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DWPF SMECT PVV Sample Characterization and Remediation

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SRNL-STI-2013-00289

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Prepared for
U.S. Department of Energy

Keywords: *DWPF, SMECT, PVV, Characterization*

Retention: *Permanent*

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May 2013

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

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ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Dr. Chris Martino for photographs taken and for assistance in some aspects of this work while the authors were unavailable. We also acknowledge the assistance of Dr. Chuck Coleman in preparing materials for the digestions and all the Shielded Cells personnel for supporting this work including preparing samples and testing the material.

EXECUTIVE SUMMARY

On April 2, 2013, a solid sample of material collected from the Defense Waste Processing Facility's Process Vessel Vent (PVV) jumper for the Slurry Mix Evaporator Condensate Tank (SMECT) was received at the Savannah River National Laboratory (SRNL). DWPF has experienced pressure spikes within the SMECT and other process vessels which have resulted in processing delays while a vacuum was re-established. Work on this sample was requested in a Technical Assistance Request (HLW-DWPF-TAR-2013-002). This document reports the results of chemical and physical property measurements made on the sample, as well as insights into the possible impact to the material using remediation methods proposed by DWPF. DWPF was interested in what the facility could expect when the material was exposed to either 8M nitric acid or 90% formic acid, the two materials they have the ability to flush through the PVV line in addition to process water once the line is capped off during a facility outage.

Based upon the SRNL analysis of the SMECT PVV jumper sample material, the following conclusions are put forth:

a) The sample material is a heterogeneous mixture of crystalline and noncrystalline species comprising approximately 82 wt.% total solids.

b) The order of abundance of elements in the sample is: Hg>>Al>Fe>Si>Th>Ni. The Hg species is non-crystalline and was not identified.

c) The material is completely solubilized using a peroxide fusion digestion; mostly solubilized with a hot, pressurized aqua regia digestion leaving primarily Bohmite [AlO(OH)] undissolved; partially solubilized with 8M nitric acid leaving predominately Bohmite and Magnetite [Fe_3O_4] undissolved along with other trace species; and a bit less partially solubilized with 90% formic acid leaving predominately Bohmite, Magnetite, and Hg species undissolved along with other trace species.

d) The dissolution test with 8M nitric acid resulted in significant dissolution of Hg from the material and an overall mass reduction of ~52%.

e) The dissolution test with 90% formic acid resulted in far less Hg dissolution from the material, as compared to the 8M nitric acid test, and an overall mass reduction of ~31%.

Of the two proposed remediation methods presented by DWPF to soak and flush the PVV line jumper, 8M nitric acid and 90% formic acid, our testing indicates the 8M nitric acid will have the most impact of the two. The nitric acid will dissolve at least an order of magnitude more Hg from the material, though some sludge components and frit present in the material will remain. The impact of a subsequent pressurized water rinse of the line could not be simulated, so its efficacy in removing the undissolved solids is unclear.

The collection and analysis of a sample of the 8M nitric acid soak/flush solution following contact with the line could be informative in assessing the relative success of the remediation effort. If the rinse is free of Hg and other elements, there was no pluggage material to remove. If the rinse contains significant Hg and/or solids one could conclude that there are contaminants present in the jumper line. Should the flush sample come back positive for the presence of solids, further sampling might not be able to determine whether the PVV jumper line is clear of all materials after all flushing has been completed; this would require a visual inspection.

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LIST OF ABBREVIATIONS AND ACRONYMS

AR	Aqua Regia
ARG	Analytical Reference Glass
CVAA	Cold Vapor Atomic Absorption Spectroscopy
DWPF	Defense Waste Processing Facility
EDS	Energy Dispersive X-Ray Spectroscopy
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
PF	Peroxide Fusion
PVV	Process Vessel Vent
SEM	Scanning Electron Microscopy
SMECT	Slurry Mix Evaporator Condensate Tank
SRNL	Savannah River National Laboratory
TAR	Technical Assistance Request
XRD	X-Ray Diffraction

1.0 Introduction

On April 2, 2013, a solid sample of material collected from the Defense Waste Processing Facility's Process Vessel Vent (PVV) jumper for the Slurry Mix Evaporator Condensate Tank (SMECT) was received at the Savannah River National Laboratory (SRNL). DWPF has experienced pressure spikes within the SMECT and other process vessels which have resulted in processing delays while a vacuum was re-established. Work on this sample was requested in a Technical Assistance Request (TAR)[1]. This document reports the results of chemical and physical property measurements made on the sample, as well as insights into the possible impact to the material using DWPF's proposed remediation methods. DWPF was interested in what the facility could expect when the material was exposed to either 8M nitric acid or 90% formic acid, the two materials they have the ability to flush through the PVV line in addition to process water once the line is capped off during a facility outage.

2.0 Experimental Procedure

2.1 Receipt Inspection

The sample arrived at SRNL in a DWPF primary container marked PC-121 and was loaded into the Shielded Cells. It was comprised of 8.255 g of heterogeneous, both in color and grain size, solids which were mottled gray and crumbly in appearance. Bigger pieces of the material broke up easily, though some larger pieces did stick to the spatula during our attempt to homogenize the material prior to sampling for x-ray diffraction (XRD) and scanning electron microscopy (SEM), precluding the use of a mortar and pestle to further homogenize the material. The sample did not stick to the stainless steel primary container used to ship the container to SRNL.

2.2 Compositional Characterization

Three SEM probe tips were used to collect solids for analysis by Energy Dispersive x-ray Spectroscopy (EDS) and to obtain SEM images, and 102 mg of material was submitted for XRD. The range of particle sizes for the material is shown in Figure 2-1 prior to drying and digestion for elemental analysis. The material was dried at 110 °C for several days prior to digestion by aqua regia (AR)[2] or alkali peroxide fusion (PF)[3]. The AR digestions were done in triplicate along with an Analytical Reference Glass (ARG)[4] and the PF digestions were conducted on a single sample to check the results obtained by the DWPF Laboratory. The AR digestions were analyzed by inductively coupled plasma – atomic emission spectroscopy (ICP-AES), inductively coupled plasma – mass spectroscopy (ICP-MS), and cold vapor atomic absorption (CVAA) spectroscopy for Hg. The PF digestion was analyzed by ICP-AES.

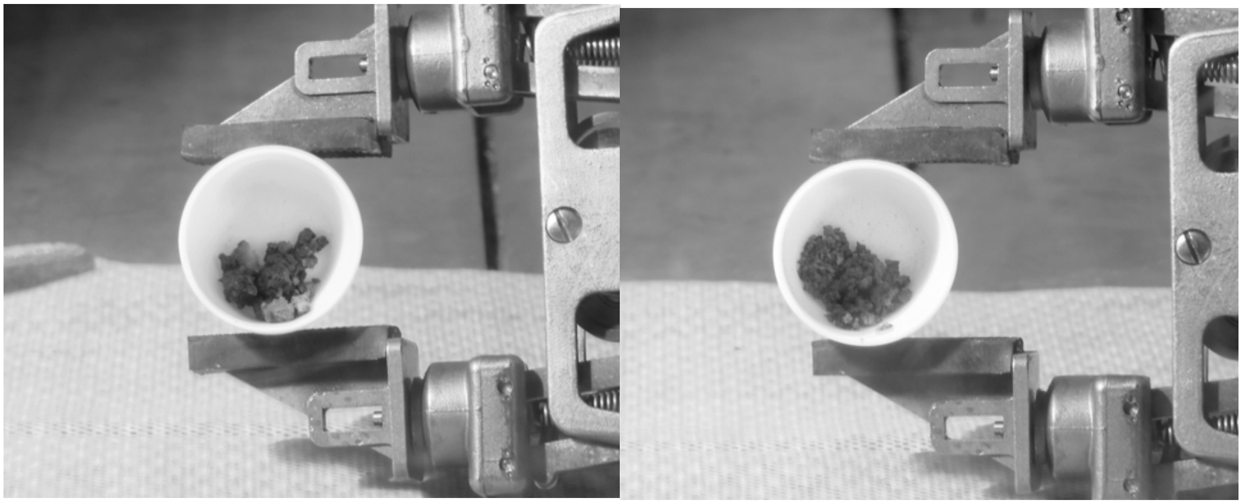

Figure 2-1. DWPF SMECT PVV Solids Prior to Drying at 110 °C

2.3 Sample Leaching Study

SRNL exposed two samples of approximately 0.5 g each of undried SMECT PVV solids to 150 mL of 8M nitric acid and two separate 0.5 g samples to 90% formic acid overnight. The leachate was then analyzed by ICP-AES, ICP-MS and CVAA for Hg, while the remaining solids were collected by vacuum filtration, rinsed with deionized water, air dried and submitted for SEM and XRD analyses. The mass of solids remaining following each of the leach tests was determined in order to calculate the percent of dissolution observed in each test.

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 As Received Material

The material when dried at 110 °C was approximately 82 wt.% total solids (%RSD 7.6) with a range of 76 – 88 wt.% for the three replicates.

The XRD spectra obtained for the as-received SMECT PVV material is shown in Figure 3-1. Two species are confirmed, Bohmite [$AlO(OH)$] and Magnetite [Fe_3O_4], the remaining species shown in Figure 3-1 are speculative. A Hg compound is suspected in the material, but no match could be obtained in the spectral database. This is in contrast to the Hg that was found by XRD in the GC Line Filter Assembly and identified as a mixture of $Hg_4(OH)(NO_3)_3$ and $Hg_{10}(OH)_4(NO_3)_6$.[5] There are also a number of major unassigned peaks in the SMECT PVV sample spectrum.

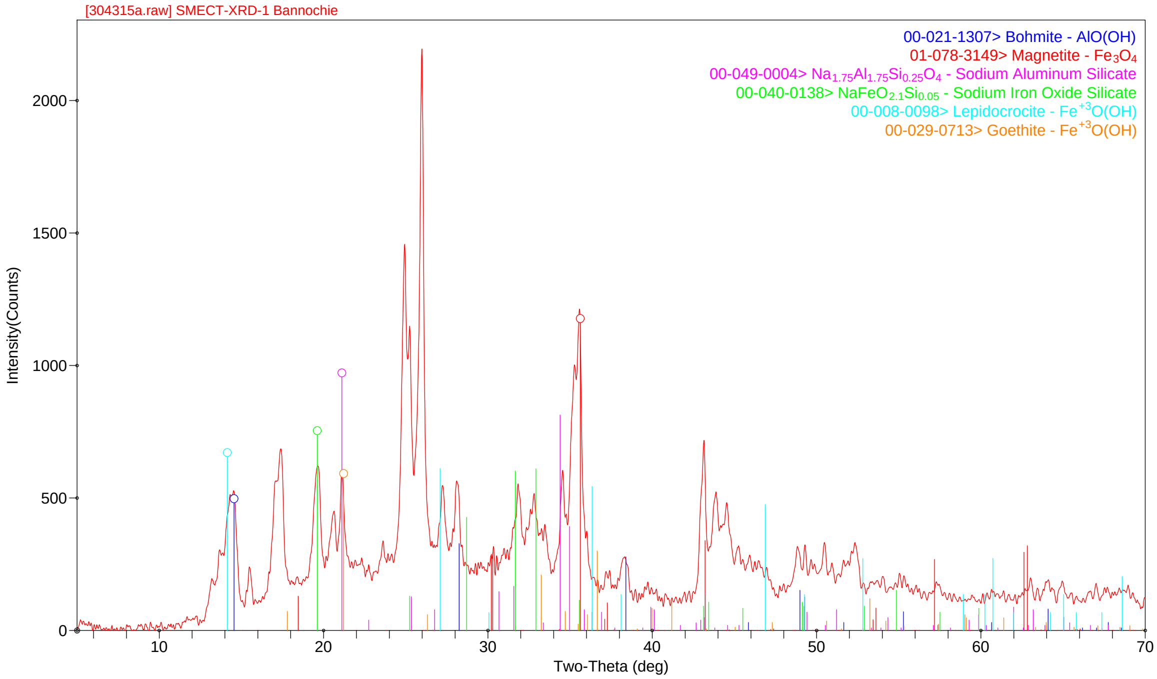

Figure 3-1. XRD Spectra of As-Received SMECT PVV Material

SEM images were captured for the as-received material collected on each of the three probes submitted. An EDS raster scan of the material indicated the presence of Al, Fe, Hg, and Si, and lesser amounts of Na, K, Ca, Cu, and Ni. Spot analyses showed material that was primarily Hg, a mixture of Hg and Al/Fe silicates, Th containing species, Si species, and primarily Al species. The SEM image from which the raster scan was taken is shown in Figure 3-2, and Figure 3-3 provides the EDS spectra obtained for this scan area.

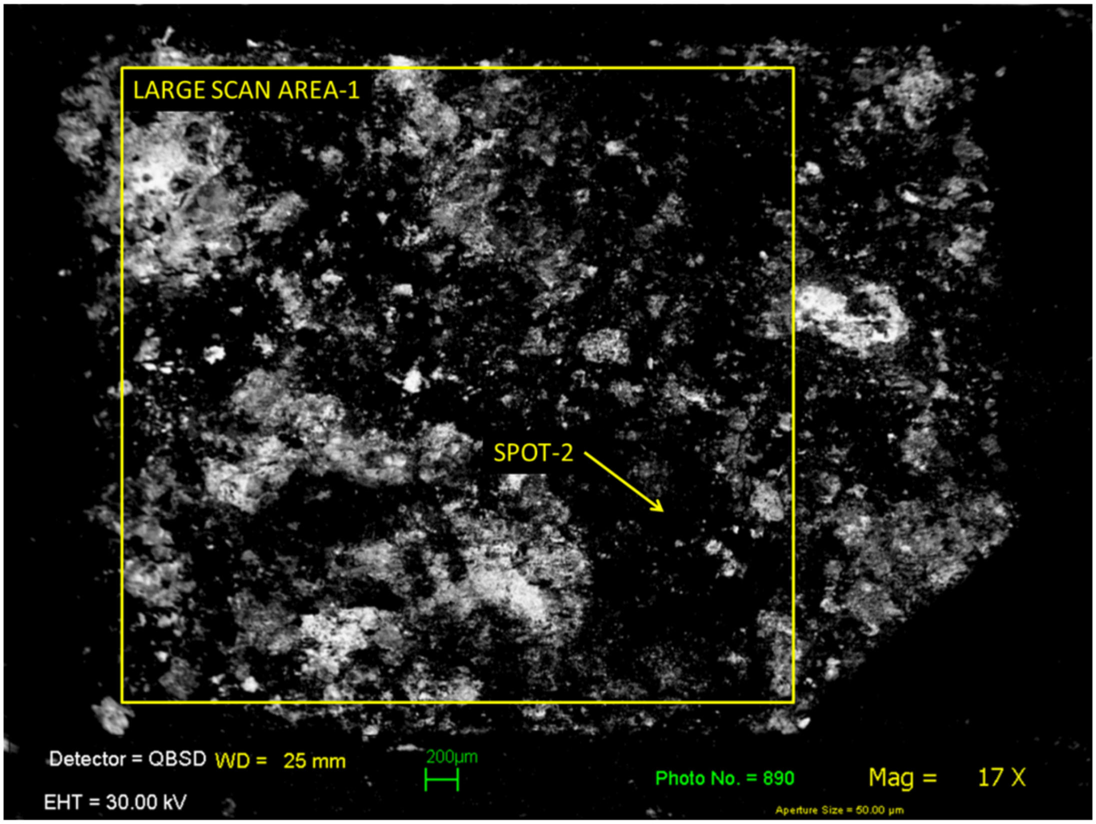

Figure 3-2. SEM image showing area of raster scans where Al, Fe, Hg, Si, Na, K, Ca, Cu, and Ni were identified. Spot 2 is the Carbon Tape Background area that was scanned.

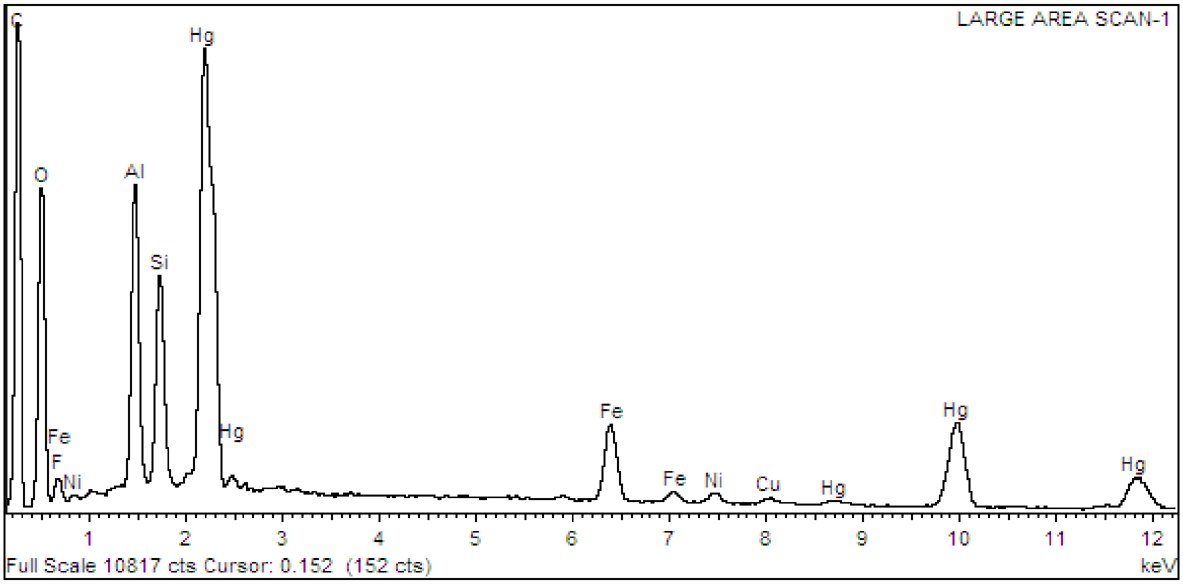

Figure 3-3. EDS spectra of large scan area shown in Figure 3-2.

Thorium was not identified in the raster scan shown in Figure 3-2, but it was identified in a number of EDS spot analyses taken on the submitted samples. Figure 3-4 shows one of the EDS spectra that identified the presence of Th in the material. In addition to the EDS spectra, ICP-AES and ICP-MS data collected from the AR digestion of the dried solids also indicated the presence of Th (Table 3-1).

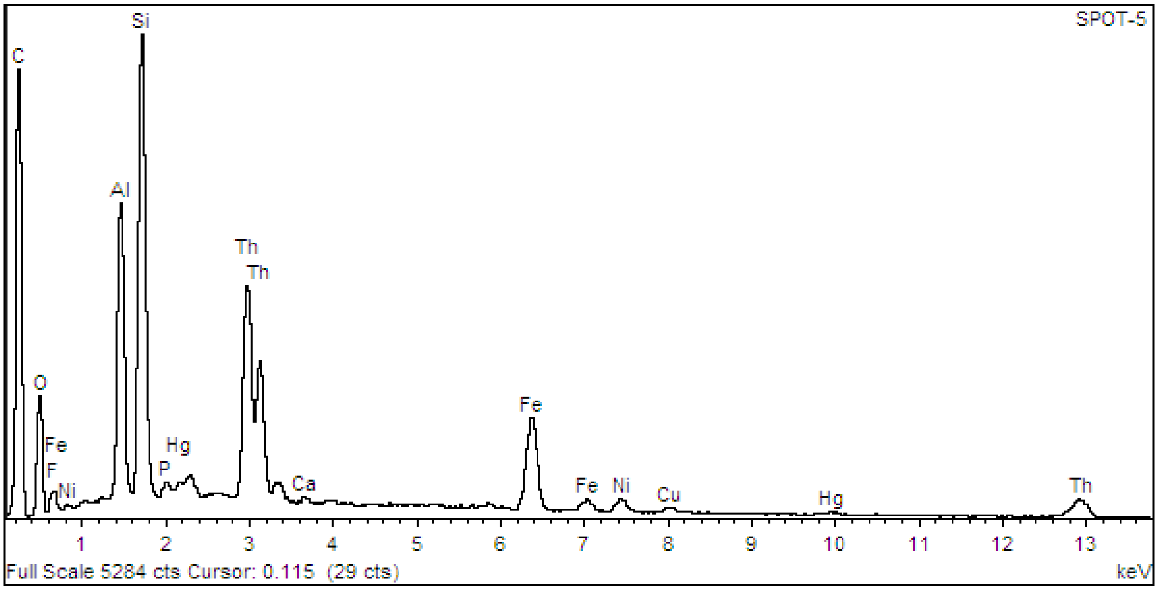

Figure 3-4. EDS spectra of a spot analysis showing the presence of Th in the SMECT PVV sample.

The elemental composition derived from measurements of digested sample at both DWPF and SRNL is summarized in Table 3-1. Unless otherwise indicated in the table the data was obtained by ICP-AES measurements. Values ≥0.1 wt.% as determined by at least one analytical method or laboratory are included in the table. The relative order of abundance of elements is Hg>>Al>Fe>Si>Th≈Ni.

Table 3-1. Elemental Composition of the Digested DWPF SMECT PVV Sample in Wt.% of Total Dried Solids (%RSD) [No. of Replicates]. Data obtained via ICP-AES unless otherwise indicated.

Element	DWPF PF[a] wt.% TS	SRNL AR[b] wt.% TS	SRNL PF[a] wt.% TS
Al	**7.26** (3.3) [4]	2.96 (18) [3]	**7.83** [1]
Ca	**0.0393** (28) [4]	**0.0252** (11) [3]	0.301 [1]
Cr	0.161 (9.1) [4]	0.0289 (36) [3]	0.0393 [1]
Fe	**5.20** (5.2) [4]	4.42 (18) [3]	**5.12** [1]
Hg	22.9[c] (1.0) [2]	**16.3**[d] (8.2) [3]	NA
Mn	**0.152** (8.5) [4]	0.119 (20) [3]	**0.150** [1]
Na	NA	**0.0994** (11) [3]	NA
Ni	**0.836** (6.6) [4]	0.650 (6.9) [3]	**0.764** [1]
P	NA	**0.0900** (14) [3]	DL[f]
Si	**3.76** (9.8) [4]	NA	**2.63** [1]
Th	0.746 (7.3) [4]	**0.915**[e] (19) [3]	**1.00** [1]
U	0.147 (19) [4]	**0.0616**[e] (9.2) [3]	DL[f]
Zr	NA	**0.186** (13) [3]	NA

NA ≡ Not Available, a) PF ≡ peroxide fusion, b) AR ≡ aqua regia digestion, c) DWPF cold chem digestion analyzed with a Hg analyzer, d) CVAA, e) ICP-MS, f) Detection Limit

Values with the highest confidence level are shown in bold, but the heterogeneous nature of the solids analyzed may be the source of much of the uncertainty and variability in the data.

3.2 Nitric and Formic Acid Leaching

Leachate samples from an overnight soak of the as-received SMECT PVV solids at room temperature in 8M nitric acid or 90 wt.% formic acid were collected and submitted for analysis as previously described in Section 2.3. The elemental results are shown in Table 3-2 for the nitric acid leach. Only constituents found at levels above the detection limit are provided in the table. The large amount of Th in the material resulted in ICP-AES interferences for U, so the U concentrations were reported from ICP-MS measurements. There is a fair amount of variability between the two replicates which seems to support the heterogeneous nature of the material. For this reason the two replicate leach tests were not averaged.

Table 3-2. Elemental Composition in mg/L of Leachate and mg/g of Dissolved SMECT PVV Material for the 8M Nitric Acid (N. A.) Leachate

Element	mg/L Leachate N. A. Repl. 1	mg/g Dissolved Material N. A. Repl. 1	mg/L Leachate N. A. Repl. 2	mg/g Dissolved Material N. A. Repl. 2
Al	2.84	1.57	2.91	1.76
Ba	0.129	0.0711	0.0752	0.0455
Ca	0.800	0.441	0.480	0.290
Ce	0.484	0.267	0.431	0.261
Cr	0.107	0.0590	0.0742	0.0449
Cu	0.120	0.0662	0.0868	0.0525
Fe	21.1	11.6	13.7	8.29
Hg[a]	861	475	625	378
La	0.0790	0.0436	0.0518	0.0313
Li	0.0824	0.0454	0.0398	0.0241
Mg	0.186	0.103	0.564	0.341
Mn	1.45	0.800	0.737	0.446
Na	4.35	2.40	2.57	1.55
Ni	2.56	1.41	1.78	1.08
P	1.74	0.960	1.13	0.683
Si	1.54	0.849	1.04	0.629
Sr	0.0221	0.0122	0.0133	0.00804
Th	4.61	2.54	4.67	2.82
Ti	0.927	0.511	0.593	0.359
U[b]	2.32	1.26	1.28	0.761
Zn	0.285	0.157	0.0947	0.0573
Zr	1.85	1.02	1.45	0.877

a) CVAA, b) ICP-MS

By far the largest contributor to the dissolved mass is from Hg containing species. In the case of the 8M nitric acid leach, there was a loss of mass of 51% for Replicate 1 and 53% for Replicate 2.

The elemental results are shown in Table 3-3 for the formic acid leach. Again, only constituents found at levels above the detection limit are provided in the table. There was less variability between the two formic acid replicates than what was observed between the nitric acid replicates. During sample preparation prior to analysis, a 10x dilution of the formic acid leachate resulted in a cloudy solution, so a decision was made to analyze the sample with a 20x dilution, which produced a clear diluent. The high dilution relative to the nitric acid leachates (2x) resulted in the higher detection limits for many of the elements. The most notable difference when comparing the two data sets is the observation that far less

Hg dissolved into the formic acid leaches than was recorded for the nitric acid leaches. Outside of Hg, there were roughly equivalent amounts of Al, Ca, Mn, Na, and Zn; far less Fe, Th, and U; and more Si dissolved by the formic acid leach. Excluding the difference in Hg, there was roughly an equivalent mass of other elements dissolved in the two acids. In the case of the 90% formic acid leach, there was a loss of mass of 29% for Replicate 1 and 34% for Replicate 2.

Table 3-3. Elemental Composition in mg/L of Leachate and mg/g of Dissolved SMECT PVV Solids for the 90% Formic Acid (F. A.) Leachate

Element	mg/L Leachate F. A. Repl. 1	mg/g Dissolved Solids F. A. Repl. 1	mg/L Leachate F. A. Repl. 2	mg/g Dissolved Solids F. A. Repl. 2
Al	2.74	3.00	2.95	2.68
Ca	0.847	0.927	0.948	0.862
Fe	8.05	8.81	8.56	7.78
Hg[a]	0.0963	0.105	0.0990	0.0900
Mg	0.152	0.166	0.128	0.116
Mn	1.15	1.26	0.979	0.890
Na	3.95	4.32	3.62	3.29
Ni	1.28	1.40	1.20	1.09
Si	3.29	3.60	4.29	3.90
Sr	0.0150	0.0164	0.0120	0.0109
Th[b]	0.220	0.241	0.264	0.240
U[b]	0.845	0.925	0.846	0.769
Zn	0.165	0.181	0.156	0.142

a) CVAA, b) ICP-MS

The solids collected from each of the leaching characterizations are shown in Figure 3-5 and Figure 3-6. The solids did not "collapse" upon introduction and soaking in either acid. After they were recollected from the leachate, the solids remained tacky following rinsing with deionized water and air drying.

Figure 3-5. Leached solids collected from overnight exposure to 8M nitric acid.

Figure 3-6. Leached solids collected from overnight exposure to 90% formic acid.

The solids collected from the leach analyses were submitted for XRD and SEM examination. The XRD spectra collected on the solids remaining following the nitric acid leach are shown in Figure 3-7 and those following the formic acid leach are shown in Figure 3-8. As was observed for the initial as-received SMECT PVV solids (Figure 3-1), the solids following both leach tests indicate the presence of Bohmite and Magnetite, along with a number of other absorption peaks which could not be assigned to structures in the spectral database.

The EDS examination of the SEM samples did show the presence of distinguishable Hg content despite the 8M nitric acid leach having preferentially dissolved Hg as demonstrated by the ICP-AES data presented previously in Table 3-2. Figure 3-9 shows the light areas of high Hg content (Spot 1) in a sample that was largely comprised of Al, Fe, and Si (Spots 2 and 3). It is unclear whether this area of Hg is due to undissolved Hg that may have dissolved if given longer exposure to the 8M nitric acid, or if it is a Hg species that was not removed when the leach solution was rinsed from the sample with deionized water, allowing it to reprecipitate on the other undissolved compounds during air drying of the sample prior to analysis.

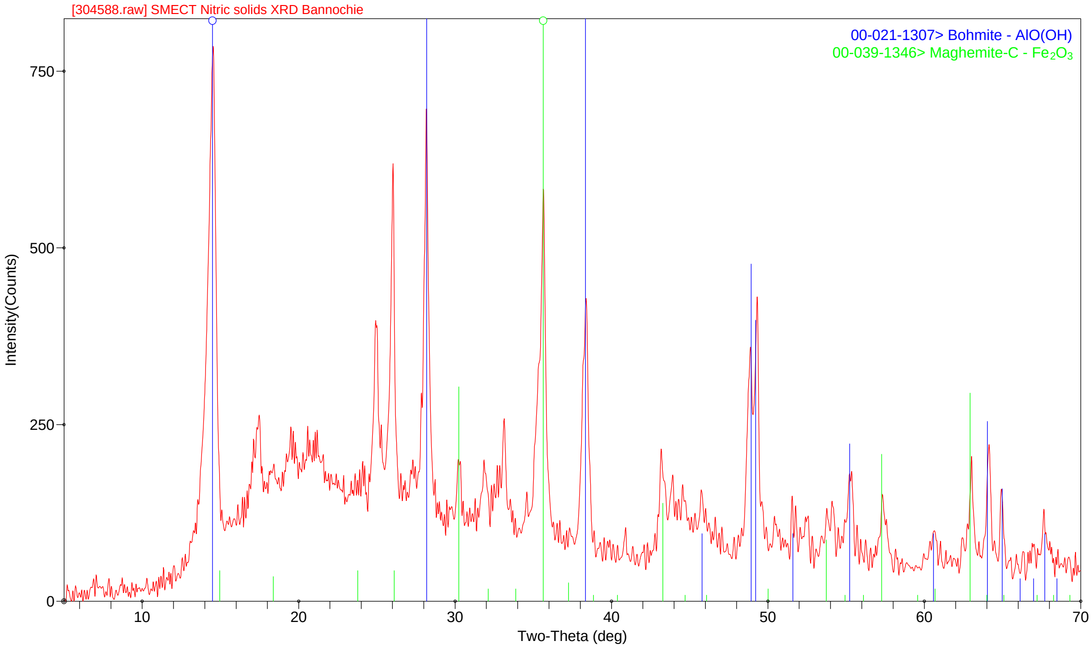

Figure 3-7. XRD spectra of residual solids collected after an 8M nitric acid leach of DWPF SMECT PVV solids.

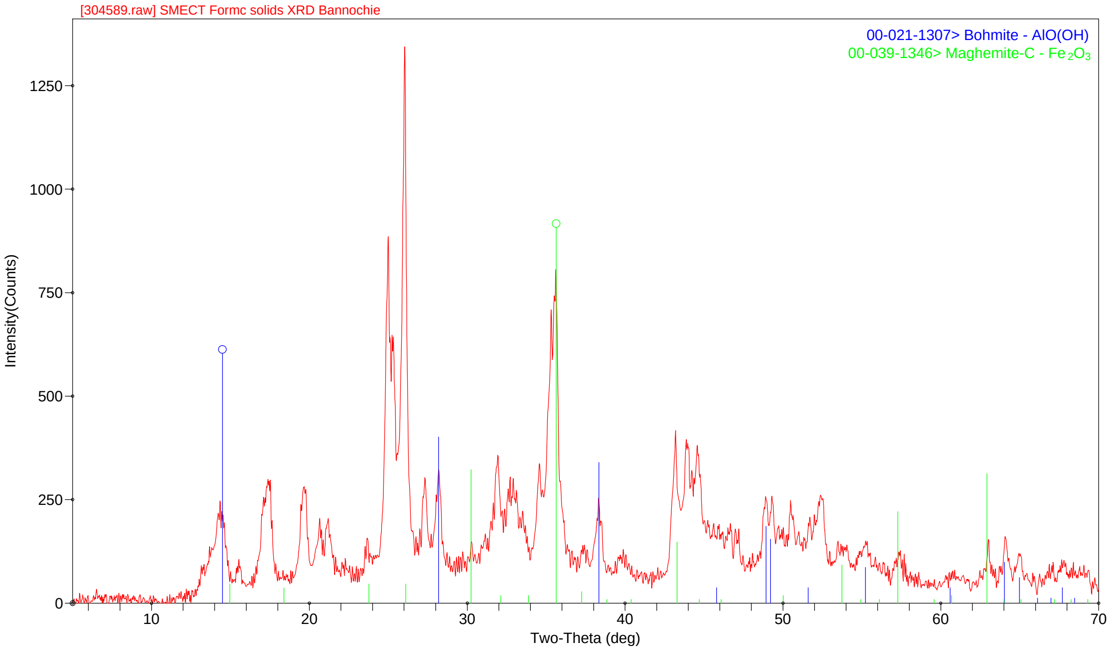

Figure 3-8. XRD spectra of residual solids collected after a 90% formic acid leach of DWPF SMECT PVV solids.

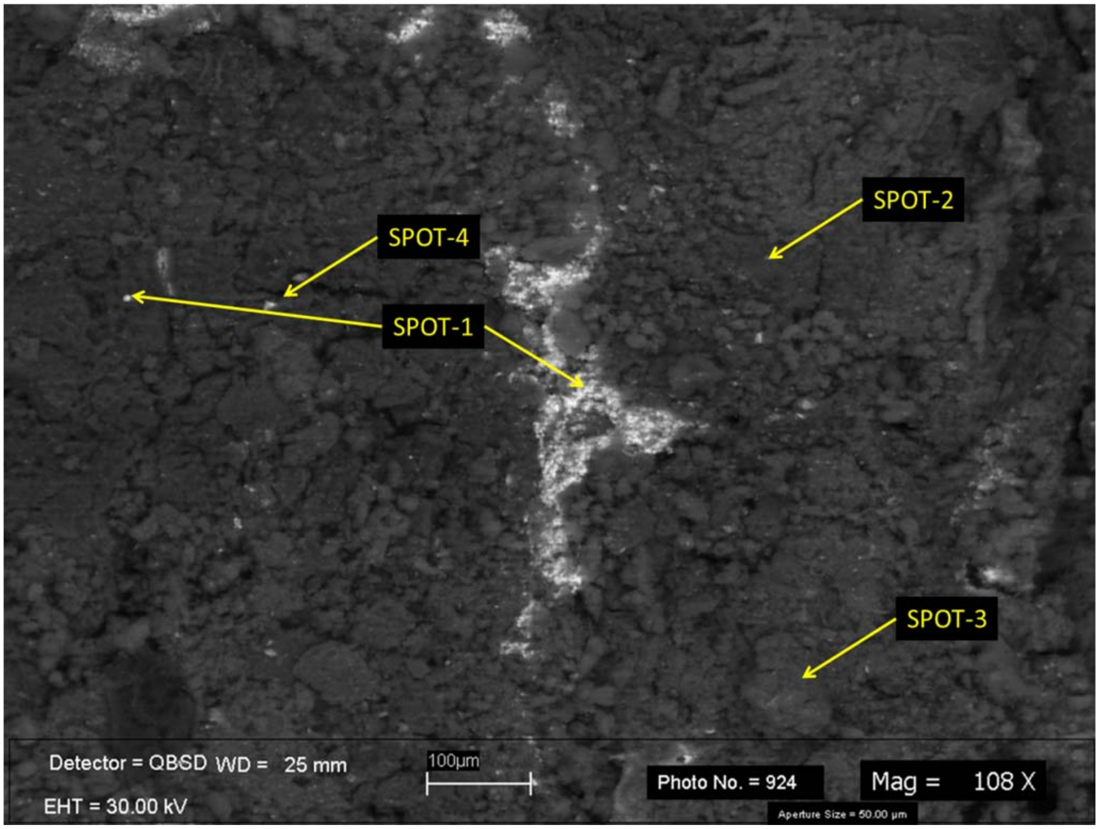

Figure 3-9. SEM image showing area of high Hg content (Spot 1) in nitric acid leached SMECT PVV solids.

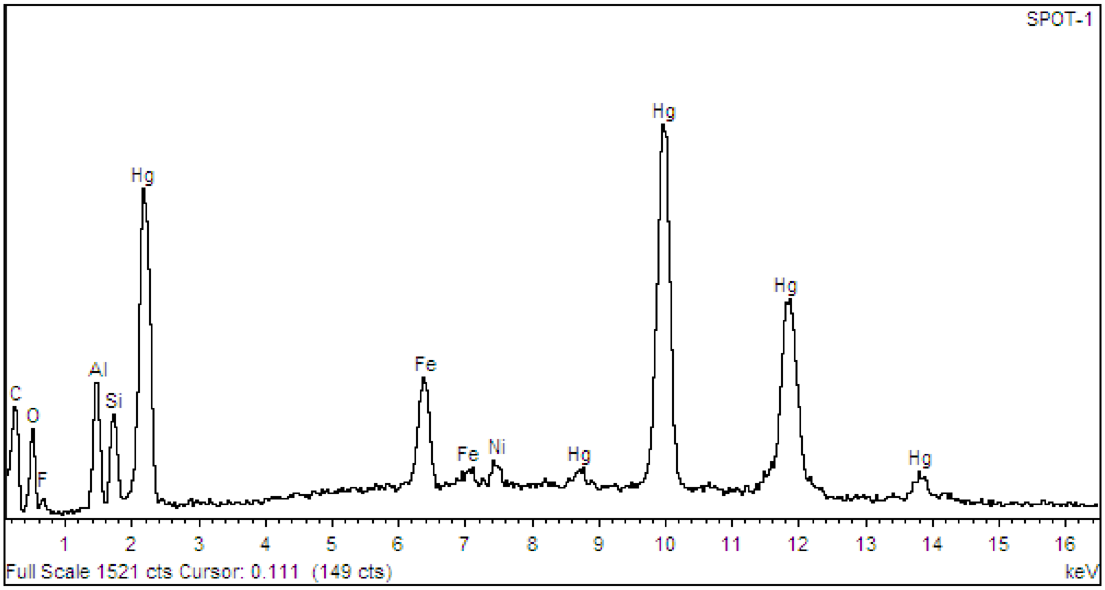

Figure 3-10. EDS spectra from Spot 1 showing the presence of Hg in the post nitric acid leached SMECT PVV sample

The SMECT PVV solids collected following a 90% formic acid leach and deionized water rinse showed broad areas of Hg containing compounds consistent with the much smaller dissolution of Hg that occurred from the sample when it was exposed to the formic acid leach (see data in Table 3-3). Spots labeled 1 in Figure 3-11 indicate primarily Hg containing compounds, as do Spots 4 – 6 in Figure 3-12. The remaining spots (2 and 3) were primarily Al and Si containing materials, possibly resulting from entrained frit.

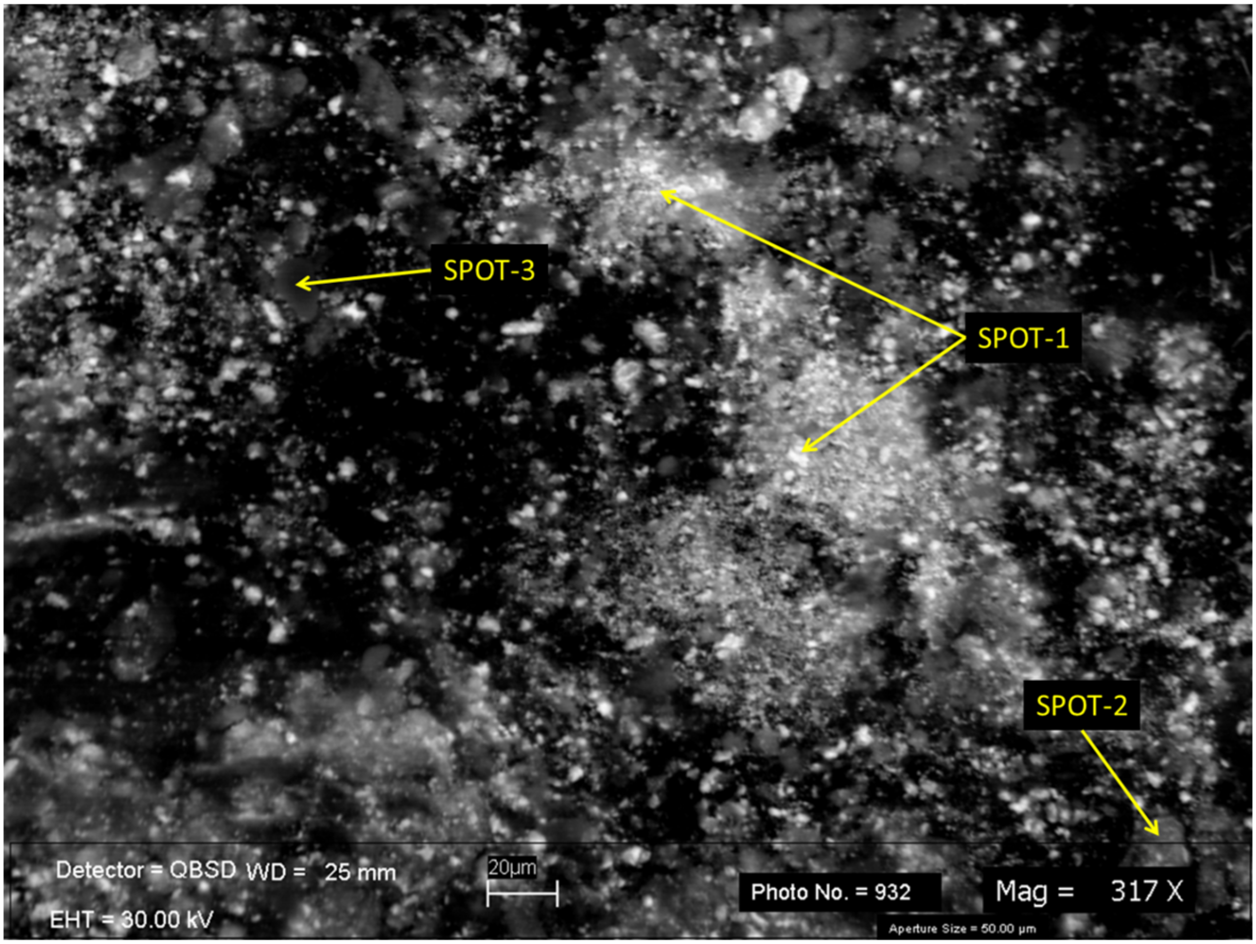

Figure 3-11. SEM image showing area of high Hg content (Spot 1) in formic acid leached SMECT PVV solids.

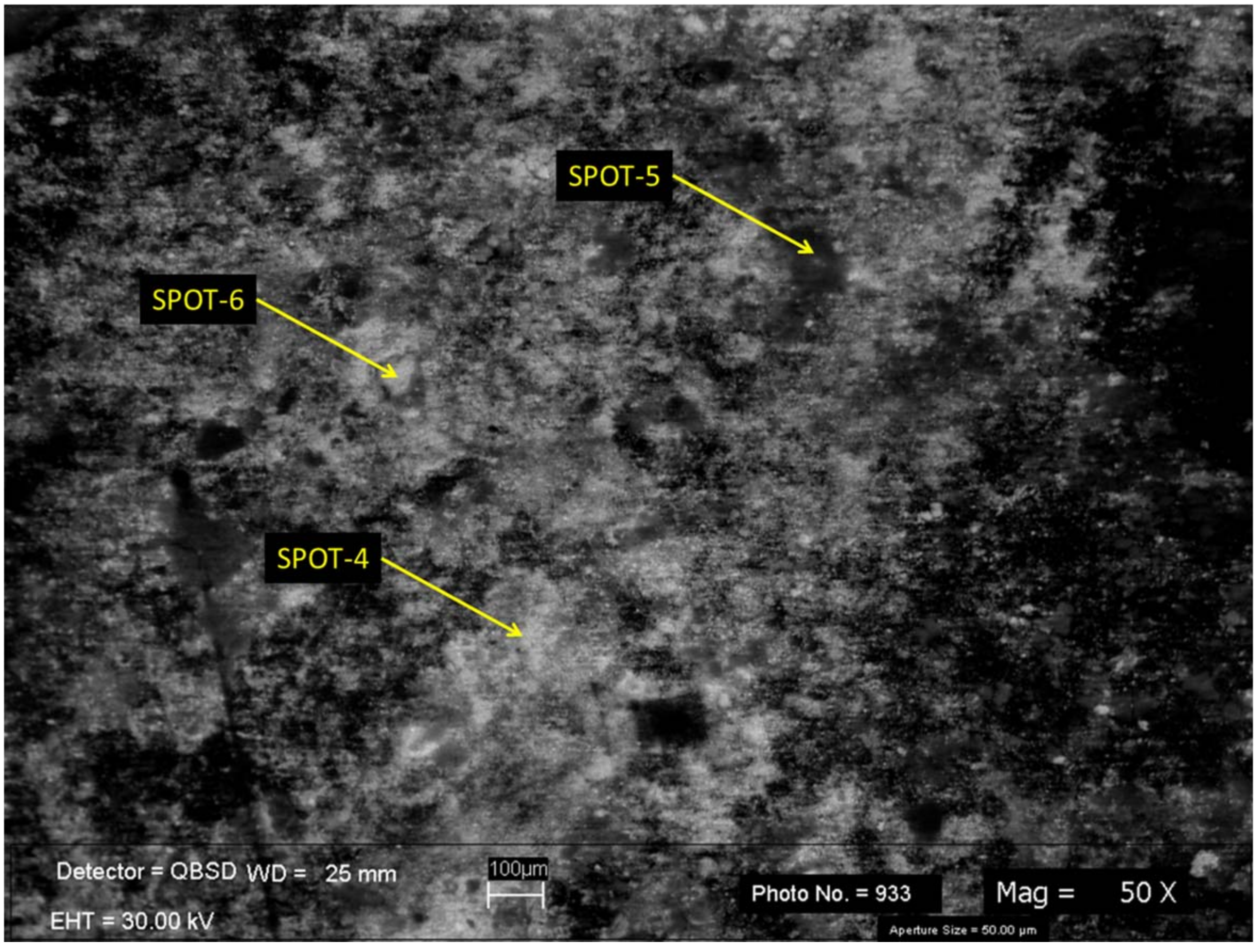

Figure 3-12. SEM image showing areas of Hg content (Spot 4, 5, and 6) in formic acid leached SMECT PVV solids.

3.3 Unanswered Question

What was not determined for the DWPF SMECT PVV sample was how much of the 18% loss on drying was due to moisture vs. possible elemental Hg loss. There was no visible sign of elemental Hg, but the presence of an amalgam with other constituents in the sample cannot be ruled out with the information collected to date.

4.0 Conclusions

Based upon the SRNL analysis of the SMECT PVV jumper sample material, the following conclusions are put forth:

a) The sample material is a heterogeneous mixture of crystalline and non-crystalline species comprising approximately 82 wt.% total solids.

b) The order of abundance of elements in the sample is: Hg>>Al>Fe>Si>Th≈Ni. The Hg species is non-crystalline and was not identified.

c) The material is completely solubilized using a peroxide fusion digestion; mostly solubilized with a hot, pressurized aqua regia digestion leaving primarily Bohmite [AlO(OH)] undissolved; partially solubilized with 8M nitric acid leaving predominately Bohmite and Magnetite [Fe_3O_4] undissolved along with other trace species; and a bit less partially solubilized with 90% formic acid leaving predominately Bohmite, Magnetite, and Hg species undissolved along with other trace species.

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e) The dissolution test with 90% formic acid resulted in far less Hg dissolution from the material, as compared to the 8M nitric acid test, and an overall mass reduction of ~31%.

5.0 Recommendations

Of the two proposed remediation methods presented by DWPF to soak and flush the PVV line jumper, 8M nitric acid and 90% formic acid, our testing indicates the 8M nitric acid will have the most impact of the two. The nitric acid will dissolve at least an order of magnitude more Hg from the material, though some sludge components and frit present in the material will remain. The impact of a subsequent pressurized water rinse of the line could not be simulated, so its efficacy in removing the undissolved solids is unclear.

The collection and analysis of a sample of the 8M nitric acid soak/flush solution following contact with the line could be informative in assessing the relative success of the remediation effort. If the rinse is free of Hg and other elements, there was no pluggage material to remove. If the rinse contains significant Hg and/or solids one could conclude that there are contaminants present in the jumper line. Should the flush sample come back positive for the presence of solids, further sampling might not be able to determine whether the PVV jumper line is now clear of all materials after all flushing has been completed, this would require a visual inspection.

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