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Underground Tank Vitrification: A Pilot-Scale In Situ Vitrification Test of a Tank Containing a Simulated Mixed Waste Sludge

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components. The XRF method produced significantly better results than the SW-846 method (6010) in this case. The XRF data for each of the two samples are relatively similar and the values are consistent with expectations based on soil composition and the composition of other items (e.g., concrete, tank sludge, limestone gravel). The expected degree of homogeneity of the vitrified mass, illustrated in Table 8.1, is evident from the two samples analyzed by the XRF technique. However, the data from the two samples analyzed via the SW-846 method do not indicate the expected degree of homogeneity, particularly for CaO and K_2O. In addition, it is apparent that all of the silicates in the product were not dissolved into solution during the sample preparation phase for the SW-846 method because the values for SiO_2 are much lower than expected.

8.2 METAL PHASE

Three samples of the metal phase found at the bottom of the solidified melt were submitted for compositional analyses by SW-846 methods, including methods 7471 for mercury and 7421 for lead. Additionally, method 6010 involving an ICP scan was performed. The analytical results are presented in Table 8.4. The particular laboratory analyzing these samples encountered extreme difficulties with the cesium analyses and, consequently, produced useless data (the reported detection limit exceeded expected cesium concentrations). Note that many of the metal samples had glass phases intermixed with the metal. Therefore, acid digestion sample preparation methods did not result in total dissolution of the entire sample including the glass phase. However, the ratio of the metal species in the sample is thought to be representative. Eight additional metal samples were analyzed via XRF, and the results are presented in Table 8.5 along with the XRF results of a 304 series stainless steel. The only significant difference between the results in Tables 8.4 and 8.5 is the cadmium concentrations; those values reported for the SW-846 methods are much higher than the XRF values. The commercial laboratory that performed these SW-846 analyses had difficulty in obtaining consistent values for lead, mercury, and cadmium, even with blank pretest samples. Based on the thermal history of the metal phase, it is suspected that most of the cadmium would have been volatilized rather than pooled at the base of the melt since cadmium is a vapor at 765°C, well below the melting point of stainless steel (1427°C), and cadmium oxide has a vapor pressure approximately 400 mm of mercury at 1484°C (Lide 1990). Considering mass balance information discussed later in this section and the laboratory's difficulty in obtaining consistent and reasonable values for the metals of interest, it is suspected that the XRF data for cadmium in the metal phase are more accurate.

Three samples of the metal were submitted for TCLP analyses, and the results are presented in Table 8.6. The leachate extract from the metal waste form was below regulatory limits for all metals. Only

TABLE 8.4. Composition of Metallic Phase via SW-846 Methods[a,b]

Species	Metal Composition (ppm) Sample M4	Sample M5	Sample M6	Average Composition
Ag	22.55	27.20	18.30	22.68
Ba	2.70	13.66	8.54	8.30
Cd	856.53	1,183.95	628.97	889.82
Co	1,959.51	373.03	1,654.70	1,329.08
Cr	20,798.30	6,239.10	23,344.90	16,794.10
Cu	2,230.50	923.05	1,474.40	1,542.65
Fe	721,599.60	1,065,905.40	568,806.80	785,437.27
Hg	6.8	8.7	4.7	6.7
Mn	225.86	5,510.40	172.01	1,969.42
Ni	63,511.20	10,232.70	53,524.90	42,422.93
Pb	171.70	267.60	156.55	198.62
Va	628.90	719.88	585.74	644.84
Zn	442.12	426.67	802.24	557.01

(a) SW-846 methods 7471 and 7421 used for mercury and lead, respectively, following acid digestion. Balance of components measured via ICP scan.
(b) Metallic samples had undissolved glass phases.

cadmium concentrations in the leach extract approached the regulatory limit. Several observations can be made from the compositional data. Considering that the vast majority of the metal is from the tank (304L stainless), it is apparent that the chromium from the stainless steel was oxidized and dissolving into the glass phase while iron from the soil was reduced to its metallic state. As expected, the chromium oxide from the original sludge layer remained in its oxide form and was dissolved into the glass matrix. This is not surprising based on the more negative reduction potentials of these metals relative to others, such as iron and lead (Lide 1990). Additionally, no cesium and minimal amounts of strontium (10 to 250 μg/g) were found in the metal phase samples. Relative to the toxic metals, mercury, and cadmium were not found as expected based on their relative volatility. Barium remained an oxide and was largely dissolved in the vitrified product, as was lead.

TABLE 8.5. Metal Phase Composition via X-Ray Fluorescence

Species	Sample Number[a] M8-S	M8-S2	M10-S1	M10-S2	M9-S1	M9 Nodules	M7-S1	M7-S2	Average	304 Series SS
Values in %										
As	0.019	0.058	0.032	0.014	0.111	0.11	0.037	0.038	0.052	0. 01
Co	ND[b]	0.113	ND	ND	0.145	0.078	0.023	ND	0.045	ND
Cr	3.03	3.3	15.43	4.92	4.49	0.268	4.44	9.51	5.674	18. 08
Cu	0.393	0.544	0.368	0.493	0.868	0.768	0.4	0.337	0.521	0.156
Fe	88.3	86.3	72.4	82.1	83.8	85.1	84.9	81.1	83.000	69.5
Ga	0.02	0.026	0.007	0.018	0.016	0.021	0.013	0.03	0.019	ND
Hg	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mn	ND	ND	1.115	0.169	0.07	ND	ND	ND	0.169	1.726
Mo	0.53	0.707	0.541	0.622	0.273	0.514	0.314	0.409	0.489	0.123
Nd	ND	0.001	0.044	0.027	0.002	0.001	0	0.007	0.010	0.104
Ni	7.7	8.76	9.89	11.31	9.84	12.82	9.72	8.34	9.798	10.17
Pb	0.004	0.122	ND	ND	0.215	0.099	ND	0.002	0.055	ND
Se	0.007	0.003	ND	ND	ND	ND	0.004	0.003	0.002	0.004
Ti	ND	ND	0.118	0.198	ND	0.201	ND	0.072	0.074	0.043
Va	ND	0.061	0.096	0.032	0.027	0.01	0.079	0.17	0.059	0.055
Zn	0.01	0.039	0.046	0.044	0.141	0.062	0.076	0.048	0.058	0.047
Rb	ND	ND	0.005	0.021	0.003	0	0	0.003	0.004	0.004
Sr	ND	ND	0.004	0.025	0.004	0.001	0.011	0.01	0.007	0.002
Yt	ND	0.001	ND	0.005	0.008	0.001	0	0.007	0.003	0.004
Zr	0.002	0.001	0.008	0.035	0.002	0.006	0.021	0.008	0.010	ND
Values in ppm										
Ag	ND	26	ND	ND	ND	ND	ND	ND	3.250	ND
Ba	ND	ND	155	727	ND	ND	ND	210	136.500	ND
Cd	ND	ND	41	ND	ND	102	ND	ND	17.875	ND
Cs	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sn	300	298	419	448	251	219	72	106	264.125	71

(a) Samples included glass phases. Also, samples M8-S, M10-S, and M7-S were split to obtain samples M8-S1, M10-S2, and M7-S2.
(b) ND = not detected.

TABLE 8.6. TCLP Results of Metal Phase Samples[a]

Species	Sample M1	Sample M2	Sample M3	Average	Limit
As	0.01	0.01	0.01	0.01	5.00
Ba	0.07	0.05	0.12	0.08	100.00
Cd	0.83	0.43	0.89	0.72	1.00
Cr	0.32	0.65	0.22	0.40	5.00
Pb	0.19	0.13	0.11	0.14	5.00
Hg	<0.00040	<0.00040	<0.00040	<0.00040	0.20
Se	0.01	0.01	0.01	0.01	1.00
Ag	0.05	0.05	0.05	0.05	5.00

(a) Values in ppm.

8.3 SURROUNDING SOIL ANALYSES

Most surrounding soil samples were analyzed primarily using SW-846 methods with one blank and one posttest sample analyzed by XRF. Results are provided in Table 8.7.

3.1 Strontium

Surrounding soil analyses were relatively consistent for strontium with the exception of samples X-2, BC-A, BC-B, 100-D, and 70-F. Sample X-2 was collected at a 30-cm (1-ft) depth in Hanford soil adjacent to the south side of the block in the 100° to 400°C isoband. Sample 70-F was collected approximately 1-m directly below the block in Hanford soil in the 70° to 100°C isoband. Hanford soil has a higher concentration of naturally occurring strontium; consequently, the higher value of strontium in these two samples is not surprising. Samples BC-A and BC-B were collected from the soil/melt interface (crust) at the bottom of the block. In this narrow interfacial region, the temperatures ranged from the melting temperature of ORNL soil (approximately 1550°C) to just below the fusion temperature. Both samples show about twice the background levels of strontium. However, samples SC-A and SC-B, which are side crust samples at a 5-ft depth at the original level of the tank sludge, do not indicate any significant increase in strontium concentrations above background levels. Based on results from numerous ISV tests that show extremely high retentions of strontium in the vitrified product (Buelt et al. 1987), it is suspected that no consistent or significant quantities of strontium evolved from the melt to the surrounding soils. This conclusion is further substantiated by the mass balance information discussed in Section 8.6.