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# Supplementary Information on K-Basin Sludges

Prepared for the U.S. Department of Energy  
Office of Environmental Restoration and Waste Management

**FLUOR DANIEL HANFORD, INC.**



Richland, Washington

Hanford Management and Integration Contractor for the  
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# Supplementary Information on K-Basin Sludges

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**SUPPLEMENTARY INFORMATION ON K BASIN SLUDGES**

**ABSTRACT**

*Three previous documents in this series have been published covering the analysis of: K East Basin Floor and Pit Sludge, K East Basin Canister Sludge, and K West Basin Canister Sludge. Since their publication, additional data have been acquired and analyses performed. It is the purpose of this volume to summarize the additional insights gained in the interim time period.*

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## SUPPLEMENTARY INFORMATION ON K BASIN SLUDGES

### 1.0 INTRODUCTION

The two water-filled K Basins are currently utilized to store metallic uranium spent fuel from the Hanford N Reactor. Open canisters house the fuel in K East Basin while sealed canisters are used in K West Basin. Associated with this fuel is sludge which consists of various proportions of fuel, structural corrosion products, wind blown materials, and miscellaneous constituents such as ion exchange materials (both organic and inorganic) and paint chips. Three previous campaigns were conducted to sample sludge from the K East Basin floor (and Weasel Pit), the K East Basin canisters, and the K West Basin canisters. Extensive chemical and physical property determinations were performed on each group of samples and the results summarized in references Makenas (1996; 1997; 1998a). These analyses were done for a number of reasons but chief among these was to facilitate development of a pathway for disposal of the sludge after the spent fuel is removed from the basins. Tables 1.1, 1.2, and 1.3 list the sludge samples taken in each campaign and Figure 1.1 shows the locations of the K East floor and canister samples. A campaign to sample additional K East floor and canister sludge is currently in the execution stage (Makenas 1998b).

Since publication of the results from these campaigns, a number of additional analyses of sludge (Silvers 1998) and interpretations of data have been performed and these are the subject of this current document. The supplemental analyses were performed with sludge material archived from the original samples listed in Tables 1.1 to 1.3 and the reader will find that the subsample numbers referred to in the text are traceable to these original samples.

Table 1.1. Samples Extracted from K East Basin Floor and Weasel Pit.

Final Sample Number (KES-)	Type Sample <sup>a</sup>	Sample Location		Under Slot?	Bay Coverage <sup>c</sup>	Depth Measure? <sup>d</sup>	Along Wall <sup>e</sup>	Canister On Side of Interest <sup>f</sup>
		Lattice Location <sup>b</sup>	North/South					
L-01	N	1257	South	Yes	E/NW	No	No	1256
A-02	N	4516	North	Yes	C/SW	Yes	No	4517
B-03	N	2935	South	Yes	C/SE	Yes	No	2934
C-04	N	2771	North	Yes	C/NE	Yes	No	2770 <sup>g</sup>
N-05	N	1268	South	Yes	E/NW	No	No	1267
J-06	N	0133	South	Yes	E/SE	Yes	No	0132
G-07	N	5253	North	Yes	W/NE	No	No	5254
H-08	N	6755	South	Yes	W/NW	No	No	6754
O-09	N	6070	North	Yes	W/NW	Yes	No	6070
F-10	N	6718	North	Yes	W/SW	No	No	6719
E-11	N	1424	South	Yes	E/SW	No	No	1423
K-12	N	0168	North	Yes	E/NE	Yes	No	0169 or 0167
M-13	R	1266	North	Yes	E/NW	No	No	1267
D-14	R	2771	South	Yes	C/NE	Yes	No	2770
I-15	N	West of 6722	In Slot to Pit <sup>h</sup>	Yes	W/SW	Yes (6722)	No	--
P-16	N	Slot West	N/A	Yes	--	No	No	--
Q-17	N	Slot Mid	N/A	Yes	--	No	No	--
R-18	N	Open Mid North	N/A	Yes	--	No	Yes	--
S-19	N	Open Mid South	N/A	Yes	--	No	No	--
T-20	R	Open East End	N/A	Yes	--	No	No	--

Table 1.1. Samples Extracted from K East Basin Floor and Weasel Pit. (Continued)

Footnotes

<sup>a</sup>N--Normal, R--Research.

<sup>b</sup>Lattice location and sub-location for sample in main basin. "North" or "South" are indicated as to which side of the empty cubical sampling should be made to be adjacent to canister of interest. For Weasel Pit see Figure 1.1.

<sup>c</sup>A secondary variable is general coverage of the three bays in the main basin ("E" = East, "C" = Central and "W" = West bays). The quadrant of the bay in which the sample is located is also indicated (e.g., "NW" = Northwest, etc).

<sup>d</sup>Was there a direct measurement of sludge depth made (and video recorded) in 1994 campaign (Baker 1995a).

<sup>e</sup>Sampling cannot be made next to wall (not directly under slot) though depths were measured in some locations in 1994.

<sup>f</sup>This is the location of the fuel canister of interest. In an empty cubical the canister of interest should be directly adjacent to sampling location (i.e., reason for the indicated "north" or "south" portion of sample location). Sample 0 taken between barrels of the same canister.

<sup>g</sup>Sample taken 12 in west of 6722 in transfer channel slot but still 15.2 cm (6 in.) into Main Basin.

<sup>h</sup>Original position was 2769, sample was taken in 2771 north next to empty canister, nearest fueled canister is 2770 which is shown on table, within 10.2 cm (4 in.) to sample KES-D-14.

Table 1.2. Samples Extracted from K East Basin Canisters.

Full Sample Number	Shorten Sample Number	K East Cubical Location	Canister Barrel	Number of Fuel Elements in Barrel <sup>1</sup>		Initial Fuel <sup>235</sup> U (wt%)	Estimated Average Fuel Burnup (Mwd/MTM)	Canister		Canister Barrel has Bottom Holes/Slots?
				Inners	Outers			Type	Barrel Material	
96-01A/1845E	96-01	1845	East	4 <sup>2</sup>	5	0.947	0	MKII	SS	No
96-04/2711E	96-04	2711	East	7	7 (2)	0.947	2600	MKI	SS	No
96-05/3128W	96-05	3128	West	6 (2)	6 (3)	0.947	2600	MKII	SS	No
96-06/5465W	96-06	5465	West	6	6 (3)	0.947	1870	MKI	Al	?
96-08/2350E	96-08	2350	East	7	7 (5)	0.947	2220	MKI	Al	?
96-09/4638E	96-09	4638	East	0	0	--	No fuel	MKI	Al	Yes
96-11/6073W	96-11	6073	West	0	0	--	No fuel	MKI	SS	No
96-13/5055W	96-13	5055	West	6	6 (3)	0.947/ 0.711	1680	MKI	Al	?
96-15/6070W	96-15	6070	West	1 (1)	7 (4)	0.947	1580	MKI	Al	?

<sup>1</sup>Number of elements with damage visible from top of barrel are shown in parentheses.

<sup>2</sup>An approximately 1 1/2 in. long bolt (debris) sitting on top of one inner element, see Appendix A.

Table 1.3. Samples Extracted from K West Basin Canisters.

Sludge Sample Number	Sludge Sample Container Number <sup>1</sup>	Canister Number in K West	Canister Barrel <sup>2</sup>	Fuel Type <sup>3</sup>	Canister Type <sup>4</sup>	Measured Cesium in Water (mCi/Barrel)
96-02/2246M	96-02	2246 <sup>5</sup>	Marked	MIV/BE/11.6	MKII/SS	932
96-03/6743U	96-03	6743	Unmarked	MIA/AM/13.2	MKII/SS	N/M <sup>6</sup>
96-16/6603M	96-16	6603	Marked	MIV/BE/17.0/D <sup>7</sup>	MKII/SS	766
96-17/6513M	96-17	6513	Marked	MIA/AM/13.2	MKII/SS	4419
96-21/2667M	96-21	2667	Marked	MIA/AM/12.5	MKI/SS	5787
96-23/1860U	96-23	1890	Unmarked	NAT/7E/11.8	MKI/Al	1111
96-24/2660M	96-24	2660	Marked	MIA/AM/12.8	MKI/SS	3517
96-25/1164M	96-25	1164	Marked	MIA/AM/13.7	MKI/SS	2018
96-26/2660U	96-26	2660	Unmarked	MIA/AM/12.8	MKI/SS	177

<sup>1</sup>The primary sample containers are marked with this number.

<sup>2</sup>There were seven fuel assemblies in each barrel.

<sup>3</sup>Type/model/percent <sup>240</sup>Pu/grade.

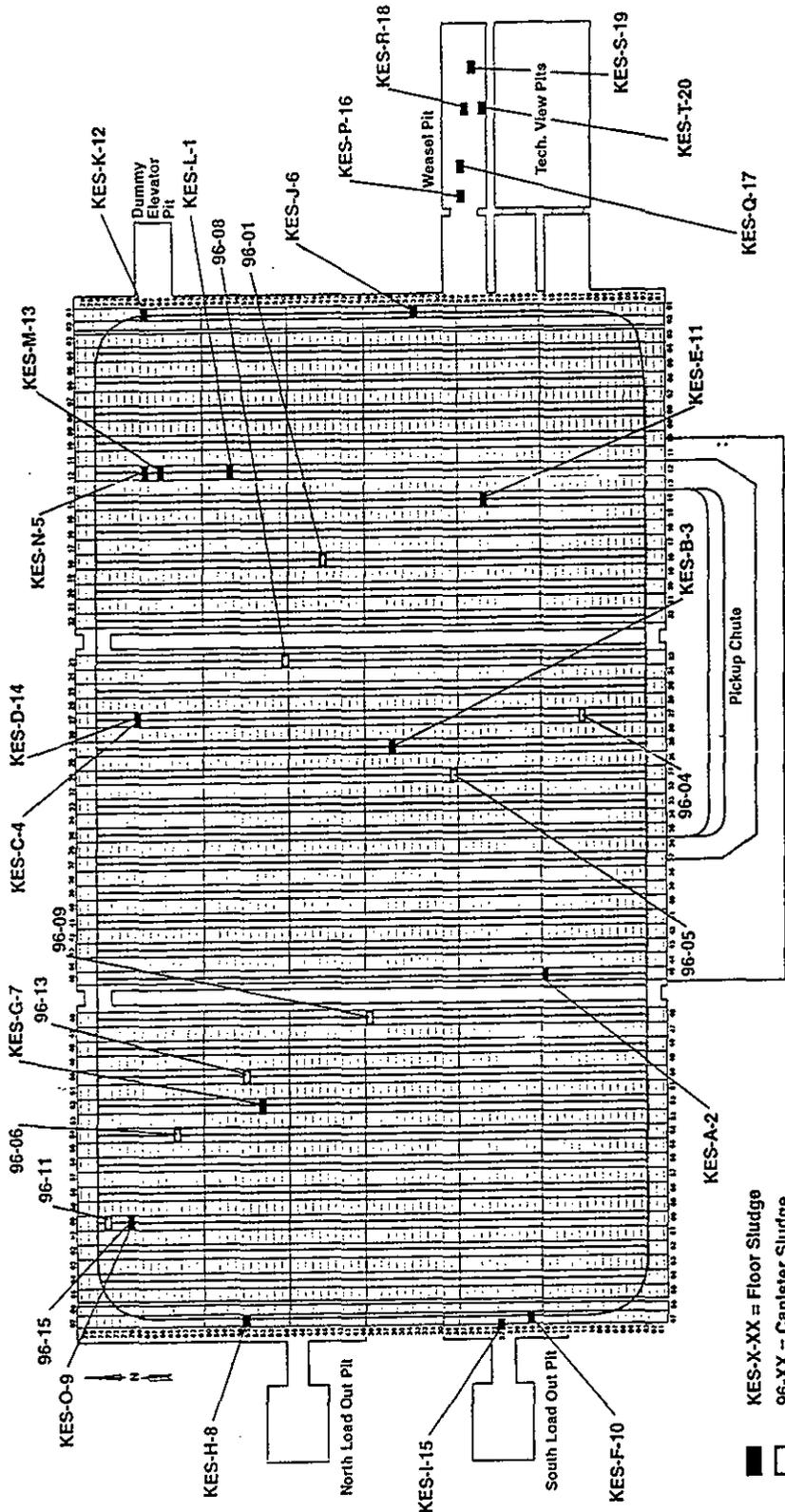
<sup>4</sup>Canister model/barrel material all MK I canisters had aluminum lids.

<sup>5</sup>Original lid number was 1512.

<sup>6</sup>N/M = Not measured.

<sup>7</sup>Repackaged and moved from K East Basin.

Figure 1.1. Locations of Sludge Samples Taken from K East Basin Floor and Canisters.



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## 2.0 RESULTS AND DISCUSSION

The following sections discuss newly generated data, new analysis, or new presentations of the data.

### 2.1 CHEMISTRY OF K EAST FLOOR AND WEASEL PIT SLUDGE

In the previous report on K East Floor and Weasel Pit sludge (Makenas 1996) statistics (mean values, standard deviations, etc.) are presented based on the combined data set including both Floor and Weasel Pit material. It has, however, occasionally been useful, in efforts such as criticality calculations, to separately utilize the data subset from each location. Therefore, Tables 2.1 and 2.2 present a summary of the appropriate data for each of the two areas where concentrations are given per milliliters of settled sludge.

### 2.2 SUMMARY OF K BASIN SLUDGE PROCESSING SCOPING STUDY

The baseline chemical treatment process for K Basin sludge is attempted nitric acid dissolution of all particulate material which passes a 0.25 in. screen (Flament 1998). The acid insoluble fraction (residual solids) will be stabilized (possibly by leaching/rinsing and grouting), packaged, and transferred to the Hanford Environmental Restoration Disposal Facility (ERDF). The liquid fraction is to be diluted with depleted uranium for uranium criticality safety and with iron nitrate for plutonium criticality safety, and neutralized with sodium hydroxide. The liquid fraction and associated precipitates are to be stored in the Hanford Tank Waste Remediation Systems (TWRS) pending vitrification. It is expected that most of the polychlorinated biphenyls (PCBs), associated with some K Basin sludges, will remain with the residual solids for ultimate disposal to ERDF. Trace quantities of PCBs within the liquid fraction will be further removed by filtration and by precipitation during the neutralization step.

The K Basin Sludge Processing Scoping Study (Scoping Study) was performed in the first half of FY 1998 by Pacific Northwest National Laboratory (PNNL) as part of the supplemental analyses of K East (KE) Basin and K West (KW) Basin canister sludge samples. The purpose of the Scoping Study was to provide an early assessment of the acid dissolution process and to identify potential problems and limitations of process assumptions that may need more in-depth examination. The study focused on characterizing the behavior of the sludges during dissolution, the sludge dissolution rates, and the extent of sludge dissolution (i.e., quantity and composition of residual solids). The compositions of the residual solids were also evaluated against the current ERDF Waste Acceptance Criteria (WAC) (Bechtel 1998).

Table 2.1. Chemistry of K East Floor Sludge.

Main Basin - per mL settled sludge	Analyte	Units	MIN	MAX	N	MEAN	STD DEV	RSD
Co60		uCi/mL	8.46E-02	2.01E+00	14	7.35E-01	5.05E-01	68.7
Cs137		uCi/mL	2.73E+01	1.48E+03	14	1.77E+02	3.82E+02	215.7
Cs134		uCi/mL	< 3.83E-02	8.83E-01				
Eu154		uCi/mL	< 1.87E-02	8.90E+00	12	1.79E+00	2.41E+00	134.8
Eu155		uCi/mL	< 5.41E-02	4.10E+00	13	7.58E-01	1.07E+00	140.9
Ce/Pr144		uCi/mL	< 2.93E-01	1.15E+01				
Nb94		uCi/mL	< 1.23E-02	4.50E-01				
RuRh106		uCi/mL	< 4.27E-01	1.68E+01				
Ra226		uCi/mL	< 5.86E-01	2.20E+01				
Tl208		uCi/mL	< 9.51E-02	1.19E+01				
Bi212		uCi/mL	< 7.59E-02	3.55E+00				
Eu152		uCi/mL	< 1.40E-02	4.84E-01				
Sb125		uCi/mL	< 3.02E-02	3.75E+00				
Am241- GEA		uCi/mL	1.82E-01	5.35E+01	14	9.61E+00	1.38E+01	143.9
Alpha		uCi/mL	4.52E-01	1.11E+02	14	2.14E+01	2.92E+01	136.1
Beta		uCi/mL	2.07E+01	3.09E+03	14	4.04E+02	8.21E+02	203.3
Pu239/240		uCi/mL	1.84E-01	4.48E+01	14	8.88E+00	1.16E+01	130.7
Pu238		uCi/mL	2.83E-02	1.09E+01	7	7.79E-01	5.44E-01	69.8
Np237		uCi/mL	< 7.21E-04	8.54E-03	6	1.36E-03	5.21E-04	38.4
Cm243/244		uCi/mL	< 1.14E-01	1.28E+01				
Am241- AEA		uCi/mL	1.57E-01	5.60E+01	14	9.60E+00	1.44E+01	150.4
Sr90		uCi/mL	1.77E+00	1.38E+03	14	1.63E+02	3.66E+02	225.1
U-las		ug/mL	1.31E+03	2.16E+04	6	8.76E+03	7.20E+03	82.2
U-PNL		ug/mL	1.44E+03	4.27E+05	14	5.59E+04	1.11E+05	198.8
U-ICP		ug/mL	1.14E+03	9.18E+04	11	2.30E+04	2.41E+04	104.7
Al		ug/mL	8.54E+03	4.26E+04	11	1.80E+04	9.72E+03	53.9
Ca		ug/mL	2.68E+02	5.58E+03	11	1.69E+03	1.66E+03	98.2
Cd		ug/mL	1.90E+01	5.75E+01	11	3.96E+01	1.29E+01	32.5
Cr		ug/mL	4.15E+01	4.86E+02	11	2.07E+02	1.67E+02	80.7
Cu		ug/mL	2.46E+01	4.25E+02	11	1.94E+02	1.26E+02	64.8
Fe		ug/mL	6.92E+03	2.73E+05	11	9.05E+04	9.02E+04	99.7
K		ug/mL	< 6.25E+01	1.21E+03	1	1.21E+03		
Mg		ug/mL	1.28E+02	1.03E+03	11	5.45E+02	2.93E+02	53.8
Mn		ug/mL	6.14E+01	4.51E+02	11	1.75E+02	1.15E+02	65.4
Na		ug/mL	9.03E+01	1.49E+04	11	1.50E+03	4.44E+03	295.0
Pb		ug/mL	4.20E+01	3.63E+02	11	1.62E+02	1.11E+02	68.7
Zn		ug/mL	5.44E+01	6.50E+02	11	3.13E+02	1.98E+02	63.4
Zr		ug/mL	2.82E+01	2.65E+02	11	1.27E+02	7.63E+01	60.0
Ag		ug/mL	< 1.02E+00	1.65E+01	1	1.74E+00		
B		ug/mL	< 4.01E+01	1.18E+02	10	7.48E+01	2.73E+01	36.6
Ba		ug/mL	2.32E+01	2.30E+02	8	7.89E+01	6.77E+01	85.7
Be		ug/mL	1.76E+00	2.64E+01	10	1.29E+01	6.60E+00	51.0
Sm & Se		ug/mL	< 1.02E+01	1.65E+02				
Tl		ug/mL	< 2.04E+01	3.31E+02				
TIC		ug/mL	7.50E+00	1.63E+03	12	7.35E+02	4.46E+02	60.7
TOC		ug/mL	3.87E+02	4.03E+03	11	1.05E+03	1.06E+03	100.5
TC		ug/mL	6.68E+02	6.55E+03	11	1.99E+03	1.71E+03	85.8
CN		ug/mL	< 3.11E-01	1.34E+00				
OHdemand		moles OH/mL	1.24E-04	4.00E-04	10	2.35E-04	8.80E-05	37.4
TGA (222S)		ug/mL	7.55E+05	9.78E+05	7	8.87E+05	8.00E+04	9.0
DSC - wet wt (222S)		Joules/mL	0.00E+00	7.43E+01	7	1.06E+01	2.81E+01	264.6
DSC - dry wt (222S)		Joules/mL	0.00E+00	2.30E+02	7	3.29E+01	8.69E+01	264.6
SO4		ug/mL	2.45E-02	7.89E+00	14	2.74E+00	2.72E+00	99.2
PO4		ug/mL	< 2.45E-02	2.38E+00				
NO3		ug/mL	3.46E-02	2.15E+00	6	5.68E-01	8.09E-01	142.4
NO2		ug/mL	< 1.41E-02	9.04E-01				
Cl		ug/mL	1.70E-02	4.40E-01	12	2.34E-01	1.28E-01	54.7
F		ug/mL	< 1.08E-03	1.62E+00	2	8.28E-01	1.12E+00	135.2
NH3		ug/mL	< 7.52E-02	1.23E+01				

Table 2.1. Chemistry of K East Floor Sludge. (Continued)

Main Basin - per mL settled sludge		MIN	MAX	N	MEAN	STD DEV	RSD
Analyte	Units						
TGA (PNNL)	ug/mL	1.24E+05	9.80E+05	12	6.39E+05	2.79E+05	43.7
DSC - wet wt (PNNL)	joules/mL	0.00E+00	9.68E+00	12	8.07E-01	2.79E+00	346.4
residue	ug/mL	5.80E+03	4.45E+05	14	7.21E+04	1.12E+05	155.4
U233	ug/mL set <	1.41E-02 <	4.18E+00				
U234	ug/mL set	1.10E-01	3.49E+01	14	4.26E+00	9.07E+00	212.6
U235	ug/mL set	1.00E+01	3.10E+03	14	3.97E+02	8.06E+02	203.0
U236	ug/mL set	1.10E+00	2.12E+02	14	3.47E+01	5.64E+01	162.4
U238	ug/mL set	1.43E+03	4.24E+05	14	5.55E+04	1.10E+05	198.8

Table 2.2. Chemistry of K East Weasel Pit Sludge.

Weasel Pit - per mL settled sludge Analyte	Units	MIN	MAX	N	MEAN	STD DEV	RSD
Co60	uCi/mL	3.67E-01	2.34E+00	6	1.43E+00	6.44E-01	45.2
Cs137	uCi/mL	7.59E+01	5.04E+02	6	2.89E+02	2.04E+02	70.5
Cs134	uCi/mL	< 2.07E-01 <	4.13E-01				
Eu154	uCi/mL	2.95E-01	1.98E+00	6	1.21E+00	6.04E-01	50.1
Eu155	uCi/mL	1.68E-01 <	1.29E+00	3	5.50E-01	3.95E-01	71.9
Ce/Pr144	uCi/mL	< 2.55E+00 <	5.31E+00				
Nb94	uCi/mL	< 1.55E-01 <	2.21E-01				
RuRh106	uCi/mL	< 3.31E+00 <	7.98E+00				
Ra226	uCi/mL	< 4.61E+00 <	1.09E+01				
Tl208	uCi/mL	< 3.91E-01 <	7.09E+00				
Bi212	uCi/mL	< 1.74E-01 <	2.30E+00				
Eu152	uCi/mL	< 8.18E-02 <	7.02E-01				
Sb125	uCi/mL	<	2.27E+00				
Am241- GEA	uCi/mL	1.68E+00	1.17E+01	6	7.49E+00	3.87E+00	51.6
Alpha	uCi/mL	3.78E+00	2.81E+01	6	1.78E+01	8.74E+00	49.0
Beta	uCi/mL	1.54E+02	1.30E+03	6	7.74E+02	5.39E+02	69.7
Pu239	uCi/mL	2.17E+00	1.49E+01	6	8.90E+00	4.45E+00	50.0
Pu238	uCi/mL	< 7.96E-01 <	4.06E+00	2	1.16E+00	7.07E-03	0.6
Np237	uCi/mL	1.10E-03 <	7.78E-03	4	1.49E-03	3.76E-04	25.2
Cm243/244	uCi/mL	< 1.20E+00 <	4.75E+00				
Am241- AEA	uCi/mL	1.97E+00	1.12E+01	6	7.17E+00	3.41E+00	47.6
Sr90	uCi/mL	4.61E+01	3.70E+02	6	2.17E+02	1.35E+02	62.4
U-las	ug/mL	1.35E+04	3.67E+04	4	2.72E+04	1.12E+04	41.1
U-PNL	ug/mL	1.43E+04	7.53E+04	6	4.23E+04	2.57E+04	60.7
U-ICP	ug/mL	1.33E+04	8.71E+04	6	5.50E+04	2.53E+04	46.0
Al	ug/mL	1.75E+04	5.87E+04	6	3.60E+04	1.61E+04	44.7
Ca	ug/mL	3.95E+03	3.31E+04	6	1.45E+04	1.16E+04	79.8
Cd	ug/mL	2.62E+01	7.64E+01	6	4.61E+01	1.70E+01	36.8
Cr	ug/mL	4.60E+02	1.91E+03	6	1.01E+03	4.92E+02	49.0
Cu	ug/mL	1.84E+02	9.47E+02	6	4.20E+02	2.75E+02	65.4
Fe	ug/mL	1.33E+05	5.22E+05	6	2.77E+05	1.33E+05	48.0
K	ug/mL	4.75E+02	2.54E+03	4	1.61E+03	5.62E+02	34.9
Mg	ug/mL	9.77E+02	4.82E+03	6	2.14E+03	1.43E+03	66.9
Mn	ug/mL	2.74E+02	9.84E+02	6	5.12E+02	2.66E+02	52.0
Na	ug/mL	2.48E+02	2.88E+03	6	1.05E+03	1.00E+03	95.4
Pb	ug/mL	2.90E+02	1.08E+03	6	5.13E+02	2.84E+02	55.5
Zn	ug/mL	5.22E+02	2.09E+03	6	1.05E+03	5.50E+02	52.5
Zr	ug/mL	2.53E+02	1.06E+03	6	5.55E+02	2.98E+02	53.8
Ag	ug/mL	< 9.30E+00 <	3.77E+01				
B	ug/mL	6.89E+01	7.66E+02	4	2.71E+02	3.31E+02	121.8
Ba	ug/mL	9.92E+01	5.64E+02	5	3.81E+02	2.37E+02	62.1
Be	ug/mL	1.01E+01	2.43E+01	5	1.69E+01	5.88E+00	34.9
Sm & Se	ug/mL	< 9.30E+01 <	3.77E+02				
Tl	ug/mL	< 1.86E+02 <	7.55E+02				
TlC	ug/mL	1.10E+03	3.26E+03	5	1.92E+03	8.39E+02	43.7
TOC	ug/mL	1.72E+03	2.60E+03	5	2.12E+03	3.82E+02	18.0
TC	ug/mL	2.58E+03	4.98E+03	5	3.86E+03	1.08E+03	27.9
CN	ug/mL	< 7.14E-01 <	9.24E-01				
OHdemand	moles OH/mL	1.50E-04	3.91E-04	4	2.66E-04	1.19E-04	44.8
TGA (222S)	ug/mL	6.99E+05	8.05E+05	4	7.47E+05	4.40E+04	5.9
DSC - wet wt (222S)	Joules/mL	0.00E+00	0.00E+00	4	0.00E+00	0.00E+00	
DSC - dry wt (222S)	Joules/mL	0.00E+00	0.00E+00	4	0.00E+00	0.00E+00	
SO4	ug/mL	2.35E+00	2.03E+01	5	9.78E+00	7.83E+00	80.0
PO4	ug/mL	< 3.65E-02 <	9.04E-01				
NO3	ug/mL	1.29E-01 <	4.27E-01	1	1.29E-01		
NO2	ug/mL	< 3.19E-02 <	3.27E-01				
Cl	ug/mL	1.13E-01	5.28E-01	5	2.52E-01	1.79E-01	71.2
F	ug/mL	< 3.28E-02 <	3.41E-01	3	1.49E-01	1.66E-01	111.6
NH3	ug/mL	< 1.15E+00 <	1.49E+00				

Table 2.2. Chemistry of K East Weasel Pit Sludge. (Continued)

Weasel Pit - per mL settled sludge Analyte	Units	MIN	MAX	N	MEAN	STD DEV	RSD
TGA (PNNL)	ug/mL	2.91E+05	5.70E+05	4	4.70E+05	1.23E+05	26.2
DSC - wet wt (PNNL) residue	joules/mL ug/mL	0.00E+00	0.00E+00	4	0.00E+00	0.00E+00	
		9.42E+04	4.12E+05	6	2.31E+05	1.20E+05	51.8
U233	ug/mL set <	1.40E-01 <	7.37E-01				
U234	ug/mL set	1.02E+00	5.26E+00	6	3.04E+00	1.78E+00	58.5
U235	ug/mL set	9.95E+01	5.27E+02	6	2.94E+02	1.80E+02	61.1
U236	ug/mL set	1.06E+01	5.64E+01	6	3.20E+01	1.95E+01	60.9
U238	ug/mL set	1.42E+04	7.47E+04	6	4.20E+04	2.55E+04	60.7

### 2.2.1 Description of Testing

The dissolution behavior in nitric acid was examined for three types of actual K Basin sludge samples. These sludge samples were selected because of anticipated challenges to the nitric acid dissolution of the KE Basin sludge during the planned pretreatment operations. Two of the samples contained relatively high iron concentrations (one from the KE Weasel Pit and one from KE canisters). Iron compounds can co-precipitate with transuranic elements and can exist in forms that are resistant to nitric acid dissolution. The third sample primarily consisted of ion exchange (IX) material collected from the KE Basin floor. The IX material is approximately 65 wt% organic ion exchange resin (OIER) beads and 35 wt% inorganic IX material (Schmidt 1998a). This testing was conducted to determine how well the IX material could be decontaminated (i.e., extent of radionuclides removed) in nitric acid and whether the OIER would sorb significant levels of radionuclides when co-dissolved with sludge. The potential for OIER to form nitrated organic compounds (reactive) was also examined. For the OIER testing, subsamples of both neat ("as collected") material and material spiked with high-uranium (and TRU) -content canister sludge were dissolved in nitric acid. Before the radioactive samples were tested, the dissolution methodology was tested using samples of fresh, nonradioactive OIER beads.

The sludge dissolution testing was conducted with 10 M nitric acid at 25 °C, 60 °C, and 95 °C over an 8-hour dissolution period as described in the test instructions (Bredt 1997). For the KE canister and Weasel Pit sludges, a series of approximately 2-g sludge sample aliquots (settled sludge basis) were digested in vials with 20 ml of acid. During the dissolutions, liquid samples were collected at 2 hours, 4 hours, 6 hours, and 8 hours and analyzed for select radionuclides and key metal cations (i.e., uranium, iron, aluminum) to track the rate of dissolution. When the 8-hour dissolution period was complete, the solutions were centrifuged, and the supernatant was decanted from the acid insoluble residual solids. The residual solids were rinsed with deionized (DI) water, dried, and digested by caustic fusion, and the resulting solutions were analyzed for select radionuclides by alpha energy analysis (AEA) and gamma energy analysis (GEA) and for metals by inductively coupled plasma alpha energy spectroscopy (ICP-AES). X-ray diffraction (XRD) analysis of the residual solids was performed to identify crystalline phases.

For the IX material testing, approximately 1-g aliquots (wet sample basis) of the IX material sample were added to a series of vials. Between 0.4 g and 1 g (settled sludge basis) of the high-uranium-content canister sludge was added into the reaction vials for half of these tests. Next, 20 ml of room-temperature 10 M nitric acid were added to each vial, and the vials were left at ambient temperature for 2 hours. At this time, half of the tests were concluded, and digestion was continued in the other half (including both spiked and unspiked material) at 60 °C for an additional 6 hours. When the digestions were finished, the contents of the vials were filtered, and the residual OIER (and other solids) were rinsed with nitric acid and DI water. The filtered solutions were analyzed for select radionuclides and for metals via ICP-AES. The solids were digested by caustic fusion and were analyzed for select radionuclides by AEA and GEA and for metals by ICP-AES.

A detailed description of the testing and results obtained from the Scoping Study is provided in Appendix A. Key observations and findings from this work are summarized below.

### 2.2.2 Results from Dissolution of K East Weasel Pit and Canister Sludge

Gel formation (not anticipated prior to these scoping tests) was readily apparent when the Weasel Pit and canister sludge samples were digested at temperatures of 60 °C and 95 °C. The volume occupied by the gel was observed to increase with increasing processing temperature and agitation. The gel was isolated and was found to contain amorphous material as well as quartz and approximately 23 wt% anorthosite [a mixture of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ )]. The anorthite is most likely an acid insoluble composition identified in previous work (Terry 1983). Little or no gel formation was observed in the dissolutions conducted at 25 °C.

During K Basin sludge treatment processing, gel formation could impact sludge transport or the solid/liquid separation step, and increase the radionuclide content in the residual solids (i.e., via entrapment or absorption of soluble species). Consequently, nonradioactive tests were conducted to determine sources potentially contributing to the gel formation. Samples of Hanford blow/sand, collected near the K Basins, were digested in nitric acid (several concentrations) at temperatures up to boiling. In some of these tests, the gel formation observed was similar to that seen during dissolution of actual sludge samples. Based on this testing, it was speculated that the Hanford blow/sand, known to be present in K Basin sludge, contributes to the formation of gel.

The analyses of the liquid samples (collected at various intervals during the testing) showed that, as expected, the dissolution rates for iron are highly dependent on temperature. For both the Weasel Pit and canister sludges, the dissolution rates for iron increased by a factor of four when the dissolution temperature was increased from 25 °C to 60 °C. However, increases in temperature have a limited effect on aluminum solubilization. Due to the resistant nature of anorthosite (Note: all the aluminum in the insoluble solids was bound within the anorthosite at 60 °C and 95 °C), no additional solubilization of aluminum is likely to be achieved by increasing the dissolution temperature from 60 °C to 95 °C.

The weight percent residual solids (centrifuged) on a wet basis, after a dissolution step, increased with temperature for both the Weasel Pit and canister sludges. However, on a dry solids basis, the weight percent residual solids decreased as the dissolution temperature increased. It is assumed that more solids dissolution is occurring at higher temperatures resulting in the observed decrease in weight percent residual on a dry basis. The larger volume of gel formed at higher temperatures retained a greater volume of interstitial liquid, resulting in the higher weight percent solids (centrifuged) on a wet basis. Dissolution of the Weasel Pit sludge yielded 50 wt% to 70 wt% residual solids (dry basis). The residual solids from the canister sludge dissolution ranged from 12 wt% to 23 wt% (dry basis).

The residual solids from the acid dissolution of the canister sludge sample contained  $^{137}\text{Cs}$  at a concentration 6 to 17 times greater than the ERDF WAC (Bechtel 1998). The ERDF WAC for  $^{137}\text{Cs}$  is  $32 \text{ Ci/m}^3$ . In comparison, the residual solids from the Weasel Pit sludge dissolution contained  $^{137}\text{Cs}$  at a concentration 3 to 4 times greater than the ERDF WAC. The  $^{137}\text{Cs}$  decontamination factors for the residual solids were 12 to 16 for the Weasel Pit sludge and 6 to 17 for the canister sludge. Increasing the dissolution temperature from  $25^\circ\text{C}$  to  $60^\circ\text{C}$  had little effect on the  $^{137}\text{Cs}$  removal from the Weasel Pit sludge residual solids. For the canister sludge, increasing the dissolution temperature from  $60^\circ\text{C}$  to  $95^\circ\text{C}$  reduced the  $^{137}\text{Cs}$  concentration in the residual solids by a factor of 2. [Decontamination factors (DFs) were calculated by dividing the analyte activity in the dry residual solids (e.g.,  $\text{nCi/g } ^{137}\text{Cs}$ ) by the analytes activity in the initial sludge on a dry weight basis.]

The TRU activity (calculated as the sum of the alpha activity from the plutonium, americium, and curium isotopes) in the insoluble residues was reduced by a factor of 20 to 35 for Weasel Pit sludge and 15 to 25 for canister sludge, but still exceeded the ERDF TRU WAC ( $100 \text{ nCi/g}$ ). The TRU activity in the insoluble residues from Weasel Pit sludge was between  $450 \text{ nCi/g}$  and  $780 \text{ nCi/g}$  and between  $7,500 \text{ nCi/g}$  and  $13,000 \text{ nCi/g}$  for the residual solids from the canister sludge. Increasing processing temperatures had no measurable effect on the plutonium decontamination and had an adverse effect on the  $^{241}\text{Am}$  decontamination. While increasing the processing temperature had an adverse effect on the  $^{241}\text{Am}$  decontamination of samples tested, more effective dissolution of the solids at higher temperatures would reduce the volume of waste that will need to be leached and/or disposed. From these results, a TRU leaching step will most likely be required for the acid insoluble residual solids generated by the process.

Almost all of the uranium in the Weasel Pit and canister sludge samples dissolved within the first 2 hours at both  $25^\circ\text{C}$  and  $60^\circ\text{C}$ . However, in one test with the canister sludge sample, 8 hours were required to effectively dissolve the uranium. The effective ERDF WAC for uranium is  $0.012 \text{ Ci/m}^3$  or  $980 \mu\text{g U/g}$  dry solids (ERDF criterion of  $0.0026 \mu\text{g/ml}$  divided by the assumed density of  $2.66 \text{ g/ml}$ ). The canister sludge residues ranged from  $0.009 \text{ g U/g}$  to  $0.023 \text{ g U/g}$  or  $0.018 \text{ g U/ml}$  to  $0.046 \text{ g U/ml}$ . This level is 10 to 25 times the ERDF WAC. The uranium concentrations in the Weasel Pit Sludge residual solids were  $0.0036 \text{ g/g}$  to  $0.0050 \text{ g/g}$ , or 4 to 5 times the ERDF WAC.

The cumulative impact of the radionuclide concentrations in the residual solids, with respect to ERDF criteria was evaluated with the "sum of fractions" method (10 CFR 61.55). When two or more radionuclides are present in a waste to be dispositioned to ERDF, the concentration of each constituent in the waste must be divided by the appropriate ERDF limit. The quotients are then summed and the sum must be less than or equal to one for the waste to be acceptable for disposal. The "sum of fractions" is about 40 times above the ERDF limit for the Weasel Pit residual solids and about 500 to 800 times greater than the limit for the residual solids from the canister sludge. Although there is significant variability between duplicate tests (i.e., relative percent difference for duplicates ranged from 16% to 54%), the overall trend for the residual solids is that the "sum of fractions" increases with increasing dissolution temperature.

A fraction of the radionuclides assigned to the residual solids may have been dissolved species trapped within the interstitial liquid associated with the gel. This could explain why TRU concentrations tended to increase with increasing dissolution temperature (i.e., greater volume of gel was generated at higher temperatures). For future testing or actual processing, it is important that the residual solids be thoroughly rinsed before analysis to ensure that soluble species are completely removed.

### 2.2.3 Results from the Dissolution of Sludge Containing Ion Exchange Material

No significant dissolution of the IX material occurred under the conditions of this study. Scatter in the data resulting from variable amounts of interstitial liquid makes precise quantification of dissolution difficult. Future bead digestion studies should be conducted such that calculations can be easily referenced to a dry basis.

Results from Fourier transform infrared (FTIR) analyses of the residual solids from the dissolution tests showed that, under the most severe dissolution conditions tested (10 M nitric acid, 25 °C/2 hours, followed by 60 °C/6 hours), no nitration of the organic backbone of the OIER was detected. However, at higher temperatures and longer dissolution periods, the generation of reactive nitrated organic compounds may be a concern.

The IX material in the KE Basin sludge sample has a high affinity for the plutonium(IV) nitrate complex, as well as an affinity for uranium. Distribution coefficients of between 4 ml/g and 86 ml/g were measured for plutonium. The lower values were measured in concentrated uranium solutions (i.e., tests in which the high-uranium-content canister sludge was added) where bead loading approached the maximum resin capacity. The uranium distribution coefficients ( $K_d$ ) were measured between 3 ml/g and 7 ml/g in high-uranium solutions. A distribution coefficient is the concentration of analyte on solid per gram of solid divided by the concentration of analyte in milliliters of equilibrium solution. It should be noted that these measured  $K_d$ 's for plutonium are lower than the expected literature value of 500 ml/gm. With decreased uranium loading the measured  $K_d$  could approach the expected value.

The ERDF WAC for TRU, 100 nCi/g, was exceeded for all IX material residuals, including those not spiked with high-uranium-content canister sludge. This suggests the IX material was already partially loaded with radionuclides or were not sufficiently rinsed of sludge before nitric acid dissolution. In the neat IX material tests, the TRU content was reduced from 800 nCi/g (prior to digestion) to 150 nCi/g to 200 nCi/g in the residual (after 6 hours at 60 °C). In the testing conducted with IX material spiked with the high-uranium-content canister sludge, the TRU level in the IX material residual exceeded the ERDF WAC by a factor of 400 to 500 (after dissolution at 6 hours at 60 °C). These results indicate that separating the IX material before acid dissolution will result in a material much easier to decontaminate for disposal to ERDF. The IX material remaining with the sludge that is subjected to acid dissolution will sorb high levels of TRU.

Dissolution of IX material with 10 M nitric acid at both 25 °C and 60 °C is effective in stripping  $^{137}\text{Cs}$  from OIER to levels approximately equal to the ERDF WAC of 32 Ci/m<sup>3</sup>.

From a "sum of fractions" analysis, the impact of sludge spiking is very apparent, as it increases the "sum of fraction" by a factor of approximately 20 to 300 in comparison to the neat, unspiked IX material residual solids. With the neat IX material residual solids, the "sum of fractions" is about 4 to 8 times above the ERDF limit. The "sum of fractions" for the residual solids from the IX material spiked with sludge are 130 to 1200 times greater than the ERDF WAC limit.

#### 2.2.4 Conclusions from Processing Study

The Scoping Study provided preliminary confirmation of the feasibility of the K Basin sludge dissolution process. The study was also successful in identifying areas within the process that will require more in-depth examination during process development testing. New information generated from the Scoping Study includes: (1) discovery and characterization of gel formation during sludge dissolution and (2) determination/confirmation that IX material have a high propensity to sorb TRU during dissolution (i.e., indication that IX material beads should be removed from K Basin sludge before acid dissolution).

The compositions of the residual solids were also compared against the ERDF WAC to determine whether, and to what extent, further washing/leaching would be necessary before the residual solids could be dispositioned ERDF. These comparisons provide insight into the ability of the nitric acid dissolution step to decontaminate the residual solids. However, for the following reasons, the comparison cannot be used to draw definitive conclusions on whether the residual solids generated within the K Basin Sludge Pretreatment Process will be acceptable for disposal to ERDF. First, in the comparisons above, the residual solids are compared to ERDF WAC on the basis of sludge type (i.e., KE Canister Sludge Composite and KE Areas Sludge Composite), whereas, in the baseline process, all residual solids from K Basins sludge dissolutions will be accumulated and mixed in one tank, which will effectively average the residual solids composition. This averaging will have a dramatic effect on the analyte concentrations in the residual solids from KE Basin, since the less contaminated KE Areas (i.e., floor and pit) residual solids will account for most of the residual solids mass. The more highly contaminated residual solids from the KE canisters and fuel washing will account for only about 1% of total mass.

Second, the baseline process includes a leaching step that will be performed to further decontaminate the residual solids. This leaching step has not been taken into consideration within the comparisons made above. Third, in the baseline process, the leached residual solids will be immobilized in a grout matrix before disposition to ERDF. In accordance with

ERDF rules, compliance with the ERDF WAC will be based upon the concentrations of the analytes within the grout matrix (e.g., TRU activity per unit mass of grout). Therefore, while the ERDF criteria provide a benchmark for comparison and evaluation of nitric acid dissolution, for the reasons discussed, the comparisons cannot be used to make absolute judgments on the efficacy of the process.

## **2.3 EVALUATION OF POLYCHLORINATED BIPHENYLS DATA FROM K EAST BASIN SLUDGE SAMPLES**

The original data for PCBs in K East floor sludge were generated by two different laboratories and utilizing two different instruments. Therefore, an additional review and evaluation of the analyses for PCBs in K East Basin sludge samples was performed. The focus of this review was to provide the best interpretation of the quantitative PCB data presented in Makenas (1996). The details of the evaluation are given in Appendix B and a summary of the evaluation is provided below. This effort, after adjustment to both data sets, resulted in much closer agreement on the PCB concentrations.

### **2.3.1 Summary of Evaluation for Polychlorinated Biphenyls Data**

The evaluation of the PCB analytical data was focused primarily on the quantitative data generated by the Hanford 222-S Laboratory using gas chromatography (GC) with an electron capture detector (ECD), and the data generated by the PNNL 325 Laboratory using gas chromatography/mass spectroscopy (GC/MS) with the use of an Arocolor 1254 standard. Other PCB analytical data were generated from several screening techniques; however, as these data are considered to be semi-quantitative, they were not evaluated in detail.

Table 2.3 shows the originally reported data (Makenas 1996) and adjusted PCB concentrations for the three samples of primary interest. Samples KES-P-16 and KES-R-18 were collected from the Weasel Pit. Sample KES-I-15 was collected from the main basin, 6 in. east of the mouth of the South Load Out Pit.

The reported values were adjusted for several reasons described briefly in this section and in detail in Appendix B. The PCB concentrations provided in the last column of Table 2.3 are believed to most accurately represent the actual PCB concentrations in the Weasel Pit. For Sample KES-I-15, the value shown in the next to the last column, is the most accurate available.

Table 2.3 shows that the adjusted results from both analytical techniques tend to converge. However, the concentrations at which they converge indicate that Samples KES-R-18 and KES-I-15 contained PCBs at concentrations greater than 50,000  $\mu\text{g}/\text{kg}$  (50 ppm).

Table 2.3. Comparison of Quantitative Polychlorinated Biphenyls Data on K East Basin Sludge from 222-S Laboratory (Gas Chromatography/Electron Capture Detector) and 325 Laboratory (Gas Chromatography/Mass Spectroscopy); Settled, Centrifuged, and Dry Sludge Bases.

Sample ID/ 325 Laboratory ID	222-S Laboratory GC/ECD Reported PCB Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> , (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	325 Laboratory GC/MS Reported PCB Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> , (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	Adjusted <sup>5</sup> GC/ECD PCB Conc. Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> , (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	Adjusted <sup>6</sup> GC/MS PCB Conc. Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> , (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>
KES-I-15	101,000 (104,000) [180,000]	no data (no data)	63,000 ( 65,000) [110,000]	no data (no data)
KES-P-16/ 96-00538	40,000 (47,000) [79,000]	16,000 (19,000) [32,000]	29,000 (34,000) [57,000]	31,000 (36,000) [60,000]
KES-P-16D/ 96-00538D		15,000 (18,000) [30,000]		40,000 (47,000) [79,000]
KES-R-18/ 96-00540	180,000 (220,000) [400,000]	19,000 (23,000) [42,000]	110,000 (130,000) [240,000]	43,000 (53,000) [97,000]
KES-R-18D/ 96-00540D		70,000 ( 86,000) [160,000]		140,000 (170,000) [310,000]
KES-R-18MS/ 96-00540MS		62,000 ( 76,000) [140,000]		110,000 (130,000) [240,000]
KES-R18MSD/ 96-00540MSD		43,000 (53,000) [97,000]		82,000 (100,000) [180,000]

<sup>1</sup>Concentrations on per  $\mu\text{g}/\text{kg}$  sludge basis. Note: to convert to ppm, divide  $\mu\text{g}/\text{kg}$  by 1,000 (e.g., 40,000  $\mu\text{g}/\text{kg}$  = 40 ppm).

<sup>2</sup>PCB concentration on a settled sludge basis.

<sup>3</sup>PCB concentration on a centrifuged sludge basis--values in table are in parentheses.

<sup>4</sup>PCB concentration on a dry sludge basis.

<sup>5</sup>Adjusted GC/ECD PCB concentrations (222-S Laboratory), determined from using chromatograph peak heights.

<sup>6</sup>Adjusted GC/MS PCB concentrations (325 Laboratory), adjusted for both solvent recovery and surrogate recovery.

The PCB data in Makenas (1996, Appendix H) are reported on a "centrifuged sludge" basis. Table 2.3 provides PCB concentrations on a "settled sludge" and a "centrifuged sludge" and "dry sludge" basis. Use of the PCB concentrations on a settled sludge basis is more appropriate for regulatory purposes than use of the concentrations on a centrifuged sludge basis. The settled sludge basis is more likely to reflect the form of the sludge in the basin. For this evaluation, conversion of the concentrations to the settled sludge basis reduced the estimated PCB concentration by 3% to 18%. PCB concentrations on a "dry sludge" basis are included in Table 2.3. The rules under TSCA were recently amended in a manner that suggests PCB waste designation determinations should be made on "dry basis" PCB concentrations for most solids.

For K East Basin sludge samples analyzed by GC/MS at the 325 Laboratory that were reported as "non-detects" for PCB in Makenas (1996) "less than" concentrations were determined by assuming an on-column quantification limit of 10 ng (based on experience and discussions with the analyst) and using data on extraction recoveries and sample masses. From this analysis, the estimated "less than values" are shown in Table 2.4 for the other K East Basin sludge samples analyzed. The actual PCB concentrations, on settled, centrifuged, and dry sludge bases, are between the less than values and zero.

Table 2.4. Estimated Quantification Limits for Non-Detect K East Basin Sludge Samples Analyzed by Gas Chromatography/Mass Spectroscopy at the 325 Laboratory.

Sample ID	PCB Aroclor 1254, Settled Sludge Basis, $\mu\text{g}/\text{kg}$ <sup>1</sup> Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>
KES-L-1	<17,000 (<26,000) [<87,000]
KES-A-2	<14,000 (<20,000) [<51,000]
KES-N-5	<79,000 (<14,000) [<66,000]
KES-H-8	<16,000 (<17,000) [<45,000]

<sup>1</sup>Concentrations on per  $\mu\text{g}/\text{kg}$  sludge basis. Note: to convert to ppm, divide  $\mu\text{g}/\text{kg}$  by 1,000 (e.g., 40,000  $\mu\text{g}/\text{kg}$  = 40 ppm).

<sup>2</sup>PCB concentration on a settled sludge basis.

<sup>3</sup>PCB concentration on a centrifuged sludge basis--values in table are in parentheses.

<sup>4</sup>PCB concentration on a dry sludge basis.

### 2.3.2 Discussion of Adjustments

Adjustments were made to the data reported in Reference Makenas (1996) as a result of the review provided in Appendix B. At the 222-S Laboratory, quantification of the GC/ECD data was performed with a single point calibration and by comparing peak areas from the standard (Aroclor 1254) with the peak areas from the K East Basin sludge sample extracts. When these were examined, the chromatographs showed evidence of contamination-based shouldering, which, based on previous experience, can result in an over-estimation of the PCB concentration. The chromatographs were re-evaluated by comparing peak heights of the standard to those of the sample extracts. Under SW-846, in Method 8080A (Organochlorine Pesticides and PCBs), peak heights or peak areas are acceptable quantification techniques. The result of using peak heights for quantification is that the estimated PCB concentrations were reduced by 28% to 41% from that initially reported (Makenas 1996).

Semi-volatile organics analyses (SVOA) performed at the 325 Laboratory initially indicated that PCB may be present in certain K East Basin sludge samples (Silvers 1995). An Aroclor 1254 standard, along with a blank, was analyzed to confirm the presence of PCB by comparison with this standard. The concentrations were quantified. The "on-column" concentrations ranged from 17% to 130% of that obtained from the Aroclor 1254 standard. During examination of these data, we found that a step in the quantification procedure was inadvertently omitted for the PCB data only. The omission of the step was confirmed in a discussion with the analyst. The reported PCB concentrations from this data set did not take into account the fraction of solvent recovered during the sample extractions. Further examination of the data, and write-ups on the data (Silvers 1995), indicated that between the time the samples were extracted and measured (after removal from the hot cell), some evaporation of solvent from the extracts had occurred.

SVOA data, obtained concurrently with the PCB data (i.e., from same extract injections), showed that SVOA surrogates added to the sludge sample during the extraction step were over-recovered. The extent of over-recovery correlated with notes on organic analysis bench sheet (page D03-017 of Silvers, 1995), indicating probable evaporation. Assuming that all over-recoveries resulted from evaporation prior to measurement of the extract volumes, the surrogate recoveries were used as internal standard to correct the estimated PCB concentrations. The over-recoveries acted to reduce the estimated PCB concentrations by 9% to 48% from the values corrected to account for the quantification error. The net effect from accounting for both the omission in the quantification procedure and the over recoveries is that the adjusted PCB concentrations are from 70% to 160% greater than the values previously reported. These adjusted PCB concentrations (shown in Table 2.3) are believed to more accurately reflect the concentrations present in the sludge samples analyzed.

### 2.4 ANALYSIS OF RESIDUAL SOLIDS AFTER ACID DIGESTION

The original analyses of K East floor and Weasel Pit sludge were done by acid digestion of sludge followed by wet chemistry analysis of the resulting liquid. Residuals which did not dissolve in the acid solutions were weighed

and subjected to X-Ray diffraction but never chemically analyzed. For the current effort archive samples of K East floor (Samples L-01 and N-05) and from the K East Weasel Pit (Sample Q-17) were subjected to additional analysis specifically targeted to assess the contribution of acid digest residuals on the composition of virgin sludge. This was done by utilizing caustic fusion as a more aggressive dissolution technique. Where sample volume allowed (Samples L-01 and Q-17) samples were first digested with acid ( $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HCl}$ ) and the undigested residuals subsequently subjected to caustic ( $\text{KOH}$  and  $\text{KNO}_3$ ) fusion.

For Sample N-13 the limited archive material dictated that only caustic fusion (without the acid digestion step) could be performed. The liquid resulting from both processes were analyzed. Table 2.5 compares the current acid digest analyses with previous data. Tables 2.6 through 2.8 show where acid insoluble materials (such as  $\text{SiO}_2$  and  $\text{TiO}_2$  implied by previous XRD work) make a significant contribution to the overall sludge composition. The uranium concentrations of the residual material appear to be anomalously high. This could be due to trapping of uranium-rich acid digest liquid in the filtered residual solids.

## **2.5 DIFFERENTIAL SCANNING CALORIMETRY AND THERMO-GRAVIMETRIC ANALYSIS IN AIR**

Most of the previous Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) work on K Basin sludge has been done utilizing a nitrogen atmosphere. This choice was motivated by a particular accident scenario for Waste Tank storage. These previous analyses with K East Basin sludges demonstrated primarily weight losses due to water evolution. The most recent work on K West canister sludge (Silvers 1997; Makenas 1998a), utilizing an air atmosphere, has indicated a number of exotherms and a weight gain which are probably due to oxidation of reactive sludge. An attempt has now been made to produce similar information (utilizing air) for K East Basin sludge. Subsamples from archived material of the original K East Basin samples were run for TGA/DSC. The results are discussed in detail in Appendix C. The differences in results obtained for air versus nitrogen atmospheres, seen previously for K West canister sludge, were not observed for the K East floor and canister sludge cases. An example of the nitrogen versus air comparison is given in Figure 2.1 with other examples given at the end of Appendix C.

## **2.6 DIFFERENTIAL SCANNING CALORIMETRY AND THERMO-GRAVIMETRIC ANALYSIS OF RESIN BEADS**

A previous study (Pool 1998) of the energetics associated with organic resin beads in sludge relied on uncontaminated (in a radioactive sense) beads obtained directly from the manufacturer. Some of these were treated (prior to DSC and TGA) with nitric acid to simulate the effects on beads of stripping transuranic elements. The results of the TGA/DSC work with radioactive beads (Figure 2.2a) recovered from K East Basin (with and without exposure to acid stripping) are given in Appendix D. Exothermic reactions at high temperatures (Figure 2.2b) were observed in DSC for all radioactive bead samples with the

Table 2.5. Comparison of New and Previous Composition (ICP) Data for Acid Digested Sludge.

Analyte	As-Settled				OldData ug/g dry L01	New,Old ug/g dry RPD
	NewData ug/g dry L01	NewData ug/g cf L01	NewData ug/g as L01	NewData ug/mL as L01		
Al	65972	1.98E+04	1.20E+04	1.39E+04	64600	2.10
Ca	6019	1.80E+03	1.11E+03	1.28E+03	2570	80.31
Fe	80977	2.43E+04	1.48E+04	1.70E+04	81500	-0.64
Na	1144	3.43E+02	2.11E+02	2.43E+02	694	48.97
Si	15503	4.64E+03	2.83E+03	3.26E+03		
U	466097	1.40E+05	8.51E+04	9.79E+04	327000	35.08
Zn	715	2.14E+02	1.31E+02	1.50E+02	647	9.99
Zr	591	1.77E+02	1.08E+02	1.24E+02	621	-4.95

Analyte	As-Settled				OldData ug/g dry N05	New,Old ug/g dry RPD
	NewData ug/g dry N05	NewData ug/g cf N05	NewData ug/g as N05	NewData ug/mL as N05		
Al	94800	6.22E+04	5.00E+04	5.55E+04	105000	-10.21
Ca	34400	2.26E+04	1.81E+04	2.01E+04	28900	17.38
Fe	166000	1.09E+05	8.75E+04	9.71E+04	169000	-1.79
Na	4880	3.20E+03	2.57E+03	2.86E+03	1140	124.25
Si	55300	3.63E+04	2.92E+04	3.24E+04		
U	109000	7.15E+04	5.75E+04	6.38E+04	101000	7.62
Zn	1290	8.46E+02	6.80E+02	7.55E+02	1260	2.35
Zr	483	3.17E+02	2.55E+02	2.83E+02	518	-6.99

Analyte	As-Settled				OldData ug/g dry Q17	New,Old ug/g dry RPD
	NewData ug/g dry Q17	NewData ug/g cf Q17	NewData ug/g as Q17	NewData ug/mL as Q17		
Al	49305	1.04E+04	5.91E+03	8.92E+03	30400	47.44
Ca	9170	1.94E+03	1.11E+03	1.68E+03	5130	56.50
Fe	176865	3.74E+04	2.12E+04	3.20E+04	167000	5.74
Na	10929	2.31E+03	1.31E+03	1.98E+03	309	189.00
Si	212854	4.50E+04	2.55E+04	3.85E+04		
U	76900	1.62E+04	9.22E+03	1.39E+04	72700	5.61
Zn	640	1.35E+02	7.68E+01	1.16E+02	656	-2.47
Zr	169	3.57E+01	2.03E+01	3.07E+01	377	-76.19

[Dry (d), centrifuged (cf), and as-settled (as), values provided]

Table 2.6. Comparison of Acid Digest and Caustic Fusion Composition Results for K East Floor Sample L-01 (Dry Basis).

		KES-L-01-B			
				Residue Wt (g)	0.097
				Initial Wt (g)	1.241
Multiplier=		403.0	4282.7		
ALO#=#		Acid Digest	Fusion-Residue		
Client ID=#		97-3119 @5	97-3119-Ni @2		
		KES-L-01 B	KES-L-01-B	Acid Soluble	Acid Insoluble
				KES-L-01-B	KES-L-01-B
Det. Limit (ug/mL)		ug/g	ug/g	ug/g	ug/g
(Analyte)					Total KES-L-01-B
					ug/g
0.025 Ag	(31)	--	--	(31)	(31)
0.06 Al	63,200	35,600		63,200	65,972
0.25 As	--	--		--	--
0.05 B	(121)	(725)		(121)	177
0.01 Ba	237	(200)		237	253
0.01 Be	52.5	--		52.5	52.5
0.1 Bi	(237)	--		(237)	(237)
0.25 Ca	5,100	11,800		5,100	6,019
0.015 Cd	152	--		152	152
0.2 Ce	(94)	--		(94)	(94)
0.05 Co	--	--		--	--
0.02 Cr	365	(656)		365	416
0.025 Cu	631	(421)		631	664
0.05 Dy	(79)	--		(79)	(79)
0.1 Eu	--	--		--	--
0.025 Fe	78,400	33,100		78,400	80,977
2 K	--	n/a		--	--
0.05 La	(82)	--		(82)	(82)
0.03 Li	(48)	--		(48)	(48)
0.1 Mg	--	(2,820)		--	(220)
0.05 Mn	331	(2,020)		331	488
0.05 Mo	(137)	--		(137)	(137)
0.15 Na	(299)	14,700		(299)	1,443
0.1 Nd	548	--		548	548
0.03 Ni	(45)	n/a		(45)	(45)
0.1 P	445	(574)		445	490
0.1 Pb	(103)	--		(103)	(103)
0.75 Pd	(985)	--		(985)	(985)
0.3 Rh	(599)	--		(599)	(599)
1.1 Ru	--	--		--	--
0.5 Sb	--	--		--	--
0.25 Se	--	--		--	--
0.5 Si	(400)	194,000		(400)	15,103
1.5 Sn	(2,160)	--		(2,160)	(2,160)
0.015 Sr	63.1	(115)		63.1	(9)
1.5 Te	--	--		--	--
1 Th	--	--		--	--
0.025 Ti	113	6,250		113	487
0.5 Tl	--	--		--	--
2 U	458,000	104,000		458,000	8,097
0.05 V	(28)	--		(28)	(28)
2 W	--	--		--	--
0.05 Y	(27)	--		(27)	(27)
0.05 Zn	688	(346)		688	(27)
0.05 Zr	526	(833)		526	(65)

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Table 2.7. Comparison of Acid Digest and Caustic Fusion Composition Results for K East Weasel Pit Sample Q-17 (Dry Basis).

		KES-Q-17-A				
				Residue Wt (g)	0.823	
				Initial Wt (g)	1.512	
Multiplier=		330.7	1606.4			
ALO#=		Acid Digest	Fusion-Residue			
Client ID=		97-3120 @5	97-3120-Ni @2			
		KES-Q-17 A	KES-Q-17-A	Acid Soluble	Acid Insoluble	Total
				KES-Q-17 A	KES-Q-17 A	KES-Q-17 A
Det. Limit (ug/mL)	(Analyte)	ug/g	ug/g	ug/g	ug/g	ug/g
0.025	Ag	(10)	--	(10)	--	(10)
0.06	Al	21,600	50,900	21,600	27,705	49,305
0.25	As	--	--	--	--	--
0.05	B	294	(91)	294	(50)	344
0.01	Ba	110	1,590	110	865	975
0.01	Be	(11)	--	(11)	--	(11)
0.1	Bi	(134)	--	(134)	--	(134)
0.25	Ca	4,930	7,790	4,930	4,240	9,170
0.015	Cd	78.5	--	78.5	--	78.5
0.2	Ce	--	--	--	--	--
0.05	Co	(25)	--	(25)	--	(25)
0.02	Cr	421	(44)	421	(24)	445
0.025	Cu	313	(53)	313	(29)	342
0.05	Dy	--	--	--	--	--
0.1	Eu	--	--	--	--	--
0.025	Fe	176,000	1,590	176,000	865	176,865
2	K	--	n/a	--	n/a	--
0.05	La	--	--	--	--	--
0.03	Li	(11)	--	(11)	--	--
0.1	Mg	1,010	(322)	1,010	(175)	1,185
0.05	Mn	330	(330)	330	(180)	510
0.05	Mo	(54)	--	(54)	--	(54)
0.15	Na	(424)	19,300	(424)	10,505	10,929
0.1	Nd	(117)	--	(117)	--	(117)
0.03	Ni	102	n/a	102	n/a	102
0.1	P	488	(168)	488	(91)	579
0.1	Pb	357	--	357	--	357
0.75	Pd	(417)	--	(417)	--	(417)
0.3	Rh	(116)	--	(116)	--	(116)
1.1	Ru	(673)	--	(673)	--	(673)
0.5	Sb	--	--	--	--	--
0.25	Se	--	--	--	--	--
0.5	Si	2,750	386,000	2,750	210,104	212,854
1.5	Sn	4,970	--	4,970	--	4,970
0.015	Sr	(43)	318	(43)	173	216
1.5	Te	--	--	--	--	--
1	Th	--	--	--	--	--
0.025	Ti	191	635	191	346	537
0.5	Tl	--	--	--	--	--
2	U	76,900	--	76,900	--	76,900
0.05	V	(31)	--	(31)	--	(31)
2	W	--	--	--	--	--
0.05	Y	--	--	--	--	--
0.05	Zn	640	--	640	--	640
0.05	Zr	169	--	169	--	169

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
2) Values in brackets [ ] are within 10-times detection limit with errors likely to exceed 15%.  
3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Table 2.8. Caustic Fusion Composition Results for K East Basin Floor Sample N-05.

		KES-N-05-A
	Multiplier=	1431.6
	ALO#=	KOH Fusion-Only
	Client ID=	97-3122-Ni @2 KES-N-05-A
Det. Limit (ug/mL)	(Analyte)	ug/g
0.025	Ag	--
0.06	Al	94,800
0.25	As	--
0.05	B	808
0.01	Ba	249
0.01	Be	(64)
0.1	Bi	(189)
0.25	Ca	34,400
0.015	Cd	248
0.2	Ce	--
0.05	Co	--
0.02	Cr	574
0.025	Cu	822
0.05	Dy	--
0.1	Eu	--
0.025	Fe	166,000
2	K	n/a
0.05	La	--
0.03	Li	--
0.1	Mg	4,910
0.05	Mn	1,050
0.05	Mo	--
0.15	Na	4,880
0.1	Nd	(222)
0.03	Ni	n/a
0.1	P	(847)
0.1	Pb	(440)
0.75	Pd	--
0.3	Rh	--
1.1	Ru	--
0.5	Sb	--
0.25	Se	--
0.5	Si	55,300
1.5	Sn	(4,400)
0.015	Sr	(94)
1.5	Te	--
1	Th	--
0.025	Ti	1,500
0.5	Tl	--
2	U	109,000
0.05	V	--
2	W	--
0.05	Y	--
0.05	Zn	1,290
0.05	Zr	(483)

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "--" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

acid treated beads exhibiting the largest magnitude enthalpies. Such an observation was not made for virgin beads by Pool (1998). Whether this represents a true difference or simply a variation in experimental technique (such as residual nitrate from varying degrees of washing after treatment) remains to be evaluated.

## 2.7 PARTICLE SIZE DISTRIBUTION

Unlike the two canister sludge campaigns, particle size determinations for K East Basin floor sludge were only performed using a laser scattering technique. Subsequent campaigns for K East and K West also added determinations via sieving. Laser scattering measured particle size distributions up to a maximum size of 700  $\mu\text{m}$  (i.e., only sees material that will pass through a Tyler 24 sieve size). Since the in-basin sludge sampling technique potentially could acquire particles up to 0.64 cm (0.25 in.) in diameter, the question could be posed as to the fraction of K East floor sludge material existing as particles larger than that measurable by the laser technique. To address this question several archive samples of K East floor sludge were run through sieves (with controlled water additions), Figure 2.3. The sample designation sieve sizes and material mass fractions collected on the sieves are given in Tables 2.9, 2.10, and 2.11 respectively. One can see from Table 2.11 and Figure 2.4 that the two floor samples, by weight (and by inference volume) are primarily made up of large particles whereas the Weasel Pit samples are finer. However, the reader should be cognizant of the effects of sludge layers (i.e., that selectively sieving sludge sample layers may not be representative of the entire sludge depth, see Table 2.9) which cannot be evaluated at this time.

Table 2.9. K East Floor and Weasel Pit Samples Analyzed by Wet Sieving.

Sample	Origin	Comment
KES-H-08	Floor K East	Primarily ion exchange beads. Standing water noted on both samples shipped to PNNL. Both samples shipped to PNNL were composited.
KES-M-13A	From top layer of KES-M-13	As-received appeared dry. No bottom layer sample available.
KES-S-19	Weasel Pit K East	As-received appear dry.
KES-T-20	Bottom layer of KES-T-20	As-received appeared dry. Ion exchange beads noted in this sample. No top layer sample available.
SUP MIX	K East canister supernate	SUP MIX is a liquid composite of mixing nearly equal portions of decanted liquid from the nine K East Basin canister samples and filtered through a 0.45 $\mu\text{m}$ membrane.

Table 2.10. Sieve Sizes Used for Wet Sieving.

Tyler Size	USA Equivalent	Sieve Opening (in.)	Sieve Opening (mm)
6	6	0.132	3.35
8	8	0.0937	2.36
14	16	0.0469	1.18
24	25	0.0278	0.710
42	45	0.0139	0.355

Table 2.11. Weight Percent Dry Solids Separated by Sieve Size During the Sieving Analysis.

Sample	Tyler 6	Tyler 8	Tyler 14	Tyler 24	Tyler 42	Beaker
KES-H-08	0	0	3	66	23	8
KES-M-13A	NM	NM	NM	41	24	35
KES-S-19	1	1	4	8	22	65
KES-T-20	1	1	5	12	24	57

NM = Not measured.

Figure 2.1. Comparison of Thermo-Gravimetric Analysis in Air and Nitrogen Atmospheres for K East Canister Sample 96-13.

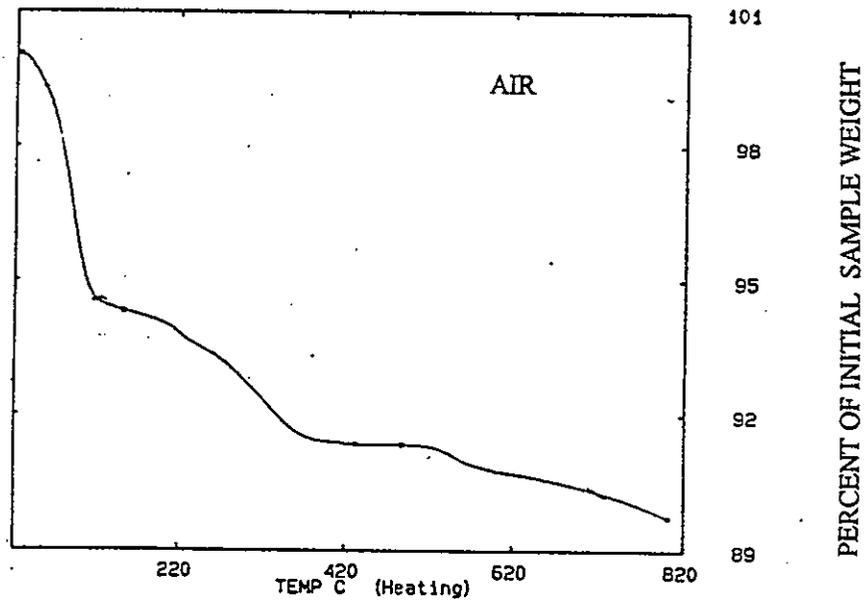
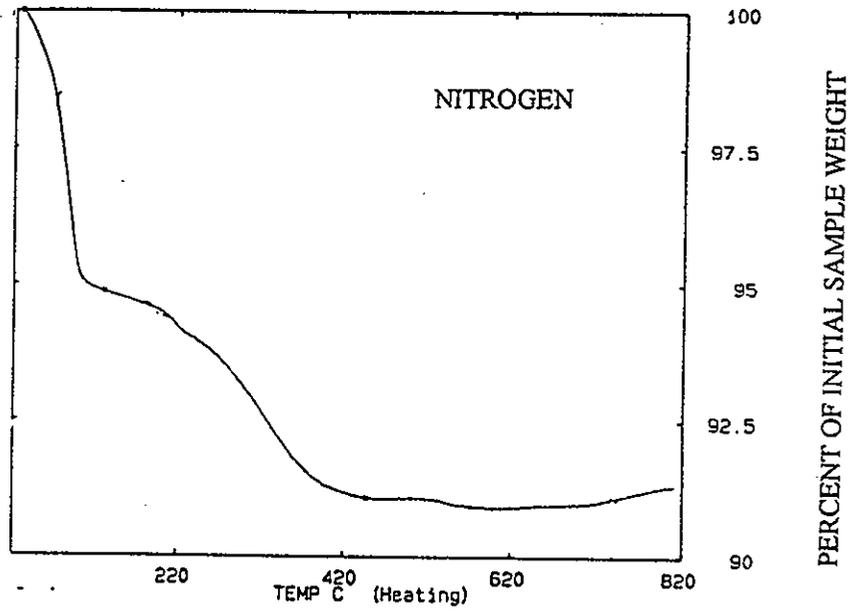


Figure 2.2a. Tyler 24 Sieved Fraction from KE Sample H-08. Sieve openings are 0.710 mm. This fraction is primarily ion exchange beads and white particulates. Note two distinct populations of light and dark beads. White particles are Zeolon, an inorganic ion exchange material used at K Basins.

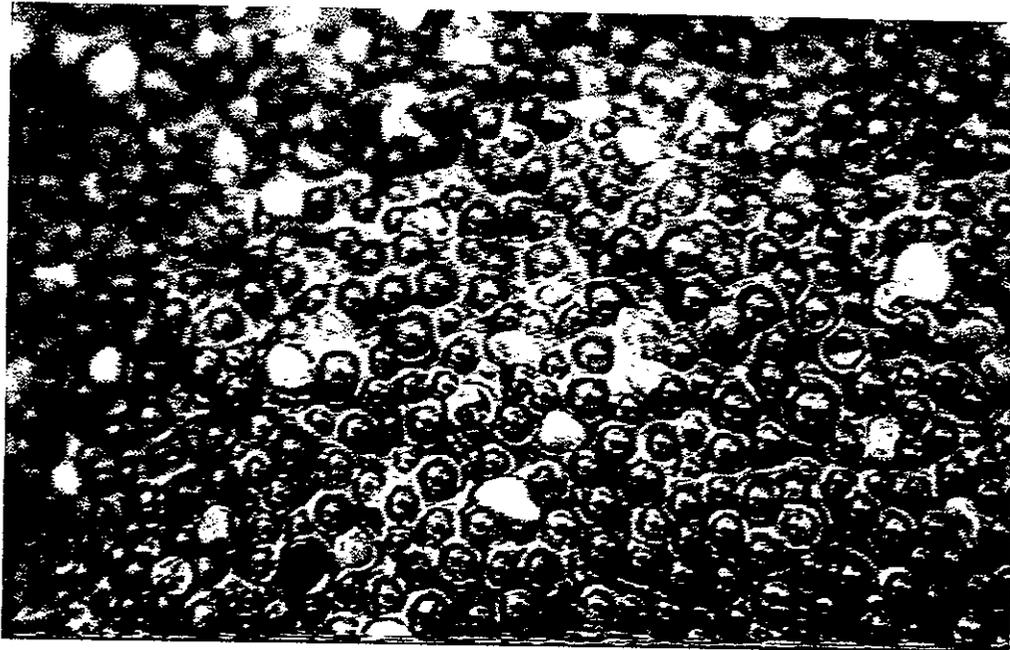


Figure 2.2b. Differential Scanning Calorimetry for a Sample of Untreated Dark Resin Beads Recovered from K East Floor Sample H-08. The indicated exotherm is larger for other beads subjected to nitric acid treatment.

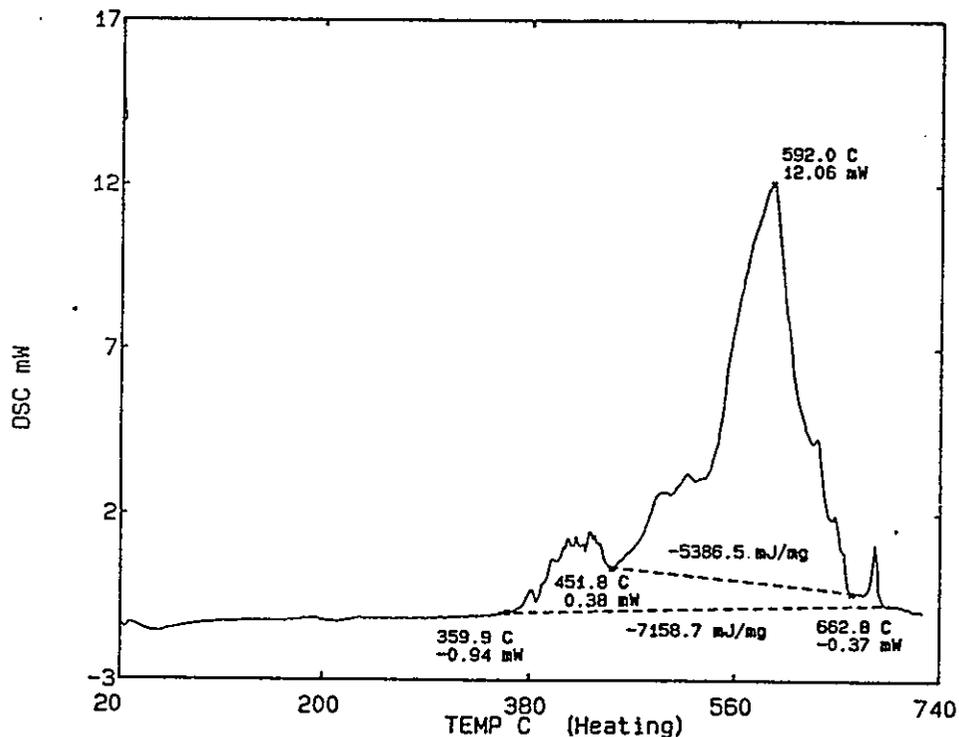
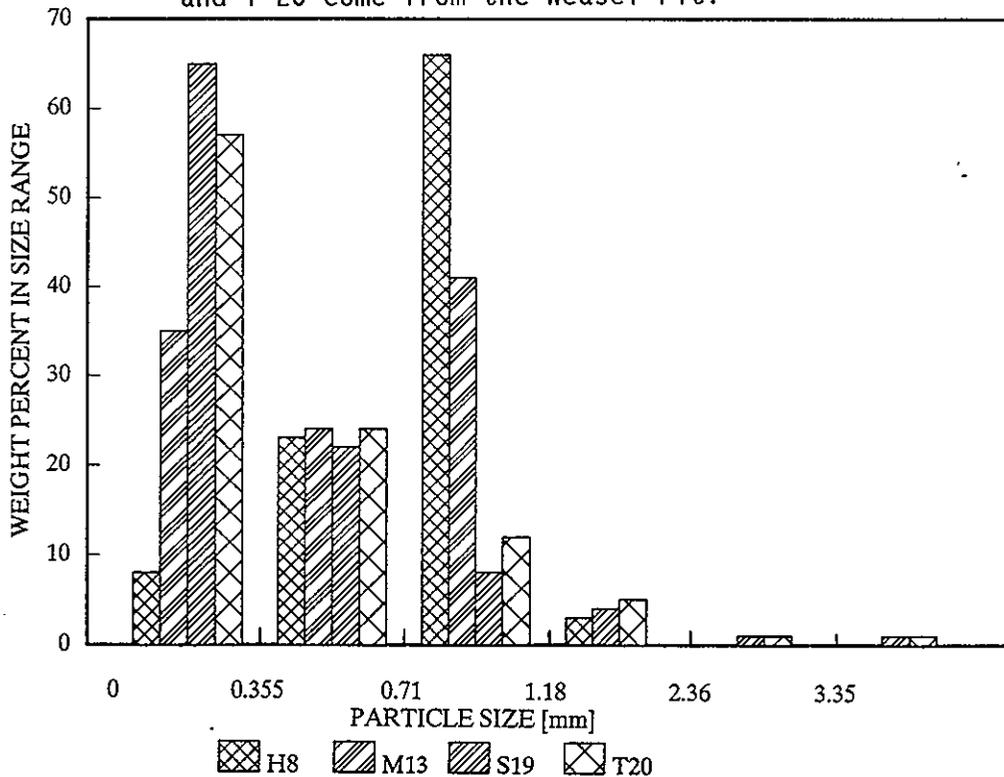


Figure 2.3. Sludge Particles on a Tyler 24 (0.710 mm opening) Sieve. Particles are from K East Weasel Pit Sludge Sample S-19.



Figure 2.4. Particle Size Distribution for K East Basin Floor and Pit Sludge Utilizing Sieving. Note Sample H-08 is primarily composed of resin beads and Samples S-19 and T-20 come from the Weasel Pit.



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**A P P E N D I X   A**

**K BASIN SLUDGE PROCESSING SCOPING STUDY**

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## SECTION A1: INTRODUCTION

This appendix describes work performed by Pacific Northwest National Laboratory (PNNL) for Duke Engineering & Services Hanford (DESH), under letter of instruction DESH-9758893, as part of the supplemental analyses of K East (KE) Basin and K West (KW) Basin canister sludge samples. This work was performed to provide initial guiding information on the proposed treatment of KE Basin sludge using nitric acid described under the Phase I Testing Plan (Delegard et al. 1998). This work was not intended to be a comprehensive study of the dissolution process, but a scoping study conducted to provide early identification of potential problems and limitations of assumptions that may need more in-depth examination as part of the design evolution of the sludge treatment process.

The dissolution behavior of three actual basin samples in nitric acid was examined. Two of the samples initially selected were sludges with a high iron content (one from the KE Weasel Pit and one from KE canisters), and the third was primarily composed of ion exchange (IX) material from the KE floor. The IX material is mainly organic ion exchange resin beads (OIER) (~65 wt%) and some inorganic ion exchange material (~35 wt%). This work was done with 10 M nitric acid at 25°C, 60°C, and 95°C over an 8-hour dissolution period. To examine the adsorption of plutonium and uranium on the IX material, actual K Basin sludge samples high in plutonium and uranium were added to some of the IX material samples before addition of acid. Prior to work with radioactive materials, the dissolution methodology was tested using samples of fresh Purolite beads. See Section A2.2 for further description of the test approach.

### A1.1 K EAST BASIN SLUDGE BACKGROUND

Approximately 43.1 m<sup>3</sup> of sludge have accumulated in the KE Basin. This material is located in the storage canisters, as well as on the floor and in associated pits. Characterization has shown the sludge is primarily uranium oxide, windblown sand, and aluminum and iron oxides and hydroxides. Minor components identified during characterization include organic and inorganic ion exchange materials, paint chips, and polychlorinated biphenyls (PCBs). The concentrations of these components vary by location and depth; however, the total inventory of the various components has not been accurately quantified.

Current remediation plans require removal and treatment of the sludge. The baseline treatment process is nitric acid dissolution of all particulate material less than ¼ inch. The acid-insoluble fraction is to be transferred to the Hanford Environmental Restoration Disposal Facility (ERDF). The liquid fraction is to be diluted with depleted uranium for uranium criticality safety and iron nitrate for plutonium criticality safety, and neutralized with sodium hydroxide. The liquid fraction and associated precipitates are to be stored in the Hanford Tank Waste Remediation Systems (TWRS) pending vitrification.

Based on the current baseline, two sludge process streams from KE Basin will require treatment (Pearce 1998). Stream 1 will be composed of sludge less than 6350 µm (¼ inch) from the Weasel Pit, various other basin pits, the floor area, as well as particles less than 250 µm generated during canister and fuel washing steps. Stream 2, KE dropout drum sludge, will be composed of particles between 250 and 6350 µm generated during canister and fuel washing steps.

Two sludge components were identified to be potential complications to the processing baseline: OIER beads (Purolite NRW-37, Schmidt 1998) and high-iron sludge. Both components could be insoluble in nitric acid and both have the potential to entrain greater than 100  $\mu\text{Ci/g}$  of plutonium in the insoluble solids, exceeding the TRU (transuranic) Waste Acceptance Criterion (WAC) for disposal to ERDF (Bechtel 1998). Literature for similar organic resins show a distribution coefficient for plutonium of approximately 1000 in 10 M nitric acid, raising a criticality concern (Katz et al. 1986). [The distribution coefficient is the ratio of a particular species concentration on a material (e.g., residual solids) compared to its concentration in solution.] In addition, exposure of some organic anion beads to concentrated nitric acid has resulted in nitration of the aromatic rings, creating an explosion hazard (Harland 1994).

## **A1.2 SLUDGE SAMPLE COLLECTION AND STORAGE**

Sludge samples from the basin floor and Weasel Pit were collected from KE Basin by Westinghouse Hanford Company in August and September 1995. These samples were collected at various depths in the sludge, near aluminum and stainless steel canisters, and at various distances from corroding fuel. Sampling of the canister sludge occurred in April 1996. The sludge sample material remaining after characterization activities was stored only to maintain the material for minor follow-on questions; hence, storage had been basically "as is" in the labs at the end of the initial work. During storage, the samples dried and formed materials that range from fine powders to hard chunks. The only exception to this drying is sample KES-H-08, which had a visible standing liquid layer during the scoping work described in this appendix.

## SECTION A2: EXPERIMENTAL

This section describes the samples selected for testing, as well as the experimental approach. All work was conducted under PNNL Quality Assurance Plan MCS-033. Data and observations made during the nitric acid treatment are recorded in test instructions. Videotape images were also collected during the nitric acid treatment step.

### A2.1 DESCRIPTION OF SLUDGE SAMPLES

This scoping study was designed to assess the potential effects of high-iron sludge and OIER beads on the processing baseline. Four sludge samples were used in this work: KES-H-08 (KE Floor), KES-T-20 (KE Weasel Pit), 96-08 (KE Canister), and 96-06 M/L (KE Canister). Table A2.1 lists the samples, along with information from the chain of custody and observations made during characterization. Characterization of the solids began with digestion of the sludges in nitric acid followed by hydrogen peroxide and hydrochloric acid. Table A2.2 lists some of the resulting inorganic and radiochemical analyses.

#### A2.1.1 Ion Exchange (IX) Material Sample

Sample KES-H-08 was collected from the basin floor near the north Load Out Pit. Sieving work showed this sample was approximately 65 wt% round OIER beads. In addition to the round OIER beads, other material, including white particles between 355 and 1180  $\mu\text{m}$ , were observed in sample KES-H-08 (see Figure A2.1). These white particles appeared similar to Zeolon-900, an inorganic mordenite used as an ion exchange material at KE Basin. Results from the x-ray diffraction (XRD) analysis of sample KES-H-08 showed the presence of mordenite ( $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ ). A subsequent evaluation of the KES-H-08 sample showed that it contains ~65 wt% OIER and 35 wt% inorganic ion exchange material, presumably Zeolon-900 (Schmidt 1999).

The material from KES-H-08 used in this work was sieved prior to testing. Sieving was performed to remove oxide sludge and obtain a sample containing primarily IX material. Manufacturer specifications for the OIER indicate that <2% of the beads are smaller than 400  $\mu\text{m}$ . Given this lower limit for the bead diameter, a Tyler 42 sieve with 355  $\mu\text{m}$  openings was used for the separation. The KES-H-08 sample was placed on the Tyler 42 sieve, and KE Basin supernatant was flowed over the sample. The KE Basin supernatant used for this work was prepared by mixing roughly equal volumes of supernatant decanted from each of the nine KE canister sludge samples shipped to PNNL in 1996. The sample was rinsed with the supernatant until no more small dark particles were visible and the rinse passing through the sieve appeared to be clear. The rinse was collected in a clean jar, but not analyzed. White particles (~1 mm) could not be separated from the beads (see Figure A2.1). Again, these particles appeared to be similar in shape and color to Zeolon-900, and are most likely the mordenite identified in the bulk sample by XRD. Following sieving, samples of the IX material were collected in screw cap vials. They formed a wet clump, but no standing liquid was visible.

#### A2.1.2 Weasel Pit Sludge Sample, KES-T-20

Sample KES-T-20 was collected by isolating a vertical column of sludge in the Weasel Pit using an "Isolation Tube." Details of the sample collection can be found in Makenas et al. (1996). Sample KES-T-20 was transferred to the 222-S Laboratory where settling studies were performed. Following

resettling of the material at 222-S, the sample was split into an upper and a lower sample. Material collected from the upper portion of the resettled sample was identified as KES-T-20 Top, while material from the lower portion was identified as KES-T-20 Bottom. The bottom layer was used in this testing. In the remainder of this appendix, KES-T-20 Bottom, as listed in Table A2.1, is referred to as KES-T-20 (T-20). Characterization of this sample showed 24 wt% iron, 5.3 wt% aluminum, and 5.8 wt% uranium on a dry weight basis. As Table A2.2 shows, approximately 33% of sample KES-T-20 remained following the analytical acid digestion procedure (i.e., nitric acid, hydrogen peroxide, and hydrochloric acid).

**Table A2.1** KE Basin Sludge Samples Used in the Scoping Study

Sample Number	Sampling Location	Date Sampled	Comments
KES-H-08	Floor north of North Load Out Pit	8/29/95	Sample is round OIER (~65 wt%) and organic ion exchange material (35 wt%)
KES-T-20 Bottom	Along south wall of Weasel Pit	9/19/95	Bottom layer of KES-T-20
96-06 M/L	KE Cubicle 5465, West Barrel	4/17/96	Interface sample collected between 96-06 M and 96-06 L
96-08	KE Cubicle 2350, East Barrel	4/10/96	Sample is browner than most of the KE canister sludges

**Table A2.2** Major Elemental and Radiochemical Constituents for Samples Used in the Scoping Study (Makenas et al. 1996; 1997)

Analyte	KES-H-08	KES-T-20 Bottom	96-06 L	96-06 M	96-06 Average <sup>a</sup>	96-08
Al	1.87E+04	5.30E+04	1.04E+04	1.45E+04	1.25E+04	7.9E+04
Fe	1.51E+04	2.40E+05	1.20E+03	1.80E+03	1.50E+03	7.3E+04
U	3.14E+03	5.84E+04	8.43E+05	8.26E+05	8.35E+05	4.0E+05
<sup>137</sup> Cs	1.44E+02	5.50E+02	7.85E+02	3.20E+02	5.53E+02	1.18E+03
<sup>241</sup> Am <sup>b</sup>	3.43E-01	6.54E+00	7.58E+01	8.08E+01	7.83E+01	7.73E+01
<sup>89/90</sup> Sr	9.66E+01	3.03E+02	1.98E+03	1.78E+03	1.88E+03	9.40E+02
<sup>238</sup> Pu	6.18E-02	1.27E+00	1.61E+01	1.83E+01	1.72E+01	1.74E+01
<sup>239/240</sup> Pu	4.03E-01	7.98E+00	9.29E+01	1.04E+02	9.85E+01	9.35E+01
Insoluble Solids <sup>c</sup>	9.73E+05	3.26E+05	NA	NA	NA	NA

Units for Al, Fe, U, and Insoluble Solids are in  $\mu\text{g/g}$  of dried sludge.

Units for <sup>137</sup>Cs, <sup>241</sup>Am, <sup>89/90</sup>Sr, <sup>238</sup>Pu, and <sup>239/240</sup>Pu are in  $\mu\text{Ci/g}$  of dried sludge.

<sup>a</sup> 96-06 Average is the average for samples 96-06 L and 96-06 M, and is assumed to be the concentrations in 96-06 M/L.

<sup>b</sup> <sup>241</sup>Am measured by alpha energy analysis.

<sup>c</sup> Residual solids from analytical digestion procedure using HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub>.

NA, not analyzed or not enough residual to analyze.

### **A2.1.3 High-Iron Canister Sludge, 96-08**

Sample 96-08 was collected from the east barrel in KE cubicle position 2350. Characterization of this sample showed 7.3 wt% iron, 7.9 wt% aluminum, and 40 wt% uranium on a dry basis. An acid-insoluble fraction of 96-08 was analyzed by XRD and found to primarily be SiO<sub>2</sub> and an as-yet unidentified crystalline material. It is not known what fraction of 96-08 was insoluble in the acid digestion technique.

### **A2.1.4 High-Uranium and TRU Canister Sludge, 96-06**

As shown in Table A2.2, KE canister sludge sample 96-06 M/L, contains high concentrations of U and Pu. Sample 96-06 M/L was added (spiked) to some of the IX material samples in this work to examine the adsorption of Pu and U on the material. Sample 96-06 M/L was collected from the west barrel in KE cubicle position 5465. During the characterization work, sample 96-06 was dispersed in supernatant and allowed to settle. The settled solids stratified into three distinct layers: an upper layer (96-06 U), a middle layer (96-06 M), and a lower layer (96-06 L). These three layers were collected as unique samples; to prevent commingling of the layers, the interfaces were also collected as separate samples, 96-06 U/M and 96-06 M/L. Samples 96-06 U/M and 96-06 M/L were not characterized; however, as seen in Table A2.2, results for samples 96-06 M and 96-06 L are similar (with the exception of <sup>137</sup>Cs). This similarity suggests 96-06 M/L can be characterized as an average of the two with less than 10% error for most analytes.

### **A2.1.5 Sludge Reconstitution**

All samples with the exception of the IX material from KES-H-08 were rewet in KE Basin water before testing. Rewetting was required due to drying that occurred during storage. Approximately 15 grams of material were removed from each of the archive jars and placed in unique vials. Sufficient KE supernatant was then added to each of the vials to submerge the solids. The vials were then shaken until the supernatant and solids were well mixed. Approximately 24 hours later, the samples were sonicated at 40 Watts for 90 seconds to break up any agglomerate formed during the drying process. The solids were then left undisturbed for 3 days to allow settling. After 3 days, the standing liquid on all samples was clear. This clear liquid was removed using a pipette. The settled solids were stirred to produce a homogeneous sludge and then analyzed for weight percent water by drying 1-gram aliquots at 105°C until a stable mass was reached.

## **A2.2 APPROACH**

The goal of this work was to provide preliminary information on the behavior of KE Basin sludges during nitric acid dissolution and identify any potential complications that may need to be investigated as part of further process development testing. A limited test matrix (Table A2.3) was developed with two temperatures (ambient and 60°C) and three samples (96-08, KES-T-20, and IX material from KES-H-08). Ambient cell temperature during the work was between 25°C and 27°C. Initially, for the high-iron canister sludge, it was only planned to conduct tests 98-08 1 through 98-08 4 (Table A2.3). However, tests 98-08 5 through 98-08 10 were later added to the test matrix to further investigate gel formation during sludge dissolution (see Section A3.1).

Table A2.3 Test Matrix for Scoping Study

Test Number	Sludge Sample Mass, g (dry wt basis)	10 M HNO <sub>3</sub> , ml	Temperature and Duration
OIER, Neat (H-08)			
H-08 1	0.494	20	25°C/2 hr
H-08 2	0.413	20	25°C/2 hr
H-08 3	0.382	20	25°C/2 hr then 60°C/6 hr
H-08 4	0.402	20	25°C/2 hr then 60°C/6 hr
OIER (H-08) + High-Uranium Canister Sludge (96-06)			
H-08 5	0.344 (H-08)/0.1563 (96-06)	20	25°C/2 hr
H-08 6	0.436 (H-08)/0.1422 (96-06)	20	25°C/2 hr
H-08 7	0.383 (H-08)/0.1886 (96-06)	20	25°C/2 hr then 60°C/6 hr
H-08 8	0.452 (H-08)/0.3313 (96-06)	20	25°C/2 hr then 60°C/6 hr
High-Iron Canister Sludge (96-08)			
96-08 1	1.230	20	25°C/8 hr
96-08 2	1.062	20	25°C/8 hr
96-08 3	1.057	20	60°C/8 hr
96-08 4	1.241	20	60°C/8 hr
96-08 5	1.021	20	25°C/6 hr
96-08 6	1.035	20	25°C/6 hr
96-08 7	1.049	20	60°C/6 hr
96-08 8	1.105	20	60°C/6 hr
96-08 9	1.329	20	95°C/6 hr
96-08 10	1.009	20	95°C/6 hr
Weasel Pit Sludge (T-20)			
T-20 1	1.219	20	25°C/8 hr
T-20 2	1.189	20	25°C/8 hr
T-20 3	1.185	20	60°C/8 hr
T-20 4	1.152	20	60°C/8 hr

A nitric acid concentration of 10 M was used for all samples. To identify problems in the procedure (e.g., nitration of organics, excessive offgassing) prior to work with radioactive materials, the dissolution methodology was tested on samples of fresh ion exchange resin, i.e., Duolite C-3 (cation exchanger), Purolite NRW-100 (anion exchanger), and Purolite NRW-400 (cation exchanger). Purolite NRW-37 currently used in the basin is a mixed bed resin containing both Purolite NRW-100 and Purolite NRW-400. Duolite may have been used in the past at the K Basins.

#### **A2.2.1 Nonradioactive Tests**

Fresh Duolite C-3, Purolite NRW-100, and Purolite NRW-400 were used to develop and test the dissolution methodology. Approximately 1-gram aliquots were transferred in quadruplicate into 40-ml glass vials (a total of 12 vials). Twenty milliliters of 10 M nitric acid were added, using a pipette, to each of the 12 vials. Adding the acid to the Purolite NRW-400 produced vapors, and the beads immediately turned a darker shade of amber. No vapors were observed in the NRW-100 or Duolite samples. Both types of Purolite and the Duolite beads floated for between 30 seconds and 3 minutes before sinking in the acid. After approximately 30 seconds, the Duolite samples began to bubble vigorously.

Two vials of each resin type were placed in an aluminum block heater at 60°C. The other two vials of each resin type were left on the counter at approximately 23°C. Every 30 to 60 minutes the samples were swirled and video images collected. After 50 minutes, most of the Duolite material at 60°C had dissolved; the Duolite at 23°C was partially dissolved, while the Purolite samples at both temperatures had experienced no noticeable dissolution. After 6 hours, the Duolite material at 60°C contained no visible solids; the Duolite at 23°C contained undissolved solids, while the Purolite samples at both temperatures had experienced no noticeable dissolution.

The Purolite samples were vacuum filtered using Gelman FP Vericel (polyvinylidene fluoride, PVDF) 0.2- $\mu$ m membranes (Gelman catalog #66476). The filtered Purolite beads were collected and retained for spectroscopic analysis using Fourier transform infrared (FTIR) and Raman. The Duolite C-3 material plugged the filter media and was not retained. Since the beads collected from the basin do not appear to be Duolite, no further attempt was made to separate the Duolite residue from the acid.

#### **A2.2.2 Weasel Pit (KES-T-20) and Canister (96-08) Sludge Tests**

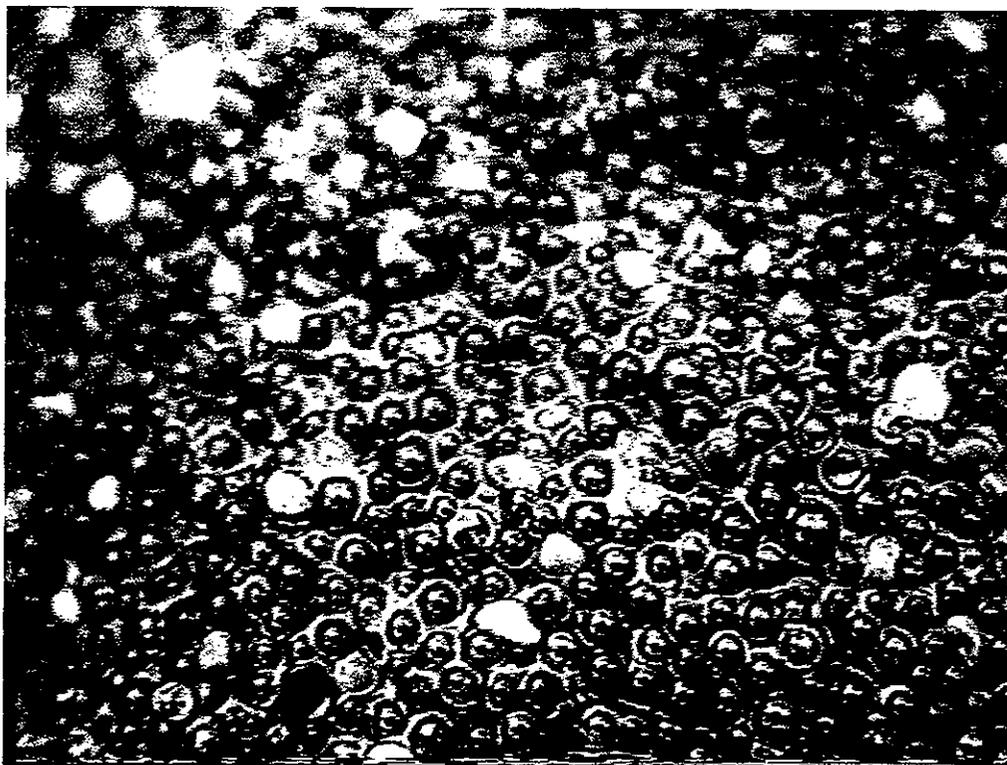
The as-settled sludge samples, 96-08 and KES-T-20, were stirred, and four aliquots of approximately 2 grams were removed from each sample and placed in unique vials labeled 96-08 1 through 96-08 4 and T-20 1 through T-20 4. Twenty milliliters of room-temperature nitric acid were added to each of the vials. Vials 96-08 1, 96-08 2, T-20 1, and T-20 2 were left at ambient temperature while the remaining vials were placed in a block heater at 60°C. Approximately 2, 4, 6, and 8 hours after addition of the acid, the samples were stirred, and 1-ml aliquots of the solutions were removed. The aliquots were immediately filtered through a 0.2- $\mu$ m PVDF syringe filter (Gelman catalog #4406). After 8 hours, the vials were centrifuged at approximately 500 x g (500 times the force of gravity) for 5 minutes. The supernatant was then decanted, and 20 ml of deionized (DI) water were added to the solids. The vials were shaken and then centrifuged for 30 minutes at approximately 750 x g. The rinse water was decanted, and the solids were dried at 105°C until a stable mass was reached.

The solutions filtered at 2, 4, 6 and 8 hours were analyzed for metals by inductively coupled plasma alpha energy spectroscopy (ICP-AES). The solutions filtered at 8 hours were also analyzed for select radionuclides. The solids were digested by fusion, and the resulting solution was analyzed for select radionuclides by alpha energy analysis (AEA) and gamma energy analysis (GEA) and for metals by ICP-AES.

### A2.2.3 IX Material (KES-H-08) Testing

The IX material sieved from KES-H-08 was stirred, and eight 1-gram aliquots were removed and placed in unique vials labeled H-08 1 through H-08 8. Between 0.4 and 1 gram of sludge from sample 96-06 M/L was added to samples H-08 5 through H-08 8. Twenty milliliters of room-temperature nitric acid were added to each of the vials. All eight vials were left at ambient (~25°C) for 2 hours. After 2 hours, samples H-08 3, H-08 4, H-08 7, and H-08 8 were transferred to a heat block at 60°C. At this same time, samples H-08 1, H-08 2, H-08 5, and H-08 6 were vacuum filtered through a 0.2- $\mu$ m PVDF membrane (Gelman catalog #66476). The filtrates were collected for later analysis, and the filtered solids were rinsed with 10 ml of 10 M nitric acid and then 10 ml of DI water. At 4 and 6 hours, samples H-08 3, H-08 4, H-08 7, and H-08 8 were stirred. At 8 hours, samples H-08 3, H-08 4, H-08 7, and H-08 8 were vacuum filtered through a 0.2- $\mu$ m PVDF membrane. The filtrates were collected for later analysis, and the filtered solids were rinsed with 10 ml of 10 M nitric acid and then 10 ml of DI water.

The filtered solutions were analyzed for select metals by ICP-AES and for select radionuclides. The solids were digested by fusion, and the resulting solution was analyzed for select radionuclides by AEA and GEA and for metals by ICP-AES.



**Figure A2.1** Sieved fraction from sample KES-H-08. This fraction is primarily organic ion exchange beads (OIER) and inorganic ion exchange material (white particulates approximately 1 mm in diameter).

## SECTION A3: RESULTS

This section presents the results for the treatment (in 10 M nitric acid) of the three types of K Basin sludge samples: canister sludge (96-08), Weasel Pit sludge (KES-T-20) and IX material sieved from KES-H-08 (with and without sludge spiking). These results include percent insoluble solids, extent of dissolution for selected radioisotopes and metals after 8 hours, as well as concentrations of selected metals in solution as a function of time over 8 hours. Also presented are the results of organic analyses including total organic carbon (TOC) and semi-volatile organic analysis (SVOA) conducted on the acid solutions from sample KES-H-08 after 8 hours, and FTIR analyses of fresh and acid-digested nonradioactive PuroLite resin beads and filtrate.

### A3.1 GEL FORMATION IN CANISTER (96-08) AND WEASEL PIT (KES-T-20) SLUDGE

The gel formation during sludge dissolution was not anticipated from previous sludge characterization or process design work prior to performing the testing and analyses associated with the Supplementary Information on K Basin sludge. Acid digestions performed as part of the previous sludge characterization efforts were less aggressive in some cases and were not videotaped. It is likely that gel formation had occurred previously, but was not observed.

During the dissolution of samples 96-08 and KES-T-20, a gel precipitate was observed in digestions at 60°C. The gel was first observed after 4 hours in sample 96-08, and after 2 hours in sample KES-T-20. No gel was observed in samples digested at 25°C. Figures A3.1 and A3.2 show samples 96-08 and KES-T-20 at 0, 2, 4, 6 and 8 hours into the digestion at 25°C. Figures A3.3 and A3.4 show samples 96-08 and KES-T-20 at 0, 2, 4, 6 and 8 hours into the digestion at 60°C. As can be seen in Figure A3.3, the gel in sample 96-08 was first observed as a structure that was in the liquid but attached to the wall of the vial and connected by a “tail” to the settled solids. When the sample was stirred at 4 hours, the structure was lost, and the material settled to the bottom of the vial, forming a fluffy gel. The material was observed to be similar to “Jello” when the vial was lightly jarred.

Indications of gel formation in sample KES-T-20 were observed after 2 hours (Figure A3.4). Unlike sample 96-08, the gel in KES-T-20 started as fine particles in the settled solids. These fine particles were noted when the sample was swirled after 2 hours. When the 25°C samples were swirled at 2 hours, the liquid clouded and turned to a dark black-brown that did not clear for at least 5 minutes. When the 60°C samples were swirled at 2 hours, the solids formed a floc that settled, leaving a clear solution after several seconds. When the 60°C KES-T-20 samples were swirled at 4, 6 and 8 hours, the settled solids layer became progressively thicker and displayed the same Jello-like behavior as the gel observed in the 60°C samples from 96-08.

A second set of subsamples from 96-08 were digested in an effort to produce samples to characterize the gel observed at 60°C. Six 2-gram subsamples each were weighed into 40-ml vials labeled 96-08 5 through 96-08 10. Twenty milliliters of nitric acid at room temperature were added to each of the vials. Vials 96-08 5 and 96-08 6 were left at ambient temperature (approximately 25°C); vials 96-08 7 and 96-08 8 were placed in an aluminum block heater at approximately 60°C; and vials 96-08 9 and 96-08 10 were placed in an aluminum block heater at approximately 95°C. All samples were swirled approximately every 30 minutes and video images captured every hour. Swirling the samples and collecting the video images required removing the samples from the heater blocks for about 2 minutes. The temperature of the samples during this time out of the heater blocks was not monitored.

The samples at 25°C and 60°C displayed the same behavior as observed at these temperatures during the initial run. A gel was observed in the 60°C samples after approximately 3 hours, and no gel formation was observed at 25°C. Gel formation and solids dissolution in the 95°C samples appeared to occur sooner. When the vials at 95°C were removed from the heater block after 1.5 hours, gel was observed on the bottom of the vial and floating on the surface. The floating gel appeared to have entrained bubbles. While the gel was observed after 1.5 hours, it is possibly formed sooner. When the vials at 95°C were swirled for the same amount of time, the gel volume increased (see Figure A3.5). One explanation for this increase in gel volume is that the swirled material resettled to formed a less dense solids packing. It is also possible that the increase in volume resulted from precipitation of additional material from the acid solution. In this precipitation mechanism, swirling would raise the gel off the bottom of the vessel and into the acid solution. If the acid solution was supersaturated with respect to the gel, then the gel would have acted as nucleation sites for further gel precipitation. This mechanism is unlikely, though, since convection was observed in the vials before swirling began, which would have exposed a supersaturated solution to the gel.

After 6 hours, the solids in the 95°C 96-08 samples appeared to mainly be gel, with a few small black specks evenly distributed throughout (see Figure A3.5). The 60°C samples had less gel than the 95°C samples. The non-gel solids, as well as a few black specks, were visible and again evenly distributed throughout.

After 6 hours, 5 ml of solution were removed from both of the vials at 95°C and immediately filtered through a 0.2- $\mu$ m PVDF membrane (Gelman catalog #4406). Next, all the vials (96-08 5 through 96-08 10) were centrifuged at approximately 1000 x g for 15 minutes. The supernatant was then decanted, and 20 ml of DI water were added to the solids. The vials were shaken and then centrifuged for 15 minutes at approximately 1000 x g. The rinse water was decanted and discarded. The solids were dried at 105°C until a stable mass was reached.

The filtered solutions from the 95°C tests were analyzed for metals by ICP-AES and radionuclides by AEA and GEA. The solids were analyzed for crystalline species by XRD, for select radionuclides by AEA and GEA, and for metals by ICP-AES.

### **A3.2 GEL FORMATION FROM ACID DIGESTION OF HANFORD SAND**

It was proposed that the gel formation was the result of nitric acid digestion of windblown sand that has collected in the basins, as they are not closed structures. Tests were conducted using nonradioactive sand from around the K Basin area in an attempt to duplicate the gel formation.

A supply of representative Hanford sand was acquired, which consisted of particles (less than 0.25 inch) of dirt, rock, and other materials found on the Hanford Site. The material was collected by DESH on August 8, 1997, from the area just outside the transfer bay roll-up doors at both the K East and West Basins.

For each test, approximately 2 grams of the Hanford sand were weighed into 20-ml vials. Other solid additives, if required, were weighed into the vial. Next, a measured quantity of DI water was added to the vial followed by an aliquot of nitric acid calculated to bring the solution to the desired acid molarity. The solution was well mixed, and then the vial was capped. The vials were then placed in an oven and digested at 50°C. Table A3.1 provides the specific conditions for each test, and indicates whether gel was formed.

**Table A3.1** Test Conditions and Qualitative Results from Acid Digestion of Hanford Sand

Test No.	Nitric Acid (ml)	Nitric Acid (M)	Hanford Sand, g	Additives, g	Heating at 50°C	Gel Presence (qualitative)
1	10	10	2.036	none	no	trace
2	10	8	1.9896	none	yes	present
3	10	10	2.0421	none	yes	some
4	10	3	1.9772	none	yes	trace
5	10	12	~2	none	yes	present
6	10	10	1.9948	Rust, 0.0539	yes	some
7	10	10	2.0692	Fe(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	yes	present
8	10	14	2.1516	none	yes	significant

Immediately upon addition of the acid to the Hanford sand, specific particles in the mixtures began to bubble. No precipitate or gel was immediately observed; the nature of the bubbling particles is unknown, although CaCO<sub>3</sub>, commonly found in Hanford soils, will produce CO<sub>2</sub> bubbles when exposed to acid.

After about 4 hours, the vials were removed from the oven and examined for any signs of the gel formation, and then placed back in the oven overnight. In general, the gel was visible after 4 hours. However, for Tests 1 and 4 (Table A3.1), no gel was observed until after the overnight digestion. Figure A3.6 shows an example of the gel formed during this work with Hanford sand.

In addition to the Hanford sand, a set of samples was prepared using crystalline SiO<sub>2</sub> and nitric acid to determine if the gel could be reproduced with only silica and acid. Two samples were prepared with silica and nitric acid at ~10 M; one with cold OIER beads added and one without any beads. An additional control sample was prepared using DI water and silica. None of the samples displayed the floating gel that was observed in the tests prepared with the Hanford sand. It is possible that a trace of gel material was present but was unobservable due to its similarity to the white silica solids. However, lightly shaking the sample did not suspend much of the white solids; thus it was concluded that very little or no gel was formed.

Qualitatively, the molarity of the nitric acid used in each test had a noticeable effect on the formation of the gel, with higher concentrations tending to yield more formation of the gel. It was also noted that the application of heat appeared to be necessary to properly form the material in this particular matrix. It is also suspected that the formation of the gel may be assisted by, or attributed to, one or more subcomponents of the Hanford sand. Test 2 (Table A3.1) with 8 M nitric acid, appeared to have more gel formation than Test 3 at 10 M nitric acid. Due to inhomogeneity of Hanford sand, the composition of the aliquot used for the tests likely differed, and more of the particular component(s) responsible for the gel formation may have been present in the 8 M test than in the 10 M test. However, in actual K Basin

sludge samples, the gel formation may also be enhanced by other components that are not specific to the materials found in the Hanford sand.

The gel formed from the nitric acid digestion of the Hanford sand was separated from the settled solids using a pipette and collected in a single vial. The vial was then centrifuged at approximately 1000 x g for 15 minutes. The acid was decanted and 20 ml of DI water were added to the solids. The solids were resuspended, and the vial was centrifuged again. The DI water was decanted; fresh water was added; and the solids were resuspended. The vial was centrifuged for a third time; the water was decanted; and the solids were dried at 105°C until a stable mass was reached.

The dried gel was then analyzed by XRD for crystalline phases. Three major crystalline phase were identified: quartz ( $\text{SiO}_2$ ), albite [ $\text{Na}(\text{Si}_3\text{Al})\text{O}_8$ ], and anorthite [ $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$ ].

### A3.3 ORGANIC ANALYSES (FTIR, TOC, AND SVOA) PERFORMED ON IX MATERIAL SAMPLES

Fourier transform infrared (FTIR), TOC, and SVOA analyses were performed on selected acid solutions and IX material residual samples following digestion to assess the impact of nitric acid on the organic resin bead backbone. The FTIR analysis was conducted on the IX material residual solids H-08 1 through H-08 8 to determine if nitration of the beads was occurring. Results of FTIR analyses showed that, under the conditions of this work (10 M nitric acid, 25°C for 2 hours followed by 60°C for 6 hours), no nitration of the organic backbone was detected, although this could be a concern at higher temperatures over longer digestion periods.

The filtered solutions from H-08 1 through H-08 8 were subjected to TOC and SVOA analyses to quantify the amount of organic materials introduced into the solution during nitric acid treatment of the OIER beads. The TOC values ranged between 26 and 129  $\mu\text{gC/g}$  with no obvious temperature dependence.

### A3.4 X-RAY DIFFRACTION RESULTS

X-ray diffraction analyses were conducted on the acid-insoluble residual solids from samples 96-08 and KES-T-20 to identify crystalline phases. The residual solids were rinsed with DI water to remove any interstitial acid, and then dried at 105°C until a stable mass was reached. In most cases, the samples were left at 105°C for approximately 72 hours. The samples were ground using a mortar and pestle and mounted on a glass slide using a mixture of amyl acetate and collodion.

Table A3.2 lists the crystalline phases identified by XRD. All samples contained amorphous material that could not be identified by XRD. Quartz ( $\text{SiO}_2$ ) and goethite [ $\text{FeO}(\text{OH})$ ] were found in many of the residual solids from both 96-08 and KES-T-20. For the 96-08 residual solids following digestion at 95°C (96-08 9 and 96-08 10), quartz and anorthite were the primary peaks identified. Anorthite has a set of three strong peaks in the diffraction pattern at approximately 28 degrees. This is the same area of the diffraction pattern that contains several of the unknown peaks identified in other residual samples. It is therefore likely that anorthite is present in most residuals, but not identified by the database.

**Table A3.2** Summary of Crystalline Phases Identified in Dry Residual Solids by XRD Analysis

Sample	Temp, °C	Common Name	Formula
96-08 1	25	Goethite	FeO(OH)
		7 Unknowns	
96-08 2	25	Goethite	FeO(OH)
		Lepidocrocite	FeO(OH)
		Quartz	SiO <sub>2</sub>
		5 Unknowns	
96-08 3	60	Goethite	FeO(OH)
		Quartz	SiO <sub>2</sub>
		4 Unknowns	
96-08 4	60	Goethite	FeO(OH)
		Quartz	SiO <sub>2</sub>
		4 Unknowns	
96-08 9	95	Quartz	SiO <sub>2</sub>
		Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
		1 Unknown	
96-08 10	95	Quartz	SiO <sub>2</sub>
		Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
		1 Unknown	
T-20 1	25	Goethite	FeO(OH)
		Iron Hydroxide	Fe(OH) <sub>3</sub>
		Trevorite	NiFe <sub>2</sub> O <sub>4</sub>
		3 Unknowns	
T-20 2	25	Goethite	FeO(OH)
		Iron Hydroxide	Fe(OH) <sub>3</sub>
		2 Unknowns	
T-20 3	60	Goethite	FeO(OH)
		Quartz	SiO <sub>2</sub>
		2 Unknowns	
T-20 4	60	Goethite	FeO(OH)
		6 Unknowns	

### A3.5 INSOLUBLE RESIDUAL SOLIDS FROM ACID DIGESTION OF SLUDGE SAMPLES

Following exposure to 10 M nitric acid, the insoluble residual solids were separated from the acid solutions. The residual solids in samples H-08 1 through H-08 8 were separated using vacuum filtration, rinsed with 10 ml of 10 M nitric acid, and then rinsed with 10 ml of DI water (see Figure A3.7 for images of KES-H-08 during dissolution). The wet residual solids (mostly beads) were weighed, and the calculated wt% wet residual are listed in Table A3.3. Scatter is seen in the wt% wet residual for samples H-08 1 through H-08 8. While the data in Table A3.3 suggest up to 32 wt% dissolution at 60°C for sample H-08 4, the duplicate shows a mass gain of 15 wt%. This scatter is the result of differing amounts of interstitial water between samples. Overall, the observations suggest qualitatively that no significant dissolution of the IX material occurred. It is recommended that future IX material digestion studies be conducted such that calculations can easily be referenced to a dry basis.

The samples 96-08 1 through 96-08 10 and T-20 1 through T-20 4 were centrifuged, and the acid was decanted. Approximately 20 ml of DI water were then added to the 96-08, and T-20 solids and the samples were centrifuged again and decanted to remove the water. The rinsed centrifuged solids were weighed and then placed in an oven at 105°C until a stable mass was reached. The wt% wet and wt% dry residual solids are listed in Table A3.3. The residual solids results for samples 96-08 1 through 96-08 4 and T-20 1 through T-20 4 are plotted in Figure A3.8, and the results for sample 96-08 5 through 96-08 10 are plotted in Figure A3.9.

The results show that the wt% residual centrifuged solids (wet basis) increase with temperature for both 96-08 and KES-T-20. In contrast, for both of these samples, the wt% residual dry solids values decrease with temperature. One possible explanation for this observation is that hydrates are formed at 60°C, or only small quantities are formed at 25°C. Dehydration of these hydrates at 105°C could then account for the observation. However, no hydrates were identified by XRD. Consequently, it is more likely that the gel, formed at 95°C and 60°C is trapping a greater percentage of interstitial water at the higher digestion temperatures. The loss of interstitial water at 105°C seems a more likely explanation for this trend in the wt% solids data.

**Table A3.3** Weight Percent Wet and Dry Residual Solids Following Exposure to 10 M Nitric Acid

Sample	Temperature and Duration	Wet Residual, wt% <sup>(a)</sup>	Dry Residual	
			wt%	RPD
H-08 1	25°C/2 hr	73	NM	NA
H-08 2	25°C/2 hr	78	NM	NA
H-08 3	25°C/2 hr then 60°C/6 hr	115	NM	NA
H-08 4	25°C/2 hr then 60°C/6 hr	68	NM	NA
H-08 5	25°C/2 hr	98	NM	NA
H-08 6	25°C/2 hr	84	NM	NA
H-08 7	25°C/2 hr then 60°C/6 hr	66	NM	NA
H-08 8	25°C/2 hr then 60°C/6 hr	85	NM	NA
96-08 1	25°C/8 hr	44	22	9%
96-08 2	25°C/8 hr	41	20	
96-08 3	60°C/8 hr	65	12	8%
96-08 4	60°C/8 hr	65	13	
96-08 5	25°C/6 hr	54	21	9%
96-08 6	25°C/6 hr	51	23	
96-08 7	60°C/6 hr	69	16	32%
96-08 8	60°C/6 hr	77	22	
96-08 9	95°C/6 hr	82	12	0%
96-08 10	95°C/6 hr	94	12	
T-20 1	25°C/8 hr	73	70	1%
T-20 2	25°C/8 hr	82	69	
T-20 3	60°C/8 hr	106	49	4%
T-20 4	60°C/8 hr	107	51	

<sup>(a)</sup> Wet residuals from 96-08 and T-20 were centrifuged.

NM = Not measured. The residual OIER bead samples were not dried, so calculation of wt% on a dry basis was not possible.

NA = not applicable.

RPD = relative percent difference.

### A3.6 RADIOCHEMISTRY

Following completion of the digestion, residual solids and filtered liquids were analyzed for selected radionuclides. The compositions of the residual solids were compared against the ERDF Waste Acceptance Criteria (WAC) (Bechtel 1998) to determine whether, and to what extent, further washing/leaching would be necessary before the residual solids could be dispositioned ERDF. These comparisons provide insight into the ability of the nitric acid dissolution step to decontaminate the residual solids. However, for the following reasons, the comparison cannot be used to draw definitive conclusions on whether the residual solids generated within the K Basin Sludge Pretreatment Process will be acceptable for disposal to ERDF. First, in the comparisons below, the residual solids are compared to ERDF WAC on the basis of sludge type (i.e., IX material, KE canister sludge, KE Weasel Pit sludge), whereas, in the baseline process, all residual solids from K Basin sludge dissolutions will be accumulated and mixed in one tank, which will effectively average the residual solids composition. This averaging will have a dramatic effect on the analyte concentrations in the residual solids from KE Basin, since the less contaminated KE floor and Weasel Pit) residual solids will account for most of the residual solids mass. The more highly contaminated residual solids from the KE canisters and fuel washing will account for only about 1% of total residual solids mass from nitric acid dissolution of the KE Basin sludge.

Second, within the baseline K Basin Sludge Pretreatment Process, the IX material may be removed from the K Basin sludge prior to the acid dissolution step. Third, the baseline process includes a leaching step to further decontaminate the residual solids. This leaching step has not been taken into consideration within the comparisons made below. Fourth, in the baseline process, the leached residual solids will be immobilized in a grout matrix before disposition to ERDF. In accordance with ERDF rules, compliance with the ERDF WAC will be based on the concentrations of the analytes within the grout matrix (e.g., TRU activity per unit mass of grout). Therefore, while the ERDF criteria provide a benchmark for comparison and evaluation of nitric acid dissolution, for the reasons discussed, the comparisons cannot be used to make absolute judgments on the efficacy of the nitric acid dissolution process.

The radionuclides most likely limiting the ERDF acceptance of K Basin residual solids are  $^{137}\text{Cs}$  ( $32 \text{ Ci/m}^3$  or  $32 \mu\text{Ci/ml}$ ) and TRU ( $100 \text{ nCi/g}$ ). The TRU isotopes have individual limits:  $^{241}\text{Am}$ ,  $0.05 \text{ Ci/m}^3$  ( $50 \text{ nCi/ml}$ );  $^{238}\text{Pu}$ ,  $1.5 \text{ Ci/m}^3$  ( $1500 \text{ nCi/ml}$ ); and  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ,  $0.029 \text{ Ci/m}^3$  ( $29 \text{ nCi/ml}$ ) each. Because  $^{239}\text{Pu}$  comprises about 3/4 of the  $^{239/40}\text{Pu}$  activity, and the  $^{238}\text{Pu}$  acceptance criterion is high relative to its prevalence and the respective  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  criteria, the limiting plutonium isotope is  $^{239}\text{Pu}$ . The  $^{239}\text{Pu}$  criterion of  $29 \text{ nCi/ml}$  is equivalent to  $39 \text{ nCi } ^{239/240}\text{Pu/ml}$ . The effective uranium limit for disposal to ERDF,  $0.0026 \text{ g U/ml}$ , has the potential to restrict certain K Basin residual solids. The final waste form for residual solids (of which IX material will be a constituent) must meet these levels to allow disposal to ERDF. Note that the ERDF WAC limit for  $^{238}\text{U}$  and its daughters is  $0.012 \text{ Ci/m}^3$ . With 8 alpha and 6 beta decays in the  $^{238}\text{U}$  decay chain and a specific activity of  $3.36 \times 10^{-7} \text{ Ci } ^{238}\text{U/g}$ , the specific activity of the  $^{238}\text{U}$  chain is  $4.7 \times 10^{-6} \text{ Ci/g}$ . The ERDF limit for  $^{238}\text{U}$  thus is  $0.00256 \text{ g } ^{238}\text{U/ml}$  ( $[0.012 \text{ Ci/m}^3]/[4.7 \times 10^{-6} \text{ Ci/g}] = [2.56 \times 10^3 \text{ g/m}^3] = 0.00256 \text{ g } ^{238}\text{U/ml}$ ). The ERDF limit for  $^{235}\text{U}$  (daughters *not* included) is  $0.0027 \text{ Ci/m}^3$  and the specific activity of  $^{235}\text{U}$  is  $2.16 \times 10^{-6} \text{ Ci/g}$ . Thus, the ERDF limit for  $^{235}\text{U}$  is  $0.0013 \text{ g } ^{235}\text{U/ml}$ . The relative limits of the two uranium isotopes, and the nominal 0.7%  $^{235}\text{U}$  enrichment of the K Basin sludge, mean that  $^{238}\text{U}$  concentration limits ERDF disposal. Therefore, the effective uranium limit for disposal to ERDF is  $0.0026 \text{ g U/ml}$ .

The cumulative impact of the radionuclide concentrations in the IX material residual solids, with respect to ERDF criteria, was also evaluated with the "sum of fractions" method (10 CFR 61.55). When two or more radionuclides are present in a waste to be dispositioned to ERDF, the concentration of each

constituent in the waste must be divided by the appropriate ERDF limit. The quotients are then summed, and the sum must be less than or equal to 1 for the waste to be acceptable for disposal.

The solids were prepared by KOH fusion in nickel crucibles, while the filtered solutions were analyzed directly. Cesium-137 was quantified using GEA. Strontium-90 was chemically separated from the samples and quantified. Plutonium was chemically separated and quantified by AEA. Americium and curium were chemically separated and quantified by AEA.

Results from these analyses are listed in Tables A3.4 and A3.5 for the residual solids and filtered liquids, respectively. The solids results are listed in nCi per g of residual solids after drying at 105°C. The liquids are reported in nCi per milliliter.

### A3.6.1 IX Material from Sample KES-H-08

As shown in Table A3.4, the total TRU for all the residual solids from the IX material samples is in excess of the ERDF limit of 100 nCi/g. While TRU elements are not limited to plutonium, americium, and curium, these are the only TRU elements present in the waste in measurable quantities. Therefore, in this report total TRU is defined as the sum of all detectable alpha activities from plutonium, americium, and curium isotopes. Since canister sludge was not added to samples H-08 1 through H-08 4, the level of TRU suggests the IX material was already partially loaded with radionuclides or was not sufficiently rinsed of sludge before the nitric acid treatment. The IX material was prepared by sieving with K Basin water until no solids were visible on them, and the rinse ran clear. This rinsing process was assumed to be similar to the method that might be used in the K Basin Sludge Pretreatment Process to clean the beads.

Figure A3.10 shows the TRU concentrations for the non-spiked or neat IX material tests (i.e., without high-uranium canister sludge spiking). The figure shows that acid dissolution reduced the TRU concentration from about 800 nCi/g to below 200 nCi/g (25°C/2 hr, then 60°C/6 hr), which is close to the ERDF TRU criterion (assuming a density of 1 g/ml for the OIER residual solids). For the dissolutions at 60°C/6 hr, it is apparent from Figure A3.10 that <sup>241</sup>Am is more readily leached from the IX material than the Pu isotopes. While the Pu activity decreased from 460 Ci/g to an average of 148 Ci/g, dropping by a factor of 3, the <sup>241</sup>Am decreased from 340 Ci/g to an average of 21 Ci/g, dropping by a factor of 16. A similar TRU figure was not prepared for the IX material tests with sludge spiking, since the variability in the quantities of sludge used for spiking (Table A2.3) makes graphical interpretation of the data difficult.

The data from Tables A3.3 and A3.4 can be combined with the masses of the initial bead samples and the masses of the dry residual solids to calculate the total TRU on the non-spiked beads before the nitric acid treatment. These total TRU values are listed in Table A3.6. The results in Table A3.6, which shows the TRU content in the IX material before nitric acid treatment, compare well with the total TRU value of 808 nCi/gram reported in Makenas et al. (1996) for sample KES-H-08.

Table A3.4 Results from Radiochemical Analysis for Dried Residual Solids

Sample	<sup>238</sup> Pu	<sup>239/240</sup> Pu	<sup>241</sup> Am	<sup>243/244</sup> Cm	Total TRU <sup>(1)</sup>	<sup>90</sup> Sr	<sup>60</sup> Co	<sup>137</sup> Cs	<sup>137</sup> Cs (Ci/m <sup>3</sup> )
H-08 1	2.46E+01	1.46E+02	7.69E+01	5.63E-01	2.48E+02	1.17E+04	9.99E+00	3.03E+04	3.03E+01
H-08 2	2.98E+01	1.86E+02	1.17E+02	4.30E+00	3.37E+02	1.11E+04	8.79E+00	3.36E+04	3.36E+01
H-08 3	2.31E+01	1.15E+02	2.18E+01	3.14E+00	1.63E+02	2.20E+03	<2.7E+00	1.45E+03	1.45E+00
H-08 4	2.94E+01	1.29E+02	2.03E+01	7.53E+00	1.86E+02	2.39E+03	<2.5E+00	1.76E+03	1.76E+00
H-08 5	4.97E+02	3.76E+03	1.07E+03	3.85E+00	5.33E+03	2.81E+03	<1.6E+01	4.35E+04	4.35E+01
H-08 6	6.51E+02	5.05E+03	2.45E+03	9.36E+00	8.16E+03	6.90E+04	1.34E+01	1.05E+05	1.05E+02
H-08 7	4.27E+03	3.35E+04	2.17E+03	<2E+01	3.99E+04	2.31E+04	<8E+00	1.32E+04	1.32E+01
H-08 8	5.22E+03	4.20E+04	3.10E+03	<5E+01	5.03E+04	3.34E+04	<7.4E+00	1.71E+04	1.71E+01
96-08 1	1.37E+03	8.64E+03	3.04E+03	5.10E+02	1.35E+04	3.88E+03	1.67E+03	1.98E+05	5.25E+02
96-08 2	7.24E+02	4.77E+03	1.96E+03	5.96E+01	7.51E+03	4.64E+03	1.86E+03	2.07E+05	5.51E+02
96-08 3	7.06E+02	5.00E+03	2.99E+03	6.74E+01	8.76E+03	3.97E+03	1.06E+03	1.42E+05	3.78E+02
96-08 4	9.95E+02	6.90E+03	4.36E+03	3.92E+03 <sup>(2)</sup>	1.62E+04 <sup>(2)</sup>	6.16E+03	1.23E+03	1.66E+05	4.42E+02
96-08 9	3.50E+02	5.38E+03	4.55E+03	2.34E+02	1.05E+04	NA	5.10E+02	6.77E+04	1.80E+02
96-0810	3.70E+02	6.33E+03	5.55E+03	8.28E+01	1.23E+04	NA	5.44E+02	7.72E+04	2.05E+02
T-20 1	5.74E+01	4.00E+02	9.86E+01	1.91E+00	5.58E+02	2.42E+04	1.23E+03	3.37E+04	8.96E+01
T-20 2	4.13E+01	2.41E+02	1.72E+02	1.31E+00	4.56E+02	2.12E+04	1.25E+03	4.30E+04	1.14E+02
T-20 3	6.70E+01	4.34E+02	2.78E+02	1.92E+00	7.81E+02	2.59E+04	1.32E+03	4.46E+04	1.19E+02
T-20 4	5.46E+01	3.51E+02	2.29E+02	0.00E+00	6.35E+02	1.90E+04	7.06E+02	4.57E+04	1.22E+02

Units are nCi/g with the exception of <sup>137</sup>Cs, which is also listed in Ci/m<sup>3</sup>.

NA, not analyzed.

(1) TRU = (<sup>238</sup>Pu) + (<sup>239/240</sup>Pu) + (<sup>241</sup>Am) + (<sup>243/244</sup>Cm).

(2) The <sup>243/244</sup>Cm result for 96-08 4 was unusually high and is suspect. This result was used to calculate total TRU for 96-08 4.

**Table A3.5** Results from Radiochemical Analysis for Filtered Liquids

Sample	<sup>238</sup> Pu	<sup>239/240</sup> Pu	<sup>241</sup> Am AEA	<sup>243/244</sup> Cm	<sup>90</sup> Sr	<sup>60</sup> Co	<sup>137</sup> Cs
H-08 1	4.05E-01	2.53E+00	3.26E+00	2.53E-02	NM	NM	NM
H-08 2	3.36E-01	2.17E+00	2.50E+00	2.23E-02	NM	NM	NM
H-08 3	3.70E-01	2.42E+00	3.64E+00	2.61E-02	NM	NM	NM
H-08 4	4.68E-01	2.15E+00	4.27E+00	3.14E-01	NM	NM	NM
H-08 5	1.23E+02	9.47E+02	6.89E+02	8.32E-01	NM	NM	NM
H-08 6	1.16E+02	9.06E+02	6.91E+02	<2E+00	NM	NM	NM
H-08 7	1.17E+02	9.27E+02	1.06E+03	<3E+00	NM	NM	NM
H-08 8	1.80E+02	1.43E+03	1.72E+03	<3E+00	NM	NM	NM
96-08 1	8.76E+02	5.69E+03	4.74E+03	1.37E+01	3.54E+04	1.62E+01	4.45E+04
96-08 2	7.44E+02	4.86E+03	4.47E+03	2.57E+01	3.07E+04	1.21E+01	3.81E+04
96-08 3	8.12E+02	5.13E+03	4.60E+03	1.06E+02	3.16E+04	2.43E+01	3.96E+04
96-08 4	9.28E+02	5.73E+03	4.87E+03	1.77E+01	3.58E+04	3.38E+01	4.66E+04
96-08 9	1.10E+03	7.19E+03	6.00E+03	2.95E+01	NM	4.18E+01	5.78E+04
96-0810	1.07E+03	5.55E+03	4.47E+03	1.95E+01	NM	3.22E+01	4.37E+04
T-20 1	5.85E+01	4.11E+02	3.38E+02	8.27E-01	2.33E+04	1.99E+01	4.41E+04
T-20 2	5.93E+01	3.61E+02	3.03E+02	0.00E+00	2.86E+04	1.82E+01	4.84E+04
T-20 3	5.77E+01	3.87E+02	3.47E+02	5.38E-01	2.72E+04	6.21E+01	4.69E+04
T-20 4	5.25E+01	3.85E+02	3.35E+02	9.24E-01	2.55E+04	7.07E+01	4.35E+04

Units are nCi/ml.

NM = GEA and <sup>90</sup>Sr analyses were not performed on the filtered liquid from samples H-08, and <sup>90</sup>Sr was not analyzed on samples 96-08 9 and 96-08 10.

**Table A3.6** Total TRU Content of Non-spiked IX Material Before Nitric Acid Treatment

Sample	Total TRU (nCi/g dry)
H-08 1	6.67E+02
H-08 2	8.44E+02
H-08 3	7.68E+02
H-08 4	6.47E+02

The ERDF limit for <sup>137</sup>Cs is 32 Ci/m<sup>3</sup>. The <sup>137</sup>Cs activity reported by Makenas et al. (1996) was 144 μCi/g for the dried sample KES-H-08. A density of 1 g/ml is assumed for the IX material. The manufacturer-reported density of wet Purolite NRW-37 is 1.2 g/ml. However, the dry IX material appears to float for a short time when added to water, so the assumption of 1 g/ml for the dry IX material appears reasonable. Assuming a density of 1 g/ml, the activity for the IX material is equal to 144 Ci/m<sup>3</sup>. Assuming a density of 1 g/ml for the acid-treated IX material, the activity after treatment for the non-spiked IX material was 32 Ci/m<sup>3</sup> for the samples treated at 25°C and 16 Ci/m<sup>3</sup> at 60°C. The activity after treatment for the sludge-spiked IX material was 75 Ci/m<sup>3</sup> for the sample treated at 25°C and 15 Ci/m<sup>3</sup> at 60°C. These results show that the treatment with nitric acid is effective in stripping <sup>137</sup>Cs from the IX material, and the ERDF limit of 32 Ci/m<sup>3</sup> is satisfied with 10 M nitric acid at a treatment temperature between 25°C and 60°C.

Figure A3.11 shows the  $^{137}\text{Cs}$  concentrations for the neat IX material tests (i.e., without high-uranium canister sludge spiking). This figure shows that a very significant improvement in  $^{137}\text{Cs}$  decontamination was achieved by continuing the dissolution for 6 hours at  $60^\circ\text{C}$ .

Following dissolution of the sludge in nitric acid, Pu(IV) forms an anionic complex with nitrate. At high nitric acid concentrations, the Purolite anion exchange resin has a high affinity for this complex (Katz et al. 1986). This affinity is expressed as a distribution coefficient,  $K_d$ , that is the ratio of a particular species concentration on the resin compared to its concentration in solution. The  $K_d$ s for Pu and U were calculated for each of the H-08 samples (U was measured by ICP-AES and is described in Section A3.7). The calculated  $K_d$  values are listed in Table A3.7. While scatter is seen in the calculated  $K_d$  values, the data show the IX material has a measurable affinity for Pu under these acidic conditions, with  $K_d$ s ranging from 4 to 86. Assuming 1 L of IX material was introduced into the dissolver with 1000 L of solution, between 0.4% and 8.6% of the Pu should be anticipated to exchange onto the IX material.

The uranium content in the residual solids of the sludge-spiked beads (H-08 5 through H-08 8) was approximately 0.03 g U/g dry residual solids [0.25 milli-equivalents (meq) U/g dry residual solids]. The total capacity of the anion beads is 1.3 meq/ml wet (vendor specification for Purolite A-400 anion exchange resin). Assuming the wet resin is 40 wt% water, contains 50 wt% anion resin, and has a density of 1 g/ml, the anion capacity of the residual solids is approximately 1 meq/g dry residual solids. These results suggest the residual solids (at 0.3 meq/g) are nearing their total anion capacity (1 meq/g). Therefore, higher  $K_d$ s could be observed at lower loadings. The high uranium loading on the anion resin likely was responsible for the lower plutonium  $K_d$ s.

Based on the effective ERDF criterion for uranium,  $2600\ \mu\text{g/ml}$ , the uranium content in the non-spiked IX material residual solids is less than the ERDF limit, while the uranium content in the sludge-spiked IX material is 8 to 16 times above the limit (assuming a density of 1 g/ml for the IX material residual solids).

The results of the “sum of fractions” analysis on the IX material residual solids are provided in Table A3.8. From this table, the impact of sludge spiking (samples H-08 5 through H-08 8) is very apparent, as it increases the “sum of fraction” by a factor of approximately 20 to 300 [in comparison to the non-spiked IX material (samples H-08 1 through H-08 4)]. It is also clear from this table that  $^{239}\text{Pu}$  provides the largest contribution to the “sum of fractions.”

**Table A3.7**  $K_d$  Values Calculated for H-08 Samples

Sample	Temperature, $^\circ\text{C}$	$K_d^{(1)}$ for Pu	$K_d^{(1)}$ for U
H-08 1	25	58	NA <sup>(2)</sup>
H-08 2	25	86	NA
H-08 3	60	49	NA
H-08 4	60	61	NA
H-08 5 <sup>(3)</sup>	25	4.0	4.7
H-08 6 <sup>(3)</sup>	25	5.6	7.0
H-08 7 <sup>(3)</sup>	60	36	3.2
H-08 8 <sup>(3)</sup>	60	29	3.3

(1)  $K_d$ s are in units of ml/g.

(2) NA = Insufficient U to quantify in the residual solids of the non-spiked samples.

(3) H-08 sample spiked with sludge from sample 96-06.

Table A3.8 Sum of Fractions (ERDF Limit) for Residual Solids from IX Material (KES-H-08)

Radionuclide	ERDF Limit <sup>(1)</sup> for Radionuclide, Ci/m <sup>3</sup>	Fraction <sup>(2)</sup> of ERDF Limit for Sample							
		H-08 1	H-08 2	H-08 3	H-08 4	H-08 5 <sup>(3)</sup>	H-08 6 <sup>(3)</sup>	H-08 7 <sup>(3)</sup>	H-08 8 <sup>(3)</sup>
<sup>238</sup> Pu	1.5E+00	0.02	0.02	0.02	0.02	0.33	0.43	2.9	3.5
<sup>239</sup> Pu	2.90E-02	3.8	4.8	3.0	3.3	97	130	870	1100
<sup>241</sup> Am	5.00E-02	1.5	2.3	0.44	0.41	21	49	43	62
<sup>243/244</sup> Cm	1.25E+02	0.00	0.00	0.00	0.00	0.00	0.00		
<sup>90</sup> Sr	7.00E+03	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
<sup>137</sup> Cs	3.2-E+01	0.95	1.1	0.05	0.06	1.4	3.3	0.41	0.53
<sup>238</sup> U + daughters	2.60E-03	0.00	0.00	0.00	0.00	8.1	12	11	16
Sum of Fractions		6.3	8.2	3.5	3.8	130	190	930	1200

Radionuclide concentrations calculated by assuming a density of 1.00 g/mL for the IX material residual solids.

- (1) From ERDF WAC (Bechtel 1998).
- (2) Fraction = concentration of radionuclide divided by ERDF limit.
- (3) H-08 sample spiked with sludge from sample 96-06.

While both the anion and cation resin were present in the samples during this testing, it is assumed that only the anion resin has an affinity for Pu under high nitric acid conditions. Therefore the  $K_d$  measured for the samples is reduced by the dilution with the cation resin. The anion resin has the lower density and was noted collecting in the vortex when samples were stirred. Rinsing with DI water may result in Pu transfer to the cation resin. If the anion and cation resins should separate from each other during processing due to their different densities, the  $K_d$  would be expected to differ from those measured here.

### A3.6.2 Residual Solids from Weasel Pit (KES-T-20) and Canister (96-08) Sludge

As shown in Table A3.4, the total TRU activities for the insoluble residual solids from KES-T-20 and 96-08 were in excess of the ERDF limit of 100 nCi/g. Sample KES-T-20 residual solids exceeded this limit by a factor of approximately 6, while sample 96-08 residual solids exceeded it by a factor of approximately 100. Figures A3.12 and A3.13 compare the TRU activity of the starting materials to the activity of the residual solids. Note the  $^{137}\text{Cs}$  activities before and after treatment are on different scales in both figures. While Table A3.3 shows that more of the solids were dissolved at increasing temperatures, this increased dissolution had no measurable effect on the TRU activity per gram of residual solids on a dry basis. The TRU activity in the KES-T-20 residual solids is between approximately 450 and 780 nCi/g. The TRU activity in the 96-08 residual solids is between approximately 7,500 and 13,000 nCi/g.

Since the XRD analysis could not identify all major phases present in the residual solids, it is not readily apparent as to what techniques/leachants could be employed to leach the remaining TRU from the solids. It should be noted that since less residual solids remain at higher temperature, less material will need to be leached and/or disposed of as TRU waste following treatment at higher temperatures.

Figures A3.14 and A3.15 compare the  $^{137}\text{Cs}$  activity of the initial KES-T-20 and 96-08 sludge to the residual solids. In both plots,  $^{137}\text{Cs}$  is plotted on a log scale. The ERDF limit for  $^{137}\text{Cs}$  activity is 32 Ci/m<sup>3</sup>. As with the TRU isotopes, all residuals were in excess of the ERDF limit. If these solids are to be grouted prior to disposal at ERDF, then a dilution factor of 20:1 (grout:waste) may be required to meet the ERDF  $^{137}\text{Cs}$  activity limit. As with the TRU nuclides, more effective dissolution at higher temperatures does not seem to reduce the specific  $^{137}\text{Cs}$  activity of all the residual solids, but does reduce the volume of waste that will need to be leached and/or disposed. For sample KES-T-20, processing temperatures had no significant effect on the  $^{137}\text{Cs}$  activity of the residuals (between 90 and 120 Ci/m<sup>3</sup>).

The cumulative impact of the radionuclide concentrations in the Weasel Pit and canister sludge residual solids, with respect to ERDF criteria, was evaluated with the "sum of fractions" method (10 CFR 61.55). The results of the "sum of fractions" analysis are provided in Table A3.9. For the calculations, a density of 2.66 g/ml was assumed for the residual solids (from both the Weasel Pit and canister sludge). The XRD results indicate the residual solids are primarily amorphous material (probably quartz), quartz with anorthite, and iron oxide/hydroxides. The theoretical density of quartz is 2.66 g/ml (Linde 1993). The "sum of fractions" is about 40 times above the ERDF limit for the Weasel Pit residual solids and about 500 to 800 times greater than the limit for the residual solids from the canister sludge. The uranium content of the residual solids from KES-T-20 is 4 to 5 times above the limit, while the uranium content of the residual solids from 96-08 is about 10 to 25 times the uranium ERDF limit. Table A3.9 shows that  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  (primary TRU isotopes) provide the largest contributions to, and dominate, the "sum of fractions." Although there is significant variability between duplicates, there does not appear to be any identifiable correlation between the "sum of fractions" data and temperature.

**Table A3.9** Sum of Fractions (ERDF Limit) for Residual Solids from Weasel Pit (KES-T-20) and Canister Sludge (96-08)

Radionuclide	ERDF Limit <sup>(1)</sup> for Radionuclide, Ci/m <sup>3</sup>	Fraction <sup>(2)</sup> of ERDF Limit for Sample/Test Condition									
		96-08 1 25°C 8 hr	96-08 2 25°C 8 hr	96-08 3 60°C 8 hr	96-08-4 60°C 8 hr	96-08 9 95°C 6 hr	96-08 10 95°C 6 hr	T-20 1 25°C 8 hr	T-20 2 25°C 8 hr	T-20 3 60°C 8 hr	T-20 4 60°C 8 hr
<sup>238</sup> Pu	1.5E+00	2.4	1.3	1.3	1.8	0.62	0.66	0.10	0.07	0.12	0.10
<sup>239</sup> Pu	2.90E-02	600	330	340	470	370	440	28	17	30	24
<sup>241</sup> Am	5.00E-02	160	100	160	230	240	300	5.3	9.2	15	12
<sup>243/244</sup> Cm	1.25E+02	0.01	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00
<sup>90</sup> Sr	7.00E+03	0.00	0.00	0.00	0.00	NM <sup>(3)</sup>	NM <sup>(3)</sup>	0.01	0.01	0.01	0.01
<sup>137</sup> Cs	3.2-E+01	17	17	12	14	5.6	6.4	2.8	3.6	3.7	3.8
<sup>238</sup> U + daughters	2.60E-03	13	9.5	14	19	19	23	3.7	4.1	5.1	4.3
<b>Sum of Fractions</b>		790	460	530	730	640	770	40	34	54	44

Radionuclide concentrations calculated by assuming a density of 2.66 g/mL for Weasel Pit and canister sludge residual solids.

(1) From ERDF WAC (Bechtel 1998).

(2) Fraction = concentration of radionuclide divided by ERDF limit.

(3) <sup>90</sup>Sr not measured.

Table A3.10 lists the decontamination factors calculated for  $^{238}\text{Pu}$ ,  $^{239/240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{137}\text{Cs}$ , and U. These factors were calculated by dividing the analyte activity (or concentration in the case of U) in the dry residual solids by the analytes activity in the initial sludge on a dry weight basis. The analyte activities in the dry residual solids for Pu,  $^{241}\text{Am}$ ,  $^{137}\text{Cs}$  were taken from Table A3.4, while the concentration for U was taken from Table A3.14 (see Section A3.7.2). The values for the initial sludge were taken from Table A2.2.

**Table A3.10** Decontamination Factors for Residual Solids from Canister Sludge (96-08) and Weasel Pit Sludge (KES-T-20) Following Dissolution in 10 M Nitric Acid

Sample	Temp., °C	Time, hr	$^{238}\text{Pu}$	$^{239/240}\text{Pu}$	$^{241}\text{Am}$	$^{137}\text{Cs}$	U
T-20 1	25	8	22.1	20.0	66.4	16.3	16.2
T-20 2	25	8	30.8	33.1	38.0	12.8	14.6
T-20 3	60	8	19.0	18.4	23.5	12.3	11.7
T-20 4	60	8	23.3	22.7	28.6	12.0	13.9
96-08 1	25	8	12.7	10.8	25.5	6.0	32.0
96-08 2	25	8	24.0	19.6	39.4	5.7	43.0
96-08 3	60	8	24.6	18.7	25.9	8.3	28.6
96-08 4	60	8	17.5	13.6	17.7	7.1	21.1
96-08 9	95	6	49.7	17.4	17.0	17.4	21.1
96-08 10	95	6	47.0	14.8	13.9	15.3	17.5

While there is up to a 50% difference between some duplicates, the decontamination factor for  $^{241}\text{Am}$  and U appear to decrease with increasing processing temperatures. For sample KES-T-20 the average  $^{241}\text{Am}$  decontamination factor drops from 52 to 26 between 25°C and 60°C, and for sample 96-08 the average  $^{241}\text{Am}$  decontamination factor drops from 32 to 15 between 25°C and 95°C. For sample KES-T-20, the average U decontamination factor drops from 15 to 13 between 25°C and 60°C, and for 96-08 the average U decontamination factor drops from 38 to 19 between 25°C and 95°C. This indicates that a fraction of the  $^{241}\text{Am}$  and U are in phases that are either insoluble to nitric acid under these conditions or less soluble than other species dissolving in the solids at higher temperatures.

The results in Table A3.10 show that, with the exception of samples 96-08 9 and 96-08 10, the decontamination factors for  $^{241}\text{Am}$  are higher than those for the Pu isotopes. This indicates the dissolution is more selective in removing  $^{241}\text{Am}$  from the residual solids in comparison with Pu isotopes. While the decontamination factor for  $^{238}\text{Pu}$  appears to increase with temperature for sample 96-08, this trend is not seen in sample KES-T-20. The factor for  $^{238}\text{Pu}$  increases from an average of 18 at 25°C to 48 at 95°C for sample 96-08. However, the average Pu decontamination factor (averaged for  $^{238}\text{Pu}$  and  $^{239/240}\text{Pu}$ ) for sample KES-T-20 appears to drop from 26 at 25°C to 21 at 60°C. In addition, no trend is seen with temperature in the decontamination factors for  $^{239/240}\text{Pu}$  for either 96-08 or KES-T-20. This suggests scatter and/or sample inhomogeneity is more important in the decontamination factors for Pu than temperature.

The decontamination factors for  $^{238}\text{Pu}$  should be similar to those for  $^{239/240}\text{Pu}$ , as no isotopic effects are anticipated during nitric acid dissolution. However, the decontamination factors for the Pu isotopes in samples 96-08 9 and 96-08 10 averaged 48 for  $^{238}\text{Pu}$  and only 16 for  $^{239/240}\text{Pu}$ . The cause of this inconsistency is unknown. The decontamination factor for  $^{137}\text{Cs}$  increases with temperature for sample 96-08 from 6 to 16 between 25°C and 95°C. However, for sample KES-T-20 the value did not change upon increasing the temperature from 25°C to 60°C, remaining at approximately 12-14.

Based on this data set, the decontamination factors show increasing processing temperature has no measurable effect on the Pu decontamination of the residual solids, only limited effect on  $^{137}\text{Cs}$  decontamination, and an adverse effect on U and  $^{241}\text{Am}$  decontamination. For sample 96-08, the  $^{137}\text{Cs}$  activity in the residual solids decreased by up to a factor of  $\sim 3$  with increasing processing temperature, with average activities of 540, 410, and 190  $\text{Ci}/\text{m}^3$  at 25°C, 60°C, and 95°C, respectively.

### A3.7 ELEMENTAL COMPOSITION BY INDUCTIVELY COUPLED PLASMA

Filtered liquids and residual solids were analyzed for selected element concentrations by ICP-AES. Liquid samples were analyzed following dilution to reduce the acid concentrations to levels acceptable to the instrument. Solids were prepared using a KOH fusion in nickel crucibles. These data were collected to determine the rate and extent of solids dissolution, as well as the effect of temperature on solids dissolution.

#### A3.7.1 IX Material from Sample KES-H-08

After 2 hours at ambient temperature, samples H-08 3, H-08 4, H-08 7 and H-08 8 were transferred to a heat block at 60°C. At this same time, samples H-08 1, H-08 2, H-08 5, and H-08 6 were vacuum filtered. The filtrates were collected for ICP-AES analysis, and the filtered residual solids were then rinsed with 10 ml of 10 M nitric acid and then 10 ml of DI water. After total 8-hour contact with the acid, samples H-08 3, H-08 4, H-08 7 and H-08 8 were vacuum filtered. The filtrates were collected for ICP-AES analysis, and the filtered residual solids were then rinsed with 10 ml of 10 M nitric acid and then 10 ml of DI water. The filtered solids were fused, and the resulting solution was analyzed by ICP-AES. The results for the residual solids and liquids are listed in Tables A3.11 and A3.12, respectively.

For the unspiked IX material, the average aluminum concentration in the residual solids decreased from 5.5  $\mu\text{g}/\text{g}$  dry to 3.25  $\mu\text{g}/\text{g}$  dry between 25°C and 60°C, respectively. In addition to increasing temperature, the total digestion time increased from 2 to 8 hours, and decoupling these independent factors is not possible with this limited data set. However, for samples 96-08 and T-20, to be discussed later, increasing temperature and digestion time affected the rate of aluminum dissolution. Therefore, if aluminum is present in the IX material as sludge adsorbed on the surface, then both temperature and digestion times should affect the dissolution efficiency of aluminum.

Iron showed a similar trend to aluminum. The iron concentration in the unspiked IX material residual solids decreased from an average of 3000  $\mu\text{g}/\text{g}$  dry (2 hr at 25°C) to 760  $\mu\text{g}/\text{g}$  dry (2 hr at 25°C then 6 hr at 60°C). As with aluminum, the individual contributions of dissolution time and dissolution temperature to the iron content cannot be determined from this data set; however, it is likely similar to samples 96-08 and T-20 in which both temperature and time affect the extent of iron dissolution.

Similar interpretations of aluminum and iron dissolution trends in tests with spiked IX materials are not made because of the variability in the quantities of sludge used for spiking.

**Table A3.11** Elemental Composition of Insoluble Residual Solids from IX Material (KES-H-08)

Sample	Dissolution Conditions	Al	Fe	Na	U
H-08 1	25°C/2 hr	5.45E+03	3.29E+03	2.80E+03	<3.6E+03
H-08 2	25°C/2 hr	5.54E+03	2.64E+03	2.60E+03	<3.8E+03
H-08 3	25°C/2 hr then 60°C/6 hr	3.80E+03	8.20E+02	2.80E+03	<3.9E+03
H-08 4	25°C/2 hr then 60°C/6 hr	2.70E+03	7.00E+02	2.30E+03	<3.3E+03
H-08 5 <sup>(1)</sup>	25°C/2 hr	5.33E+03	1.80E+03	2.70E+03	2.10E+04
H-08 6 <sup>(1)</sup>	25°C/2 hr	7.40E+03	7.20E+03	3.00E+03	3.10E+04
H-08 7 <sup>(1)</sup>	25°C/2 hr then 60°C/6 hr	5.17E+03	8.30E+02	2.60E+03	2.90E+04
H-08 8 <sup>(1)</sup>	25°C/2 hr then 60°C/6 hr	4.10E+03	1.20E+03	4.00E+03	4.10E+04

Units are in  $\mu\text{g/g}$  dry residual solids.

(1) H-08 sample spiked with sludge from sample 96-06.

### A3.7.2 Weasel Pit (KES-T-20) and Canister Sludge ( 96-08) Samples

Samples of the liquid phase were collected during the digestion of material from KES-T-20 and 96-08. The liquid subsamples were immediately filtered and analyzed for metals by ICP-AES. The primary metals identified in 96-08 liquids were Al, Fe, and U, while B, Ca, Cr, and Mg were also found in KES-T-20 liquids. The results from these liquid analyses are listed in Table A3.13. Following the digestion, the residual solids were rinsed and dried at 105°C until a stable mass was reached. The resulting dried residual solids were prepared by fusion and analyzed for metals by ICP-AES. The primary metals identified in both 96-08 and KES-T-20 residual solids were Al, Ca, Fe, Mg, Na, Si, Ti, and U. The results from these analyses (dry weight basis) are listed in Table A3.14. Neither residual solids nor liquids from samples 96-08 5 through 96-08 8 were analyzed by ICP-AES.

To better evaluate the rate of dissolution, the data in Tables A3.13 and A3.14 were normalized based on the initial starting masses (i.e., grams of each analyte dissolved per gram of original sludge). The normalization was performed by first calculating the amount of sludge that was placed in the vial on a dry weight basis using the weight fraction solids determined in this work and the wet mass of sludge added. The liquid concentrations in  $\mu\text{g/ml}$  were multiplied by 20 ml (the total volume of acid) and  $10^{-6}\text{g}/\mu\text{g}$  to determine the total mass of each analyte in solution. This mass in the liquid was then divided by the mass of initial sludge on a dry basis to determine the grams of each element that dissolved per gram of initial dry sludge. Table A3.15 lists the mass and wt% solids data used in the calculation. The residual solids concentrations in  $\mu\text{g/g}$  were multiplied by the number of grams of residual solids on a dry basis and  $10^{-6}\text{g}/\mu\text{g}$  to determine the total grams of analyte in the residual solids. This mass in the residual solids was then divided by the mass of initial sludge on a dry basis to determine the mass of each element that did not dissolve per gram of initial dry sludge. Tables A3.16 and A3.17 list the normalized data for the liquids and solids, respectively.

Table A3.12 Elemental Composition of Filtered Liquids from IX Material (KES-H-08)

Analyte	Al	Ba	Ca	Cd	Fe	Mg	Mn	Na	U
H-08 1	2.54E+02	1.00E+01	2.60E+02	1.30E+00	3.95E+01	4.00E+01	2.70E+00	9.40E+02	<3.3E+01
H-08 2	2.15E+02	9.13E+00	2.30E+02	1.10E+00	3.66E+01	3.60E+01	2.50E+00	8.21E+02	<3.3E+01
H-08 3	2.38E+02	8.99E+00	2.40E+02	1.10E+00	9.22E+01	4.00E+01	3.30E+00	7.31E+02	3.80E+01
H-08 4	2.38E+02	9.26E+00	2.60E+02	1.10E+00	8.20E+01	4.10E+01	3.20E+00	7.82E+02	4.10E+01
H-08 5	2.52E+02	7.19E+00	1.80E+02	9.20E-01	4.59E+01	3.50E+01	2.00E+00	6.48E+02	4.45E+03
H-08 6	3.08E+02	9.66E+00	2.50E+02	1.20E+00	5.89E+01	4.60E+01	2.80E+00	8.62E+02	4.41E+03
H-08 7	4.31E+02	9.86E+00	2.40E+02	1.20E+00	1.07E+02	<6.6E+01	3.40E+00	7.41E+02	9.05E+03
H-08 8	5.66E+02	1.19E+01	2.80E+02	1.40E+00	1.92E+02	7.00E+01	4.00E+00	8.62E+02	1.24E+04

Units are in  $\mu\text{g/ml}$ .

**Table A3.13** Elemental Composition of Filtered Liquids from Weasel Pit (KES-T-20) and Canister Sludge (96-08)

Sample	Time, hr	Al	B	Ca	Cr	Fe	Mg	U
96-08 1	2	1.90E+03	ND	ND	ND	3.44E+02	ND	1.41E+04
96-08 1	4	2.66E+03	ND	ND	ND	5.65E+02	ND	1.70E+04
96-08 1	6	3.17E+03	ND	ND	ND	7.85E+02	ND	1.85E+04
96-08 1	8	4.13E+03	ND	ND	ND	1.21E+03	ND	2.26E+04
96-08 2	2	2.57E+03	ND	ND	ND	4.37E+02	ND	2.02E+04
96-08 2	4	3.07E+03	ND	ND	ND	6.49E+02	ND	1.98E+04
96-08 2	6	3.55E+03	ND	ND	ND	9.24E+02	ND	2.03E+04
96-08 2	8	3.61E+03	ND	ND	ND	9.67E+02	ND	2.02E+04
96-08 3	2	3.98E+03	ND	ND	ND	2.30E+03	ND	2.08E+04
96-08 3	4	4.23E+03	ND	ND	ND	3.11E+03	ND	2.10E+04
96-08 3	6	4.15E+03	ND	ND	ND	3.35E+03	ND	2.05E+04
96-08 3	8	4.20E+03	ND	ND	ND	3.77E+03	ND	2.06E+04
96-08 4	2	4.62E+03	ND	ND	ND	2.80E+03	ND	2.33E+04
96-08 4	4	4.77E+03	ND	ND	ND	3.38E+03	ND	2.36E+04
96-08 4	6	4.68E+03	ND	ND	ND	3.75E+03	ND	2.28E+04
96-08 4	8	4.89E+03	ND	ND	ND	4.23E+03	ND	2.39E+04
96-08 9	6	5.52E+03	ND	ND	ND	5.72E+03	ND	2.87E+04
96-08 10	6	4.32E+03	ND	ND	ND	4.42E+03	ND	2.26E+04
T-20 1	2	2.69E+03	1.08E+02	1.44E+03	1.25E+01	8.56E+02	9.60E+01	3.26E+03
T-20 1	4	2.83E+03	8.73E+01	1.40E+03	1.41E+01	1.24E+03	1.03E+02	3.09E+03
T-20 1	6	3.16E+03	8.26E+01	1.52E+03	1.63E+01	1.71E+03	1.19E+02	3.14E+03
T-20 1	8	3.30E+03	5.65E+01	1.52E+03	1.78E+01	2.10E+03	1.26E+02	3.15E+03
T-20 2	2	2.75E+03	9.68E+01	1.28E+03	1.25E+01	9.58E+02	9.58E+01	2.79E+03
T-20 2	4	3.17E+03	8.74E+01	1.39E+03	1.47E+01	1.41E+03	1.11E+02	2.88E+03
T-20 2	6	3.50E+03	8.50E+01	1.49E+03	1.65E+01	1.79E+03	1.25E+02	2.96E+03
T-20 2	8	3.62E+03	8.00E+01	1.51E+03	1.77E+01	2.13E+03	1.31E+02	2.96E+03
T-20 3	2	3.46E+03	9.71E+01	1.43E+03	2.32E+01	5.19E+03	1.35E+02	3.14E+03
T-20 3	4	3.66E+03	8.71E+01	1.47E+03	2.61E+01	6.95E+03	1.49E+02	3.18E+03
T-20 3	6	3.94E+03	8.15E+01	1.53E+03	2.98E+01	9.68E+03	1.68E+02	3.22E+03
T-20 3	8	4.00E+03	7.92E+01	1.55E+03	3.14E+01	1.15E+04	1.76E+02	3.26E+03
T-20 4	2	3.14E+03	9.11E+01	1.35E+03	2.05E+01	4.57E+03	1.26E+02	3.12E+03
T-20 4	4	3.54E+03	2.28E+02	1.42E+03	2.55E+01	7.59E+03	1.50E+02	3.14E+03
T-20 4	6	3.75E+03	8.46E+01	1.50E+03	2.87E+01	9.93E+03	1.70E+02	3.13E+03
T-20 4	8	3.87E+03	8.02E+01	1.51E+03	3.06E+01	1.23E+04	1.76E+02	3.20E+03

Units are in  $\mu\text{g/ml}$ .

ND: Concentrations of B, Ca, Cr, and Mg were above the detection limit, but within 10 times the detection limit.

**Table A3.14** Elemental Composition of Residual Solids from Weasel Pit (KES-T-20) and Canister Sludge (96-08)

Sample	Al	Ca	Fe	Mg	Na	Si	Ti	U
T-20 1	1.53E+04	3.35E+03	2.32E+05	2.64E+03	7.78E+03	2.00E+05	3.23E+03	3.60E+03
T-20 2	1.64E+04	3.70E+03	2.30E+05	2.17E+03	7.74E+03	2.00E+05	2.39E+03	4.00E+03
T-20 3	1.72E+04	5.58E+03	1.92E+05	2.52E+03	1.01E+04	2.22E+05	4.09E+03	5.00E+03
T-20 4	1.82E+04	6.61E+03	1.21E+05	2.64E+03	9.69E+03	2.89E+05	2.83E+03	4.20E+03
96-08 1	5.14E+04	1.11E+04	2.57E+05	5.15E+03	1.15E+04	1.32E+05	3.40E+03	1.25E+04
96-08 2	4.90E+04	6.10E+03	2.89E+05	3.32E+03	9.99E+03	8.09E+04	2.15E+03	9.30E+03
96-08 3	3.86E+04	1.12E+04	1.35E+05	4.73E+03	1.57E+04	2.55E+05	3.76E+03	1.40E+04
96-08 4	3.22E+04	1.29E+04	1.64E+05	5.90E+03	1.26E+04	2.18E+05	4.74E+03	1.90E+04
96-08 9	4.54E+04	2.09E+04	3.45E+04	8.43E+03	2.04E+04	2.98E+05	5.37E+03	1.90E+04
96-08 10	4.34E+04	1.77E+04	2.82E+04	7.09E+03	1.86E+04	3.20E+05	4.96E+03	2.29E+04

Units are in  $\mu\text{g/g}$  dry residue.

**Table A3.15** Mass and Weight Percent Solids Data Used to Calculate Normalized Concentrations

Sample	Initial Wet, g	Wt Fraction Solids	Initial Dry, g	Insoluble Dry, g	Wt % Dissolved
T-20 1	2.3197	0.525	1.219	0.8555	29.8
T-20 2	2.2625	0.525	1.189	0.8217	30.9
T-20 3	2.2549	0.525	1.185	0.5757	51.4
T-20 4	2.1928	0.525	1.152	0.5898	48.8
96-08 1	2.443	0.504	1.230	0.2741	77.7
96-08 2	2.1083	0.504	1.062	0.2078	80.4
96-08 3	2.0982	0.504	1.057	0.1267	88.0
96-08 4	2.4632	0.504	1.241	0.1637	86.8
96-08 9	2.3228	0.572	1.329	0.157	88.2
96-08 10	1.7635	0.572	1.009	0.125	87.6

**Table A3.16** Normalized Elemental Composition of Filtered Liquids from Weasel Pit (KES-T-20) and Canister Sludge (96-08)

Sample	Time, hr	Al	B	Ca	Cr	Fe	Mg	U
96-08 1	2	3.09E-02	ND	ND	ND	5.59E-03	ND	2.30E-01
96-08 1	4	4.33E-02	ND	ND	ND	9.18E-03	ND	2.76E-01
96-08 1	6	5.16E-02	ND	ND	ND	1.28E-02	ND	3.00E-01
96-08 1	8	6.71E-02	ND	ND	ND	1.97E-02	ND	3.68E-01
96-08 2	2	4.84E-02	ND	ND	ND	8.24E-03	ND	3.81E-01
96-08 2	4	5.77E-02	ND	ND	ND	1.22E-02	ND	3.73E-01
96-08 2	6	6.68E-02	ND	ND	ND	1.74E-02	ND	3.82E-01
96-08 2	8	6.80E-02	ND	ND	ND	1.82E-02	ND	3.81E-01
96-08 3	2	7.54E-02	ND	ND	ND	4.36E-02	ND	3.93E-01
96-08 3	4	8.00E-02	ND	ND	ND	5.88E-02	ND	3.97E-01
96-08 3	6	7.86E-02	ND	ND	ND	6.34E-02	ND	3.87E-01
96-08 3	8	7.95E-02	ND	ND	ND	7.14E-02	ND	3.90E-01
96-08 4	2	7.44E-02	ND	ND	ND	4.52E-02	ND	3.75E-01
96-08 4	4	7.69E-02	ND	ND	ND	5.46E-02	ND	3.81E-01
96-08 4	6	7.55E-02	ND	ND	ND	6.04E-02	ND	3.68E-01
96-08 4	8	7.88E-02	ND	ND	ND	6.82E-02	ND	3.85E-01
96-08 9	6	1.08E-01	ND	ND	ND	1.12E-01	ND	5.62E-01
96-08 10	6	8.46E-02	ND	ND	ND	8.66E-02	ND	4.43E-01
T-20 1	2	4.41E-02	1.78E-03	2.36E-02	2.04E-04	1.41E-02	1.58E-03	5.36E-02
T-20 1	4	4.64E-02	1.43E-03	2.30E-02	2.31E-04	2.04E-02	1.69E-03	5.08E-02
T-20 1	6	5.18E-02	1.36E-03	2.49E-02	2.68E-04	2.81E-02	1.95E-03	5.16E-02
T-20 1	8	5.42E-02	9.27E-04	2.49E-02	2.92E-04	3.45E-02	2.07E-03	5.17E-02
T-20 2	2	4.63E-02	1.63E-03	2.16E-02	2.10E-04	1.61E-02	1.61E-03	4.70E-02
T-20 2	4	5.34E-02	1.47E-03	2.34E-02	2.47E-04	2.38E-02	1.88E-03	4.85E-02
T-20 2	6	5.88E-02	1.43E-03	2.50E-02	2.78E-04	3.01E-02	2.11E-03	4.98E-02
T-20 2	8	6.09E-02	1.35E-03	2.53E-02	2.98E-04	3.58E-02	2.20E-03	4.98E-02
T-20 3	2	5.84E-02	1.64E-03	2.42E-02	3.91E-04	8.76E-02	2.28E-03	5.31E-02
T-20 3	4	6.18E-02	1.47E-03	2.49E-02	4.40E-04	1.17E-01	2.51E-03	5.37E-02
T-20 3	6	6.65E-02	1.38E-03	2.58E-02	5.04E-04	1.63E-01	2.84E-03	5.44E-02
T-20 3	8	6.75E-02	1.34E-03	2.62E-02	5.30E-04	1.94E-01	2.97E-03	5.50E-02
T-20 4	2	5.45E-02	1.58E-03	2.35E-02	3.57E-04	7.93E-02	2.18E-03	5.42E-02
T-20 4	4	6.15E-02	3.95E-03	2.46E-02	4.43E-04	1.32E-01	2.60E-03	5.45E-02
T-20 4	6	6.51E-02	1.47E-03	2.60E-02	4.99E-04	1.72E-01	2.95E-03	5.44E-02
T-20 4	8	6.72E-02	1.39E-03	2.63E-02	5.32E-04	2.14E-01	3.06E-03	5.56E-02

Units are in g/g initial dry sludge.

ND = not detected.

**Table A3.17** Normalized Elemental Composition of Residual Solids from Weasel Pit (KES-T-20) and Canister Sludge (96-08)

Sample	Al	Ca	Fe	Mg	Na	Si	Ti	U
T-20 1	1.07E-02	2.35E-03	1.63E-01	1.85E-03	5.46E-03	1.40E-01	2.27E-03	2.53E-03
T-20 2	1.13E-02	2.56E-03	1.59E-01	1.50E-03	5.35E-03	1.38E-01	1.65E-03	2.77E-03
T-20 3	8.36E-03	2.71E-03	9.33E-02	1.22E-03	4.91E-03	1.08E-01	1.99E-03	2.43E-03
T-20 4	9.32E-03	3.38E-03	6.20E-02	1.35E-03	4.96E-03	1.48E-01	1.45E-03	2.15E-03
96-08 1	1.15E-02	2.48E-03	5.73E-02	1.15E-03	2.56E-03	2.94E-02	7.57E-04	2.78E-03
96-08 2	9.59E-03	1.19E-03	5.66E-02	6.50E-04	1.95E-03	1.58E-02	4.21E-04	1.82E-03
96-08 3	4.63E-03	1.34E-03	1.62E-02	5.67E-04	1.88E-03	3.06E-02	4.51E-04	1.68E-03
96-08 4	4.25E-03	1.70E-03	2.16E-02	7.79E-04	1.66E-03	2.88E-02	6.25E-04	2.51E-03
96-08 9	5.36E-03	2.47E-03	4.08E-03	9.96E-04	2.41E-03	3.52E-02	6.35E-04	2.25E-03
96-08 10	5.13E-03	2.09E-03	3.33E-03	8.38E-04	2.20E-03	3.78E-02	5.86E-04	2.71E-03

Units are in g/g initial dry sludge.

Figures A3.16 through A3.21 are graphs that show the normalized concentrations of U, Fe, and Al in solution versus time for subsamples of 96-08, and 96-08 at 25°C and 60°C. Figure A3.16 shows that with the exception of the duplicate 25°C 96-08 samples, the uranium dissolution in 96-08 was independent of temperature and was complete within the first 2 hours. It is unclear why the uranium in the 96-08 duplicate at 25°C required the full 8 hours to dissolve. Figure A3.17 shows for sample KES-T-20 more uranium dissolved at 60°C compared to similar durations at 25°C. Table A2.2 shows that samples 96-08 and KES-T-20 contain 0.40 and 0.058 g U/g dry sludge, respectively. The normalized concentration of uranium in solution after 8 hours at 60°C was 0.39 and 0.055 g U/g dry sludge. From these values, approximately 95% of the uranium in these samples dissolved within 8 hours of contact at 60°C. Most of this uranium in 96-08 and KES-T-20 dissolved within the first 2 hours at both temperatures.

Figures A3.18 and A3.19 plot the normalized iron concentration in the solutions. Both plots show that the dissolution rate for iron at 60°C is four times higher than at 25°C. Table A2.2 shows sample 96-08 and KES-T-20 contain 0.073 and 0.24 g Fe/g dry sludge, respectively. The normalized iron in solution after 8 hours at 60°C was 0.070 and 0.20 g Fe/g dry sludge. These values suggest that the dissolution is near completion after 8 hours. However, Table A3.17 shows that the solids after 8 hours still contain a normalized 0.019 and 0.077 g Fe/g dry solids for 96-08 and KES-T-20, respectively, so approximately 26% of the iron in 96-08 and 32% of the iron in KES-T-20 is undissolved after 8 hours at 60°C. This is presented graphically in Figures A3.18 and A3.19.

Figures A3.20 and A3.21 plot the normalized aluminum concentration in the solutions. The dissolution of aluminum in sample KES-T-20 was approximately 20% higher after the first 2 hours at 60°C compared to 25°C, but the rates after the first 2 hours were comparable at both temperatures. Figure A3.18 shows that aluminum dissolution for 96-08 at 60°C slowed dramatically after approximately 4 hours at roughly 0.079 g Al/g dry solids. The total aluminum in 96-08 from Table A2.2 is 0.079 g Al/g dry sludge, suggesting complete dissolution. However, the data in Table A3.17 show that the solids after 8 hours still contained a normalized 0.004 g Al/g dry sludge. The sample results in Table A2.2 were collected using an acid preparation step, while the results in Table A3.17 were collected using a fusion preparation step. The fusion results here suggest sample 96-08 contains a nitric acid-insoluble Al residual solids. This observation matched the identification of anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) by

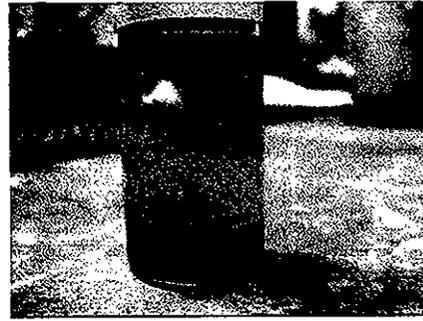
XRD in the 96-08 95°C acid-insoluble residual solids. Anorthite, a mineral found in Hanford sediments, was not positively identified in KES-T-20 acid-insoluble residual solids, but peaks in the XRD spectra suggest it is present.

Figures A3.20 and A3.21 compare the normalized aluminum content of the liquid and residual solids fractions after 8 hours for samples of 96-08 and KES-T-20. Figures A3.22 and A3.23 compare the normalized iron content of the liquid and residual solids after 6 to 8 hours for samples 96-08 and KES-T-20. Figure A3.22 includes the 6-hour normalized data as well, showing that 0.0037 g Fe/g dry sludge, or 5% of the total iron, remained undissolved after 6 hours at 95°C for sample 96-08. Figure A3.24 shows that there is no additional dissolution of aluminum achieved by increasing the dissolution temperature from 60°C to 95°C for 96-08. Figure A3.25 shows that only an additional 4% of the aluminum in KES-T-20 is dissolved by increasing the dissolution temperature from 20°C to 60°C.

Given the formula for anorthite ( $\text{Ca Al}_2\text{Si}_2\text{O}_8$ ), the mole ratio of Al to Ca should be 2 for the 96-08 residual solids at 60°C and 95°C. However, the Al to Ca ratio is closer to 3, suggesting a different formula for anorthite that includes sodium (approximate formula is  $\text{Ca}_{(1-x)}\text{Na}_{(2x)}\text{Al}_2\text{Si}_2\text{O}_8$ ). This structure with sodium is commonly called anorthosite and is a mixture of albite ( $\text{NaAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). This new formula is supported by the observation that, as shown in Table A3.17, Ca and Na do not appear to be dissolving. As well, both albite and anorthite were identified by XRD in the gel residual solids. With the concentrations in Table A3.14, the  $x=0.38$  and  $0.45$  for gel residual solids can be calculated from 96-08 9 and 96-08 10, respectively. Given the analytical uncertainty of  $\pm 10\%$  for these concentrations, the values for  $x$  strongly suggest the presence of Al, Na, and Ca in an acid-insoluble anorthosite phase within the gel. Assuming anorthosite is present in the 96-08 9 and 10 residual solids as  $(\text{Ca}_{(0.585)}\text{Na}_{(0.830)}\text{Al}_2\text{Si}_2\text{O}_8)$  and all the aluminum in the gel residual solids is present as anorthosite, then using the Al concentrations in Table A3.17, the gel residual solids are 23 wt% anorthosite. It has been shown that only anorthosite containing more than 60% anorthite can be acid leached (Terry 1983). Therefore, since this anorthosite is approximately 59% anorthite, additional acid leaching is unlikely to be effective at dissolving this phase. Acid leaching of anorthite breaks down the mineral and produces high-silica gels (Terry 1983).



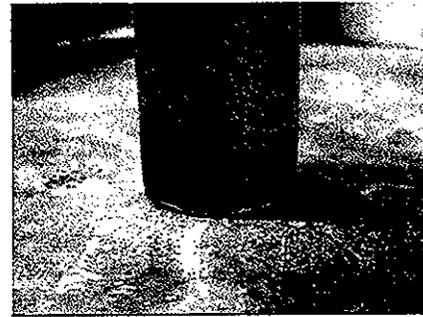
0 hr



2 hr



4 hr



6 hr



8 hr

**Figure A3.1** Canister Sludge (96-08) at 0, 2, 4, 6, and 8 hours in 10 M nitric acid at 25°C



0 hr



2 hr



4 hr



6 hr



8 hr

**Figure A3.2** Weasel Pit Sludge (KES-T-20) at 0, 2, 4, 6, and 8 hours in 10 M nitric acid at 25°C



0 hr



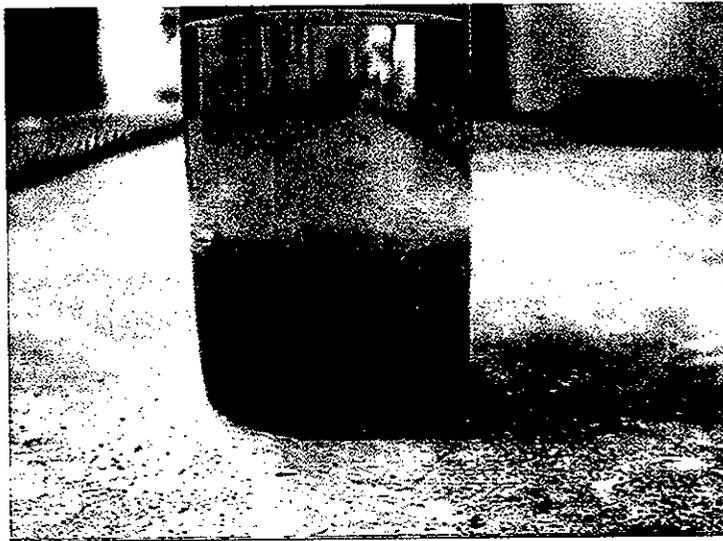
2 hr



4 hr



6 hr



8 hr

**Figure A3.3** Canister Sludge (96-08) at 0, 2, 4, 6, and 8 hours in 10 M nitric acid at 60°C



0 hr



2 hr



4 hr

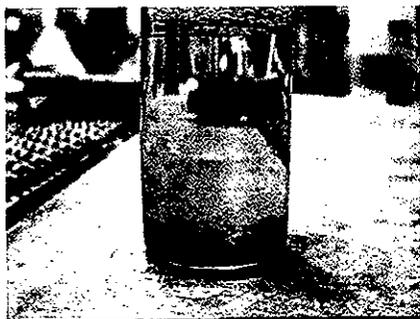


6 hr

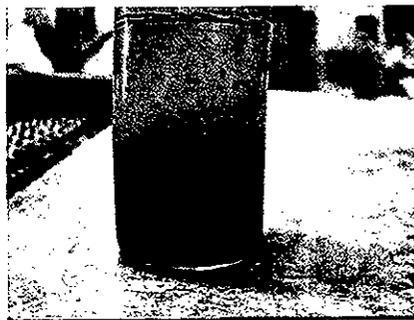


8 hr

**Figure A3.4** Weasel Pit Sludge (KES-T-20) at 0, 2, 4, 6, and 8 hours in 10 M nitric acid at 60°C



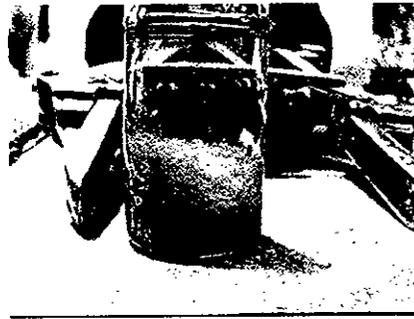
1.5 hr Before Swirling



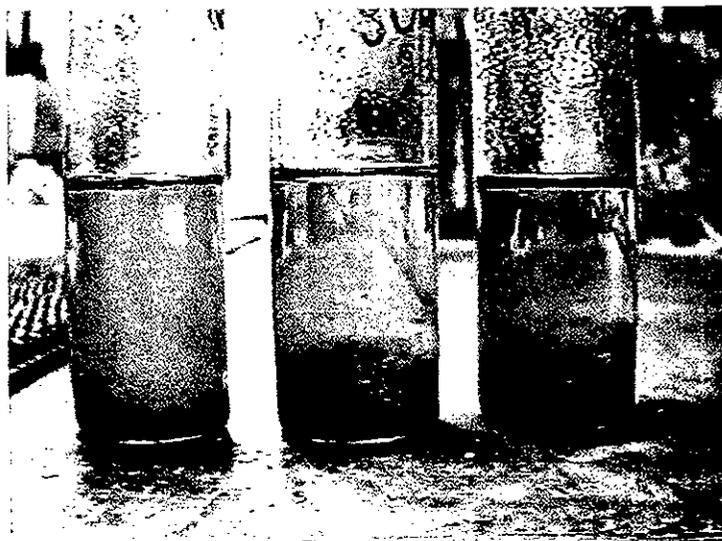
1.5 hr After Swirling



2 hr

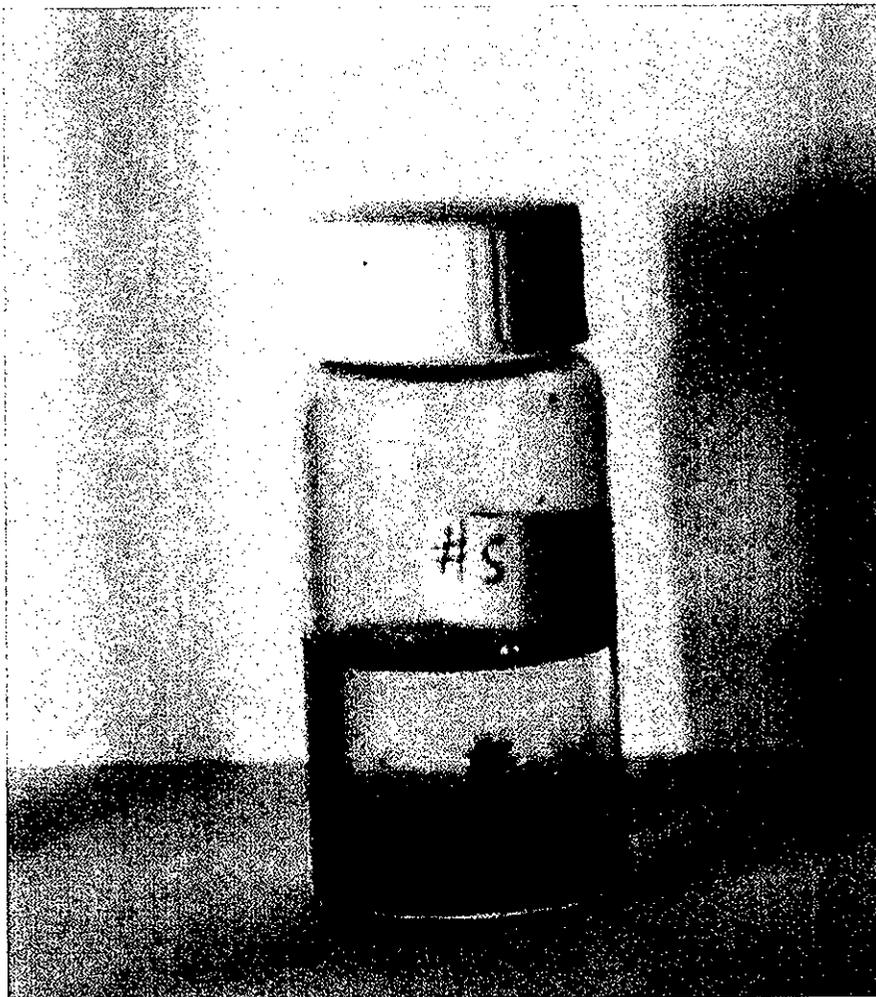


4 hr



6 hr

**Figure A3.5** Photographs of Canister Sludge (96-08) digested at 95°C in 10 M nitric acid. The top two photographs show an increase in settled solids volume after swirling. All other photographs were taken before swirling. Photograph at the bottom compares the samples at 25°C, 60°C and 95°C after 6 hours.



**Figure A3.6** Gel Formed from Acid Digestion ( $12\text{ M HNO}_3$ ) of Nonradioactive Hanford Sand at  $50^\circ\text{C}$ , 4 hr.



0 hr



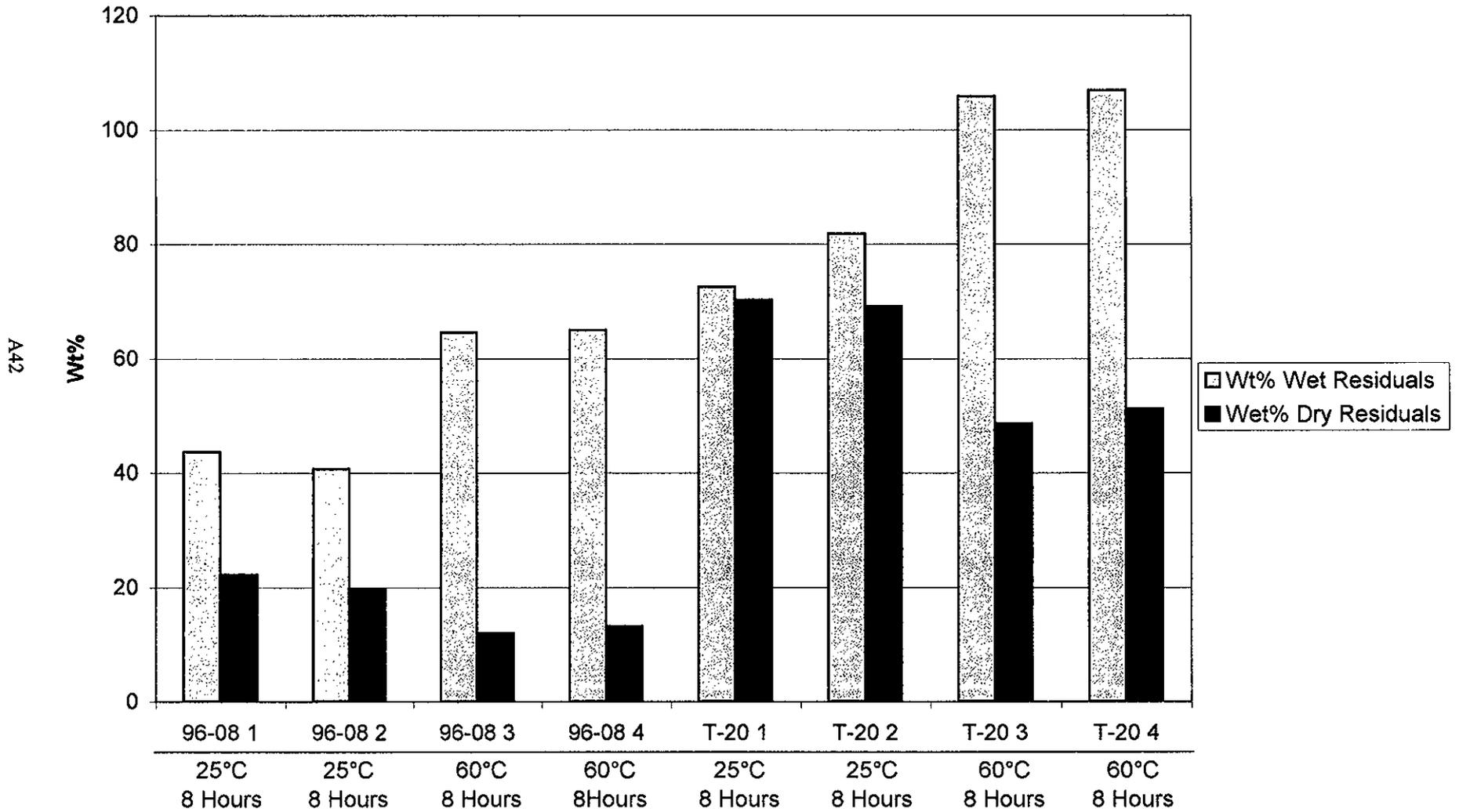
2 hr



8 hr

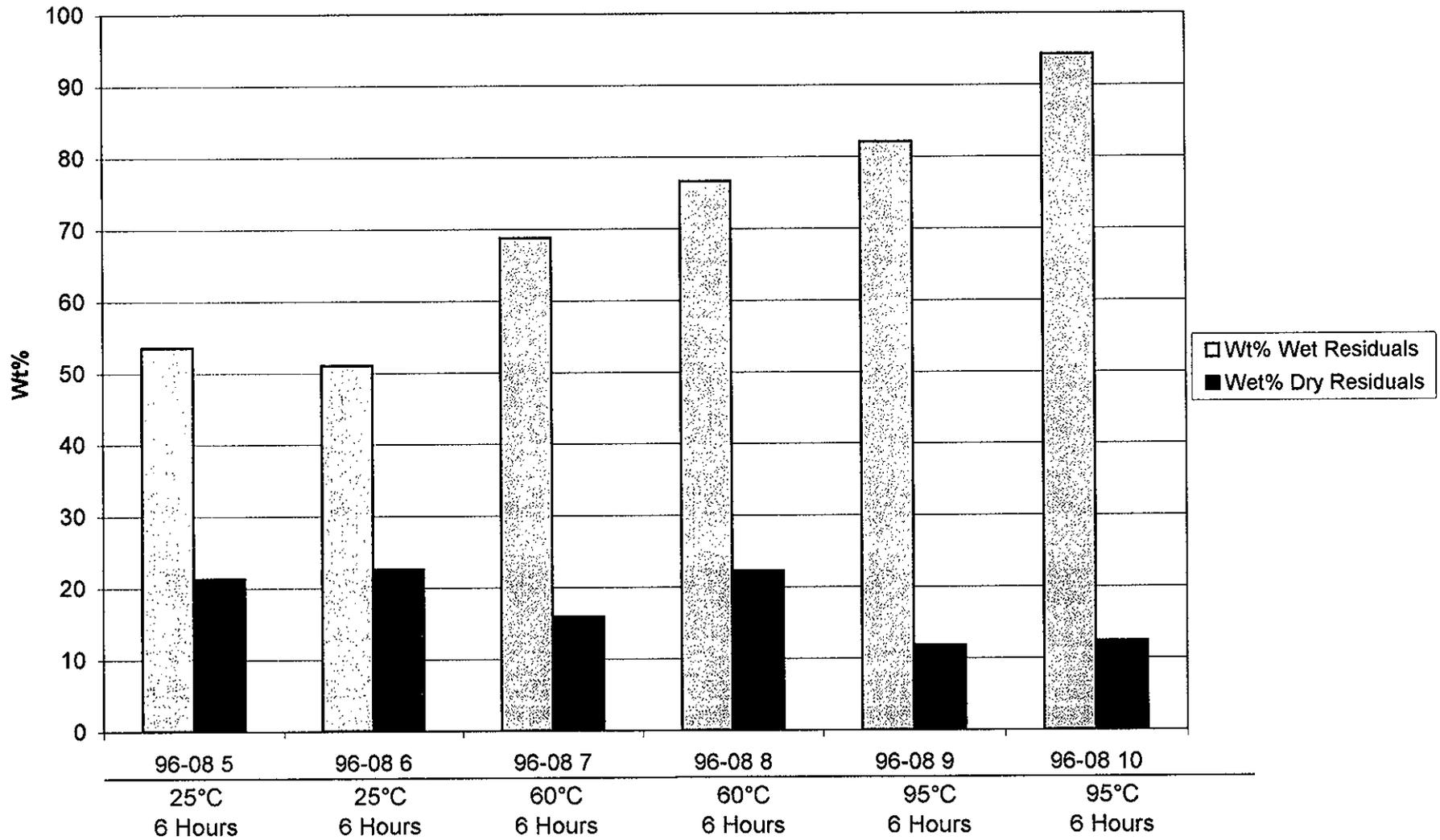
**Figure A3.7** OIER Beads Sieved from Sample KES-H-08 at 0, 2, and 8 hours in 10 M Nitric Acid. Sample was held at 25°C for the first 2 hours then heated to 60°C for the next 6 hours. Sample was swirled before images were collected.

**Figure A3.8 Weight Percent Residual Solids For Canister Sludge (96-08) and Wesel Pit Sludge (KES-T-20) After Contact with 10 M Nitric Acid**

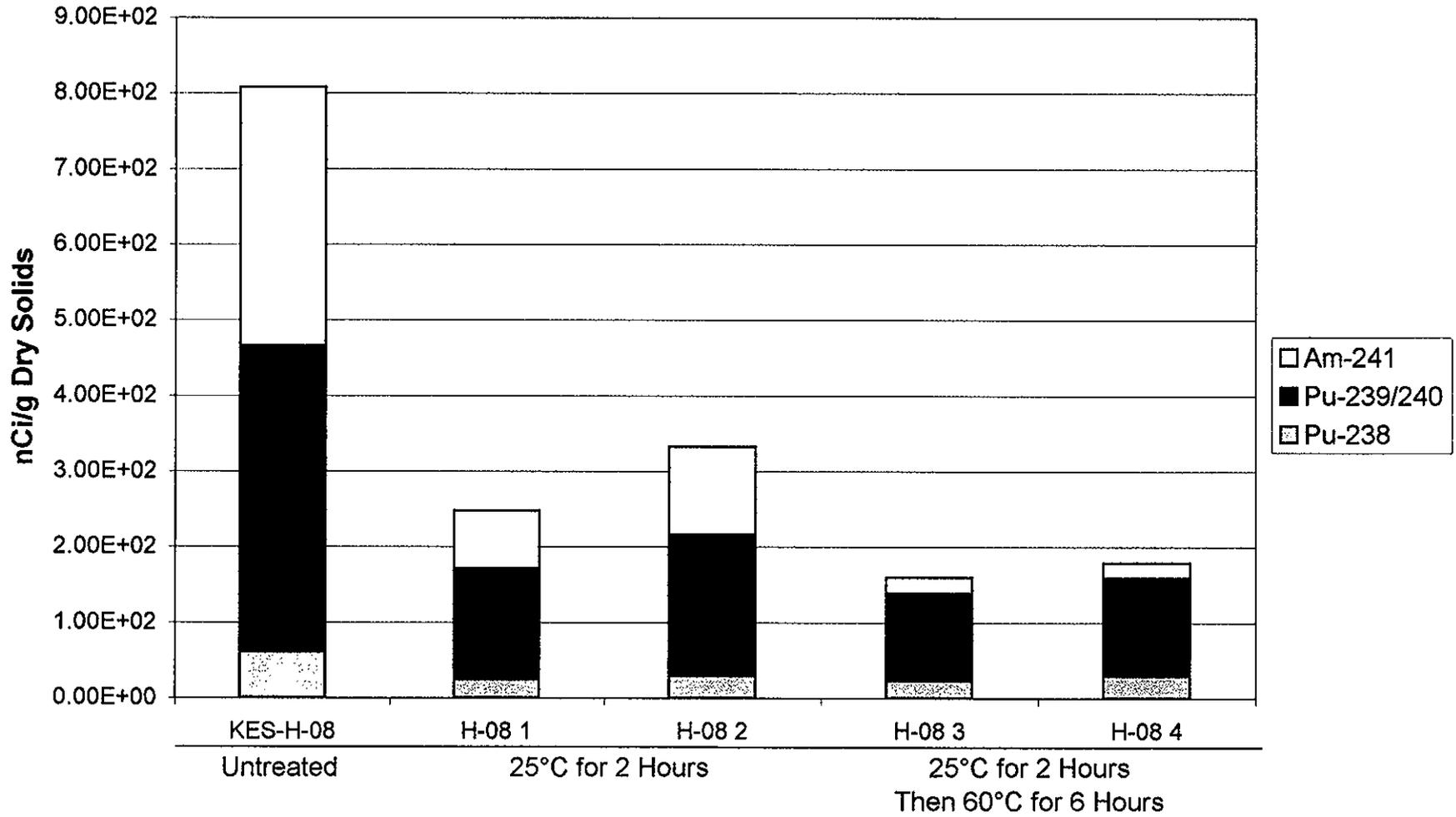


**Figure A3.9 Weight Percent Residual Solids from Canister Sludge (96-08) Following Contact with 10M Nitric Acid for 6 Hours**

A43

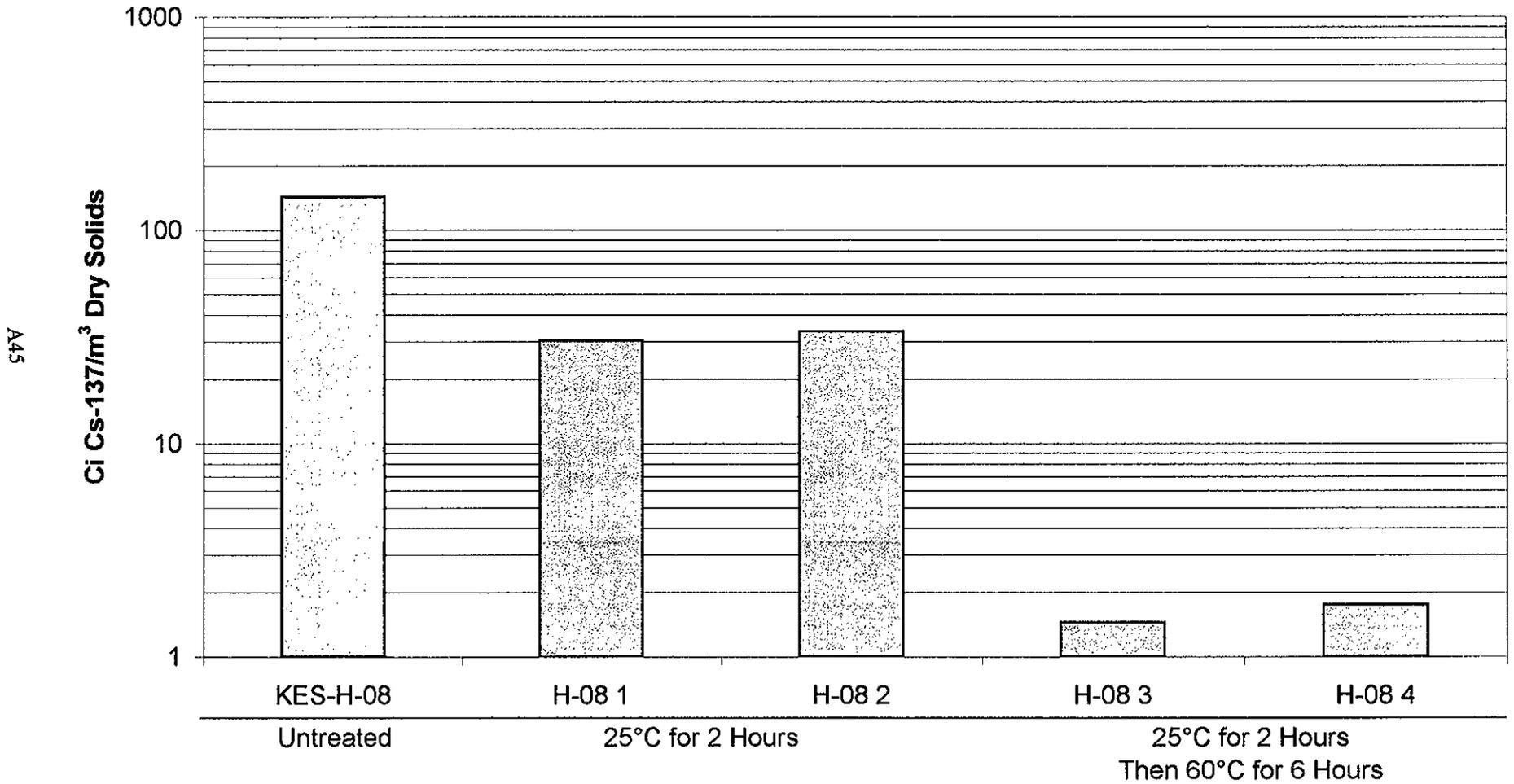


**Figure A3.10 Transuranic Content of OIER (KES-H-08) Compared to the Residual Solids After Contact with 10 M Nitric Acid**

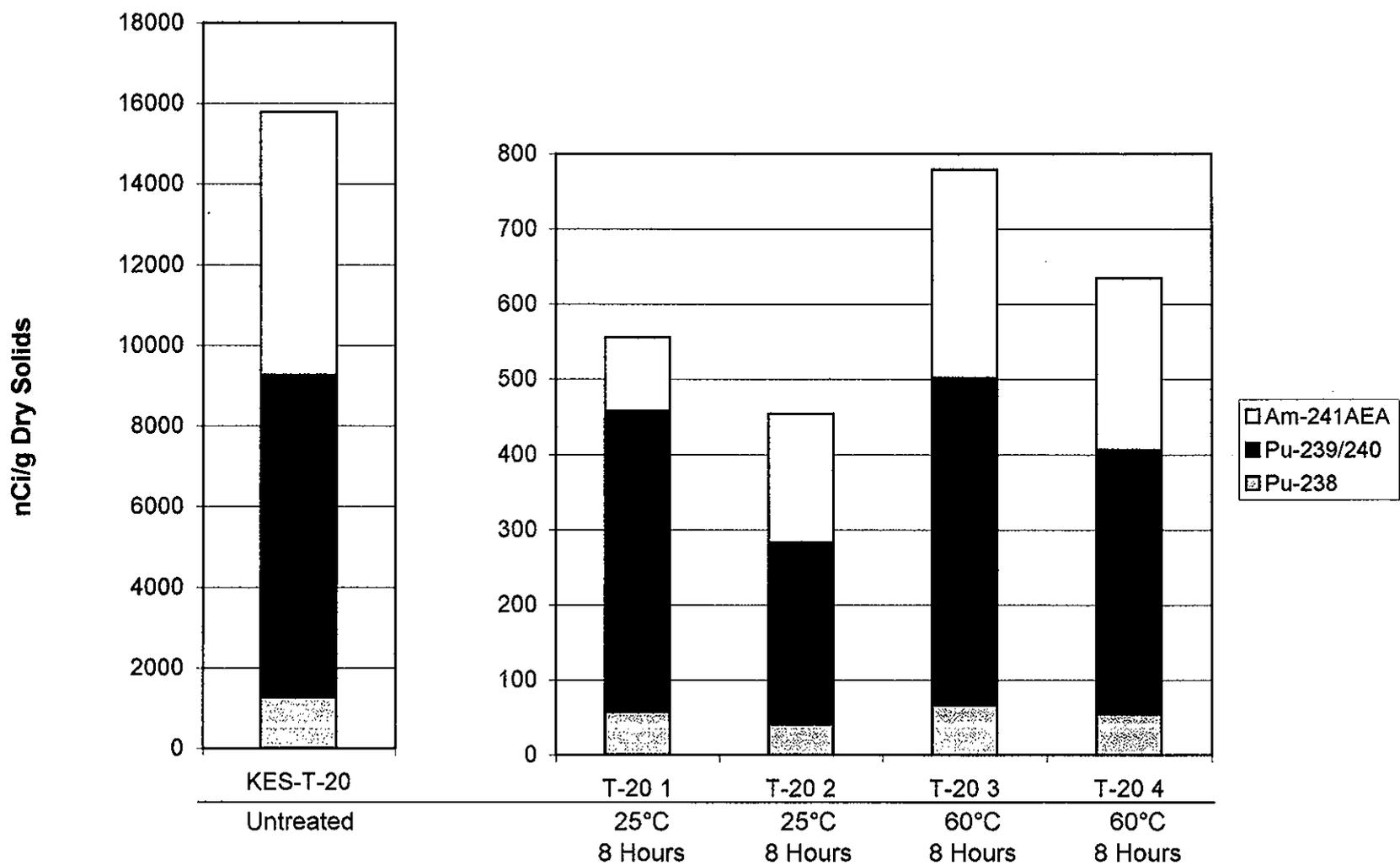


A44

Figure A3.11 Cesium-137 Activity in OIER (KES-H-08) Compared to Residual Solids After Contact with 10 M Nitric Acid. A Density of 1.00 g/ml Assumed.



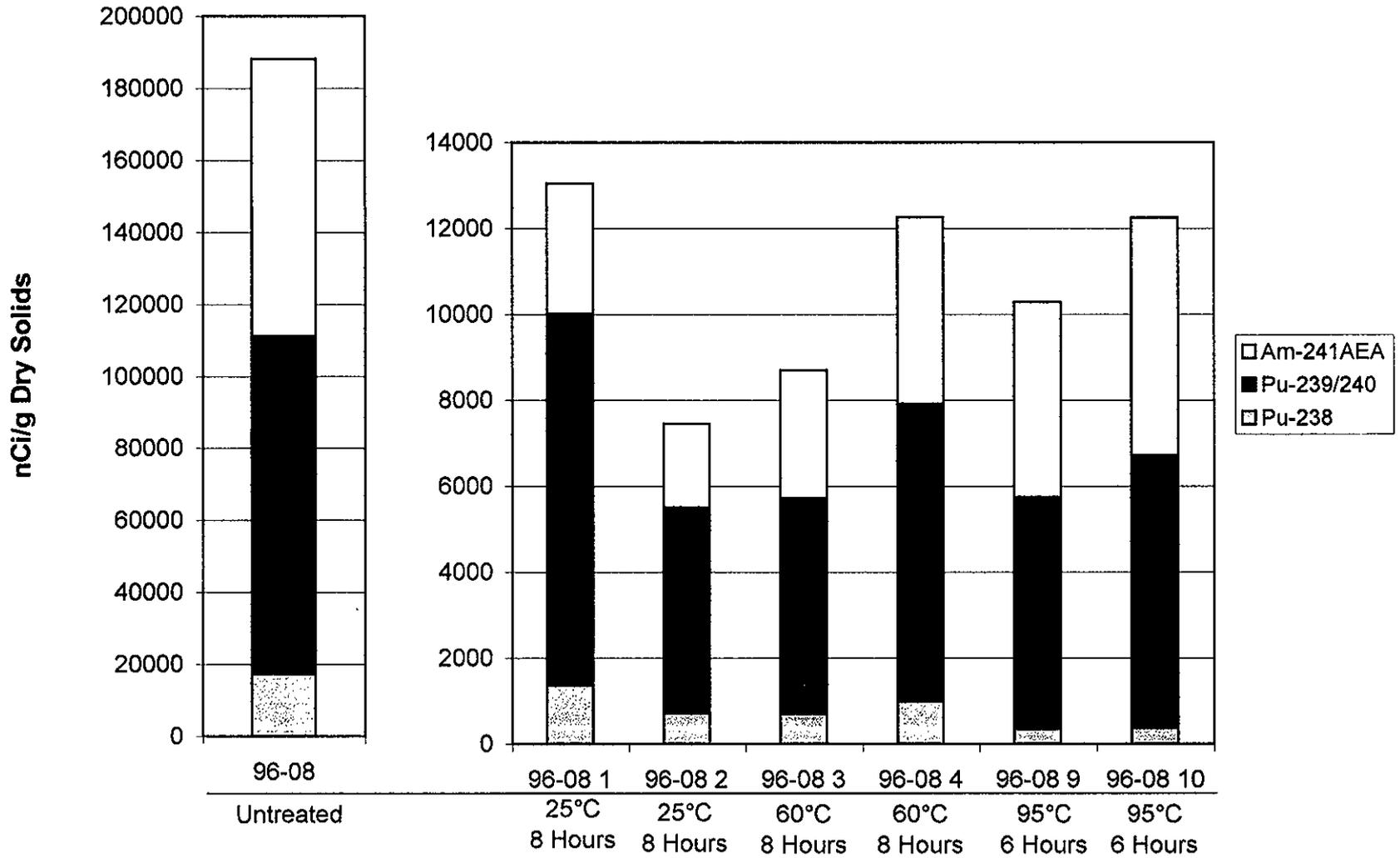
**Figure A3.12 Transuranic Content of Weasel Pit Sludge (KES-T-20) Compared to Residual Solids After Contact with 10 M Nitric Acid**



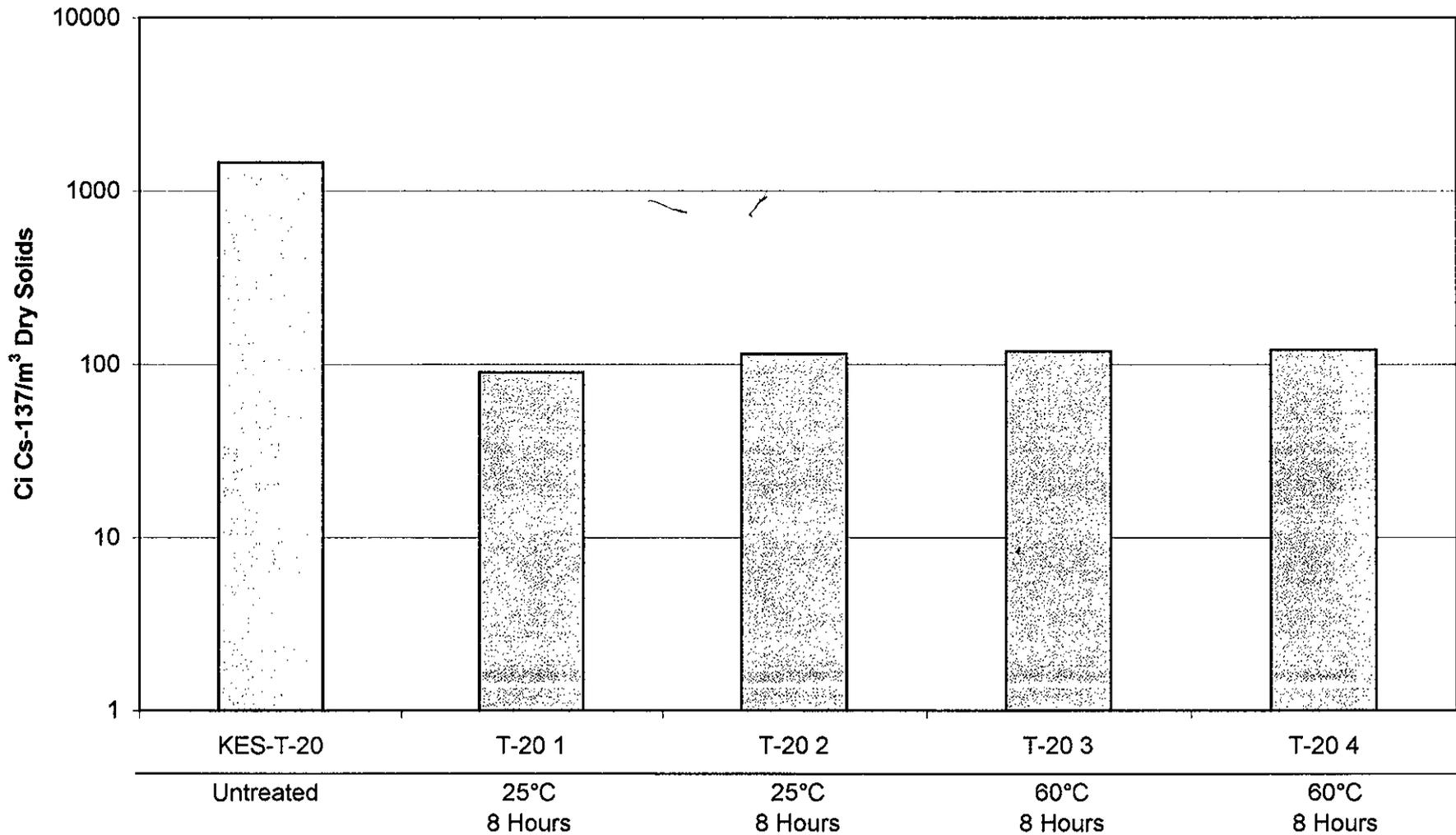
A46

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**Figure A3.13 Transuranic Content of Canister Sludge (96-08) Compared to Residual Solids After Contact with 10 M Nitric Acid**



**Figure A3.14 Cesium-137 Activity in Weasel Pit Sludge (KES-T-20) Compared to Residual Solids After Contact with 10 M Nitric Acid. A Density of 2.66 g/ml Assumed.**



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**Figure A3.15 Cesium-137 Activity in Canister Sludge (96-08) Compared to Residual Solids After Contact with 10 M Nitric Acid. A Density of 2.66 g/ml Assumed.**

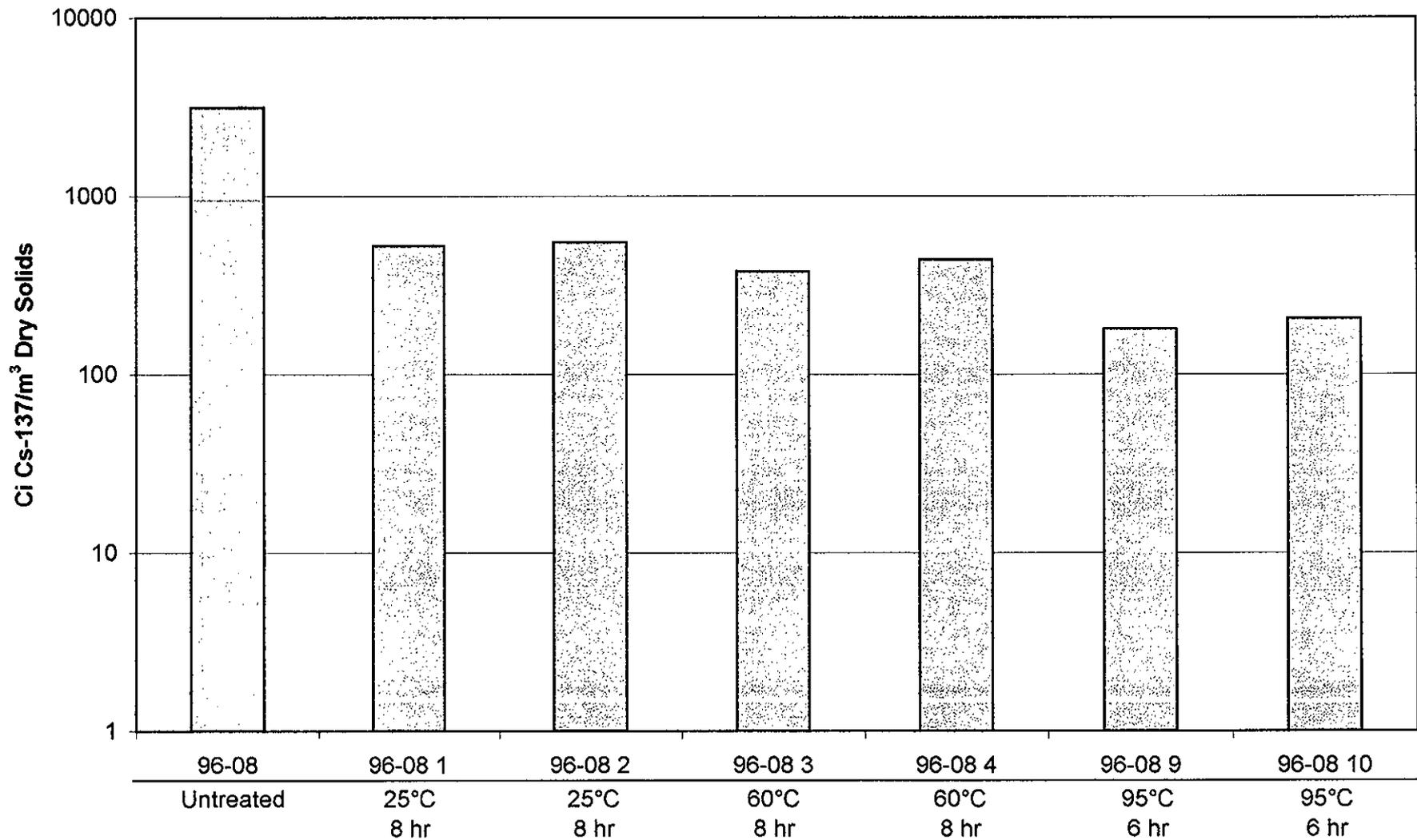
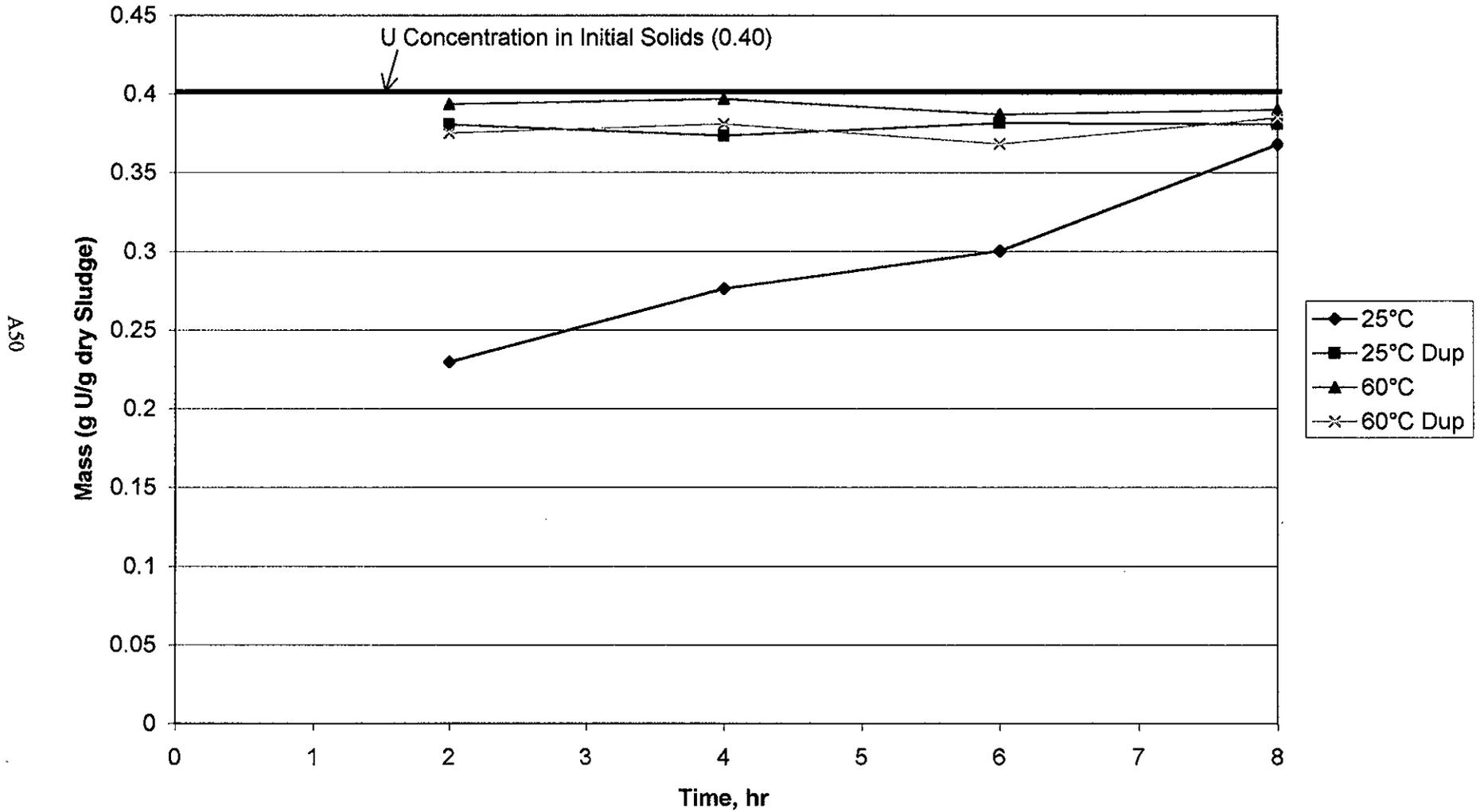
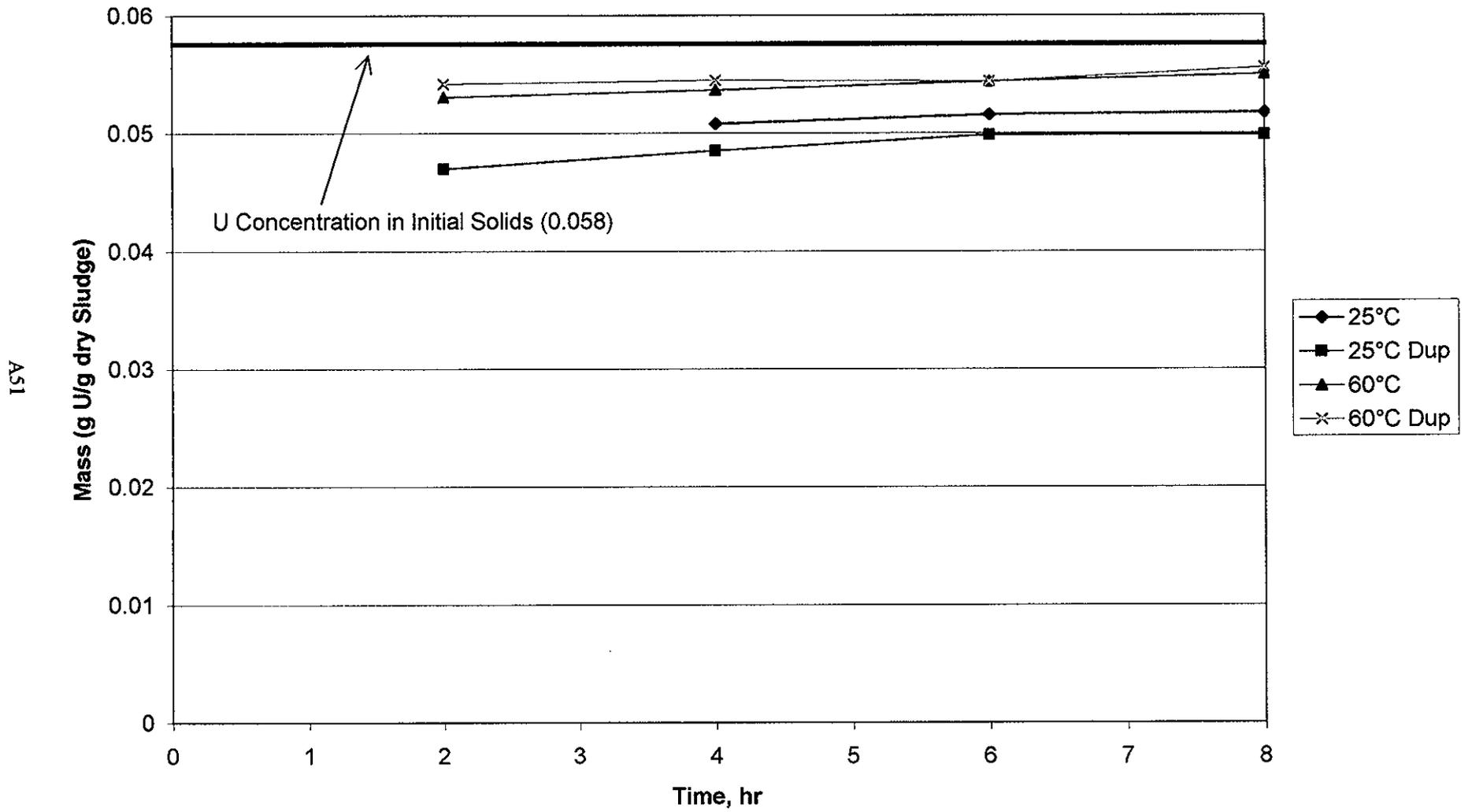


Figure A3.16 Normalized Uranium in Solution During Dissolution of Canister Sludge (96-08) in 10 M Nitric Acid



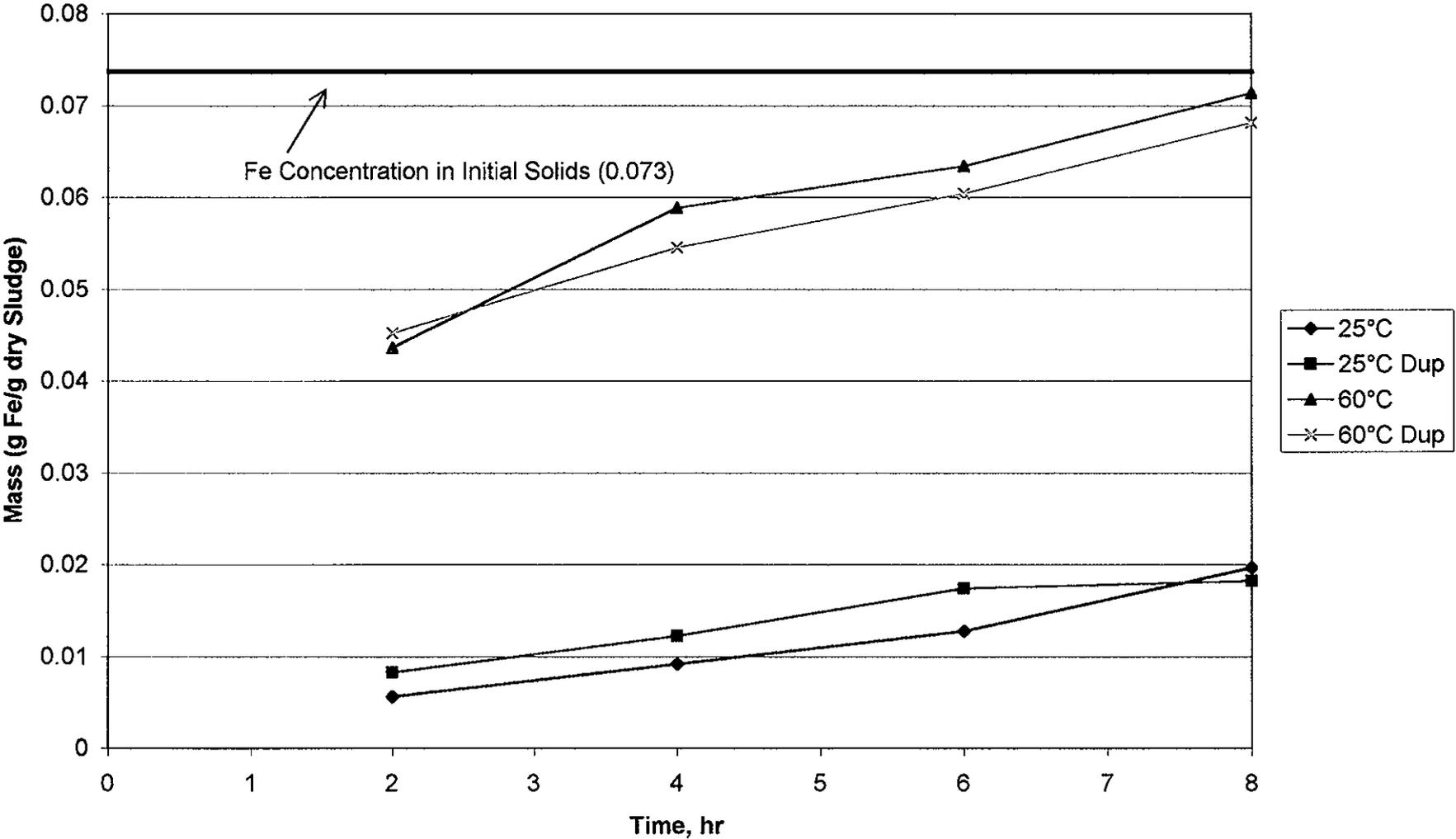
A50

Figure A3.17 Normalized Uranium in Solution During Dissolution of Weasel Pit Sludge (KES-T-20) in 10 M Nitric Acid



A51

Figure A3.18 Normalized Iron in Solution During Dissolution of Canister Sludge (96-08) in 10 M Nitric Acid



A52

Figure A3.19 Normalized Iron in Solution During Dissolution of Weasel Pit Sludge (KES-T-20) in 10 M Nitric Acid

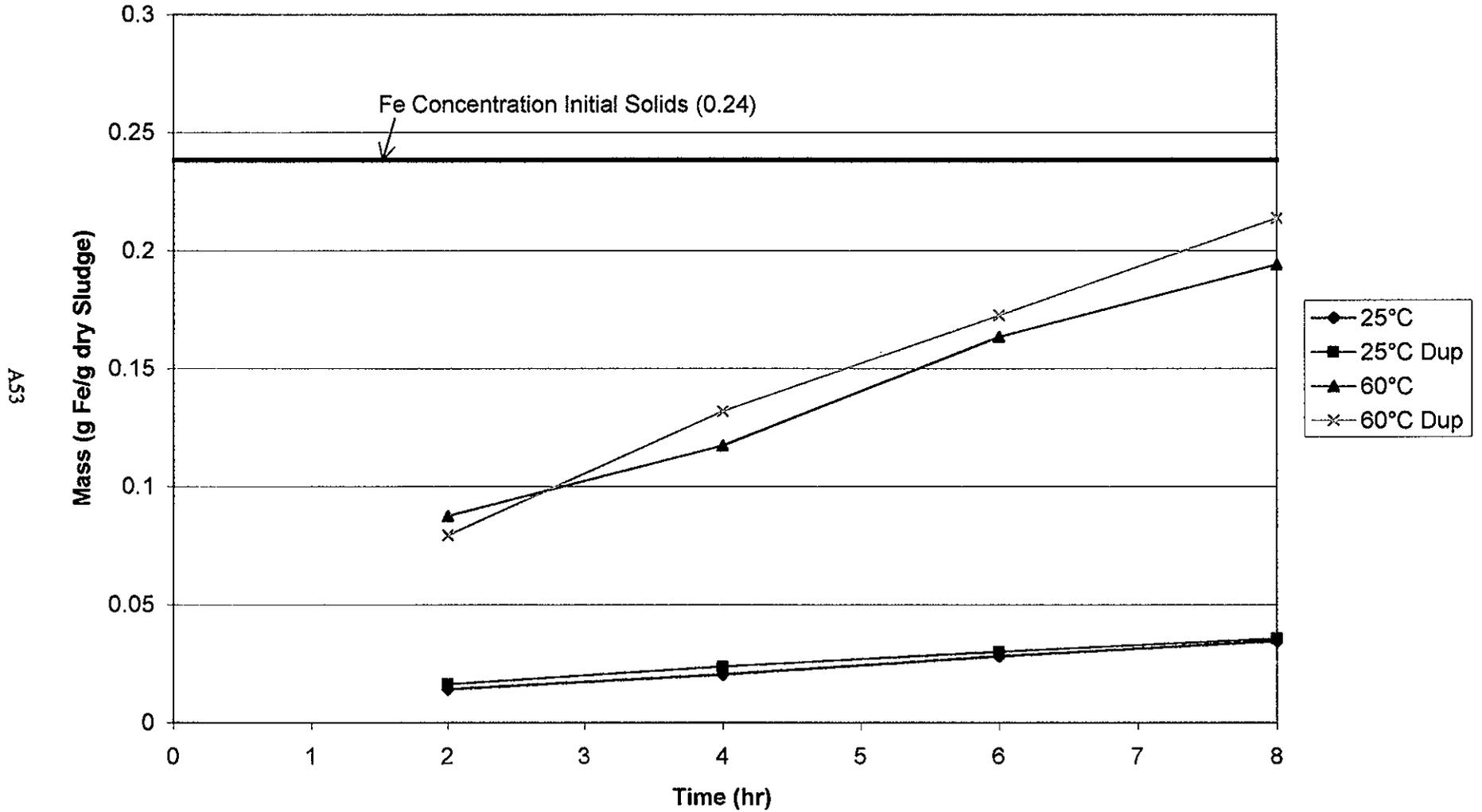
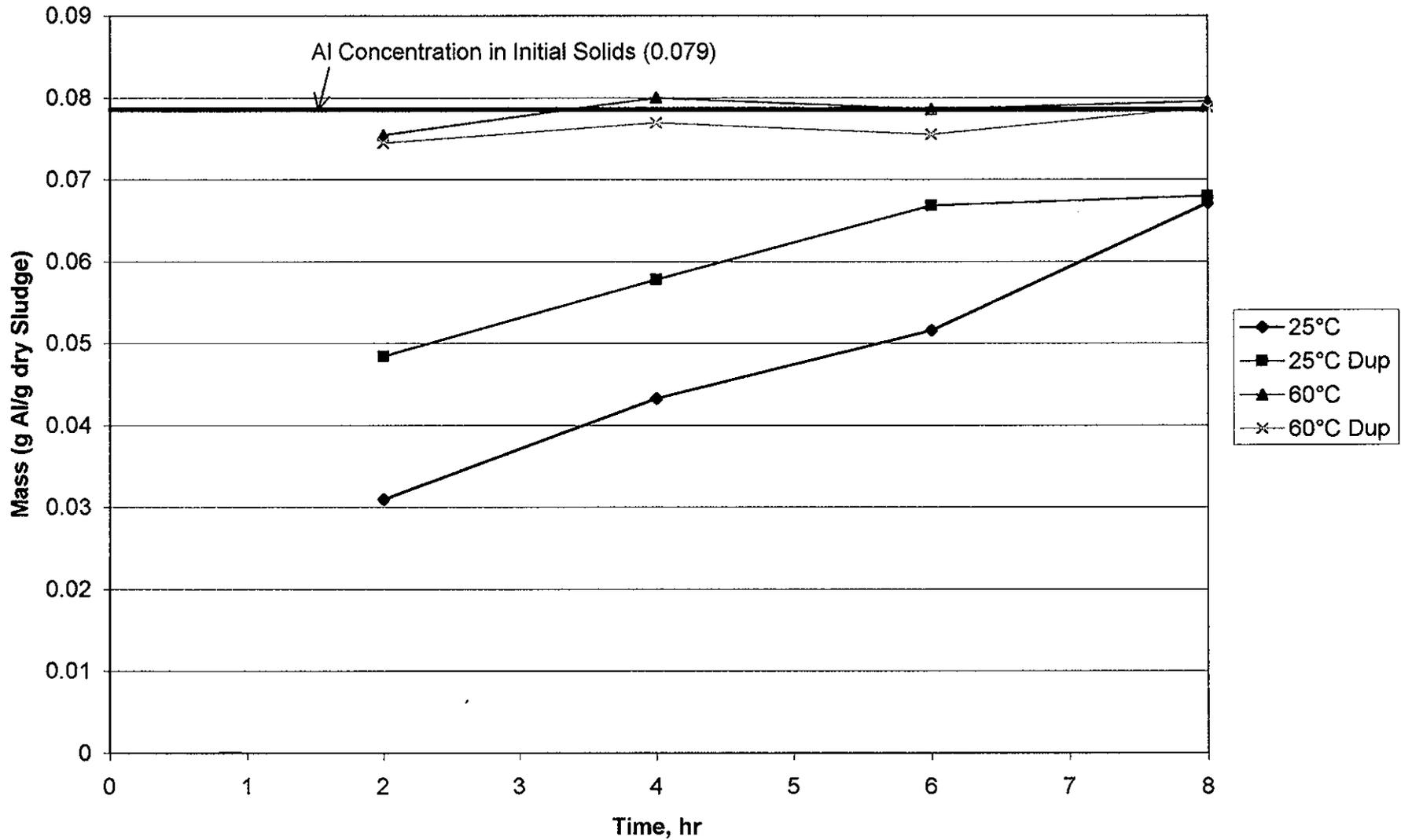


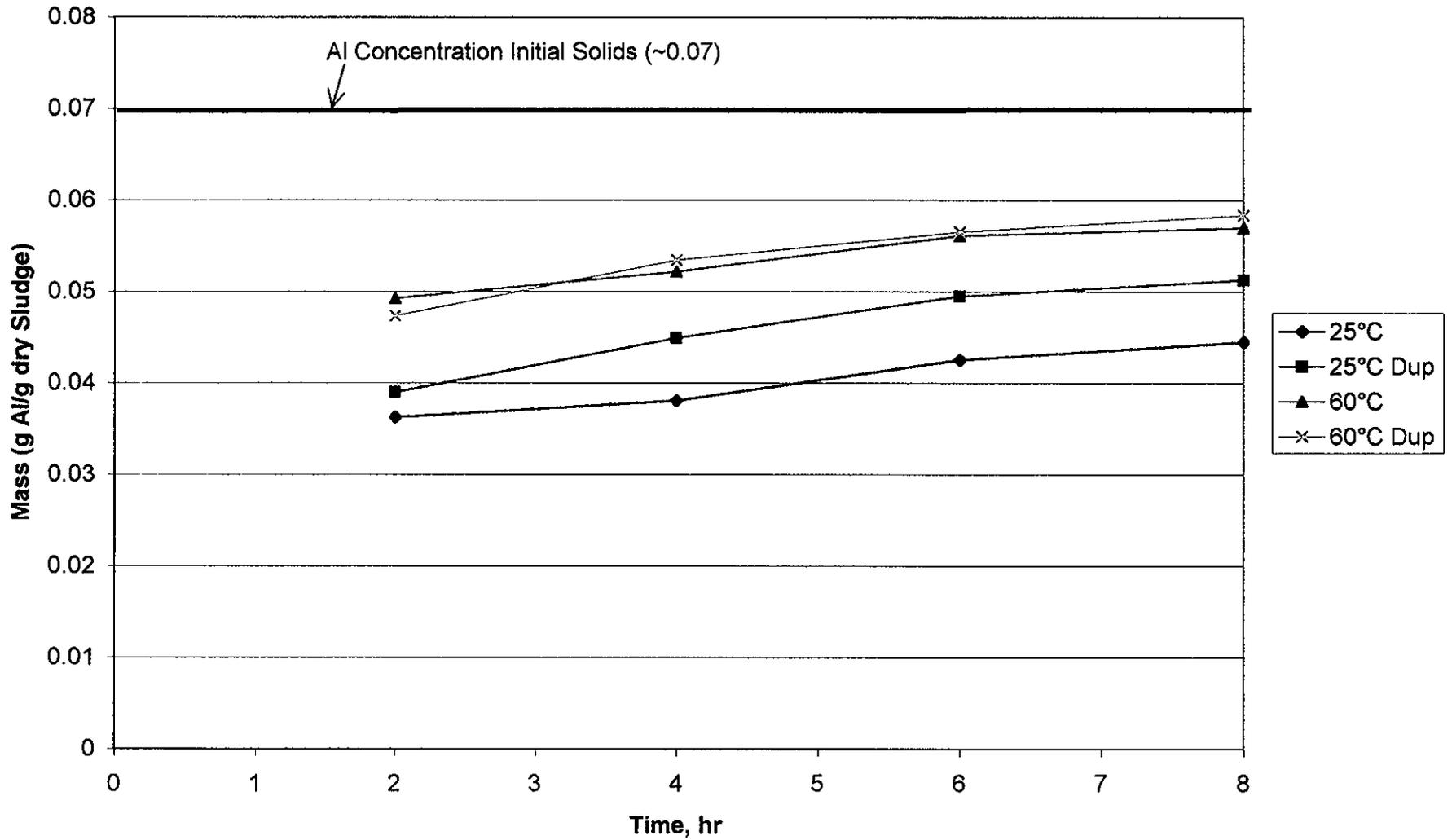
Figure A3.20 Normalized Aluminum in Solution During Dissolution of Canister Sludge (96-08) in 10 M Nitric Acid



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Figure A3.21 Normalized Aluminum in Solution During Dissolution of Weasel Pit Sludge (KES-T-20) in 10 M Nitric Acid



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Figure A3.22 Iron Distribution for Canister Sludge (96-08) After Contact with 10 M Nitric Acid

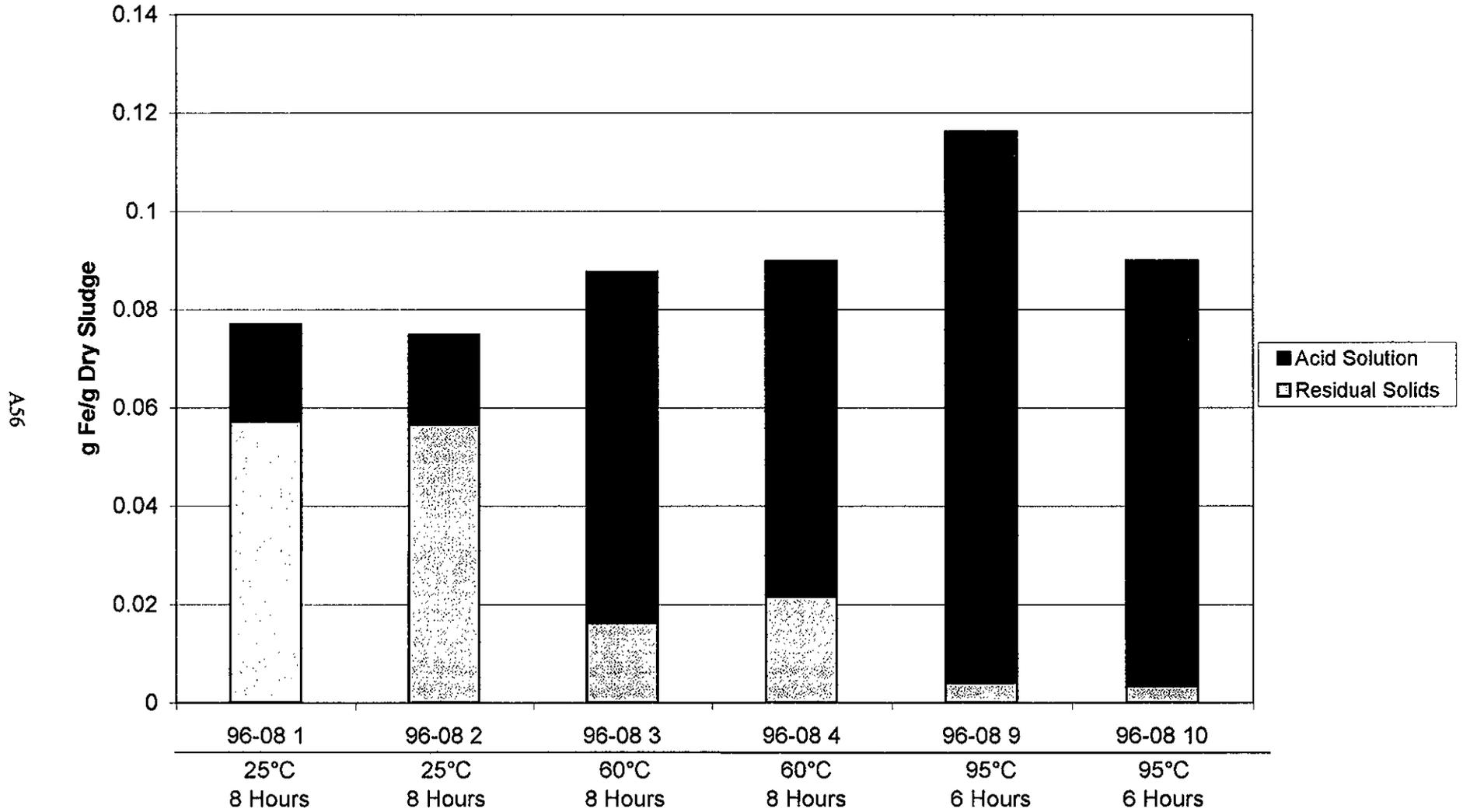
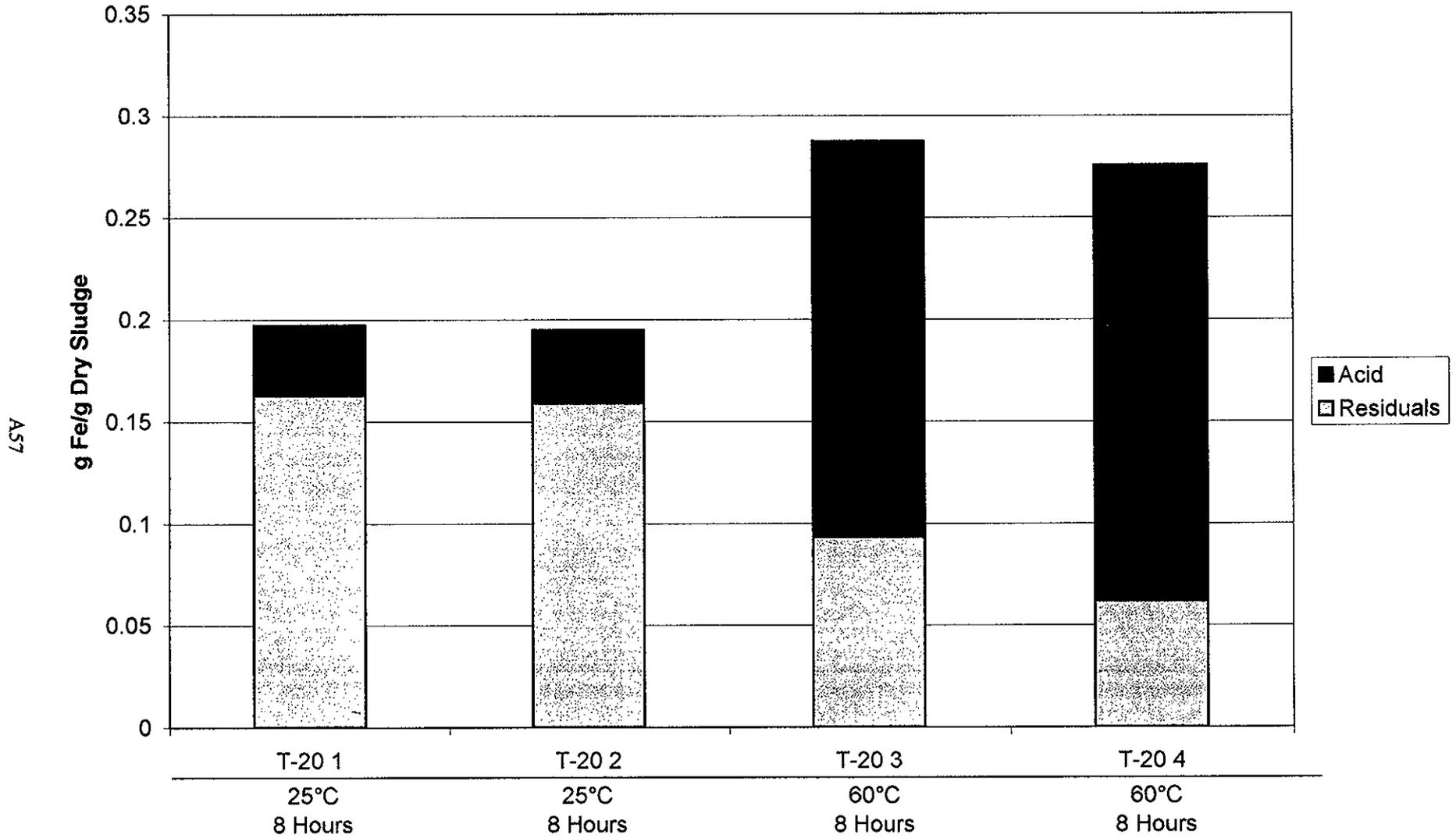


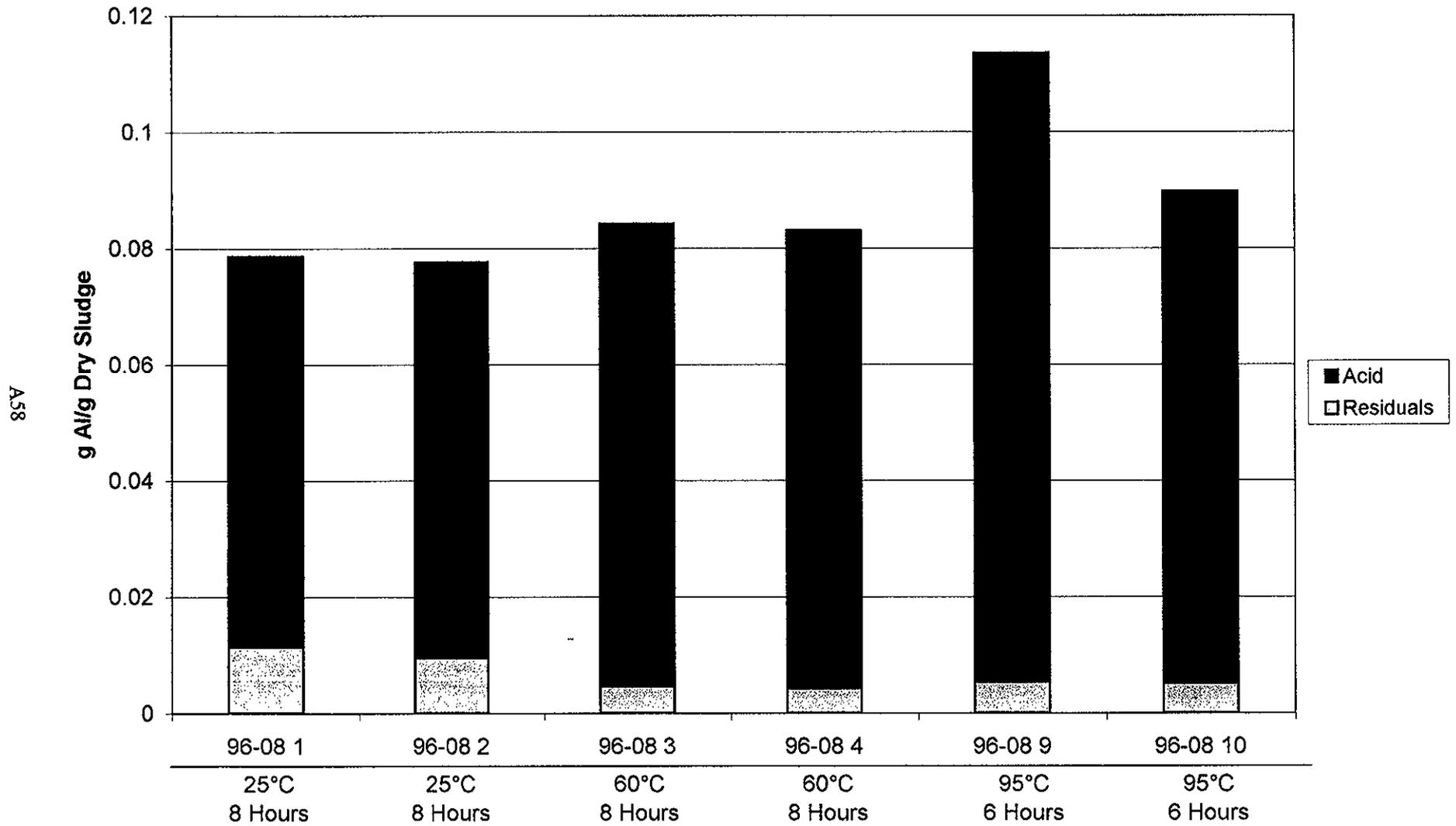
Figure A3.23 Iron Distribution for Weasel Pit Sludge (KES-T-20) After Contact with 10 M Nitric Acid



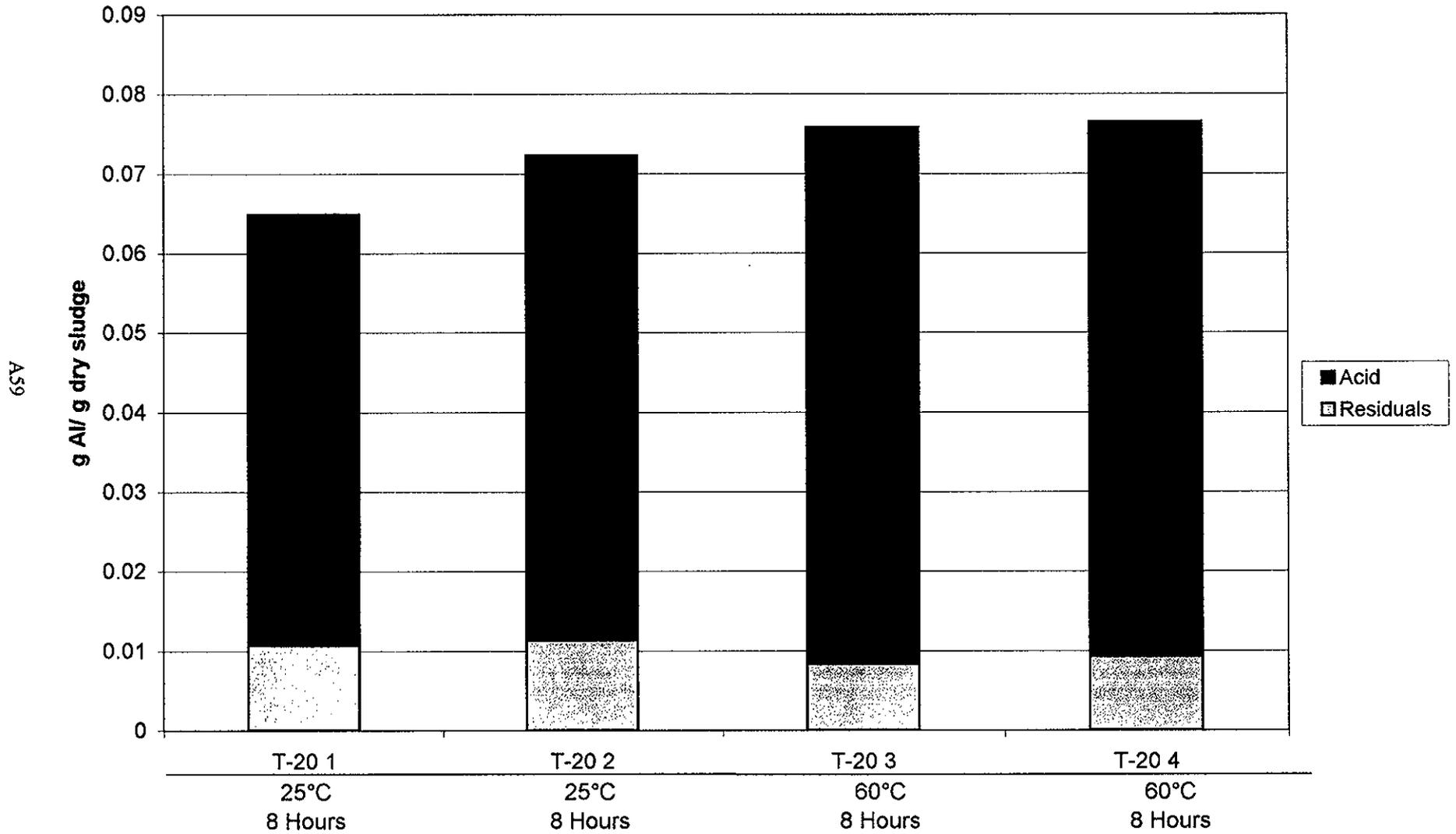
AS7

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**Figure A3.24 Aluminum Distribution for Canister Sludge (96-08) After Contact with 10 M Nitric Acid**



**Figure A3.25 Aluminum Distribution for Weasel Pit Sludge (KES-T-20) After Contact with 10 M Nitric Acid**



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**A P P E N D I X B**

**EVALUATION OF POLYCHLORINATED BIPHENYLS DATA  
FROM K EAST BASIN SLUDGE SAMPLES**

A. J. Schmidt and A. H. Zacher

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**APPENDIX B****EVALUATION OF POLYCHLORINATED BIPHENYLS DATA  
FROM K EAST BASIN SLUDGE SAMPLES****B.1 SCOPE**

The evaluation provided here examines the applicability and the implied confidence of the detection and quantification of polychlorinated biphenyls (PCBs) in the K East Basin sludge samples. The focus of this effort was to provide the best interpretation of the existing quantitative PCB data in context to its use for designating the sludge in the K East Basin with respect to EPA and related regulations from the standpoint of the methods used to accurately detect and measure the concentration (i.e., greater than or less than the 50 ppm threshold range).

**B.2 SUMMARY OF EVALUATION**

The evaluation of the PCB analytical data focused primarily on the quantitative data generated by the 222-S Laboratory using gas chromatography (GC) with an electron capture detector (ECD), and the data generated by the 325 Laboratory using gas chromatography/mass spectroscopy (GC/MS) with the use of an Aroclor 1254 standard. Other PCB analytical data were generated from several screening techniques; however, as these data are considered to be semi-quantitative, they were not evaluated in detail.

Table B1 shows the originally reported data (Makenas 1996) and adjusted PCB concentrations for the three samples of primary interest. Samples KES-P-16 and KES-R-18 were collected from the Weasel Pit. Sample KES-I-15 was collected from the main basin, 6 in. east of the mouth of the South Load Out Pit.

The reported values were adjusted for several reasons described in detail within this document. It is believed that the PCB concentrations provided in the last column of Table B1, "Adjusted GC/MS PCB Concentrations," most accurately represent the actual PCB concentrations in the Weasel Pit. For sample KES-I-15, the value shown in the next to the last column to the far right, "Adjusted GC/ECD PCB Concentration," is the most accurate available. Additional sampling and analysis of this sludge will most likely produce similar results.

Table B1 shows that the adjusted results from both analytical techniques tend to converge. However, the concentrations at which they converge indicate that Samples KES-R-18 and KES-I-15 contain PCBs at concentrations (generally on a dry basis) greater than 50,000  $\mu\text{g}/\text{kg}$  (50 ppm).

Table B1. Comparison of Quantitative Polychlorinated Biphenyls Data on K East Basin Sludge from the 222-S Laboratory Gas Chromatography/Electron Capture Detector and the 325 Laboratory Gas Chromatography/Mass Spectroscopy; Settled, Centrifuged, and Dry Sludge Bases.

Sample ID/ 325 Laboratory ID	222-S Laboratory GC/ECD Reported PCB Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	325 Laboratory GC/MS Reported PCB Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	Adjusted <sup>5</sup> GC/ECD PCB Conc. Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>	Adjusted <sup>6</sup> GC/MS PCB Conc. Aroclor 1254, $\mu\text{g}/\text{kg}^1$ Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>
KES-I-15	101,000 (104,000) [180,000]	no data (no data)	63,000 ( 65,000) [110,000]	no data (no data)
KES-P-16/ 96-00538	40,000 (47,000) [79,000]	16,000 (19,000) [32,000]	29,000 (34,000) [57,000]	31,000 (36,000) [60,000]
KES-P-16D/ 96-00538D		15,000 (18,000) [30,000]		40,000 (47,000) [79,000]
KES-R-18/ 96-00540	180,000 (220,000) [400,000]	19,000 (23,000) [42,000]	110,000 (130,000) [240,000]	43,000 (53,000) [97,000]
KES-R-18D/ 96-00540D		70,000 ( 86,000) [160,000]		140,000 (170,000) [310,000]
KES-R-18MS/ 96-00540MS		62,000 ( 76,000) [140,000]		110,000 (130,000) [240,000]
KES-R18MSD/ 96-00540MSD		43,000 (53,000) [97,000]		82,000 (100,000) [180,000]

<sup>1</sup>Concentrations on per  $\mu\text{g}/\text{kg}$  sludge basis. Note: to convert to ppm, divide  $\mu\text{g}/\text{kg}$  by 1,000 (e.g., 40,000  $\mu\text{g}/\text{kg}$  = 40 ppm).

<sup>2</sup>PCB concentration on a settled sludge basis.

<sup>3</sup>PCB concentration on a centrifuged sludge basis--values in table are in parentheses.

<sup>4</sup>PCB concentration on a dry sludge basis.

<sup>5</sup>Adjusted GC/ECD PCB concentrations (222-S Laboratory), determined from using chromatograph peak heights.

<sup>6</sup>Adjusted GC/MS PCB concentrations (325 Laboratory), adjusted for both solvent recovery and surrogate recovery.

While the PCB data in Makenas (1996, Appendix H) are reported on a "centrifuged sludge" basis, Table B1 provides PCB concentrations on a "settled sludge," "centrifuged sludge," and "dry sludge" bases. Use of the settled sludge basis may be more appropriate for regulatory purposes than use of the centrifuged sludge basis because it more likely reflects the form of the sludge in the basin. Conversion of the concentrations from centrifuged basis to the settled sludge basis reduced the estimated PCB concentration by 3% to 18%. Sludge basis are included in Table B1. The rules under TSCA were recently amended in a manner that suggests PCB waste designation determinations should be made on "dry basis" PCB concentrations for most solids (RF Vol. 63, No. 124, June 29, 1998).

For K East Basin sludge samples analyzed by GC/MS at the 325 Laboratory that were reported as "non-detects" for PCB in Reference 2, "less than" concentrations were determined by assuming an on-column quantification limit of 10 ng (based on experience and discussions with the analyst) and using data on extraction recoveries and sample masses. The estimated "less than values" (i.e., actual PCB concentration, on a settled sludge, centrifuge sludge, and dry sludge basis, is between the less than value and zero) are shown in Table B2 for the other K East Basin sludge samples analyzed.

Table B2. Estimated Quantification Limits for Non-Detect K East Basin Sludge Samples Analyzed by Gas Chromatography/Mass Spectroscopy at the 325 Laboratory

Sample ID	PCB Aroclor 1254, Settled Sludge Basis, $\mu\text{g}/\text{kg}$ <sup>1</sup> Settled <sup>2</sup> (Centrifuged) <sup>3</sup> [Dry] <sup>4</sup>
KES-L-1	<17,000 (<26,000) [<87,000]
KES-A-2	<14,000 (<20,000) [<51,000]
KES-N-5	<79,000 (<14,000) [<66,000]
KES-H-8	<16,000 (<17,000) [<45,000]

<sup>1</sup>Concentrations on per  $\mu\text{g}/\text{kg}$  sludge basis. Note: to convert to ppm, divide  $\mu\text{g}/\text{kg}$  by 1,000 (e.g., 40,000  $\mu\text{g}/\text{kg}$  = 40 ppm).

<sup>2</sup>PCB concentration on a settled sludge basis.

<sup>3</sup>PCB concentration on a centrifuged sludge basis--values in table are in parentheses.

<sup>4</sup>PCB concentration on a dry sludge basis.

In examining the results from the 325 Laboratory for Sample KES-R-18, it was important to note the wide variability in the concentration from the sample, duplicate, matrix spike, and matrix spike duplicate. This variability indicated that PCBs were not uniformly distributed in the sludge sample. It also could explain some of the differences in results between the two laboratories. Further sample homogenization and use of larger samples for performing the extraction would likely result in data that more accurately reflect the PCB concentration in the K East Basin sludge. SW-846 Method 8080A (Organochlorine Pesticides and PCBs) refers back to Methods 3540 (Soxhlet Extraction) and 3550 (Sonication Extraction) for extraction of solids samples. Method 3540 calls for a sample size of at least 10 g after grinding the sample to less than 1 mm. Method 3550 calls for a 30-g sample, if the contaminant concentrations are low, and a 2-g sample if the contaminant is expected to be at medium to high concentrations. Due to radiological concerns, samples used for PCB analysis were only in the range of 0.5 g to 2 g.

### **B.3 SUMMARY OF ADJUSTMENTS TO PREVIOUSLY REPORTED DATA**

#### **B.3.1 Gas Chromatography/Electron Capture Detector Data (222-S Laboratory)**

At the 222-S Laboratory, quantification of the GC/ECD data was performed with a single point calibration and then comparing peak areas from the standard with the peak areas from the K East Basin sludge sample extracts. In examining these data, it was observed that the chromatographs showed evidence of contamination-based shouldering, which, based on previous experience, results in an overestimation of the PCB concentration. The chromatographs were re-evaluated by comparing peak heights of the standard to those of the sample extracts. Under SW-846, in Method 8080A (Organochlorine Pesticides and PCBs), use of either peak heights or peak areas is acceptable as a quantification technique. The result of using peak heights for quantification was that the estimated PCB concentrations were reduced by 28% to 41% from what was reported by Makenas (1996). Because of the peak contamination-based shouldering, use of peak heights most likely results in a more accurate measurement of PCB concentration from these GC/ECD data.

#### **B.3.2 Gas Chromatography/Mass Spectroscopy Data (325 Laboratory)**

Semi-volatile organics analyses (SVOA) performed at the 325 Laboratory initially indicated that PCBs may be present in certain K East Basin sludge samples. An Aroclor 1254 standard, along with a blank, was analyzed to provide confirmation of the presence of PCB. From comparison to this standard, the PCB concentrations of the samples were quantified. The "on-column" concentrations ranged from 17% to 130% of that obtained from the Aroclor 1254 standard.

In examining these data, it was found that a step in the quantification procedure was inadvertently omitted for the PCB data only. The omission of the step was confirmed in a discussion with the analyst. The reported PCB concentrations from this data set did not take into account the fraction of solvent recovered during the sample extractions. As a result, the reported concentrations were only one-fifth to one-half of what should have been reported.

Further examination of the data, and write-ups on the data (Silvers 1995), indicated that between the time the samples were extracted and measured (after removal from the hot cell), significant evaporation of solvent from the extracts occurred. SVOA data, obtained concurrently with the PCB data (i.e., from same extract injections), showed that SVOA surrogates added to the sludge sample during the extraction step were over-recovered (see Table B6). The extent of over-recovery correlated with notes on the organic analysis bench sheet [page D03-017 of Silvers (1995)], indicates probable evaporation. The surrogate recoveries were used as internal standards to correct the estimated PCB concentrations (i.e., it was assumed that all over-recoveries resulted from evaporation prior to measurement of the extract volumes). The over-recoveries acted to reduce the estimated PCB concentrations by 9% to 48% from the values corrected to account for the quantification error. The net effect from accounting for both the omission in the quantification procedure and the over-recoveries is that the adjusted PCB concentrations are from 70% to 160% greater than the values previously reported.

The adjusted PCB concentrations are shown in Table B1 and are believed to most accurately reflect the concentrations present in the sludge samples analyzed. The adjustments have resulted in much closer agreement of PCB concentrations determined by the two methods.

#### **B.4 RECOMMENDATIONS FOR FUTURE ANALYSES**

Specific recommendations to obtain more accurate data on PCB concentrations in future analyses of K East Basin sludge are as follows: (1) use as large a sludge sample as possible for the extraction; (2) use recognized PCB sample extraction and cleanup techniques; and (3) use a multi-point calibration with Aroclor 1254 standards rather than a single point calibration. If the analysis is to be performed with GC/ECD, a cleanup technique such as the use of Florisil or sulfuric acid/permanganate will likely reduce potential errors associated with interfering contaminants.

As noted on Page 3-7 of Silvers (1995), the methods used for the preparation and analysis of PCBs by 325 Laboratory were tailored for SVOAs, not PCBs. Consequently, sample biases are not completely known. Silvers further recommends that follow-on analyses be performed with recognized PCB preparation and analysis methodology to more accurately determine concentrations.

## **B.5 DETAILED DISCUSSION OF ADJUSTMENTS TO PREVIOUSLY REPORTED DATA**

The following two sections provide details and justification for the adjustments made to the PCB concentrations reported in Makenas (1996).

### **B.5.1 Adjustment of Gas Chromatography/Electron Capture Detector Polychlorinated Biphenyls Data from 222-S Laboratory**

The 222-S Laboratory "voluntarily" performed PCB confirmation analyses using GC/ECD. An examination of the PCB data generated from the 222-S Laboratory GC/ECD analysis was performed for this review. Areas in which there are some uncertainties with the reported data and where there is a possibility for other interpretations have been outlined in the following paragraphs.

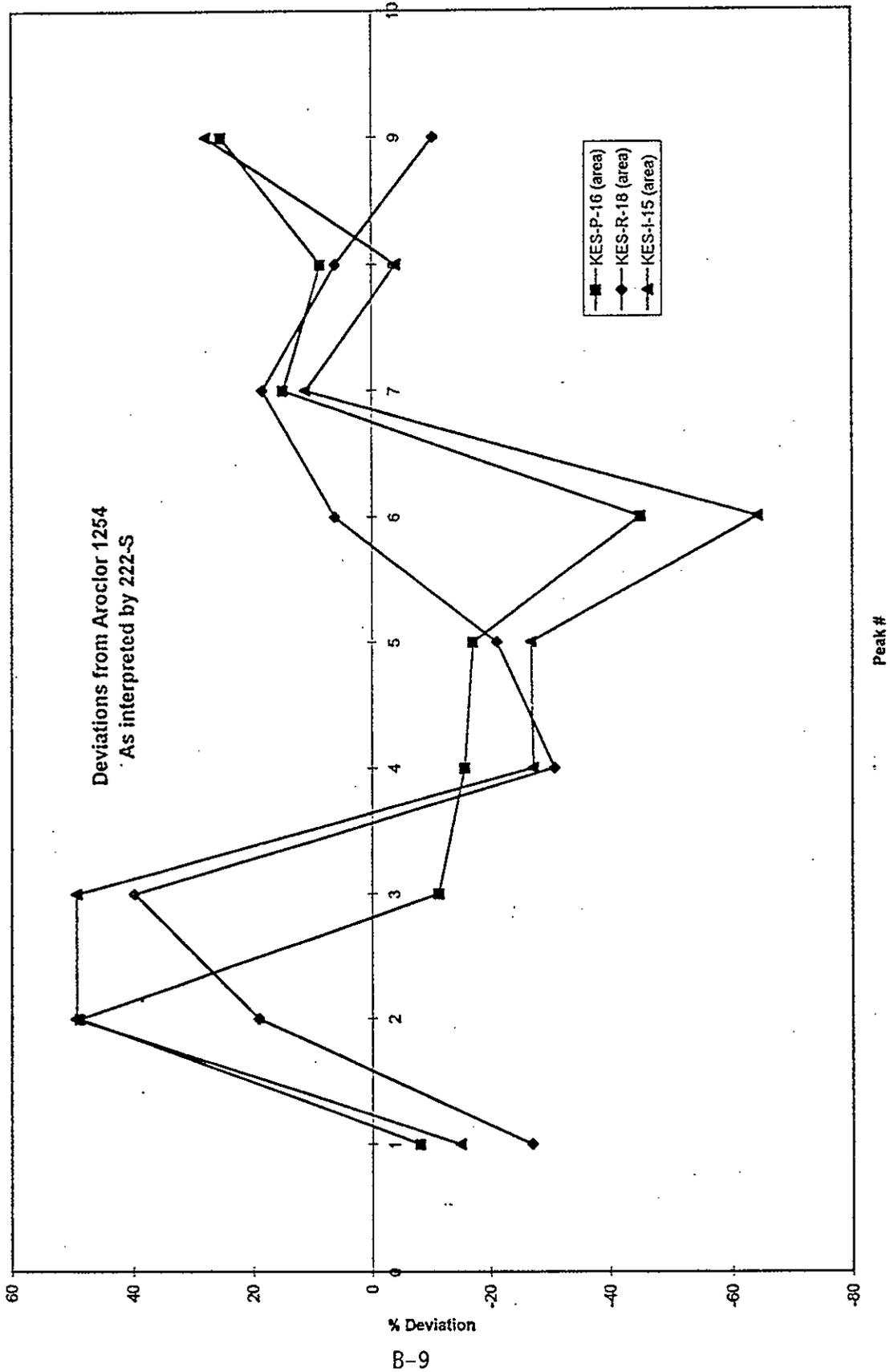
Two primary mechanisms for GC/ECD interference were examined: extraneous contaminant peaks and contaminant shouldering/smearing. In the case of contaminant peaks, there are a number of compounds that can interfere with PCB analysis on a GC/ECD by having similar residence time as PCB and covering or augmenting the response of a particular PCB congener or co-eluting congener set. The one of primary concern is phthalate esters. This interference is specifically listed in Method 8080A as a potential for interference (SW846), and is also identified as present in the samples from the SVOA (Miller 1996).

Recent experience (Schmidt 1996) in PCB analysis showed that compounds similar to phthalate esters leached into the PCB extraction solvents, such as plasticizers coming into contact with the solvent or coming into contact with the vessels used for the extraction. This experience included the use of plastic-fiber reinforced lab towels for drying the glassware during cleaning procedures. Plasticizers leached from the laboratory towels were found to co-elute on a standard PCB analysis with 7-CB, 8-CB, and 9-CB congeners, which would appear to augment the response from the latter peaks on the analysis of Aroclor 1254, thereby skewing the apparent average upwards.

The area response of each sample analyzed for PCB via GC/ECD by the 222-S Laboratory was normalized and reported as a deviation from the Aroclor 1254 standard. Figure B1 shows that there are observable trends in the deviations in some of the samples. The peaks that were chosen to be tracked in the analysis procedure by the laboratory have been assigned numbers 1 through 9 based on their elution time from the GC, 1 being the first tracked peak eluted from the column.

As a general rule, PCB congeners with higher numbers of chlorines attached will elute later on the column, and those with lesser numbers of chlorines will elute faster. The standard breakdown for Aroclor 1254 is given in Erickson (1992). The positive deviations in the last of the nine tracked peaks may indicate the presence of phthalate esters or other contaminants augmenting the response in these peaks. The positive deviations in the first three of the tracked peaks may indicate contamination or partial degradation

Figure B1. Gas Chromatography/Electron Capture Detector  
Area Response Deviation from Aroclor 1254 Standard.



of higher chlorinated PCBs in the mixture to lesser chlorinated species that would register in the first few peaks. This is possible but would also have to occur with an apparent loss of the higher chlorinated species. While the trend of distinct positive deviations of 10% to 50% from an Aroclor 1254 profile among most of the samples in the peaks 7 through 9 is indicative of contamination, no attempt was made to account for this apparent over-reporting in the current analysis. Quantitatively accounting for this apparent contamination would require an appropriate extract cleanup step and reanalysis of the sample extract on GC/ECD.

When examining the ECD chromatograms from the 222-S Laboratory that were created by overlaying the sample and the Aroclor 1254 chromatograms, it is apparent that there are some smeared peak contaminations that are being quantified as if they are PCBs, when, in fact, they may not be. This is especially obvious in the chromatogram for Sample KES-I-15 where a large wide peak appears to be overlaid across tracked peaks 1, 2, and 3. Attachment A of this Appendix contains the chromatographs generated via GC/ECD by 222-S Laboratory in which the samples are compared against the Aroclor 1254 standard. This may be indicative of some co-solvation of the PCB and contaminant organics, column degradation/fouling, low injector temperatures, or some other unspecified phenomenon, but determining the cause of the peak shouldering was beyond the scope of the analytical work. Some degree of peculiar tailing is common on many of the tracked peaks across all three of the GC/ECD analyzed samples, which would suggest that future samples should be subjected to an appropriate sample cleanup or diluted slightly to mitigate the effects of a potential contaminant. There may be other alternatives for interpreting the data without as much interference from the unusual tailing problems.

In our experience with GC/ECD analysis of PCBs in oil phase (Schmidt 1996), we found that the analysis was sensitive to a particular contamination that would appear to co-elute with various PCB congeners. When certain unspecified hydrocarbon oils were present in a high enough concentration PCB sample, the normally very sharp PCB peaks on the GC/ECD would display the usual sharp peak with a wide, smeared shoulder attached. In the previous PCB analysis (Schmidt 1996), comparison of the GC/ECD chromatograms generated with the smeared shoulder with samples that were diluted beyond the critical concentration of the contaminating organics indicated that the peak response heights of the sharp primary peak could be ratioed to PCB concentration, while the added, smeared shoulder appeared to be extra detected mass after adjusting for the sample dilution. Consequently, the GC/ECD data from 222-S Laboratory were requantified by using peak heights rather than peak areas to mitigate the effects of the potential contamination.

A method (LA-523-434) based on EPA Method 8080A for PCB analysis was used by 222-S Laboratory for identification and quantification of the detectable PCB in the form of specific Aroclor mixes. Method 8080A allows some options in interpretation of the chromatograms retrieved from the GC/ECD. Method 8080A allows the user to select chromatogram comparison based on target peak areas or target peak heights. While it is often considered standard to measure concentrations based on reported area of a sample, in some cases, it may be desirable to measure peak heights to generate quantitative data. In

addition, taking into account the presence of potential contaminant tailing as detailed previously, along with previous experience with interpretation of incompletely cleaned samples, more applicable results may be yielded.

The chromatograms for the samples from the 222-S Laboratory from Miller (1996) "Appendix C, Gas Chromatography/Electron Capture Detector Chromatograms of PCB Analyses" were used with a micrometer to measure the heights of the peaks of each of the three samples and the standard in units taken from the response on the y-axis. Table B3 provides a comparison of the results of "area" and "height" interpretations of the data. The values in Table B3 are "as injected" and are representative of the concentration of PCBs in the injection vial. For reported values, the concentrations were adjusted for the sample size and extraction partition. In addition, in the chromatogram interpretation by the 222-S Laboratory, one peak was considered an outlier, and was eliminated from the original interpretation from Samples KES-I-15 and KES-P-16. For the analysis presented in Table B3, the peak was included and marked "all peaks."

Table B3. Comparison of "Area" and "Height" On-Column Quantifications.

Sample ID 222-S Laboratory ID	On-Column PCB Concentration, pg/ $\mu$ l $\pm$ One Standard Deviation, Expressed as Percent of Mean		
	KES-P-16 S95K000142	KES-R-18 S95K000143	KES-I-15 S95K000151
Area (1 peak del.)	134 $\pm$ 22%	710 $\pm$ 24%	227 $\pm$ 29%
Area (all peaks)	127 $\pm$ 28%	710 $\pm$ 24%	210 $\pm$ 38%
Height (all peaks)	95 $\pm$ 24%	428 $\pm$ 13%	141 $\pm$ 29%

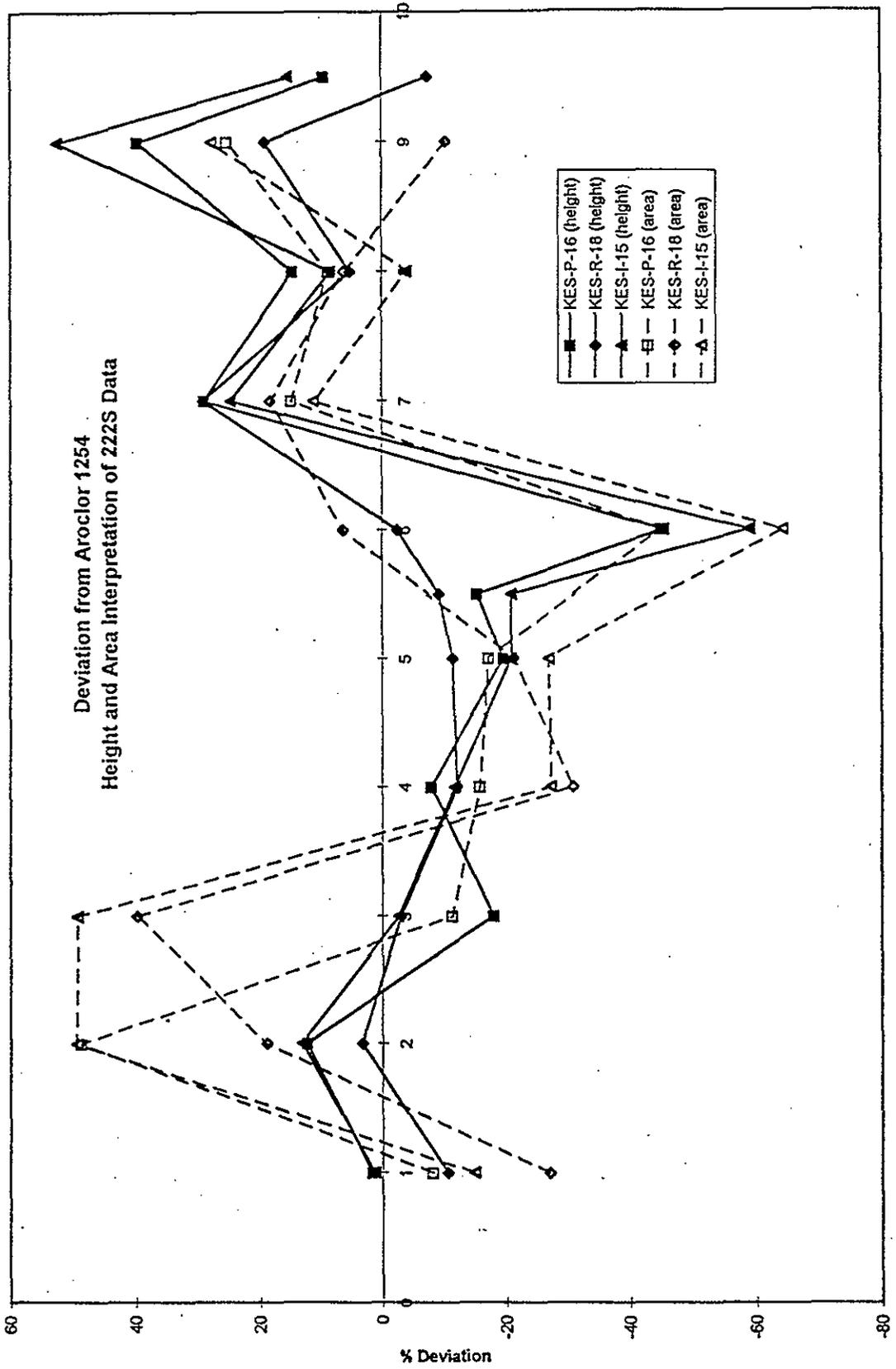
The "height" interpretation shows tighter standard deviations from an Aroclor 1254 profile and lower estimated concentrations. Figure B2 adds the newly interpreted data using the peak heights to generate a similar "percent deviation" chart against the standard Aroclor 1254 profile.

Two peaks in the Aroclor profile were not used in the original interpretation. These two peaks have been incorporated into the reanalysis and are shown in the figure as Peak Number 5.5 and Peak Number 9.5.

From Figure B2, the height interpretation method seems to eliminate large deviations in the sample profile from a standard Aroclor 1254. It does not, however, appear to mitigate deviations from the profile on the higher chlorinated biphenyls, but the augmentation of the profile in the higher congeners may be a function of potential contamination from phthalate esters or other contaminants as described previously.

Figure B3 was prepared to demonstrate the validity of the assumption discussed above that the GC/ECD data should conform to a standard Aroclor 1254 profile. Figure B3 plots the deviation from the Aroclor 1254 standard for the

Figure B2. Comparison of Gas Chromatography/Electron Capture Detector Area and Height Response Deviation from Aroclor 1254 Standard.



data generated from the GC/MS at the 325 Laboratory. This figure shows that the samples can be expected to conform to an Aroclor 1254 standard. In general, GC/MS is less sensitive to contaminant interferences than GC/ECD.

Table B4 compares the results of the "area" and "height" quantifications on a centrifuged sludge basis. The in-vial concentrations were used to back out the original concentrations of the extracted samples using similar calculations as performed by 222-S Laboratory.

Table B4. Comparison of "Area" and "Height" Quantifications of Gas Chromatography/Electron Capture Detector Analysis.

Sample ID	All Concentrations Reported in $\mu\text{g/g}$ , Centrifuged Sludge Basis			
	222-S Laboratory ID	Reported by 222-S	Area, All Peaks	Height Interpretation
KES-P-16	S95K000142	47	45	34
KES-R-18	S95K000143	220	same	130
KES-I-15	S95K000151	104	97	65

As noted previously, quantification of the GC/ECD data was performed by comparing the chromatographs generated from the sample analyses to a chromatograph generated from a single analysis of an Aroclor 1254 standard. For all three samples, the on-column PCB was greater than that of the standard. Table B5 shows the extent of the extrapolation used for performing the quantifications, both for the height method and for the area method. As shown in Table B5, the "on-column" concentrations of PCBs were significantly higher than the Aroclor 1254 standards. Although both methods extrapolate significantly beyond the standard, the extent of extrapolation appears to be less with the use of the height method for quantification. Data that are well beyond the calibration standard are subject to more variability. While the samples were well above the calibration standard, review of the chromatograms revealed no signs of detector saturation.

Table B5. Comparison "On-Column" Polychlorinated Biphenyls of Samples Relative to Aroclor 1254 Standard Used for Quantification of Gas Chromatography/Electron Capture Detector Analysis.

Sample ID Number	Laboratory ID	On-Column PCB Concentration of Sample Relative to Aroclor 1254 Standard, Percent	
		Area Method	Height Method
KES-P-16	S95K000142	130%	100%
KES-R-18	S95K000143	710%	430%
KES-R-15	S95K000151	210%	140%

In the current review of the calculations performed to quantify the GC/ECD analysis, the calculations used for the generation of the reported data assumed recoveries from the sample extraction were 100%. The method used, Method LA-523-434, also indicates that an analyte recovery of 100% is assumed. However, page 30 of Miller (1996) indicates that only a single contact extraction was performed. If a single extraction was performed and only a portion of the extraction solvent was recovered, the results for the GC/ECD analyses should be adjusted upwards. To address this concern, copies of the sample log books for the extraction and handling of the samples analyzed via GC/ECD would have to be reviewed (this was beyond the scope of the current review).

#### **B.5.1 Adjustment of Gas Chromatography/Mass Spectroscopy Polychlorinated Biphenyls Data from 325 Laboratory**

It is important to note the 325 Laboratory was not requested by the Sample Analysis Plan (Welsh 1995) to perform quantitative PCB analyses. A single PCB Aroclor 1254 standard was injected to provide confirmation of PCB only after the SVOA screening indicated the probable presence of PCBs in some samples. This single standard was also used to quantify the PCB concentrations in the K East Basin samples.

In reviewing the PCB data generated at the 325 Laboratory from samples injected on 8 and 9DEC96 (Silvers 1995), two items were found that could have a significant impact the interpretation of the data. First, in the work-up of the data to calculate the concentration of PCB in the centrifuged sludge, the fraction of solvent recovered during the original single contact extraction of the organics from the sludge was not accounted for. In the calculations of final PCB concentrations (per mass sludge), it was assumed that all PCB in the original sludge sample was extracted and contained within the concentrated extract. However, based on page D03-017 of Silvers (1995), only a fraction of the solvent used for the organics extraction was recovered. As a result, the PCB concentrations reported by the 325 Laboratory underestimate the actual PCB concentrations. Table B6 shows the estimated PCB concentration when the solvent recovery is accounted for. It should be noted that in the SVOA determinations, the percent recovery of the extraction solvent was accounted for in the calculations for the reported concentrations.

The second item is the SVOA surrogate recoveries. Sample extracts were concurrently analyzed for both SVOAs and PCBs. As the original intent of the analyses was to examine the sample for SVOAs, SVOA surrogates and SVOA matrix spikes were added to the sludge samples during sample extraction. Depending upon the sample, 8 to 19 semi-volatile organic compounds were added to each sample as surrogates and matrix spikes. For a number of these samples (some of which were concurrently analyzed for PCB), unusually high surrogate recoveries were obtained. On page D03-007 of Silvers (1995), the high recoveries were attributed to evaporation of recovered solvent before recording the recovered solvent volume. Sample extracts for which evaporation losses were suspected are noted on page D03-017. By assuming that the average SVOA surrogate recovery should be 100%, corrected PCB concentrations can be calculated (Table B6). The net effect of the over-recoveries is to decrease the reported PCB concentration. However, the omission of the extraction recovery has a larger effect on the final estimated PCB concentrations.

Table B6. Adjustments to Polychlorinated Biphenyls Data Generated from Gas Chromatography/Mass Spectroscopy by 325 Laboratory

Laboratory ID/ Sample ID	Reported PCB Aroclor 1254 ( $\mu\text{g}/\text{kg}$ ) <sup>1</sup>	Reported Solvent Recovery from Extraction <sup>2</sup>	Corrected <sup>3</sup> PCB Aroclor 1254 ( $\mu\text{g}/\text{kg}$ ) <sup>1</sup>	Average SVOA Surrogate Recovery	Adjusted <sup>4</sup> Solvent Recovery from Extraction	Final <sup>5</sup> Estimated PCB Conc. Aroclor 1254 ( $\mu\text{g}/\text{kg}$ ) <sup>1</sup>
96-00538/ KES-P-16	19,000	35% <sup>6</sup>	54,000	150%	53%	36,000
96-00538D/ KES-P-16D	18,000	20% <sup>6</sup>	90,000	190%	38%	47,000
96-00540/ KES-R-18	23,000	40%	58,000	110%	44%	53,000
96-00540D/ KES-R-18D	86,000	30% <sup>6</sup>	290,000	170%	51%	170,000
96-00540MS/ KES-R-18MS	76,000	50%	150,000	120%	60%	130,000
96-00540MSD/ KES-R-18MSD	53,000	50%	110,000	110%	55%	100,000

## Notes:

<sup>1</sup>Concentrations on per kg centrifuged sludge basis.

<sup>2</sup>Based on ml's of solvent recovered from 10 ml aliquot of extraction solvent added to sample.

<sup>3</sup>Reported PCB concentration divided by fraction of extraction solvent recovered.

<sup>4</sup>Calculated fraction of solvent recovered if actual surrogate recovery was 100%.

<sup>5</sup>PCB concentration corrected for both solvent recovery and surrogate recovery.

<sup>6</sup>Bench sheet noted that caps on these samples were slightly loose, and solvent may have evaporated, resulting in high surrogate recoveries.

It should be noted that by using the surrogate recoveries as internal standards, it is effectively assumed that the PCBs behave identically to the surrogates, both during the extraction and all subsequent sample handling prior to injection.

As noted previously, quantification of the GC/MS data was performed by comparing sample data to a single point analysis of an Aroclor 1254 standard and a sample blank. Only one of the six quantified samples had a greater "on-column" PCB mass than the standard. Table B7 compares the "on-column" PCB of the samples relative to the standard. Data that are well beyond or well below (e.g., KES-P-16, KES-P-16D, and KES-R-18) the calibration standard are subject to more variability.

Table B7. Comparison "On-Column" Polychlorinated Biphenyls of Samples Relative to Aroclor 1254 Standard Used for Quantification of Gas Chromatography/Mass Spectroscopy Analyses.

Sample ID Number	Laboratory ID	On-Column PCB Concentration of Sample Relative to Aroclor 1254 Standard, Percent
KES-P-16	96-00538	22%
KES-P-16D	96-00538D	34%
KES-R-18	96-00540	17%
KES-R-18D	96-00540D	100%
KES-R-18MD	96-00540MS	130%
KES-R-18MSD	96-00540MSD	56%

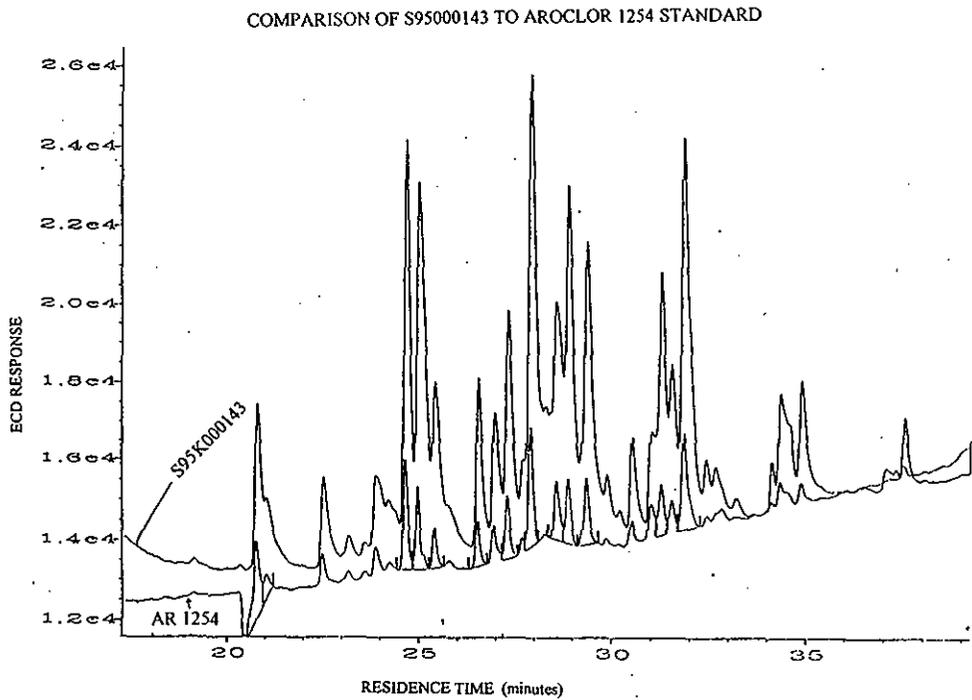
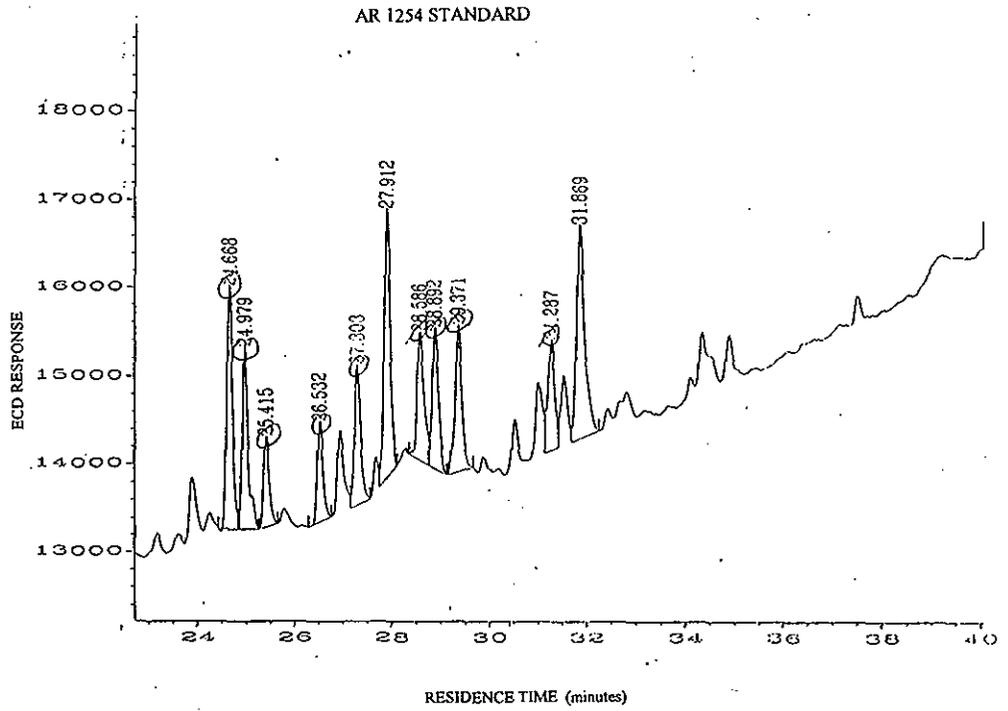
## B.6 REFERENCES

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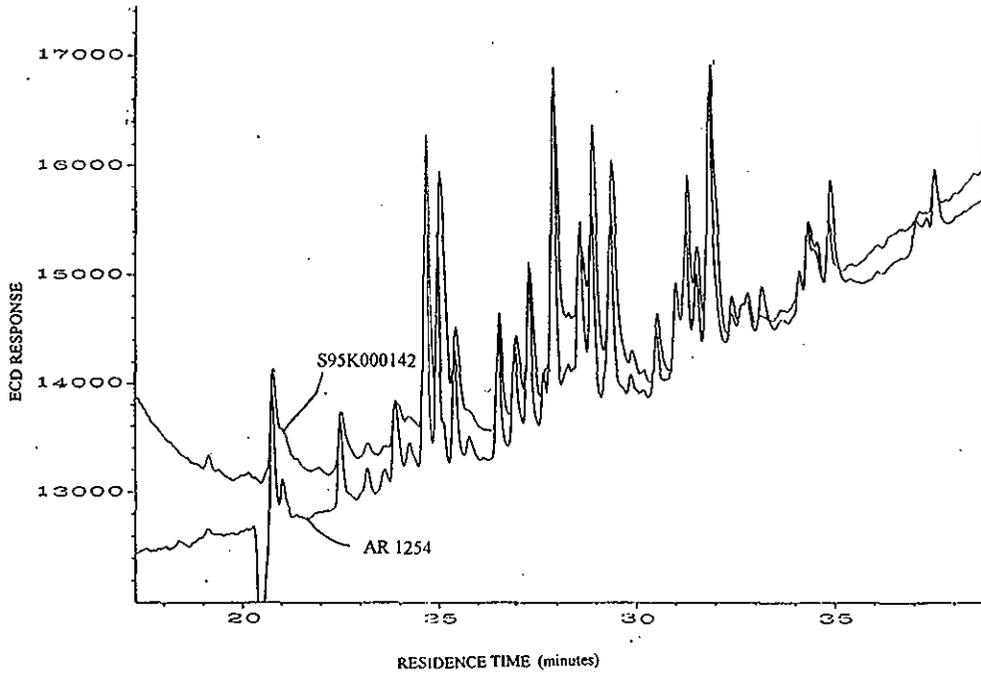
**ATTACHMENT A OF APPENDIX B**

**CHROMATOGRAPHS GENERATED VIA GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR  
IN 222-S IN WHICH THE SAMPLES ARE COMPARED  
AGAINST THE AROCLOR 1254 STANDARD**

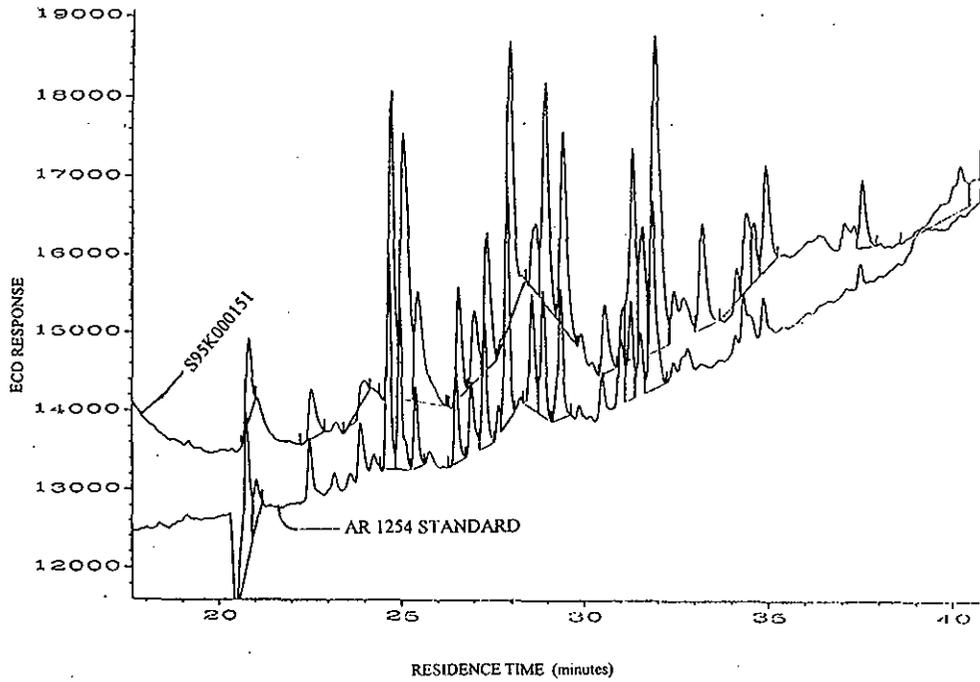
(Taken from WHC-SD-SNF-DP-004 Rev. 1 Appendix C)



COMPARISON OF S95K000142 TO AR 1254 STANDARD



COMPARISON OF S95K000151 TO AROCLOR 1254 STANDARD



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A P P E N D I X C

DIGITAL SCANNING CALORIMETRY AND THERMO-GRAVIMETRIC ANALYSIS OF SLUDGE IN AIR

(Excerpted from the work of J. M. Tingey in Silvers 1998)

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## Thermal Analysis

Archive samples of the settled solids from canisters 96-05 and 96-13 taken from the K East Basin and sludge samples from the K East Basin floor (KES-L-01) and Weasel Pit (KES-P-16) were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis/Differential Thermal Analysis (TG/DTA) in both nitrogen and air atmospheres. The analyses were performed on a Seiko Series 5200 Thermal Analysis System according to PNNL technical procedure PNL-ALO-508 "Laboratory Procedure for Operation of the Differential Scanning Calorimeter (DSC), Thermogravimetric Analyzer (TG), and High Temperature Differential Thermal Analyzer (DTA) and DSC". Between 6 and 26 mg of sample were placed in platinum pans, and the temperature of the sample was increased at a constant rate (5 K/min) from ambient temperature to 993 K in the DSC and 1073 K in the TG/DTA. The energy required to increase the temperature of the sample (DSC), the mass of the sample (TG), and the changes in the temperature of the sample (DTA) in relation to a reference sample (an empty platinum pan) were monitored as a function of temperature.

The calibration of the thermal analysis system was checked weekly with an indium standard and a calibrated weight. The literature values for the enthalpy and onset temperatures of indium are 28.59 J/g and 429.75 K. The measured values for the onset temperature of indium was 429.8 K for both the DSC and the DTA. The enthalpy of the indium as measured by DSC is 28.3 J/g. The deviation of the measured values from the reported values is 1% for the enthalpy and within experimental error for the onset temperatures. A lead standard was also run on the DSC. The literature values for the onset temperature and enthalpy of the solid to liquid phase transition for lead are 600.7 K and 23.22 J/g. The measured values were 600.7 K and 23.7 J/g. The deviation of the measured values from the reported values is 2% for the enthalpy and within experimental error for the onset temperature.

The results of these analyses and the previously reported analyses are given in Tables I and II. The results of these analyses was similar below 550 K for all the samples under both cover gases, but significant differences were observed above 550 K. All of the data is based on wet weights. For more consistency between samples, the data can be calculated on a dry weight basis for all transitions except for the first transition which is the evaporation of water from the sample.

The first transition occurs between ambient temperature and up to 460 K. This transition is endothermic and is due to the evaporation of water from the sample, and a significant sample mass loss is associated with this transition. This transition was observed in all samples under all conditions. The enthalpy for this transition is dependent upon the amount of water in the sample (wt% solids) and varies between samples. The previously analyzed samples had more water in the samples; therefore, this enthalpy and mass loss associated with this transition is larger in these samples. This water evaporation endotherm consists of multiple endotherms which cannot be resolved. The multiple endothermic transitions are indicative of evaporation of water from different environments (inner and outer coordination spheres and waters of hydration) and were expected.

Significant water evaporates at ambient temperatures as the cover gas passes over the sample; therefore, many of the samples had lost substantial water before the analyses were begun. This loss of water is indicated by the DSC curves beginning below the baseline and the TG curves beginning at masses less than 100% of the original mass. Due to the premature loss of water, an accurate enthalpy for the evaporation of water cannot be determined for all samples. Generally, a greater than value is reported for the enthalpy of this transition. The mass loss associated with this transition is based on mass of the original sample (100% mass).

The second transition is also observed in all the samples under both cover gases. This endothermic transition occurs between 415 and 600 K. The onset temperature and enthalpy for this transition ranges from 450 to 485 K and 5 to 80 J/g. The enthalpy of the transition varies between the samples because of the differences in chemical composition of the sample including the amount of water associated with the sample. A significant mass loss is associated with this transition.

Additional transitions at higher temperatures are observed in most of the samples. These transitions are all exothermic with the exception of KES-P-16 in air. An endothermic transition with an enthalpy of 126 J/g was observed between 574 and 719 K. This transition has an onset temperature of 600 K. Since this transition was observed in only this sample, a duplicate run should be performed to validate this endothermic transition. Exothermic behavior was observed in KES-L-01 with a nitrogen cover gas and 96-05 and 96-13 with both air and nitrogen cover gases. In the previously analyzed samples exothermic behavior was observed only in 96-13. This

exothermic behavior begins at approximately 600 K and is completed by 850 K. An overall mass loss is associated with this exothermic behavior although some small weight gains may be associated with this behavior. Several transitions are observed as part of this exothermic behavior.

No significant difference was observed between nitrogen and air atmospheres. Generally, the enthalpy of the exothermic behavior seemed depressed in the air atmosphere compared to the nitrogen atmosphere, but no different transitions were observed as the cover gas was changed from nitrogen to air.

Table I. Differential Scanning Calorimeter Results

Sample	Atmosphere	Temp. Range (K)	Onset Temp. (K)	Enthalpy (J/g)
KES-L-01 A	Nitrogen	295 - 581	*	> 200
		441 - 531	481.6	40.6
		592 - 873	**	-103.4
	Air	295 - 581	*	> 170
		459 - 541	482.9	29.9
KES-L-01 (Previous Analysis)	Nitrogen	292 - 394	*	1061
		430 - 552	461	13.2
KES-L-01 Dup. (Previous Analysis)	Nitrogen	280 - 389	*	886
		443 - 519	464	11.8
KES-P-16 B	Nitrogen	298 - 581	*	> 193
		468 - 581	480.7	48.2
	Air	295 - 474	*	> 184
		474 - 574	482.2	15.0
		574 - 719	600.5	126
KES-P-16 (Previous Analysis)	Nitrogen	307 - 387	*	*
		415 - 587	449	77.1
KES-P-16 Dup. (Previous Analysis)		310 - 390	*	268
		425 - 599	454	77.5
96-05	Nitrogen	307 - 461	*	> 160.5
		472 - 522	**	7.2
		565 - 852	624.2	-1074
	Air	304 - 471	*	373
		471 - 541	483.6	15.0
		553 - 777	607.7	-909
		675 - 709	677.1	***
		709 - 777	739.4	***

96-05 (Previous Analysis)	Nitrogen	294 - 370	*	204
		383 - 413	**	0.6
		450 - 532	477.1	15.8
96-05 Dup. (Previous Analysis)		296 - 400	*	184
		454 - 518	467.5	15.5
96-13	Nitrogen	304 - 447	*	> 254
		463 - 521	**	4.7
		560 - 830	616.9	-1075
	Air	294 - 456	*	389
		472 - 516	478.9	5.5
		582 - 701	589.1	-179
96-13 (Previous Analysis)	Nitrogen	295 - 415	*	*
		453 - 517	466	7.7
		610 - 805	631	-44.9
96-13 Dup. (Previous Analysis)	Nitrogen	300 - 460	*	*
		460 - 527	469	6.7
		689 - 801	696	-16.7

\* This transition began at the start of the run; therefore, it was not possible to determine the onset temperature. The transition begins below the baseline; therefore, the enthalpy of this transition is reported as a greater than value.

\*\* This transition was so small that it was difficult to obtain an accurate onset temperature

\*\*\* The transition could not be resolved from previous transitions; therefore, the enthalpy for this transition is included in the reported enthalpy for the encompassing transition.

Table II. Thermogravimetric Analysis Results

Sample	Atmosphere	Temp. Range (K)	Onset Temp. (K)	Mass Loss (%)
KES-L-01 A	Nitrogen	298 - 426	*	8.1
		426 - 819	483.4 (89.5%)	8.8
		819 - 1084	**	0.7
	Air	297 - 431	*	8.8
		431 - 743	484.5 (88.8%)	8.7
		743 - 1079	**	1.3
KES-L-01 (Previous Analysis)	Nitrogen	290 - 373	*	37.7
		459 - 520	459	0.8
	Nitrogen	293 - 390	*	66.7
		447 - 538	471	1.3
KES-P-16 B	Nitrogen	301 - 426	*	3.8
		426 - 844	476.7 (95.0%)	7.4
	Air	298 - 426	*	2.5
		426 - 703	503.6 (96.2%)	16.4
		703 - 1079	**	0.7
KES-P-16 (Previous Analysis)	Nitrogen	309 - 373	*	4.6
		471 - 565	494	5.8
	Nitrogen	307 - 373	*	4.8
		471 - 577	495	6.2
96-05	Nitrogen	298 - 435	*	5.5
		435 - 739	485.8 (94.0%)	3.9
		788 - 923	804.3 (90.6%)	0.3

96-05	Air	298 - 419	*	5.5
		419 - 677	482.5 (93.9%)	3.7
		677 - 795	662.7 (90.8%)	-0.2
		795 - 925	805.9 (91.0%)	0.7
		925 - 1079	**	0.8
96-05 (Previous Analysis)	Nitrogen	295 - 413	*	19.8
		413 - 600	ND	1.4
	Nitrogen	295 - 400	*	15.5
		400 - 605	ND	1.2
96-13	Nitrogen	301 - 424	*	5.2
		424 - 721	466.7 (94.6%)	3.7
		788 - 851	796.2 (91.1%)	0.2
		920 - 1084	**	-0.4
	Air	298 - 418	*	5.6
		418 - 710	471.4 (94.1%)	3.1
		779 - 918	797.1	0.7
		918 - 1079	**	0.9
96-13 (Previous Analysis)	Nitrogen	295 - 418	*	15.0
		418 - 713	ND	2.3
	Nitrogen	300 - 446	*	3.4
		446 - 531	ND	1.0
		531 - 704	ND	1.3

\* The mass loss began at the start of the run; therefore, it was not possible to determine the onset temperature.

\*\* The mass loss was too gradual to obtain an accurate onset temperature.

ND Not Determined

Figure C1. Comparison of Thermo-Gravimetric Analysis in Air and Nitrogen Atmospheres for K East Floor Sample L-01.

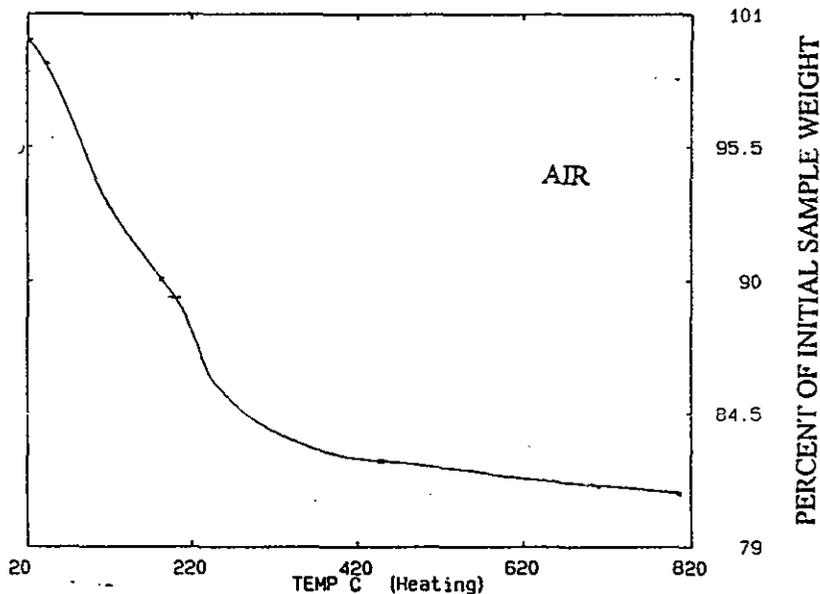
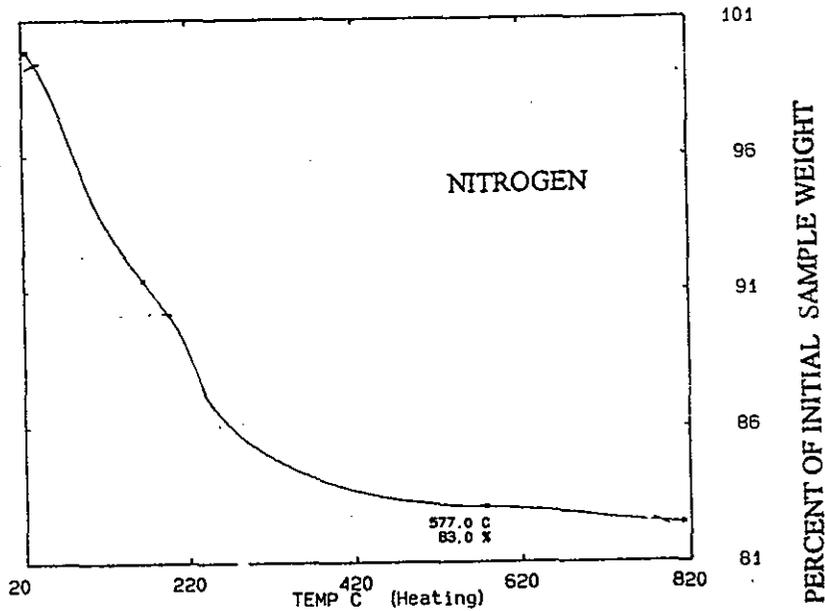


Figure C2. Comparison of Thermo-Gravimetric Analysis in Air and Nitrogen Atmospheres for K East Weasel Pit Sample P-16.

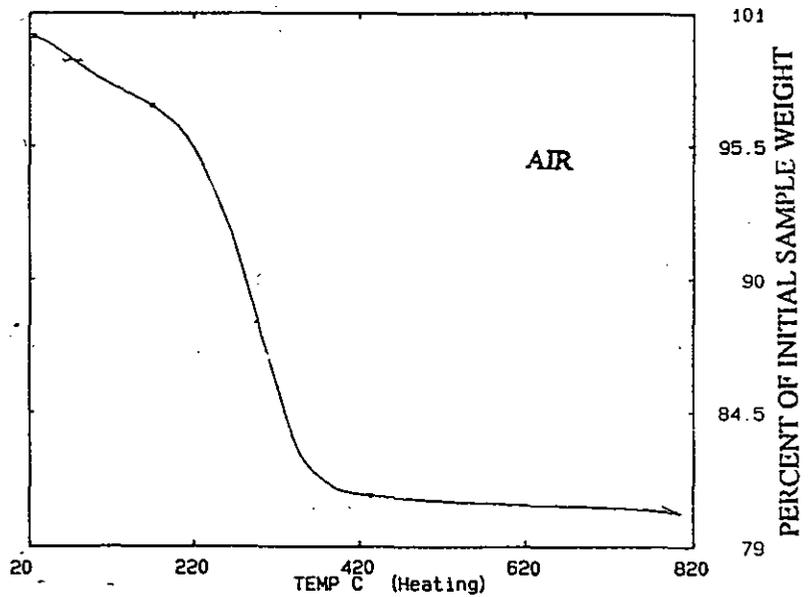
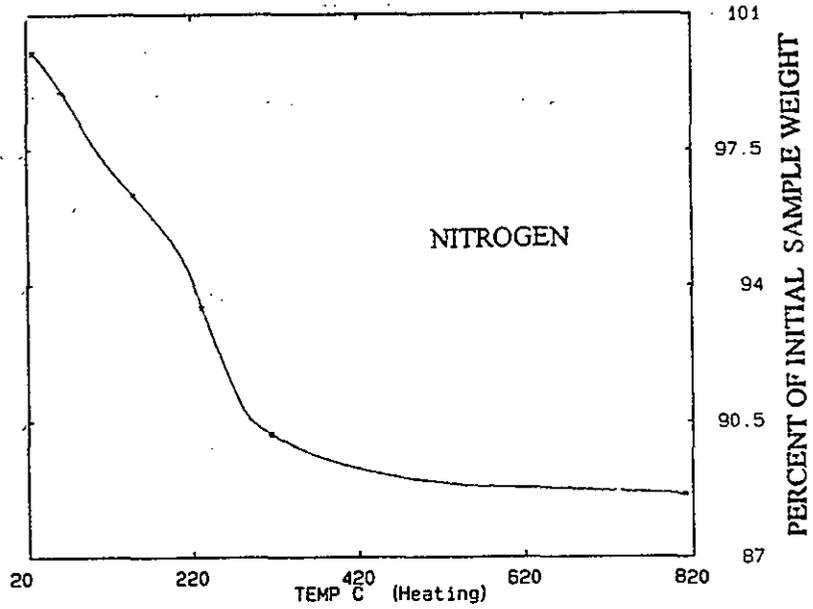


Figure C3. Comparison of Thermo-Gravimetric Analysis in Air and Nitrogen Atmospheres for K East Canister Sample 96-05.

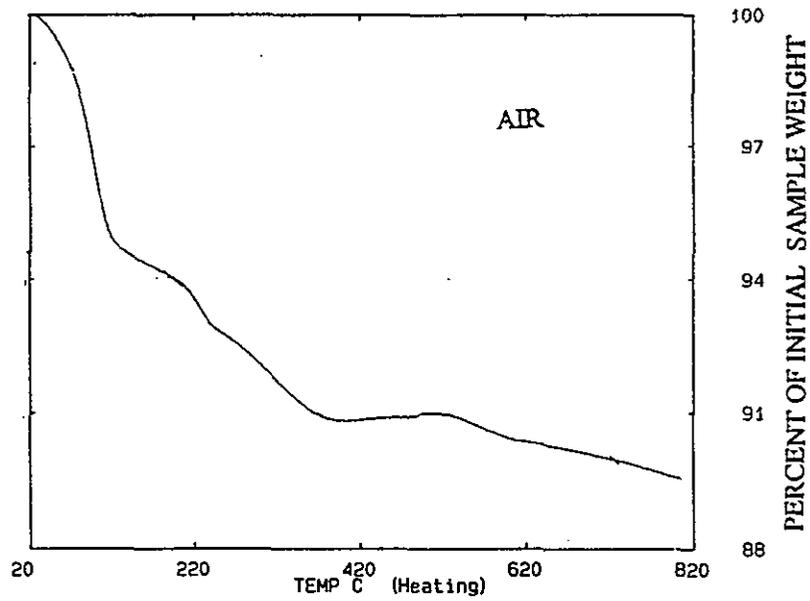
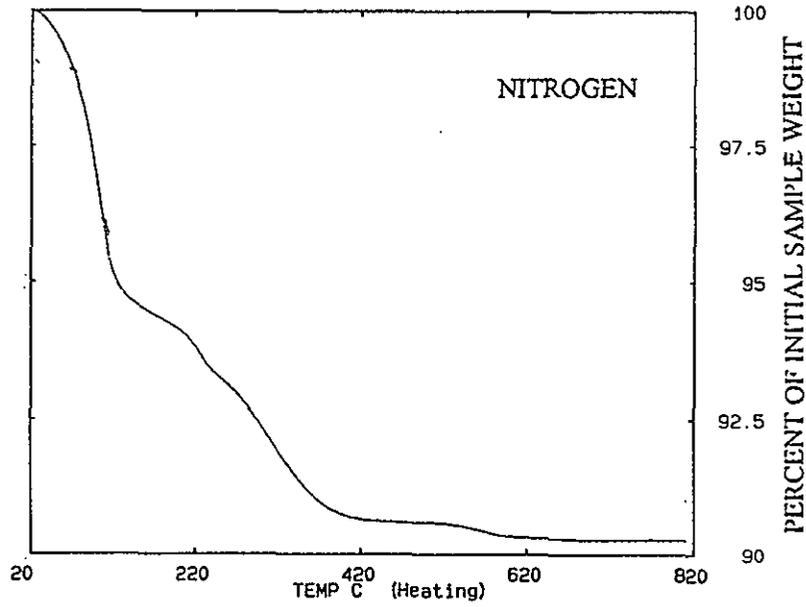
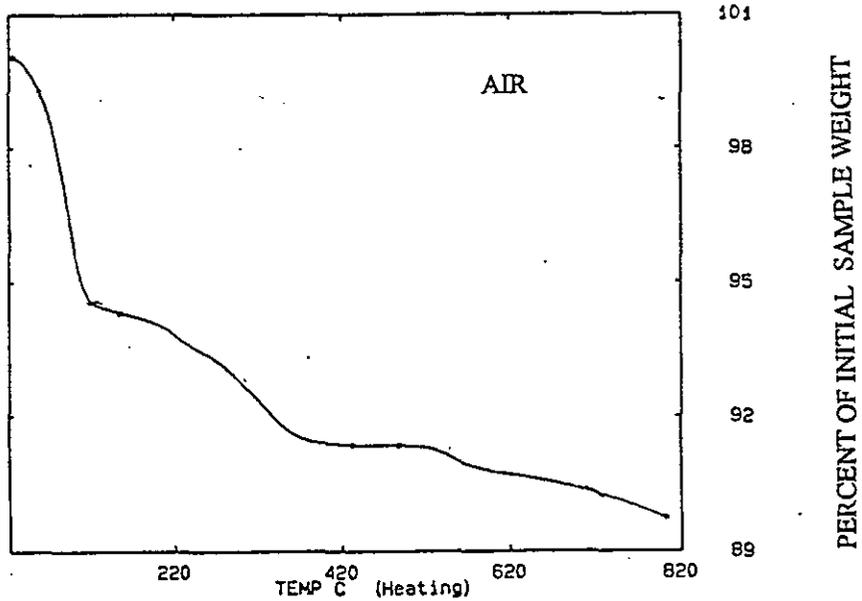
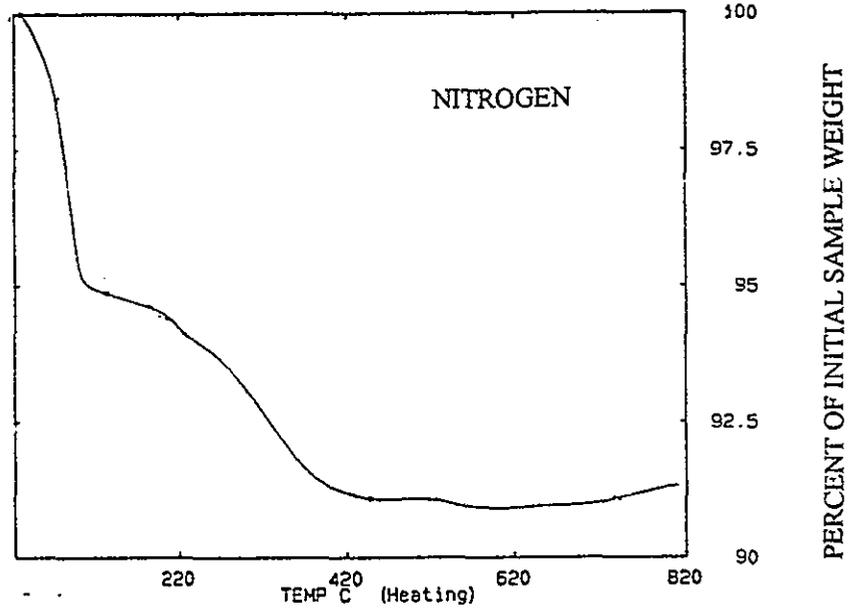


Figure C4. Comparison of Thermo-Gravimetric Analysis in Air and Nitrogen Atmospheres for K East Canister Sample 96-13.



A P P E N D I X D

DIGITAL SCANNING CALORIMETRY AND THERMO-GRAVIMETRIC  
ANALYSIS OF RADIOACTIVE RESIN BEADS

J M Tingey

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## APPENDIX D

### SUPPLEMENTAL THERMAL ANALYSIS OF K-EAST BASIN SAMPLES

#### D.1 INTRODUCTION

This report describes work performed by Pacific Northwest National Laboratory (PNNL) for Duke Engineering & Services Hanford (DESH) under letter of instruction (LOI) DESH-9758893. Under this LOI, the thermal properties of organic ion exchange resins (OIER) were measured. These OIER materials are present in the K East Basin, and the OIER thermal properties could affect the proposed treatment of K East Basin sludge using nitric acid.

#### D.2 BACKGROUND

Approximately 2100 metric tons of irradiated N Reactor fuel are currently stored at two retention basins on the Hanford site: K East and K West Basins. This material was to be reprocessed through PUREX to recover the plutonium; however, the closure of PUREX in December of 1992 left no immediate disposal path for this spent nuclear fuel. Some of the fuel stored in these basins has begun to corrode. Visual observations indicate that fuel corrosion begins at defects in the weld areas or at areas damaged when the elements, embrittled by irradiation, were discharged from the reactor (Swanson 1988).

N Reactor fuel is a metallic uranium alloy, unlike most commercial fuels which are uranium oxide based. This metallic uranium alloy contains 700 ppm to 900 ppm aluminum, 365 ppm to 735 ppm carbon, 300 ppm to 400 ppm iron, 124 ppm silicon, and 100 ppm nickel (Geiger 1989). To prevent corrosion, the metallic uranium fuel elements were clad with Zircaloy-2, a zirconium alloy containing nuclear grade zirconium with 1.5% tin. During corrosion the exposed uranium swells as it is converted from metal to oxide causing the cladding to split, exposing more metal, and providing additional sites for corrosion to occur. Swelling of the fuel elements also causes any oxide layers to spall, exposing even more metal.

In the K East and K West Basins, the fuel elements are stored in canisters made from two connected barrels that are 8 in. in diameter and 27 in. long. Three canister types, Mark 0 (MK-0), Mark I (MK-I) and Mark II (MK-II), were used in K East Basin. These canisters were fabricated from either aluminum (MK-0 and some of the MK-I canisters) or stainless steel (MK-II and some of the MK-I canisters). The MK-0 canister bottoms are perforated while the MK-I and MK-II canister bottoms are solid. The canisters in K East Basin have no lids, while the canisters in K West Basin were filled with a dilute  $\text{KNO}_3$  solution and sealed under  $\text{N}_2$  using a graphite-based gasket material (Grafoil) between the lid and canister.

Approximately  $43.1 \text{ m}^3$  of sludge has accumulated in the K East Basin. Sludge has been observed in the storage canisters as well as on the floor and in associated pits. The sludge is primarily uranium oxide, windblown sand,

and aluminum and iron oxides and hydroxides. Minor components identified include organic and inorganic ion exchange materials, fine uranium metal particles, paint chips, Grafoil, and polychlorinated biphenyls. The concentrations of these components vary by location and depth in the basins.

Current remediation plans require removal and treatment of the sludge. The original process baseline included disposal of sludge directly to the Hanford Double-Shell Tanks pending vitrification. The Tank Waste Remediation Systems (TWRS) has limits on the energetics of materials that can be received for storage; therefore, the energetics of the sludge have been studied (Makenas 1996; Makenas 1997 and 1998). The current baseline process includes treatment in nitric acid of all particles less than 1/4 in. in diameter. The acid-insoluble fraction is to be transferred to the Environmental Restoration Disposal Facility (ERDF). Due to criticality concerns the liquid fraction is to be diluted with depleted uranium and iron followed by treatment with NaOH. The liquid fraction and associated precipitates are to be stored in the Double-Shell Tanks pending vitrification. An alkaline rinse (1 M NaOH) of the acid-treated resin followed by a water rinse has been proposed prior to disposal to eliminate potential safety concerns by removing the nitrate oxidant.

Prior to the characterization campaign, approximately 14 different sludge types were identified in the K East Basin based on appearance, location, and settling behavior. Analyses of the sludges confirm they are an inhomogeneous mixture varying in composition with location and depth.

Two sludge components were identified as potential complications to the processing baseline: organic ion exchange resin (Purolite NRW-37) (Schmidt 1998) and high iron sludge. Purolite NRW-37 is a mixture of Purolite NRW-100 (cation exchange) and NRW-400 (anion exchange) resin beads. Both components are insoluble in nitric acid and have the potential to entrain greater than 100 nCi/g of plutonium in the insoluble solids, exceeding the TRU limit for disposal to ERDF, and raising criticality concerns (Katz 1986). An additional concern is that exposure of some organic anion exchange resin beads to concentrated nitric acid has resulted in nitration of the aromatic rings creating an explosion hazard (Harland 1994). Retention of nitrate in the resin by ion exchange or sorption also is of concern because of nitrate's oxidation properties.

Distribution coefficients of approximately 1000 for plutonium in similar organic anion exchange resins at 10 M nitric acid are reported in the literature. In 10 M nitric acid the plutonium and uranium distribution coefficients of organic ion exchange resin beads collected from the floor of the K East Basin appear to be below the literature values. The measured distribution coefficients were approximately 50 for plutonium and 5 for uranium (Bredt et al., 1998).

The manufacturer specification for Purolite NRW-37 shows that 93% of the beads are between 400  $\mu\text{m}$  and 1200  $\mu\text{m}$ . Since the beads have been found on the K East floor, they are anticipated to be present in Stream 1 from K East Basin processes. Stream 1 of the K East Basin process includes all sludge from the basin floor and weasel pit and sludge particles >250  $\mu\text{m}$  in diameter from the canisters. Stream 1 of the K West Basin process includes only floor sludge.

The beads have also been found in some K East canisters, and since greater than 98% of the beads are larger than 250  $\mu\text{m}$ , organic ion exchange resin beads should be anticipated in Stream 2 from both K West and K East Basin processes. Stream 2 from both Basins includes sludge from both empty and full canisters and the fuel wash process. In the K East Basin the sludge particles allowed into this stream range in size from 1/4 in. to 250  $\mu\text{m}$ . In the K West Basin the sludge particles range in size from 1/4 in. to 500  $\mu\text{m}$ .

### D.3 SAMPLE DESCRIPTION

Sludge samples were collected from K East Basin by DESH. Sampling of the floor and Weasel Pit sludges occurred in August and September of 1995. These samples were collected at various depths in the sludge, near aluminum and stainless steel canisters, and at various distances from corroding fuel. Sampling of the canister sludge occurred in April of 1996. Canister sludge samples were collected from empty canisters and canisters containing fuel, stainless steel and aluminum canisters, and canisters with intact fuel as well as canisters with damaged fuel. All samples were collected using a vacuum extraction tube with 0.635 cm diameter ports.

Characterization of the K Basin sludges was conducted at PNNL and 222-S laboratories (Makenas et al., 1996, 1997, and Makenas 1998). Following characterization, most of the residual samples were shipped to PNNL's 325 Building hot cells for storage. During storage the samples dried, forming materials that range from fine powders to hard chunks. The only exception was sample KES-H-08 which had visible standing liquid.

Sample KES-H-08 was collected from the basin floor near the north Load Out Pit. Sieving work showed this sample was approximately 65 wt% round Organic Ion Exchange Resin (OIER) beads. In addition to the OIER beads, white particles between 355  $\mu\text{m}$  and 1180  $\mu\text{m}$  in diameter were also observed. These white particles are similar to Zeolon-900, an inorganic mordenite used as an ion exchange material at K East Basin. X-ray diffraction (XRD) analyses of KES-H-08 and Zeolon-900 identified the presence of mordenite  $[(\text{Na}_2, \text{Ca}, \text{K}_2)\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 7\text{H}_2\text{O}]$ , an orthorhombic zeolite mineral, in both materials (Schmidt et al., 1998).

Prior to the testing described in this report, KES-H-08 was wet-sieved to remove oxide sludge and obtain a sample containing primarily OIER beads. Manufacturer specifications for these beads indicate that <2% of the beads should be smaller than 400  $\mu\text{m}$ . Given this lower limit for the bead diameter, a Tyler 42 sieve with 355  $\mu\text{m}$  openings was used for the separation. The KES-H-08 sample was placed on the Tyler 42 sieve, and the sample was washed with K East Basin supernate until no more small dark particles were visible and the rinse passing through the sieve appeared to be clear. The rinse was collected in a clean jar, but not analyzed. Small (approximately 1 mm) white particles were not separated from the beads. These particles appeared to be similar in shape and color to Zeolon-900, and are the mordenite identified in the bulk sample by XRD (Pool et al., 1998). Following sieving, the beads were collected in a screw cap vial. They formed a wet clump, but no standing

liquid was visible. A subsample of the beads was air dried. Using a pair of tweezers, the dried beads were then separated into a dark and a light fraction. The resulting samples were labeled H-08 Dark and H-08 Light. The NRW-37 component resins, NRW-100 cation exchange resin and NRW-400 anion exchange resin are dark red and amber in color, respectively.

Additional subsamples of OIER beads obtained from sieved KES-H-08 were digested in nitric acid at 298 K and 333 K. The detailed experimental approach for this testing can be found in a previous letter report (Bredt et al., 1998). The beads sieved from KES-H-08 were stirred and eight 1-gram aliquots were removed and placed in unique vials labeled H-08 1 through H-08 8. Between 0.4 and 1 gram of sludge from Sample 96-06 M/L was added to Samples H-08 4 through H-08 8. Sample 96-06 is the middle and lower layers of settled solids from the material suctioned from the west canister barrel of K East Basin cubical 5465. This very corroded canister contained fuel elements in poor condition. Twenty milliliters of room-temperature nitric acid was added to each of the vials. All eight vials were left at ambient temperature (approximately 298 K) for 2 hours. After 2 hours, Samples H-08 3, H-08 4, H-08 7, and H-08 8 were transferred to a heat block at 333 K, and Samples H-08 1, H-08 2, H-08 5, and H-08 6 were vacuum filtered through a 0.2  $\mu\text{m}$  PVDF membrane. At 4 hours and 6 hours, Samples H-08 3, H-08 4, H-08 7, and H-08 8 were stirred and at 8 hours these samples were vacuum filtered through a 0.2  $\mu\text{m}$  PVDF membrane. The filtrates from all the samples were collected for later analysis, and the filtered solids were rinsed with 10 ml of 10 M nitric acid followed by 10 ml of DI H<sub>2</sub>O. In this report these filtered solids are called treated organic ion exchange resin beads.

A small portion of Sample H-08 was processed through the nominal flowsheet for organic ion exchange resin processing followed by an acid wash and finally an alkaline wash of the sample. The nominal flowsheet process is treatment of the organic ion exchange resin with 6 M HNO<sub>3</sub> at 368 K. This sample was then washed in 0.32 M HNO<sub>3</sub> (2%) at ambient temperature for several days (approximately 25 times the volume of acid to volume of resin). The resulting washed resin was rinsed twice with approximately the same volume of 0.32 M HNO<sub>3</sub> as was used to wash the sample. The acid was decanted and the resin beads were vacuum filtered. The resulting solids were rinsed with deionized water at a water to resin ratio of approximately 20:1 and allowed to dry in air at ambient temperature. A subsequent alkaline wash of a portion of this sample included a rinse with 50 ml of 1 M NaOH per gram of resin. The resin was washed for 1 hour and agitated every 15 minutes. The wash solution is decanted from the resin, and three water rinses of 50 ml of H<sub>2</sub>O per gram of treated resin are performed for each sample. The resin was then allowed to dry overnight in an air atmosphere at ambient temperature.

The preparation of the sample materials described in this report are summarized in Table D.1. The non-radioactive organic ion exchange resins were analyzed in their as-received condition from the vendors. The NRW-100 and NRW-400 ion exchange resins are nuclear grade resins based on the standard Purolite ion exchange resins C-100 and A-400, respectively. NRW-100 is a cation exchange resin and NRW-400 is an anion exchange resin. The resin

matrix for both exchangers is polystyrene cross-linked with divinylbenzene (DVB). The NRW-100 and NRW-400 contain nuclear sulfonic and Type I quaternary ammonium functional groups, respectively. NRW-100 is received from the vendor in the  $H^+$  form and the NRW-400 is received in the  $OH^-$  form. Duolite C-3 cation exchange resin contains a methylene sulfonic functional group which is similar to the NRW-100 functional group, but the resin matrix in Duolite C-3 is a phenol-formaldehyde condensate instead of a polystyrene copolymer. This phenolic resin consists of granular particles (irregular in shape) in contrast to the spherical polystyrene resin beads. The Duolite C-3 resin was used to investigate the impact of Duolite ARC-359 in the K Basins. Duolite ARC-359 is also a methylene sulfonic functionalized phenol-formaldehyde resin, but is not currently being produced. Duolite ARC-359 was used at the K Basins but has not been observed in the K Basin sludges characterized to date.

Graphite was observed in the X-Ray Diffraction of samples from the K West canister sludge (Makenas 1998). The graphite in these samples comes from the Grafoil used to seal the canisters in K West Basin. Grafoil is a graphite-based gasket material that is extremely heat resistant and chemically inert. The minimum carbon content for nuclear grade Grafoil is 99.5%. The functional temperature range for standard Grafoil is 33 K to 3250 K in neutral or reducing atmospheres and 33 K to 725 K in oxidizing atmospheres. Grafoil can even be used in concentrated nitric acid at temperatures up to 310 K. As the concentration of nitric acid decreases the upper functional temperature increases (360 K in 0% to 10% nitric acid).

#### D.4 APPROACH

The energetics and mass losses of the filtered solids from H-08 1 through H-08 8 were analyzed as function of temperature by Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) on a Seiko Series 5200 Thermal Analysis System according to PNNL technical procedure PNL-ALO-508, "Laboratory Procedure for Operation of the Differential Scanning Calorimeter (DSC), Thermo-Gravimetric Analysis (TGA), and High Temperature Differential Thermal Analyzer (DTA)." The nonradioactive ion exchange resins were analyzed on a Seiko Series 6200 Thermal Analysis System according to the same procedure as the radioactive samples.

Approximately 5 mg of organic ion exchange material or sample was placed in a copper pan with copper mesh placed on top of the sample to prevent sample from being ejected from the pan during energetic exothermic events. Simultaneous DTA and TGA analyses are performed on the same sample, but a separate sample is used for the DSC analysis. During the majority of the DSC analyses, the temperature of the sample was increased from ambient to approximately 993 K at a constant rate of 5 K/minute. During the majority of the DTA/TGA analyses, the temperature of the sample was increased from ambient temperature to approximately 1073 K at a constant rate of 5 K/minute. The temperature was increased to only 773 K on the initial DSC and DTA/TGA analyses of the nonradioactive organic ion exchange resins. The energy required to increase the temperature of the sample was monitored as a function

of temperature for the DSC analyses. The mass of the sample (TGA) and the change in the temperature of the sample in relation to a reference sample (an empty pan) (DTA) were monitored as a function of temperature in the DTA/TGA analyzer. These analyses were performed in both flowing nitrogen and air atmospheres.

The results from these analyses indicated large exothermic behavior (>20,000 J/g) from the treated organic ion exchange resins in air above 675 K in copper pans. A large increase in the mass of these samples (>100%) was also observed in air above 825 K in copper pans. Visual observation of the copper pans exposed to air at these elevated temperatures indicate substantial corrosion to the pan. To determine whether the large exothermic behavior and large increase in mass are due to the oxidation of the copper pans from the volatilization of nitrogen oxide gases in an air environment, thermal analyses of cerium nitrate under air cover gas were performed by the same method described above in both copper and platinum pans. Thermal analysis of one of these treated organic ion exchange samples (H-08 6) was repeated in platinum and copper pans to verify the results obtained previously and the effect of copper pans on these results.

Approximately 15 mg of cerium nitrate or 1 mg of the treated organic ion exchange sample was placed in a sample pan. The cerium nitrate was 99.9% hydrous and came from Research Chemicals in Phoenix, Arizona. The lot number for the cerium nitrate was Ce-N-3-020. The cerium in the nitrate salt is in the +3 oxidation state, and the chemical formula for this material is  $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ .

Platinum lids and copper mesh were placed on top of the treated organic ion exchange sample in platinum and copper pans, respectively, to prevent the sample from being ejected from the pan during energetic exothermic events. Copper mesh was placed on the duplicate cerium nitrate sample in the copper pans to determine the impact of the copper mesh on the results. The cerium nitrate samples were performed in duplicate in both copper and platinum pans. Treated organic ion exchange resin samples were analyzed only once in each pan material during these additional analyses.

DSC of cerium nitrate and the treated organic ion exchange resins were performed over the same temperature range and at the same ramp rate as the previous analyses. DTA/TGA analyses of cerium nitrate and the treated organic ion exchange resins were also performed over the same temperature range and at the same ramp rate as the previous analyses in copper pans, but in platinum pans the temperature of the sample was increased from ambient temperature to approximately 1223 K at a rate of 5 K/minute. The temperature limit for copper pans is 1073 K; therefore, this was the temperature limit of these analyses. These analyses were performed only in a flowing air atmosphere. The parameters for each run are reported in Table D.2.

Aliquots of H-08 resin beads treated according to the nominal flowsheet (6 M  $\text{HNO}_3$  at 368 K for 10 hours) were analyzed by DSC and DTA/TGA in platinum pans with platinum lids over the same temperature range and ramp rate as the cerium nitrate samples in platinum pans and lids. Aliquots obtained prior to and after the alkaline wash were analyzed.

The temperature calibration of the DTA/TGA and the temperature and enthalpy calibration of the DSC were checked with indium and lead standards. The balance calibration of the TGA was checked with calibrated weights. The literature values for the enthalpy and onset temperature for the melt of indium and lead are 28.59 J/g and 429.75 K (indium), and 23.22 J/g and 600.65 K (lead) (Matsuo et al., 1985). The measured values for the onset temperatures and enthalpies are listed in Table D.3. Since these analyses were conducted over several months, multiple calibration checks were performed. The average enthalpy and onset temperature for indium and lead are 27.8 J/g  $\pm$  1.3 J/g and 429.8 K  $\pm$  0.4 K (indium) and 23.0 J/g  $\pm$  0.9 J/g and 601.2 K  $\pm$  0.4 K (lead). The largest deviation for the measured values of the indium and lead melts from the literature values is less than 12% for the enthalpy and within 1 K for the onset temperature. The measurements of the check weights on the TGA were all within 0.5% of the actual mass of the check weights.

## D.5 RESULTS

The energetics and mass losses associated with virgin organic ion exchange resins (Purolite NRW-100 and NRW-400 and Duolite C3) and Grafoil observed in the K Basin sludges are presented in Tables D.4 and D.5, respectively. All of the resins exhibit significant mass losses between ambient and 420 K. These mass losses and the endotherm associated with these mass losses are due to the evaporation of water from the solids. The Purolite ion exchange resins have much larger mass losses and enthalpies than are observed for the Duolite resin. The cover gas composition does not change the mass loss or enthalpy associated with this transition. Above 420 K both endothermic and exothermic transitions are observed with associated mass losses. In an air cover gas the exothermic behavior is dominant, and mass gains are observed above 920 K. This mass gain is observed at lower temperatures (800 K) for the Duolite resin. No mass gains were observed under a nitrogen cover gas. The enthalpy of the exothermic reactions was very large in air sometimes exceeding -10,000 J/g and always greater than -4000 J/g.

Both the energetics and mass loss as a function of temperature for the untreated H-08 samples are reported in Tables D.6 and D.7, respectively. It was hypothesized that the H-08 light samples are Purolite NRW-400 resin and the H-08 dark samples are Purolite NRW-100 resin. Under a nitrogen cover gas the H-08 dark samples and the Purolite NRW-100 have endothermic and exothermic transitions which are unresolved. These transitions occur between 550 K and 800 K. In the H-08 light samples the exothermic behavior observed under a nitrogen cover gas between 600 K and 900 K is much more energetic (larger enthalpy) than was observed in either of the virgin Purolite ion exchange resins. In air the energetics of all of the untreated H-08 samples (both light and dark) are dominated by the exothermic behavior. The enthalpy of this exothermic behavior is approximately -7000 J/g. Significant increases in the mass of the sample were observed above 925 K in an air environment. Some mass gain was observed in H-08 light samples above 875 K in a nitrogen environment, but this mass increase was much smaller than was observed in air. The mass losses and enthalpies associated with the evaporation of water are

smaller in these samples than was observed for the virgin Purolite resins; therefore, the water evaporation endotherm in these samples is small compared to the transitions observed at higher temperatures. This decrease in mass loss and enthalpy may be due to more complete drying of these samples prior to analysis than was done for the virgin resins.

The treated H-08 samples exhibited similar behavior to the untreated samples. The DSC and TGA results for two of the treated samples (H-08 3 and H-08 6) in both air and nitrogen atmospheres are reported in Tables D.8 and D.9, respectively. Large exothermic transitions were observed above 720 K in both nitrogen and air cover gases. No mass gains were observed under nitrogen cover gas, whereas large mass gains were observed above 825 K in an air atmosphere. The enthalpy of the exothermic behavior of these samples under an air atmosphere ( $>25,000$  J/g between 675 K and 875 K) was also much larger than was observed for other samples, but no new transitions were observed.

The Grafoil exhibited limited energetics below 800 K in either air or nitrogen environments. Above 800 K a small mass loss was observed in nitrogen while in air the sample was consumed. Both of these mass losses are associated with exothermic behavior.

To determine whether large mass gains observed above 825 K and the energetic exothermic behavior in the treated organic ion exchange resin beads are due to the oxidation of the copper pans from the volatilization of nitrogen oxide gases in an air environment, thermal analyses of cerium nitrate under air cover gas were performed in both copper and platinum pans. Thermal analysis of one of the treated organic ion exchange samples (H-08 6) was also repeated in platinum and copper pans to verify the results obtained previously and the effect of copper pans on these results. The energetics and mass loss associated with the cerium nitrate salt and the treated organic ion exchange samples analyzed in these later experiments are presented in Tables D.10 and D.11, respectively.

The mass loss and energetics observed for the cerium nitrate in both platinum and copper pans indicate that the cerium nitrate loses its six waters and is converted to ceric oxide ( $\text{CeO}_2$ ). In the copper pans, a small mass gain (approximately 1% of the original mass or 0.15 mg) is observed above 680 K in the TGA analysis of the cerium nitrate. There is some difference in the temperature at which mass changes were observed above 680 K in the copper pan with a copper mesh lid compared to the copper pan with no lid, but mass gains were observed in both analyses. No significant mass gains were observed in the TGA analysis of the cerium nitrate in platinum pans.

The mass loss and energetics observed for the treated organic ion exchange sample in the copper pan is similar to the results reported previously. A large mass increase was observed above 800 K. This mass gain was not complete by the end of the analyses. The maximum temperature of this analysis was limited by the operating range of the copper pans; therefore, this transition could not be analyzed to completion. The mass increase observed in the platinum pans over this temperature range (1.6%) was much smaller than was observed in copper (60.7%). Thermal analyses in both copper and platinum exhibited the large exothermic behavior ( $>26,000$  J/g) between 650 K and 850 K.

The enthalpy above 650 K of the alkaline-washed and acid-washed (dilute acid) H-08 samples processed through the nominal flowsheet were significantly less exothermic than was observed in the treated samples. The onset temperature of the large exothermic transition shifted to higher temperatures in the alkaline-washed samples but did not shift on the acid-washed samples. This shift resulted in the majority of the energy associated with the alkaline-washed sample not being observed by DSC with its limited temperature range, but the full transition was observed in the DTA/TGA. The DSC and DTA/TGA results in both air and nitrogen atmospheres of the H-08 sample processed under the nominal flowsheet conditions with and without (acid-washed only) the alkaline wash are reported in Tables D.12 and D.13, respectively.

## D.6 CONCLUSIONS

The thermal behavior of the H-08 treated and untreated samples are indicative of organic ion exchange resins, but their behavior above 420 K does not match well with that observed in the virgin Purolite resins. The mass losses and enthalpies associated with the evaporation of water in the H-08 are much smaller than was observed for the virgin Purolite resins. This may be due to additional drying in the H-08 samples prior to analysis. Large exothermic behavior was observed in all H-08 samples above 675 K. The enthalpies of these exothermic transitions were much larger in the treated samples (more exothermic than  $-25,000$  J/g or  $-28,000$  J/g on a dry weight basis) than was observed in the untreated samples (approximately  $-7000$  J/g or approximately  $-8300$  J/g on a dry weight basis).

This large exothermic behavior was observed in both air and nitrogen atmospheres for the treated sample. This exothermic behavior is due to the oxidation of the organic ion exchange resin. In air the  $O_2$  in the air provides the primary oxidant. The enthalpies associated with this oxidation are similar to the literature values for the oxidation (enthalpy of combustion) of ethyl benzene ( $-43,100$  J/g) (Himmelblau 1982). The enthalpy of combustion of ethyl benzene is expected to be similar to that of the polystyrene which makes up approximately 92% of the weight of the organic ion exchange resin. In nitrogen the oxidant for this exothermic reaction is the nitrate associated with the treated resin beads and the nitrate in the sample from the evaporation of the nitric acid solutions in which the beads were treated. This should provide excess nitrate for the oxidation of the organic ion exchange resin to proceed to completion. Thorough washing of the organic ion exchange resin, decreases the enthalpy of the exothermic reaction in nitrogen to approximately  $-7000$  J/g but does not completely eliminate this transition. Some nitrate still remains in the organic ion exchange resin. Similar reactions have been observed with organic anion exchange resins in nitric acid (Hyder et al., 1997; Bartenev et al., 1998).

An alkaline wash of the resin does not significantly reduce the enthalpy of the large exothermic behavior in nitrogen compared to the acid-washed sample but does shift the onset from approximately 775 K to approximately 1000 K. The alkaline wash also replaces the nitrate anion coordinated with the functional group of the resin with hydroxide resulting in a lower mass loss associated with the decomposition of the organic ion exchange resin.

The exothermic behavior observed in the treated organic ion exchange samples between 650 K and 850 K in an air atmosphere is not an anomaly of the copper pans, nitrogen oxide gases and air environment. This behavior is observed in treated organic ion exchange samples analyzed in both copper and platinum pans, but no similar behavior is observed with cerium nitrate in either copper or platinum pans in an air atmosphere. The large mass gain observed above 800 K does appear to be an anomaly associated with these treated samples in copper pans under an air atmosphere. Similar behavior was not observed in platinum pans or in the analyses of the cerium nitrate salt in platinum or copper pans. Nitrogen oxide gases appear to be formed at lower temperatures in the cerium nitrate salt than is observed in the treated organic ion exchange samples. The release of this gas at lower temperature may decrease its corrosivity from that observed in the organic ion exchange samples. Visual observations of the copper pan prior to and after completion of the analysis indicates that the copper pan was oxidized. It is recommended that all thermal analyses at temperatures greater than 800 K in an air atmosphere be performed in platinum pans.

During the processing of the organic ion exchange resin, the resin should remain wet. A potential for energetic reactions is present, if the temperature of the beads approaches or exceeds 440 K. Similar reactions were observed in Russia and are reported in the literature (Hyder et al., 1997 and Bartenev et al., 1998). This potential for energetic reactions is based on the mass of the organic ion exchange resin, the thermal conductivity of the organic ion exchange resin, and the temperature of the organic ion exchange resin. The thermal conductivity of the resin decreases significantly upon drying increasing the ability for the resin to reach elevated temperature. Water also provides a mechanism for the energy associated with these slurries to be removed as the water evaporates.

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Table D.1. Sample Material Preparation.

Sample	Material Preparation	Results Location
Purolite NRW-100	As-received from vendor	Tables 4 & 5
Purolite NRW-400	As-received from vendor	Tables 4 & 5
Duolite C3	As-received from vendor	Tables 4 & 5
Grafoil	As-received from vendor	Tables 4 & 5
H-08 Dark	Dark fraction of resin beads separated by hand from wet-sieved KES-H-08	Table 6 & 7
H-08 Light	Light fraction of resin beads separated by hand from wet-sieved KES-H-08	Table 6 & 7
H-08 3	Wet-sieved KES-H-08, digested in 10 M HNO <sub>3</sub> for 2 hr at 293 K and 6 hr at 333 K, vacuum filtered and rinsed with 10 M HNO <sub>3</sub> followed by distilled water.	Tables 8 & 9
H-08 6	Wet-sieved KES-H-08 plus 96-06 M/L, digested in 10 M HNO <sub>3</sub> for 2 hr at 293 K, vacuum filtered and rinsed with 10 M HNO <sub>3</sub> followed by distilled water.	Tables 8, 9, 10, & 11
Cerium Nitrate	As-received from vendor	Tables 10 & 11
Water-Washed DVT3	Wet-sieved KES-H-08 processed through the nominal flowsheet (6 M HNO <sub>3</sub> , 368 K, 10 hr) followed by 0.32 M HNO <sub>3</sub> washes, vacuum filtration, and a deionized water rinse.	Tables 12 & 13
Alkaline-Washed DVT3	Wet-sieved KES-H-08 processed through the nominal flowsheet (6 M HNO <sub>3</sub> , 368 K, 10 hr) followed by 0.32 M HNO <sub>3</sub> washes, vacuum filtration, a deionized water rinse, alkaline wash (1 M NaOH, 293 K, 1 hr), decant, and deionized water rinses.	Tables 12 & 13

Table D.2. Parameters for Thermal Analyses of Copper Pan Effect.

Run	Analysis	Sample	Pan	Lid	Temperature Range (K)
1	TGA/DTA	Cerium Nitrate	Platinum	None	Ambient - 1223 K
2	TGA/DTA	Cerium Nitrate	Platinum	None	Ambient - 1223 K
3	TGA/DTA	Cerium Nitrate	Copper	Cu	Ambient - 1073 K
4	TGA/DTA	Cerium Nitrate	Copper	None	Ambient - 1073 K
5	TGA/DTA	H-08 6	Platinum	Pt	Ambient - 1173 K
6	DSC	Cerium Nitrate	Platinum	None	Ambient - 993 K
7	DSC	Cerium Nitrate	Platinum	None	Ambient - 993 K
8	DSC	Cerium Nitrate	Copper	Cu	Ambient - 993 K
9	DSC	Cerium Nitrate	Copper	None	Ambient - 993 K
10	DSC	H-08 6	Platinum	Pt	Ambient - 993 K
11	TGA/DTA	H-08 6	Copper	Cu	Ambient - 1073 K
12	DSC	H-08 6	Copper	Cu	Ambient - 993 K

Table D.3. Calibration Data.

Date	Standard	Onset Temperature (K)		Enthalpy (J/g)
		DSC	TGA/DTA	
10/9/97	Indium	429.6	429.9	28.9
12/9/97	Indium	429.0	430.0	28.8
1/2/98	Indium	429.9	-----	27.8
1/20/98	Indium	-----	430.1	-----
1/26/98	Indium	429.9	429.2	27.6
2/5/98	Indium	430.0	430.1	28.7
2/9/98	Indium	-----	429.7	-----
9/21/98	Indium	429.8	429.8	28.3
	Lead	600.7	-----	23.7
11/17/98	Indium	430.0	430.1	26.7
	Lead	601.3	600.2	23.3
11/20/98	Indium	430.1	430.1	25.2
	Lead	601.5	600.6	21.9
12/09/98	Indium	430.1	430.9	26.0
	Lead	601.6	600.7	22.2
12/17/98	Indium	430.2	430.2	26.5
12/11/98	Lead	601.7	600.8	23.7
Literature Values	Indium	429.75		28.59
	Lead	600.65		23.22

Date	Measured Mass (mg)		
11/17/98	2.076	5.014	20.028
11/20/98	2.055	4.998	20.034
12/09/98	2.052	4.987	20.022
12/11/98	2.069	4.996	20.061
<b>Actual Mass</b>	<b>2.065</b>	<b>5.006</b>	<b>20.034</b>

Table D.4. Differential Scanning Calorimetry Results for Virgin Organic Ion Exchange Resins and Grafoil.

Sample	Cover Gas	Run	Temperature Range (K)		Onset	
			Start	End	Temperature (K)	Enthalpy (J/g)
Purolite-NRW 100	N2	1	299	400		934.7
			509	601	528.8	75.5
			611	701	631.5	-35.8
Purolite NRW 100	N2	2	298	490		934
			490	588	554.2	54
			588	754		-71
Purolite-NRW 400	N2	1	299	391		973.1
			391	465		-120
			628	675	628	-14.7
			675	709		10.3
Purolite NRW 400	N2	2	828	857	835.6	8.5
			304	379		640
			384	458		-104
			656	730		29
Duolite C3	N2	1	753	832		16
			305	438		92.2
			438	517	450.5	35.6
Duolite C3	N2	2	517	984		-1270.1
			302	425		109.6
			433	520	441.1	39.2
Grafoil	N2	1	520	949		<-506
			300	969		>790
Grafoil	N2	2	454	522		5
			302	970		>530
Purolite NRW 100	Air	1	479	516		1
			299	423		815
			513	593	528.2	35
Purolite NRW 100	Air	2	593	696		-47
			305	422		790
			523	585	526.2	38.8
			585	977		-4181
			691	707	698.2	
Purolite NRW 400	Air	1	713	930	780.2	
			930	958	933.2	
			297	426		878
			586	685	608.2	-31
Purolite NRW 400	Air	2	691			
			302	416		983
			445	883	535.2	-4132
Duolite C-3	Air	1	665	735	688.2	
			735	883		
			305	434		117.3
Duolite C-3	Air	2	483	760	656.2	-3241
			435	528	439.2	33.4
			296	415		248
Grafoil	Air	1	476	828	643.2	-9036
			458	518	451.2	15.5
Grafoil	Air	2	554	853	611.2	-254
			862			
			459	511	449.2	2.3
Grafoil	Air	2	623	813	644.2	-89.4
			839		944.2	

Table D.5. Thermo-Gravimetric Analysis and Differential Thermal Analysis Results for Virgin Organic Ion Exchange Resins and Grafoil.

Sample	Gas	Run	Temperature (K)		Onset	% of Original Mass				
			Start	End		Onset	Loss			
Purolite NRW-100	N2	1	298	460.7	535.2	49.1	48.8			
			460.7	615.7			18.5			
			615.7	726.4			5.4			
Purolite NRW-100	N2	2	726.4	1041.7	533	49.4	3.7			
			301	458.3			48.9			
			458.3	615			17.6			
Purolite NRW-400	N2	1	615	729.1	656.4	19.8	5.7			
			729.1	1073			3.4			
			298	553			67.6			
Purolite NRW-400	N2	2	553	761	654.2	20.6	22.1			
			761	1081			2.4			
			298	430			61.9			
Duolite C-3	N2	1	430	551	654.2	20.6	5.8			
			551	766			23.4			
			766	1069			2.6			
Duolite C-3	N2	2	302	416	654.2	20.6	11.8			
			416	592			21.4			
			592	761			9.8			
Duolite C-3	N2	2	761	1073	654.2	20.6	9.2			
			299	416			13.3			
			416	594			22			
Grafoil	N2	1	594	755	654.2	20.6	9.3			
			755	973			8.6			
			973	1073			0.8			
Purolite NRW-100	N2	2	428	701	654.2	20.6	0.1			
			701	952			-0.1			
			952	1084			0.2			
Purolite NRW-100	Air	3	No Significant Mass Change (0.2%)					1.6		
			737	1086	814	100	47.7			
			296	473	538.4		23			
Purolite NRW-100	Air	2	473	773	538.4	538.5	47.4			
			300	465			20.3			
			465	723			25.5			
Purolite NRW-400	Air	1	723	919	538.5	538.5	25.5			
			919	1073			-3.3			
			296	430			60.5			
Purolite NRW-400 (aluminum pan)	Air	2	430	611	538.5	538.5	8			
			689	Sample ejected from the pan at the start of this transition						
			304	416			57.5			
Purolite NRW-400	Air	2	416	547	538.5	538.5	7			
			547	722			14.2			
			722	851			29.5			
Duolite C-3	Air	1	851	1070	538.5	538.5	1.1			
			300	379			10.2			
			379	622			475.2	84.1	24.4	
Duolite C-3	Air	2	610	775	475.2	475.2	60.4			
			300	386			10.6			
			386	613			475.2	83.9	22.8	
Duolite C-3	Air	2	633	804	475.2	475.2	60.9			
			804	1073			698.2	60.5	60.9	
			804	1073			824.2	3.9	-23.2	
Grafoil	Air	1	855	1011	824.2	824.2	92.8			
			656	900			695.3	100.3	-9.5	
			900				1012.8	109.8	109	

Table D.6. Differential Scanning Calorimetry Results for Untreated Organic Ion Exchange Resin from K East Basin (H-08).

Sample	Cover Gas	Run	Temperature(K)		Onset	Enthalpy (J/g)
			Start	End		
H-08 Dark	N2	1	305	407	----	70.6
			467	522	491.8	12
			554	633	576.4	-24
			633	678	----	*
			678	812	----	**
H-08 Dark	N2	2	305	450	----	96.5
			450	533	487.8	10.9
			582	801	605.2	**
			801	891	----	-18
H-08 Dark	Air	1	569	975	623.5	-7947.9
H-08 Dark	Air	2	613	970	643.8	-7158.7
H-08 Light	N2	1	397	522	430.3	109.4
			522	603	554.4	138.2
			647	737	661.1	-208.5
			737	971	742.4	****
H-08 Light	N2	2	407	520	430.9	61.4
			525	608	554.4	183.3
			613	703	619.8	187.8
			703	819	----	-195.6
			819	971	850.7	****
H-08 Light	Air	1	325	463	320.2	-95.4
			463	887	----	-6519
			556	663	574.1	***
			663	719	671.9	***
			719	887	740.9	***
H-08 Light	Air	2	461	886	477.3	-7286
			570	662	----	***
			662	709	----	***
			709	886	728.3	***

\* This exothermic transition was too energetic for the DSC to measure the enthalpy.

\*\* This temperature range contains a combination of exothermic and endothermic transitions that cannot be resolved.

\*\*\* The enthalpies for these transitions could not be resolved; therefore, the sum of the enthalpies for these transitions are reported over the entire temperature range of these transitions.

\*\*\*\* These large exothermic transitions were not complete at the upper temperature range of the DSC; therefore, an enthalpy is not reported. The exotherms are larger than 2000 J/g for run 1 and 350 J/g for run 2.

---- The onset temperature could not be determined for these transitions.

Table D.7. Thermo-Gravimetric Analysis and Differential Thermal Analysis Results for Untreated Organic Ion Exchange Resin From K East Basin (H-08).

Sample	Gas	Run	Temperature (K)		Onset	Ratio of Original Mass (%)	
			Start	End		Onset	Loss
H-08 Dark	N2	1	303	641			15.4
			641	936	649.4	84.6	25.4
			936	1027	944.9	59.2	5.8
H-08 Dark	N2	2	305	618			14.2
			618	893	651.8	85.7	25.1
			893	1086	938.7	59.2	10
H-08 Dark	Air	1	298	598			15.2
			598	923	651.1	83.9	34.4
			923	1084			-28.1
H-08 Dark	Air	2	300	576			14.7
			642	739	651.4	85.3	7.8
			739	760			-0.6
			760	900	773.4	78	21.7
			900	1020	903.5	52.7	-15.4
			1020	1059			1
H-08 Light	N2	1	1059	1084			-3.6
			303	559			13.3
			559	623	564.2	86.6	2.3
H-08 Light	N2	2	623	960	652.1	83.9	8.3
			303	440			8.9
			440	529	456.9	90.6	5.9
			529	613	556.6	84.6	18.3
H-08 Light	N2	3	613	879	662.3	62.8	45.7
			879	1087			1.8
			324	524			10.1
			524	608	552	85.4	5.6
			608	738	657.3	66.8	16.2
H-08 Light	Air	1	738	862			2.5
			862	1086	941.2	61.9	-7.3
			298	435			10.1
			435	520	455.2	89.3	5.8
			520	708	559.9	82.9	33.1
			708	723	705.3	50.9	-1.1
			723	811	755	53.4	16.2
			811	923	817.8	36.2	-28.8
H-08 Light	Air	2	923	1059	959.3	68.3	-24.8
			1059	1084	1062.5	91	-15.2
			309	445			10.8
			445	519	456.8	88.7	4.7
			519	592	561.7	83.2	11.6
			592	719			14.4
			719	832	766.5	57.7	20.7
			832	950	865.6	38.1	-5.1
			950	1041	976.8	42.7	5.3

Table D.8. Differential Scanning Calorimetry Results for Treated Organic Ion Exchange Resin from K East Basin (H-08).

Sample	Cover Gas	Temperature (K)		Onset	Enthalpy (J/g)
		Range			
H-08 3	Nitrogen	295	- 436	----	308
		634	- 950	669	-43778
H-08 3	Air	295	- 453	----	169
		581	- 769	680.1	-22438
		769	- 852	773.6	
		863	- 973	867.8	**
H-08 6	Nitrogen	296	- 425	----	304
		479	- 574	----	-75
		574	- 637	----	-18
		637	- 721	----	-16
		721	- 973	----	**
H-08 6	Air	295	- 418	----	113
		576	- 721	598.5	-37750
		721	- 835	738.3	
		835	- 977	----	**

\*\* These large exothermic transitions were not complete at the upper temperature range of the DSC; therefore, an enthalpy cannot be reported.

---- The onset temperature could not be determined for these transitions.

Table D.9. Thermogravimetric Analysis and Differential Thermal Analysis Results For Treated Organic Ion Exchange Resin From K East Basin (H-08)

Sample	Cover Gas	Temperature (K)		Ratio of Original Mass (%)	
		Range	Onset	Onset	Loss
H-08 3	Nitrogen	298 - 471	----	----	17.0
		471 - 632	535.2	81.1	13.7
		632 - 815	677.2	59.0	20.1
		815 - 1081	----	----	4.6
H-08 3 dup.	Nitrogen	298 - 455	----	----	18.5
		455 - 763	537.1	77.3	48.6
		763 - 1081	----	----	6.8
H-08 3	Air	297 - 473	----	----	21.5
		497 - 648	538.2	77.0	23.3
		648 - 825	707.8	50.7	27.1
		825 - 1077	853.7	27.9	-132.3
H-08 6	Nitrogen	298 - 504	----	----	16.7
		504 - 786	553.8	81.5	25.5
		786 - 1086	----	----	5.1
H-08 6	Air	298 - 488	----	----	15.7
		488 - 698	546.1	83	16.7
		698 - 796	764.9	66.3	18
		796 - 1079	818.2	48.2	-136.9

---- The onset could not be determined for these transitions.

Table D.10. Differential Scanning Calorimetry Results For Copper Pan Effect

Run	Sample	Pan	Temperature (K)		Enthalpy (J/g)
			Range	Onset	
6	Cerium Nitrate	Pt	296 - 499		898
			499 - 581		235
7	Cerium Nitrate	Pt	296 - 436		938
			442 - 495		67
			495 - 589		248
8	Cerium Nitrate	Cu with Lid	295 - 433		1074
			433 - 497		71
			497 - 597		280
			688 - 720	685.6	-34
			799 - 879	792.0	-72
			879 - 973		-114
9	Cerium Nitrate	Cu	303 - 423		712
			440 - 494		58
			494 - 596		241
			700 - 730		-12
10	H-08 6	Pt with Lid	729 - 838	775.2	-27267
11	H-08 6	Cu with Lid	654 - 840	679.0	-26212

Table D.11. Thermo-Gravimetric Analysis and Differential Thermal Analysis Results for Copper Pan Effect.

Run	Sample	Pan	Temperature (K)		Ratio of Original Mass (%)	
			Range	Onset	Onset	Loss
1	Cerium Nitrate	Pt	298 - 338			2.5
			338 - 428	354.9	96.0	14.2
			428 - 728	449.6	82.4	43.1
2	Cerium Nitrate	Pt	300 - 339			2.6
			339 - 430	355.4	95.9	14.4
			430 - 493	452.1	82.0	7.2
			493 - 909			35.9
3	Cerium Nitrate	Cu with Lid	299 - 338			2.7
			338 - 424	353.5	95.8	14.5
			424 - 492	448.7	81.7	7.0
			492 - 684	504.4	74	34.4
			684 - 862			-1.1
			862 - 1083			0.9
4	Cerium Nitrate	Cu	300 - 338			2.8
			338 - 435	355.3	95.6	15.1
			435 - 496	452.2	81.1	6.4
			496 - 734	503.5	73.9	35.3
			734 - 927			1.0
			927 - 1083			-1.4
						11.6
5	H-08 6	Pt with Lid	299 - 459			11.6
			459 - 696	547.8	85.6	24.6
			696 - 855	770.3	56.4	37.6
			855 - 1187			-1.6
11	H-08 6	Cu with Lid	299 - 442			12.1
			442 - 657	543.3	84.9	17.6
			657 - 721	677.2	68.8	4.3
			721 - 834	761.4	65.6	20.6
			834 - 1004			-48.3
			1004 - 1026			1.4
			1026 - 1083			-12.4

Table D.12. Differential Scanning Calorimetry Results For Washed Organic Ion Exchange Resin From K East Basin (H-08)

Sample	Cover Gas	Temperature (K)		Enthalpy (J/g)
		Range	Onset	
Water-Washed DVT3	Nitrogen	296 - 386	----	381
		386 - 673	705.6	-1415
		673 - 973	----	-7401
	Air	573 - 654	594.7	
		654 - 759	716.6	-30112
		759 - 883	776.7	
Alkaline- Washed DVT3	Nitrogen	295 - 388	----	697
		388 - 671	----	-1450
		671 - 805	----	-450
	805 - 966	----	**	
	Air	294 - 453	----	997
		454 - 601	465.0	-548
628 - 859		674.4	-9246	

\*\* This large exothermic transition was not complete at the upper temperature range of the DSC; therefore, an enthalpy cannot be reported.

---- The onset temperature could not be determined for these transitions.

Table D.13. Thermogravimetric Analysis and Differential Thermal Analysis Results For Washed Organic Ion Exchange Resin From K East Basin (H-08)

Sample	Cover Gas	Temperature (K)		Ratio of Original Mass (%)	
		Range	Onset	Onset	Loss
Water-Washed DVT3	Nitrogen	300 - 403	----	----	9.0
		403 - 501	468.0	88.3	6.3
		501 - 638	539.8	82.5	21.0
		638 - 996	670.3	61.0	21.0
		996 - 1238	----	----	2.1
	Air	300 - 410	----	----	9.0
		410 - 510	443.6	89.8	4.5
		510 - 689	543.1	84.9	20.6
		689 - 768	748.7	61.1	25.4
		768 - 891	802.1	38.9	10.7
		891 - 1238	----	----	-0.5
	Alkaline- Washed DVT3	Nitrogen	298 - 403	----	----
403 - 517			464.1	88.7	8.4
517 - 622			534.1	82.1	3.8
622 - 861			680.0	77.5	22.0
861 - 1238			----	----	4.1
Air		298 - 418	----	----	10.0
		418 - 656	449.4	89.0	6.7
		656 - 848	698.0	82.7	18.6
		848 - 1074	1004.5	64.8	22.3
		1074 - 1237	----	----	-0.3

---- The onset temperature could not be determined for these transitions.

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