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Characterization of Three Samples Taken From the Off Gas System of DWPF Melter One

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC09-96SR18500

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LIST OF ACRONYMS

ADS	Analytical Development Section
CSEM	Contained Scanning Electron Microscopy
CXRD	Contained X-Ray Diffraction
DWPF	Defense Waste Processing Facility
EDAX	Energy Dispersive S-Ray Analysis
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Excitation Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
PC	Primary Container
RSD	Relative Standard Deviation
SB	Sludge Batch
SRAT	Sludge Receipt Adjustment Tank
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TRM	Telerobotic Manipulator

INTRODUCTION AND SUMMARY

The first melter (Melter One) in the Defense Waste Processing Facility (DWPF) operated for more than eight years. It has been removed from service and replaced by Melter Two. For six of the eight years Melter One had been in radioactive operations immobilizing SRS high level waste sludges into a stable borosilicate glass for disposal in a geologic repository. Prior to DWPF radioactive operations there were two years of testing and qualification runs with nonradioactive simulated sludge.

During the eight years of DWPF operation an off gas system was attached to the melter to condense steam generated in the melter plenum and collect any entrained solids or volatilized species. This off gas system had been in operation during processing of Sludge Batches 1A and 1B and a portion of Sludge Batch 2. During the replacement of Melter One in 2002, DWPF had the opportunity to take samples of three deposits from the off gas system. One of the three samples came from deposits in the off gas system just above the film cooler in the primary off gas line. Here the temperature was nominally 350-400°C. [1] Thus there was no possibility of off gas condensate water contacting this deposit. The other two samples were taken from deposits at the inlet and the bottom of the quencher. Here the temperatures were ~350°C and <100°C, respectively. These three samples of the deposits were taken on 11/18/02 and transported to SRTC on 5/8/03 for characterization.

The primary objective of this characterization was to determine if there was any evidence for the accumulation of fissile material relative to the element Fe in the deposits. Secondary objectives were to determine their chemical and crystalline compositions and determine what species could be leached from the deposits and appear in condensate water going to the SRS Tank Farm system. Results are summarized below.

- There was no evidence of accumulation of fissile material relative to Fe. The ratio of Fe to fissile material in the deposits was nominally 600 in the sample from the primary line and nominally 800 to 2000 in the deposits from the quencher. This ratio in Sludge Batch 2 (SB2) is 560 [2] and the critically safe ratio is 160 [3]).
- The chemical composition of the samples was a mixture of sludge and glass species. The element Si was a major component (14-20 weight percent) in all three deposits. The deposit from the primary line contained ~12 wt. % Na, and ~6% Fe and S. In the two deposits from the quencher, the Na and S were considerably lower and the Fe correspondingly higher. All the deposits contained U-235 fission products and actinide elements.
- From the chemical compositions, evidence was obtained for the some volatility of Cs-137, Tc-99 and Hg from the melter. However, data obtained from the analysis of three glass samples from the melter during processing Sludge Batch 1A, indicate that >93% of the Cs-137 and Tc-99 are retained in the molten glass and immobilized. [4] The element Hg is streamed stripped in the DWPF from the sludge prior to the vitrification process. It has been shown that 92% of the Hg can be removed by this process. [2]. Detection of Hg in the off gas system indicates that a small amount of Hg reaches the melter and is volatilized.

- The chemical compositions of the samples also indicate that molten glass containing dissolved sludge is not getting from the melter into the off gas system where the samples were collected.
- A water leach test indicated that 93% of the S and 74 % of the Na could be dissolved from the sample of deposits in the primary off gas line where the temperature was nominally 400°C. A much lower percentage (10-20%) from the deposits taken from the quencher. There was also evidence of B leaching from the deposits. These results are consistent with the extensive analyses of off gas deposits obtained from several melter campaigns performed during the development of the DWPF process. [5,6] In the present study the fraction of Si and U dissolved from all three deposits was only ~1-2%. The major anion leached was sulfate. This result suggests that one soluble species that may be going to the Tank Farm system from the melter off gas condensate water is sulfate, presumably Na_2SO_4. No soluble chlorides or fluorides were detected in the leachates from the off gas deposits.
- The primary crystalline compound in all three deposits was Fe_2O_3 consistent with the results in References 4 and 5. The deposit from the primary line also contained Na_2SO_4; however this compound was not present in the deposits from the quencher. No evidence was obtained for the presence of crystalline NaCl. Not detecting crystalline NaCl is in contrast with results from analyses of deposits from off gas lines attached to melters used to develop the DWPF process.[5,6] However, the deposits taken in that study were taken further up the off gas line. Also the presence of NaCl in the off gas system would be very dependent on its concentration in the melter feed being processed.
- Examination by Scanning Electron Microscopy indicated that the deposits had primarily rounded particles rather than distinct crystals. Also the elements were not distributed uniformly throughout the deposits indicating that the deposits were mixtures of chemical compounds. This observation is also consistent with previous studies.[5,6]

EXPERIMENTAL

Obtaining Samples of Off Gas Deposits

Samples were taken from deposits at three different locations in the off gas system. They were obtained by suspending the primary off gas line and the quencher of the off gas system from the main process crane in the DWPF melt cell after the off gas line had been disconnected from Melter One. The samples were then obtained remotely. The telerobotic manipulator (TRM) was used to manipulate sharp-edged sample cups on the end of long rods to scrape samples from the areas of interest. These areas were the primary off gas line just past the film cooler, the inlet of the quencher, and the bottom of the quencher near its exit. Each sample was then poured from its sample cup into a new primary sample stainless steel container for transport to SRTC. The sampling location and the designation for the primary container (PC) for each sample are shown in Figure 1

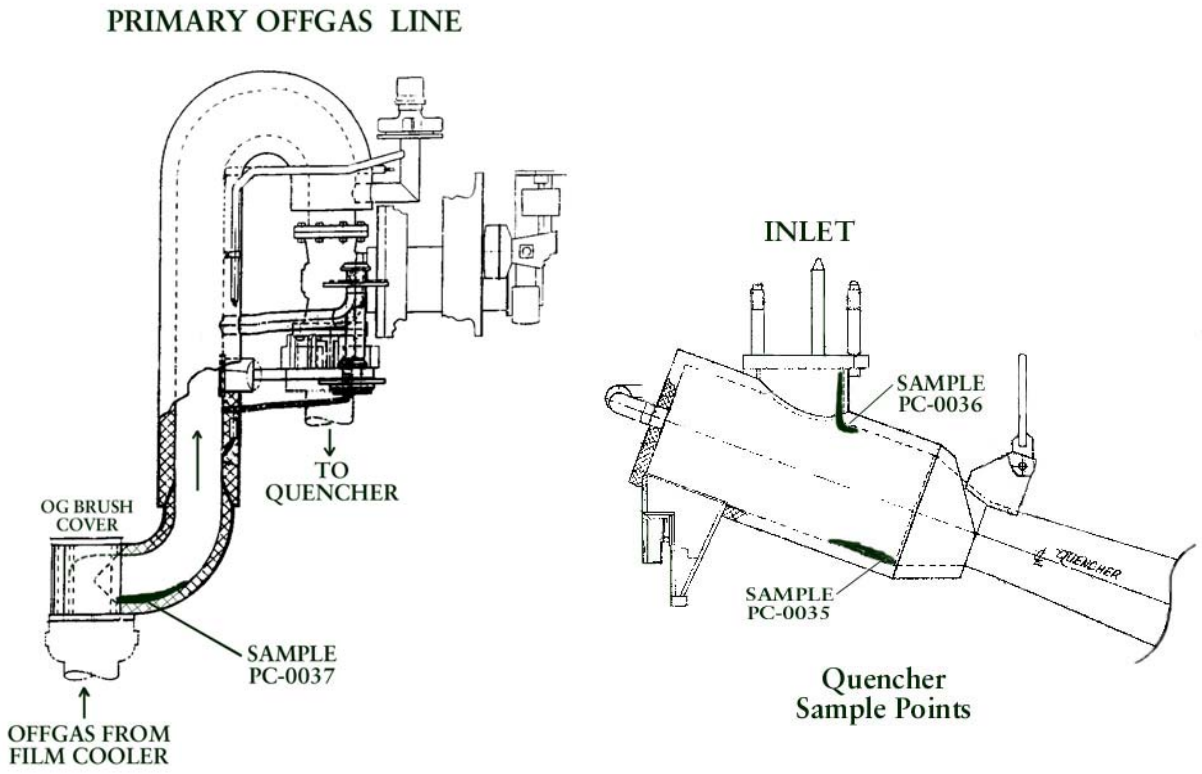

Figure 1. Locations in the DWPF Melter One Off Gas System of the Deposits Sampled (The PC designations for each sample indicate the primary containers that the samples were placed in for transport to SRTC.)

The sample from the primary off gas system just past the film cooler was placed into PC0037. The sample from the inlet to the quencher was placed into PC0036 and the sample from the bottom of the quencher into PC0035. The primary containers with their respective samples were then transported to SRTC. At SRTC the containers were placed in the Shielded Cells. Here they were opened and the samples removed and characterized.

Visual Observations and Weights

At SRTC the samples were poured from their primary containers into small weighed glass jars. The jars were then weighed again to obtain the weights of the samples. Throughout this report the samples will be designated by the number of their primary container. Sample 0036 from the inlet to the quencher weighed 7.211 grams. This sample was the easiest to obtain using the long rod attached to the TRM. The other two samples were more difficult to obtain and consequently smaller amounts of sample resulted. Sample 0035 from the bottom of the quencher and weighed 0.869 grams and Sample 0037 from the primary off gas line and weighed 0.837 grams. Visually, the appearances of the samples were identical. All were black and granular. They were primarily in small pieces with particle sizes ranging from approximately 0.5 to 8mm. The larger particles were easily broken with a micro spatula into smaller particles. These larger particles

were broken up but no attempt was made to grind and homogenize the samples. They were just mixed in the jars by using the micro spatula held by the manipulator.

Composition of the Off Gas Samples

Small amounts of each sample were dissolved remotely in sealed Teflon vessels by the mixed acid technique developed by the Analytical Development Section (ADS) of SRTC. [7] This method is used to dissolve DWPF glass and uses a mixture of HF, HNO_3, and HCl acids. Boron is used in the method; thus the element cannot be determined by this method. The mixed acid method was chosen to ensure that any silicates that may be in the samples were dissolved. Teflon vessels that could be tightly sealed were used to ensure that any elements volatilized during the procedure such as Hg were retained in the solutions during the dissolution. At the end of the dissolution procedure there were no visible solids in any of the acid solutions indicating that the entire amount of each sample had been dissolved. A standard glass was dissolved and analyzed with the samples to check if the dissolutions were performed correctly and the analyses were accurate. Results for the standard glass indicated that this was the case. A blank dissolution (no sample was present) was also performed to check for impurities in the reagents or radioactive contamination that might have resulted from performing the dissolutions remotely in the Shielded Cells. Results of the blank indicated that concentrations of impurities and contaminants were negligible compared to concentrations of the analytes measured.

For Samples 0035 and 0037 only small amounts (~0.1 grams) of duplicate samples were dissolved because of the limited amount of sample obtained. For Sample 0036 where a larger amount of off gas sample was obtained, triplicate samples were dissolved, two weighing ~0.1 grams and one weighing~ 0.25 grams as called for in the procedure [5]. Aliquots of the resulting solutions were removed from the Shielded Cells and submitted to ADS for analysis. They were analyzed by Inductively Coupled Plasma Excitation Spectroscopy (ICP-ES) for elemental concentrations, Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for U-235 fission products and actinides, and counting techniques for gamma emitters and Sr-90.

RESULTS AND DISCUSSION

Results for the compositions of the three off gas samples are in Tables 1, 2, and 3. Each Table, gives the concentrations measured in the individual samples, the average of the two or three replicates and the percent relative standard deviation (%RSD) of the results.
Results for the three off gas samples are in Tables 1, 2, and 3. Each Table, gives the concentrations measured in the individual samples, the average of the two or three replicates and the percent relative standard deviation (%RSD) of the results.

Table 1. Composition of Melter Off Gas Sample 0037 Taken from the Primary Off Gas Line of the Melter

Elements Measured by ICP-ES

Concentrations are given in weight percent.

Element	0037-1(a)	0037-2(b)	Average	%RSD
Ag	0.08	0.07	0.08	9.5
Al	1.21	1.25	1.23	2.6
Ca	0.63	0.62	0.62	1.5
Cd	0.48	0.42	0.45	9.1
Cr	0.16	0.20	0.18	12
Cu	0.01	0.01	0.01	0.4
Fe	5.11	5.14	5.13	0.4
Hg	<0.01	ND	ND	ND
Li	0.34	0.37	0.34	7.4
Mg	0.46	0.48	0.46	3.5
Mn	0.74	0.75	0.75	0.8
Na	11.43	12.08	11.75	3.9
Ni	0.18	0.26	0.22	26
S	6.82	6.45	6.64	3.9
Si	20.00	18.30	19.15	6.3
Sn	0.26	0.21	0.24	13
Sr	0.13	0.13	0.13	1.9
U	1.24	1.21	1.22	1.8

Radionuclides Measured by Gamma Beta Counting

Concentrations are given in microcuries/gram.

Sr-90	9.40E+02	9.22E+02	9.31E+02	1.3
Cs-137	2.71E+03	2.40E+03	2.56E+03	8.8

Isotopes Measured by ICP-MS

Concentrations are given in weight percent.

Tc-99	1.19E-02	1.30E-02	1.25E-02	6.1
Mo-100	7.06E-04	9.94E-04	8.50E-04	24
Ru-101	4.70E-03	5.92E-03	5.31E-03	16
Ru-102	3.94E-03	5.13E-03	4.53E-03	19
Rh-103	1.73E-03	1.69E-03	1.71E-03	1.9
Ru-104	2.34E-03	3.04E-03	2.69E-03	19
Pd-105	9.93E-05	1.34E-04	1.17E-04	21
U-233	5.08E-05	5.22E-05	5.15E-05	1.9
U-234	1.46E-04	1.42E-04	1.44E-04	2.1
U-235	5.85E-03	5.75E-03	5.80E-03	1.3
U-236	4.12E-04	3.76E-04	3.94E-04	6.4
Np-237	3.81E-04	2.96E-04	3.39E-04	18
U-238	1.32E+00	1.42E+00	1.37E+00	5.2
Pu-239	2.73E-03	2.54E-03	2.63E-03	5.1
Pu-240	2.21E-04	2.05E-04	2.13E-04	5.3
Am-241	1.08E-04	9.66E-05	1.02E-04	7.8

(a) 0.105 grams dissolved and diluted to 100 mL

(b) 0.106 grams dissolved and diluted to 100 mL.

Table 2. Composition of Melter Off Gas Sample 0036 Taken from the Inlet to the Quencher on the Off Gas Line of the Melter

Elements Measured by ICP-ES

Concentrations are given in weight percent.

Element	0036-1 (a)	0036-2 (b)	0036-3 (c)	Average	%RSD
Ag	0.01	0.01	0.01	0.01	19
Al	3.40	3.25	2.47	3.04	16
Ca	0.45	0.54	0.42	0.47	13
Cd	0.15	0.16	0.13	0.15	10
Cr	0.18	0.14	0.16	0.16	12
Cu	0.02	0.02	0.02	0.02	9.3
Fe	18.5	17.5	20.6	18.9	8.3
Hg	0.52	ND	ND	ND	ND
Li	0.17	0.14	0.16	0.17	9.1
Mg	0.60	0.57	0.57	0.60	2.7
Mn	1.93	1.95	1.55	1.81	13
Na	1.06	0.78	1.12	0.99	18
Ni	0.42	0.38	0.30	0.37	17
S	1.09	1.12	1.38	1.20	14
Si	19.9	19.9	19.9	18.9	6.5
Sn	0.29	0.23	0.32	0.28	17
Sr	0.09	0.12	0.09	0.10	17
U	1.84	1.55	1.82	1.74	9.5
Radionuclides Measured by Beta or Gamma Counting					
Concentrations are given in microcuries/gram.					
Sr-90	9.83E+02	7.24E+02	7.66E+02	8.25E+02	17
Cs-137	2.77E+02	3.19E+02	2.58E+02	2.84E+02	11
Isotopes Measured by ICP-MS					
Concentrations are given in weight percent.					
Tc-99	2.74E-03	2.55E-03	2.07E-03	2.45E-03	14
Mo-100	6.59E-03	4.06E-03	4.21E-03	4.95E-03	29
Ru-101	1.02E-01	3.24E-02	3.75E-02	5.73E-02	68
Ru-102	8.49E-02	2.82E-02	3.19E-02	4.83E-02	66
Rh-103	5.77E-03	5.80E-03	4.15E-03	5.24E-03	18
Ru-104	4.70E-02	1.70E-02	1.77E-02	2.72E-02	63
Pd-105	7.57E-04	2.71E-04	2.46E-04	4.25E-04	68
U-233	9.76E-05	1.21E-04	6.85E-05	9.56E-05	27
U-234	1.79E-04	1.88E-04	1.43E-04	1.70E-04	14
U-235	6.77E-03	6.74E-03	6.22E-03	6.57E-03	4.7
U-236	4.83E-04	5.32E-04	3.85E-04	4.67E-04	16
Np-237	2.56E-04	3.36E-04	2.85E-04	2.92E-04	14
U-238	1.47E+00	1.42E+00	1.40E+00	1.43E+00	2.3
Pu-239	3.48E-03	5.08E-03	4.39E-03	4.32E-03	19
Pu-240	2.90E-04	4.21E-04	3.18E-04	3.43E-04	20
Am-241	1.01E-04	2.32E-04	2.15E-04	1.83E-04	39

(a) 0.244 grams dissolved and diluted to 250 mL.
(b) 0.102 grams dissolved and diluted to 100 mL.
(c) 0.097 grams dissolved and diluted to 100 mL.

Table 3. Composition of Melter Off Gas Sample 0035 Taken From the Bottom of the Quencher on the Off Gas Line of the Melter

Elements Measured by ICP-ES

Concentrations are given in weight percent.

Element	0035-1(a)	0035-2 (b)	Average	%RSD
Ag	0.02	0.01	0.02	9.0
Al	5.38	4.45	4.92	13
Ca	0.68	0.51	0.59	19
Cd	0.13	0.12	0.13	2.9
Cr	0.15	0.15	0.15	0.1
Cu	0.02	0.02	0.02	14
Fe	17.2	20.6	18.9	12.7
Hg	0.77	ND	ND	ND
Li	0.15	0.12	0.15	11
Mg	0.97	0.71	0.97	19
Mn	2.76	2.73	2.75	0.7
Na	0.98	0.85	0.91	10
Ni	0.44	0.40	0.42	6.4
S	1.28	1.02	1.15	16
Si	14.1	14.1	14.1	0.1
Sn	0.27	0.31	0.29	7.8
Sr	0.15	0.11	0.13	19
U	3.19	2.31	2.75	23

Radionuclides Measured by Beta or Gamma Counting

Concentrations are given in microcuries/gram.

Sr-90	1.34E+03	8.50E+02	1.09E+03	32
Cs-137	4.25E+02	4.25E+02	4.25E+02	0.0

Isotopes Measured by ICP-MS

Concentrations are given in weight percent.

Tc-99	4.35E-03	4.66E-03	4.50E-03	5.0
Mo-100	2.23E-03	2.31E-03	2.27E-03	2.3
Ru-101	2.90E-03	3.43E-03	3.16E-03	12
Ru-102	3.45E-02	4.20E-02	3.83E-02	14
Rh-103	2.99E-02	3.54E-02	3.26E-02	12
Ru-104	5.87E-03	7.18E-03	6.52E-03	14
Pd-105	1.74E-02	1.95E-02	1.84E-02	8.1
U-233	2.09E-04	1.31E-04	1.70E-04	32
U-234	3.81E-04	2.59E-04	3.20E-04	27
U-235	1.38E-02	9.34E-03	1.15E-02	27
U-236	9.90E-04	6.76E-04	8.33E-04	27
Np-237	5.38E-04	3.81E-04	4.59E-04	24
U-238	3.18E+00	2.15E+00	2.67E+00	27
Pu-239	5.74E-03	6.17E-03	5.96E-03	5.1
Pu-240	4.10E-04	4.98E-04	4.54E-04	14
Am-241	2.52E-04	1.70E-04	2.11E-04	27

(a) 0.104 grams dissolved and diluted to 100 mL.
(b) 0.097 grams dissolved and diluted to 100 mL.

The results in Tables 1-3 indicate that all the samples of off gas deposits contain the major components in the radioactive sludge and glass frit along with U-235 fission products and actinides. In all three deposits, Si is a major component (14 to 20 weight percent).

In Table 1 it can be seen that the agreement between the results for major elements measured by ICP-ES for Sample 0037 is within nominally 5% or better. However the agreement in the other two samples as shown in Tables 2 and 3 is not as as good (10-20% RSR). This trend is also indicated for the minor elements measured by beta-gamma counting or by ICP-MS. When quadruplicate glass samples from the DWPF melter are ground and dissolved the agreement between the results especially for the major elements is usually 5% or better.[8] The disagreement between replicate samples from the deposits is not unexpected because it has been shown that off gas deposits are agglomerates of compounds rather than a homogeneous mixture.[5,6] The data in the three Tables does show that the composition of Sample 0037 is different from the other two in that Sample 0037 contains relative high concentrations of Na and S compared to the other two samples. Also Hg was detected and measured in Samples 0036 and 0035 and not detected in Sample 0037. Further information can be obtained by comparing ratios of concentrations of elements in each sample with their respective ratios in actual sludge.

By comparing the ratios of different elements in the off gas samples with respective ratios in the sludge that was processed in Melter One, information can be obtained concerning whether certain elements are enhanced in the off gas samples. This can indicate whether the ratio of Fe to fissile material is different in the off gas samples compared to the melter feed and whether there is volatility of any elements from the melter. Table 4 shows calculated ratios of selected elements or isotopes in the off gas samples compared to their respective ratios calculated from concentrations measured for the selected species in SB2.[2,9] Even though the off gas system had been on the melter while processing SB1A, SB1B, and a portion of SB2, SB 2 was chosen for this comparison because it was the last sludge being processed before the melter was removed. For the off gas samples, results of individual dissolved samples rather than averages were used to calculate the ratios because of the inhomogeneity of the samples. The concentrations of all the elements except Cs-137 and Sr-90 are given in weight percent. For the radionuclides Cs-137 and Sr-90 the concentrations are microcuries per gram of sample. The concentrations used to calculate the ratios for SB2 elements are given in References 2 and 9.

Table 4. Ratios of Concentrations of Selected Elements in the Off Gas Samples Compared to Their Respective Ratios in Sludge Batch 2

Ratio (a)	Off Gas Samples							SB2
	0037-1	0037-2	0036-1	0036-2	0036-3	0035-1	0035-2	Sludge(b)
Fe/Al	4.2	4.1	5.5	5.4	8.3	3.2	4.6	4.1
Fe/Sr-90	1.8E+02	1.8E+02	5.3E+01	4.1E+01	3.7E+01	7.8E+01	4.1E+01	1.9E+02
Fe/U	4.1	4.3	10.1	11.3	11.3	5.4	8.9	3.1
Fe/(U233+Pu-239+U-235)(c)	593	617	1792	1470	1933	873	1318	560
Hg/Fe	<2.0E-03	NA	NA	2.8E-02	NA	4.5E-02	NA	7.4E-04(d)
Cs-137/Fe	531	466	14.9	18.2	12.5	24.7	20.6	12.0
Cs-137/Sr-90	2.89	2.60	0.281	0.440	0.336	0.318	0.500	0.061
Tc-99/Fe	2.3E-03	2.5E-03	1.5E-04	1.5E-04	1.0E-04	1.3E-04	2.3E-04	3.1E-05
Tc-99/Sr-90	1.3E-05	1.4E-05	2.8E-06	3.5E-06	2.7E-06	1.7E-06	5.5E-06	1.6E-07
Fe/Si	3.9	3.6	1.1	1.1	0.85	0.82	0.69	19.8
Li/Si	0.017	0.020	0.008	0.007	0.009	0.010	0.009	0.069(e)

(a) The ratios that have Sr-90 and Cs-137 concentrations in them have uCi/g for concentrations of these radionuclides and weight percent for concentrations of the other elements in the ratios.
(b) Calculated from data published in References 2 and 9.
(c) The fissile element Pu-241 was not measured but based on analyses of other SB2 (see Ref.9) and its short half life (15y) its concentration is expected to have negligible effect on this ratio.
(d) This is the ratio of Hg to Fe in the SRAT product of the SRAT qualification run performed at SRTC. See Reference 2.
(e) This is the ratio of Li to Si in Frit 200. See Reference 8.

The ratios of Fe to Al in four of the five off gas samples agree fairly well with that in SB2. This implies that the deposits are entrained sludge or glass particles and that there is no segregation between these two elements during entrainment in the off gas. These particles are splashed, volatilized carried from the melter surface and then caught in the off gas stream. This also indicates that the Fe present in the samples did not result from Fe or its corrosion products being scraped off the off gas system itself by the sharp edged sampling cup attached to the TRM. Scraping of Fe or its corrosion products from the quencher could be hypothesized as a possible reason for the high ratio in Sample 0036-3. However the quencher is made of an Allcorr alloy that does not contain Fe.[10] The primary off gas line at the film cooler is fabricated of Inconel 690 that can contain up to 11% Fe.[10] The metals of both components contain only a trace of Al. [10] Thus is appears that essentially all the Fe and Al in the off gas deposit results from entrainment of radioactive sludge being fed to the melter.

The ratios for Fe/Sr-90 and Fe/U in Sample 0037, the sample from the primary off gas system also agree fairly well those in SB2 also supporting the results from the Fe/Al ratios. The Fe/Sr-90 and Fe/U ratios are higher in the Samples 0036 and 0035 (except for Sample 0035-1) suggesting segregation of these elements further down the off gas system. It appears that relatively less Sr-90 and U are being carried down the off gas system compared to Fe. Perhaps,

Sr-90 and U which are both heavier than Fe settle out faster in the off gas system than Fe. Note that this segregation was not evident for Al and Fe.

The results for the ratios of the concentration of Fe to the sum of the U-233, Pu-239, and U-235 concentrations are all greater than 160, the criticality safe ratio for DWPF sludge operations.[3] This ratio for Sample 0037 agrees with that measured in SB2 indicating no enhancement of fissile material in that sample. The ratios of iron to fissile are higher in the other two off gas deposits indicating depletion of the fissile material in these samples further down the off gas system. Results for all three deposits confirms that fissile material is not accumulating at these three locations in the off gas system.

The ratios involving Hg, Cs-137, and Tc-99, in Samples 0036 and 0035 are all larger than their respective ratios in SB2. The ratios involving Cs-137 and Tc-99 in Sample 0037 are also larger than the corresponding ratios in SB2. The larger ratios suggest that there is some volatilization of these elements from the melter. The presence of Hg in two of the off gas deposits indicates that some Hg had reached the DWPF melter even though Hg is steam stripped from the sludge in the Sludge Receipt Adjustment Tank (SRAT) process. For example, in the SB2 campaign at SRTC, it was shown that 92% of the Hg in the sludge had been steam stripped from sludge by the SRAT process in that campaign.[2] Apparently at least some of the Hg that reached the melter had volatilized. For Sample 0037 taken from the primary off gas line, Hg was not detected. This suggests that it was still volatile at this position in the off gas system. At this position, just past the film cooler, the temperature of the off gas is nominally 400°C [1]; thus, Hg volatilization could still occur. The temperature at the quencher is lower, ~350°C at the inlet and 50-100°C at the exit [1] and thus some Hg apparently condensed. It has been shown in other studies that Cs-137 and Tc-99 can be volatilized during laboratory scale melter tests (~10% for Cs-137 and ~60% for Tc-99). [11] The higher ratios for Cs-137 and Tc-99 to Fe and Sr-90 than in SB2 indicate some volatilization of these radionuclides from the DWPF melter. However analyses of three glass samples taken from the DWPF melter pour stream during the SB1A campaign indicate that 93% or greater of the Tc-99 and Cs-137 are retained in the melt and solidified in the glass. [4]

Finally, the results for the Fe/Si ratios in Table 4 clearly indicate that the samples analyzed are mixtures of sludge and frit. They are not pristine sludge, pristine Frit 200, or pristine HLW glass. In SB2 sludge the ratio Fe/Si is 19.8 due to the small amount of Si present compared to Fe.[2] In SB2 glass the ratio is 0.33.[8] Apparently, molten glass with dissolved sludge is not getting from the melter to the off gas system. The ratio Li/Si in the last row of Table 4 indicates that the deposits for some reason are depleted in Li or enhanced in Si since the ratio of Li/Si in Frit 200 is 0.069.[8]

Hot Water Leach of Samples

A sample of each of the off gas samples was leached with hot deionized water to determine the fraction of water soluble elements and anions that were in each of the samples. Studies made during vitrification of nonradioactive simulated sludges indicated that off gas deposits contained water soluble alkali borates, halides, and sulfates.[5,6] It was expected that if chlorides or

fluorides were present in the radioactive off gas samples, this technique would indicate such. A known amount of each sample (approximately 0.1 grams) was put into 90 mL of water in a beaker (covered with Al foil) for 2.5 hours at 80°C. After the heating the solutions were removed from the oven and weighed to determine the exact amount of water remaining. (Less than 10mL of water was lost in each test.) All the resulting solutions still contained solids. Each solution was carefully sampled while it was still hot and then analyzed by ICP-ES and gamma counting. The solutions were also analyzed by Ion Chromatography (IC) to determine the amount of water soluble anions dissolved from the samples. After the leaching only the appearance of sample 0037 had changed while the others remained black. The black color of sample 0037 had become lighter and appeared to be dark sand. Results of the leach test were calculated in terms of weight percent of the dissolved element or anion in the original sample. This was calculated by knowing the amount dissolved element or anion (calculated from the volume of the final solution and the measured concentration of that element in the solution) and by knowing the original weight of the sample leached. The fraction of the element dissolved could then be calculated by knowing the total amount of that element in the sample from the acid dissolutions (see Tables 1-3). For this calculation the average of the respective concentrations of the elements in the samples were used (see Column 4 of Tables 1-3). Fractions of anions leached could not be calculated because the total amount of each anion in the original sample was not measured. Results are in Table 5.

Table 5. Weight Percent of Elements and Anions Leached in Hot Water for the Off Gas Samples and the Fraction of Each Element Leached.(a)

Elements Measured by ICP-ES

Concentrations are wt. % of soluble element or anion in the original samples. Element	Sample Number		
	0037 (b)	0036 (c)	0035 (d)
Ag	<7E-04	<7E-04	<7E-04
Al	5.5E-02	6.0E-02	7.8E-02
Ca	1.2E-01	7.6E-02	1.1E-01
Cd	4.3E-03	3.0E-03	4.8E-03
Cr	5.4E-02	5.2E-03	7.5E-03
Cu	ND	1.5E-04	ND
Fe	5.2E-03	6.2E-02	3.9E-03
Li	2.0E-01	7.6E-03	1.0E-02
Mg	5.1E-02	4.4E-02	5.5E-02
Mn	4.0E-03	4.9E-02	6.0E-02
Na	8.7E+00	8.8E-02	1.7E-01
Ni	ND	1.9E-02	1.5E-02
S	6.1E+00	1.3E-01	2.2E-01
Si	3.4E-01	1.1E-01	6.8E-02
Sn	1.5E-02	1.2E-02	7.7E-03
Sr	2.5E-02	1.4E-02	2.1E-02
U	1.9E-02	ND	ND
B	7.5E-01	3.3E-02	1.6E-01

Fraction of Element Leached

Element	Sample Number		
	37	36	35
Ag	<0.04	<0.04	<0.04
Al	4.4E-02	2.0E-02	1.6E-02
Ca	2.0E-01	1.6E-01	1.9E-01
Cd	9.6E-03	2.0E-02	3.9E-02
Cr	3.0E-01	3.2E-02	5.2E-02
Cu	NA	9.0E-03	NA
Fe	1.0E-03	3.3E-03	2.1E-04
Li	6.1E-01	4.5E-02	7.0E-02
Mg	1.1E-01	7.3E-02	5.7E-02
Mn	5.4E-03	2.7E-02	2.2E-02
Na	7.4E-01	8.9E-02	1.9E-01
Ni	NA	5.2E-02	3.5E-02
S	9.3E-01	1.1E-01	1.9E-01
Si	1.8E-02	5.8E-03	4.8E-03
Sn	6.5E-02	4.2E-02	2.6E-02
Sr	1.9E-01	1.4E-01	1.6E-01
U	1.5E-02	NA	NA

Anions measured by IC

Fluoride	<0.02	<0.02	<0.02
Formate	<0.08	<0.08	<0.08
Nitrite	<0.08	<0.08	<0.08
Nitrate	0.025	0.017	0.050
Phosphate	<0.08	<0.08	<0.08
Oxalate	<0.08	<0.08	<0.08
Sulfate	1.7	0.033	0.067
Chloride	<0.02	<0.02	<0.02

Cs-137 Measured by Gamma Counting

Concentration is uCi of soluble Cs-137 per gram of sample			
Cs-137	2.9E-02	1.3E-03	1.9E-03

Fraction of Cs-137 Leached

Cs-137	1.1E-05	4.5E-06	4.4E-06

(a) Samples were leached at 80°C for 2.5 hours in ~80mL deionized water.
(b) For sample 0037, 0.112 grams were used and the final volume of the water was 81.8mL.
(c) For sample 0036, 0.112 grams were used and the final volume of the water was 83.1mL.
(d) For sample 0035, 0.114 grams were used and the final volume of the water was 83.4mL.

Several observations can be made concerning the results in Table 5. These are listed below.

- For all the samples, the elements Ca, Cr, Mg, Na, S, and Sr had the highest fractions leached. The element B was detected, but the fraction dissolved could not be calculated because the amount of B in the original sample was not measured. Only small fractions (<10%) of the other elements in the deposits were water soluble. This included Si and the radionuclides U and Cs-137 where the fraction soluble was small, 2% or less for U and 0.001% or less for Cs-137.
- The major anion leached was sulfate in agreement with the study using simulated sludge.[3,4]
- For the sample from the primary off gas line, Sample 0037, a sizeable fraction of S and Na were soluble, 93% for the S and 74% for the Na. Since sulfate was detected in the leachate, at least a portion of these two elements was undoubtedly associated with the compound Na_2SO_4. This agrees with the results of analysis of soluble off gas deposits from the SGM-7 melter campaign where sulfate and sodium were identified as the most abundant water soluble species in the deposits.[5,6]
- Very little fluoride or chloride were leached. This was unexpected since soluble halide salts were detected in the off gas deposits from the melters using simulated waste. Not detecting the halide salts in the radioactive deposits may have resulted from where the samples were taken. For the samples taken from the quencher, the soluble halide salts may have already been leached by the water condensate presence in the quencher. This is supported by the fact that very little sulfate was leached from these deposits compared to Sample 0037 taken from the off gas line near the film cooler. The low amounts of soluble halide salts in Sample 0037 may have resulted from the fact that the halide salts have a tendency to be deposited further down the off gas line.[5,6]

Contained X-Ray Diffraction Results

Small samples of the solids were submitted for Contained X-Ray Diffraction (CXRD) to identify any crystalline compounds present. For Sample 0037, 129 mg were submitted, for 0036, 318 mg, and for 0035, 141 mg. The samples were taken from the Shielded Cells in shielded bottles to reduce personnel dose rates. Still the dose rate for each sample through the bottle was nominally 600 mR/hr extremity (a dose rate at contact calculated from a reading at 4 cm.) and 2 mR/hr whole body (taken at 30cm.). The CXRD diffraction patterns are shown in Figures 2, 3, and 4.

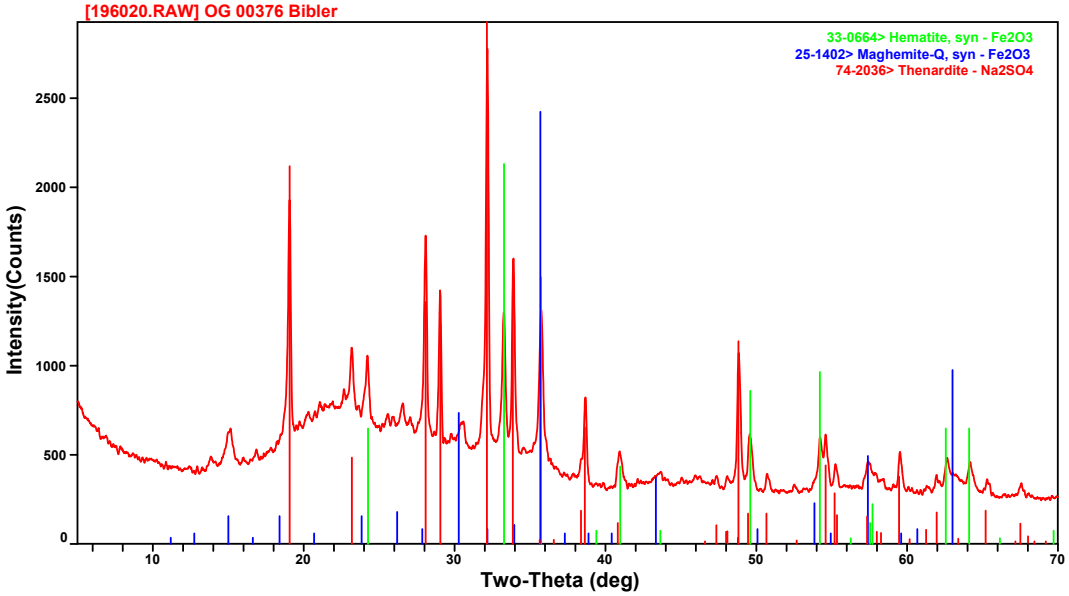

Figure 2. CXRD Pattern for Sample 0037 from the Primary Off Gas Line

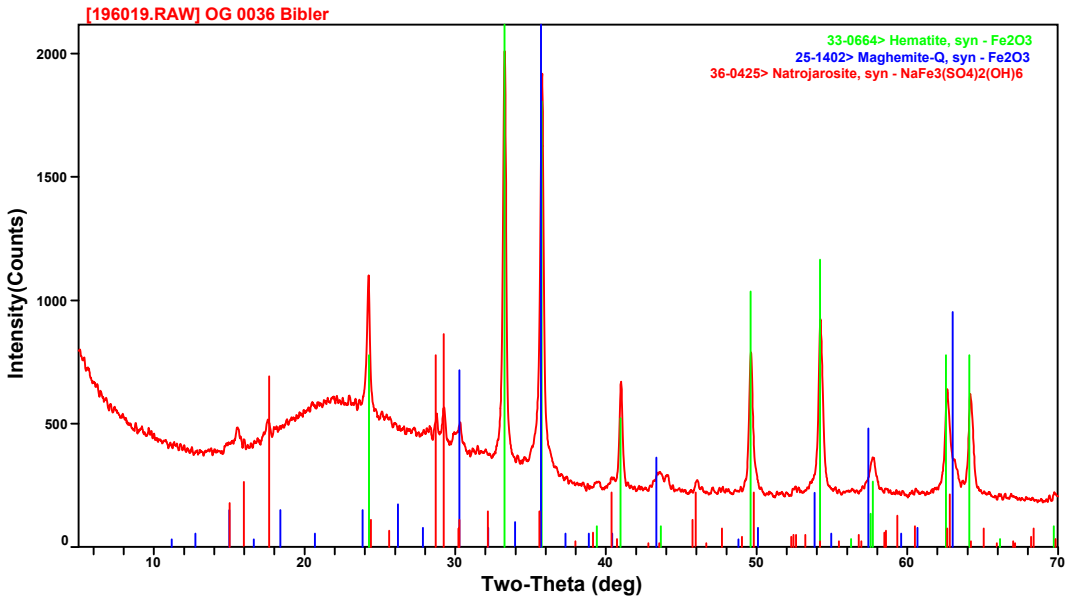

Figure 3. CXRD Pattern for Sample 0036 from the Inlet to the Quencher

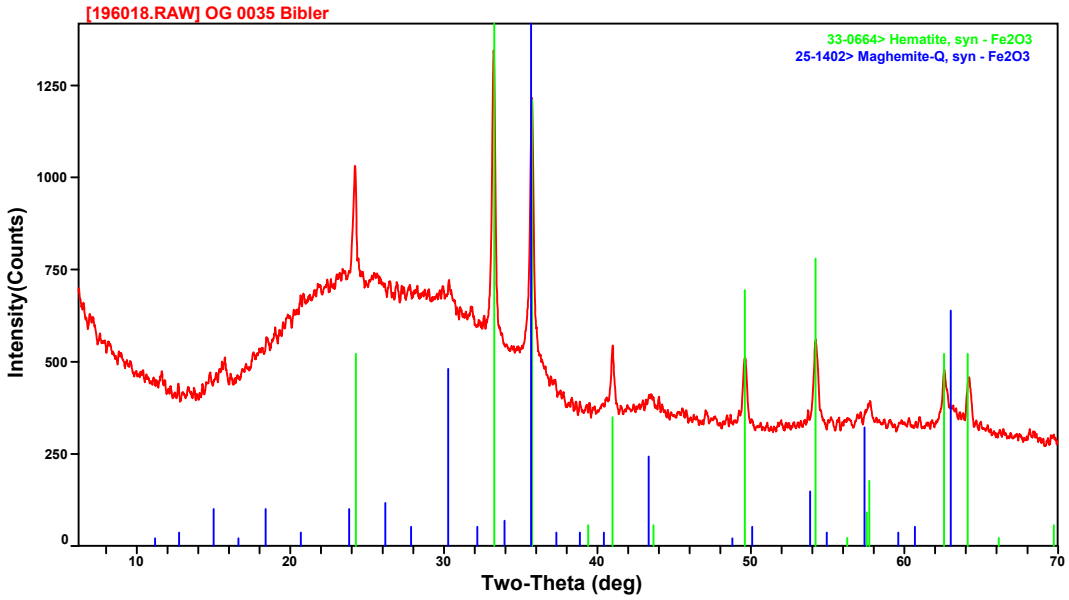

Figure 4. CXRD Pattern for Sample 0035 from the Bottom of the Quencher

The CXRD pattern for the sample from the primary off gas line (Figure 2) shows a slight amorphous hump associated with crystals of two forms of Fe_2O_3 (hematite and maghemite-Q) along with Na_2SO_4. No other crystals were detected including spinels that are usually found in devitrified SRS waste glasses. The CXRD pattern for the sample from the inlet to the quencher (Figure 3) shows a slight amorphous hump associated with the same forms of Fe_2O_3 as those in 0037 along with the compound natrojarosite which is a sulfate compound containing both Na and Fe. The CXRD pattern for the sample from the bottom of the quencher (Figure 4) shows an amorphous hump again associated with the same forms of Fe2O3. No sulfate compounds were detected in this sample suggesting that the sulfate compounds may have been dissolved from the deposit by condensate water from the melter. In none of the samples were patterns for NaCl detected as was detected in off gas samples from deposits from the melter runs with nonradioactive simulated sludges.[5,6]

Contained Scanning Electron Microscopy Results

Small samples (~10 milligrams) were taken from the Shielded Cells for examination by Contained Scanning Electron Microscopy (CSEM) and Energy Dispersive X-ray Analysis (EDAX). The micrographs of the three samples showed similar structure. Typical results are in Figures 5-7.

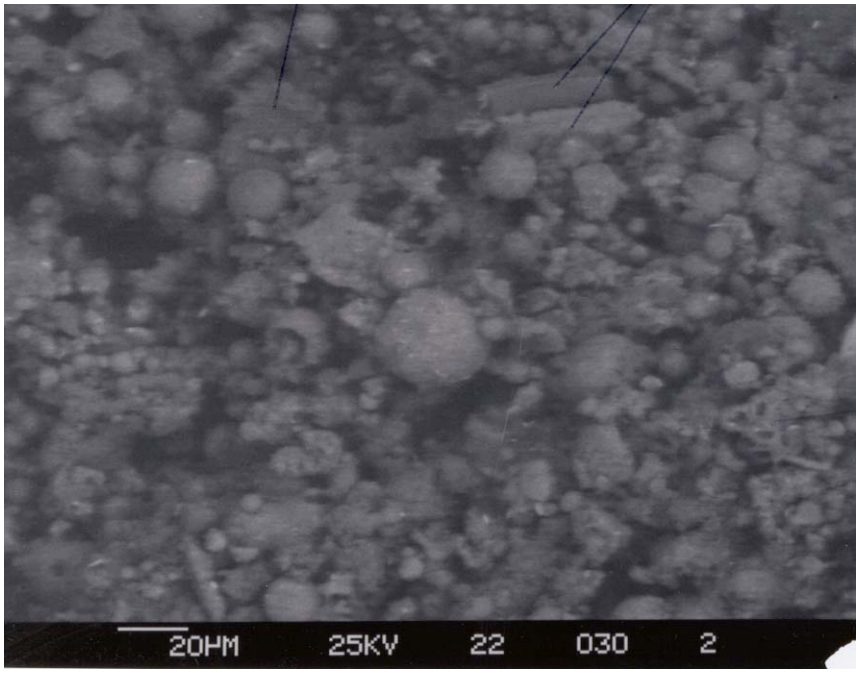

Figure 5. Typical CSEM Micrograph for Sample 0037 from the Primary Off Gas Line
(Magnification = 500X)

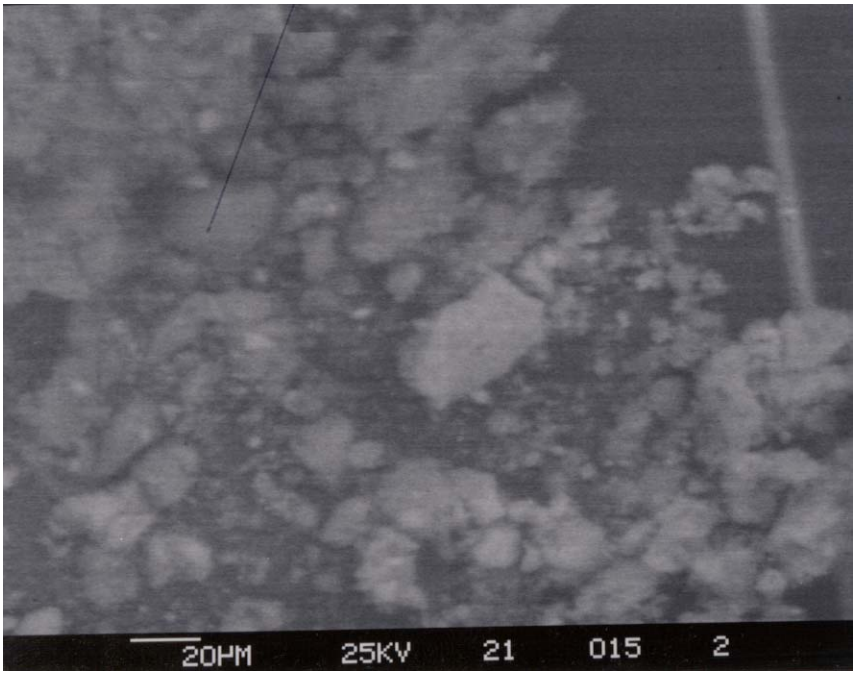

Figure 6 Typical CSEM Micrograph for Sample 0036 from the Inlet to the Quencher
(Magnification = 500X)

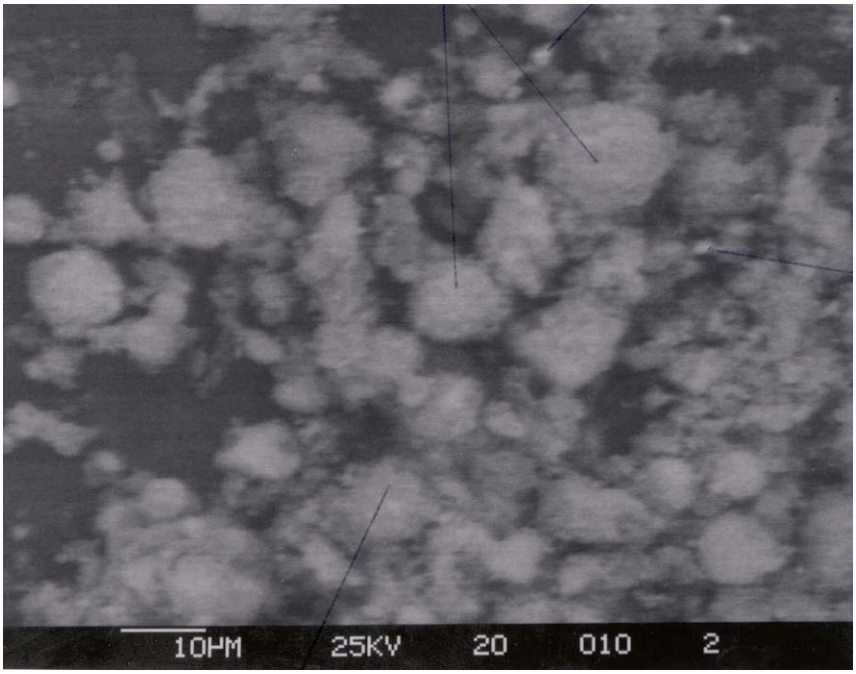

Figure 7. Typical CSEM Micrograph for Sample 0035 from the Bottom of the Quencher
(Magnification = 1000X)

As seen in the figures, all three samples had primarily rounded particles associated with a few particles that had defined crystalline edges.

More information was obtained from the EDAX analysis. The EDAX method identifies elements from their characteristic x-rays that are emitted when the element is struck by the electron beam of the microscope. The EDAX analysis indicated that on a microscopic scale, the compositions of the samples were nonhomogeneous. As expected none of the spectra resembled that for a typical SRS waste glass where Si is the primary component and Fe is a minor component. Typical EDAX spectra for the off gas samples are shown in Figures 8-13. In all the spectra the signals for Au and Pd result from the alloy used to provide a conductive coating for the sample.

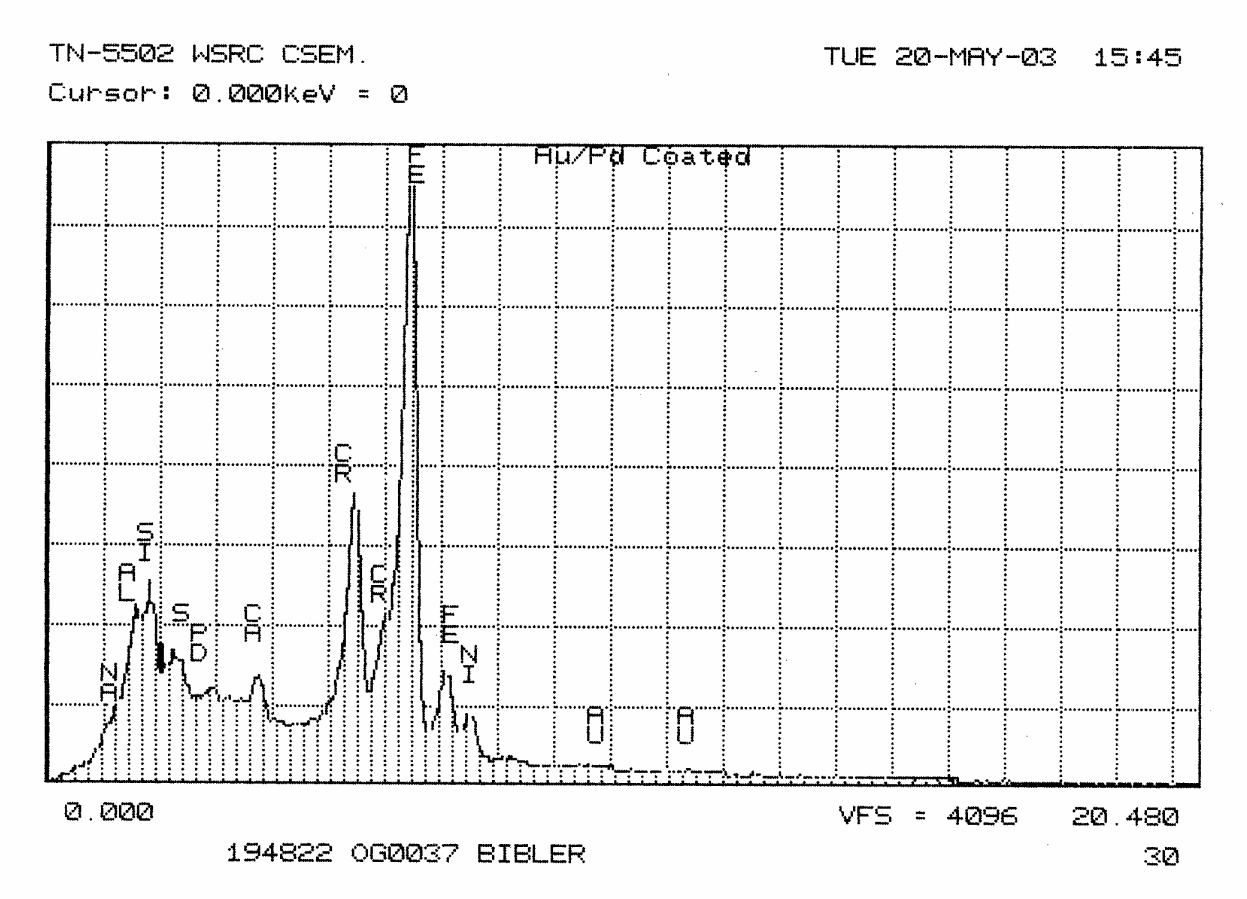

Figure 8. An EDAX Spectrum for a Particle in Figure 5 for Sample 0037 from the Primary Off Gas Line. The element Fe is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

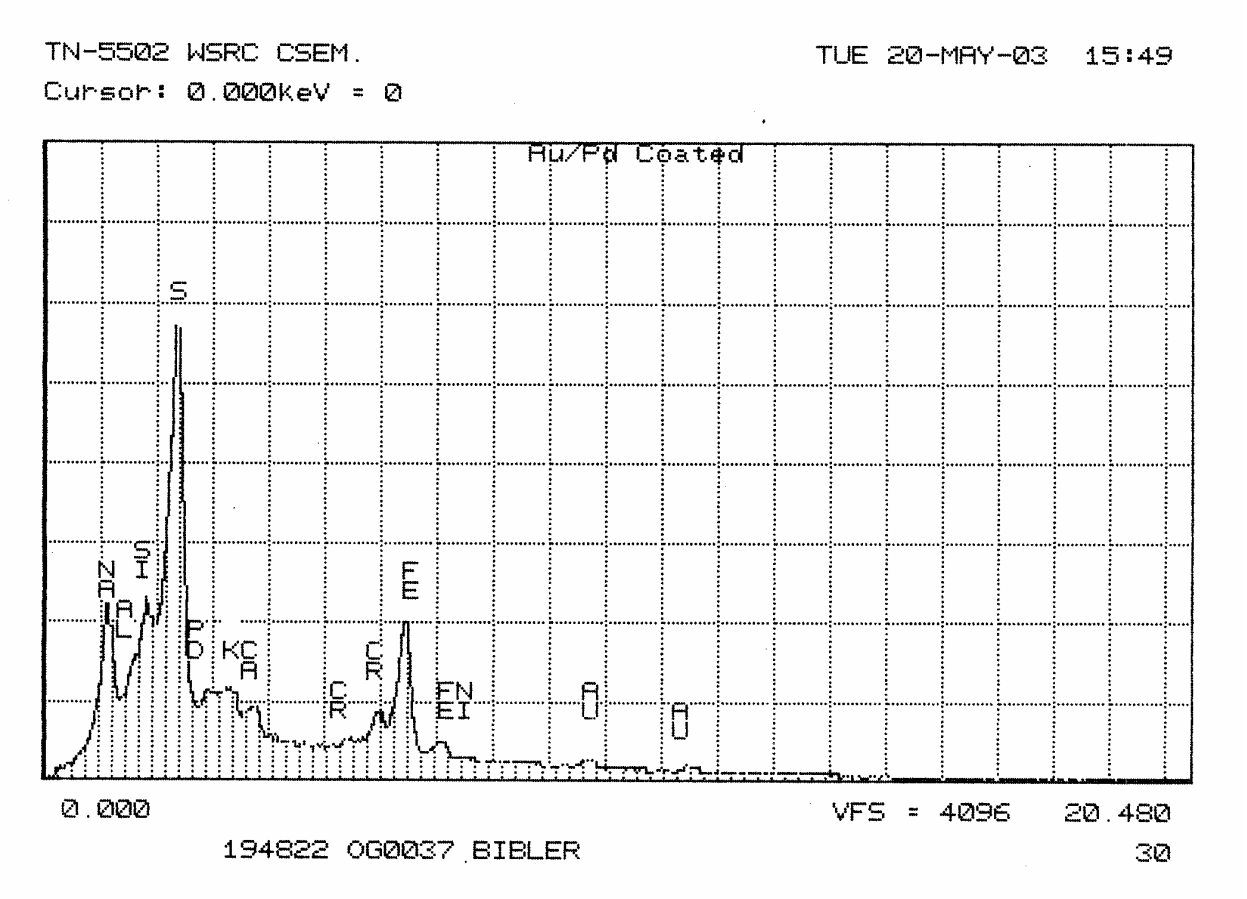

Figure 9. An EDAX Spectrum for a Particle in Figure 5 for Sample 0037 from the Primary Off Gas Line. The element S is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

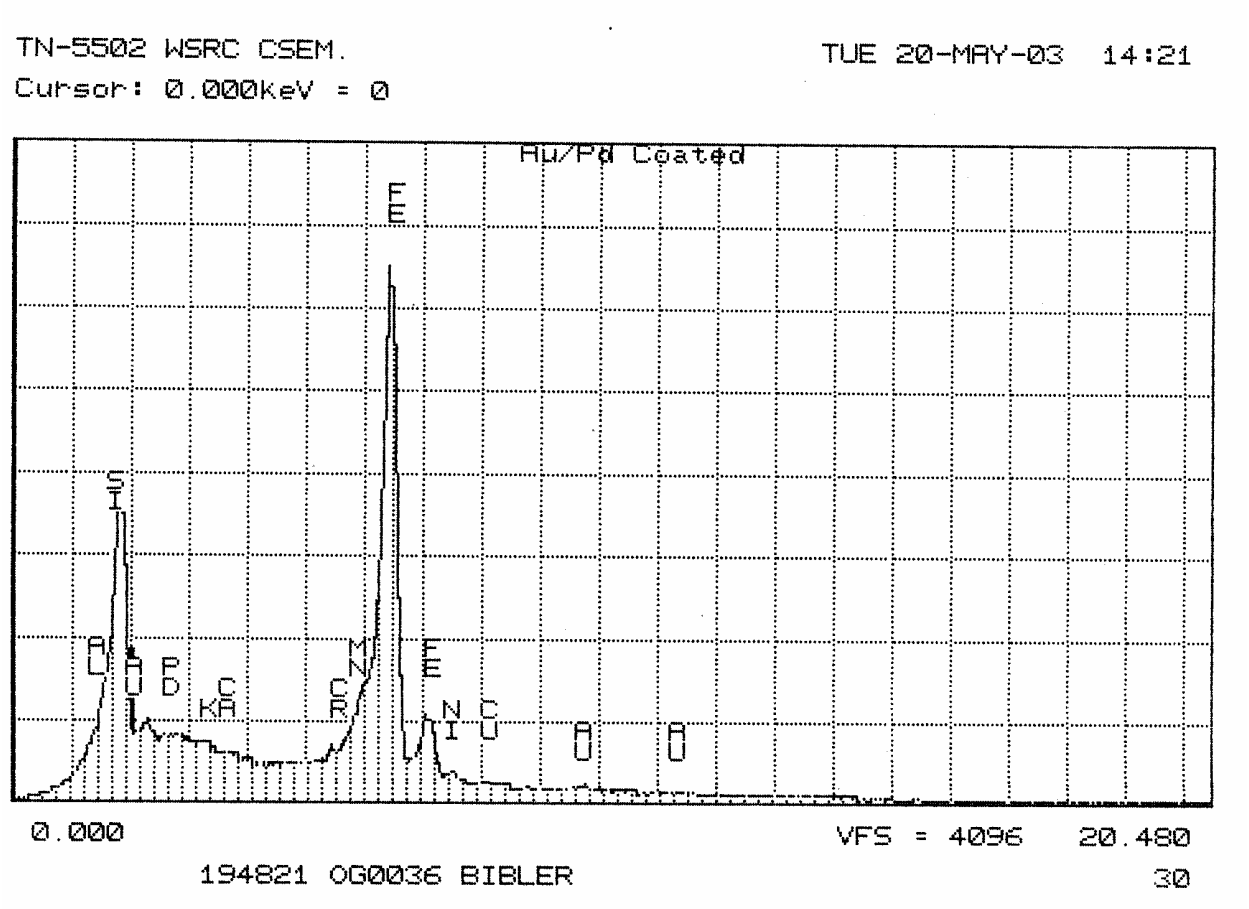

Figure 10. An EDAX Spectrum for a Particle in Figure 6 for Sample 0036 from the Inlet to the Quencher The element Fe is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

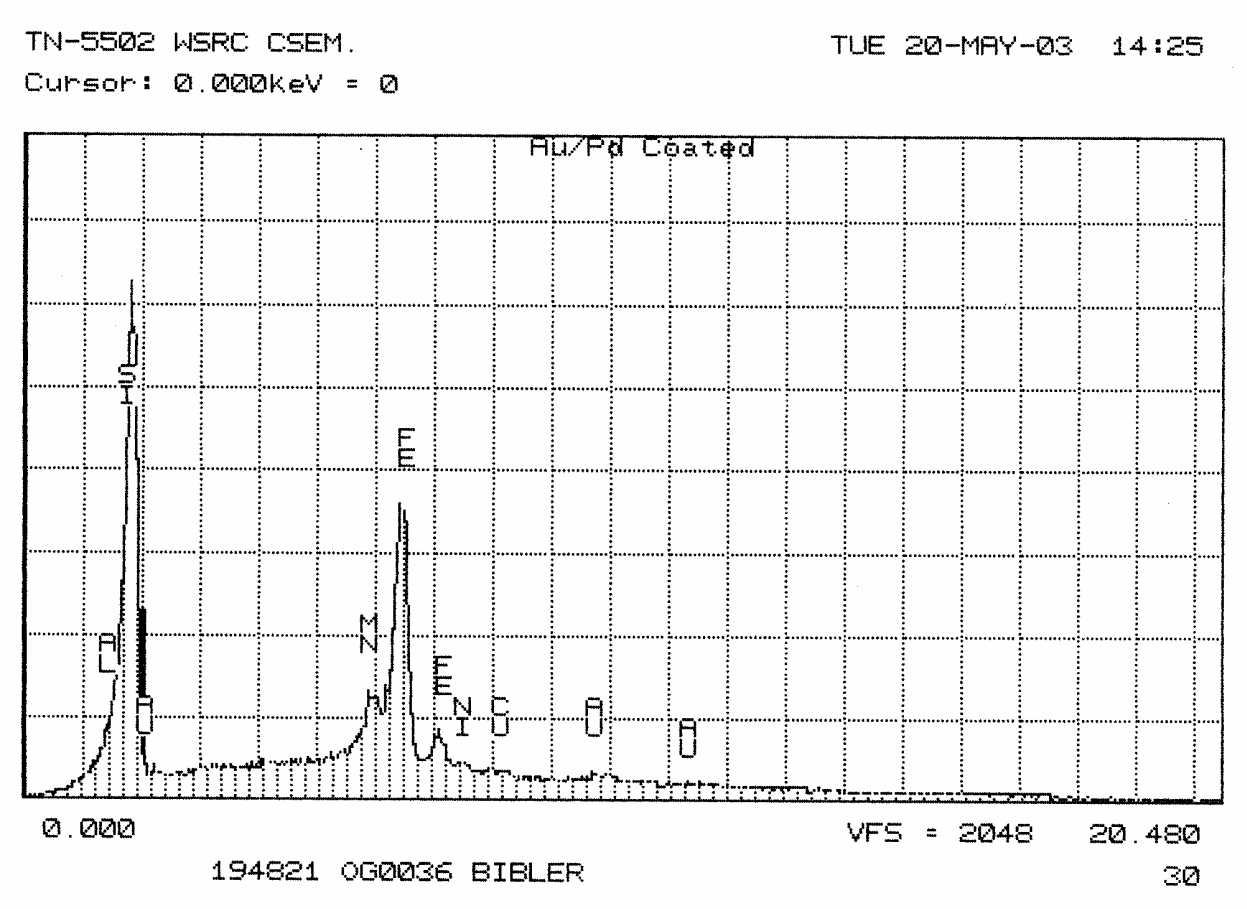

Figure 11. An EDAX Spectrum for Another Particle in Figure 6 for Sample 0036 from the Inlet to the Quencher. The element Si is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

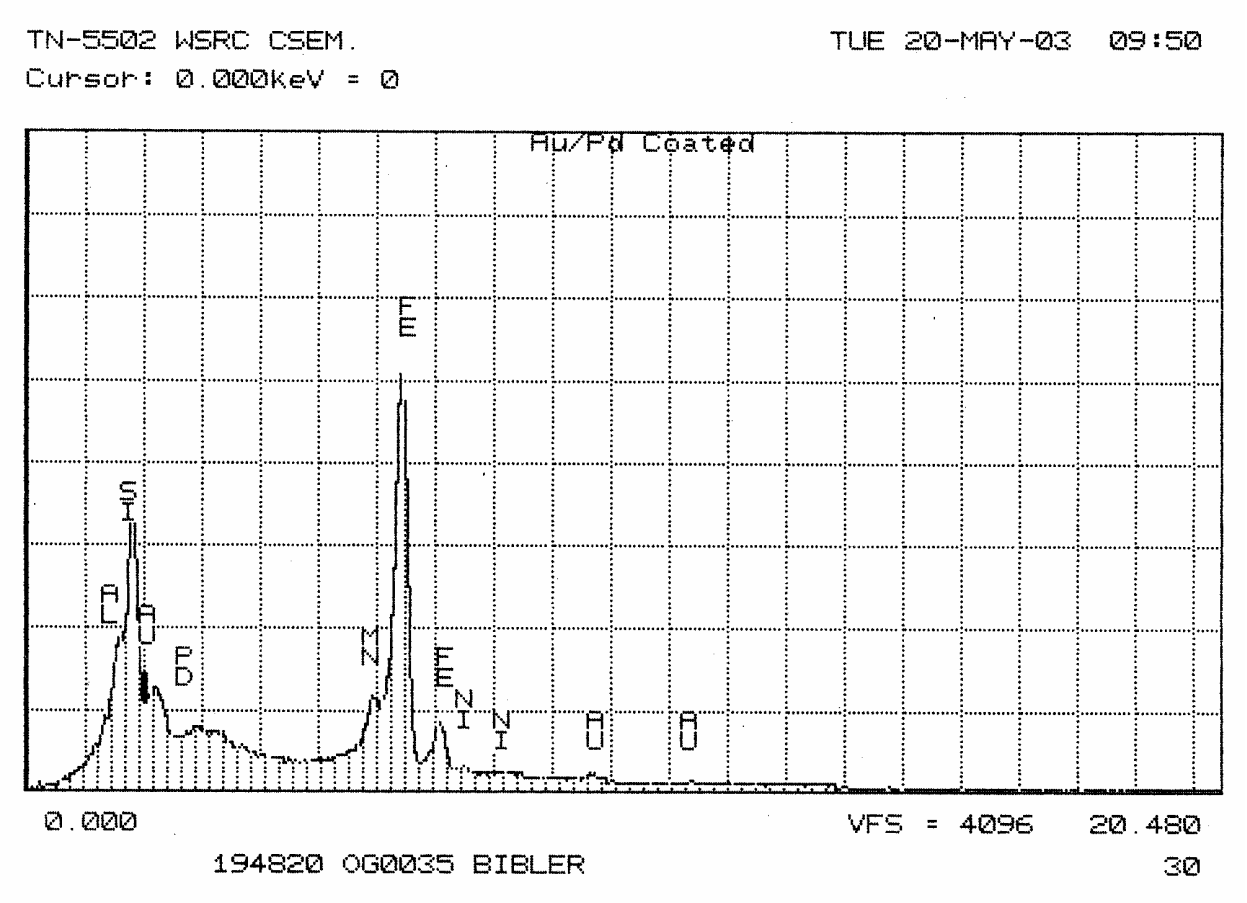

Figure 12. An EDAX Spectrum for a Particle in Figure 7 for Sample 0035 from the Bottom of the Quencher. The element Fe is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

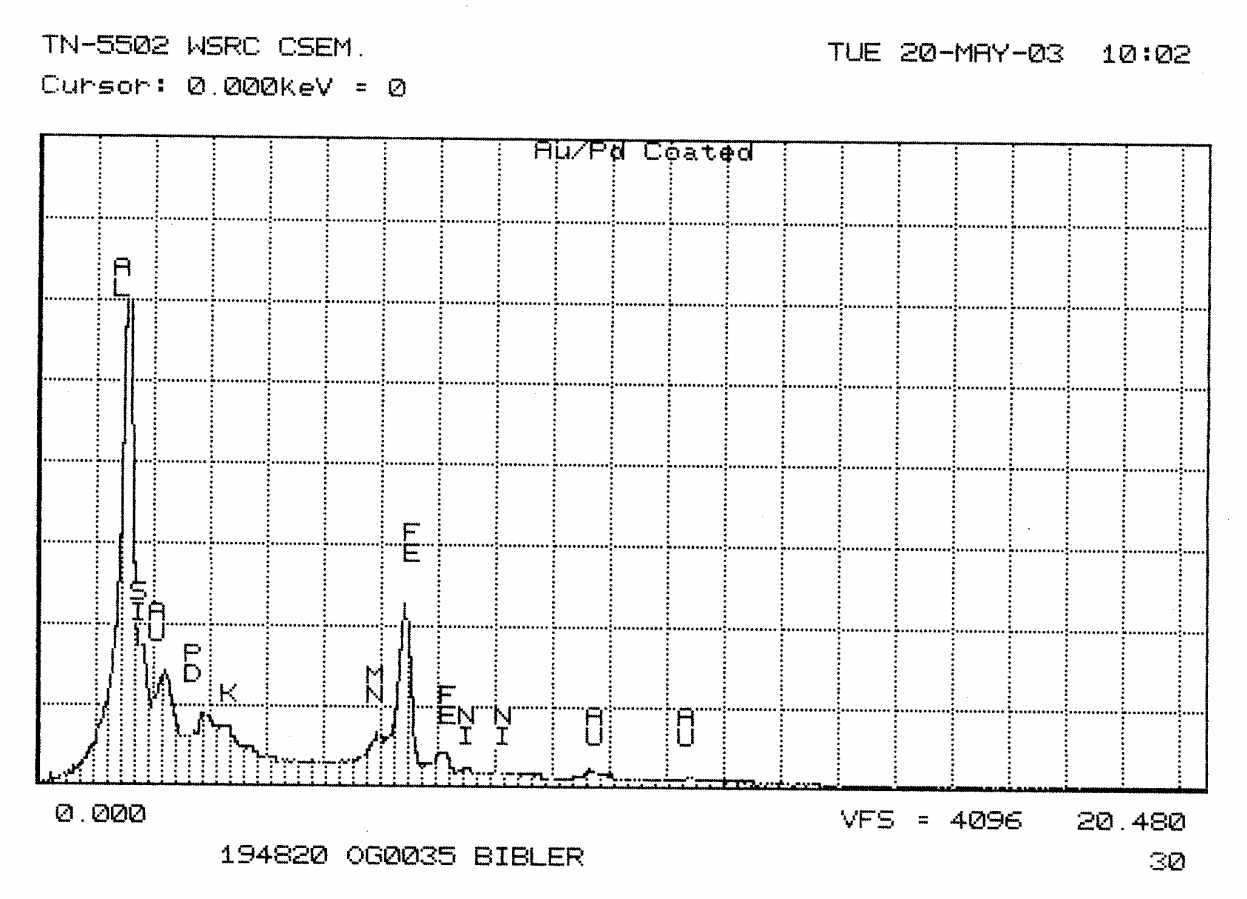

Figure 13 An EDAX Spectrum for Another Particle in Figure 7 for Sample 0035 from the Bottom of the Quencher. The element Al is a major component. (The elements Au and Pd are from the conductive alloy put on the sample.)

As seen qualitatively in Figures 9-13 the particles do not have identical compositions. This is expected since the particles are agglomerates of sludge and frit. The elements Fe, Si, Al, Na, Ca, Ni, Mn, and some U were detected in all of the particles examined in all three samples by EDAX.

CONCLUSIONS

The results in this study support the following conclusions concerning the three off gas samples.

- There was no evidence for the accumulation of fissile material relative to Fe in the samples.
- The samples were mixtures of sludge and frit.
- Some volatilization of Hg, Cs-137, and Tc-99 from the DWPF melter had occurred. (However there is evidence that greater than 93% of the Cs-137, and Tc-99 is retained in the glass in the DWPF melter.[4]

- Iron (III) oxide was the main crystalline compound in all three samples. The sample from the primary line also contained crystalline sodium sulfate that could be leached out of the sample by hot water. The samples from quencher contained very little sodium sulfate.
- No alkali halides, including NaCl were detected. This is in contrast to results for samples from off gas lines on melters using simulated sludge where NaCl was a main component of the samples.[5,6] However, those samples were taken at higher locations in the off gas line than the radioactive samples taken from the DWPF off gas line.

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