## Mercury Reduction and Removal from High Level Waste at the Defense Waste Processing Facility - 12511

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## ABSTRACT

The Defense Waste Processing Facility processes legacy nuclear waste generated at the Savannah River Site during production of enriched uranium and plutonium required by the Cold War. The nuclear waste is first treated via a complex sequence of controlled chemical reactions and then vitrified into a borosilicate glass form and poured into stainless steel canisters. Converting the nuclear waste into borosilicate glass is a safe, effective way to reduce the volume of the waste and stabilize the radionuclides. One of the constituents in the nuclear waste is mercury, which is present because it served as a catalyst in the dissolution of uranium-aluminum alloy fuel rods. At high temperatures mercury is corrosive to off-gas equipment, this poses a major challenge to the overall vitrification process in separating mercury from the waste stream prior to feeding the high temperature melter. Mercury is currently removed during the chemical process via formic acid reduction followed by steam stripping, which allows elemental mercury to be evaporated with the water vapor generated during boiling. The vapors are then condensed and sent to a hold tank where mercury coalesces and is recovered in the tank's sump via gravity settling. Next, mercury is transferred from the tank sump to a purification cell where it is washed with water and nitric acid and removed from the facility. Throughout the chemical processing cell, compounds of mercury exist in the sludge, condensate, and off-gas; all of which present unique challenges.

## INTRODUCTION

The Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) processes legacy nuclear waste generated from the production of enriched uranium and plutonium. The majority of this highly radioactive waste has resulted from past chemical dissolution and separations activities at the F-area and H-area Canyons. In the first step of the dissolution process, a 4.7 wt% solution of mercuric nitrate (or mercury(II) nitrate, $Hg(NO_3)_2$) was added to a boiling 47.4 wt% solution of nitric acid to serve as a catalyst in dissolving irradiated aluminum-clad fuel rods. This decreases the amount of time required to fully dissolve the rod material versus using only boiling nitric acid. Elemental aluminum readily forms a thin surface layer of aluminum oxide ($Al_2O_3$) upon contact with oxygen in air. This process creates a passive layer (~4 nm thick) which prevents any further oxidation of the aluminum beneath this layer. Although beneficial in many applications because of its hardness and resistance to acid, this oxide layer proves to be a hindrance during the dissolution process. On its own, boiling nitric acid is capable of penetrating the oxide layer and dissolving the aluminum and uranium; however, this takes a substantial amount of time and energy. With the addition of mercuric nitrate to the process, the processing time for dissolution is significantly reduced. It is a linear logarithmic correlation between mercury concentration and dissolution rate with a slope nearly one [1]. Mercury disrupts the aluminum oxide layer by forming an amalgam with aluminum. Once this occurs, elemental aluminum is exposed to the nitric acid solution and is readily dissolved.

The solution is then transferred to a series of mixer-settler tanks for the first cycle of the solvent extraction separation process known as Plutonium – Uranium Extraction (PUREX). This cycle

utilizes tributyl phosphate (TBP) to associate with the desired fissile materials (U and Pu) in solution and extracts them into the solvent phase (normally kerosene) for further processing. The undesired actinides, decay products, and separations chemicals, including mercuric nitrate, remain in the aqueous phase and are rejected to the waste stream. At this point, the waste stream is sent to the Tank Farm for storage prior to final disposal. The waste tanks are constructed out of carbon steel and are susceptible to corrosion. The waste is required to be neutralized prior to storage; this pH change causes the dissolved metals to precipitate as metal oxide compounds (i.e. Hg → HgO).In the tank farm, liquid waste is normally processed through an evaporator unit to remove excess water and optimize the storage space available. A result of concentrating the waste is that a fraction of the mercury is vaporized into the evaporator overheads and is collected. This mercury condensate is recycled back to the Canyons to be reintroduced into the flow process during the dissolution step. The remaining mercuric compounds in the concentrated waste are ultimately sent to DWPF as part of a sludge batch. A simplified DWPF flowsheet of the Chemical Processing Cell (CPC) is shown below in Figure 1.
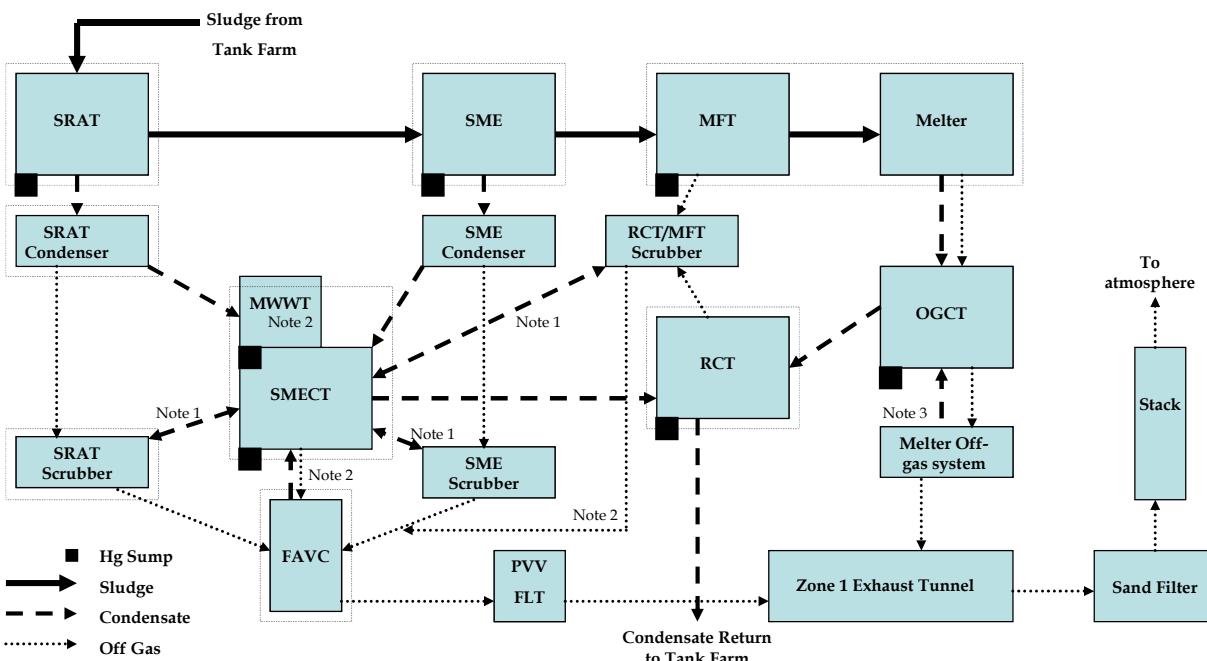


**Note 1:** SMECT liquid is used as the scrubber solution for the SRAT, SME, and MFT/RCT Scrubber. Liquid for all scrubbers drains back to the SMECT.

**Note 2:** MWWT/SMECT and RCT/MFT Scrubber vapor streams are connected to the MTH which connects to the PVV between the SME scrubber and FAVC.

**Note 3:** Melter off-gas system consists of Film cooler, quencher, condenser, HEME, and HEPA filters.

Fig. 1. Overview of the current DWPF flowsheet

Approximately 30,200 liters (8,000 gallons) of sludge is received in the Sludge Receipt and Adjustment Tank (SRAT) as part of a sludge batch sent from a 4.9 million liter (1.3 million gallon) feed tank in the H-area tank farm. The sludge is chemically adjusted in the SRAT via addition of concentrated nitric and formic acids. The acid addition in the SRAT serves several purposes:  to acidify the incoming sludge and thus adjust the slurry rheological properties, determine the redox state of the final melter feed, and reduce and separate the mercury entrained in the incoming feed. Acid is added at nominally 110-130% of the required stoichiometric amount to ensure that acid is not the limiting reagent [2]. When formic acid is added it reacts with the mercuric oxide (HgO) in the sludge resulting in elemental mercury,

water, and carbon dioxide. The elemental mercury is then steam stripped via boiling to drive mercury into the vapor phase. In the SRAT condenser the mercury condenses and coalesces along with the water vapor and then drains to the Mercury Water Wash Tank (MWWT), which is a decanter where the mercury is intended to settle. Any mercury that bypasses the MWWT, which is situated on top of the Slurry Mix Evaporator Condensate Tank (SMECT), will ultimately drain to the SMECT sump or recycle back to the SRAT during a reflux cycle. Mercury that is later stripped as vapor from the waste in the Slurry Mix Evaporator (SME) is also sent directly to the SMECT because there is no decanter. Collected mercury in the SMECT is pumped to the MWWT via a positive displacement mercury pump. From the MWWT, mercury is pumped to a Mercury Purification Cell (MPC) for nitric acid scrubbing and decontamination. In the first scrubbing step, a 12 wt% nitric acid solution flows counter to the mercury in a 5.08 cm (2 inch) diameter by 91.44 cm (36 inch) tall glass column filled with ceramic Berl saddles. After acid washing, the mercury is rinsed with process water in another identical column. The scrubbed mercury is then stored in the Mercury Hold Tank (MHT) where it can be pumped to fill smaller bottles for disposal.

The main purposes for removing mercury from the waste stream are to avoid negative impacts to the melter unit and off-gas system, and as a purge stream for mercury from the tank farm. DWPF has operational limits on the amount of mercury that can remain in the waste stream due to corrosion and plugging concerns in melter off-gas components. Mercury removal and appropriate disposal  are necessary given that the alternatives, which include either exhausting it to the atmosphere as mercury vapor or returning it to the tank farm as dissolved mercury in the condensate recycle line from the Recycle Collection Tank (RCT), are not acceptable. DWPF has process limitations on the amount of mercury permitted for each batch at the end of the SRAT process; this permissible limit is 0.80 wt% [3]. This is based on the impact to off-gas system components and the rate at which mercury accumulation drives corrective maintenance downtime for the facility. Table I shows the projected mercury content, as a percentage of total incoming mercury to the process, being retained across units in the CPC. Ideally, the amount of mercury contained in the MWWT would equate to the amount of incoming mercury.

**Table I: Projected Mercury fraction contained in CPC units**

| | |
|---|---|
| SRAT | 5% |
| SMECT | 25% |
| SME | 5% |
| RCT | 22% |
| MFT | 1% |
| Off-Gas system/Ventilation | 7% |
| MWWT | 10% |
| Vessel Jumpers | 15% |
| Scrubbers | 10% |

**DISCUSSION**

For the purposes of discussing the mercury material balance data, several terms will be defined to more clearly describe what particular mercury location is being discussed. Referring to Figure 2, *removed* and *stripped* mercury are not defined as the same thing. *Stripped* refers to the amount of mercury that is recovered in the MWWT and the amount that collects in the scrubber liquid (SMECT), as well as any mercury that does not coalesce out of the vapor phase and is carried into the Process Vessel Vent (PVV) system. *Removed* is the sum of *stripped* mercury and any mercury that drops out of the sludge and accumulates as elemental mercury at the bottom of the SRAT due to its increased density. It can also be considered as any mercury that is not suspended in the sludge slurry any longer. *Recovery efficiency* is the amount of water evaporation required during the boiling phase per amount of mercury *removed*. The amount of mercury *retained* is the amount remaining in the sludge slurry as measured by a sample analysis. The amount of incoming mercury to the process should equal the amount *removed* + *retained*; however, this will only be valid if the material balance closure is equal to 100%.
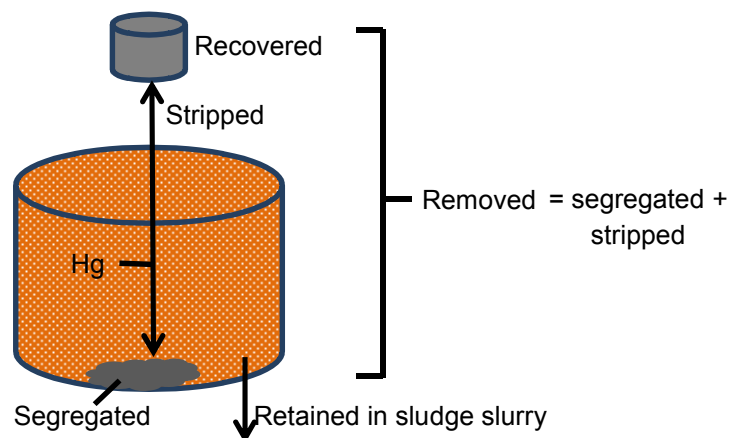


Fig. 2. Distribution of Mercury in a tank

Currently, the time to collect an appreciable amount of mercury is on the order of numerous months, which is unacceptably long. Since June 2007, over 568 liters (150 gallons) of mercury has been sent to the DWPF as part of incoming sludge [4]. With a density of 13.546 g/cm$^3$, this volume of mercury has weight of approximately 77,000 kg (17,000 pounds).This sludge normally has a mercury concentration of ~1.2 wt% (dry slurry basis) prior to processing. Approximately 80 percent of this mercury is removed during the SRAT process. However, the stripping efficiency (lb$_{steam}$/lb$_{Hg}$) based on representative data is quite low as shown in Figure 3. The data shows two cases: one starting with 68 kg (150 pounds) of mercury suspended in the sludge slurry and the other starting at 45.4 kg (100 pounds). Overall, a greater starting concentration of mercury in the sludge slurry requires a greater amount of steam per unit of mercury removal. It is suspected that as mercury coalesces into larger drops over the steam stripping run, it becomes more difficult to remove [5].
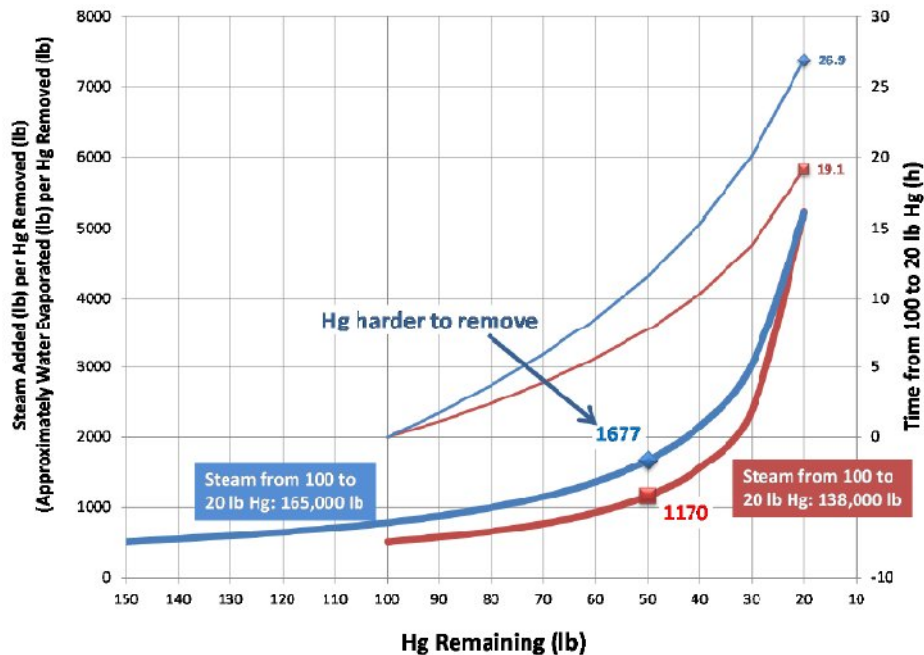
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Fig. 3. Steam required to remove Mercury [5]

The amount of mercury in the feed to the SRAT, SME, Melter Feed Tank (MFT) and Melter is known based on the incoming mercury concentration and sample results from the SRAT and SME. Table II shows the average sample results per batch run from processing of Macro-Batch 6 (completed May 2010).

Table II. Mercury removal during Macro-Batch 6 [4]

| CPC Unit | Transferred In (sludge) | Removed from sludge | |
|---|---|---|---|
| | [lbs/batch] | [lbs/batch] | [%][1] |
| SRAT | 149.6 | 117.7 | 78.7% |
| SME | 24.1[2] | 15.0 | 10.0% |
| MFT | 6.1 | 0.0 | 0.0% |
| Melter | 4.4 | 4.4[3] | 2.9% |

Note 1: Percentage of total incoming mercury to DWPF.
Note 2: Based on SRAT product sample results.
Note 2: Assuming that no mercury is stripped from the MFT; however, it is possible that some mercury separates from the MFT sludge and collects in the sump.
Note 3: Assuming all remaining mercury is vaporized in the high temperature environment of the melter.

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In addition, per samples taken from the SME, the chemically treated waste has a mercury concentration of 0.80 wt% or less. By design, the removed mercury should accumulate in the MWWT and be ultimately collected in the MPC. However, mercury has not been detected in the sump of the MWWT since the tank was replaced due to a hole in the overflow line in January 2009. Prior to its replacement, approximately 7.6 liters (2 gallons) of mercury total was transferred from the previous MWWT to the MPC, and an additional 15.2 liters (4 gallons) remained in the removed tank (based on the removed tank weight). This accounts for only 15% of the mercury removed from the incoming sludge [4].

Prior to removing the original MWWT, transfers to the MPC were successfully made and some (less than a gallon) of relatively pure mercury was collected. The next three transfers sent contaminated mercury to the cell, with each one more contaminated than the next. Subsequent transfers yielded a sludge/water mixture with only traces of mercury. It was thought all of the mercury was removed from the MWWT; yet, weighing the tank following removal revealed that up to 4 gallons remained in the tank. Mercury on the walls of the tank and crevasses likely accounted for this. More rigorous sparging of the tank prior to the final transfers may have allowed the additional 15.2 liters (4 gallons) to settle in the tank sump. The mercury that was successfully removed from the tank (approximately 7.6 liters) clogged up tanks in the MPC. It is probable that the purity of the mercury collected in the sump of the MWWT may be sludge batch dependent. Clogging problems were not as severe when purifying Macro-Batch 1 mercury; still, recovering and purifying "dirty" mercury has been extremely difficult.

The quality of mercury sent to the MPC can be strongly affected if high concentrations of antifoam (greater than ~10,000ppm) are added during batch processing. The evaporated antifoam material makes the mercury more difficult to process and may be the cause of severe pluggage in the MPC, this may be in part to the organics being introduced to the process [6]. In July 2008, mercury was successfully cleaned by the two scrubber columns and collected in the MHT; however, attempts to recirculate the mercury the following day were unsuccessful due to the formation of a clog at the bottom of the tank. The piping was removed and the clog was broken up. The material was collected in a bucket on the floor of the purification cell. Another attempt to transfer mercury occurred in January 2009 which resulted in a pluggage. As previously, the piping was unclogged with the material draining to buckets on the floor of the cell. From material gathered in the buckets, it appears that the mercury being sent to MPC may be in a compound form such as a mercury (I) nitrate hydroxide, which can form when elemental mercury comes in contact with dilute nitric acid.

During a DWPF outage occurring in October 2011, the SMECT mercury pump was removed from the tank for servicing and troubleshooting. The pump operates by allowing mercury that accumulates in the SMECT sump to flow into a collection bowl through a 2.54 cm (1 inch) outer diameter opening. This opening can be closed when transferring mercury out of the collection bowl by using an air actuated valve shaft. During this process, high pressure water is pushed into the collection bowl and the resulting pressure buildup forces the collected mercury up a line discharging to the MWWT. However, this particular pump has never functioned correctly. Following start-up tests in the early 1990's with "clean" mercury, this pump has failed to transfer any appreciable amount of mercury. It has been noted that during multiple attempts to transfer, the liquid level in the SMECT has risen. This is an indication that the valve shaft did not fully seal and seat properly on the collection bowl opening. Water was allowed to spray out through the opening and prevent the pump from achieving the pressure required for transferring. When the pump was removed from the tank, a mercury- containing mass had adhered up to a height of approximately 38.8 cm (15.25 inches) from the bottom.
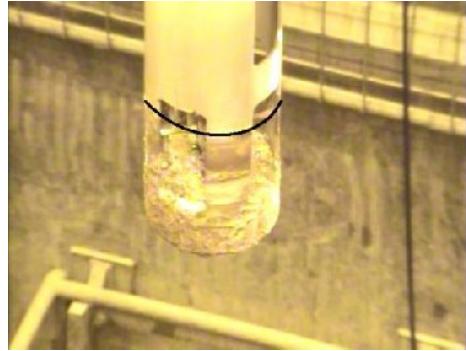
Fig. 4. Mercury mass on SMECT Hg pump (black reference line indicates max. height of Hg)

This mass is quite viscous in nature, and as the pump was being moved in the DWPF canyon by crane there were chunks of material falling off. Although this material was attached to the pump, it was removed easily during decontamination with a high pressure water jet. Based on the SMECT tank dimensions, a height of 15.25 inches on the pump indicates that up to 684.4 liters (180.8 gallons) of this material may be settled in the bottom of the SMECT. In recent laboratory studies conducted at the Savannah River National Laboratory (SRNL) using simulated sludge for Macro-Batch 7, appreciable amounts of mercury-rich deposits were noted on the vessel walls. Also, tests representing the SRAT showed some mercury-rich deposit buildup on the agitator blades. The situation was exacerbated under test conditions representing the MWWT with high antifoam concentrations, with some of the mercury on the walls turning a yellowish-green color and becoming gelatinous in nature. Analytical analysis indicates this can be a result of $Hg(OH)_2 \cdot Hg_2(NO_3)_2$. In addition to segregating at the bottom of tanks, mercury segregates and accumulates in the low points of vessel jumper connections. It is not uncommon for a small amount of mercury material (normally less than a few hundred milliliters) to spill out onto the CPC cell covers when a jumper is being removed for servicing.

The mercury concentration in the aqueous recycle stream back to the tank farm is one of the most vital unknowns for closing the mercury balance. During normal operation, the water inventory in the SMECT increases and at designated intervals it is transferred to the Recycle Condensate Tank (RCT) for chemical adjustments prior to sending the water to the tank farm. In 2011, samples from the RCT have shown signs of mercury in solution with an average concentration of 230 ppm. This reported concentration varies wildly from a low concentration of 39 ppm in June to a high of 565 ppm reported in May, just one month prior. The limit for mercury concentration in the RCT is 600 ppm [7]. Even with this fluctuating data, it is presumed that a significant amount of mercury, potentially up to 1,700 kg (~3,800 pounds), is being returned to the tank farm per year in solution, or 22% of the total mercury balance.

**PATH FORWARD**

Based upon sludge batch modeling information, it is forecasted that the mercury concentration in incoming sludge to DWPF will continue to increase. While mercury is being removed from the sludge slurry prior to entering the melter, it is not advantageous to have it continually building up at the low points in tanks. Addressing this issue is an opportunity to remove a rate limiting step in the CPC process and result in an overall DWPF production improvement. . In the near-term, a sample will be gathered from the SMECT mercury pump collection bowl and sent to SRNL for

analysis. This will allow for a better understanding of the mercury components that have segregated to the bottom of the tank and sump. A functional test will be conducted on the mercury pump to determine if there is a mechanical fault in the actuation of the valve shaft or if a pump design change is required. Another test will be to pressurize the collection bowl with water and attempt to drive mercury up the discharge line. It is vital for DWPF processing to be able to remove mercury and prevent excessive accumulation in the bottom of the tanks.

The MPC will undergo an extensive cleaning campaign. In its current condition, it is not operational and will likely have the same pluggage issues if the piping is either not replaced or extensively cleaned. Samples of the material have been collected and will be sent to SRNL for analysis. In addition, a roadmap is being developed to investigate whether purifying mercury in the MPC is a necessary step and to see if a more efficient path for disposal is available. With the significant reduction in activities at the Canyons, recycled mercury is no longer needed for fuel rod dissolution. Eliminating this purification could result in a facility cost savings.

Laboratory work will continue to investigate and better understand the effects of the antifoam on mercury. A determination is needed regarding the advantages and disadvantages of processing the sludge slurry with a higher antifoam concentration.

## CONCLUSIONS

Mercury removal from sludge waste being fed to the DWPF melter is required to avoid exhausting it to the environment or any negative impacts to the Melter Off-Gas system. The mercury concentration must be reduced to a level of 0.8 wt% or less before being introduced to the melter. Even though this is being successfully accomplished, the material balances accounting for incoming and collected mercury are not equal. In addition, mercury has not been effectively purified and collected in the Mercury Purification Cell (MPC) since 2008. A significant cleaning campaign aims to bring the MPC back up to facility housekeeping standards. Two significant investigations are being undertaken to restore mercury collection. The SMECT mercury pump has been removed from the tank and will be functionally tested. Also, research is being conducted by the Savannah River National Laboratory to determine the effects of antifoam addition on the behavior of mercury. These path forward items will help us better understand what is occurring in the mercury collection system and ultimately lead to an improved DWPF production rate and mercury recovery rate.

## REFERENCES

1. "Technical Manual 200-Area HM Process", DPSTM-200-HM, Savannah River Laboratory, July 1977.

2. Eibling, R.E., Fowler, J.R. (1981). "Mercury Reduction and Removal During High-Level Radioactive Waste Processing and Vitrification", DP-MS-81-49, November 1981.

3. Wingard, B.R., Bricker, J.M., Occhipinti, J. E. (2010). "Path Forward to Address Reduction of SRAT Cycle Time Via Reducing the Mercury Stripping Time", SRR-WSE-2010-00213, October 2010.

4. Wingard, B.R. (2010). "Path Forward to Address the Mercury Balance at the DWPF and Determine How to Recover, Transfer, and Purify Mercury in the CPC", SRR-WSE-2010-00077, April 2010.

5.  Zamecnik, J.R. (2011). "Behavior of Mercury During DWPF Chemical Process Cell Processing – Highlights of FY11 Work", SRNL-L3100-2011-00200, Rev. 0, November 2011.

6.  Hutson, L.F. (1992). "Organics in the CPC and Their Effects on the DWPF Operation", WSRC-TR-92-0006, January 1992.

7.  "Waste Compliance Plan For Radioactive Liquid Waste Transfers From the DWPF to 241-H Tank Farm", X-SD-G-00005, Rev. 22, September 2011.