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).

Characterization of Solid Materials Responsible for the Partial Blockage of the 3H Evaporator-to-Mercury Removal Tank Drain Line

L. N. Oji

June 2015

SRNL-STI-2015-00262, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2015-00262
Revision 0

Keywords: 3H Evaporator System,
Tank farms

Retention: *Permanent*

Characterization of Solid Materials Responsible for the Partial Blockage of the 3H Evaporator-to-Mercury Removal Tank Drain Line

L. N. Oji

June 2015

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

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

L. N. Oji, Advanced Characterization and Processing	Date

TECHNICAL REVIEW:

T. B. Peters, Advanced Characterization and Processing Reviewed per Manual E7 Procedure 2.60	Date

APPROVALS:

F. M. Pennebaker, Manager Advanced Characterization and Processing	Date
S. L. Marra, Manager Environmental & Chemical Process Technology Research Programs	Date
C. B. Sherburne, Process Safety & Regulatory Manager Tank Farm/ETP Process Engineering	Date

EXECUTIVE SUMMARY

In April 2015, part of the solid wet cake material responsible for partially obstructing of the drain line from the Mercury Removal Tank (MRT) on the 3H Evaporator was delivered to SRNL for analysis. The desired analytical goal was to identify the chemical components of the material responsible for the partial blockage and if possible, infer possible formation mechanisms and the best way of removing the consolidated clogging solid material from the drain line.

Chemical analysis of the “as-received” material by various spectroscopic and wet chemical techniques led to the following conclusions.

- The bulk of the “as-received” sample is elemental mercury and mercuric oxide. Additionally, there are water soluble components and some crystalline, non-water soluble solid materials.
- X-ray diffraction analysis of both the “as-received” sample and water leached/air-dried solid fraction indicate the presence of four traces crystalline mercury compounds (mercury nitride [$(Hg_2N)NO_3$], kleinite [$Hg_6Cl_3N_3H_2O$], mercuric oxide [HgO]) and a mercury sulfate complex [$Hg_4(SO_4)N_2(H_2O)$].
- FT-IR spectroscopy was also used to confirm the existence of the mercury nitride/nitrate compounds and the existence of insoluble transition metal oxalates as components of the “as-received” sample. A sparingly soluble and hygroscopic iron [II] oxalate dehydrate ($FeC_2O_4 \bullet 2H_2O$) was also identified in the “as-received” sample by FT-IR spectroscopy. Since the “as-received” sample also exhibits this characteristic hygroscopic behavior and elemental iron was identified as a relatively large component of the “as-received” sample, we concluded that this iron oxalate forms a significant proportion of the non-mercury fraction of the as-received” sample.
- Thermo-gravimetric analysis of the “as-received” sample, with the exception of the loss of water, showed no discernable exotherms due to rapid mass loss. The lack of distinct rapid mass loss with increase in temperature indicates that the “as-received” sample is not shock sensitive or energetic to pose a safety problem in the evaporators at its present composition.
- Literature reviews on mercury nitride and similar nitrated mercury compounds reveals that some of these potentially energetic mercury compounds can be synthesized under laboratory conditions in the presence of mercuric oxide and ammonia/ammonium precursors at temperatures above 100 $^{\circ}$C. This may indicate that ammonia concentration is higher than anticipated in the evaporator for this feed. Since these precursors, including oxalates, may be present in SRS Evaporator system, we recommend their continuous monitoring in SRS evaporators/ and evaporator overheads to provide the plant a warning before their concentrations reach significant limits and increase the potential for the formation of energetic nitrated mercury compounds.
- Since this heterogeneous “as-received” sample from the 3H Evaporator-to-mercury removal tank drain line is about 15 to 23 wt. % water soluble and can be leached with water at room temperature, it is concluded that aqueous cleaning with pressurized water may be a good way to dislodge this material from the drain lines when it accumulates over time.
- Due to the limited literature information on the flammability of mercury nitride, its flammability properties were inferred from its structurally analogue, mercuric nitrate ($Hg(NO_3)_2$), which is not flammable. However, both compounds are oxidizing agents and as such are capable of speeding up flames in a combustion environment. Most of the other compounds identified in the “as-received” sample, mainly the transition metal oxalates and mercury compounds are sparingly water soluble and are not flammable under the evaporator operating conditions.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectrometry
FT-IR	Fourier transform infrared
MRT	Mercury Removal Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TGA	Thermo-gravimetric Analysis
XRD	X-ray diffraction

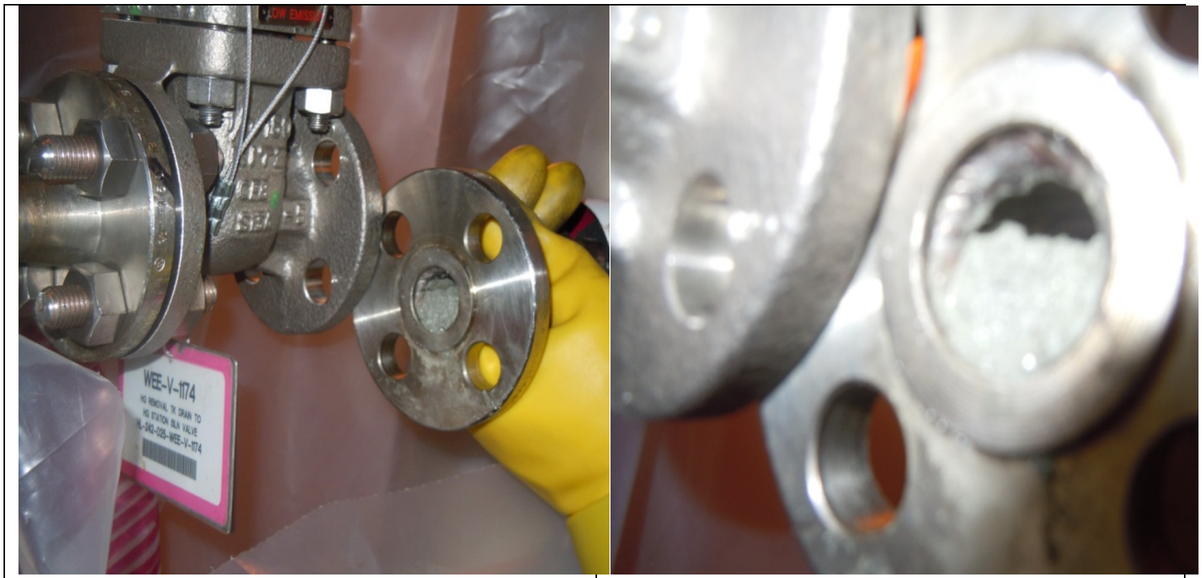
1.0 Introduction

On April 16, 2015, Savannah River Remediation (SRR) provided sample solids taken from the drain line leading from the Mercury Removal Tank (MRT) on the 3H (242-25H) Evaporator to Savannah River National Laboratory (SRNL) for analysis. The desired goal was to identify the chemical nature (elemental make-up and crystalline structure of the solid) of the solids material, which had partially plugged the drain line from the MRT on the 3H Evaporator as shown in Figure 1. Information was also requested to determine how the accumulation of the solid material can be chemically or mechanically removed from the drain line to eliminate future plugging.

The Technical Task Request, TTR-HTF-2015-00001, defined the tasks and requirements for the performance of this sample characterization by SRNL. This report contains the results of the chemical characterization and analytical identification of the nature of the solid material discovered in the drain line leading from the MRT on the 3H Evaporator.

1.1 Sample Description

Pictures of the wet and pasty solids assumed to be responsible for the partial plugging of the 3H Evaporator-to-mercury removal tank drain line sent to SRNL for analysis, are presented in Figure 2 (inserts A-D). The wet solid particles are seen smeared on the interior walls of the original glass sample container with elemental mercury globules at the bottom of the glass sample container (Figure 2, insert A and B). The visible elemental mercury was decanted into a small glass vial (Figure 2, insert C) and a Teflon-coated metal spatula was used to scrape the wet smeared sample solids down to the bottom of the original glass container. From the bottom of the glass container, the wet segregated solid material was sampled for analysis as shown in Figure 2, insert D. About a third of the total solid wet sample is seen on the tip of the Teflon-coated metal spatula along with tiny globules of what appears to be silvery elemental mercury.



Insert A Mercury transfer line almost plugged with this silvery gray material	**Insert B.** A closer look into the almost closed mercury transfer line orifice.

Figure 1, Inserts A and B, show the 3H Evaporator-to-MRT drain line almost plugged with a mysterious gray solids.

Insert A: Wet solid sample particles seen smeared on the interior walls of the original glass sample container.

Insert B: Elemental mercury visible at the bottom of the original glass sample container.

Insert C: Decanted elemental mercury from original sample is seen in a different container

Insert D: Recovered wet solid sample from the smeared glass container.

Figure 2 (inserts A-D) Pictures of solids material responsible for the partial plugging of the 3H Evaporator to MRT drain line (Sample HTF-15-44).

2.0 Experimental Details

The 3H evaporator mercury drain line sample (HTF-15-44) was received at the SRNL Shielded Cells on April 16, 2015. Inserts in Figures 1 and 2 show the different configurations of the "as-received" material. As earlier described, the glass sample holder contained wet solid sample particles which were smeared all over the interior walls of this original glass sample container. The smeared samples particles contained fine visible and silvery particles of elemental mercury. There was also a lot of segregated globules of elemental mercury at the bottom of the glass sample container as shown in Figure 2, insert B. The segregated globules of elemental mercury, at the bottom of the glass container, were decanted into a separate container and the weight of the decanted mercury determined (38.6 g) as shown in Figure 2, insert C. This was estimated to constitute about 70 % of the total "as received" sample weight.

All sample preparations were based on the wet smeared sample solid on the walls of the vessels, which was estimated to be about 30% or 16.5 g of the original “as received” total sample weight. These smeared samples on the vessel walls were pushed down and concentrated to the container bottom with a spatula as shown in Figure 2, insert D.

Aliquots of the “as received” wet solid samples (concentrated smeared samples) were submitted for solid state analysis by X-ray powder diffraction (XRD) to determine the crystallographic solid phase. The XRD spectra of the air-dried solid fraction resulting from the sample leaching with de-ionized water were also obtained for comparison.

Aliquots of the sample (average of 1.27± 0.05 g) were also digested by aqua-regia with nitric/hydrochloric acid and the resulting digested liquid sample was analyzed in duplicate by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-ES) for elemental constituents. Two aliquots of the “as-received” 3H-Evaprotator mercury drain line sample were leached with distilled and de-ionized water and the resulting leachate analyzed by ion chromatography (IC). An average of 0.965 ± 0.003 grams of the sample solids was leached with 10.01 ± 0.01 grams of distilled and de-ionized water (phase ratio of 10.4 mL/g). In this process, the solid material was thoroughly mixed with the given amount of distilled and de-ionized water, and the mixture was hand agitated for approximately five minutes and left to stand overnight before another agitation and filtering of the mixture using a 0.45 micron Nalgene filter unit. The filtrates were analyzed in duplicate for the requested anions by IC. Thus, only surface-bound and water soluble constituents are assumed to be measured in the leachate analyses.

Samples were also submitted for mercury analysis via permanganate/persulfate dissolution/ digestions and cold vapor mercury analysis.

Three types of thermo-gravimetric analysis (TGA) runs were performed with the “as-received” sample. In the first run, the TGA analysis was performed with the “as-received” sample with heating just above 210 °C. In the second TGA run, the sample was pre-dried at 50 °C before continuous heating for up to 230 °C. The third TGA run was a re-run using the residue samples from the second sample.

The Infrared spectra (FT-IR spectra) of the “as-received” sample and air-dried solid fraction resulting from the sample leaching with de-ionized water were obtained for confirmation of some the analytical species identified with IC and XRD analysis. The FT-IR spectral analysis also included optical microscope images of both the “as-received” sample and the water leached solid fraction after air-drying for 72 hours as shown in Figure 7.

3.0 Analytical Results and Discussion

Field observation of the solids collected from the 3H Evaporator-to-mercury removal tank drain line indicated that the sample was initially a dry powder which started to turn wet when introduced into the glass container shown in Figure 2 (inserts A-B and D). This observation seems to indicate that the material was hygroscopic and thus absorbed moisture from the air to become wet and pasty.

The recovered sample solid from the 3H Evaporator-to-mercury removal tank drain line was also observed to degrade a neoprene gasket (small holes observed in the gasket) which had been brought into contact with it within 24 hours. This field observation may be attributed to the reaction between elemental mercury and thiourea (an organosulfur compound-$SC(NH_2)_2$) used to crosslink chloroprene (vulcanization of chloroprene with sulfur-'atomic bridges') in the making of neoprene.[a] The organo sulfur functional group in the neoprene actually reacts with mercury in the sample since sulfur is known to reacts with elemental mercury, even at room temperatures, to form black mercuric sulfide (meta-cinnabar).[b]

3.1 XRD Spectra

The XRD spectra for the "as-received" sample (insert A) and water leached, air-dried residual solid fraction (insert B) of the 3H evaporator-to-mercury removal tank drain line sample are shown in Figure 3, inserts A and B. There is a shift in base line (elevated baseline), which indicates the presence of amorphous materials in addition to crystalline materials in the sample matrix for both the "as-received" and water leached/air-dried solid fraction.

The XRD spectra matched the spectral lines for the presence of at least five mercury bearing crystalline compounds. Two types of mercury nitrides were matched and these included one nitride with the formula [$(Hg_2N)NO_3$] and a second hydrated nitride with the formula [$Hg_2N(OH)(H_2O)_2$].

The XRD spectrum for mercury nitride [$(Hg_2N)NO_3$], kleinite [$Hg_6Cl_3N_3H_2O$], and montroydite (mercury oxide) [HgO] were identified in both the "as-received" sample and water leached/air-dried residual solid fraction XRD spectra. The hydrated mercury nitride, [$Hg_2N(OH)(H_2O)_2$], and mercury sulfate [$Hg_4(SO_4)N_2(H_2O)$] were identified only in the water leached/air-dried residual solid fraction XRD spectra only.

The hydrated mercury nitride, [$Hg_2N(OH)(H_2O)_2$], which was observed only after leaching of the "as-received" sample with water, in a phase ratio of 10.4 mL/g, may be just a hydrated derivative of the other mercury nitride [$(Hg_2N)NO_3$]. Therefore, it can be concluded that only four forms of mercury compounds were matched or identified.

3.2 Aqua Regia Digestion and Analysis for Elemental Constituents

Elemental mercury (1.02E+06 ± 2.17E+05 µg/g or 102 ± 22 wt%), as expected, formed the bulk of the elemental constituent of the "as-received" sample. Other post-digestions measurable elements included silicon (3.15 E+02 ± 3.14E+02 µg/g), iron, chromium, zinc, and aluminum as shown in Table 2. The variations and large uncertainties in the analytical results for mercury and silicon reflect the inhomogeneous nature of the "as-received" sample.

3.3 Leachate Analysis

The analysis of the de-ionized water leachates, to isolate water soluble components of the "as-received" sample, shows the presence of measurable quantities of chloride, nitrate, nitrite and sulfate and even fluoride anions (Figure 4 and Table 1). These anion analytical results confirmed the XRD information which indicated that there are other non-crystalline (amorphous) materials which are components of the "as-received" sample. The amorphous fraction of the "as-received" sample also contains other water soluble anions like oxalates and sulfates. After leaching of the sample, the resulting combined weight of the insoluble fractions from the two leaching was air-dried for 72 hours. By gravimetric measurements from leaching, approximately 15 wt. % of the original "as-received" sample seems to be water soluble. However, this value could not be confirmed from anion-cations balance determinations because of the predominant concentration of both elemental mercury and mercuric oxides in the "as-received sample" relative to the water

---

[a] http://chlorine.americanchemistry.com/Science-Center/Chlorine-Compound-of-the-Month-Library/Neoprene-The-First-Synthetic-Rubber

[b] L.N. Oji, "Mercury Disposal Via Sulfur Reactions" Journal of Enviro. Engineering, VOL. 124 No. 10, October 1998 page 945

leachable anions. The best estimate for the percent water soluble species, based on water leachable anions and cation derived from complete acid digestion of the "as received" sample, excluding most of the elemental mercury, is 23 wt. % (7.39E-06/3.20E-05*100). The total sum of the cations in the "as-received" sample was 3.20E-05 moles and that for the leachate anions came to 7.39E-06 moles as shown in Tables 1 and 2. If the total amount of elemental mercury/mercuric oxides are taken into consideration the percent water soluble species ranges from 0.14 to 0.67 wt.%. It is also worth emphasizing again that the sample was heterogeneous and so such variation in number is expected. The one sigma measurement uncertainty for IC and ICP-ES analytical results are, respectively, 10% and 20%.

3.4 Thermo-gravimetric Analysis

An aliquot of the sample (0.207g) which was heated to 210 °C partitioned into two fractions; a pool of elemental mercury and a dark brown powder. The TGA data shows that this "as-received" sample contains about 4 wt% water. However, compared to previous TGA studies involving studies of simulated SRS sludge and synthetic energetic materials (mercury fulminate and other select energetic compounds)[a, b], where there were definite changes of exotherms due to rapid mass loss, this "as-received" sample showed no discernable exotherms due to rapid mass loss (Figure 5). The 50 °C pre-dried sample run shown in Figure 5 has two small kinks on the plot which look like mass losses at about temperatures of 60°C and 110°C. These graph kinks or perturbations maybe artifacts from the TGA instrumentation or material impurities. The lack of distinct rapid mass loss with an increase in temperature indicates that the "as-received" sample is not shock sensitive or energetic to pose a safety problem in the evaporators. Hence, although the XRD spectra shows that it contains mercury nitride ($(Hg_2N)NO_3$) and kleinite mineral, there is no TGA evidence to indicate that the material, in its present configuration and make-up, is energetic.

3.5 Fourier Transform-Infra Red Analysis

Infrared analysis was performed as a follow up characterization to confirm the infrared signatures for mercury nitride $(Hg_2N)NO_3$, kleinite ($Hg_6Cl_3N_3{\bullet}H_2O$) and other non-crystalline (amorphous) materials which were not identified in the XRD spectra.

Figure 6 shows the infrared spectra for the "as-received" sample (insert A) and the solid fraction left after water leaching and air-drying for 72 hours (insert B). Each insert in Figure 6 contains two spectra (overlay spectra). Because the "as received" sample and even the post water leached solids were not homogenous or uniform across the sample matrix, it was necessary to determine the infra-red spectra at several locations and to see if there were differences. In general, the lower spectrum in each overlay spectra in the inserts reflects the majority of the samples in the bulk, while the upper spectrum in each insert represents that of fewer sample locations in the sample bulk. Looking closely at each insert and the overlay spectra, it is quite obvious that the sample in both cases ("as-receive" and leached solid fraction) is heterogeneous. This heterogeneity had also been observed in the elemental composition analysis as mentioned previously.

The FT-IR spectra for the "as-receives sample" Figure 6, insert A, has spectral peaks for the following four moieties, large nitrate peak centered at 1360 cm^{-1}, a shoulder nitrite peak at 1258 cm^{-1}, sulfate peaks centered at 1053 cm^{-1},and an oxalate peak centered at 1655 cm^{-1}. These anions were also identified by IC in the analysis of the water soluble leachates from the "as-received" sample as shown in Figure 4 and Table 1.

---

[a] F. Fondeur, W. R. Wilmarth and S. D. Fink, "Gamma radiation stability studies of mercury fulminate," WSRC-RP-99-01090, Rev. 0, Dec. 6, 19999.

[b] F. Fondeur, W. R. Wilmarth, "Synergistic and alkaline stability studies of mixtures of simulated high level waste sludge with selected energetic compounds," WSRC-RP-99-00592, Rev. 0, July.19999.

Figure 6, insert B, shows the infra-red spectra for the post water leached air dried solids. In both spectra, the sulfate peaks at 1053 cm-1 and the shoulder nitrite peak at 1258 cm-1 were virtually gone, which seems to indicate that majority of the water soluble species in the sample were sulfates and nitrites. However, the nitrate (1360 cm-1) and oxalate (1660 cm-1) peaks were still present in their original intensities. The two peaks belong to the solid fractions which are not water soluble, but are possible transition metal oxalates and nitrates like iron oxalate ($Fe_2(CO_4)•3H_2O$) or $FeC_2O_4•2H_2O$, nickel oxalates ($Ni(C_2O_4)•2H_2O$), zinc oxalates ($Zn(C_2O_4)•2H_2O$), chromium oxalate ($Cr(C_2O_4)•H_2O$ and mercury nitride ($(Hg_2N)NO_3$). It is worth mentioning that the FT-IR spectra for the oxalates mentioned here look quite similar to one another and are similar to the sample spectra shown in Figure 6 inserts.[a] Of all the possible transition metal oxalates so far mentioned here, iron [II] oxalate ($Fe(C_2O_4)•2H_2O$) is the only oxalate which is hygroscopic with poor solubility in water at 0.09 g/ 100 mL at 25 °C.[b]

As previously mentioned, field observation information on the solids collected from the 3H Evaporator-to-mercury removal tank drain line indicated that the sample was initially a dry powder which turn wet when introduced into the glass sample container. This observation is consistent with the behavior of a hygroscopic compound. In this case, we conclude that majority of the non-elemental/mercuric oxide solids in the “as-received” sample may be iron [II] oxalate dihydrate. ($Fe(C_2O_4).2H_2O$).

However, the infra-red intensity of the oxalate bands (centered at 1655 cm^{-1}) in the samples are considerably smaller than those for the cited pure transition metal oxalates [a, b]. The transition metal oxalates, excluding mercury, were selected because the elemental analysis (acid digested) data for the “as-received” solid samples (Table 2) shows that these metals are the most prevalent transition metal cations in the “as-received” sample solids results.

The characteristic NH_4^+ ion infrared bands at 3360 cm^{-1} and 2993 $cm^{-1,}$ Figure 6, insert B, may be assigned to ammonium ion stretch bands, although there are no obvious separate confirming ammonium ion deformation bands in the 1484-1390 cm^{-1} region.[c] These bands may have folded into the nitrate band centered at 1366 cm^{-1} and lying between 1500 cm^{-1} and 1100 cm^{-1}. If this is the case, then there may be another insoluble ammonium ion inorganic compound in the sample.

3.6 Flammability

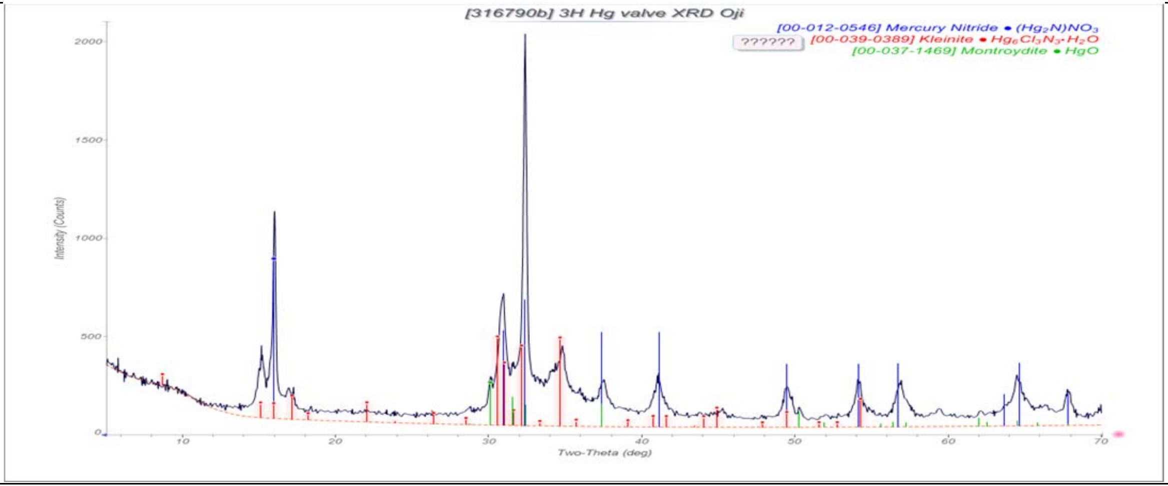
Due to the lack of literature information on the flammability of mercury nitride, its flammability properties were inferred from its structurally analogue, mercuric nitrate ($Hg(NO_3)_2$), which is not flammable. However, both compounds are oxidizing agents and as such are capable of speeding up flames in a combustion environment. All other compounds identified in the “as-received” MRT sample, mainly the transition metal oxalates are water insoluble and are not flammable. Therefore, under the evaporator operating conditions, the “as-received” MRT sample is not flammable.

---

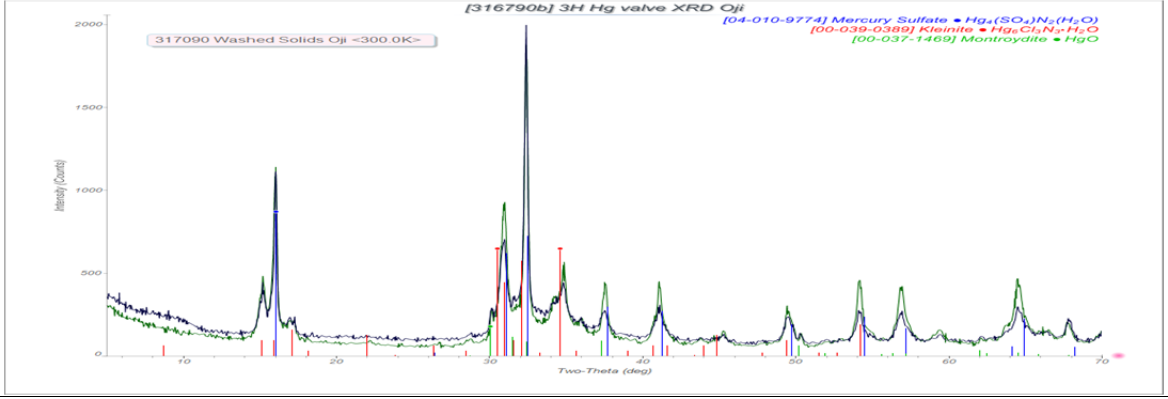
[a] http://webbook.nist.gov/cgi/cbook.cgi?ID=B6000084&Mask=80.

[b] http://www.chemicalbook.com/ChemicalProductProperty_EN_CB3179428.htm’
http://webbook.nist.gov/cgi/cbook.cgi?ID=B6000061&Mask=80

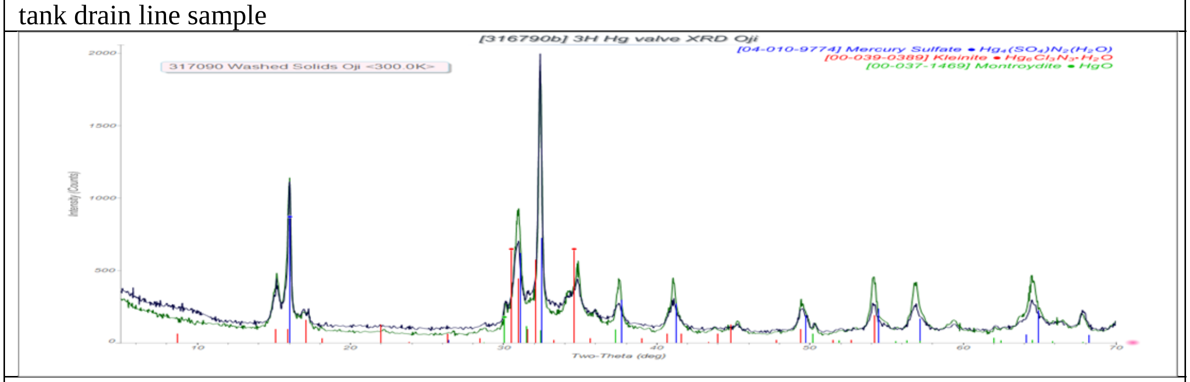
[c] K. Nakamoto, “Infrared & Raman Spectra of Inorganic and Coordination Compounds,” Page 135, Third edition, John Wiley$ Sons publication, 1978.



Insert A: "As-received" 3H evaporator-to-mercury removal tank drain line sample



Insert B: Water leached, air-dried residual solid fraction of the 3H evaporator-to-mercury removal tank drain line sample



Insert C: Water leached, air-dried residual solid fraction of the 3H evaporator-to-mercury removal tank drain line sample

Figure 3 XRD spectra for the "as-received" (insert A) water leached, air-dried residual solid fraction (insert B and C) of the 3H evaporator-to-mercury removal tank drain line sample.

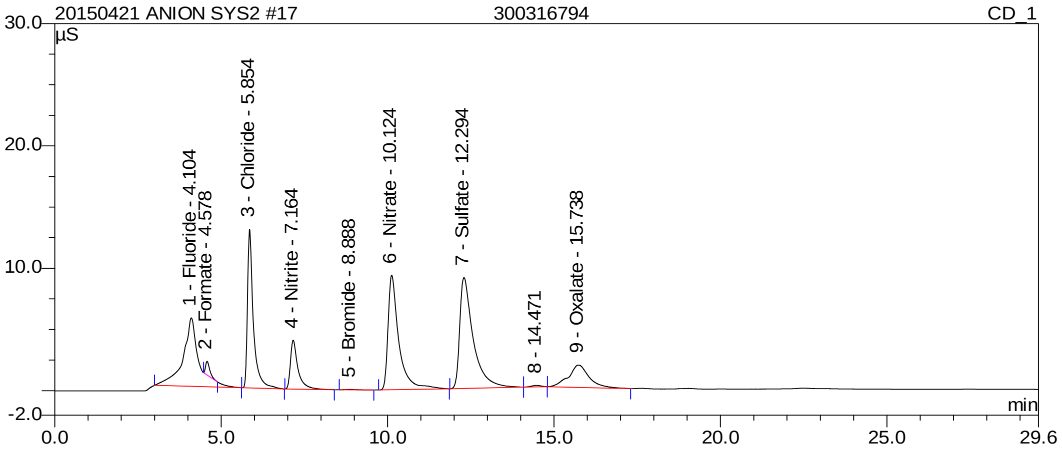


Figure 4 Anions from leachates (water soluble fraction of the original solids)

Table 1 Ion chromatography (IC) analysis from "as-received" sample Water leachate.

Anions	**Tk 3H evap-1, µg/g**	**Tk 3H evap-2, µg/g**	**Average, µg/g**	**Standard deviation**	**Mole anion/ g**
Fluoride	2.94E+01	2.60E+01	**2.77E+01**	*2.46E+00*	1.46E-06
Formate	<10.48	<10.35	**[10.41]#**	-	2.31E-07
Chloride	4.31E+01	3.38E+01	**3.84E+01**	*6.62E+00*	1.08E-06
Nitrite	2.10E+01	2.07E+01	**2.08E+01**	*1.81E-01*	4.52E-07
Nitrate	1.07E+02	9.67E+01	**1.02E+02**	*7.21E+00*	1.65E-06
Sulfate	9.55E+01	8.44E+01	**9.00E+01**	*7.86E+00*	1.87E-06
Oxalate	3.13E+01	2.59E+01	**2.86E+01**	*3.83E+00*	6.50E-07
Anion sum	-	-	**-**		**7.39E-06**

Absolute value used in anion balance calculations.

Table 2 ICP-ES data from aqua regia digestions of the "as-received" sample

Elements	300316787 3H Run 1, µg/g	300316788 3H Run 2, µg/g	Average, µg/g	Standard deviation	Mole cation/ g
Al	2.23E+01	2.30E+01	**2.27E+01**	*4.95E-01*	8.39E-07
Ca	4.45E+00	5.98E+00	**5.22E+00**	*1.08E+00*	1.30E-07
Cr	7.44E+01	7.33E+01	**7.39E+01**	*7.78E-01*	1.42E-06
Cu	5.77E+00	6.36E+00	**6.07E+00**	*4.17E-01*	9.55E-08
Fe	7.26E+02	7.10E+02	**7.18E+02**	*1.13E+01*	1.29E-05
K	<60.5	<63.5	**[62]#**	-	1.59E-06
Mn	1.50E+01	1.49E+01	**1.50E+01**	*7.07E-02*	2.72E-07
Na	<47.8	<50.4	**[49.1]#**	-	2.13E-06
Ni	6.28E+01	5.77 E+01	**6.03 E+01**	*3.61E+00*	1.03E-06
Si	9.27 E+01	5.37 E+02	**3.15 E+02**	*3.14E+02*	1.12E-05
Zn	3.21 E+01	2.04E+01	**2.63 E+01**	*8.27E+00*	4.01E-07
Cation sum	-	-	**-**		**3.20E-05**
Hg	8.63E+05	1.17E+06	**1.02E+06**		5.08E-03

Absolute value used in cation balance calculations.

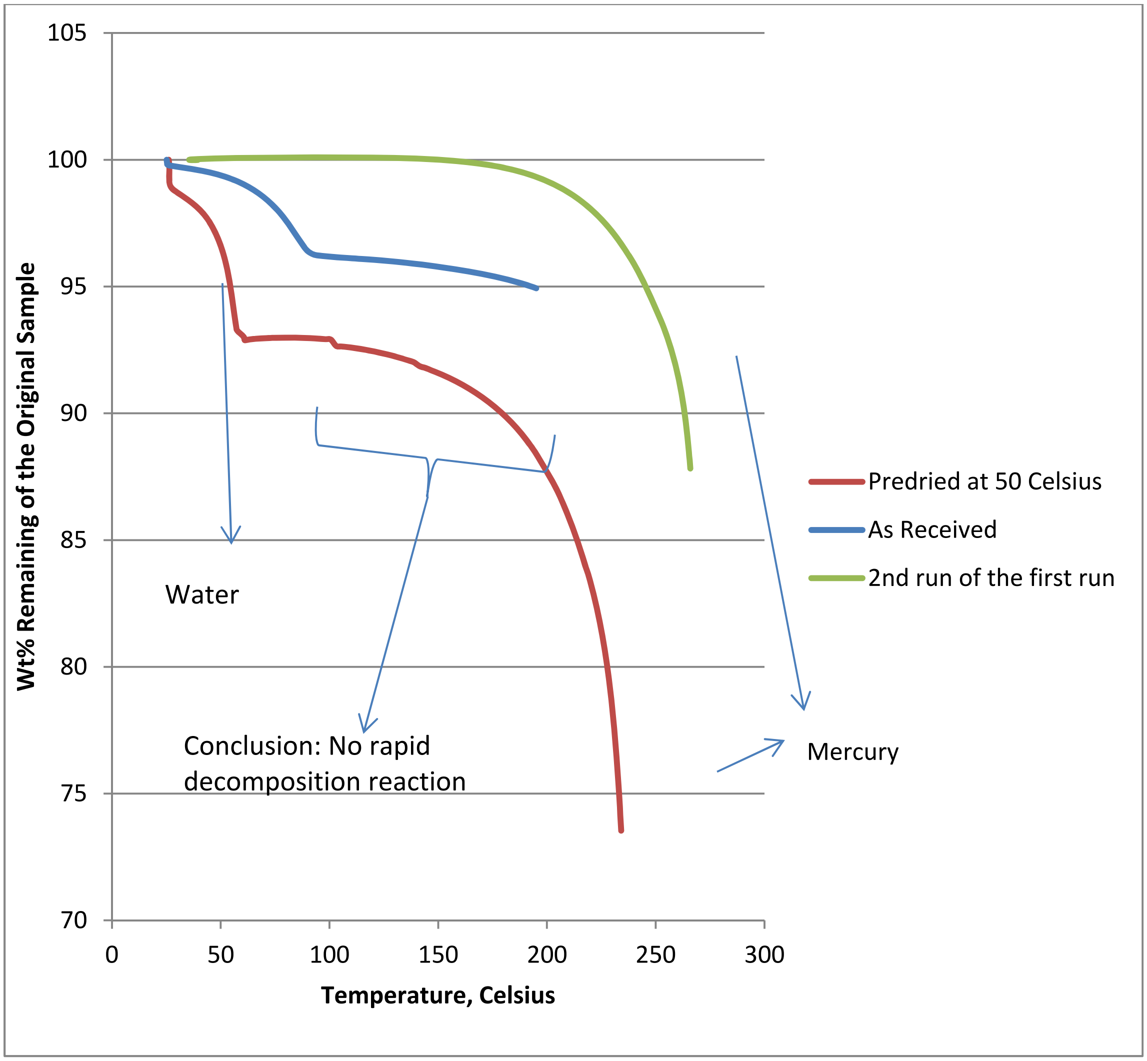
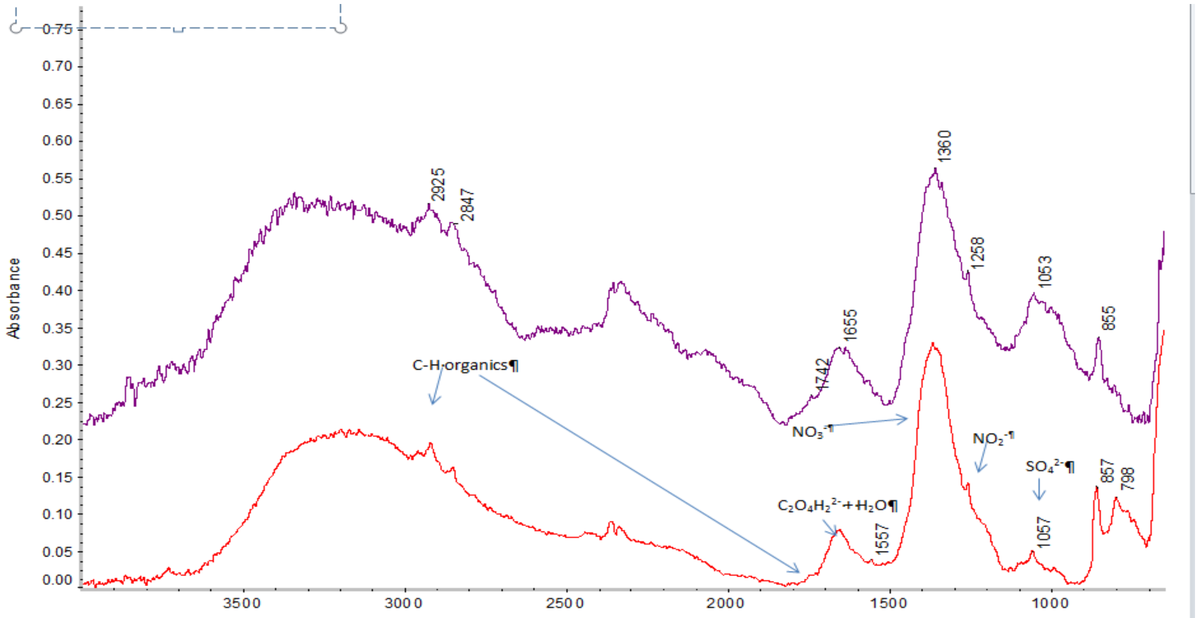
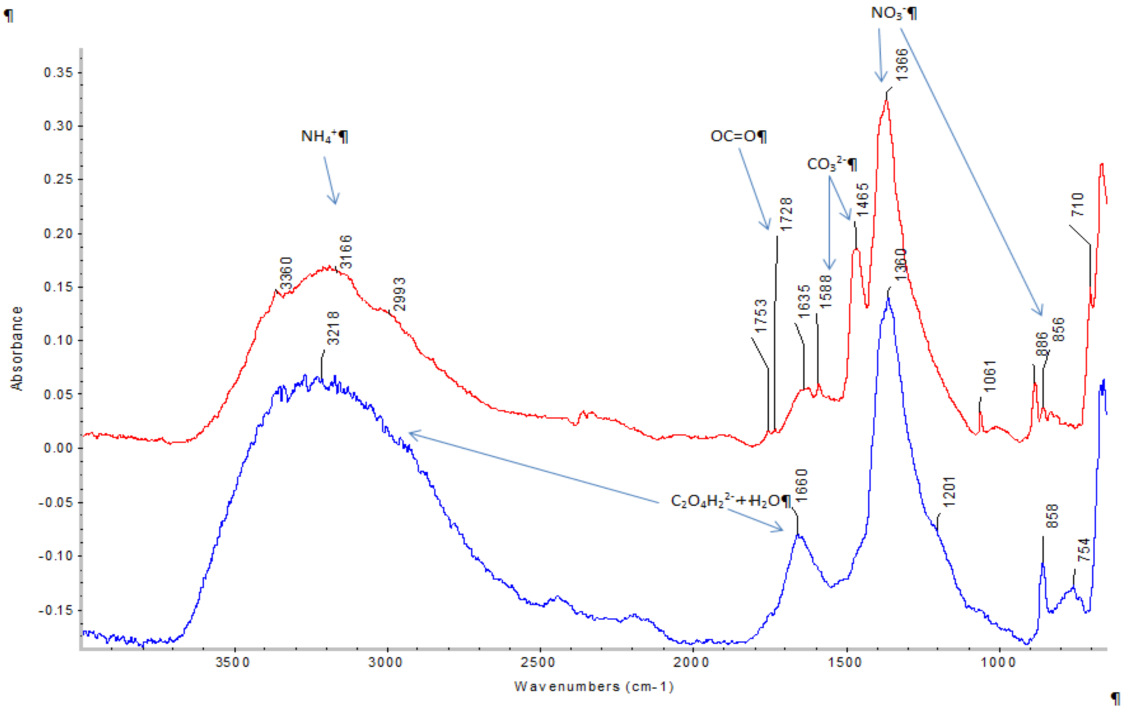


Figure 5 TGA data indicate that there is no discernable evidence of a rapid decomposition reaction.

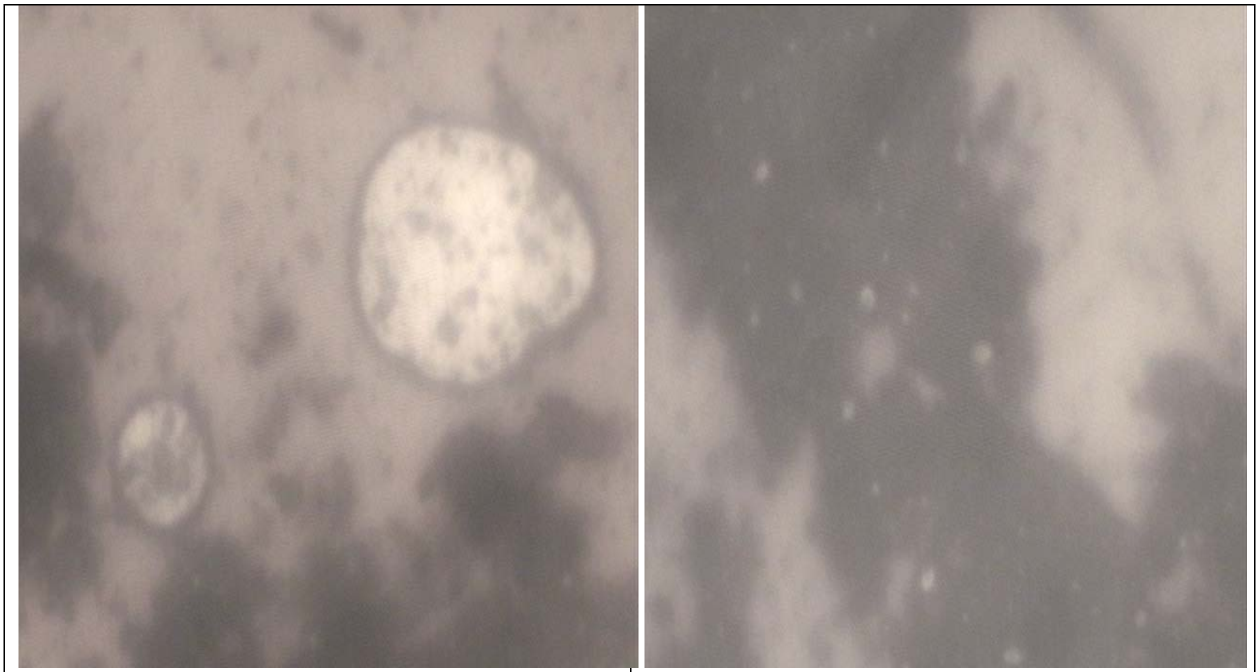


A: FT-IR Spectra of the “As Received” Sample



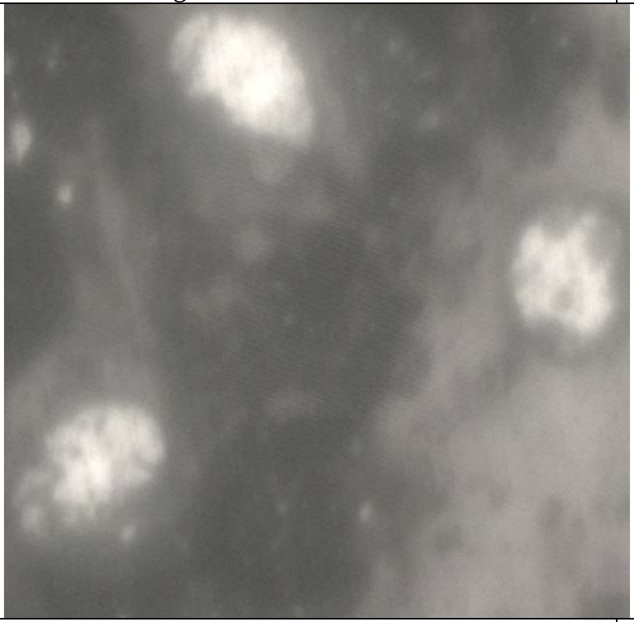
B: FT-IR Spectra for the solid fraction left after water leaching and air-drying; phase ration 10.4 mL/g

Figure 6 FT-IR spectra for the as receive sample (insert A) and solid fraction left after water leaching and air-drying for 72 hours (insert B).



Insert A: As-received sample: Mercury globules are seen in the image with fine black materials

Insert B: As-received sample: Mercury globules are seen in the image with fine black materials



NO image here.

Insert C: Solids fractions left after water leaching and air-drying; phase ratio of 10.4 mL/

Figure 7 Optical microscopic images from Infrared microscope for the as-received sample (inserts A and B) and solids fractions left after water leaching and air-drying (insert C).

4.0 Conclusions

Analysis of the wet cake material responsible for partially obstructing of the drain line from the MRT on the 3H Evaporator by various spectroscopic and wet chemical techniques shows that the “as-received” MRT sample is a mixture of several solid material fractions, water soluble composite materials and high in elemental mercury. Some of these materials are amorphous while others are crystalline.

X-ray diffraction analysis of both the “as-received” sample and water leached/air-dried solid fraction indicate the presence of about four crystalline mercury compounds, which include mercury nitride [$(Hg_2N)NO_3$], kleinite [$Hg_6Cl_3N_3 \bullet H_2O$], mercury oxide [HgO] and mercury sulfate [$Hg_4(SO_4)N_2(H_2O)$]. FT-IR spectroscopy was also used to further confirm the existence of the mercury nitride/nitrate compounds (mercury cations/nitrido anions) as well as confirm the existence of insoluble transition metal oxalates as components of the “as-received” sample. Among the possible transition metal oxalates identified by FT-IR spectroscopy, iron [II] oxalate dihydrate. ($Fe(C_2O_4) \bullet 2H_2O$), which is sparingly soluble and hygroscopic, a behavior which is also characteristic of the “as-received” MRT sample, may be one of the solid components of the material responsible for the partial obstruction of the drain line from the MRT on the 3H Evaporator.

Because some mercuric compounds, in their pure forms, are potentially energetic materials it was necessary to determine the energetics of the “as-received” MRT material by thermo-gravimetric analysis. Thermo-gravimetric analysis of the clogging sample from the mercury line, with the exception of the loss of water, showed no discernable exotherms due to rapid mass loss. This lack of distinct rapid mass loss with increase in temperature indicates that the sample is not shock sensitive or energetic to pose a safety problem in the evaporators at its present composition and concentration in the MRT sample sent in for analysis.[a]

Since this heterogeneous “as-received” sample from the 3H Evaporator-to-mercury removal tank drain line can be leached with water at room temperature, with about 15-23 wt. % of the “as-received” sample (excluding the decanted mass of elemental mercury) being water soluble, we conclude that aqueous cleaning with pressurized water is a good way to dislodge this material from the drain line when it accumulates over time.

Due to the limited literature information on the flammability of mercury nitride, its flammability properties was inferred from its structurally analogue, mercuric nitrate ($Hg(NO_3)_2$), which is not flammable. However, both compounds are oxidizing agents and as such are capable of speeding up flames in a combustion environment. Most of the other compounds identified in the “as-received” sample, mainly the transition metal oxalates and mercury compounds are water insoluble and may not be flammable under the evaporator operating conditions.

Literature reviews on mercury nitride and similar nitrated mercury compounds reveals that some of these potentially energetic mercury compounds can be synthesized under laboratory conditions in the presence of mercuric oxide and ammonia/ammonium precursors at temperatures above 100 °C.[b] This may indicate that ammonia is higher than anticipated in the evaporator for this feed.

---

[a] T. B. Peters et al, "Examination of Milton's Base ([Hg2N][OH}.2H2O and [Hg_2N](NO_3) and safety implications for Savannah river Site Waste Tanks Containing Dry Sludge, WSRC-TR-2000-00111, Rev. 0, May 15, 2000),

[b] Peter Nockemann, Gerd Meyer "Bildung von $NH_4[Hg_3(NH)_2](NO_3)_3$ und Umwandlung in [Hg_2N](NO_3)" Zeitschrift für anorganische und allgemeine Chemie 2002, Volume 628, pages 2709–2714. doi:10.1002/1521-3749(200212)628:12<2709::AID-ZAAC2709>3.0.CO;2-P

Since the precursors (ammonia/ammonium ions) may be present in SRS Evaporator system, we recommend their continuous monitoring in SRS evaporators/evaporator overheads to give the plant a heads up before their concentrations reach significant limits which will increase the potential for the formation of energetic nitrated mercury compounds.

The “as received” sample used for these tests was also analyzed for semi-volatile organic compounds including ammonium ion (NH_4^+) but no volatiles organics were detected. Therefore, it is safe to conclude that only small amounts of this mercury nitride and kleinite were present in the “as-received’ material. It is also worth noting that there is no literature-information which indicates that mercury nitride and other compounds detected in the “as-received” samples from the 3H Evaporator-to-mercury removal tank drain line are energetic materials capable of causing explosions.

In addition to continuous monitoring for the ammonia/ammonium ions precursors, it is also recommended that select organic moieties such as oxalates be monitored for in SRS evaporator overheads to minimize the formation of potentially clogging compounds in the system.

5.0 Quality Assurance

Data are recorded in SRNL Electronic Notebook: L5575-00080 SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and various AD notebooks contain the analytical/experimental data.

Nockemann, P., Meyer, G.; Z. Anorg. Allg. Chem. 628 (2002) 12, 2709-2714; Inst. Anorg. Chem., Univ. Koeln, D-50939 Koeln, Germany; G.S, Nichols, “Ammonia-Mercury System in Tritium Process,” DPST-85-571, September 4, 1985 (Acc. No. 188372).

Acknowledgements

I acknowledge the contributions of Mona Blume, M. Hightower and Shirly McCollum for preparing the samples, Mark Jones, Dr. Tom White, David Missimer, F. Fondeur and M. Crowder for providing analytical services.

Distribution:

C. J. Martino, 999-W Room 390
C. B. Sherburne, 707-7E Room 1
D. J. Martin, 241-152H
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A