512-S facility. The nominal operating volume of the PRFT is ~7,000 gallons.

SEFT – Is located in the CPC and is the receipt vessel for strip effluent stream (acidic stream containing Cs) from MCU. The nominal operating volume of the SEFT is ~9,000 gallons.

SME – Is located in the CPC and receives acidified sludge slurry from the SRAT, frit slurry from canister decontamination, antifoam additions, and acidified process frit slurry. After processing is complete, the vessel is sampled to ensure Product Composition Control System (PCCS) requirements are met. The nominal operating volume of the SME is ~9,000 gallons.

SMECT – Is located in the CPC and receives condensate from the SRAT and SME. The SMECT provides liquid supply to the Ammonia scrubbers. The SMECT contents are transferred on a regular basis to the RCT. The nominal operating volume of the SMECT is ~9,000 gallons.

SRAT – Is located in the CPC and receives sludge slurry, salt streams (ARP from the PRFT and SE from the SEFT), nitric acid, formic acid, and antifoam additions. This tank is sampled to provide input to acid calculations and is sampled after processing is complete. The nominal operating volume of the SRAT is ~9,000 gallons.

MWWT – Is located in the CPC and Receives and sends condensate back from/to the SRAT to maintain desired level in the SRAT during boiling conditions. MWWT contains a weir to minimize floating elemental mercury beads going to SMECT. The tank is utilized to send recovered Hg to the MPC. The nominal operating volume of the MWWT is ~70 to 83 gallons.

RCT – Is located in the CPC and receives condensate from the SMECT, solutions from the laboratory drains, condensate from the OGCT, and transfers of material from the Decontamination Waste Treatment Tank (DWTT). The nominal operating volume of the RCT is ~9,000 gallons.

Melter Feed Tank (MFT) – Is located in the CPC and provides feed to the melter. Receipt tank for qualified material from the SME. The nominal operating volume of the MFT is ~9,000 gallons.

OGCT – Is located in the CPC and is the receipt tank for condensate generated from the melter. The nominal operating volume of the OGCT is ~9,000 gallons.
DWTT – Is located in the CPC and receives hot and warm decontamination solutions, decontamination waste solutions from the vessels and equipment being decontaminated, drains and overflows from the Mercury Purification Process, and dissolving spent High Efficiency Mist Eliminator (HEME)/High Efficiency Particulate Air (HEPA) filter dissolutions among many of the support functions it serves. The nominal operating volume of the DWTT is ~9,000 gallons.
Melter – Is located in the Melt cell and receives material from the MFT for vitrification. The maximum volume of the melter is 1,414 gallons.

As indicated previously, DWPF has been in radioactive operation for 20 years. During these 20 years, DWPF has processed 10 different macrobatches of sludge slurry and the products generated from 13 macrobatches of salt. The information provided below in Table 1 summarizes the length of time each sludge batch was processed, the sludge batch number /source tanks/Canyon additions to the sludge batch, the sludge type (H Modified Plutonium Uranium Extraction (HM) waste or Plutonium Uranium Extraction (PUREX)), Salt Batch number, and the key observations for that particular timeframe. The total mercury concentrations for the sludge and salt batches are presented in Figure 2 and Figure 3, respectively.

Table 1 – Timeline Summary for DWPF Operation

Month/Year (Start to Finish of Sludge Batch)	Sludge Batch/Macro Batch (Source Tanks for Sludge Batch and Canyon Receipts)	Sludge Type	Salt Batch (Start of Salt Batch)	Key Observations
Finish: 3/96	Cold Runs	PUREX / HM / Blend	-	Demonstrated functionality of systems and unit operations including Hg removal. - Incoming sludge: 3.0 wt.% Hg total dried solids limit set for DWPF. SRAT Product: 0.45wt% Hg total dried solids limit set for DWPF. Number of Batches Processed: 1 thru 20. Waste Loading (WL) Target: 28%
3/96 to 9/98	Sludge Batch 1A/Macro Batch 1 (Tanks: 17, 18, 21, and 22)	Blend (PUREX/HM)	-	Started radioactive operations with Sludge - Only Operations. Feeding from Tank 51. Added dilute formic acid/copper nitrate stream to substitute for Precipitate Hydrolysis Aqueous (old salt process). Dow Corning 544 antifoam used in the process. REDOX target used equation (F-N) to balance nitric and formic acids. R&D complete in 1997 to make flowsheet change to concentrated formic acid (90 wt.%) to reduce water in the recycle stream and shorten cycle time. Number of Batches Processed: 20 - 93 Can Production: 495 cans Frit : 200 WL Target : 28%
10/98 to 11/01	Sludge Batch 1B/Macro Batch 2 (Heel of SB1A and Al dissolved Tk 42)	More HM than PUREX	-	Sludge - Only Operations feeding from Tank 51. Dow Corning 544 Antifoam used in the process. REDOX target used equation (F-3N). Hg recovered, processed, and sent back to H-Canyon (~5.4 gallons). Sludge was noted to be tacky and adhering to surfaces in the DWPF lab. Number of Batches Processed: 94 - 208 Can Production: 726 cans Frit : 200 WL Target : 28%
12/01 to 3/04	Sludge Batch 2/Macro Batch 3 (Tanks 8, 17, 18, 22, and 42(heel))	Mainly PUREX	-	Sludge - Only Operations feeding from Tank 40. Changed from Dow Corning 544 to Antifoam IIT747in the process. Processing issues with air entrainment and rheology. SME failure and melter replacement 10/18/02. Hg recovered, processed, and sent Solid Waste(~6.2 gallons). "Mercury emissions from the Zone 1 exhaust stack are limited by an environmental permit to 0.0168 pph. Mercury monitoring downstream of the stack exhaust was originally required by DHEC, however they no longer require the monitoring because the limit is greater than the highest possible mercury content (assuming the mercury content is reduced to saturation at the respective condensers maximum air flow rates and exit temperatures). The monitors were abandoned in place in 2003." Number of Batches Processed: 208 - 272 Can Production: 364 cans Frit : 200 and 320 WL Target : 28% to 32 %
3/04 to 4/07	Sludge Batch 3/Macro batch 4 (Heel of SB2, Tk 7 (Tk 18/Tk 19). Oxalate and Coal thought to be high, but were not. F& H-Canyon receipts: Am/Cm, Pu/Gd, and Np	PUREX	-	Sludge - Only Operations feeding from Tank 40. Antifoam IIT747 used in the process. Raised wash endpoint from 0.5M Na to ~1M. Implemented new REDOX correlation assigning coefficients to Nitrogen and Carbon source. Number of Batches Processed: 272 - 402 Can Production: 726 cans Frit : 202 and 418 WL Target : 34 %
05/07 to 11/08	Sludge Batch 4/Macro Batch 5 (Large heel of SB3, Tk 11. H-Canyon receipts: none)	Blend (PUREX/HM)	Salt Batch 1 (4/25/2008)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Coupled Operation started on 6/16/2008. Antifoam IIT747 used in process. Al and Hg are higher. Longer cycle times and more frequent additions of antifoam. Catalytic hydrogen production in Shielded Cells Run high. Repeated Shielded Cells run. Had to perform a decant out of Tank 40 based on slurry pump dilution. Number of Batches Processed: 402B - 467 Can Production: 314 cans Frit : 418 and 510 WL Target : 34 %
12/08 to 6/10	Sludge Batch 5/Macro Batch 6 (Tank 11 Al dissolution, Tank 7, and heel from SB4. H-Canyon receipts: Pu/Be/Gd)	Aluminum Dissolved HM	Salt Batch 1 and 2 (4/25/2008 and 1/22/2009)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Antifoam IIT747 used in process. Longer cycle times due to Hg concentration and more frequent additions of antifoam. Catalytic hydrogen production observed in DWPF. pH of SRAT/SME products very high. Installed Isolok sampler on SRAT. Eliminated small sample stream going to the RCT. Collected ~5 gallons of Hg in 2008. Resides in a 5 gallon bucket in the purification cell. Replaced the MWWT in Jan 2009. Prior to replacement,~ 2 gallons of Hg was sent to the Hg purification cell and 4 gallons remain in the MWWT. Mercury that was successfully removed from the tank (approximately 2 gallons) clogged up tanks in the purification cell. Likewise transfers made in July 2008 clogged up a tank in the purification cell. Also, noted floating material on the surface of tank. Appeared to be some sort of organic material, but not confirmed. 2010 outage revealed mercury buildup in the SRAT condenser and SRAT scrubber. Hg probe in SMECT indicated 2", but prone fluctuations. SRAT Product limit raised to 0.60 wt.% Hg total dried solids. Number of Batches Processed: 468 - 530 Can Production: 323 cans Frit : 418 WL Target : 34 %

Table 1 - Timeline Summary for DWPF Operation (Continued)

Month/Year (Start to Finish)	Sludge Batch/Macro Batch (Source Tanks for Sludge Batch and Canyon Receipts)	Sludge Type	Salt Batch	Summary
6/10 to 5/11	Sludge Batch 6/Macro Batch 7 (Tank 12 - Al dissolution, Tank 4, heel from SB5. H-Canyon receipts: Pu/Gd)	Aluminum Dissolved HM	Salt Batch 3 (5/28/2010)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Antifoam IIT747 used in process. Highest Hg concentration observed to date. Longer cycle times due to Hg concentration and more frequent additions of antifoam. pH of SRAT/SME products very high. SRAT Product limit raised to 0.80 wt.% Hg total dried solids. 8/2010 reduced steam flow to SAS#1 from 370pph to 185pph. Bubblers installed in the melter 9/2010. PISA declared due to amount of antifoam going to the melter, due to long cycle time. Revised Calculation X-CLC-S-00164 to include carbon speciation. Number of Batches Processed: 531 - 570 Can Production: 194 cans Frit : 418 WL Target : 36 %
6/11 to 12/11	Sludge Batch 7A/Macro Batch 8 (Tank 4, 7, 12 and heel from SB6. H-Canyon receipts: Pu/Gd)	Mainly HM with PUREX	Salt Batch 3, Salt Batch 4A and 4B (5/28/2010, 7/23/2011, and 9/20/2011)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Antifoam IIT747 used in process. Study undertaken to understand antifoam performance, degradation products and improved effectiveness. Report issued 9/2011 Only a 6 month batch and coil fouling issues noted. Number of Batches Processed: 570B - 608 Can Production: 198 cans Frit : 418 WL Target : 36 %
1/12 to 5/13	Sludge Batch 7B/Macro Batch 9 (Tank 7 and Heel of SB7a . H-Canyon receipts: None)	Blend (PUREX/HM)	Salt Batch 4B, Salt Batch 5, and Salt Batches 6A thru 6D (9/20/2011, 8/31/2012, 1/25/2013, 3/2/2013, 3/22/2013, and 4/17/2013)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Antifoam IIT747 used in process. Carryover events noted in SME. Potential Inadequacy in Safety Analysis (PISA) declared for sludge solids carryover in recycle on 11/8/2012. Compensatory action required pre-caustic adjustment of the RCT. DWPF Review Team 2/2013. Noted issues with Hg recovery. Number of Batches Processed: 609 - 670 Can Production: 310 cans Frit : 418 WL Target : 36 %
5/13 to present	Sludge Batch 8/Macro Batch 10 (Tank 7, Tank 12 (remaining), Tank 13 and Heel of SB7B H-Canyon receipts: Pu LAP and DE-3013)	Mainly HM with PUREX	Salt Batch 6D, Salt Batches 7A and 7B, and Salt Batch 8 (4/17/2013, 3/26/2014, 5/25/2014, and 2/19/2015)	Sludge-Only and Coupled Operation. Feeding from Tank 40. Antifoam IIT747 used in process. Sampling plan developed to sample SRAT sump, MWWT, and SMECT. Hg samples retrieved from the SRAT sump, MWWT sump, and SMECT sump on 11/2013 and sent to SRNL for analysis. Melter is currently unbubbled due to the PISA declared. PISAs declared for trapped hydrogen and antifoam. Production stopped on 5/11/2015 and restarted on 9/21/2015. Mercury sampling campaign initiated. Sampled Batches 735 (condensate streams - only), 736 (SRAT, SME, and condensate streams), and 738 (SRAT, SME, and condensate streams). Sent condensate samples to Eurofins for Analysis. 4/2015 MWWT Hg bubbler in sump of tank indicates ~2” which is ~6.6 gallons. 4/2015 the SMECT Hg bubbler indicates greater than 2”. This may be as much as 70 gallons of Hg. Number of Batches Processed: 671 – 763 (As of 7/15/2016) Can Production: 428 cans (As of 7/15/2016) Frit : 803 WL Target : 36 %

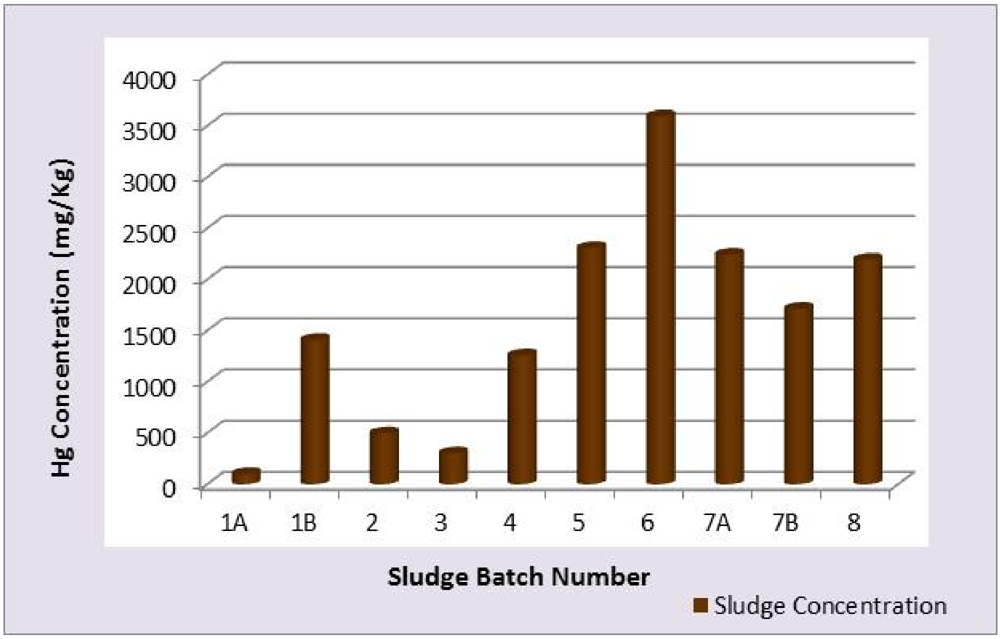


Figure 2 – Total Mercury Concentrations in mg/kg for Sludge Batches Processed in DWPF

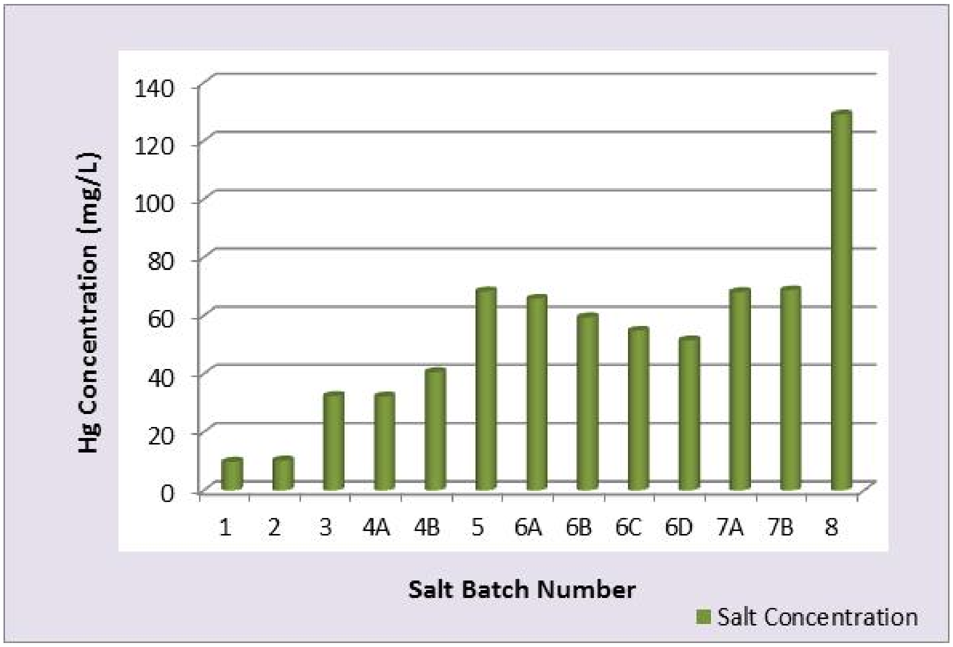


Figure 3 – Total Mercury Concentrations mg/L for Salt Batches

In reference 3, it was estimated that DWPF has received ~608 gallons of mercury (based on a total mercury analysis performed for each sludge batch, volume received into the SRAT and SRAT receipt density) based on the sludge slurry contribution alone. Since that initial estimate, DWPF has processed 28 additional SRAT batches adding another 40 gallons of mercury to the 608 gallons received making the total mercury inventory sent to DWPF ~648 gallons. See Appendix A for SB calculations. Based on the information provided in Table 1 and Appendix A, about 20% of the mercury [~124 gallons total = (23 gallons recovered + 77 gallons in the MWWT and SMECT+ 24 gallons to air emissions)] has been recovered and/or accounted for out of the ~648 gallons brought into DWPF. It is also known that low spots in the piping, filter assemblies and scrubber packing are ideal locations for mercury to collect or adhere on the surfaces. Outside of mercury holdup in DWPF process equipment, CPC sump #1 also contains some elemental mercury from an event when a MWWT drain jumper was removed and the MWWT contents were sent to the canyon sump. The actual volume of mercury present in the sump is unknown at this time, but it is not a large volume and is estimated to be ~10 gallons. Samples have also been taken from the sumps of the SMECT, SRAT, and MWWT. These samples indicate the presence of elemental mercury[11]. In some of the samples, the elemental mercury can be visually confirmed. Figure 4 contains the photographs of the SMECT, SRAT and MWWT samples.

Figure 4 - Photographs of SMECT (A), SRAT (B), and MWWT (C) Sump Samples

The picture of the MWWT in Figure 4, indicates the MWWT is dark in color and looks very dirty in comparison to the SMECT sample. Based on this information, it appears the significant amount of the mercury sent to DWPF could be returning in the recycle stream. The BDR assumed 25% of the Hg was returned to the Tank Farm in recycle stream. To confirm this, a sampling campaign was initiated at DWPF to confirm the indications of the historical data collected. Details of the recent facility sampling are found in Section 3.2. Section 2.3 provides an overview of the historical sample results for mercury.

2.3 Overview of the Historical Sample Results for Mercury

A summary of routine process samples and non-routine samples was presented in Reference 3. The methods selected for analysis varied from Cold Vapor Hg (CV-Hg), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Inductively Coupled Plasma Emissions Spectroscopy (ICP-ES). The CV-Hg and ICP-ES method will provide a quantitative measurement of the total mercury present. The ICP-ES also provides information on other analytes, but caution must be exercised when using the ICP-ES to report total Hg. Depending on the form of mercury present, the dissolution method used to prepare the solution for analysis may not be adequate to dissolve all of the different forms (organic and inorganic) of mercury present. If crystalline forms of mercury are present, the XRD can identify what crystalline form is present. This analysis is useful when trying to identify the form of mercury in order to dissolve/remove it or understand the chemistry in regards to its formation. The SEM is another tool available that can help identify whether or not mercury is present along with other elements. The SEM is also helpful determining the size and surface of particles relative to each other and relative abundance of the element in the sample. The SEM is not a quantitative technique to determine total amounts. These techniques were used to perform the analyses for the routine and non-routine samples documented below in Table 2.

Table 2 - Mercury Data from Routine Sampling or Special Sampling

Sample	Method	Result - mg/L elemental Hg basis unless otherwise indicated	Report/Memo
SMECT-4	CVHg	170	WSRC-TR-2004-00575[12]
SMECT-D	CVHg	110	WSRC-TR-2004-00575[12]
OGCT	CVHg	3.64E-02 wt.% (dried solids)	WSRC-TR-2004-00577[13]
OGCT	SEM	Detected Hg in the solids	WSRC-TR-2005-00141[9]
DWTT- SME Coil Decon	CVHg	1.94	WSRC-TR-2005-00036[14]
DWTT- HEME Dissolution	CVHg	< 4E-03wt.% (dried solids)	WSRC-TR-2005-00036[14]
RCT	CVHg	8.58E-02 wt.% (dried solids)	WSRC-TR-2004-00577[13]
PRFT	CVHg	22.4	SRNL-STI-2013-00735[15]
Quencher	ICP-ES	Range 0.12-0.15 wt.%	WSRC-STI-2007-00262[16]
Steam Atomized Scrubber (SAS)	XRD	Calomel	WSRC-STI-2007-00262[16]
SAS	ICP-ES	Range 3.42 -6.57 wt.%	WSRC-STI-2007-00262[16]
SAS - Water Leach	ICP-ES	Range 0.352-0.427 wt.%	WSRC-STI-2007-00262[16]
SME Coil Sample	CVHg	Range 2470-6160 ug/g (dried solids)	SRNL-STI-2011-00623[17]
SME Bulk Sample	CVHg	Range 501-610ug/g (dried solids)	SRNL-STI-2011-00623[17]
Quencher Sample	ICP-ES	2.37 wt.%	SRNL-STI-2011-00520[18]
Gas Chromatograph (GC) HEME/HEPA/HEPA	XRD	$Hg_4(OH)(NO_3)_3$ and $Hg_{10}(OH)_4(NO_3)_6$	SRNL-STI-2009-00602[19]
GC HEME	CVHg	Dissolved in Nitric - 59wt.%	SRNL-STI-2009-00602[19]
GC Line Particulate Material	XRD	$Hg_3CO_3(OH)\bullet 2H_2O$	SRNL-PSE-2007-00095[20]
SRAT Sump Sample	CVHg	557,000 mg/kg	SRNL-L3100-2014-00038[11]
MWWT Hg Sump Sample-Solids	CVHg	845,000 mg/kg	SRNL-L3100-2014-00038[11]
MWWT Hg Sump Sample	CVHg	436,000 mg/kg	SRNL-L3100-2014-00038[11]
SMECT Hg Sump Sample	CVHg	784,000 mg/kg	SRNL-L3100-2014-00038[11]
SMECT Hg Sump Sample Aqueous	CVHg	8,390 mg/kg	SRNL-L3100-2014-00038[11]
RCT Sample	CVHg	1.20 wt.% (dried solids)	SRNL-STI-2014-00603[21]

The results in Table 2, indicate all of the samples contain mercury. Depending on the sample location/source tank, the samples results can be quite variable with regards to concentrations. Also, based on the forms reported in Table 2, calomel or crystalline phases of mercury nitrate hydroxides based on the chemistry outline in Section 2.1 are not unexpected.

3.0 CPC Process Chemistry Behavior, DWPF Sampling Activities and Description of Analytical Methods Performed

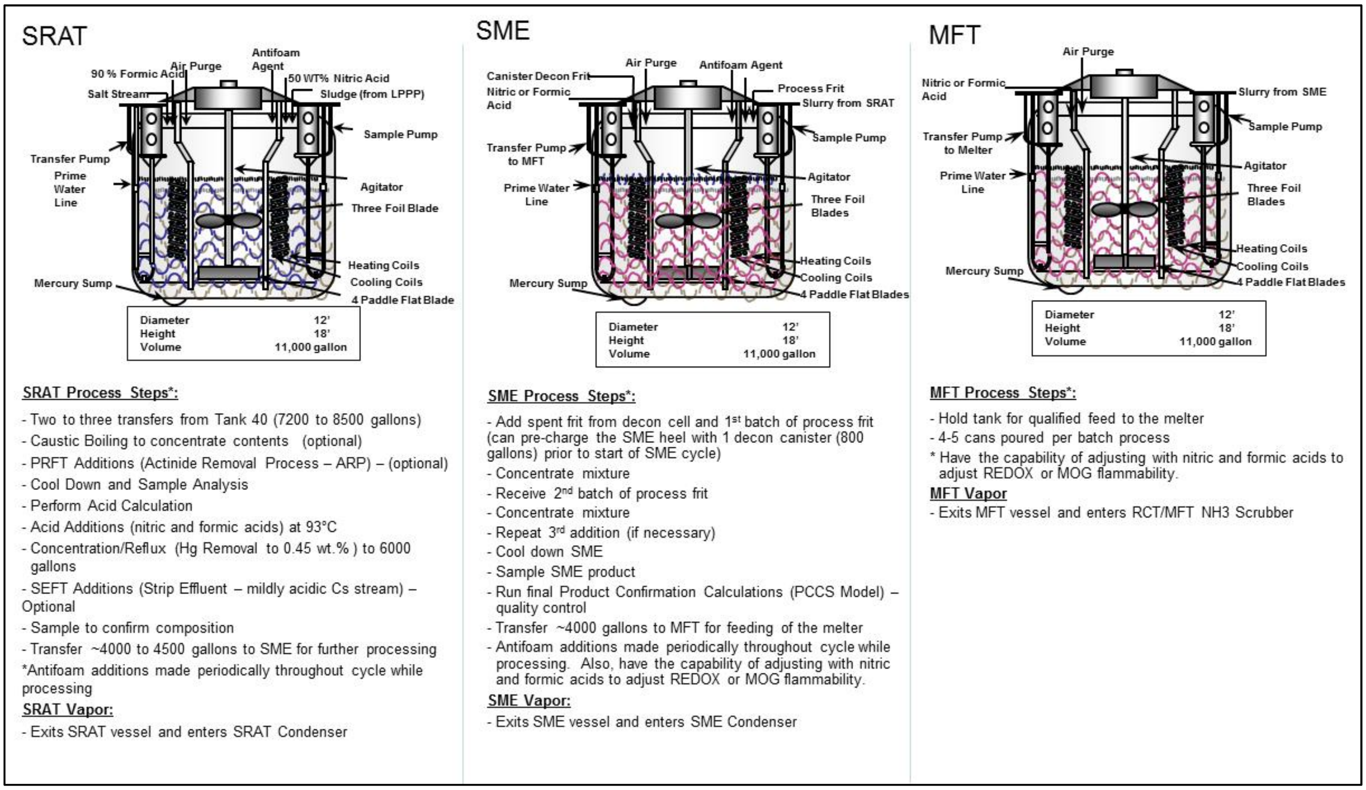
This section has been divided into four sub-sections. The overview of the main process vessels and functions can be found in Section 3.1, information regarding the sampling plan recently completed at DWPF can be found in Section 3.2, the DWPF sample preparation and analytical method for total mercury analysis can be found in Section 3.3, and the information regarding sampling and analysis performed by SRNL and Eurofins FGS can be found in Section 3.4.

3.1 Overview of the Main Process Vessels and Functions

In Section 2.2, a general purpose was provided for the main processing vessels presented in Figure 1. This section will provide more detail for the main processing vessels, functions and describe the condensing trains for DWPF.

SRAT, SME and MFT Main Processing Steps

An overview of the main processing steps for the SRAT, SME, and MFT is provided in Figure 5.



SRAT Process Steps*:

- Two to three transfers from Tank 40 (7200 to 8500 gallons)
- Caustic Boiling to concentrate contents (optional)
- PRFT Additions (Actinide Removal Process – ARP) – (optional)
- Cool Down and Sample Analysis
- Perform Acid Calculation
- Acid Additions (nitric and formic acids) at 93°C
- Concentration/Reflux (Hg Removal to 0.45 wt.%) to 6000 gallons
- SEFT Additions (Strip Effluent – mildly acidic Cs stream) – Optional
- Sample to confirm composition
- Transfer ~4000 to 4500 gallons to SME for further processing

*Antifoam additions made periodically throughout cycle while processing

SRAT Vapor:

- Exits SRAT vessel and enters SRAT Condenser

SME Process Steps*:

- Add spent frit from decon cell and 1st batch of process frit (can pre-charge the SME heel with 1 decon canister (800 gallons) prior to start of SME cycle)
- Concentrate mixture
- Receive 2nd batch of process frit
- Concentrate mixture
- Repeat 3rd addition (if necessary)
- Cool down SME
- Sample SME product
- Run final Product Confirmation Calculations (PCCS Model) – quality control
- Transfer ~4000 gallons to MFT for feeding of the melter
- Antifoam additions made periodically throughout cycle while processing. Also, have the capability of adjusting with nitric and formic acids to adjust REDOX or MOG flammability.

SME Vapor:

- Exits SME vessel and enters SME Condenser

MFT Process Steps*:

- Hold tank for qualified feed to the melter
- 4-5 cans poured per batch process

* Have the capability of adjusting with nitric and formic acids to adjust REDOX or MOG flammability.

MFT Vapor

- Exits MFT vessel and enters RCT/MFT NH3 Scrubber

Figure 5 – Main Processing Steps for the SRAT, SME, and MFT[3]

As seen in Figure 5, all of the vessels have the same diameter, height, and working volume. Both the SRAT and SME have condensers to cool the vapor stream coming off of vessel, whereas the vapor exiting the MFT enters the RCT/MFT ammonia scrubber. The sludge slurry entering the SRAT must meet the limits established in the Waste Acceptance Criteria (WAC) in order to be processed in DWPF. In the WAC, there is one criterion in regards to mercury[22]. As noted above, the nitric and formic acids are added in the SRAT. The nitric acid is an oxidizing acid, while formic acid is a reducing acid. The mix and total amount of these two acids is adjusted based on the SRAT receipt analytical results to accomplish the following goals:

- Acid base neutralization reactions - destruction of hydroxides and carbonates,
- Reaction with sodium nitrite - destruction of nitrite,
- Reduction of manganese – reduction of some fraction of MnO_2 to Mn^{+2},
- Reduction of mercury – reduction of HgO to Hg (via formic acid addition),
- Appropriate balance of nitric and formic for final glass Reduction/Oxidation (REDOX) in the melter,
- Balancing carbon and nitrogen sources to ensure MOG criteria is met,
- Minimization of hydrogen production from the noble metal catalyzed decomposition of formic acid, and
- Maximize weight percent solids.

The addition of acids during SRAT processing can result in significant off gas production and contributes to foaming of the sludge slurry. Foaming can result in a carryover of material from the SRAT into the off gas system and condensate systems (see Figure 4 for a picture of solids entrainment in the MWWT). To prevent carryover events, an antifoam agent is added to the SRAT. However the total quantity of antifoam added is limited due to its negative impact on CPC and MOG flammability. To compensate for the limited quantity of antifoam, the pounds per hour of steam added to the vessel is controlled. This can result in longer stripping times to achieve the desired mercury removal in the final product. The addition of formic acid to the tank also results in the production of hydrogen from the noble metal catalyzed decomposition of formic acid and the destruction of a large fraction of the formate added as formic acid. Due to higher levels of noble metals in the recent sludge slurry batches, the total amount of acids added has been limited due to catalytic hydrogen production. The limitation placed on total acid added during the CPC in turn constrains the ability to meet the other SRAT processing goals.

The goals of SME processing are to:

- Ensure Product Composition Control System (PCCS) limits are met by blending correct amounts of sludge and frit,
- Ensure waste loading commitment is met,
- Ensure each SME batch is below the 897 g/m^3 fissile limit (glass oxides basis),
- Ensure MOG flammability limits are met,
- Minimize hydrogen production from the noble metal catalyzed decomposition of formic acid, and
- Maximize weight percent solids.

In the SME, the main source of hydrogen production can be attributed to the process frit additions. The process frit additions contain a small amount of formic acid. During SB6 operations at DWPF, samples of the SME product were obtained to ensure that SME products meet the mercury limit established for processing of that SB through the melter. The material balance performed for the SME product indicates that some of the mercury is removed during the boiling steps of the SME (via steam stripping). The mercury removed during this step would transfer to the SMECT. As a result of the formate destruction in the SRAT and SME, the ending pH for the SME product can be high (10 to 11). The rheological properties of the products can be influenced by the ending pH and weight percent total solids. As the pH rises, the rheological properties of the sludge slurry tend to shift towards a thicker mud-like material. This has resulted in the facility targeting lower weight percent solids to compensate for the unfavorable rheological properties at elevated pH. The other phenomena observed during SME processing is coil fouling. Although the cause has not yet been determined, it is probably a combination of the chemistry (e.g. high pH) and rheological properties of the sludge slurry. The sample data for the SME coil, in Table 2, indicate the presence of mercury. The facility has compensated for this issue by targeting lower wt.% solids for the SME product and monitoring the performance of the steam coil.

Process Vessel Vent (PVV) and Mercury Transfer Header

The Process Vessel Vent (PVV) and Mercury Transfer Header provide ventilation pathways for the process tanks. Drawing M-M7-S-00005[23] provides simplified schematic of the pathway for the main process vessels and is displayed below in Figure 6.

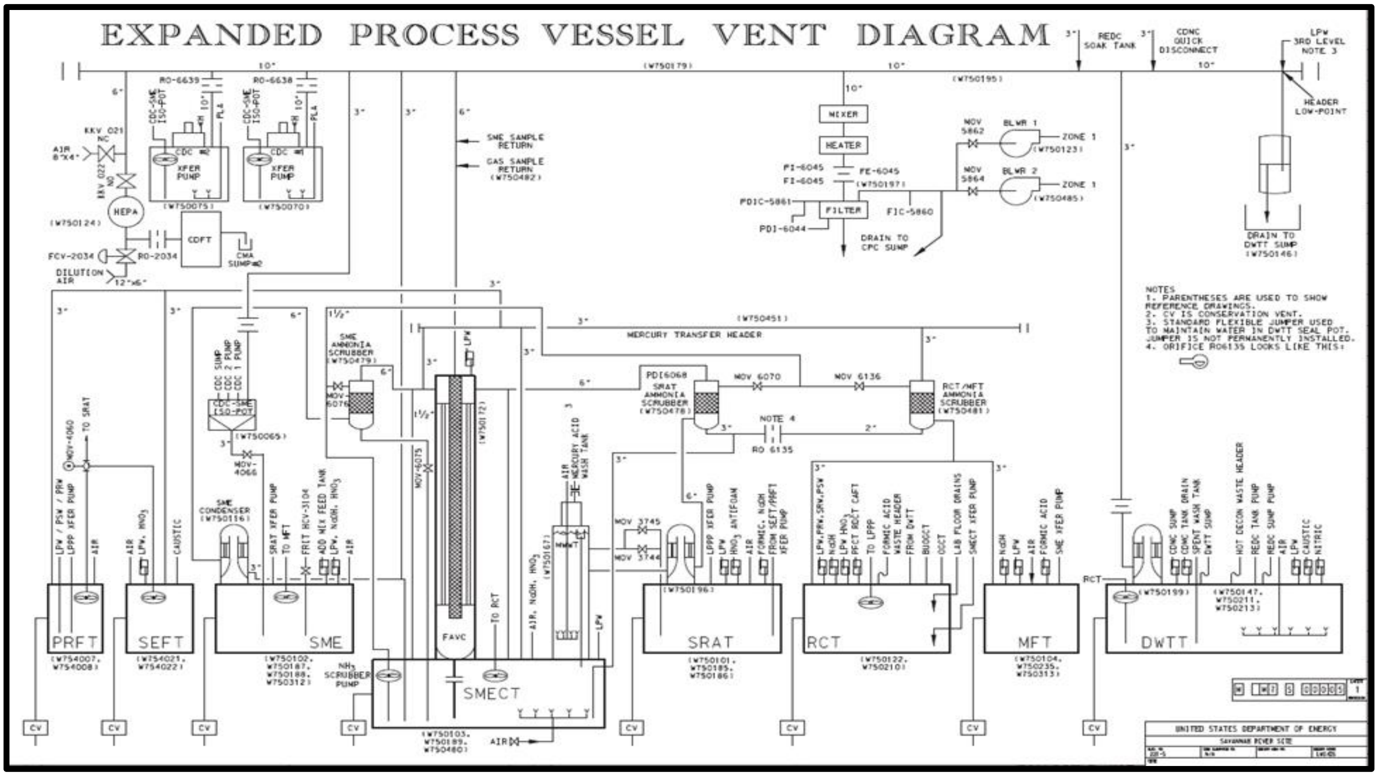


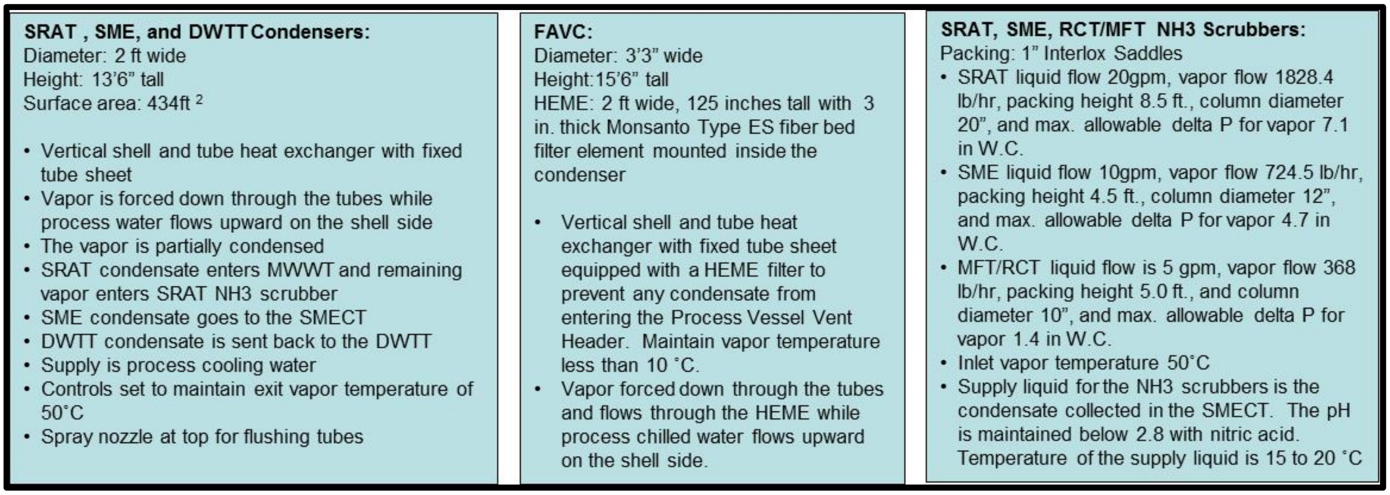
Figure 6 – Overview Drawing Process Vessel Vent (PVV) and the Mercury Transfer Header

The following observations can also be drawn from Figure 6:

- All process vessels are equipped with mercury sumps.
- The SRAT and SME ammonia scrubber vapor is directed toward the Formic Acid Vapor Condenser (FAVC) while the PRFT, SEFT, and RCT/MFT ammonia scrubber vapor is directed toward the mercury transfer header and then to the FAVC.
- The FAVC vapor is directed toward the PVV header then to Zone 1 ventilation.
- Any condensate collected from the FAVC is sent to SMECT.
- The DWTT is directly connected to the PVV header.
- The Mercury Transfer Header not only serves as a ventilation pathway for the process vessels, but was also designed to transport mercury from the process vessels to the SMECT. Once the mercury is in the SMECT, it can be transferred to the MPC via the MWWT.

Condensers and Scrubbers

Figure 7 contains technical specifications and operational information related to the condensers and scrubbers.



SRAT , SME, and DWTT Condensers:
Diameter: 2 ft wide
Height: 13’6” tall
Surface area: 434ft ^{2}

- Vertical shell and tube heat exchanger with fixed tube sheet
- Vapor is forced down through the tubes while process water flows upward on the shell side
- The vapor is partially condensed
- SRAT condensate enters MWWT and remaining vapor enters SRAT NH3 scrubber
- SME condensate goes to the SMECT
- DWTT condensate is sent back to the DWTT
- Supply is process cooling water
- Controls set to maintain exit vapor temperature of 50˚C
- Spray nozzle at top for flushing tubes

FAVC:
Diameter: 3’3” wide
Height:15’6” tall
HEME: 2 ft wide, 125 inches tall with 3 in. thick Monsanto Type ES fiber bed filter element mounted inside the condenser

- Vertical shell and tube heat exchanger with fixed tube sheet equipped with a HEME filter to prevent any condensate from entering the Process Vessel Vent Header. Maintain vapor temperature less than 10 ˚C.
- Vapor forced down through the tubes and flows through the HEME while process chilled water flows upward on the shell side.

SRAT, SME, RCT/MFT NH3 Scrubbers:
Packing: 1” Interlox Saddles

- SRAT liquid flow 20gpm, vapor flow 1828.4 lb/hr, packing height 8.5 ft., column diameter 20”, and max. allowable delta P for vapor 7.1 in W.C.
- SME liquid flow 10gpm, vapor flow 724.5 lb/hr, packing height 4.5 ft., column diameter 12”, and max. allowable delta P for vapor 4.7 in W.C.
- MFT/RCT liquid flow is 5 gpm, vapor flow 368 lb/hr, packing height 5.0 ft., and column diameter 10”, and max. allowable delta P for vapor 1.4 in W.C.
- Inlet vapor temperature 50˚C
- Supply liquid for the NH3 scrubbers is the condensate collected in the SMECT. The pH is maintained below 2.8 with nitric acid. Temperature of the supply liquid is 15 to 20 ˚C

Figure 7 – Condensers and Scrubbers Technical Specifications and Operational Information

During SB1A, 1B, and 2, the SRAT condenser operated at less than 55˚C and elemental mercury was collected in the MWWT. The observed exit vapor temperature of the SRAT condenser has steadily been increasing since SB4. The vapor temperature has been as high as 70˚C at the completion of acid addition and heat-up to boiling. During this time, several neutralization reactions are occurring along with mercury reduction producing H_2, oxides of N_2, and CO_2. As described in Figure 7, the SRAT condenser is designed to maintain the exit temperature of the vapor stream at 50˚C. Since the SRAT condenser cannot maintain the set point for the exit temperature of the vapor stream, it is assumed that very little of the mercury vapor is condensing upon exiting the SRAT condenser and is bypassing the MWWT. The next opportunity for the mercury vapor to condense is the ammonia scrubber. The ammonia scrubber solution is maintained between 15˚C and 20˚C and provides plenty of cooling capacity via direct vapor-liquid contact. Any mercury condensed in the ammonia scrubber system would collect in the SMECT. The observed increase in operating temperature of the SRAT condenser is likely due to the carryover events that have occurred. Carryover events from the SRAT and SME can deposit solids in the condensers and ammonia scrubbers, decreasing their overall efficiency and create deposit sites for elemental mercury. Figure 8 shows a picture of the mercury accumulation in the condensate drain of the SRAT ammonia scrubber to the SMECT.

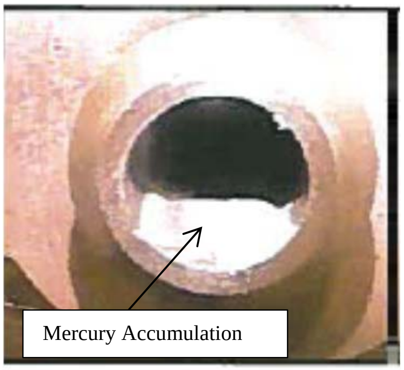


Figure 8 – Picture of Mercury Accumulation in the SRAT Ammonia Scrubber Condensate Drain to the SMECT

The FAVC vapor temperature ranges from 8 ˚C to 12 ˚C during processing. Recent pressure differentials for the SRAT, SME, and MFT/RCT scrubbers, during processing of Batch 735, are approximately +2 in WC, +23 in WC, and +10 in WC, respectively. Two out the three scrubbers are outside of the expected pressure differentials indicating that they may be partially plugged.

Main Mercury Collection Vessels – MWWT and SMECT

Figure 9 provides an overview of the MWWT and the SMECT. As indicated in Section 2.2, the MWWT has a small operating volume (~80 gallons) in comparison to the SMECT (~9,000 gallons)

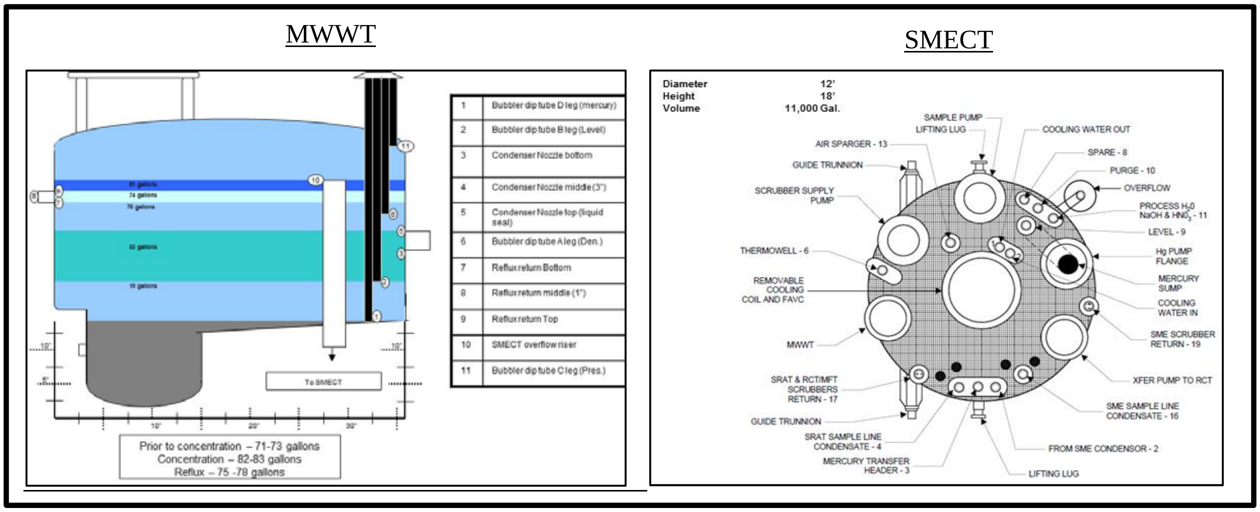


Figure 9 – Main Mercury Collection Vessels – MWWT and SMECT

The MWWT receives and sends condensate back from/to the SRAT to maintain desired level in the SRAT during boiling conditions. The MWWT is equipped with a weir to minimize floating elemental mercury beads from returning to the SMECT and is the tank utilized to send recovered Hg to the MPC. The pH of the MWWT solution could change based on SRAT processing (i.e. caustic boiling/acid additions) and contains sludge solids from carryover events as observed in Figure 4. The mercury bubbler is currently indicating ~2" of mercury in the tank. Based on the instrument scaling performed for the level instrumentation[24], this correlates to ~6.6 gallons of mercury. As noted previously, this is a very small fraction of the 637 gallons of mercury received into the facility.

The SMECT receives condensate from the SRAT, SME, and FAVC and needs a minimum level of ~4000 gallons to supply liquid to the Ammonia Scrubbers. The pH of the liquid is maintained below 2.8 with nitric acid and is continuously monitored during processing. The SMECT could contain sludge solids from carryover events, but the picture in Figure 4 shows that the liquid in the SMECT is relatively clean in comparison to that of the MWWT indicating no recent carryover event. The SMECT also serves as the collection point for elemental mercury from the scrubbers and can receive mercury from process vessels via the Mercury Transfer Header. Because it is the receipt tank for the condensate from the SRAT, SME and FAVC, frequent transfers are required to the RCT. The mercury sump and trough in the SMECT can hold approximately 10 gallons of mercury, but the mercury bubbler in the SMECT indicates greater than 2" this may be as much as 70 gallons of mercury.[3]

Melter and MOG

Figure 10 provides a simplified schematic of the flow paths for the vapor and liquid generated from the operation of the melter and MOG system.

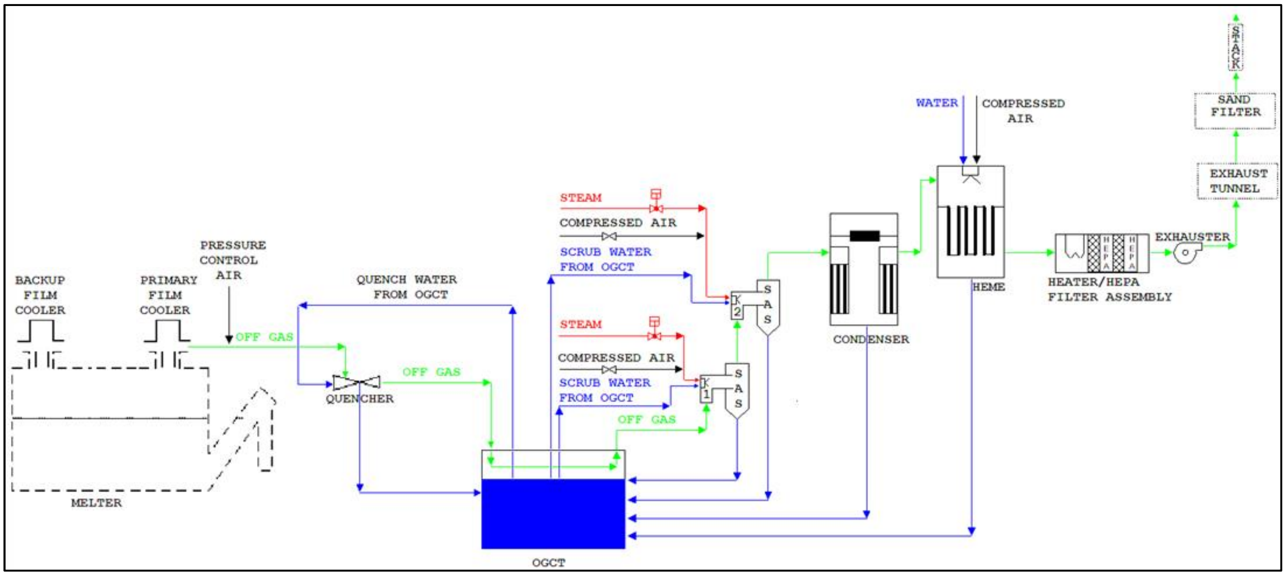


Figure 10 – Overview of the Melter Vapor and Liquid Flow Paths

As noted in previous sections, any mercury not removed in CPC operation will be sent to the melter via the MFT. The melter operates ~ 1150 ˚C and the vapors exiting the melter are cooled to ambient temperature by the time they reach the OGCT. As shown in Figure 10, the OGCT provides the liquid supply to the quencher and the SASs. Elemental mercury that has been volatilized from the melter could deposit in the MOG piping and/or could condense and collect in the OGCT. Since the OGCT is not currently agitated, the elemental Hg would settle and collect on the bottom of the tank. The pH of the OGCT in the past has been slightly acidic, thus any elemental Hg collected in this tank could dissolve. Because the OGCT is the main condensate collection for the melter, frequent transfers are made from the OGCT to the RCT. The solids collected in the bottom of the OGCT are periodically removed after treatment with nitric acid and pumped to the RCT during planned facility outages. After the vapor stream exits the OGCT, it enters a two stage SAS system followed by a condenser, HEME and HEPA filtration prior to being discharged to the exhaust tunnel. The vapor stream is then passed through a sand filter and out the stack. The liquid streams from the SAS, condenser, and HEME filter return to the OGCT.

RCT and DWTT

The RCT is the same height, diameter, and working volume as the SRAT. The RCT can receive waste from a variety of sources, but the main contributors are the DWTT, SMECT, OGCT, and sample/analytical lab waste. In-frequent transfers to the RCT include the formic acid waste header, floor drain catch tank, organic acid drain catch tank, regulated drains collection tank, effluent retention tank, catalyst feed tank, generator purge pump, deionized water purge header, process cooling water purge header, and process chilled water purge header to identify a few. Currently, Operations is still performing a caustic addition to heel of RCT for the neutralization of the acidic streams coming from the SMECT and OGCT. The waste is also adjusted with sodium nitrite to meet the corrosion control program for the Tank Farm.

The DWTT is also the same height, diameter, and working volume as the SRAT. The DWTT also receives a variety of waste streams and could include the following depending on facility operations:

- Solutions from the Hot and Warm Decontamination Waste headers,
- Contact Decontamination and Maintenance Cell (CDMC) tank drain pump(decontamination waste solutions from the vessels being decontaminated in the CDMC) and sumps,
- Remote Equipment Decontamination Cell (REDC) tank drain pump (decontamination waste solutions from the vessels being decontaminated in the REDC) and sump and filter,
- Spent wash tank (spent wash water, spills, drains and overflows from the Mercury Purification Process),
- DWTT sump (DWTT overflows and condensate from the process vessel vent header (PVVH)),

- DWTT reflux condenser, and
- HEME/HEPA filter dissolutions.

These solutions are neutralized to a pH of 7.0 prior to transfer to the RCT.

MPC and Mercury Pumps

There are two mercury pumps in the CPC; one in the MWWT and a mobile CPC mercury pump currently located in the SMECT. The MWWT mercury pump sends mercury directly to the MPC. The mobile CPC mercury pump can be placed in the SMECT, SRAT, SME, MFT, OGCT, RCT, or the SEFT. The SMECT and SRAT pump mercury directly to the MWWT; all other tanks pump mercury to the SMECT via the mercury transfer header before being transferred to the MWWT and then ultimately to the purification cell.

The MPC primarily consists of two tanks and two scrubbers. The material from the Mercury Acid Wash Tank (5 gallon capacity) is pumped through two scrubbers for cleaning with nitric acid and water before finally ending up in the Mercury Hold Tank (MHT). Per the BDR, ~2 gallons of 12 wt% nitric acid is added per gallon of elemental mercury, sparged with air ~2 hours, and then allowed to settle. The wash solution is transferred to the spent wash tank and the remaining contents are transferred to the acid scrubber first and then the water scrubber. The mercury is then checked for contaminants prior to being subjected to vacuum distillation process[6]. Mercury solubility in the acid wash is assumed to be 7.0E-03 wt.%. The distilled mercury is then transferred to mercury storage bottles for removal from the facility[6].

Figure 11 contains pictures of the Control Unit for Operating the Mobile CPC Mercury Pump, MWWT Mercury Pump and the DWPF Mercury Purification Cell

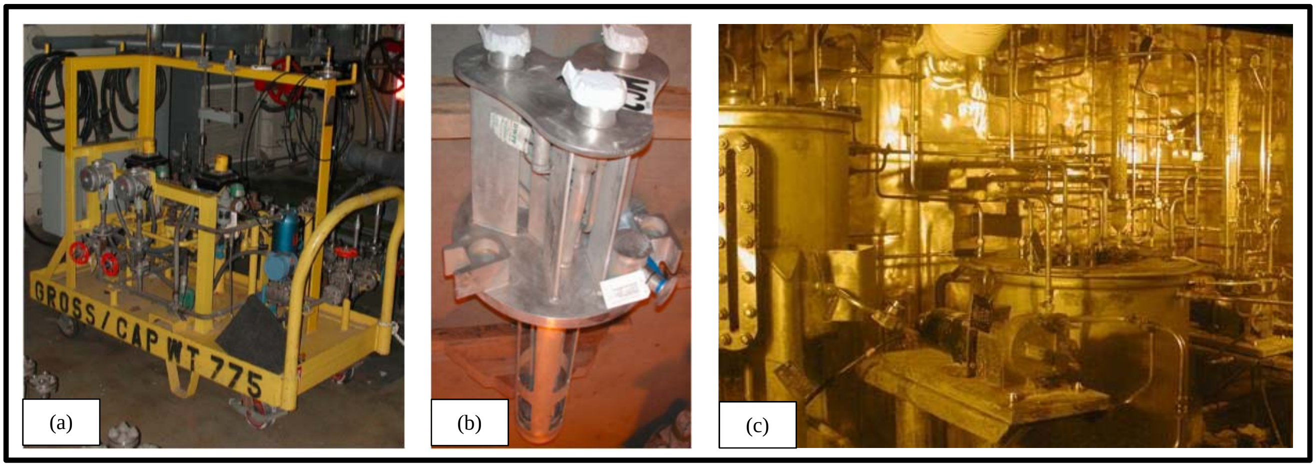


Figure 11 – Pictures of (a) Control Unit for Operating the Mobile CPC Mercury Pump, (b) MWWT Mercury Pump and (c) DWPF Mercury Purification Cell

3.2 Recent DWPF Facility Sampling

Based on the low recovery of elemental mercury at DWPF, a sampling campaign was conducted in the facility and includes the following tanks and batches:

- SRAT receipt (Batches 736, 738-747) and SRAT product (Batches 736-747)
- SME receipt and SME product (Batches 736 and 738)
- SMECT condensate data (Batches 735, 736, and 738)
- OGCT condensate data (Batches 735, 736, and 738)
- RCT condensate data (Batches 735, 736, and 738)

It should be noted that the DWPF laboratory has the capability to analyze samples for total mercury[25], but has no capability to perform mercury speciation. Mercury speciation is important to enhance our understanding of what forms of mercury are present, so that previously defined reaction chemistry can be verified or new chemistry defined. This provides a better understanding of the DWPF unit operations performance in regards to mercury removal from the Liquid Waste System and potential mercury forms being sent back in the recycle waste to the Tank Farm. Eurofins FGS has been identified as a laboratory capable of performing mercury speciation analysis on radioactive samples. Thus, extra samples were pulled for mercury speciation by Eurofins FGS. The sample matrix performed by the DWPF Laboratory, SRNL, and Eurofins FGS is presented in Tables 3 through 6 below.

Table 3 – Samples Taken of the SRAT Receipt, SRAT Product, SME Receipt, and SME Product

Vessel and Type of Sample	736	737	738	743	744	745	746	747
SRAT - SRAT receipt	X	-	X	X	X	X	X	X
SRAT - SRAT product	X	X	X	X	X	X	X	X
SME - SME receipt	X	-	X	-	-	-	-	-
SME - SME product	X	-	X	-	-	-	-	-

X = Sample obtained.
- = No sample obtained.

The SRAT receipt, SRAT product, SME receipt and SME product samples listed in Table 3 were agitated while the samples were being taken. The total mercury analysis was performed by the DWPF Laboratory.

Table 4 – Samples Taken from the SMECT During Key Process Steps of the SRAT and SME Cycles

Tank and Part of Process During the SRAT Steps	735	736	738
SMECT - Baseline - Start of SRAT Batch	X	X*	X*
SMECT - After PRFT	-	-	X*
SMECT - After Nitric Acid	X	X	X
SMECT - After Formic Acid	X	X	X
SMECT - After Initial Concentration	X	X*	-
SMECT - After SEFT	X	X	X
SMECT - End of SRAT	X	X*	X*
Tank and Part of Process During the SME Steps	**735**	**736**	**738**
SMECT - After Second Decon Canister	X	-	-
SMECT - After Last Decon Canister	X	-	-
SMECT - After First Frit Drop	X	-	X
SMECT - After Second Frit Drop	-	-	X
SMECT - After Final SME Concentration	X	-	X*

X = Indicates sample obtained.
- = No sample obtained.
* = Indicates mercury speciation was performed.

The samples of the SMECT condensate listed in Table 4 were pulled after major process steps during the SRAT and SME cycle. Based on the SMECT sample pump location, the elemental mercury residing in the mercury sump/trench is not included. Total mercury analysis was performed by the DWPF Laboratory. Speciation of select samples, including total mercury analysis, was performed by Eurofins FGS.

Table 5 – Condensate Samples Taken from the OGCT

Batches Sampled	735	736	738
OGCT	X*	X*	X*

X = Indicates sample obtained.
* = Indicates mercury speciation was performed.

The samples of the OGCT condensate listed in Table 5 were collected with the agitator off (i.e. no solids). Based on the OGCT sample pump suction location very few solids were obtained. Total mercury analysis was performed by the DWPF Laboratory. All samples were subjected to mercury speciation, including total mercury analysis, by Eurofins FGS.

Table 6 – Samples Taken from the RCT

Batches Sampled	735	736	738
RCT SRAT Processing	X*	X*	X
RCT SME Processing	X*	X*	X

X = Indicates sample obtained.
* = Indicates mercury speciation was performed.

The samples of the RCT listed in Table 6 were performed with the agitator on (i.e. solids present). Total mercury analysis was performed by the DWPF Laboratory. Speciation of select samples, including total mercury analysis, was performed by Eurofins FGS (solids were settled prior to sampling).

3.3 DWPF Sample Preparation and Analytical Method for Total Mercury

The DWPF Laboratory typically obtains samples from the process utilizing either a Hydragard™ or ISOLOK® sampler. The type of sampler used depends on the tank being sampled. Currently, the SRAT and SME vessels are the only vessels equipped with an Isolok sampler. The remaining vessels have a Hydragard sampler. The samples are pulled into ~12mL glass vials and the entire sample is dissolved when performing the total Hg analysis. The sample analyses are performed in duplicate, so an average can be performed and a standard deviation calculated. The preparation of the samples, blanks and spikes for mercury analysis is performed per Manual SW4-15.204, procedure 6.1.[25] The summary below provides an outline of the major steps:

- Add sulfuric acid, nitric acid, and potassium permanganate to the sample, swirl and wait 15 minutes,
- Add sodium persulfate, cap the digestion vessel containing the sample, mix, and heat at ~95˚C for 2 hours in an oven,
- Remove the digestion vessels and cool for 30 minutes,
- Uncap the sample and add sodium chloride-hydroxylamine hydrochloride solution, wait 10 minutes,
- If the purple color remains add sodium chloride-hydroxylamine hydrochloride solution drop wise until the solution is clear, immediately add nitric acid, and perform a series of dilutions to remove samples from the Shielded Cell.

The sample analysis is performed by a Nippon Mercury/RA 3000 system per Manual SW4-15.204, procedure 6.2.[26]

A special request was made to determine the soluble fraction of mercury in the samples that contained solids. Therefore, the RCT and OGCT samples were first filtered and then processed per the sample preparation and analysis described above. A 0.45 micron pore size cellulous nitrate filter media was used to perform the filtration of the sample. It should be noted that filtration of the sample may remove elemental mercury, if suspended in the supernate.

3.4 Sampling and Analysis Performed by SRNL and the Eurofins FGS

Samples from the various DWPF collection tanks were collected in small stainless steel bottles. It is recognized that there could be large uncertainties with such small samples from such a large volume. Every attempt was made by operations personnel to obtain a zero headspace sample. The bottles were capped, packaged for transfer to SRNL, and SRNL received the samples into either a shielded cell (OGCT samples) or transferred directly to refrigerated storage (SMECT and RCT samples) depending on the activity of the sample and its associated radiation dose rate. For samples received into the shielded cells, an intermediate dilution of 1:100 was made into a Teflon bottle and immediately removed from the cells for refrigerated storage prior to final dilution and shipment to Eurofins FGS for mercury speciation analyses.

Table 7 - DWPF Sample Designations, Descriptions, and Shipment Designations, as Well as Eurofins FGS Shipment Numbers

Eurofins Sample Designation	DWPF Description	DWPF Sample ID	DWPF Shipment #	DWPF Laboratory Information Management System (LIMS) No.	Eurofins Shipment #
SMECT 1	SMECT: SRAT 736 Baseline	1	1	200020712	13
SMECT 2	SMECT: SRAT 736 Initial Concentration	2	2	200020769	14
SMECT 3	SMECT: SRAT 736 End of Cycle	3	1	200020775	13
SMECT 4	SMECT: SRAT 738 Baseline	10	3	200020840	15
SMECT 5	SMECT: SRAT 738 After PRFT Add't	11	1	200020844	13
SMECT 6	SMECT: SRAT 738 End of Cycle	23	3	200020860	15
SMECT 8	SMECT: SME 738 End of Cycle	13	3	200020896	16
RCT 1	RCT: Batch 736 After SRAT	8	2	200020779	14
RCT 2	RCT: Batch 736 After SME	9	2	200020827	15
RCT-5	RCT: Batch 735 SMECT Condensate from SRAT Cycle	261	N/A	200020178	5
RCT-5/RCT-8	RCT: Batch 735 SMECT Condensate After SME Cycle	437	N/A	200020225	5
OGCT-4	OGCT: During Batch 735 Operation	232	N/A	200020236	5
OGCT 1	OGCT: Batch 736 End of Batch	12	4	200020884	16
OGCT 2	OGCT: Batch 738 End of Batch	14	4	200021045	16

N/A – Not Applicable

The Eurofins FGS supplied deionized water and 250 mL pre-cleaned, clear and amber glass bottles. For Shipment #13, the Eurofins FGS also supplied preservative (1.0 mL 50% H_2SO_4) for the bottles designated for methyl- and ethylmercury analysis. For Shipments #14, #15, and #16, SRNL supplied the 1.2 mL concentrated HCl preservative for the bottles designated for methyl- and ethylmercury analysis. Triplicate samples of each material were prepared for these shipments. Each replicate was analyzed for seven Hg species: total Hg, total soluble (dissolved) Hg, elemental Hg [Hg(0)], ionic (inorganic) Hg [Hg(I) and Hg(II)], methymercury [CH_3Hg^+], ethylmercury [$C_2H_5Hg^+$], and dimethymercury [$(CH_3)_2Hg$]. The difference between the total Hg and total soluble Hg after subtracting Hg(0) gives the particulate Hg concentration, i.e. Hg adsorbed to the surface of particulate matter in the sample but without resolution of the specific adsorbed species. The analytes were determined from samples in four separate bottles: 1) MeHg and ethyl mercury; 2) DMHg; 3) total mercury and soluble total (dissolved) mercury; and 4) ionic (inorganic) mercury and elemental mercury. The ionic mercury was determined after purging the sample of elemental mercury.

Final aliquot dilutions were prepared by SRNL, packaged, and shipped to Eurofins FGS within 24-36 hours and maintained as close to 4 °C as possible. The descriptions below provide details of the Eurofins FGS methods.

Dissolved vs. Total Mercury

The samples are filtered through 0.45 µm disposable filtration devices for dissolved mercury. When using filtration, an unquantifiable fraction of the dissolved volatile species can be lost, and so understate the dissolved total Hg concentration. Analysis directly of the filter post filtration can also be used to quantify particulate mercury.

Quantification of Dimethylmercury

DMHg is first extracted from a sample aliquot (0.025 to 2.00 mL, depending upon expected concentration) by dilution into 50 mL of reagent water, and direct purging for 17 minutes at a flow rate of 200 mL/min from solution into Carbotrap columns. After collection on the Carbotrap, the columns were dried by passing nitrogen through for seven minutes. For analysis, the loaded Carbotrap column is placed in-line with a packed column isothermal GC(GC) (1-m column, 4 mm ID, packed with 15% OV-3 on Chromasorb-WAW-DMSC; held at a constant 80 °C), and thermally desorbed into an argon stream which carries the Hg species into the GC column.[27] In the column, the following species can be easily separated: elemental Hg, $(CH_3)_2Hg$, $CH_3HgC_2H_5$, and $(C_2H_5)_2Hg$. Under the conditions of these experiments, however, the only meaningful peak is $(CH_3)_2Hg$, which passes through the column with a retention time of approximately 2.5 minutes, after a meaningless “marker” peak of elemental Hg at about 1 minute.[28] The gas stream from the GC column passes through a pyrolytic column held at approximately 800 °C, which breaks down all Hg species to elemental Hg, that are then quantified by cold vapor atomic fluorescence spectrometry (CVAFS), as detailed elsewhere.[27] The mass (ng) of Hg contained in each aliquot analyzed is quantified by comparison of the measured peak heights to the slope of a calibration curve analyzed from aliquots of a $(CH_3)_2Hg$ stock solution analyzed in the same manner. The initial stock solution was custom prepared in isopropanol and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species. A working solution of 1.0 ng/mL in methanol was prepared. Recertification of the concentration is performed annually by oxidation and analysis for total mercury.

Quantification of Methyl and Ethyl Mercury

MeHg and ethylmercury were analyzed similarly to the DMHg described above, except that the aliquot of sample was diluted with a pH 4.9 acetate buffer, and the sample first ethylated for 17 minutes with sodium tetraethyl borate for methylmercury[27,28] or propylated with sodium tetrapropylborate for ethylmercury. This reagent converts CH_3Hg^+, which is non-volatile, into MeHg ($CH_3HgC_2H_5$), which is volatile. This species is then analyzed by purge and trap with Carbotrap, and isothermal GC-CVAFS. The initial calibration standard employed for MeHg was a 100 µg/mL stock solution prepared by Absolute Standards (Hamden, CT), which was used to prepare a 1 ng/mL working standard. The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO). The initial calibration standard employed for ethylmercury was a 4.4 µg/mL stock solution prepared by Applied Isotope Technologies (Sunnyvale, CA). The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO) and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species.

Quantification of Total, Inorganic, and Elemental Mercury

Prior to analysis for total Hg, bromine monochloride (0.2M BrCl in 12M HCl) was added to the samples in their collection containers, at level of 1 mL per 100 mL of sample for total mercury analysis. The samples were then allowed to digest overnight at room temperature. Aliquots of each digest (0.01 to 100 mL, depending upon concentration) were reduced to elemental Hg in reagent water by the addition of $SnCl_2$, and then the elemental Hg purged onto gold traps as a pre-concentration step.[29] The mercury contained on the gold traps was desorbed and reabsorb on Carbotraps then analyzed by thermal desorption at 450 °C into a cold vapor atomic fluorescence detector (CVAFS), using the dual amalgamation technique. Peak heights were accessed by chart recorder, and the mass (ng) present in the sample calculated by comparison to a standard curve spanning the range of 0-2.00 ng Hg. The calibration standard employed is 10,000 µg/mL Hg diluted to a working laboratory concentration (10 ng/mL). The accuracy of this standard is verified daily by the analysis of the National Institute of Standards and Technology (NIST) NIST-1641d (mercury in river water matrix) reference material, which is diluted 200x with 1% BrCl solution prior to use. Inorganic mercury is determined using the same procedure after purging the sample to remove elemental mercury without the addition of BrCl that will give results of both ionic and elemental mercury. Elemental mercury is determined as well using the same procedure except without the addition of BrCl and $SnCl_2$.

4.0 DISCUSSION/RESULTS

This section has been divided into three sub-sections. Section 4.1 contains a data summary for the PRFT and SEHT. Section 4.2 contains a data summary for the mercury results obtained for the SRAT and SME receipt and product samples listed in Table 3. Section 4.3 contains a data summary for the mercury results for the condensate data listed in Tables 4 through 6.

4.1 Mercury Results for the PRFT and SEHT Samples

In order to confirm that the sludge slurry was the largest contributor to the total mercury sent to DWPF, samples from the PRFT and the SEHT were analyzed. The PRFT was analyzed on two separate occasions for total mercury; once by SRNL and once by the DWPF Laboratory. Samples of the SEHT are pulled on a regular basis and analyzed by SRNL. Mercury analysis was typically not performed on samples of the SEHT, because it was thought that very little mercury should be present in the SE stream and that the majority of the mercury should be in the decontaminated salt solution (DSS).[30] Since there was very little sample data[31] available on mercury and no speciation data, a sample was taken from the SEHT. The SEHT sample was prepared by SRNL and then shipped to Eurofins FGS for speciation. The SEHT is the hold tank for SE at MCU. The SEFT at DWPF receives the SE stream from the SEHT at MCU. Since a sample could not be retrieved from the SEFT, the sample results from the SEHT were used to evaluate the potential mercury contribution from the SE.[32] The mercury results for the PRFT are reported in Table 8, Table 9 contains the SRNL results for total mercury reported for SEHT Samples 6/2009 SE RCRA, MCU-15-382, MCU-14-666, and MCU -15-562/563/564, and the speciation results for Salt Batch 7B the SEHT are reported in Figure 12.

Table 8 – Mercury Results Reported for the PRFT[a]

PRFT Sample	Average Hg Elemental Basis (mg/L)
SRNL June 2013 PRFT Sample	22.4[a]
DWPF October 2015 PRFT Sample (LIMS ID 200020964)	20.0

[a] Converted to mg/L using data from Reference 15 (3.59E-02/100*5.96/100 *1000mg/g*1000 mL/L*1.049 g/mL)

The PRFT sample analyzed by SRNL was a sub-sample taken from the composite of 11 door stops. [15] The other PRFT sample was pulled during the processing of SRAT Batch 739 and was pulled specifically for mercury analysis. The results presented in Table 8 agree well with each other even though the sample pulls were approximately 16 months apart and different salt batches were being processed at the time.

Table 9 – Mercury Results for SEHT Samples 6/2009 SE RCRA, MCU-15-382, MCU-14-666, and MCU -15-562/ -563/ -564

MCU SEHT Sample Identification Number[a]	SRNL LIMS Identification Number	Mercury Results (mg/L) – Elemental Basis
6/2009 SE RCRA	300261156	1.09[b]
MCU-15-382	300316049	54.5[c]
MCU-14-666	300316268	<0.1[c]
MCU-15-562/-563/-564	300316274	82.2[c]

[a] See Appendix B
[b] Analyzed by CV-Hg
[c] Analyzed by CV-Hg Digested

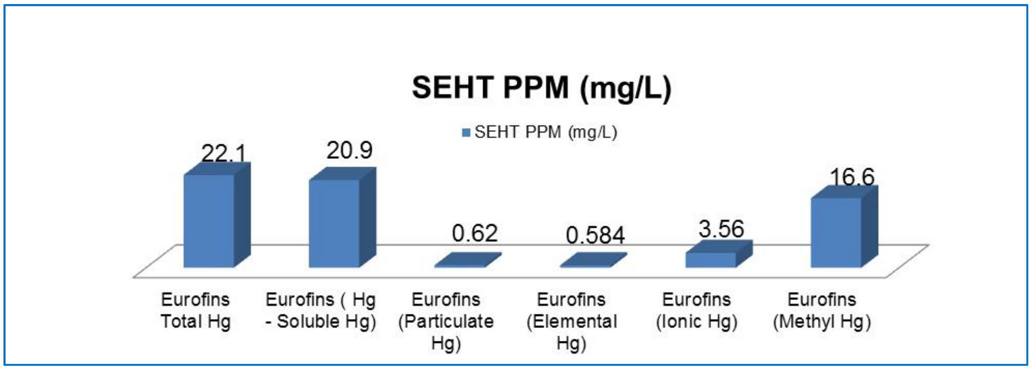
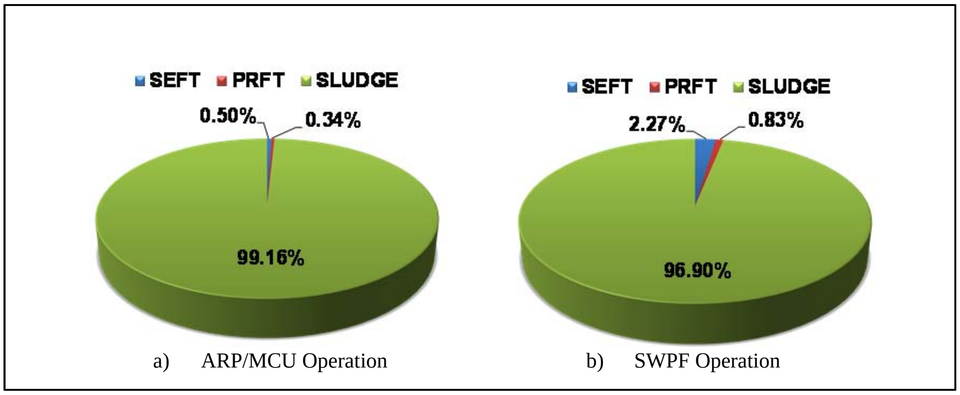


Figure 12 – Mercury Results Reported for the Salt Batch 7B SEHT (Sample Id: MCU-15-722, June 15, 2015) Sample on Elemental Hg Basis

The SEHT sample results reported in Table 9 and Figure 12 show variability in the total mercury. It should be noted that Sample 6/2009 SE RCRA was taken prior to MCU transition to the Next Generation Solvent (NGS) in December of 2013. Based on the analysis performed by Eurofins FGS, the total mercury concentration for the SEHT is about the same observed for PRFT samples. Speciation of the SEHT samples show that the majority of the mercury is soluble and mainly MeHg (~80%). In reference 30, the author summarized that the ionic mercury present in the salt solution should partition to the aqueous phase and the elemental mercury, DMHg and some of the MeHg present in the salt solution should partition to the solvent in the extraction stage at MCU. The author also noted that the DMHg present in the solvent would more than likely decompose to MeHg under acidic conditions and the MeHg would likely be removed from the solvent under acidic conditions. Speciation of the solvent samples has been completed as well[33] and confirms the conclusions drawn in reference 30. Although difficulties were encountered in the analysis due to the types of organics in the solvent, the results indicated the presence of elemental, ionic, and MeHg in the solvent and the presence of DMHg was inconclusive.

Currently under the NGS flowsheet, the only time the solvent comes into contact with an acidic stream in MCU is in the strip contactors. Under the BobCalix flowsheet at MCU, the solvent came into contact with acidic streams twice; scrub and strip contactors. The efficiency of removal during these short contact times is not known. The efficiency of removal of these mercury compounds could explain the differences in the total mercury observed in Table 9 and provide insight to the relative amount of the mercury species present in the SE in Figure 12.

The presence of mercury in the PRFT and SEHT samples, although low in comparison to the sludge slurry being processed at DWPF (see Figure 2), was unexpected in regards to the concentrations present. The mercury presence in the PRFT could be attributed to the remaining heel of salt solution at 512-S prior to batch washing and filter cleaning activities. The presence of mercury in the solvent and SEHT was discussed above. Regardless of the sources of mercury for the PRFT and SEHT, the impact of the mercury on the DWPF process must be considered. Below is an attempt to determine the impact to the distribution of mercury in DWPF as a function of ARP/MCU operation and proposed operations for the Salt Waste Processing Facility (SWPF). This information is presented in Figure 13.



a) ARP/MCU Operation b) SWPF Operation

Figure 13 – Distribution of Total Mercury (Elemental Basis) for Coupled Operation in DWPF; a) ARP/MCU operation b) SWPF Operation

To determine the impact of the PRFT and SEFT to the distribution of total mercury assumed for DWPF in Figure 13, certain assumptions were made for ARP/MCU operation and SWPF operation. The ARP/MCU graphic is based on 6,000 gallons of SB8 SRAT receipt (2181 mg/Kg)[bc] including the addition of 2,000 gallons of PRFT and 3,000 gallons SEFT (based on the Eurofins FGS analysis). The MeHg (based on elemental mercury contribution) is estimated to be 8.3 mg/L in SRAT product. The SWPF graphic is based on 6,000 gallons of SB8 SRAT product including the addition of 5,000 gallons of PRFT and 14,000 gallons SEFT. The MeHg (expressed as mercury) is estimated to be 51 mg/L in SRAT product. The mercury compounds present in the SEFT will likely survive the SRAT process due to the sequencing steps for the addition of nitric and formic acids and SE. Specifically, formic acid is added during SRAT processing to reduce the mercury compounds to their elemental state so that the elemental mercury can be removed via steam stripping. Because the SEFT addition follows the formic acid addition, the mercury contribution from the SEFT remains unreduced. The unreduced mercury compounds will likely survive the SRAT and SME process and be sent forward to the melter unless they can be steam stripped. There are published data that investigated steam distillation as an option for removing and concentrating MeHg from water samples.[34, 35] Based on the information presented in Figure 13, the sludge slurry contribution to the total mercury remains the dominant source for mercury for both ARP/MCU and SWPF operation. Although the salt stream contributions are small, they do increase during SWPF production based on the volume added. Using the basis of operation for ARP/MCU and SWPF in Figure 13, the total mercury potentially sent to the melter per SRAT batch is 0.25 kg of mercury and 1.2 kg of mercury, respectively from the SEFT addition alone.

4.2 Mercury Results Obtained for the SRAT and SME Receipt and Product Samples

SRAT and SME samples were taken and analyzed by the DWPF Laboratory as prescribed in Table 3, Section 3.3, and Section 3.4. The results of the samples can be found below in Figure 14 and
Figure 15. Table 10 contains the volume, density and other trends to help identify the differences performed for each SRAT and SME batch processed. The SRAT total steam flow and PRFT, SRAT and SME volumes reported in Table 10 were obtained from a data acquisition program called PI ProcessBook Version 3.2.0.0. The PI tags for the SRAT total steam flow, PRFT, SRAT, and SME levels are FQI3000, DLI1170, DLI3025, and DLI3109, respectively. The remaining data in Table 10 were obtained from the DWPF Laboratory and an Excel spreadsheet called "CPC Chem Coverage SB8" maintained on a network server. The LIMS identification number is provided for each sample.

---

[b] *Average mercury concentration using first 11 batches. DWPF LIMS identification numbers: (200016862, 2000117009, 2000117076, 200011712,2000117185, 2000117257, 2000117335, 2000117397, 2000117454, 2000117500, and 2000117542).*

[c] *Example Calculation for Mercury for ARP/MCU Operation* :$\left(6000\ gallons * \frac{3.785\ Liters}{Gallons} * \frac{1.13Kg}{L} * \frac{2181\ mg}{Kg} * \frac{1\ g}{1000mg} * \frac{1\ Kg}{1000g}\right)$, $\left(2000\ gallons * \frac{3.785\ Liters}{Gallons} * \frac{21.2\ mg}{L} * \frac{1\ g}{1000mg} * \frac{1\ Kg}{1000g}\right)$, $\left(3000\ gallons * \frac{3.785\ Liters}{Gallons} * \frac{22.1\ mg}{L} * \frac{1\ g}{1000mg} * \frac{1\ Kg}{1000g}\right)$

Table 10 – Information Regarding the SRAT and SME Cycles Performed for SRAT Batches 736 Through 747

SRAT Cycle

Batch Number **(DWPF LIMS ID SRAT Receipt)** **(DWPF LIMS ID SRAT Product)**	**736*** **(200020733)** **(200020776)**	**737** **(200020788)** **(200020823)**	**738** **(200020846)** **(200020859)**	**743** **(200021179)** **(200021196)**	**744** **(200021203)** **(200021237)**	**745** **(200021304)** **(200021321)**	**746** **(200021333)** **(200021353)**	**747** **(200021337)** **(200021400)**
PRFT Volume Added (gallons)	0	0	2,703	1,569	0	2,749	2,086	3,516
SRAT Receipt Volume for Acid Calculation (gallons)	8,178	8,314	8,429	8,129	8,552	8,329	8,224	7,891
SRAT Receipt Wt.% Solids	16.25	14.29	14.40	14.79	13.46	14.56	15.02	14.40
Nitric Acid Added (gallons)	125	100	105	110	115	100	110	110
Formic Acid Added (gallons)	310	280	315	265	280	325	310	295
SEFT Volume (gallons)	1,884	1,960	1,978	2,571	2,216	3,410	3,568	3,805
Final SRAT Volume (gallons)	6,424	6,235	6,049	5,895	6,414	6,282	6,149	6,259
Final Wt.% Solids	22.32	20.22	21.58	21.08	20.52	20.78	21.38	19.45
REDOX Target	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Total Pounds of Steam Added	75,014	75,389	78,837	113,990	75,488	76,526	75,154	80,717
pH of Final SRAT Product	7.7	7.4	7.5	7.4	7.1	7.7	7.7	7.7
Density of SRAT Receipt (g/mL)	1.130	1.102	1.100	1.095	1.087	1.088	1.107	1.115
Density of SRAT Product (g/mL)	1.152	1.121	1.158	1.134	1.117	1.146	1.157	1.141

SME Cycle

Batch Number **(DWPF LIMS ID SME Receipt)** **(DWPF LIMS ID SME Product)**	**736*** **(200020777)** **(200020820)**	**737** **(-)** **(200020838)**	**738** **(200020887)** **(200020894)**	**743** **(-)** **(200021233)**	**744** **(-)** **(200021263)**	**745** **(-)** **(200021327)**	**746** **(-)** **(200021369)**	**747** **(-)** **(200021418)**
SME Receipt Volume (gallons)	8,861	7,001	5,963	6,099	6,897	7,304	5,952	7,045
Volume of SRAT Product Transferred (gallons)	4,877	4,738	4,853	4,764	5,279	4,890	4,801	5,015
Canisters Deconned**	1	5	1	5	2	1	5	3
Pounds of Frit Added**	10,942	9,439	10,930	9,800	10,571	9,756	10,037	8,450
Final Volume of the SME (gallons)	9,672	7,673	7,163	6,859	7,202	7,058	6,384	6,400
SME Product Wt.% Solids	28.1	31.6	31.6	34.5	32.2	35.2	36.5	35.7
Predicted REDOX Based on Analytical Data**	0.13	0.16	0.16	0.10	0.14	0.16	0.16	0.12
pH of Final SME Product	7.9	7.3	8.1	7.9	7.3	7.5	7.7	7.7
Density of SME Receipt (g/mL)	1.132	-	1.088	-	-	-	-	-
Density of SME Product (g/mL)	1.178	1.241	1.262	1.221	1.254	1.246	1.260	1.268

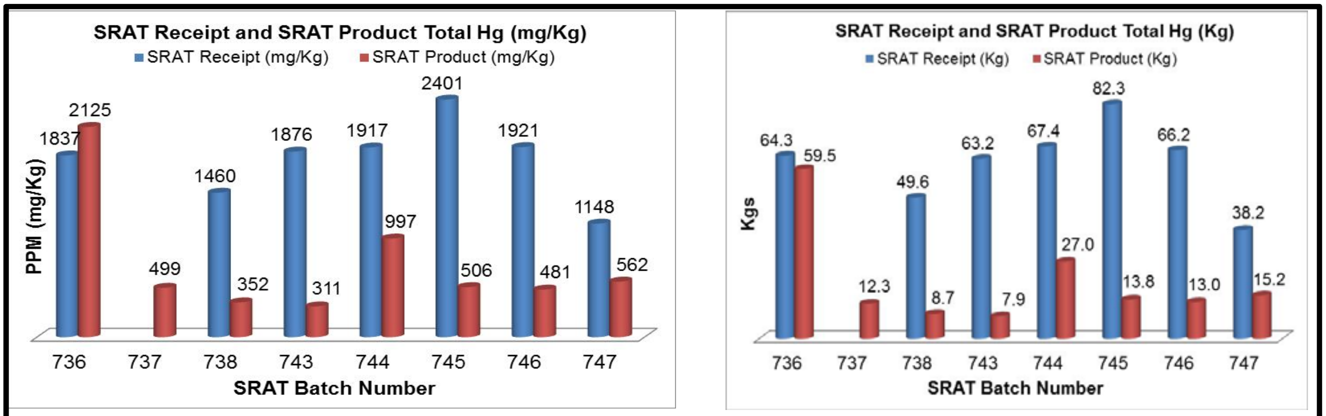
* Batch 735 was last batch processed prior to the Antifoam PISA declaration (5/11/2015). Processing resumed on 9/21/2015 with Batch 736.
\- indicates data not available.
** Maintained in an Excel spreadsheet located on network server: WG09DATA\\Sample Data-Folder\CPC Chem Coverage SB8.xlsm.

As noted in Table 10, ARP was added to SRAT Batches 738, 743, and 745 through 747. SE was added to all of the SRAT batches. Batches that have ARP and SE additions extend the cycle time of the batch, due to the water removal required to maintain a constant volume. The water that is removed during these additions is collected in the SMECT. The other factor that influences the time at boiling is the initial mercury concentration and the time required to steam strip the mercury from the SRAT based on the steam flow rate. The amount of steam required to remove one pound of mercury was experimentally determined[8]. When the mercury concentration is above 0.8 wt.% (dried solids basis) mercury in the feed ~ 750 pounds of steam per pound of mercury is required. As the mercury concentration decreases, more steam is required to achieve the targeted endpoint. If a target endpoint of 0.45 wt.% is desired, ~ 1388 pounds of steam per pound of mercury is required per Reference 8. The total pounds of steam added to each SRAT batch is calculated based on the starting amount of mercury and the desired endpoint. The total pounds of steam added to each SRAT Batch are reflected in Table 10. Batch 743 appears to have the highest steam flow rate. The potential reason for this is probably due to an issue with the SEFT transfer pump and keeping the SRAT at temperature while the trouble shooting of the transfer pump was completed. The other SRAT batches ranged from 75,000 to 81,000 pounds of steam. No anomalies were noted in the ending pH of the SRAT Batches, the ending pH ranged from 7.1 to 7.7. The glass REDOX target was the same for all batches (0.15).

The starting and ending volumes reported in Table 10 for the SME appear to be quite variable and range from ~5,900 to 9,700 gallons. Based on the SME receipt volume, the frit amount will vary based on the targeted waste loading (WL). The pH ranges from 7.3 to 8.1. The predicted glass REDOX based on the SME analytical data ranged from 0.10 to 0.16 with the majority of the data being ± 0.01 within the target.

The mercury results for the SRAT receipt and SRAT product samples vs. the SRAT Batch number are plotted in Figure 14. The results in Figure 14 are reflected in concentration (mg/kg) and mass (kg). The colors blue and red in Figure 14 represent the SRAT receipt and SRAT product, respectively. To calculate the total mass of mercury in the receipt and product samples, the concentration of mercury, the volume of the tank, and the density are needed. A sample calculation for SRAT receipt 736 is shown below.

Mass of mercury in SRAT Batch 736 receipt sample: $\left(8178\ gallons * \frac{3.785\ Liters}{Gallons} * \frac{1.13Kg}{L} * \frac{1837\ mg}{Kg} * \frac{1\ g}{1000mg} * \frac{1\ Kg}{1000g}\right) = 64.3\ Kg$. This methodology was used for the SME receipt and SME product results.



(a) Concentration (mg/L)

(b) Mass (kg)

Figure 14 – Mercury Results for the SRAT Receipt and SRAT Product Samples; (a) Concentration (mg/kg) (b) Mass (kg)

The concentrations reported for the SRAT receipt in Figure 14 were compared to the average mercury concentration taken from the first 11 batches (2,181 mg/kg) of SB8 during transition at DWPF and to the mercury value for the SB8 Waste Acceptance Product Specification (WAPS) sample (1.86wt.% or $\frac{1.86g\ mercury}{100g\ dried\ solids} * \frac{17.21g\ dried\ solids}{100\ g\ slurry} * \frac{1000\ mg}{1g} * \frac{1000\ g}{1kg} =$ 3201mg/kg).[36]

The comparison of the data shows that the SB8 sample has the highest concentration followed by SRAT Batch 745, and then the average for the first 11 batches. The mercury concentration of the WAPS sample should be highest due to a couple of facts: first, is that it was taken shortly after the transfer from Tank 51which avoids the dilution over time from the slurry pump operation in Tank 40; and second, is the sludge is not diluted from the transfer line flush from Tank 40 to LPPP. To check if this latter assumption was reasonable, a nominal 800 gallons of flush water was used to dilute a 5000 gallon transfer from Tank 40 using the results of the SB8 WAPS sample. This was compared to the results using the average of the first 11

SRAT batches. The data agree within ~20%. This is acceptable due to the difficulty in measuring mercury in the sludge slurry between two different laboratories. Another observation noted when comparing the data is the variation in the mercury concentration in the SRAT receipt. The variability in this data could be due to the efficiency of mercury removal in the previous batch (~1100 to 1600 gallon heel remains behind in the vessel after the completion of the batch) and/or analytical error. Based on the SRAT product data presented in Figure 14 , the majority of the mercury was reduced and removed from the final product with the exception of Batch 736 and Batch 747. The reason for this lower recovery is unknown and no anomalies were noted in the data collected for these two batches in Table 10.

Based on the mass of mercury in the SRAT receipt and the mass of mercury remaining in the SRAT product (reported in Figure 14), an estimate of the total mass of mercury removed to the condensate stream can be completed. This data is presented in kg and is found below in Table 11.

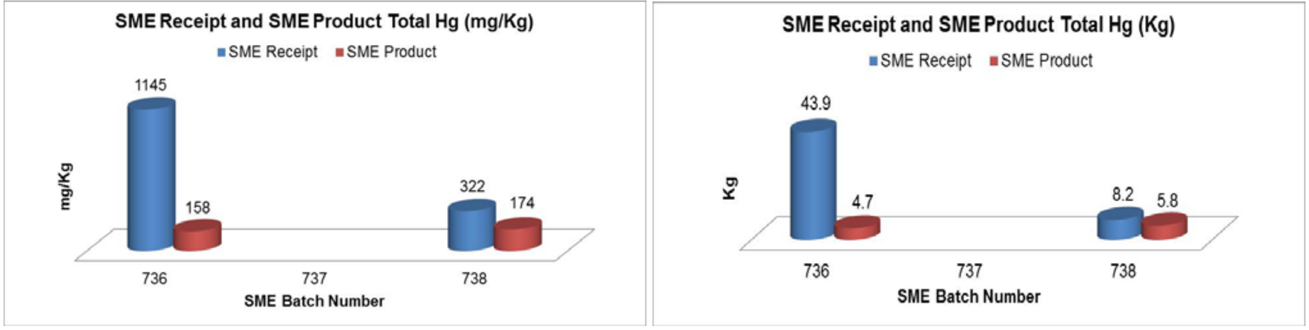
Table 11 – Potential Total Mass of Mercury Removed from the SRAT to the Condensate Stream

Batch Number	Potential Hg Mass Removed to Condensate Stream (kg)
736	4.7
737	-
738	40.8
743	55.3
744	40.4
745	68.6
746	53.2
747	23.0

- indicates data not available

The mercury removed from the SRAT process vessel has a couple of potential paths depending on the form of mercury including; the MWWT, the SMECT, depositing in the CPC off gas system, and/or exiting as a vapor as mentioned in previous sections. If the form of mercury is assumed to be elemental mercury, the volume of mercury (assuming 13.59 g/mL for density) ranges from 0.09 to 1.34 gallons based on the mass reported in Table 11. 1.34 gallons of mercury should be easily seen in the MWWT, however the mercury level indication is currently inoperable. The SMECT is a much larger vessel than the MWWT, thus this amount of mercury would be harder to detect. The condensate data reported in Section 4.3 will help substantiate the analytical data presented in this section and the assumptions made in the BDR.

The mercury results for the SME receipt and SME product samples vs. the SME Batch number are plotted in Figure 15. Although sample analysis is performed for every SME product, mercury is not a required analysis. The results in Figure 15 are reflected in concentration (mg/kg) and mass (kg). The colors blue and red in Figure 15 represent the SME receipt and SME product, respectively.



(a) Concentration (mg/kg)

(b) Mass (kg)

Figure 15 - Mercury Results for the SME Receipt and SME Product Samples; (a) Concentration (mg/kg) (b) Mass (kg)

The results for SME Batch 736 indicate that the mercury was reduced during the SRAT cycle and steam stripped during the SME cycle. The reason for this is unknown. The mercury that was steam stripped during the SME cycle would reside in the SMECT. The data for SME Batch 738 is what one would typically expect when analyzing the SME receipt and SME product for mercury. Based on a subtraction of the SME product from the SME receipt, 39.2 kg of mercury would be in the SMECT from Batch 736 and 2.4 kg of mercury would be in the SMECT from Batch 738.

4.3 Mercury Results for the SMECT, OGCT and RCT Samples

SMECT, OGCT, and RCT samples were taken and analyzed by the DWPF Laboratory as prescribed in Tables 4 through 7, Section 3.3, and Section 3.4. The results of the samples are summarized below.

SMECT

As indicated previously, samples were taken from the SMECT (when possible) for major process steps of the SRAT and SME cycles. This was completed to try and help answer the following questions:

- Is the steam stripped mercury bypassing the MWWT and residing in the SMECT?
- Are there organic species of mercury residing/being formed in the SMECT and being transferred to the RCT?
- Does the nitric acid enhance the dissolution of elemental mercury from the SMECT?

Table 12 contains the volumes and densities of the samples pulled from the SMECT. Where densities are not available the data were obtained from the PI data acquisition program. The PI tags for the volume and density are DLI3123 and DDI3122, respectively.

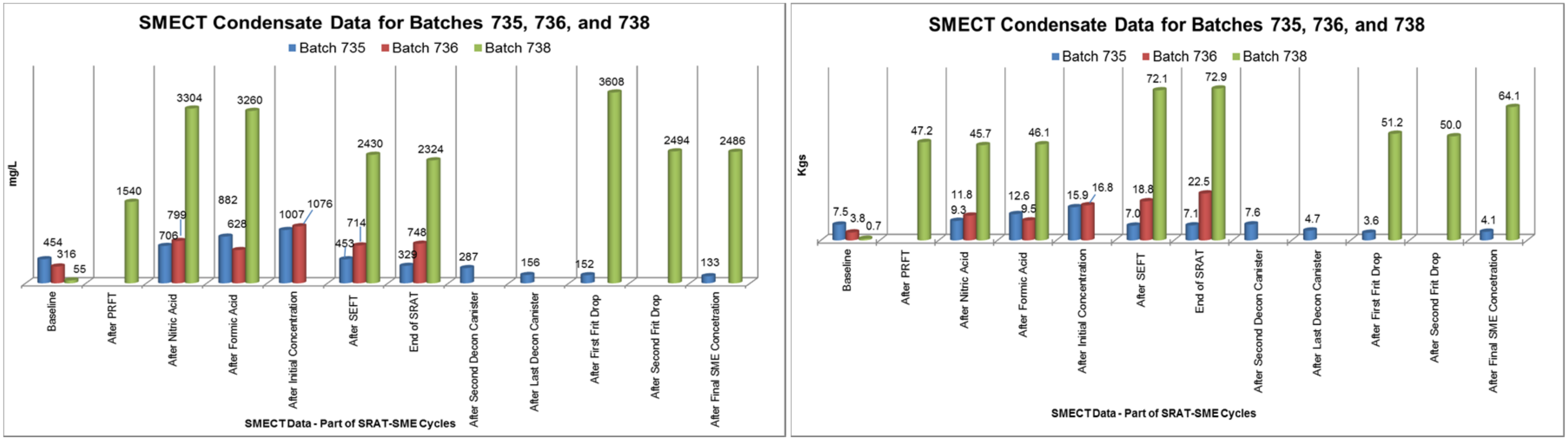
Table 12 – Volumes, Density, and LIMS Numbers for the SMECT Samples

Tank and Part of Process During the SRAT Steps	Batch 735 Volume Density LIMS Number	Batch 736 Volume Density LIMS Number	Batch 738 Volume Density LIMS Number
SMECT - Baseline - Start of SRAT Batch	Volume: 4,370 gallons Density: 1.01 g/mL 200020168	Volume: 3,250 gallons Density: 1.028 g/mL 200020712*	Volume: 3,522 gallons Density: 1.028 g/mL 200020840*
SMECT - After PRFT	-	-	Volume: 8,094 gallons Density: 1.1 g/mL 200020844*
SMECT - After Nitric Acid	Volume: 3,489 gallons Density: 1.008 g/mL 200020175	Volume: 3,916 gallons Density: 1.036 g/mL 200020765	Volume: 3,657 gallons Density: 1.053 g/mL 200020852
SMECT - After Formic Acid	Volume: 3,764 gallons Density: 1.007 g/mL 200020179	Volume: 4,002 gallons Density: 1.033 g/mL 200020768	Volume: 3739 gallons Density: 1.048 g/mL 200020854
SMECT - After Initial Concentration	Volume: 4,170 gallons Density: 1.007 g/mL 200020181	Volume: 4,133 gallons Density: 1.034 g/mL 200020769*	-
SMECT - After SEFT	Volume: 4,105 gallons Density: 1.0096 g/mL 200020187	Volume: 6,938 gallons Density: 1.09 g/mL 200020772	Volume: 7,838 gallons Density: 1.092 g/mL 200020857
SMECT - End of SRAT	Volume: 5,733 gallons Density: 1.01 g/mL 200020190	Volume: 7,947gallons Density: 1.09 g/mL 200020775*	Volume: 8,288gallons Density: 1.092 g/mL 200020860*

Tank and Part of Process During the SME Steps	Batch 735 Volume Density LIMS Number	Batch 736 Volume Density LIMS Number	Batch 738 Volume Density LIMS Number
SMECT - After Second Decon Canister	Volume: 7,003 gallons Density: 1.009 g/mL 200020200	-	-
SMECT - After Last Decon Canister	Volume: 7,921 gallons Density: 1.01 g/mL 200020207	-	-
SMECT - After First Frit Drop	Volume: 6,277 gallons Density: 1.01 g/mL 200020209	-	Volume: 3,750 gallons Density: 1.039g/mL 200020889
SMECT - After Second Frit Drop	-	-	Volume: 5,372 gallons Density: 1.076 g/mL 200020891
SMECT - After Final SME Concentration	Volume: 8,167 gallons Density: 1.01 g/mL 200020211	-	Volume:6,786 gallons Density: 1.08 g/mL 200020896*

- No sample obtained.
* Indicates mercury speciation was performed.

The mercury results for the SMECT vs. the SRAT and SME process steps are plotted in Figure 16. The results in Figure 16 are reflected in concentration (mg/L) and mass (kg). The colors blue, red, and green in Figure 16 represent Batch 735, 736, and 738, respectively.



(a) Concentration (mg/L)

(b) Mass (kg)

Figure 16 – Comparison of SMECT Total Mercury Results as a Function of SRAT and SME Process Steps for Batch 735, 736, and 738; (a) Concentration (mg/L) (b) Mass (kg)

As seen in Figure 16, the mass of mercury in the SMECT condensate continues to rise during the SRAT Cycle. This confirms that the majority of mercury is by-passing the MWWT. The increase in mercury associated “After Nitric Acid” addition is likely due to the condensate return from the MWWT to the SMECT. The MWWT collects liquid from the SRAT condenser. This liquid is acidic most likely due to reactions of NOx species in the off gas with water to form nitrous and nitric acids. The nitrous acid should further decompose to nitric acid, NO, and water. The NOx species are formed from the decomposition of nitrite in SRAT when acids are added. In between SRAT batches, the nitric acid solution collected in the MWWT remains in continuous contact with the elemental mercury present in the sump of the MWWT and reacts with the mercury to produce either mercurous nitrate ($Hg_2(NO_3)_2$) or mercuric nitrate ($Hg(NO_3)_2$) and nitric oxide. Mercurous nitrate is the likely form of mercury due to the low nitric acid concentration, excess mercury, and low temperatures[37]. The formation of mercuric nitrate requires high nitric acid concentrations and higher temperatures. Equation 19 provides the reaction chemistry for the formation of mercurous nitrate.

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O \qquad \text{Equation 19}$$

The mercury continues to rise in the SMECT “After Formic Acid” and “After Concentration” due to the reduction and steam stripping of mercury that occurs during SRAT processing. Very minor increases are noted “After SEFT” and “End of SRAT”. For the processing of Batch 735, transfers out of the SMECT were not restricted (operations emptied the tank as needed). For Batches 736 and 738, the transfers out the SMECT were restricted when possible (operations minimized the number of transfers out of the tank). As in the case for the MWWT, a dilute nitric acid stream (from addition of nitric acid directly to SMECT and collection of acidic condensate from the SRAT) is also in contact with the elemental mercury in the sump and trench of the SMECT at ~ 25˚C. Under these conditions, the mercury in the sump would slowly react with the dilute nitric acid to likely produce mercurous nitrate as well. For Batch 738 carryover events occurred during the SRAT cycle resulting in more nitric acid additions to the SMECT. The carryover event only contributed ~16% to the mass of mercury present. The data comparing the mercury collected in the SMECT vs. the mercury removed from the SRAT process for Batch 736 and Batch 738 are shown in Table 13.

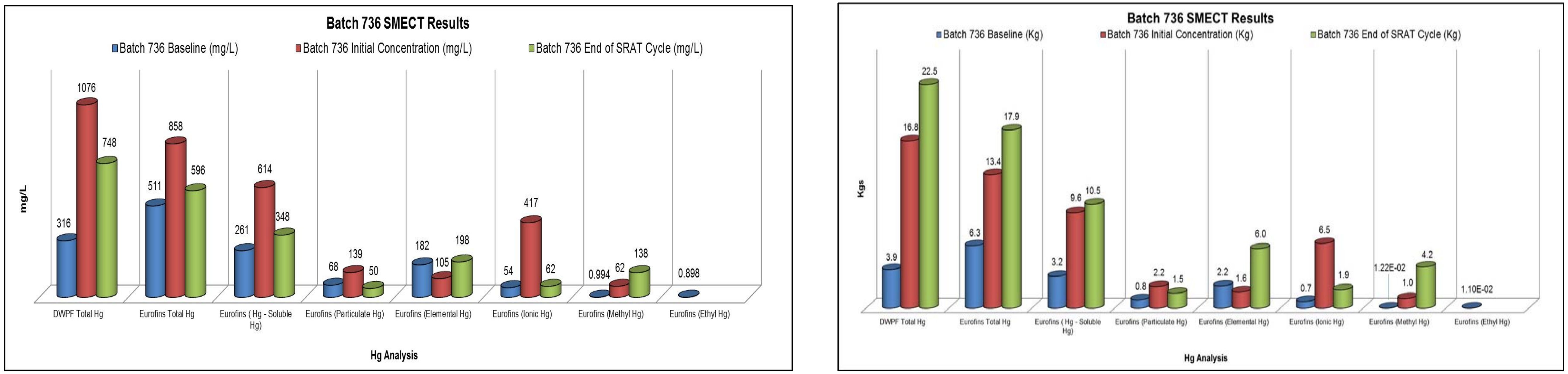
Table 13 – Comparison of the Mercury Mass Removed to the Mercury Mass in the SMECT for SRAT Batches 736 and 738

Batch Number	Total Mercury Mass (kg) in SMECT*	Total Mass (kg) of Mercury Removed From SRAT Process
SRAT Batch 736 Summary	18.7	4.7
SRAT Batch 738 Summary	72.2	40.8

* The sample analysis is representative of the solution above the elemental mercury in the sump and trench in the SMECT.

The data presented in Table 13 confirms that there is more mercury present in the SMECT than removed from the SRAT. This difference is thought to be due to the reaction of the elemental mercury present in the SMECT with nitric acid. Also, Batch 738 had a carryover event which would increase the mercury concentration in the SMECT based on the contribution of mercury from the sludge slurry. The reaction chemistry occurring in the MWWT and SMECT with elemental mercury in the sumps of these vessels makes the material balance closure very difficult for the SRAT vessel. The only conclusion that can be drawn is that the mercury concentration present in the SMECT is variable due to elemental mercury present in the sump, the contribution of mercury from the MWWT, and condenser and scrubber efficiency in removing steam stripped mercury.

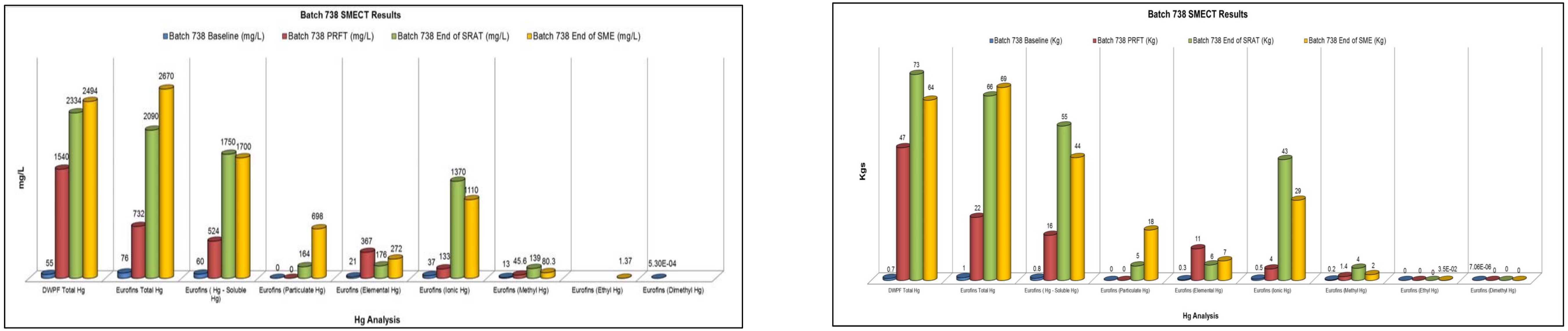
The SMECT speciation data from Eurofins FGS and the total mercury results reported from the DWPF Laboratory collected for SRAT Batch 736[38,39] and SRAT Batch 738[40,41] are presented in Figure 17 and Figure 18, respectively. The results in Figure 17 and Figure 18 are reflected in concentration (mg Hg/L) and mass (kg). The colors blue, red, and green in Figure 17 represent the baseline, initial concentration, and end of SRAT cycle samples, respectively. The colors blue, red, green and orange in Figure 18 represent the baseline, PRFT, end of SRAT cycle, and end of SME cycle samples, respectively.



(a) Concentration (mg Hg/L)

(b) Mass (kg)

Figure 17 – Speciation Data for SMECT Baseline, Initial Concentration and End of SRAT Cycle for Batch 736; (a) Concentration (mg/L) (b) Mass (kg)[38,39]



(a) Concentration (mg Hg/L)

(b) Mass (kg)

Figure 18 - Speciation Data for SMECT Baseline, PRFT, End of SRAT Cycle, and End of SME Cycle for Batch 738; (a) Concentration (mg Hg/L) (b) Mass (kg)[40,41]

For Batch 736, two out of the three total Hg values are within 20% of each other. From the Eurofin data, ionic Hg appears to be the highest in the SMECT after "Initial Concentration" which coincides with nitrous oxide production in the SRAT and MeHg appears to increase over the cycle. The potential causes of the MeHg being present in the SMECT could be due to a couple of sources. The first source is the SE. The SE is added during boiling conditions in the SRAT and the MeHg present in the stream could be steam stripped. Based on the SE volume added to Batch 736 and concentration reported in Figure 12, this only accounts for ~ 0.12 kg of the 4.2 kg calculated to be in the SMECT if all of the MeHg present in the SE is steam stripped. Other potential sources of MeHg are a reaction of degraded antifoam products with ionic mercury present in the SRAT and SME which is subject to steam stripping, the formation of MeHg in the CPC off gas train, and formation of MeHg in the SMECT itself. It is also noted that ethyl mercury was present in the baseline sample for Batch 736, but it was not present in the other samples retrieved from the SMECT. The ethyl mercury concentration is low and is likely create from the same sources as the MeHg.

Antifoam is added during SRAT and SME processing to prevent foam overs into the CPC off gas system. The antifoam agent is combination of two wetting agents that are siloxane polyalkyleneoxides and subject to degradation under SRAT and SME processing conditions. As noted earlier, Hg^{+2} species are available in the sludge slurry to react with the methyl groups present in the antifoam and produce DMHg and MeHg. These compounds are more than likely produced while the sludge slurry is caustic and hot [42] (heat up to acid addition and caustic boiling conditions of the SRAT) and/or after the completion of formic acid addition (due to SE addition). The MeHg produced during the SRAT and SME cycles could be steam stripped contributing to the mass observed in the SMECT. The DMHg is very volatile and would readily leave the SRAT and SME vessels.[43] Upon contact of DMHg with acidic conditions in the off gas system, the DMHg would degrade rapidly to MeHg and condense out in either the condensers or ammonia scrubbers and reside in the SMECT.[43,44] The other source where MeHg could be produced is the SMECT itself. The antifoam degrades in the SRAT and SME to produce volatile and flammable components including hexamethyldisiloxane, trimethylsilanol and propanal. Some of these volatile components condense and have been detected in the condensate [45] along with the presence of ionic mercury. It is possible that these conditions produce MeHg, however literature surveys do not address the reaction chemistry for the conditions in the SMECT. To prove formation, experimentation would have to be completed.

For Batch 738 two out of the four samples for total mercury are within 10% of each other. There were two carryover events during the SRAT cycle. Like Batch 736, the total mercury mass increases during the SRAT cycle. From the Eurofins data, ionic Hg appears to be the highest in the SMECT at "End of SRAT". MeHg appears to increase over the SRAT cycle like it did for Batch 736. About 4 kg of MeHg is produced in Batches 736 and 738. This appears to be independent of the amount of total mercury present in the SMECT. The methyl and ionic mercury present at the "End of SME" appears to be diluted by the condensate from the SME cycle. Also, ethyl mercury was detected in the SMECT at the "End of SME cycle". The source of ethyl mercury is likely from the antifoam added to the SRAT and SME vessels.

The speciation data from Batch 736 and 738 were put on a percentage basis to determine if any trends exist for the samples analyzed. This data is found in Table 14.

Table 14 - Eurofins FGS Data for Batches 736 and 738 on a Percentage Basis

	Batch 736 Baseline (%)	Batch 736 Initial Concentration (%)	Batch 736 End of SRAT Cycle (%)	Batch 738 Baseline (%)	Batch 738 PRFT (%)	Batch 738 End of SRAT (%)	Batch 738 End of SME (%)
Eurofins (Particulate Hg)	13.3	16.2	8.4	0	0	7.8	26
Eurofins (Elemental Hg)	35.6	12.2	33.2	28	50.1	8.4	10
Eurofins (Ionic Hg)	10.6	48.6	10.3	49.1	18.2	65.6	42
Eurofins (Methyl Hg)	0.19	7.2	23.1	17.7	6.2	6.7	3
Eurofins (Ethyl Hg)	0.18	-	-	-	-	-	5.13E-04
Eurofins (Dimethyl Hg)	-	-	-	7.0E-04	-	-	-
Total Identified by Speciation*	59.9%	84.2%	75.0%	94.8%	74.5%	88.5%	80.9%

- Indicates detection limit. This data was not included in the table.

* Based on Total Hg analyzed by Eurofins FGS. Calculated numbers used for particulate Hg. The totals represent the upper limit for recovery of species.

As can be seen in Table 14, a low recovery for the speciation was obtained for the "Baseline" sample of Batch 736. The other data indicate that 75% to 95% of the total mercury species were identified. Eurofins FGS has indicated that they believe the MeHg determination is likely biased low. The data indicate that there is a large percentage of elemental, ionic and MeHg present. Based on the current conditions (collection point for elemental mercury, low pH, dilute nitric acid solution, etc.) of the SMECT, this is not unexpected.

<u>OGCT</u>

Samples were taken from the OGCT for Batches 735, 736, and 738 as outlined in Section 3.2, 3.3 and 3.4. The sample taken for Batch 735 was also filtered (to remove suspended solids) and analyzed to determine what fraction of mercury was soluble. It should be noted that the process of filtering the sample will remove elemental mercury. Samples of the OGCT were taken at the beginning and at the end of processing the material through the melter for Batch 736 and Batch 738. This gives two separate data points for comparison. The data are presented in Figure 19 and the color blue represents the concentration in mg/L and red represents the mass in kg. The volume, density, and LIMS numbers for the OGCT Samples used to convert the concentrations to mass are found in Table 15. The PI tags for the volume and density are DLI3486 and DDI6143, respectively.

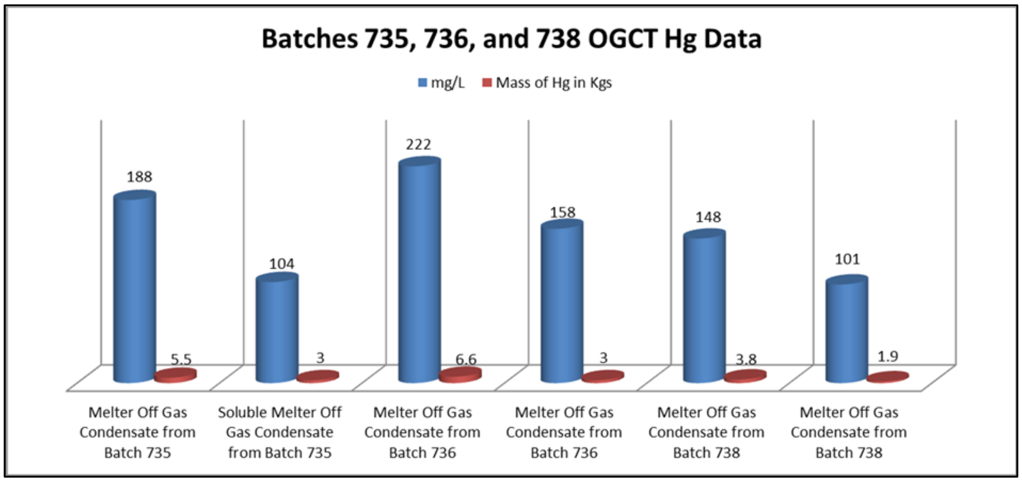


Figure 19 – OGCT Condensate Data for Batches 735, 736, and 738 Analyzed by the DWPF Laboratory; mg/L and kg

Table 15 - Volumes, Density, and LIMS Numbers for the OGCT Samples

OGCT Batch Number	Volume, Density, and LIMS Number
Batch 735	Volume:7,782 gallons, Density: 1.0 g/mL, and 200020225
Batch 736	Volume: 7,882 gallons, Density: 1.0 g/mL, and 200020836
Batch 736	Volume: 4,996 gallons, Density: 1.07 g/mL, and 200020884
Batch 738	Volume: 6843 gallons, Density: 1.0 g/mL, and 200021025
Batch 738	Volume: 5029 gallons, Density: 1.0 g/mL, and 200021036

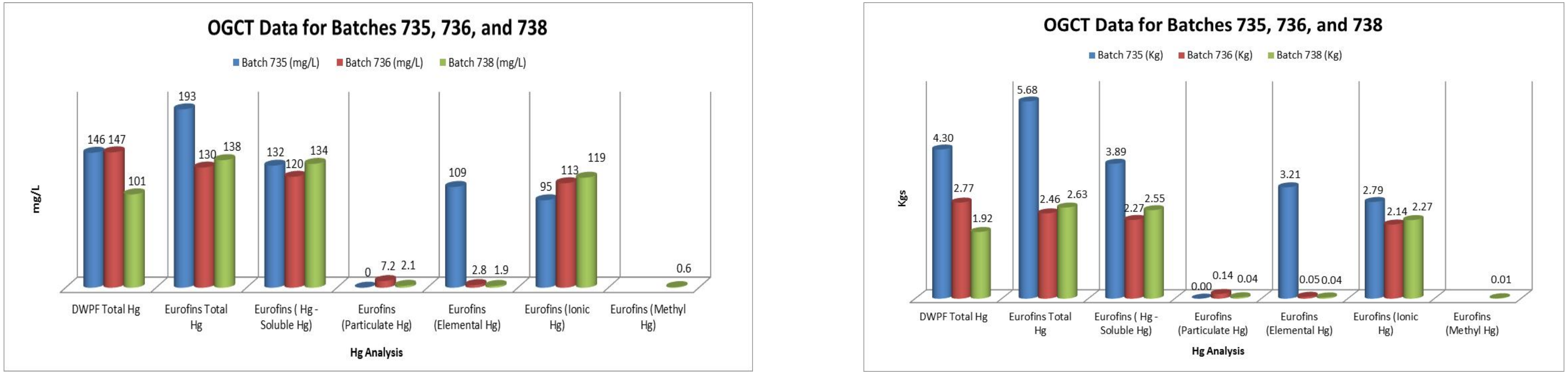
For Batch 735, approximately 55% of the mercury present in the OGCT is soluble. The concentration of mercury residing in the OGCT is dependent on the efficiency of the front end chemistry completed in the CPC. Any residual mercury remaining in the SME product is sent to the melter and is volatilized off. As noted in Figure 19, there is some variation in the OGCT data within a batch processed. As a check of the mercury in the OGCT, the data from Batch 736 and Batch 738 SME products were compared to the OGCT results. The amount calculated for the OGCT batch were added together and then compared to the mass of mercury for the SME. These data can be found in Table 16.

Table 16 – Comparison of Mercury Remaining in the SME to the Mercury Observed in the OGCT for Batch 736 and Batch 738

Batch 736 OGCT Sample Results (kg)	Hg Remaining in SME Batch 736 (kg)	Batch 738 OGCT Sample Results (kg)	Hg Remaining in SME Batch 738 (kg)
9.6	4.7	5.7	5.8

As observed in Table 16, the mercury in the OGCT for Batch 736 was much higher than Batch 738. Prior to the processing of Batch 736 through the melter, the facility had been in an outage. The OGCT liquid is acidic (mainly nitric acid) as in the SMECT. Also, the OGCT is not agitated, thus the entrained solids and elemental mercury would settle to the bottom of the tank. The samples taken from the OGCT are only representative of what is in the supernate and do not consider the contribution from the solids collected in the tank. Based on this, similar reactions are expected to occur in the OGCT as described in Equation 19. The data for Batch 738 agree well despite the influence of the heel in the MFT.

The OGCT speciation data from Eurofins FGS and the total mercury results reported from the DWPF laboratory collected for Batch 735[46], Batch 736, and Batch 738 are presented in Figure 20. The data are reflected in concentration (mg Hg/L) and mass (kg). The colors blue, red, and green in Figure 20 represent the OGCT results for Batch 735, Batch 736, and Batch 738. The speciation data from Batch 735, Batch 736, and 738 were shown as percentage of the total mercury to determine if any trends exist for the samples analyzed. This data is found in Table 17.



(a) Concentration (mg Hg/L)

(b) Mass (kg)

Figure 20 - Speciation Data for OGCT for Batch 735, Batch 736 and 738; (a) Concentration (mg/L) (b) Mass (kg)[41,46]

Table 17 - Eurofins FGS Speciation Data for OGCT Batches 735, 736 and 738 on a Percentage Basis

	Batch 735	Batch 736	Batch 738
Eurofins (Particulate Hg)	0[#]	5.5	1.5
Eurofins (Elemental Hg)	56.5	2.2	1.4
Eurofins (Ionic Hg)	49[#]	86.9	86.2
Eurofins (Methyl Hg)	-	-	4.7E-04
Total Identified by Speciation*	106%[#]	95%	89%

[#] Batch 735 was the first sample set analyzed by Eurofins FGS. It should be noted that these values are impacted due to the failure to remove elemental mercury prior to performing analyses for particulate and ionic mercury.
- Indicates detection limit. This data was not included in the table.
* Based on Total Hg analyzed by Eurofins FGS. Calculated numbers used for particulate Hg. The totals represent the upper limit for recovery of species.

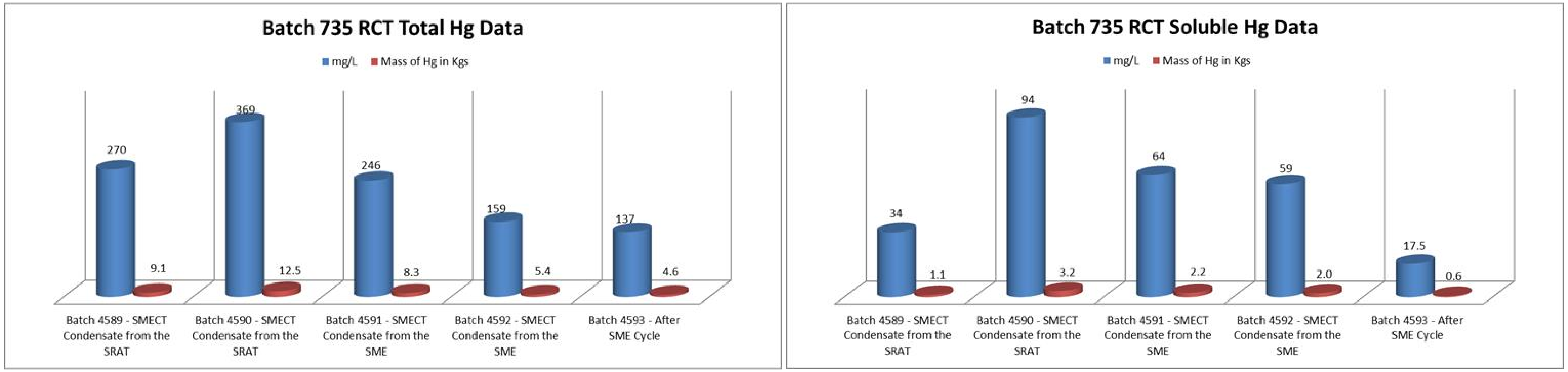
As can be seen from the data presented in Table 17, Batch 735 had over 100% recovery. These samples were among the first set of samples sent to Eurofins Frontier Global Science, Inc. and the ionic mercury was determined without purging the samples of elemental mercury prior to the measurement of ionic mercury, and therefore the ionic mercury value is expected to be high, possibly entirely due to elemental mercury. Since some of this elemental mercury is removed in the filtration step, this solution species removal gets attributed to particulate mercury. This problem was corrected for Batch 736 and Batch 738 and the data indicate that 89% to 95% of the species were identified. One out of three Eurofins FGS samples was within 12% of the total Hg values reported by the DWPF laboratory and the other two samples are within 37% of each other. For Batches 736 and 738 the majority of the mercury appears to be ionic. For Batch 735, the mercury appears to be divided between ionic and elemental mercury. There was MeHg detected in Batch 738, however based on the operating temperature of the melter MeHg and organic carbon species are not expected to survive the vitrification process. Therefore this considered an anomalous data point based on the results for Batch 735 and Batch 736. However, the MeHg data was included in the table for completeness. The mercury results reported for the OGCT are not unexpected based on its current operation and chemistry.

RCT

Samples were taken from the RCT for Batches 735, 736, and 738 as outlined in Section 3.2, 3.3, and 3.4. During the RCT sample pulls for Batch 736, SRAT Batch 737 was also being processed. Therefore, the RCT had a combination of the condensate from both batches. This is how the facility is typically operated. Batch 735 and Batch 738 were conducted differently in order to isolate the contributions from the SRAT and SME processing to gain insight and note differences in the condensate returning to the Tank Farm. The volume, density, and LIMS numbers for the RCT samples used to convert the concentrations to mass are found in Table 18. The PI tags for the volume and density are DLI6140 and DDI6143, respectively. The samples analyzed by the DWPF Laboratory are presented in Figure 21. As was done for the OGCT for Batch 735, the RCT was analyzed for total and soluble mercury. It should be noted that the RCT contains solids and these solids were present in the samples. To determine the soluble fraction, the sample was filtered and then digested.

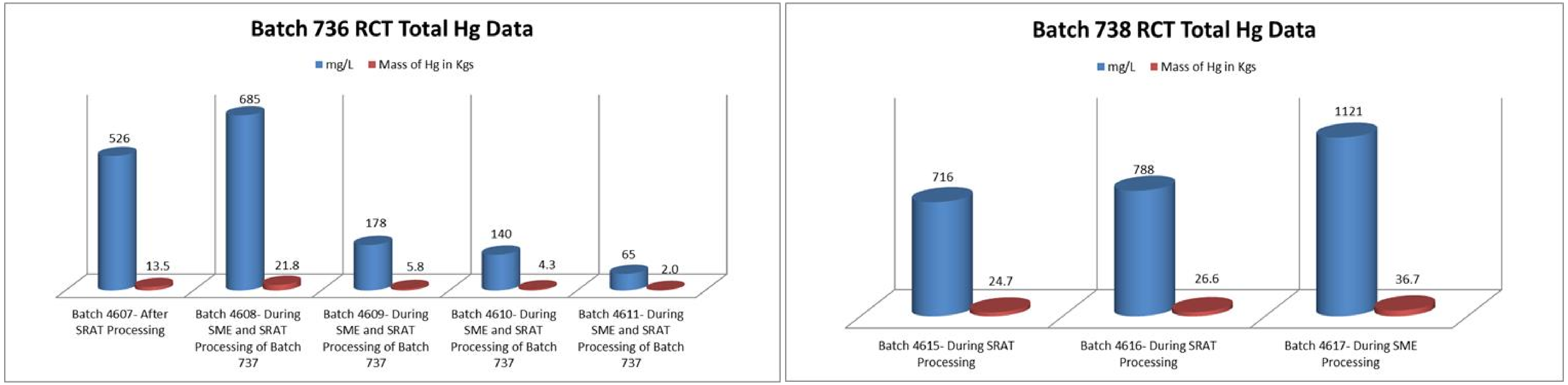
Table 18 - Volumes, Density, and LIMS Numbers for the RCT Samples

RCT Batch Number	Volume, Density, and LIMS Number
Batch 735- RCT Batch 4589	Volume:8,922 gallons, Density: 1.00 g/mL, and 200020178
Batch 735- RCT Batch 4590	Volume: 8,933 gallons, Density: 1.00 g/mL, and 200020185
Batch 735- RCT Batch 4591	Volume: 8,925 gallons, Density: 1.00 g/mL, and 200020203
Batch 735- RCT Batch 4592	Volume: 8,909 gallons, Density: 1.00 g/mL, and 200020208
Batch 735- RCT Batch 4593	Volume: 8,889 gallons, Density: 1.00 g/mL, and 2000200225
Batch 736 – RCT Batch 4607	Volume:6,801, gallons, Density: 1.00 g/mL, and 2000200779
Batch 736 – RCT Batch 4608	Volume:8,412 gallons, Density: 1.00 g/mL, and 2000200805
Batch 736 – RCT Batch 4609	Volume:8,606 gallons, Density: 1.00 g/mL, and 2000200810
Batch 736 – RCT Batch 4610	Volume:8,108, gallons, Density: 1.00 g/mL, and 2000200827
Batch 736 – RCT Batch 4611	Volume:8,078 gallons, Density: 1.00 g/mL, and 2000200832
Batch 738 – RCT Batch 4615	Volume:8,906 gallons, Density: 1.00 g/mL, and 2000200882
Batch 738 – RCT Batch 4616	Volume:8,653 gallons, Density: 1.00 g/mL, and 2000200899
Batch 738 – RCT Batch 4617	Volume:8,512 gallons, Density: 1.00 g/mL, and 2000200903



(a) Batch 735 - Total

(b) Batch 735 - Soluble



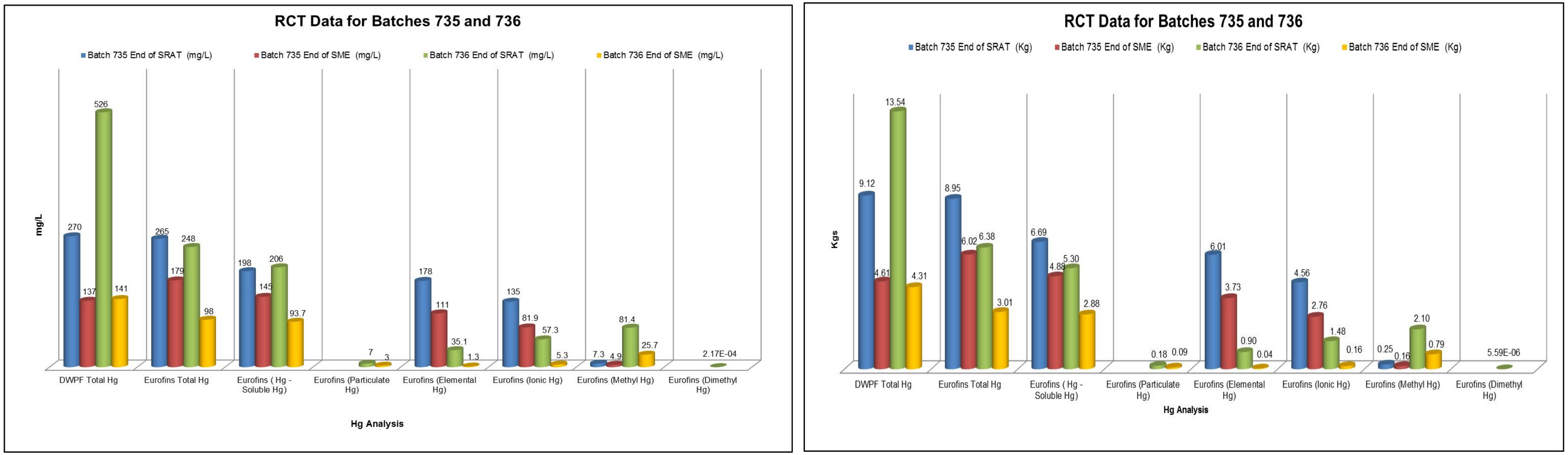
(d) Batch 736 - Total

(c) Batch 738 - Total

Figure 21 - RCT Condensate Data for Batches (a) 735-Total, (b) 735- Soluble, (c) 736 - Total, and (d) 738 – Total Analyzed by the DWPF Laboratory; mg/L and kgs

For Batch 735, the soluble mercury ranges from 12% to 37% and ~ 40 kg of mercury was returned to the Tank Farm using the total mercury results reported. For Batch 736 (contains Batch 737 condensate) and Batch 738, it appears 47.4 kg and 88 kg are returned to the Tank Farm, respectively. The increase in mercury for Batch 738 is more than likely due to the carryover events that occurred during SRAT processing. The results for Batch 735 and Batch 736 appear to agree within reason. Based on the data for the SMECT and OGCT, the results observed in the RCT are not unexpected.

The RCT speciation data from Eurofins FGS and the total mercury results reported from the DWPF Laboratory collected for Batch 735and Batch 736 are presented in Figure 22. The data are reflected in concentration (mg/kg) and mass (kg). The colors blue and red represent the end of the SRAT and end of the SME processing for Batch 735, respectively. The green and orange represent the end of the SRAT and end of the SME processing for Batch 736, respectively.



(a) Concentration (mg Hg/L)

(b) Mass (kg)

Figure 22 - Speciation Data for RCT for Batch 735 and Batch 736; (a) Concentration (mg Hg/L) (b) Mass (kg)[39,46]

Table 19 - Eurofins FGS Speciation Data for RCT Batches 735 and 736 on a Percentage Basis

	Batch 735 End of SRAT	Batch 735 End of SME	Batch 736 End of SRAT	Batch 736 End of SME
Eurofins (Particulate Hg)	0[#]	0[#]	2.8	3.1
Eurofins (Elemental Hg)	67.2	62	14.2	1.4
Eurofins (Ionic Hg)	50.9[#]	45.7[#]	23.1	5.4
Eurofins (Methyl Hg)	2.7	2.7	32.8	26.2
Eurofins (Dimethyl Hg)	*	*	8.7E-05	*
Total Identified by Speciation*	121%	111%	73%	36%

[#] Batch 735 was the first sample set analyzed by Eurofins FGS. It should be noted that these values are impacted due to the failure to remove elemental mercury prior to performing analyses for particulate and ionic mercury.

* Based on Total Hg analyzed by Eurofins FGS. Less than data left out of table. Calculated numbers used for particulate Hg. The totals represent the upper limit for recovery of species.

Only one sample compared well between DWPF and Eurofins FGS for total Hg. Two out of the four are within 31% and one sample is within 53% for total Hg. The RCT batches containing SMECT condensate from the SRAT cycle appear to be higher in Hg than the RCT batches containing SMECT condensate from SME processing. This trend holds for all of the speciation. The mass of MeHg in Batch 736 "End of SRAT" RCT sample correlates to the mass of MeHg transferred from the SMECT. As can be seen from the data presented in Table 19, the percentages vary quite a bit. The RCT samples for Batch 735 are impacted by the same issue as Batch 735 OGCT samples. The ionic mercury for these samples was measured prior to the elemental mercury from the sample and therefore it is by the high levels of elemental mercury present. The variation in the results for Batch 736 could be due to the fact that the solids were settled out from the samples. If mercurous nitrate or mercuric nitrate is present, it would react with the caustic that is in the RCT. The caustic is added to the RCT to meet the Tank Farm transfer requirements. During neutralization of the acidic streams, mercurous oxide or mercuric oxide could be produced based on the forms of mercury in the SMECT and OGCT. The mercurous oxide and mercuric oxide would settle in out of solution during interim storage in the Tank Farm. Mercurous oxide is chemically unstable and rapidly decomposes to form HgO and Hg upon the application of heat. The mercury results reported for the RCT are not unexpected based on its current operation and chemistry. This however does not agree with the assumption in the BDR that ~75% of the mercury would be recovered. It appears that based on the current reaction chemistry, that 25% to 57%[47] is retained in DWPF, when looked at on an individual batch basis. To improve the recovery of mercury in DWPF, the elemental mercury that resides in the MWWT and SMECT should be removed to prevent its reaction with the nitric acid present in these tanks.

5.0 CONCLUSIONS

The following conclusions can be made about the data presented in this report:

- Sludge slurry, PRFT (MST/sludge solids) and SE are three main streams that are received at DWPF for processing. Based on the total mercury analyses of the SE and PRFT, the total contribution of the mercury to the DWPF coupled operations is less than 1% during ARP/MCU operations. This percentage increases to around 4% during Salt Waste Processing Facility (SWPF) operations. Based on speciation analysis, SE is also a source of MeHg. The likely source of MeHg is the salt solution fed to ARP/MCU which contains a small fraction of DWPF recycle material.
- The majority of the reactions related to the mercury chemistry, outlined in the BDR, were consistent with the mercury analysis of the products and condensate streams. The exception to this was the reaction chemistry for the OGCT and the identification of methyl and ethyl mercury (via sample analysis) in the SMECT.
- No mercury speciation has been performed on a sample of sludge slurry. This is needed to confirm the forms of mercury assumed in the BDR are correct.
- Mercury speciation data was obtained for the SMECT, OGCT, and RCT. Mercury species present in all three process vessels include ionic, elemental, and particulate mercury.
- Ethyl mercury was found in one of the SMECT samples taken from Batch 736. It was also found in one sample taken from Batch 738. MeHg was found in all of the SMECT samples and appears to increase over the cycle time of the batch. Possible sources include:
    - Reaction of the degradation products of antifoam with ionic mercury species present in the condensate,
    - Steam stripping of MeHg produced/added (SE) during SRAT and SME processing, and
    - The decomposition of DMHg to MeHg under acidic conditions, if present. It should be noted that the DMHg was found in one sample from Batch 738 at a low concentration.
- Nitrous/nitric acid is produced as a by-product of the neutralization reactions in the SRAT and is collected in the MWWT and SMECT. Nitric acid additions are also made to the SMECT to maintain the pH acidic. These acids can react with the elemental mercury present in the tank's sump and trench forming mercurous nitrate and potentially mercuric nitrate.
- The mercury mass balances performed during SRAT and SME cycles indicate that a significant amount of elemental mercury potentially resides in the SMECT and is not removed via the MWWT.
- The concentration of mercury in the OGCT depends on mercury reduction/ strip efficiency of the CPC (i.e. SRAT and SME processing). Mercury not removed during the CPC process volatilizes in the melter and is condensed in the OGCT.
- The amount of mercury in the RCT is dependent on the mercury content of the SMECT and the OGCT. Thus, the mercury concentration is expected to vary batch to batch based on the CPC operation, the rate of formation for mercurous/mercuric nitrate and other mercury species, and MOG operation. Based on the limited data sets, the SMECT appears to be the largest contributor of elemental mercury to the RCT.
- Mercury material balance closure is challenging due to the changing conditions (solubility and forms) of condensate streams. Based on the results of individual batches, it appears between 25% and 57% of the mercury is currently

retained after feed preparation steps are complete. This is inconsistent with the BDR assumption that 75% would be retained/removed at DWPF during SRAT processing.

- SRAT Batch 736 indicates mercury is not consistently being removed from the SRAT as intended. Based on the results of the SME, it appears the mercury was reduced during the SRAT, but not steam stripped. The reason for this is unknown.
- The sequence of the caustic addition to the RCT has changed to be earlier in the process. The presence of elemental mercury in the RCT samples supports the assumption in the BDR that since mercury slowly oxidizes in caustic, the oxidation should occur during the long term storage in the Tank Farm.
- The analytical results obtained for the RCT samples did not include solids analysis (sample was decanted to remove solids). Thus, the BDR assumption in regards to elemental mercury adsorbing on to the RCT solids could not be evaluated.

6.0 RECOMMENDATIONS AND FUTURE WORK

- Nitric acid additions should be tailored to minimize the amount of nitric acid added to the SMECT to minimize oxidation of elemental mercury present in the tank's sump and trench.
- Complete the path forward actions outlined in SRR-WSE-2015-00055.
- If possible, the SRAT Product mercury analysis should be continued, to ensure the type of behavior observed during Batch 736 was an anomaly.
- Based on the formation of ethyl mercury and MeHg during CPC operations and its potential impact to Saltstone grout, efforts should be made to investigate the following:
    - More stable antifoams for the pH conditions of the CPC,
    - Minimization of the antifoam amounts added during CPC processing, when possible,
    - The mechanism of ethyl mercury and MeHg production in the SMECT. Currently, literature surveys indicate no published data to address the reaction chemistry for the conditions that exist in the SMECT, and
    - Complete feasibility studies related to sludge speciation, conversion of organic mercury to elemental mercury, and grout formulations to retain higher organic mercury content as funded under Environmental Management Technology Development Program (Fiscal Year 2016).

7.0 REFERENCES

[1] J.L. Folk, "Evaluation of Mercury in the Liquid Waste Process Facilities", WDED-15-10, February 3, 2015.
[2] V. Jain, H. Shah, J. E. Occhipinti, W. R. Wilmarth, R. E. Edwards, "Evaluation of Mercury in Liquid Waste Processing Facilities Phase I Report", SRR-CES-2015-00012, Rev. 1, August 13, 2015.
[3] T.L. Fellinger, "Presentation – Mercury Overview for DWPF", SRR-WSE-2015-00025, Rev. 1, May 10, 2015.
[4] G.C. Winship, "Defense Waste processing Facility Mercury Removal Study", Y-AES-S-00002, Rev.0, October 2015.
[5] M.A. Sudduth, et.al, "Path Forward to Address Mercury Removal and Disposal from DWPF Streams", SRR-WSE-2015-00055, Rev. 0, November 17, 2015.
[6] "Basic Data Report, Defense Waste Processing Facility, Sludge Plant, Savannah River Plant, 200-S Area", WSRC-RP-92-1186, Rev. 139, July, 1992.
[7] G. Fuseya, "The Solubility of Mercuric Oxide in Sodium Hydroxide Solutions", J. Am. Chem. Soc., 1920, 42 (3), pp 368–371, DOI: 10.1021/ja01448a004, March 1920.
[8] D.A. Janes, "Mercury Recovery Design Basis", DPST-82-893, September, 1982.
[9] M.S. Hay and T.L. Fellinger, "Characterization and Dissolution Test Results for the January 2005 DWPF Off Gas Condensate Tank Samples", WSRC-TR-2005-00141, Rev.0, May 16, 2005.
[10] J. R. Zamecnik and A. S. Choi, "Modeling the Impact of Elevated Mercury in Defense Waste Processing Facility Melter Feed on the Melter Off-Gas System – Preliminary Report", SRNL-STI-2009-00149, Rev.1, August 2010.
[11] J.M. Pareizs, J.R. Zamecnik, C.J. Coleman, and D.P. Lambert, "Analysis of DWPF Mercury Samples", SRNL-L3100-2014-00038, Rev.0, March 20, 2014.
[12] N.E. Bibler and T.B. Edwards, "Composition of Condensate Samples from the Sludge Receipt and Adjustment Tank and Slurry Mix Evaporator in the DWPF", WSRC-RP-2004-00575, Rev. 0, August 2004.

[13] T.L. Fellinger and N.E. Bibler, “Results for the DWPF Slurry Mix Evaporator Condensate Tank, Off Gas Condensate Tank and Recycle Collection Tank Samples (U)”, WSRC-TR-2004-00577, Rev.0, December 21, 2004.

[14] T.L. Fellinger and N.E. Bibler, “Results for the DWPF Decontamination Waste Treatment Tank Samples (U)”, WSRC-TR-2005-00036, Rev. 0, January 25, 2005.

[15] C.J. Bannochie and C.L. Crawford, “Characterization of a Precipitate Reactor Feed Tank (PRFT) Sample from the Defense Waste Processing Facility (DWPF)”, SRNL-STI-2013-00735, Rev. 0, May 4, 2014.

[16] K.E. Zeigler and N.E. Bibler, “Characterization of the DWPF Melter Off – Gas Quencher, and Steam Atomized Scrubber Deposit Samples”, WSRC-STI-2007-00262, Rev.0, May 2007.

[17] C.A. Nash, M.E. Stone, and M.S. Hay, “Analyses and Comparison of Bulk and Coil Surface Samples from the DWPF Slurry Mix Evaporator”, SRNL-STI-2011-00623, Rev.0, February 2012.

[18] J.D. Newell, “Characterization of DWPF Melter Off-Gas Quencher Sample”, SRNL-STI-2011-00520, Rev.0, November 14, 2011.

[19] C.J. Bannochie and K.J. Imrich, “DWPF GC Filter Assembly Sampling, and Analysis”, SRNL-STI-2009-00602, Rev. 0, November 2009.

[20] K.E. Zeigler and N.E. Bibler, “Analysis of DWPF SRAT Off – Gas GC Sample Line Debris”, SRNL-PSE-2007-00095, Rev.0, April 27, 2007.

[21] C.J. Bannochie, D.J. Adamson, W.D. King, “Characterization of DWPF Recycle Condensate Tank Materials, SRNL-STI-2014-00603, Rev.1, April 2015.

[22] J.W. Ray, “Waste Acceptance Criteria for Sludge, ARP, and MCU Process Transfers to 512-S and DWPF (U)”, X-SD-G-00008, Rev. 20, January 6, 2016.

[23] D. Smith, “Defense Waste Processing Facility – Expanded Process Vessel Vent Diagram” M-M7-S-00005, Rev.1, November 11, 2009.

[24] G. Moesta, “Mercury Water Wash Tank Liquid Level Scaling Computation”, S350-ZZZL-3742, Rev. 2 May 21, 2002.

[25] B. Wilson, “Sample Preparation and Vessel Cleaning”, Manual SW4-15.204, Procedure 6.1, Rev. 13, November 5, 2012.

[26] B. Wilson, “Sample Analysis”, Manual SW4-15.204, Procedure 6.2, Rev. 9, December 11, 2012.

[27] L. Liang, N.S. Bloom; M. Horvat, “Simultaneous Determination of Mercury Speciation in Biological Materials by GC/CVAFS after Ethylation and Room-Temperature Precollection”, *Clin. Chem*., 1994, 40/4: 602-607.

[28] N.S. Bloom, “Method Validation Study for Dimethyl Mercury in Air”, Final Report to the US Army Corps of Engineers in response to RFP No. 0685107-013, February 10, 2000.

[29] N.S. Bloom, E.A. Crecelius, "Determination of Mercury in Seawater at Sub-Nanogram per Liter Levels", *Mar. Chem*., 1983, 14: 49-59.

[30] C. Martino, “Organic Mercury in Caustic Side Solvent Extraction” SRNL-WHM-2004-00008, Rev.0, November 10, 2004.

[31] T. Peters, “Mercury Data from Various MCU Samples”, E-mail Communication, April 2, 2015.

[32] C.J. Bannochie, “Results of Hg Speciation Testing on MCU Strip Effluent Hold Tank (SEHT) and Decontaminated Salt Solution Hold Tank (DSSHT) Materials”, SRNL-L3100-2015-00150, Rev. 1, September 21, 2015.

[33] C.J. Bannochie, “Results of Hg Speciation Testing on 3Q15 Tank 50, Salt Solution Feed Tank (SSFT), and Solvent Hold Tank (SHT) Materials”, SRNL-L3100-2015-00144, Rev. 1, August 13, 2015.

[34] Karl C. Bowles and Simon C. Apte, “Determination of Methylmercury in Natural Water Samples by Steam Distillation and Gas Chromatography-Atomic Fluorescence Spectrometry”, Anal. Chem. 1998**,** 70, 395-399.

[35] R.J. Flett, and G. Gill, “Comparison of Two Methods for the Measurement of Methyl Mercury Concentrations in Penobscot River Sediments”, 10th International Conference on Mercury as a Global Pollutant (ICMGP), Halifax, Nova Scotia, Canada, July 24-29, 2011. Web site link:http://www.flettresearch.ca/Reference/Poster%20for%2010th%20ICMGP%20-%20MMHg%20Distillation%20vs%20KBr%20extraction%20July%202011.pdf

[36] C.J. Bannochie, “Tank 40 Final Sludge Batch 8 Chemical Characterization Results”, SRNL-STI-2013-00504, Rev.0, September 2013.

[37] D.T. Hobbs, “Impact of Nitric Acid Reacting with Elemental Mercury in the 2H-Evaporator Pot and Mercury Collection Tank” SRT-LWP-2000-00119, Rev.1, August 18, 2000.

[38] C.J. Bannochie, “Results of Hg Speciation Testing on DWPF SMECT-1, SMECT-3, and SMECT-5 Samples”, SRNL-L3100-2015-00218, Rev. 0, February 2016.

[39] C.J. Bannochie, “Results of Hg Speciation Testing on 4Q15 Tank 50, SMECT-2 and RCT-1 Samples”, SRNL-L3100-2015-00219, Rev. 1, February 2016.

[40] C.J. Bannochie, “Results of Hg Speciation Testing on DWPF SMECT-4, SMECT-6, and RCT-2 Samples,” SRNL-L3100-2016-00016, Rev. 0, February 2016.

[41] C.J. Bannochie, “Results of Hg Speciation Testing on DWPF SMECT-8, OGCT-1, and OGCT-2 Samples”, SRNL-L3100-2016-00018, Rev. 0, February 2016.

[42] W.R. Wilmarth, S.W. Rosencrance, and C.E. Duffey, “Studies of Mercury in High Level Waste”, WSRC-TR-2003-00238, Rev.1, March 31, 2004.

[43] T.L. Fellinger, H.P. Boyd, J.M. Bricker, C.J. Martino, J.R. Zamecnik, and W.R. Wilmarth, “Literature and Data Review for Evaluating the Production of Dimethyl Mercury in the Defense Waste Processing Facility”, X-ESR-S-00258, Rev.0, May 2015.

[44] W.E. Wilmarth, S.W. Rosencrance, E. Presbo, J. Garcia, P. Swartzendruber, E. Von der Geest, and N. S. Bloom, “Synthesis and Detection of Dimethylmercury Under High Level Waste Conditions”, WSRC-MS-2005-00161, Rev.0, March 11, 2005.

[45] M.S. Hay and C.J. Martino, “Analysis of Condensate Samples in Support of the Antifoam Degradation Study”, SRNL-STI-2015-00698, Rev.0, January 2016.

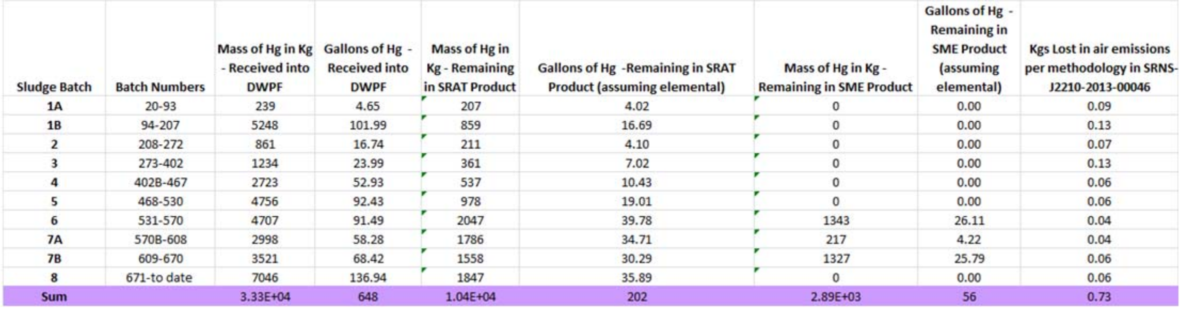
[46] C.J. Bannochie and C.L. Crawford, “Results of Hg Speciation Testing on DWPF Batch 735 RCT and OGCT Samples”, SRNL-L3100-2015-00105, Rev.1, June19, 2015.

[47] T.L. Fellinger, “Documentation of the Analytical Results for the Condensate Samples Taken During Defense Waste Processing Facility (DWPF) Batch 735 and Sampling Recommendations for DWPF Batch 736”, SRR-WSE-2015-00028, Rev. 1, June 18, 2015.

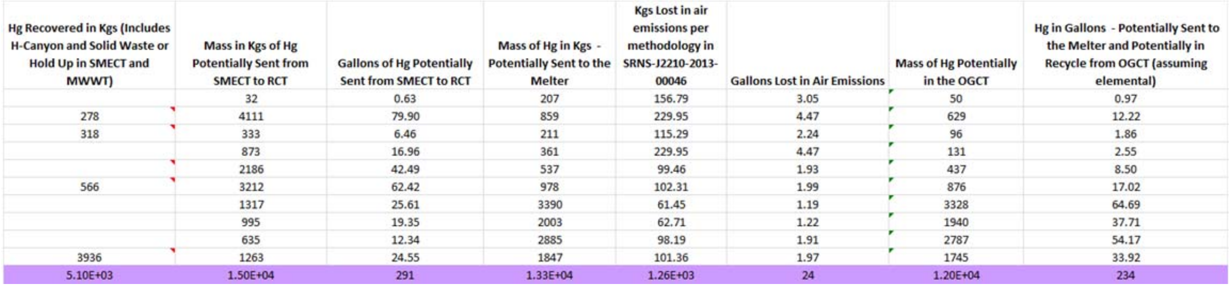
DISTRIBUTION

George Matis, 704-S
Joel Cantrell, 704-S
Kent Fortenberry, 766-H
Richard Edwards, 766-H
Ryan McNew, 766-H
Eric Freed, 704-S
Jeff Ray, 704-27S
Mark-L Johnson, 704-24S
John Iaukea, 704-S
Jon Bricker, 766-H
Roberto Gonzalez, 707-H
Mark A. Smith, 707-H
Pauline Hang, 704-S
Tom Temple, 704-S
Keith Sandroni, 210-S
Gordon Smith, 210-S
Irvin Rubin, 210-S
Mark Sautman, 703-41A
Daniel Burnfield, 703-41A
Hasmukh Shah, 766-H
Maria Rios-Armstrong, 766-H
Bill Holtzscheiter, 766-H
Bill Wilmarth, 773-A
Chris Martino, 999-W
Tom Colleran, 773-67A
Frank Pennebaker, 773-42A
Bob Petras, 707-3E
Azi Samadi, 704-27S
Andy Sudduth, 704-25S
Chris Bannochie, 773-42A
Vijay Jain, 766-H
John Occhipinti, 704-56H
Bruce Klein, 704-S
Kevin Brotherton, 704-27S
Grant Thomas, 704-27S
Austin Chandler, 704-27S
Lauryn Jamison, 704-27S
DCC, 766-H

APPENDIX A – DWPF Mercury Mass Balance for Sludge Slurry

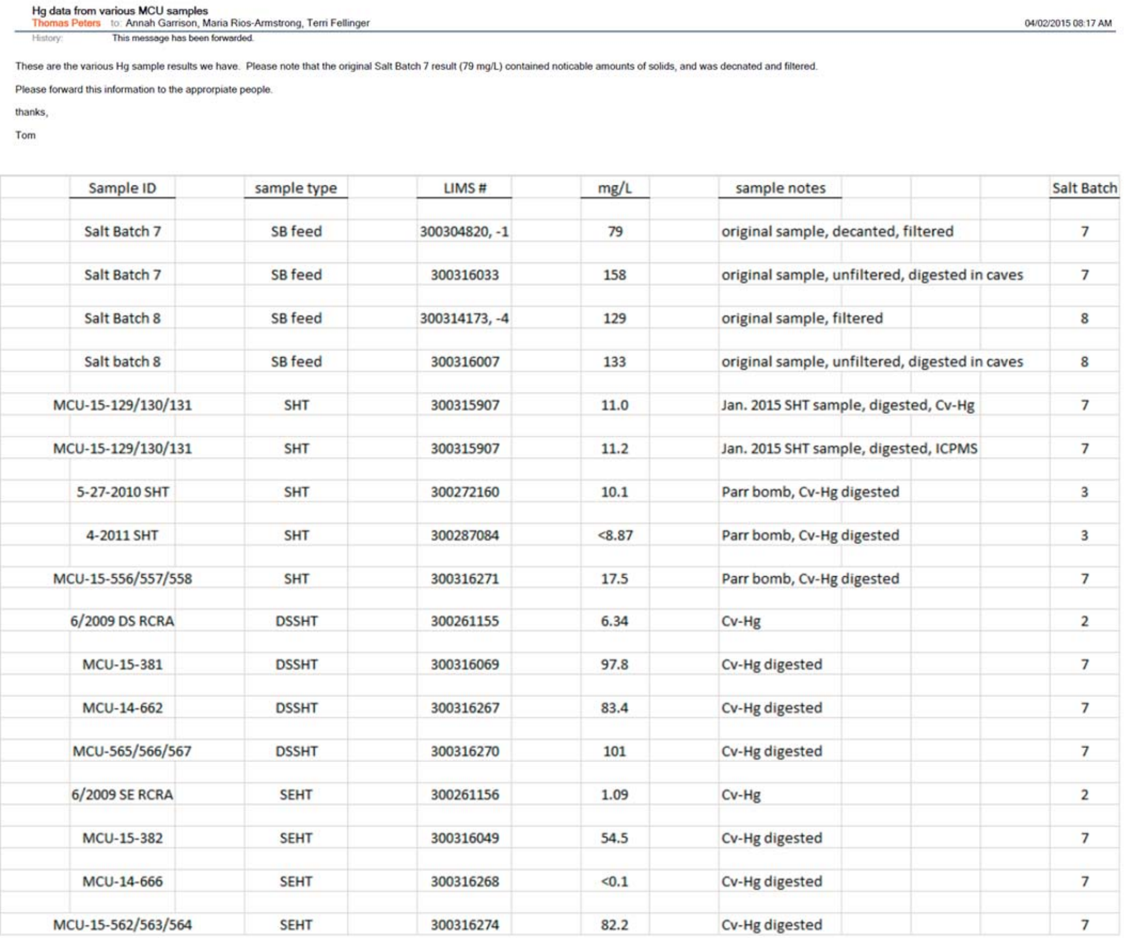


Sludge Batch	Batch Numbers	Mass of Hg in Kg - Received into DWPF	Gallons of Hg - Received into DWPF	Mass of Hg in Kg - Remaining in SRAT Product	Gallons of Hg -Remaining in SRAT Product (assuming elemental)	Mass of Hg in Kg - Remaining in SME Product	Gallons of Hg - Remaining in SME Product (assuming elemental)	Kgs Lost in air emissions per methodology in SRNS-J2210-2013-00046
1A	20-93	239	4.65	207	4.02	0	0.00	0.09
1B	94-207	5248	101.99	859	16.69	0	0.00	0.13
2	208-272	861	16.74	211	4.10	0	0.00	0.07
3	273-402	1234	23.99	361	7.02	0	0.00	0.13
4	402B-467	2723	52.93	537	10.43	0	0.00	0.06
5	468-530	4756	92.43	978	19.01	0	0.00	0.06
6	531-570	4707	91.49	2047	39.78	1343	26.11	0.04
7A	570B-608	2998	58.28	1786	34.71	217	4.22	0.04
7B	609-670	3521	68.42	1558	30.29	1327	25.79	0.06
8	671-to date	7046	136.94	1847	35.89	0	0.00	0.06
Sum		3.33E+04	648	1.04E+04	202	2.89E+03	56	0.73



Hg Recovered in Kgs (Includes H-Canyon and Solid Waste or Hold Up in SMECT and MWWT)	Mass in Kgs of Hg Potentially Sent from SMECT to RCT	Gallons of Hg Potentially Sent from SMECT to RCT	Mass of Hg in Kgs - Potentially Sent to the Melter	Kgs Lost in air emissions per methodology in SRNS-J2210-2013-00046	Gallons Lost in Air Emissions	Mass of Hg Potentially in the OGCT	Hg in Gallons - Potentially Sent to the Melter and Potentially in Recycle from OGCT (assuming elemental)
	32	0.63	207	156.79	3.05	50	0.97
278	4111	79.90	859	229.95	4.47	629	12.22
318	333	6.46	211	115.29	2.24	96	1.86
	873	16.96	361	229.95	4.47	131	2.55
	2186	42.49	537	99.46	1.93	437	8.50
566	3212	62.42	978	102.31	1.99	876	17.02
	1317	25.61	3390	61.45	1.19	3328	64.69
	995	19.35	2003	62.71	1.22	1940	37.71
	635	12.34	2885	98.19	1.91	2787	54.17
3936	1263	24.55	1847	101.36	1.97	1745	33.92
5.10E+03	1.50E+04	291	1.33E+04	1.26E+03	24	1.20E+04	234

APPENDIX B – Mercury Results for SEHT



Hg data from various MCU samples
Thomas Peters to: Annah Garrison, Maria Rios-Armstrong, Terri Fellinger 04/02/2015 08:17 AM
History: This message has been forwarded.

These are the various Hg sample results we have. Please note that the original Salt Batch 7 result (79 mg/L) contained noticable amounts of solids, and was decnated and filtered.

Please forward this information to the approrpiate people.

thanks,

Tom

Sample ID	sample type	LIMS #	mg/L	sample notes	Salt Batch
Salt Batch 7	SB feed	300304820, -1	79	original sample, decanted, filtered	7
Salt Batch 7	SB feed	300316033	158	original sample, unfiltered, digested in caves	7
Salt Batch 8	SB feed	300314173, -4	129	original sample, filtered	8
Salt batch 8	SB feed	300316007	133	original sample, unfiltered, digested in caves	8
MCU-15-129/130/131	SHT	300315907	11.0	Jan. 2015 SHT sample, digested, Cv-Hg	7
MCU-15-129/130/131	SHT	300315907	11.2	Jan. 2015 SHT sample, digested, ICPMS	7
5-27-2010 SHT	SHT	300272160	10.1	Parr bomb, Cv-Hg digested	3
4-2011 SHT	SHT	300287084	<8.87	Parr bomb, Cv-Hg digested	3
MCU-15-556/557/558	SHT	300316271	17.5	Parr bomb, Cv-Hg digested	7
6/2009 DS RCRA	DSSHT	300261155	6.34	Cv-Hg	2
MCU-15-381	DSSHT	300316069	97.8	Cv-Hg digested	7
MCU-14-662	DSSHT	300316267	83.4	Cv-Hg digested	7
MCU-565/566/567	DSSHT	300316270	101	Cv-Hg digested	7
6/2009 SE RCRA	SEHT	300261156	1.09	Cv-Hg	2
MCU-15-382	SEHT	300316049	54.5	Cv-Hg digested	7
MCU-14-666	SEHT	300316268	<0.1	Cv-Hg digested	7
MCU-15-562/563/564	SEHT	300316274	82.2	Cv-Hg digested	7