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Studies of Mercury in High Level Waste Systems

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Studies of Mercury in High Level Waste Evaporator Systems

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INTRODUCTION

Background

During nuclear weapons production, nuclear reactor target and fuel rods were processed in F- and H-Canyon, respectively. For the target rods, a caustic dissolution of the aluminum cladding was performed prior to nitric acid dissolution of the uranium metal targets in the large canyon dissolvers. The fuel rods consisted of a uranium-aluminum alloy and were processed in H-Canyon. To dissolve the aluminum cladding and the U-Al fuel, mercury in the form of soluble mercury (II) nitrate was added as a catalyst to accelerate the dissolution of the aluminum. During the late 1970's and 1980's, F-Canyon began to process plutonium-containing residues that were packaged in aluminum cans and thus required the use of mercury as a dissolution catalyst.

Following processing to remove uranium and plutonium using the solvent extraction process termed the Plutonium-Uranium Recovery by EXtraction (PUREX) process, the acidic waste solutions containing fission products and other radionuclides were neutralized with sodium hydroxide. Upon neutralization, two separate waste streams are created with the first being a transition metal-laden sludge and the second being a dilute supernate. The sludge/supernate slurry is discharged from the canyon facilities for storage in carbon steel tanks. The F- and H-Area tank farms consisted of 51 nominally 1 million-gallon tanks. In order to conserve tank space, the dilute waste supernate is evaporated. Historically, the waste was evaporated to the point that certain sodium salts (nitrate and nitrite) would crystallize into a saltcake in the drop tank.

The mercury used in canyon processing is fractionated between the sludge and supernate that is transferred from the canyons to the tank farm. The sludge component of the waste is currently vitrified in the Defense Waste Processing Facility (DWPF). The vitrified waste canisters are to be sent to the federal repository for High Level Waste. The mercury in the sludge, presumably in an oxide or hydroxide form (HgO or $Hg(OH)_2$) is reduced to elemental mercury by the chemical additions and high temperatures in the Slurry Receipt and Adjustment Tank (SRAT), steam stripped and collected in the Mercury Collection Tank. The mercury in the dilute supernate is in the form of mercuric ion (Hg^{2+}) and is soluble. During evaporation, the mercuric ion is reduced to elemental mercury, vaporizes into the overheads system and is collected as a metallic liquid in the Mercury Removal Tank shown schematically in Figure 1.

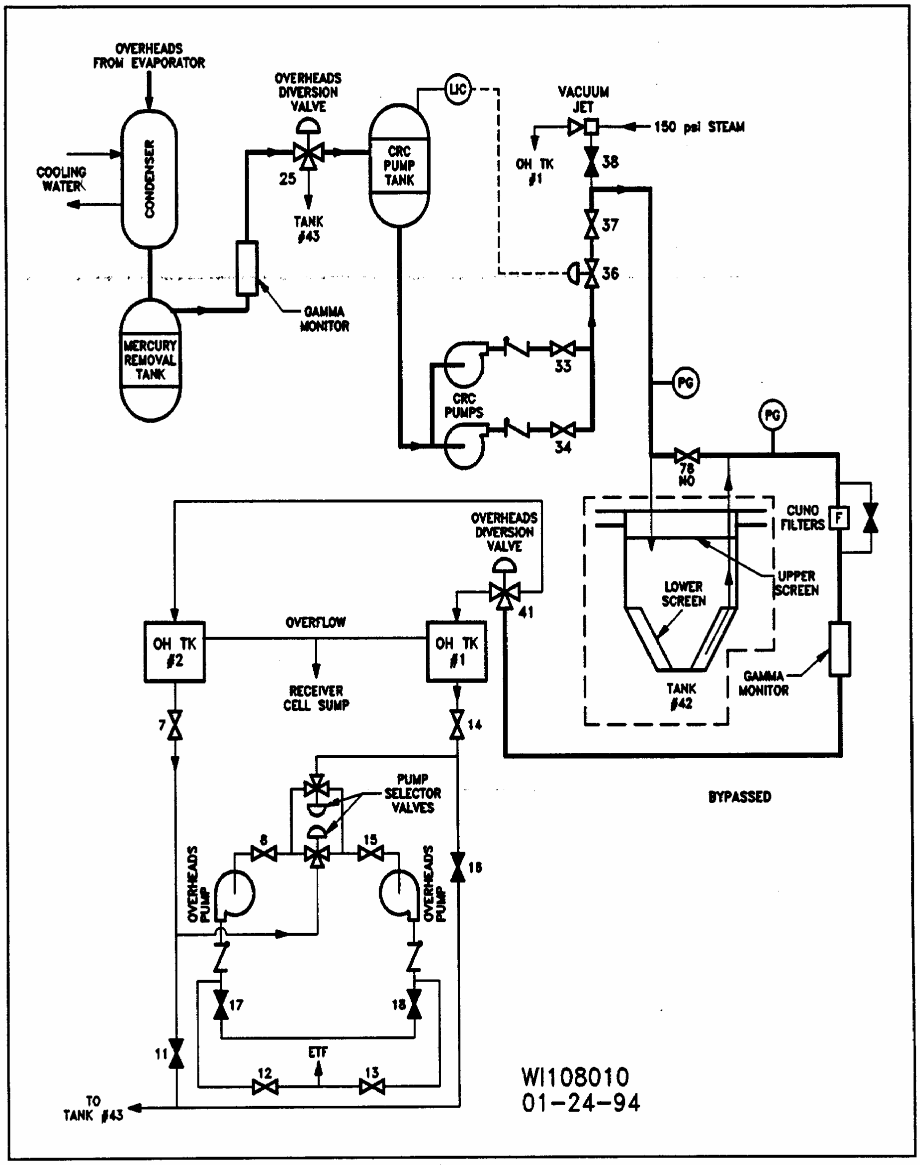

Figure 1. 2H Basic Overheads System

Currently the CRC column and Tank 42 equipment is by-passed

Chronology of Mercury Vapor Discovery

During a startup of the 3H Evaporator in summer 2001, samples taken from the evaporator overheads and analyzed by the Effluent Treatment Facility (ETF) lab for mercury were found to contain mercury levels above the ETF Waste Acceptance Criteria (WAC) limit of 2 mg/L. As a result of this, the 3H Evaporator was operated under a special procedure and deviation after July 13, 2001 to collect data to aid in understanding the high levels of mercury in the overheads. Based on the data collected, it was determined that the high mercury levels were probably the result of high mercury concentrations in the feed and high steam flow rates (high temperatures) in the evaporator. During this testing, a quarterly sample was transported to the Savannah River Technology Center (SRTC) to be checked for compliance with the WAC. The mercury analysis gave a result approximately 1/50th of that found by the ETF lab in a sample pulled during the same week. Discussions were initiated, and it was noted that while both labs used essentially the same analytical method (atomic absorption) SRTC had not been digesting the mercury samples prior to analysis whereas the ETF lab had been. SRTC had believed that since the samples contained primarily distilled water and showed little signs of contamination, especially with organics, that digestion of the mercury was unnecessary. A round-robin test was run with SRTC, ETF and Central Lab in F Area analyzing the same sample. This time all labs digested the mercury samples prior to analyzing and obtained similar results. From this it was concluded that even the very small amount of organic contamination found in the samples (on the order of 10 - 20 mg/L) was sufficient to complex the mercury and interfere with analysis.

Also in June of 2001, elevated levels of mercury vapor were discovered in the 3H Evaporator service building during a routine survey. These elevated levels were not expected based on the process model for the system and experience with operating other waste evaporators on site. The higher concentrations of mercury vapor were recorded in the overheads cell area. Speculation on why the elevated mercury levels were found in the 3H system and not the 2H system suggested several design and operational differences. SRTC was requested to examine the chemistry of mercury in support of issue resolution.

As will be described in detail in other parts of this report, liquid samples of the evaporator overheads were analyzed to better understand the mercury vapor results. Analysis of the liquid overheads samples determined the presence of both elemental and organomercury species. The presence of organomercury species in the liquid was unexpected.

Controls were put in place to protect the workers from the elemental mercury vapors and a program was developed to better understand the organomercury species. At the time, there was no routine method available to detect organomercury vapors. An outside laboratory, with extensive experience in measuring low levels of organomercury in vapors and liquids, was contracted to assist with developing a sampling plan to measure concentrations of organomercury in the 3H Evaporator service building.

The intent of this report is to document the systematic review of mercury chemistry that assisted in resolving and identifying mercury issues associated with the High Level

Waste system. The report will be revised as new information is obtained. This report also partially fulfils requests made by the Closure Business Unit.[1]

RESULTS AND DISCUSSION

Once the mercury concentrations in the overheads liquids were confirmed by the Effluent Treatment Facility (ETF) and the Savannah River Technology Center, the focus shifted to understanding the reasons for elevated mercury concentrations in the overhead tank's liquid and the service building's vapor space. SRTC began to explore four avenues to resolve the mercury issues. These are listed below:

- Review of Plant data for insight into mercury behavior
- Examine known information on the caustic behavior of mercury
- Review evaporator design (not discussed in this report)
- Analyze plant samples for mercury speciation

Review of Plant Data

The SRS High Level Waste evaporator systems include the evaporator along with the feed and drop tanks. The 3H Evaporator differs from the 2H and 2F Evaporators in several design features as shown in Table 1. First, the 3H Evaporator is larger with an operating volume of ~10,000 gallons versus 1750 gallons for the 2F and 2H Evaporators.[2] Secondly, the system temperatures (feed tank, pot and drop tank) are 25 °C to 35 °C hotter in the 3H Evaporator compared to the other two evaporators.

Table 1. SRS High Level Waste Evaporator Information

	2F	2H	3H
Feed Tank	26F	43H	32H
Drop Tank	46F	38H	30H*
Operating Volume (gal)	1850	1850	9760
Operating Temperature	135 °C	135 °C	160 °C
Feed Tank Temperature	30 °C	30 °C	60 °C
Drop Tank Temperature	45 °C	45 °C	80 °C

*Currently, Tank 37H is the drop tank.

As previously mentioned, mercuric species are known to be reduced to elemental mercury during the evaporation of High Level Waste supernate and is subsequently volatized into the overheads collection system. Figure 2 shows the effect of temperature on the vapor pressure of elemental mercury.[3] As observed, the vapor pressure increases by approximately one order of magnitude if the evaporator temperature is raised from 100 °C to 160 °C. The increased vapor pressure should manifest as an increase in the amount of liquid, elemental mercury collected in the overheads system for a given feed mercury concentration.

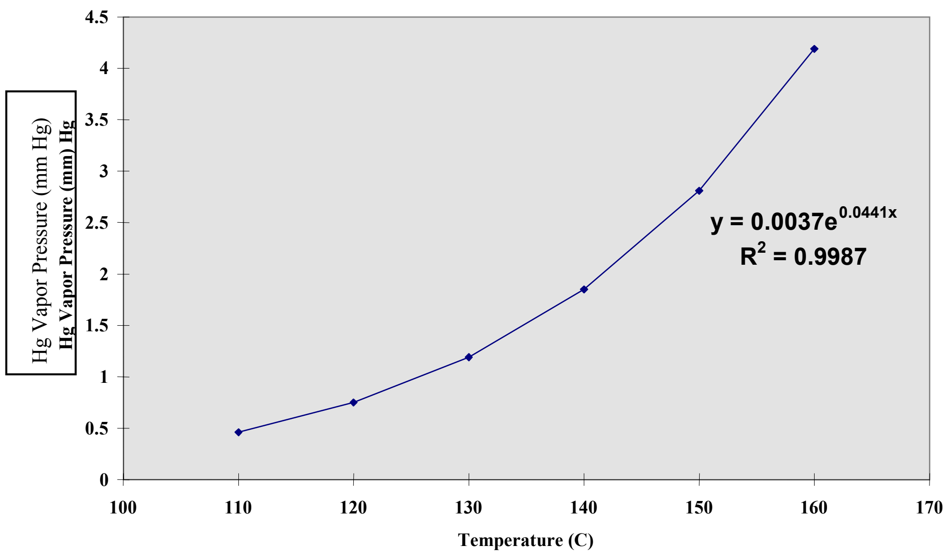

Figure 2. Mercury Vapor Pressure as a Function of Temperature

Table 2 contains a listing of the relevant plant operational data for the 3H Evaporator from August 2001 until the end of January 2002. The operational data includes the volume of condensate water generated for the dated 24-hr period, the amount of metallic mercury drained from the mercury collection tank, the evaporator pot temperatures and the Vent line temperature. JMP® software[4] was used to examine the amount of mercury produced (i.e., drained from the collection tank) against each of the other operational parameters. In particular, Figure 3 shows the plot of the evaporator pot temperature and the volume of mercury recovered from the overhead's system. The JMP® model did not show a correlation between the amount of mercury recovered versus the pot temperature. The model has a correlation coefficient (R^2) of 0.04 even though the thermodynamics of metallic mercury should drive mercury into the overheads system. The effect of increased pot and system temperature does support higher mercury levels in the 3H overhead system. However, the amount produced cannot be solely attributed to the pot temperature.

Table 2. Historical Plant Data on 3H Operation

Date	Condensate Volume (1000 gal)	Hg (mL)	Pot Temp (Deg C)	Vent Temp (Deg C)		Date	Condensate Volume (1000 gal)	Hg (mL)	Pot Temp (Deg C)	Vent Temp (Deg C)
		160	135	35		11/29/01	28	500	161	52
8/5/01	15	175	136	38		11/30/01	24	450	151	47
8/6/01	17	175	137	39		12/1/01	25	150	151	43
8/7/07	16	250	137	40		12/2/01	26	250	152	49
8/8/01	19	260	142	40		12/3/01	27	225	153	41
8/9/01	16	360	141	40		12/4/01	23	225	152	42
8/11/01	.	440	137	44		12/7/01	16	150	134	29
8/12/01	19	190	138	45		12/8/01	21	75	145	39
8/13/01	21	400	137	30		12/10/01	28	325	150	40
9/3/01	9	160	139	35		12/11/01	23	225	150	41
9/4/01	18	150	140	35		12/12/01	25	275	149	42
9/5/01	18	300	141	39		12/13/01	26	225	148	44
9/6/01	18	280	143	42		12/14/01	23	300	148	44
9/8/01	21	270	139	42		12/15/01	25	200	149	40
9/9/01	23	350	145	48		12/16/01	23	325	148	40
9/14/01	.	375	146	46		12/17/01	27	325	148	44
9/18/01	22	375	144	47		12/18/01	22	300	148	39
9/19/01	22	450	140	48		12/19/01	26	300	147	39
9/20/01	25	400	144	47		12/20/01	25	300	149	39
9/21/01	25	475	148	49		12/21/01	25	275	151	40
9/27/01	29	350	142	42		12/22/01	23	325	151	38
9/30/01	25	350	146	50		12/23/01	25	300	151	41
10/1/01	28	330	151	48		12/24/01	21	550	152	37
10/9/01	28	600	137	41		12/25/01	26	550	149	36
10/27/01	10	300	152	37		1/3/02	14	125	138	17
10/28/01	26	375	150	38		1/4/02	21	275	155	33
10/29/01	26	325	152	39		1/5/02	23	540	149	34
11/5/01	16	275	153	38		1/6/02	23	550	155	44
11/6/01	25	375	148	30		1/7/02	25	575	152	34
11/7/01	16	150	145	40		1/8/02	21	600	150	39
11/16/01	21	150	154	45		1/9/02	23	300	154	41
11/23/01	22	300	154	46		1/11/02	16	175	155	39
11/24/01	23	225	147	46		1/24/02	15	225	151	37
11/26/01	21	520	149	45		1/25/02	23	75	152	34
11/28/01	28	425	155	49		1/26/02	21	225	152	34

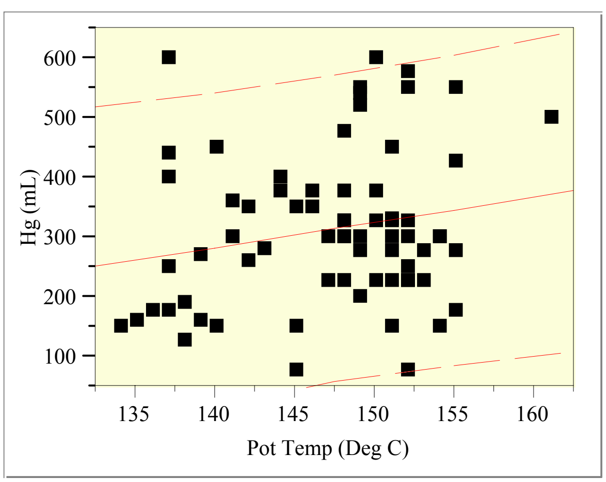

Figure 3. Plot of Operational Data for 3H Evaporator

The elevated mercury levels, associated with the 3H Evaporator compared to the 2H Evaporator, were originally thought to be related to the amount of High Level Waste sludge contained in the 3H system. Remembering that mercury partitions between the liquid supernatant phase and the insoluble sludge phase, a review of the Site's Waste Characterization Database (WG08) was performed. Figure 4 contains a representation of the 2H and 3H Evaporator systems. The sludge level in the 2H system is at a height of 58"; whereas, the sludge height is 32" in the 3H Evaporator feed tank. However, the mercury content of the sludges is quite different. The Waste Characterization Database indicates that the 2H sludge contains ~ 1700 kg of mercury in the form of mercuric oxide, HgO. The 3H sludge has a much higher mercury content and is estimated at 12,800 kg of HgO. Although this disparity in mercury content exists, solubility, reduction potential, and evaporator temperature drive the impact to mercury volatility. Therefore, the much larger mercury inventory in the 3H Evaporator system has little effect.

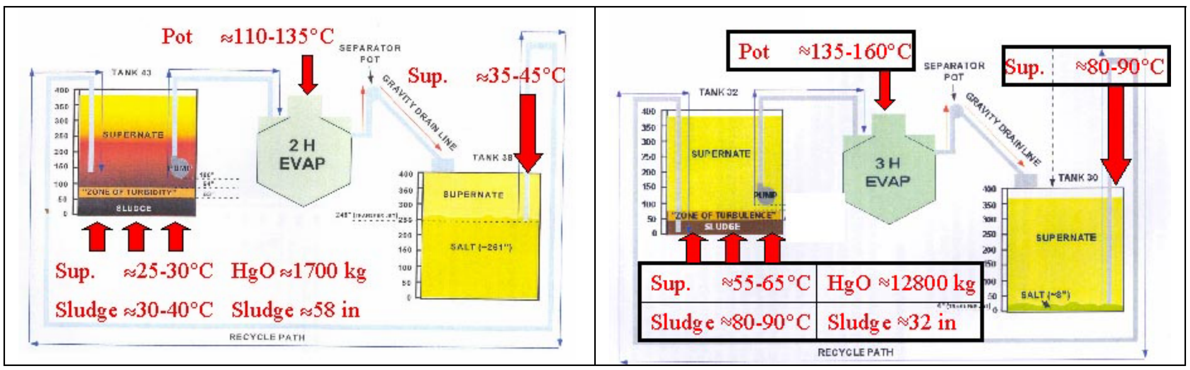

Figure 4. Comparison of 2H and 3H Evaporators

Review of Published Literature on Mercury Chemistry

The chemical understanding of the behavior of mercury species under the high pH conditions of the HLW tanks has been studied. However, several questions persist in light of elevated mercury levels in the 3H Evaporator system. The questions include:

- What is the solubility of mercuric ion as a function of temperature under high pH conditions?
- Is elemental mercury the only inorganic form of mercury that is volatized during HLW evaporation?

Three oxidation states of mercury can exist in solution concomitantly: the metal (Hg^0), mercurous ion (Hg^+ or Hg_2^{2+}) or the mercuric ion (Hg^{2+}). As early as 1920, Fuseya[5] studied the solubility of mercuric oxide in sodium hydroxide solutions for work related to HgO electrodes. Fuseya studied the Hg solubility in caustic solutions to 2 M NaOH and found mercury concentrations of 30.9 mM HgO or 6.2 g/L. However, the study lacked a filtration step to remove colloidal mercury species prior to acidification for analysis. Bibler[6] reviewed the solubility of selected metals (Cd, Pb, Mn, and Hg) for ground water application at the Savannah River Site. Figure 5 shows the distribution of hydrolysis products as a function of pH. The mercury species at pH 14 is governed by the 1,2 (x,y) species for the general formula of $Hg_x(OH)_y^{(2x-y)+}$, or $Hg(OH)_2$. The plot indicates a mercury solubility of 2.4 x 10^{-4} M or 50.4 mg/L at pH 14.

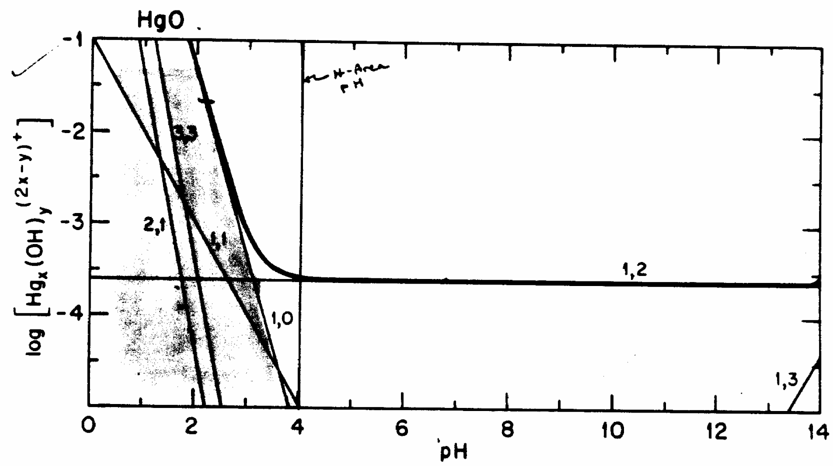

Figure 5. Distribution of Hydrolysis Products for Solutions Saturated with Hg $(OH)_2$

Zhou and Chen[7] studied the effect of temperature on the solubility of mercury in solution of potassium hydroxide in the range of 1 to 7 M KOH and 25 to 55 °C. Figure 6 shows a plot of this data taken from their report. A maximum in the mercury concentration is observed at each temperature in the KOH concentration range of 1.5 – 2 M. The ordinate in the plot has units of mole/L multiplied by 10^4; therefore, a value of 4 equates to a mercury concentration of ~80 mg/L. Temperature does appear to have a large effect on the solubility of mercuric ion. In KOH, the mercuric ion solubility would be 62 mg/L at 25 °C at 4 M hydroxide and 160 mg/L at 55 °C. This equates to a 2.6 fold increase in mercury concentration. If this data holds for sodium hydroxide solutions, the implication is that the mercury solubility in the 3H Evaporator Feed Tank (Tank 32H) would be higher in comparison to the 2H system.

In order to understand the solubility of mercury in sodium hydroxide-based systems, a commercially available software OLI chemical speciation model (OLI Software Systems, 1996) was used. The OLI software has a thermodynamic framework that predicts complex aqueous-based chemistry in equilibrium with optional vapor, nonaqueous liquid, and solid phases. The aqueous model is predictive over the general range of 0 to 300 °C, 0 to 1500 bar and 0 to 30 (molal) ionic strength. The OLI databank is extensive,

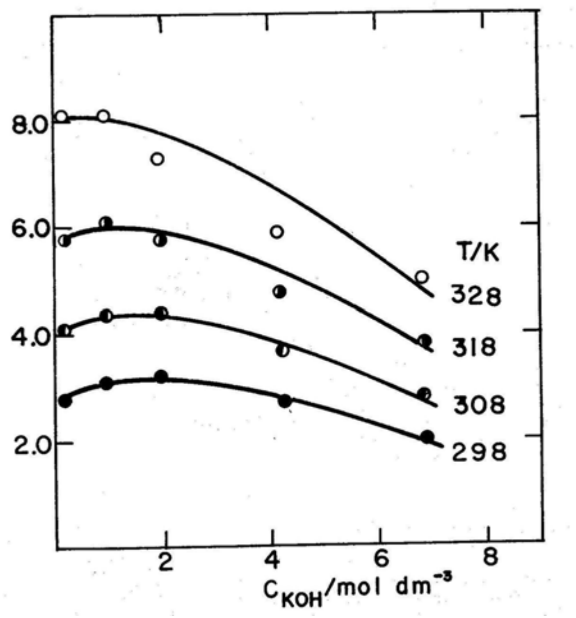

Figure 6. Mercury Concentration versus KOH Concentration

Ordinate has units of mole/L * 10^4

containing physical constants for over 3000 inorganic and organic species. The predictive framework is based on:

- the Revised Helgeson Equation of State for predicting the standard state thermodynamic properties of all species, including organics, in water;
- the Bromley-Zemaitis framework for the prediction of excess thermodynamic properties;
- the Pitzer and Setschenow formulation for the prediction of the excess thermodynamic properties calculation of molecular species in water; and
- the Enhanced SRK Equation of State for the prediction of vapor and nonaqueous, liquid-phase thermodynamic properties.

Figure 7 contains the output of the OLI modeling for mercury solubility in sodium and potassium hydroxide. The OLI database does not include nor completely agree with the work of Zhou and Chen and is a non-referenced private communication. However, the magnitude (10^{-4} M) of the mercury solubility is the same. There is a general increase in mercuric ion concentration with both increased hydroxide concentration and increased temperature.

In summary, the mercury solubility under highly alkaline conditions is fairly well known. The effect of temperature on the mercury solubility is classical, i.e.; increased temperature results in increased solubility. The higher temperature of the 3H Evaporator system should result in higher mercuric ion concentrations in the feed tank and enhance the potential for volatility when processed through the evaporator.

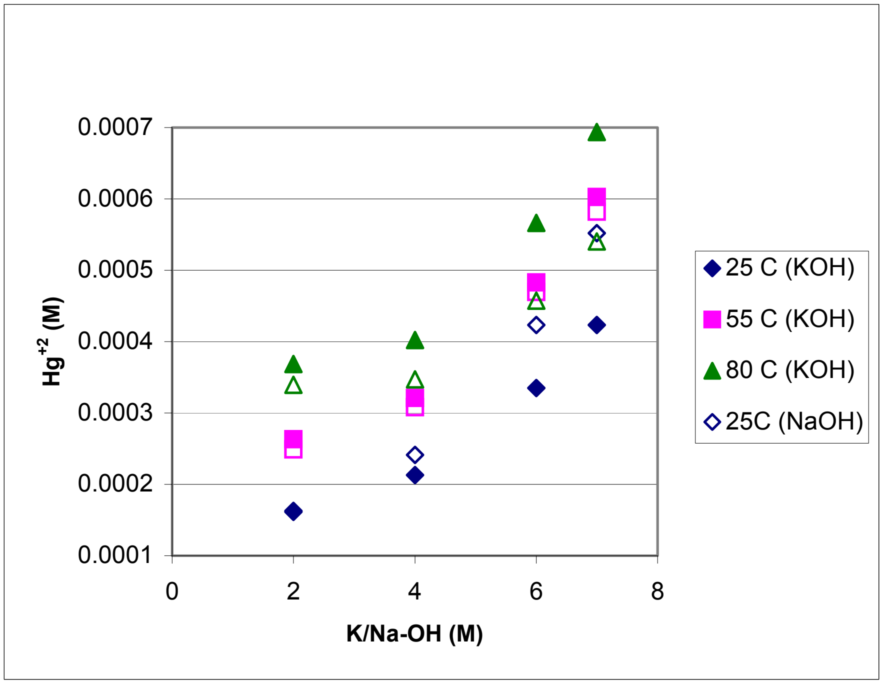

Figure 7. OLI Predicted Solubility as a Function of Caustic Concentration and Temperature

The second question regarding mercury chemistry is whether elemental mercury is the only inorganic species that volatilizes during the evaporation of HLW supernate. As previously mentioned, the chemistry of mercury is complicated by the co-existence of three oxidation states and the interrelation of these oxidation states via the disproportionation reaction shown below:

$$Hg_2^{2+} \leftrightarrow Hg^o + Hg^{2+}$$

Bibler[8] has studied the formation of elemental mercury from evaporation of aqueous systems in support of the Effluent Treatment Facility. The tests examined reducing agents for the ETF process and the effects of mercury transport to condensate water. Table 3 contains a scanned copy of a table from the referenced report. For comparison purposes, a blank containing 1 mg of mercuric (Hg^{2+}) ion was boiled and the volume reduced by a factor of 10 with very little mercury observed in the condensate phase (3.15E-3 mg). Conversely, with added reducing agent like bisulfite or stannous ion, a large fraction of the mercury was detected in the condensate.

Table 3. Reducing Agent Effect on Mercury Volatility

M. A. EBRA - 9 - DPST-86-333
March 13,1986

TABLE 1

Hg VOLATILITY

FEED SOLUTION # [a]	MERCURY IN CONCENTRATE[b]	MERCURY IN DISTILLATE[c]
1. Blank, 1 mg Hg^{2+}	.941 mg	3.15E-3 mg
2. Blank, $KMnO_4$, 1mg Hg^{2+}	.980 mg	1.98E-3 mg
3. Blank, Hg metal	1.0E-2 mg	3.87E-3 mg
4. dil $NaHSO_3$, 1 mg Hg^{2+}	.047 mg	5.70E-2 mg
5. dil $NaHSO_3$, 1 mg Hg^{2+}, 0.15M $NaNO_3$	.050 mg	3,90E-2 mg
6. dil $NaHSO_3$, 1 mg Hg^{2+}, glass wool	.039 mg	2.52E-2 mg
7. dil $NaHSO_3$, 2 mg Hg^{2+}	.066 mg	9.90E-3 mg
8. xs $NaHSO_3$, 1 mg Hg^{2+}	none detected	8.55E-2 mg
9. xs $NaHSO_3$, 2 mg Hg^{2+}	.310 mg	3.33E-2 mg
10. xs $NaHSO_3$, 2 mg Hg^{2+}, $NaNO_3$	.960 mg	2.12E-2 mg
11. dil NH_4OH, 1 mg Hg^{2+}	.756 mg	7.83E-3 mg
12. con NH_4OH, 1 mg Hg^{2+}	.916 mg	1.21E-2 mg
13. $SnCl_2$, 1 mg Hg^{2+}	none detected	1.67E-2 mg
14. $SnCl_2$, 1 mg Hg^{2+}, glass wool	none detected	1.58E-2 mg

a. See Appendix 1 for complete solution compositions

b. In a total volume of 10 mL; concentrations are an average for 3 or more runs

c. In a total volume of 90 mL; concentrations are an average for 3 or more runs

Although these tests supported ETF operation, their applicability to evaporator operation still holds. The chemical species tested do not have application to the evaporator. However, the evaporator systems do include other reducing agents in bountiful concentration like nitrite. The electrochemical potential for the mercury reduction by bisulfite and nitrite are shown below:

$$H_2SO_3 + H_2O + Hg^{2+} \text{<-->} Hg + SO_4^{2-} + 4H^+ \qquad \Delta eV=1.3$$

$$NO_2^- + 2OH^- + Hg^{2+} \text{<-->} NO_3^- + H_20 + Hg \qquad \Delta eV=1.68$$

The thermodynamic entropy or Gibb's Free Energy can be calculated from the formula

$\Delta G = -ZF\,\Delta eV$, where F=96,484 C/mole and 1eV=23.08 Cal/mol. This gives rise to favorable chemical reactions with free energies of –125 and –162 kJ/mol for bisulfite and nitrite, respectively.

The OLI-Environmental Simulation Program (ESP) was used to simulate evaporation for steady state conditions. Figure 8 shows the results of this thermodynamic modeling. As observed, the mole fraction of elemental mercury found in the overhead condensate increases with increasing evaporator pot temperature (i.e., boiling point of solution). Essentially all of the mercury partitions to the overheads above 175 °C. The higher temperatures of the 3H Evaporator leads to a higher fraction of the mercury in the HLW supernate being found in the overhead mercury collection tank.

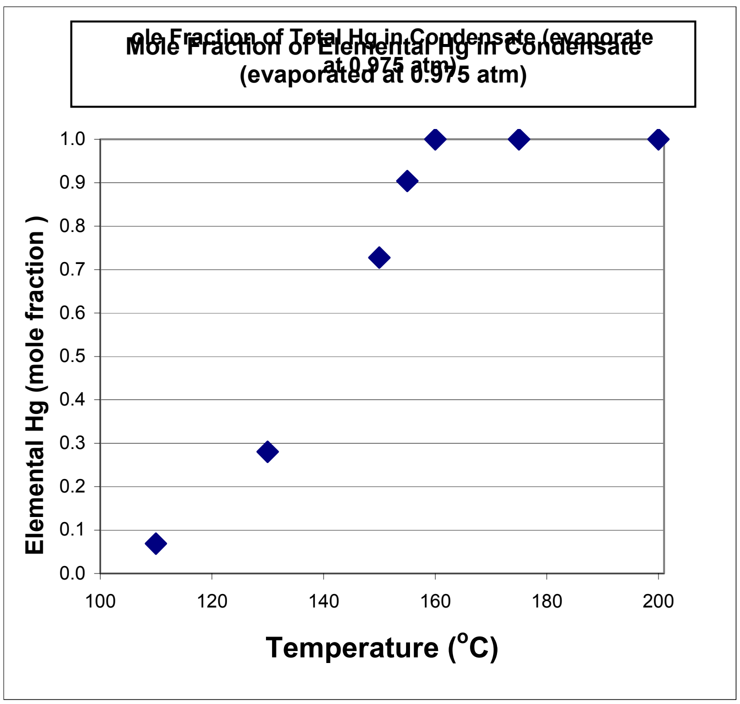

Figure 8. Mole Fraction of Elemental Hg in Condensate

Analysis of Plant Samples for Mercury Speciation

As part of the process to examine potential sources for the elevated mercury concentrations at the 3H Evaporator, one avenue that was explored was mercury speciation. Organomercury compounds traditionally have high vapor pressures. For example, dimethylmercury has a vapor pressure of 50 mm of Hg compared to 15 mm Hg for water at 25 °C. Therefore, contact was made with personnel at Frontier Geosciences, Inc. in Seattle Washington. Frontier Geosciences is a recognized world leader in developing specific methods for analyzing trace inorganic metal ions and their speciation in complex chemical systems. They are considered an expert in the chemistry of organomercury species.

The first liquid samples pulled were from the 3H overhead condensate tank on April 29, 2002. The results[9] indicated that a dimethylmercury concentration of 0.479 mg/L; well above the detection limit for Frontier's laboratory. Subsequent to that analysis a set of samples taken from the 3H, 2H and 2F overhead tanks was analyzed by the Analytical Development Section in SRTC and showed values of 0.13, 0.026, and < 0.002 mg/L, respectively. This dual laboratory confirmation clearly indicated that dimethylmercury was present and at levels that could potentially require Industrial Hygiene review for exposure control. Rosencrance and Wilmarth,[10] also, attempted to provide approaches for calculating the airborne concentrations of dimethylmercury.

A SRS path forward was developed to examine each of the evaporator liquid condensate systems along with the Effluent Treatment Plant.[11] This pathforward described the sample strategy to effectively utilize the existing resources at SRS and at Frontier Geosciences. Samples, both liquid and vapor, were collected and analyzed for monomethylmercury, dimethylmercury and total mercury from numerous locations at the 2F, 2H and 3H Evaporators along with the transfer line to the Effluent Treatment Facility and internal to the facility. Figure 9 shows a summary of the samples from each facility for samples through March of 2003. Detailed sample information is included in Appendix 1.

The 3H Evaporator has received the most sampling for dimethylmercury. There have been 16 liquid samples and 30 vapor samples. Of the liquid samples, all have tested positive for the presence of dimethylmercury. The dimethylmercury concentrations have ranged from 94 to 14,000 μg/L. For comparison purposes, selected information on dimethylmercury is shown in Table 4. Of the 30 vapor samples, 25 samples have shown dimethylmercury as being present. Five of these measurements were above the Threshold Limit Value (TLV) and three were above the Ceiling value. The concentrations have ranged from < 0.02 to > 175 $\mu g/m^3$.

As of early March 2003, 10 liquid and 10 vapor samples from the 2H Evaporator were taken and analyzed. All of the liquid samples have been positive for dimethylmercury but the maximum concentration (2200 μg/L) is not that much below the 3H system. All of the vapor samples have shown the presence of dimethylmercury but the maximum concentration measured at > 89 $\mu g/m^3$.

Figure 9. Summary of DMHg in Vapor and Liquid Samples

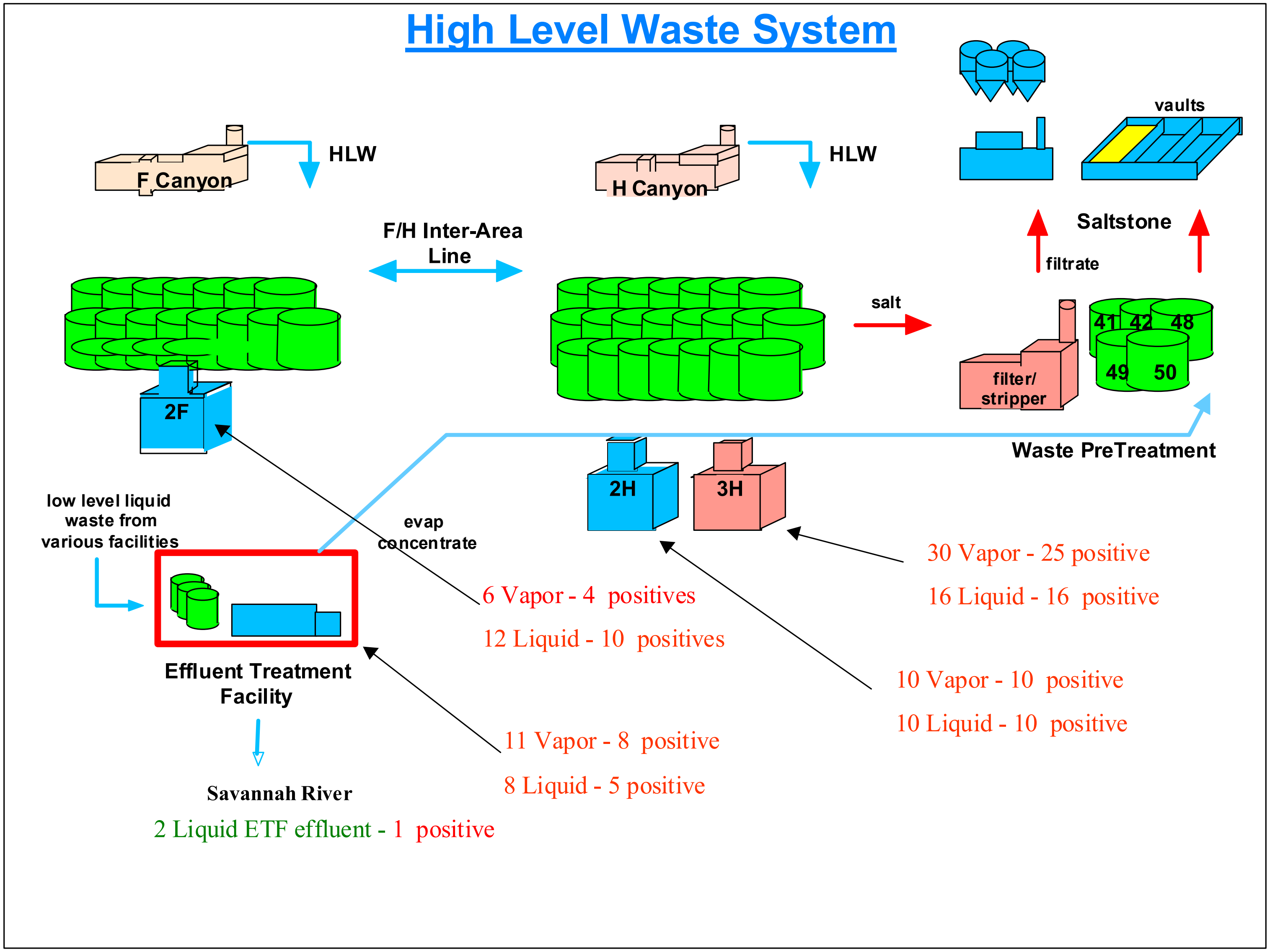

Table 4. Dimethylmercury Information

Formula: $(CH_3)_2Hg$ (molecular weight: 230.7 g/mole)
Appearance and odor: Colorless liquid with a weak, sweetish odor.
Boiling point: 95 °C Vapor density: 7.9 (air = 1)
Vapor Pressure @ 20 °C = 50 mm Hg (water = 17.3 mm Hg)
Distribution coefficient ([air]/[liquid]) = 0.31 at 25 °C
Toxicology: Causes dysfunction of central nervous system and irritates membranes and skin
Site and Regulatory Limits:
Air: OSHA TLV (8 h) = 10 μg/m^3, ACGIH STEL = 30 μg/m^3, OSHA PEL-Ceiling = 40 μg/m^3
Liquid: Site IH Guide = 100 μg/L, Fed Drinking Water Std = 2 μg/L
Discharge to Waters of State: No DMHg specific limit, total Hg limit = 2.3 μg/L

The 2F Evaporator system processes less mercury compared to the H-area systems as previously described in the Introduction to this report. Therefore, the measurements taken from the 2F system show much lower concentrations of dimethylmercury. Ten out of 12 liquid samples have tested positive with a maximum concentration of 2.6 μg/L or approximately 5 times lower than the lowest H-area liquid samples (14.1 μg/L). Four of six vapor samples have indicated the presence of dimethylmercury with a concentration that ranged from 0.012 to 0.734 μg/m3.

Because of the concentrations found in the evaporator condensates, samples were taken at the midpoints of the piping leading from the evaporators to the Effluent Treatment Facility (ETF). The ETF processes the condensate along with other wastes through evaporation, filtration, ion exchange and reverse osmosis. The samples (both liquid and vapor) were taken from the F- and H-Lift Stations along with the waste collection tank and the waste concentrate tank. Five of the 8 liquid samples were positive for the presence of dimethylmercury with a maximum concentration of 96.7 μg/L at the H-Lift Station. Vapor measurements at the H-Lift Station ventilation exhaust and the carbon column sumps showed very high dimethylmercury levels estimated at 180 μg/m^3.

A second sampling was associated with a caustic wash of an ion exchange column and subsequent discharge to a sump located at ETF. The ion exchange column is loaded with Duolite GT-73 cation exchange resin that has a high affinity for removing mercury from water in the pH range of 3 to 13. The caustic wash eliminates a bio-fouling that increases the pressure drop across the column. Samples from the vapor space in the sump at deck level were very high > 89 µg/L. The cause of this dimethylmercury detection is still under investigation.

Vapor samples were taken for six waste tanks during May, 2003. Preliminary results from this sampling evolution[12] show high levels of total mercury for all of the tanks and high levels of dimethylmercury for Tanks 38, 41, and 43. Additional samples and evaluations are planned to confirm and better understand the preliminary results.

Dimethylmercury Formation Tests

Frontier Geosciences[13] was contracted to perform initial testing into the possible formation of dimethylmercury. A simulated salt solution composition was provided to Frontier. Four organic components were chosen[14] as candidate methylating agents. The four organic compounds were digested ion exchange resin, Dow Corning H-10 antifoam, trimethylsilanol and sodium acetate. Reactions were carried out at the solution boiling point and at 50 °C in the reaction vessel shown in Figure 10.

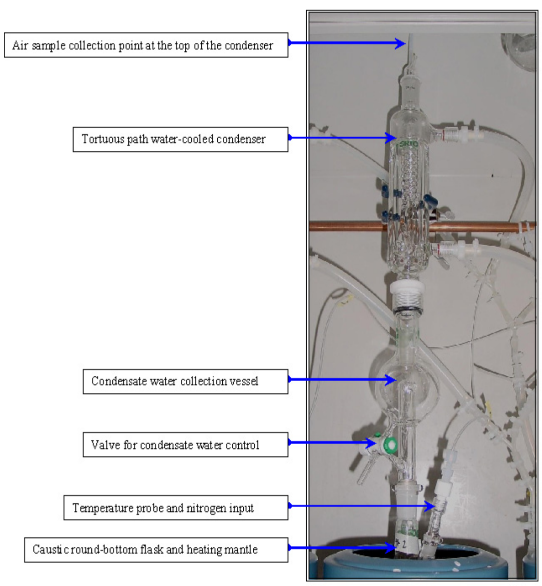

Figure 10. Dimethylmercury Reaction Vessel

Table 5 shows the results of the Frontier testing. Dimethylmercury (DMHg) was formed in tests with each of the organic species. A total of 43 tests were performed. The key findings from this testing are shown below:

- Mercury readily converted to elemental form in boiling solution
- DMHg was formed with each of the organic species tested under boiling conditions
- Highest yield of dimethylmercury formation was 0.38 % with high Hg and antifoam

- Blanks showed no DMHg formation
- DMHg was not formed under lower temperature (~50 °C) within 4 hrs
- Kinetic testing indicates higher yields near experiment end
- Formation of DMHg strongly depended on starting Hg concentration
- 4x increase in starting Hg concentration led to 620-fold increase in DMHg formation
- 10x increase in organic concentration led to 68-fold increase in DMHg formation

This dimethylmercury formation information and detection of dimethylmercury in both the liquid and vapor phases assist in the understanding of mercury release from the evaporator systems. Mercury vapor is exiting the evaporator system as elemental mercury vapor and organic mercury vapor. Reaction with organic components leads to dimethylmercury and associated volatilization.

Table 5. Summary of Simulation Test Run Results for Dimethylmercury (DMHg) Formation. This table includes the mass balance, quality assurance values, and fraction of Hg observed in the gaseous form and percentage of DMHg generated as a function of total Hg.

Test Date	Test #	Temp Degree C	Solution Base#	Heat Time (hrs.min)	Hg(II) Added (ng)	Organics Added^ Anti-Foam (ul)	Resin (ul)	TMS (ul)	Acetate (ul)	Sum Hg (ng)	Fraction Hg in Air	Mass Balance Recovery	Total DMHg (ng)	Percent DMHg Generated
12/2/2002	1	boiling	1	4		Blank Run - no organics added				61	na	na	*0.005*	*carryover*
12/2/2002	2	boiling	2	4		Blank Run - no organics added				52	na	na	*0.010*	*carryover*
12/2/2002	3	boiling	1	4	4600	Blank Run - no organics added				823	na	0.18	0.000	
12/2/2002	4	boiling	2	4	4600	Blank Run - no organics added				547	na	0.12	0.000	
12/4/2002	5	110	1	4	*4600	100	300	100	100	2466	na	0.54	**0.561**	0.0339%
12/4/2002	6	114	2	4	*4600	100	300	100	100	4034	na	0.88	0.404	0.0088%
12/4/2002	7	110	1	4	*4600	100	300	100	-	3018	na	0.66	**0.220**	0.0048%
12/4/2002	8	114	2	4	*4600	100	300	100	-	3403	na	0.74	0.000	0.0000%
12/5/2002	9	110	1	4	4600	100	300	100	100	3143	na	0.68	**0.259**	0.0056%
12/5/2002	10	114	2	4	4600	100	300	100	100	3252	na	0.71	0.037	0.0008%
12/9/2002	11	boiling	1	1.4	*4600	100	300	100	100	1857	na	0.46	0.000	0.0000%
12/10/2002	12	21	DDW	N/A	DMHg added =61.3 ng	-	-	-	-	43	na	0.68	see text	na
12/10/2002	13	boiling	1	2	DMHg added=61.3 ng	-	-	-	-	25	na	0.39	see text	na
12/10/2002	14	110	1	4.25	*4600	100	300	100	100	73	na	0.02	**0.219**	0.0048%
12/10/2002	15	110	1	4.25	*4600	100	300	100	-	210	na	0.05	**0.267**	0.0058%
12/11/2002	16	114	2	4.3	*4600	100	-	-	-	4551	1.00	0.99	**0.113**	0.0025%
12/11/2002	17	114	2	4.3	*4600	-	300	-	-	5035	1.00	1.09	0.005	0.0001%
12/11/2002	18	114	2	4.3	*4600	-	-	100	-	4663	1.00	1.01	0.005	0.0001%
12/11/2002	19	114	2	4.3	*4600	-	-	-	100	4992	1.00	1.09	0.005	0.0001%
12/12/2002	20	50	2	5.2	*4600	Blank Run - no organics added				3764	0.15	0.82	0.000	0.0000%
12/12/2002	21	53	2	5.2	*4600	100	300	100	100	3952	0.30	0.86	0.000	0.0000%
12/12/2002	22	46	2	5.2	*4600	100	300	100	-	3691	0.51	0.80	0.000	0.0000%
12/12/2002	23	47	2	5.2	*4600	100	-	-	-	4124	0.32	0.90	0.000	0.0000%
12/13/2002	24	52	2	5	*4600	-	300	-	-	4136	0.24	0.90	0.000	0.0000%
12/13/2002	25	54	2	5	*4600	-	-	100	-	3983	0.47	0.87	0.002	0.0001%
12/13/2002	26	44	2	5	*4600	-	-	-	100	3923	0.11	0.85	0.000	0.0000%
12/13/2002	27	44	1	5	*4600	Blank Run - no organics added				4236	0.09	0.92	0.000	0.0000%
12/16/2002	28	110	1	5.36	*4600	100	-	-	-	4339	1.00	0.94	**0.082**	0.0019%
12/16/2002	29	110	1	5.36	*4600	-	300	-	-	4600	1.00	1.00	0.016	0.0003%
12/16/2002	30	110	1	5.36	*4600	-	-	100	-	4546	1.00	0.99	0.002	0.0000%
12/16/2002	31	110	1	5.36	*4600	-	-	-	100	3903	1.00	0.85	0.003	0.0001%
12/17/2002	32	53	1	5	*4600	100	-	-	-	4475	0.76	0.97	0.000	0.0000%
12/17/2002	33	58	1	5	*4600	-	300	-	-	4276	0.38	0.93	0.000	0.0000%
12/17/2002	34	46	1	5	*4600	-	-	100	-	3230	0.10	0.70	0.000	0.0000%
12/17/2002	35	45	1	5	*4600	-	-	-	100	4852	0.10	1.05	0.000	0.0000%
12/19/2002	36	114	2	4.45	*18400	100	-	-	-	17354	0.97	0.94	**70.1**	**0.404%**
12/19/2002	37	114	2	4.45	*18400	1000	-	-	-	17117	0.99	0.93	**7.68**	**0.045%**
12/19/2002	38	114	2	4.45	4600	[1] 100	-	-	-	4539	0.83	0.99	**0.084**	0.0018%
12/19/2002	39	114	2	4.45	**18400	[1] 100	-	-	-	19697	0.99	1.07	**0.232**	0.0012%
12/20/2002	40	110	1	4.45	-	Blank Run - no organics added				112	0.85	na	0.008	see text
12/20/2002	41	114	2	4.45	-	Blank Run - no organics added				97	0.85	na	0.000	0.0000%
12/20/2002	42	110	1	4.45	*4600	Blank Run - no organics added				4410	0.99	0.96	0.000	0.0000%
12/20/2002	43	114	2	4.45	*4600	Blank Run - no organics added				5198	1.00	1.13	0.000	0.0000%

#Solution 1: 7 M NaOH #Solution 2: 7 M NaOH, 1 M NaNO2, 1 M NaNO3 ^See Table 3 for solution concentrations

* Hg when solution was brought to desired temperature.

** Hg added after solution was brought to temp and stable for one hour.

[1] 1 mL of antifoam was diluted in 4 mL of MQ and refluxed for 1-2 hours.

CURRENT PATH FORWARD

The investigation into mercury related issues involving High Level Waste operations has shown the thermodynamic behavior of mercury in the elemental state and as mercuric ion in solution. Additionally, the investigation has revealed that chemical reactions between mercury and organic constituents produce alkyl mercury species. The report is an attempt to centralize information and provide a reference to field measurements. Concomitant with the publication of this report are a series of additional activities. To provide an appreciation of the breadth of these activities, a subset is listed below:

- Additional liquid and vapor sampling from the three evaporator systems and ETF
- Validation sampling to ensure ventilation changes in the 3H system are effective
- Design, construction and installation of ventilation changes to the 2H Evaporator system, F and H Area Lift Stations, and possibly the 2F Evaporator system
- Additional vapor sampling of waste tank head spaces (including waste tanks independent of evaporator systems) to examine the potential for other release pathways
- Additional formation testing to examine effects of temperature, solution composition, the presence of sludge, and longer reaction times
- Degradation testing to determine dimethylmercury lifetimes under various process conditions.

SUMMARY

The chemistry and thermodynamics of mercury across the evaporation process for High Level Waste has been examined. Soluble mercuric and mercurous ions are readily reduced under the highly alkaline conditions of the waste to form elemental mercury. The mercury metal is volatilized during evaporation and condenses in the overheads system. The higher temperatures of the larger 3H Evaporator understandably results in higher mercury volumes collected. Additionally, the current 3H Evaporator feed tank contains a sludge that is very high in mercury content. The frequent recycles from the evaporator drop tank (due to limited supernate volume) cause the feed tank to be at an elevated temperature. This increases the mercury solubility and likely leads to increased leaching of mercury from the sludge.

Investigations into other aspects of mercury interactions with waste components have indicated the mercury reacts under elevated temperatures with a number of organic species to form dimethylmercury. This volatile species partitions to the overheads condensate. Liquid and vapor measurements of the overhead cell areas showed the presence of dimethylmercury. Subsequent laboratory tests also showed formation of dimethylmercury when waste simulant is spiked with mercury and organic components. Initial testing did not show formation of dimethylmercury over four hour time periods at lower temperatures (50 °C) . The sampling and detection aspects of this program are continuing. Additional formation and degradation tests are currently in the planning stage.

Initial waste tank vapor sampling has shown that dimethylmercury is present in the vapor space of several waste tanks. This sampling has also indicated that the presence of dimethylmercury is not limited to the evaporator systems since Tank 41 vapor samples were positive for dimethylmercury (Tank 41 is a salt tank that is not currently associated with the operation of any evaporator).

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- Rob Swingle for description of original mercury discussion

Appendix 1. Detailed Sample Information

DMHg = dimethylmercury, MMHg = monomethylmercury, TMHG = total methylmercury, EDMHg = estimated dimethylmercury, and THg = total mercury, Fac. = facility and Pres. = preservative

3H Evaporator Liquid Results

Sample Number	Location	Date	Fac.	Pres.	DMHg µg/L	MMHG µg/L	TMHG µg/L	THg µg/L
WSRC rep 1		4/29/02	3H	HCL		1118		1831
WSRC rep 2		4/29/02	3H	HCL		1186		1693
WSRC rep 3		4/29/02	3H	HCL		1137		1472
WSRC rep 4		4/29/02	3H	NP	405			
WSRC rep 5		4/29/02	3H	NP	503			
WSRC rep 6		4/29/02	3H	NP	530			
300179673		5/2/02	3H	NP	130			
Primary OH	Primary Overheads Sample Station	11/6/02	3H	HCL		2001.3	4896.1	7156.3
Alternate OH #1	Alternate Overheads Sample Point #1	11/6/02	3H	HCL		6427.6	10543.3	9116.3
Alternate OH #2	Alternate Overheads Sample Point #2	11/6/02	3H	HCL		7284.9	10247.8	7103.9
Primary OH	Primary Overheads Sample Station	11/6/02	3H	NP	2894.8			
Alternate OH #1	Alternate Overheads Sample Point #1	11/6/02	3H	NP	4115.7			
Alternate OH #2	Alternate Overheads Sample Point #2	11/6/02	3H	NP	2962.9			
MeOH	Alternate Overheads Sample Point #1	11/6/02	3H	MeOH	3326			
300188271	Primary Overheads Sample Station	11/6/02	3H	NP	3000			
300188272	Alternate Overheads Sample Point #1	11/6/02	3H	NP	3000			
300188273	Alternate Overheads Sample Point #2	11/6/02	3H	NP	2600			
300189349		12/3/02	3H	NP	14000			9390
300190443		1/15/03	3H	NP	1500			
WSRC-018	Primary Overheads Sample Station	2/20/03	3H	HCl			2880	3700
WSRC-017	Alternate Overheads Sample Point #1	2/20/03	3H	HCl			4360	4520
MeOH-95	Primary Overheads Sample Station	2/20/03	3H	MeOH	1960			
MeOH-94	Alternate Overheads Sample Point #1	2/20/03	3H	MeOH	93.6			
300192165		2/20/03	3H	NP	490			

3H Evaporator Vapor Results

Sample Number	Location	Date	Fac.	DMHg µg/m^3	EDMHg µg/m^3	THg µg/m^3
021106-E3H-OHSC-DMHg-WT-4	Primary Overheads Sample Station	11/6/02	3H	1.88	1.88	
021106-E3H-OHSC-STM-3	Primary Overheads Sample Station	11/6/02	3H			1.34
021106-E3H-OHRP1-DMHg-WT-3	Alternate Overheads Sample Point #1	11/6/02	3H	2.424	2.424	
021106-E3H-OHRP1-STM-2	Alternate Overheads Sample Point #1	11/6/02	3H			6.4
021106-E3H-OHRP2-DMHg-WT-2	Alternate Overheads Sample Point #2	11/6/02	3H	0.737	0.737	
021106-E3H-OHRP2-STM-1	Alternate Overheads Sample Point #2	11/6/02	3H			0.766
021106-E3H-MRB-DMHg-WT-5	Mercury Removal Station	11/6/02	3H	0.058	0.058	
021106-E3H-MRB-STM-4	Mercury Removal Station	11/6/02	3H			0.472
021106-E3H-COCRD-DMHg -WT-6	General Area/Dike	11/6/02	3H	0.168	0.168	
021106-E3H-COCRD-STM-5	General Area/Dike	11/6/02	3H			0.231
021106-E3H-OCS-DMHg-WT-7	Overheads Cell Sump/Overheads Receiver Tanks Overflow	11/6/02	3H	1.889	1.889	
021106-E3H-OCS-STM-6	Overheads Cell Sump/Overheads Receiver Tanks Overflow	11/6/02	3H			1.48
021106-E3H-ORT1-DMHg-WT-8	Overheads Receiver Tank #1 Vent	11/6/02	3H	12.065	12.065	
021106-E3H-ORT1-STM-7	Overheads Receiver Tank #1 Vent	11/6/02	3H			12.9
021106-E3H-ORT2-DMHg-WT-9	Overheads Receiver Tank #2 Vent	11/6/02	3H	13.492	13.492	
021106-E3H-ORT2-STM-8	Overheads Receiver Tank #2 Vent	11/6/02	3H			228
021203-ORT1-DMHG-1	Overheads Receiver Tank #2 Vent	12/3/02	3H	0.02	0.02	
021203-ORT2-DMHG-2	Overheads Receiver Tank #1 Vent	12/3/02	3H	<0.02	0.02	
021203-ORP1-DMHG-3	Temporary Modification/Secondary Ventilation Interface	12/3/02	3H	<0.02	0.02	
021203-ORP2-DMHG-4	Primary Overheads Sample Station	12/3/02	3H	0.03	0.03	
021203-DMHG-5	Alternate Overheads Sample Point #1	12/3/02	3H	138	138	
021203-OCD-DMHG-6	Alternate Overheads Sample Point #2	12/3/02	3H	4.15	4.15	
021203-OCS-DMHG-7	Overheads Cell Sump/Overheads Receiver Tanks Overflow	12/3/02	3H	<0.02	0.02	
021203-SVI-DMHG-8	General Area/Dike	12/3/02	3H	<0.02	0.02	
11503-ORT1-DMHg-1	Overheads Receiver Tank #1 Vent	1/15/03	3H	3.11	3.11	
11503-ORT2-DMHg-2	Overheads Receiver Tank #2 Vent	1/15/03	3H	2.37	2.37	
11503-SVI-DMHg-3	Temporary Modification/Secondary Ventilation Interface	1/15/03	3H	0.14	0.14	
11503-ORP1-DMHg-4A	Alternate Overheads Sample Point #1	1/15/03	3H	0.17	0.17	
11503-ORP1-DMHg-4B	Alternate Overheads Sample Point #1	1/15/03	3H	>175	350	
11503-ORP2-DMHg-5A	Alternate Overheads Sample Point #2	1/15/03	3H	0	0	
11503-ORP2-DMHg-5B	Alternate Overheads Sample Point #2	1/15/03	3H	>175	350	
030220-3HORT1-DMHg-1	Overheads Receiver Tank #1 Vent	2/20/03	3H	0.029	0.029	
030220-3HORT1-STM-1	Overheads Receiver Tank #1 Vent	2/20/03	3H			1.17
030220-3HHg-DMHg-8	Primary Overheads Sample Station	2/20/03	3H	0.015	0.015	
030220-3HHg-STM-8	Primary Overheads Sample Station	2/20/03	3H			1.53
030220-3HDIKE-DMHg-3	General Area/Dike	2/20/03	3H	0.025	0.025	
030220-3HDIKE-STM-3	General Area/Dike	2/20/03	3H			0.9
030220-3HPOH1-DMHg-4	Mercury Removal Station	2/20/03	3H	0.005	0.005	
030220-3HPOH1-STM-4	Mercury Removal Station	2/20/03	3H			0.59
030220-3HORT2-DMHg-2	Overheads Receiver Tank #2 Vent	2/20/03	3H	0.03	0.03	
030220-3HORT2-STM-2	Overheads Receiver Tank #2 Vent	2/20/03	3H			1.3
030220-3HSMP-DMHg-7	Overheads Cell Sump/Overheads Receiver Tanks Overflow	2/20/03	3H	0.048	0.048	
030220-3HSMP-STM-7	Overheads Cell Sump/Overheads Receiver Tanks Overflow	2/20/03	3H			0.64
030220-3HAOH1-DMHg-5	Alternate Overheads Sample Point #1	2/20/03	3H	0.014	0.014	
030220-3HAOH1-STM-5	Alternate Overheads Sample Point #1	2/20/03	3H			0.33

2H Evaporator Liquid Results

Sample Number	Location	Date	Fac.	Pres.	DMHg	MMHG	TMHG	THg
					µg/L	µg/L	µg/L	µg/L
300179674		5/2/02	2H	NP	26			
WSRC-023	Alternate Overheads Sample Point #1	2/5/03	2H	HCl			2692	1014
MeOH-04	Alternate Overheads Sample Point #1	2/5/03	2H	MeOH	1137			
WSRC-021	Alternate Overheads Sample Point #2	2/5/03	2H	HCl			4513	1276
MeOH-40	Alternate Overheads Sample Point #2	2/5/03	2H	MeOH	2193			
WSRC-028	Blank HCL	2/5/03					2E-07	0.0000149
WSRC-053	Blank HCL	2/5/03					9E-07	0.0000164
MeOH-82	Primary Overheads Sample Station	2/20/03	2H	MeOH	15.1			
MeOH-06	Primary Overheads Sample Station	2/20/03	2H	MeOH	14.1			
MeOH-11	Primary Overheads Sample Station	2/20/03	2H	MeOH	14.8			
WSRC-048	Primary Overheads Sample Station	2/20/03	2H	HCl			2120	2340
WSRC-05	Primary Overheads Sample Station	2/20/03	2H	HCl			2260	2330
WSRC-027	Primary Overheads Sample Station	2/20/03	2H	HCl			2080	2300
300192164		2/20/03	2H	NP	220			
MeOH-100	Primary Overheads Sample Station	3/4/03	2H	MeOH	957			
WSRC-024	Primary Overheads Sample Station	3/4/03	2H	HCl			2679	2932
MeOH-101	Alternate Overheads Sample Point #1	3/4/03	2H	MeOH	1226			
WSRC-055	Alternate Overheads Sample Point #1	3/4/03	2H	HCl			3190	3134
MeOH-102	Alternate Overheads Sample Point #2	3/4/03	2H	MeOH	1500			
WSRC-046	Alternate Overheads Sample Point #2	3/4/03	2H	HCl			3109	3374

2H Evaporator Vapor Results

Sample Number	Location	Date	Fac.	DMHg µg/m³	EDMHg µg/m³	THg µg/m³
030205-2HORT-DMHg-1	Between Overheads Receiver Tanks HEPAs	2/5/03	2H	>0.28	1.7	
030205-2HAOH1-DMHg-4	Alternate Overheads Sample Point #1	2/5/03	2H	>7.8	14	
030205-2HAOH2-DMHg-5	Alternate Overheads Sample Point #2	2/5/03	2H	>7.8	18	
030205-2HOF-DMHg-6	Overheads Cell Sump/Overheads Receiver Tanks Overflow	2/5/03	2H	>7.8	185	
030205-2HHg-DMHg-7	Mercury Removal Station	2/5/03	2H	4.61	4.61	
030205-2HORT-STM-1	Between Overheads Receiver Tanks HEPAs	2/5/03	2H			35.7
030205-2HAOH1-STM-4	Alternate Overheads Sample Point #1	2/5/03	2H			34.6
030205-2HAOH2-STM-5	Alternate Overheads Sample Point #2	2/5/03	2H			199
030205-2HOF-STM-6	Overheads Cell Sump/Overheads Receiver Tanks Overflow	2/5/03	2H			259
030205-2HHg-STM-7	Mercury Removal Station	2/5/03	2H			4.06
030220-2HPOH-DMHg-1	Primary Overheads Sample Station	2/20/03	2H	1.52	1.52	
030220-2H-POH-STM-1	Primary Overheads Sample Station	2/20/03	2H			0.88
030304-2HOF-DMHg-1	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/4/03	2H	>89.4	360	
030304-2HOF-STM-1	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/4/03	2H			930
030304-2HDIKE-DMHg-2	General Area/Dike	3/4/03	2H	>89.4	180	
030304-2HDIKE-STM-2	General Area/Dike	3/4/03	2H			137
030304-2HHEPA-DMHg-3	Between Overheads Receiver Tanks HEPAs	3/4/03	2H	36.9	36.9	
030304-2HHEPA-STM-3	Between Overheads Receiver Tanks HEPAs	3/4/03	2H			52
030304-2HSUMP-DMHg-4	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/4/03	2H	>89.4	360	
030304-2HSUMP-STM-4	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/4/03	2H			813

2F Evaporator Liquid Results

Sample Number	Location	Date	DMHg	TMHG	THg
			µg/L	µg/L	µg/L
300179675		5/2/02	<2		
WSRC-014	Primary Overheads Sample Station	2/4/03		16.2/29.8	3014
WSRC-020	Alternate Overheads Sample Point #2	2/4/03		15.8/23.6	515
WSRC-025	Alternate Overheads Sample Point #1	2/4/03		11.9/22.3	449
MeOH-10	Alternate Overheads Sample Point #2	2/4/03	2.63		
MeOH-2	Primary Overheads Sample Station	2/4/03	1.53		
MeOH-16	Alternate Overheads Sample Point #1	2/4/03	1.28		
300191577		2/4/03	1.3		
WSRC-044	Primary Overheads Sample Station	2/19/03		32.6	221
WSRC-016	Primary Overheads Sample Station	2/19/03		32.5	188
WSRC-039	Primary Overheads Sample Station	2/19/03		30.5	186
MeOH-98	Primary Overheads Sample Station	2/19/03	1.96, 2.33		
MeOH-15	Primary Overheads Sample Station	2/19/03	2.02		
MeOH-60	Primary Overheads Sample Station	2/19/03	1.96		
300192166		2/19/03	<10		
WSRC-034	Primary Overheads Sample Station	3/5/03		24.4	196
MeOH-103	Primary Overheads Sample Station	3/5/03	2.33		
WSRC-037	Alternate Overheads Sample Point #1	3/5/03		13.6	4247
MeOH-104	Alternate Overheads Sample Point #1	3/5/03	1.35		
WSRC-045	Alternate Overheads Sample Point #2	3/5/03		0.475	612
MeOH-105	Alternate Overheads Sample Point #2	3/5/03	0.0018		

2F Evaporator Vapor Results

Sample Number	Location	Date	DMHg	THg
			µg/m^3	µg/m^3
030305-2FSUMP-DMHg-1	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/5/03	0.734	
030305-2FSUMP-STM-1	Overheads Cell Sump/Overheads Receiver Tanks Overflow	3/5/03		1.84
030305-2FDIKE-DMHg-2	General Area/Dike	3/5/03	0.101	
030305-2FDIKE-STM-2	General Area/Dike	3/5/03		17.2
030305-2FPRIM-DMHg-3	Primary Overheads Sample Station	3/5/03	0.039	
030305-2FPRIM-STM-3	Primary Overheads Sample Station	3/5/03		1.09
030305-2FALT1-DMHg-4	Alternate Overheads Sample Point #1	3/5/03	0.012	
030305-2FALT1-STM-4	Alternate Overheads Sample Point #1	3/5/03		0.254
030305-2FALT2-DMHg-5	Alternate Overheads Sample Point #2	3/5/03	<0.004	
030305-2FALT2-STM-5	Alternate Overheads Sample Point #2	3/5/03		0.356
030305-2FHg-DMHg-6	Mercury Removal Station	3/5/03	<0.004	
030305-2FHg-STM-6	Mercury Removal Station	3/5/03		0.135

Effluent Treatment Facility Liquid Results

Sample Number	Location	Date	Fac.	Pres.	DMHg	MMHG	TMHG	THg
					µg/L	µg/L	µg/L	µg/L
300189423	H-Lift Station Sample Station	12/17/02	ETF	NP	<1			
WSRC-038	IX Effluent Sample Point	1/31/03	ETF	HCl			0.0013	0.418
MeOH-23	IX Effluent Sample Point	1/31/03	ETF	MeOH	<0.1			
WSRC-019	H-Lift Station Sample Station	2/6/03	ETF	HCl			547.3	97.9
MeOH-99	H-Lift Station Sample Station	2/6/03	ETF	MeOH	0.92			
WSRC-022	F-Lift Station Sample Station	2/6/03	ETF	HCl			6	93.6
MeOH-17	F-Lift Station Sample Station	2/6/03	ETF	MeOH	0.05			
MeOH-97	IX Effluent Sample Point	2/19/03	ETF	MeOH	0.023			
WSRC-032	IX Effluent Sample Point	2/19/03	ETF	HCl			0.0004	0.0659
WSRC-015	H-Lift Station Sample Station	2/19/03	ETF	HCl			910, 1065	28200
MeOH-13	H-Lift Station Sample Station	2/19/03	ETF	MeOH	96.7			
MeOH-96	F-Lift Station Sample Station	2/19/03	ETF	MeOH	ND (<0.002)			
WSRC-013	F-Lift Station Sample Station	2/19/03	ETF	HCl			0.548	387
WSRC-040	Waste Water Collection Tank Sample Point	3/13/03	ETF	HCl			369	455
MeOH-199	Waste Water Collection Tank Sample Point	3/13/03	ETF	MeOH	12.1			

Vapor Results

Sample Number	Location	Date	Fac.	DMHg	EDMHg	THg
				µg/m^3	µg/m^3	µg/m^3
030211-ETPCC2-DMHg-1	Carbon Column #2 Manway	2/11/03	ETF	0.047	0.047	
030211-ETPCC2-STM-1	Carbon Column #2 Manway	2/11/03	ETF			
030211-ETPSMP-DMHg-3	Carbon Columns Sump	2/11/03	ETF	<0.0011	0.0011	
030211-ETPSMP-STM-3	Carbon Columns Sump	2/11/03	ETF			0.73
030212-ETPHg-DMHg-1	Mercury Column #1 Manway	2/12/03	ETF	0.016	0.016	
030212-ETPHg-STM-1	Mercury Column #1 Manway	2/12/03	ETF			34.3
030219-HLS-DMHg-1	H-Lift Station Manhole	2/19/03	ETF	4.84	4.84	
030219-HLS-STM-1	H-Lift Station Manhole	2/19/03	ETF			0.03
030219-FLS-DMHg-2	F-Lift Station Manhole	2/19/03	ETF	<0.080	0.08	
030219-FLS-STM-2	F-Lift Station Manhole	2/19/03	ETF			0.01
030219-HLV-DMHg-4	H-Lift Station Ventilation Exhaust	2/19/03	ETF	>82	165	
030225-ETP1HgCSMP-DMHg-1	Carbon Columns Sump	2/25/03	ETF	>89.4	180	
030225-ETP1HgCSMP-DMHg-2	Carbon Columns Sump	2/25/03	ETF	>89.4	180	
030313-ETPWWCT-DMHg-1	Waste Water Collection Tank Sample Point	3/13/03	ETF	0.344	0.344	
030313-ETPWWCT-STM-1	Waste Water Collection Tank Sample Point	3/13/03	ETF			0.178
030313-ETPWCT-DMHg-2	Waste Concentrate Sample Point	3/13/03	ETF	<0.004	0.004	
030313-ETPWCT-STM-2	Waste Concentrate Sample Point	3/13/03	ETF			0.074
030313-ETPHLSV-DMHg-3	H-Lift Station Ventilation Exhaust	3/13/03	ETF	>89.4	180	
030313-ETPHLSV-STM-3	H-Lift Station Ventilation Exhaust	3/13/03	ETF			222

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REFERENCES

[1] P. Davis , Task Technical Request, “3H Evaporator Support for Fate of Mercury,” HLE-TTR-2003-031, Rev. 0,October 30, 2002.
[2] P. D. d’Entremont, “Functions and Requirements for the 2H and 3H Evaporator Flowsheet Models,” HLW-PRE-2001-0003, November 15, 2001.
[3] D. R. Lide, Editor, CRC Handbook of Chemistry and Physics, 71st Edition, CRC Press.
[4] Statistical Consulting Section, “Software Verification and Validation for Commercial Statistical Packages Utilized by the Statistical Consulting Section of SRTC,” WSRC-RP-99-00422, Rev. 0, May 21, 1999.
[5] G. Fuseya, “The Solubility of Mercuric Oxide in Sodium Hydroxide Solutions,” J. AM. Chem. Soc. (1920) 42, 368.
[6] J. P. Bibler, “Solubility Versus pH of Selected Metals …. Response”, IWT-LWP-89-0814, January 3, 1984.
[7] Zhou and Chen, Fudan Xuebao, Ziran Kexueban (1983) 22, 229.
[8] J. P. Bibler, “Mercury Volatility in the Presence of Reducing Agents,” DPST-86-333, March 13, 1986.
[9] S. W. Rosencrance and W. R. Wilmarth, “Initial Analysis Results for 3H Evaporator Overheads by Frontier Geosciences,” SRT-LWP-2002-00052. May 17, 2002.
[10] S. W. Rosencrance and W. R. Wilmarth, “Approaches to Calculation of Dimethylmercury in Air,” SRT-LWP-2002-00048, May 9, 2002.
[11] D. W. Rochelle, “2F, 2H and 3H Evaporator and ETF Mercury/Organo (Alkyl) Mercury Pathforward,” CBU-HDP-2003-00009, January 03, 2003.
[12]E-Mail, E. Prestbo to D. Thaxton, et. al., “3H and Tank DMHg and STM Results, dated June 3, 2003.
[13] E. Prestbo, J. Garcia, P. Swartzendruber, E. von der Geest, and S. Rosencrance, “Evaluation of the Potential for Chemical Formation of Dimethyl Mercury at High pH in the Presence of Selected Organics,” January 9, 2003.
[14] D. D. Walker, “Organic compounds in Savannah River High-Level Waste,” WSRC-TR-2002-00391, rev. 0, September 30, 2002.