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ORNL/ER-395

**ENVIRONMENTAL
RESTORATION
PROGRAM**

**Summary Review of the Chemical
Characterization of Liquid
and Sludge Contained in the Old
Hydrofracture Tanks,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee**



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Energy Systems Environmental Restoration Program

**Summary Review of the Chemical
Characterization of Liquid
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Hydrofracture Tanks,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee**

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Date Issued—February 1997

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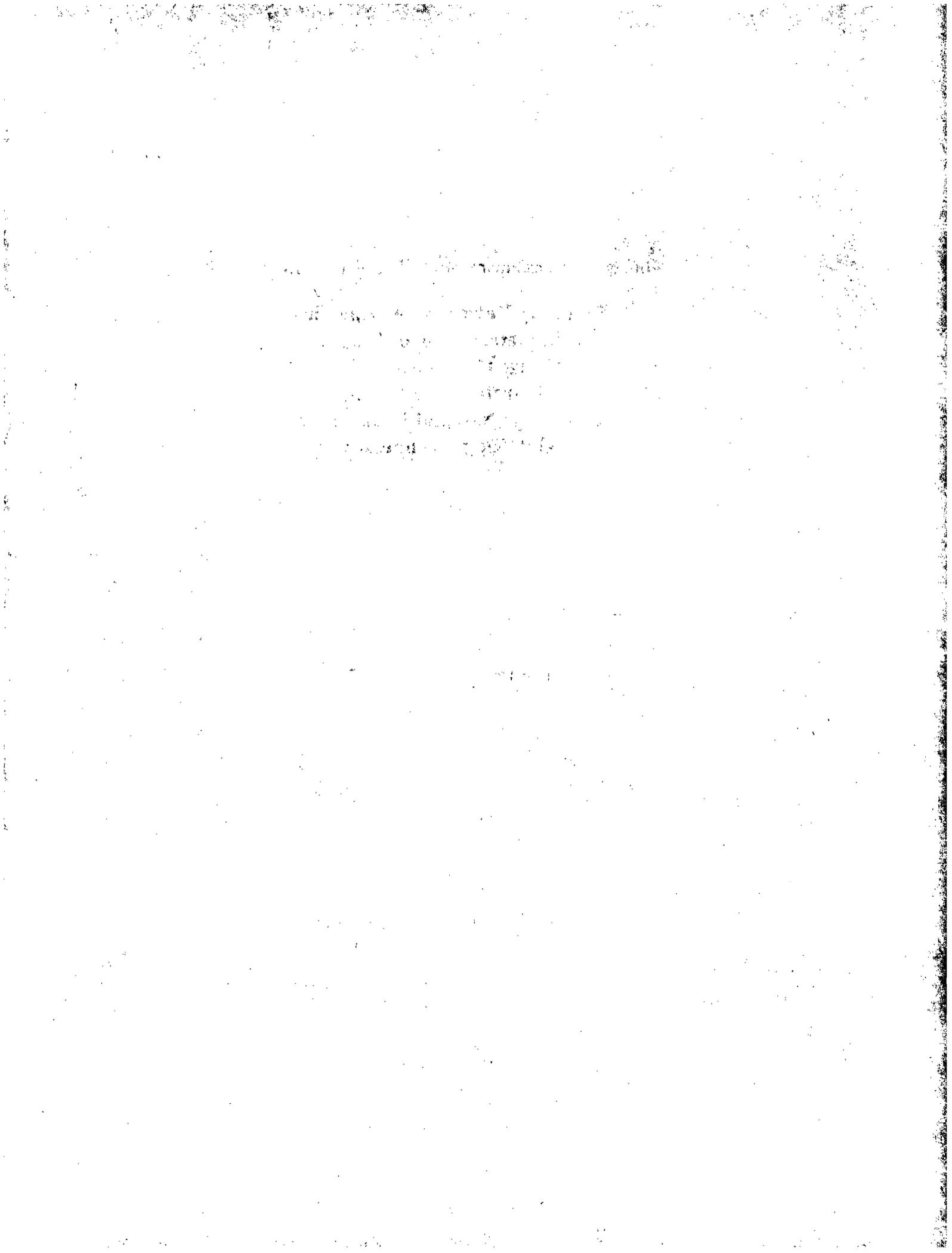
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PREFACE

This report summarizes analytical data developed from sludge and liquid samples collected from the Old Hydrofracture Facility tanks during December 1995 and January 1996. The sampling and analysis work was performed in accordance with *Addendum 2: Supplemental Sampling and Analysis Plan for the Old Hydrofracture Facility Tanks* (Energy Systems 1995). This document is not a Federal Facility Agreement milestone. This report was prepared under Work Breakdown Structure 6.1.05.20.01.15.10 (Activity Data Sheet 3305, "Inactive Tanks").

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ABBREVIATIONS

CFR	<i>Code of Federal Regulations</i>
Energy Systems	Lockheed Martin Energy Systems, Inc.
FEM	fissile equivalent mass
ICP	inductively coupled plasma
LLLW	liquid low-level waste
MS	mass spectrometry
OHF	Old Hydrofracture Facility
ORNL	Oak Ridge National Laboratory
PCB	polychlorinated biphenyl
RCRA	Resource Conservation and Recovery Act
SVOC	semivolatile organic compound
TBP	tributyl phosphate
TCLP	Toxicity Characteristic Leaching Procedure
TIC	tentatively identified compound
TRU	transuranic
VOC	volatile organic compound

EXECUTIVE SUMMARY

This report presents analytical data developed from samples collected from the five inactive tanks located at the Old Hydrofracture Facility (OHF) at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. The samples were collected during December 1995 and January 1996. The purpose of the sampling and analysis project was (1) to determine whether the tank contents meet ORNL waste acceptance criteria, as specified in the *Oak Ridge National Laboratory, Liquid Waste Treatment Systems, Waste Evaluation Criteria*, WM-WMCO-201 (Parrott et al. 1991); (2) to determine various physical properties of the tank contents that would affect the design of a sludge mobilization system; and (3) to gather information to support a baseline risk assessment (Energy Systems 1995). The report focuses on the analytical results used to evaluate the tank contents with regard to nuclear criticality safety requirements and to regulatory waste characterization.

The major issue relating to the chemical characterization is the concern for nuclear criticality based on the ratios of ^{238}U and ^{232}Th to fissile isotopes in the liquid and sludge fractions of the waste. Present waste acceptance criteria require that solutions containing ^{233}U , ^{235}U , ^{239}Pu , or ^{241}Pu must be mixed with either depleted uranium or natural thorium (according to chemical similarity) so that the resultant solution will contain at least 100 parts by weight of ^{238}U or ^{232}Th per part by weight of the fissile isotope(s). Uranium denature ratios expressed as $^{238}\text{U}/^{235}\text{U}$ -fissile equivalent mass (FEM) ratios should be in excess of 100; if they are less than 100 then there is concern relative to nuclear criticality. Average $^{238}\text{U}/^{235}\text{U}$ -FEM ratios for the sludge and liquid in the OHF tanks are 64 and 100, respectively. The low ratios are primarily due to the high concentrations of ^{233}U . These data indicate that it is important to add additional ^{238}U to these tanks so that the uranium denature ratios meet waste acceptance criteria. Simple addition of needed ^{238}U and elevation of the pH in the waste tanks in excess of 11.5 will ensure precipitation of the ^{238}U into the sludge phase, thus raising the uranium denature ratios to acceptable levels.

The chemical characterization data also indicate that wastes contained in the OHF tanks may also be in excess of two other waste acceptance criteria. Both may be due to the separation of the waste stream into liquid and sludge fractions. Waste acceptance criteria require liquid radioactive wastes added to the LLW system must not have a total radionuclide activity concentration exceeding 2×10^{10} Bq/L (2 Ci/gal) ^{90}Sr equivalent. The radiological analyses indicate that the liquid fraction of the OHF tanks contain activity levels $< 2 \times 10^{10}$ Bq/L; however, the sludge component may contain activities in excess of the 2×10^{10} Bq/L criterion. For example, if one assumes bulk densities of 1.1 to 1.3 g/mL, sludges in the OHF tanks appear to contain on the order of 10^{10} Bq/L of $^{90}\text{Sr}/^{90}\text{Y}$. Sludges also appear to contain excessive levels of transuranic (TRU) isotopes. The primary TRU isotopes in the OHF tanks include, ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Am . Concentrations of these isotopes in the liquid fraction of the OHF tanks are all well below the 3.7×10^6 Bq/kg criterion; however, sludges in all OHF tanks contain TRU activities significantly greater than the TRU criteria. Removal of free water from these wastes would be required for disposal practices; thus, on a dry weight basis, TRU activities would be on the order of 2.5 times the activities on a wet weight basis since most of the sludges contain at least 60% water. These characterization data strongly indicate that sludge in the OHF would be TRU wastes if processed accordingly.

Analyses of the liquid and sludge fractions for Resource Conservation and Recovery Act (RCRA) metals revealed that the OHF tanks contain RCRA wastes. For example, mercury levels in the liquid fraction of all five tanks exceed the RCRA limit (0.2 mg/L). Tank 3 contains an extremely

high mercury concentration (12.8 mg/L), greater than 60 times the RCRA limit. Liquid waste in two of the tanks (tanks 3 and 4) contain concentrations of chromium (16.6 and 8.4 mg/L, respectively) in excess of the RCRA limit (5 mg/L). Based on total concentrations of RCRA metals in the sludge fraction, it appears that the sludge in the OHF tanks will also be in excess of regulatory limits. However, this can only be determined by characterization of the final waste form using the Toxicity Characteristic Leaching Procedure (TCLP). Since the TCLP removes only the extractable fraction of RCRA metals from the waste form, it is impossible to determine their regulatory status until the final waste form is characterized using this test. Analyses of TCLP/RCRA organic compounds in the liquid and sludge fractions contained in the OHF tanks showed concentrations below regulatory levels, indicating the wastes are not a concern with respect to their concentrations of TCLP/RCRA organic compounds.

The above assessment of the chemical characteristics of the liquid and sludge contained in the OHF tanks is based on the samples collected. The representativeness of these samples has not been verified. The ORNL/ER-13 report (Autrey et al. 1990) showed that the analyses of liquid samples taken from varying depths in the OHF tanks were not appreciably different, indicating that liquid samples are likely representative samples of the liquid phase. However, the sludge samples were taken from only one location within the individual tank and are probably not representative; thus, it would be prudent to collect additional sludge samples to verify the range in chemical/radionuclide compositions. Possibly more important is to investigate differences in physical properties of sludge within the tanks. These data will be needed before suitable engineering efforts can be developed for treatment and disposal of these wastes.

1. INTRODUCTION

This report is intended to review and summarize the results of the chemical characterization data recently obtained on the liquid and sludge components contained in the Old Hydrofracture Facility (OHF) tanks. The project objectives of the characterization effort were outlined in the sampling and analysis plan, *Addendum 2: Old Hydrofracture Facility Tanks Sampling and Analysis Plan* prepared by CDM Federal Programs Corporation and published as ORNL RAP/LTR-88/24 (Energy Systems 1995). As a format for this report, the decision criteria are addressed as outlined in Table 3.1 of the sampling and analysis plan. The intent is to summarize the characterization results that directly pertain to these decision criteria. Since publication of the sampling and analyses plan (the ORNL RAP/LTR-88/24 report) there have been some suggested changes in the acceptable criticality ratios for $^{238}\text{U}/^{235}\text{U}$ and $^{238}\text{U}/^{233}\text{U}$ as well as methods in which these ratios are to be calculated. This report does not address these suggested changes. The decision criteria for the sampling and analysis plan (as presented in Table 3.1 of the ORNL RAP/LTR-88/24 report) are reproduced in Table 1.1.

As a matter of perspective, analytical data obtained from this recent characterization effort are compared to that obtained in an earlier 1988 effort. The intent is to determine if any differences are apparent, thus giving an indication of potential changes in levels and distributions of contaminants between the liquid and sludge phases. Such an effort may be effective in identifying specific ageing processes and may be helpful in adopting better waste management plans as well as the development of more effective methods for remediation of the waste tanks.

Table 1.1. Project objectives and decision determinants^a

Objectives	Analytical parameters	Decision criteria	Methods of determination
1. Determine whether nuclear criticality safety is a concern	Total U	If total U > 250 g, then further assessment is needed	Method 6010A
	Uranium isotopics: (²³³ U, ²³⁴ U, ²³⁵ U, ²³⁶ U, ²³⁸ U); and ²³⁸ U/ ²³⁵ U + ²³³ U ratio	If ²³⁸ U/ ²³⁵ U + ²³³ U < 100, then NCS concern exists	Method AC-MM-40100
	Plutonium isotopics: (²³⁹ Pu, ²⁴⁰ Pu, ²⁴¹ Pu, ²⁴² Pu); ²³² Th/ ²³⁹ Pu + ²⁴¹ Pu ratio; and Total Th	If ²³² Th/ ²³⁹ Pu + ²⁴¹ Pu < 100, then NCS concern exists	Method CASD-AM-RML-RA11 (for Pu isotopics) Method 6010A (for Total Th)
2. Determine whether ORNL LLLW acceptance criteria are met	Total radionuclide activity (Bq/L, Ci/gal)	If total radionuclide activity $\geq 2 \times 10^{10}$ Bq/L (2 Ci/gal), then further assessment is needed	Method CASD-AM-EPA-900.0 (for gross alpha/beta) Method CASD-AM-EPA-901.1 (for gamma scan)
	²³³ U, ²³⁵ U, ²³⁹ Pu, ²⁴¹ Pu	If ≤ 100 parts of matrix by weight ²³⁸ U or ≤ 100 parts of matrix by weight ²³⁹ Th, then further assessment is needed	Method CASD-AM-RML-RA11 (for Pu isotopics) Method AC-MM-40100 (for U isotopics)
	TRU isotopes (Np, Pu, Am, Cm)	If TRU isotopes or ²³³ U contribute total specific activity $\geq 3.7 \times 10^6$ Bg/Kg (100 nCi/g), then the material is considered TRU and further assessment is needed	Method CASD-AM-RML-RA04
	RCRA metals	RCRA toxicity characteristics	Methods 6010A, 7000A, and 7470
	Volatile organic compounds	If RCRA limits are exceeded, then further assessment is needed	Methods 8240/8260
	Semivolatile organic compounds	If RCRA limits are exceeded, then further assessment is needed	Method 8270
	Nonhalogenated volatile organic compounds	If RCRA limits are exceeded, then further assessment is needed	Method 8015
	Anions	N/A	Method 9056
	PCBs: Aroclor-1016, Aroclor-1221, Aroclor-1232, Aroclor-1242, Aroclor-1248, Aroclor-1254, Aroclor-1260	If levels > 2 ppm at the source of the PCB material, then further assessment is needed (50 ppm if waiver granted)	Method 8080
	Total suspended solids	N/A	Method 160.2
Total dissolved solids	N/A	Method 160.1	

Table 1.1 (continued)

Objectives	Analytical parameters	Decision criteria	Methods of determination
3. Perform a baseline risk assessment to help determine risk that would be created by loss of tank contents		If risk $\geq 1 \times 10^{-4}$, then further assessment is needed	
	^{233}U (Bq/g, Bq/L)	N/A	Method AC-MM-40100
	^{244}Cm , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am	N/A	Method CASD-AM-RML-RA04
	Gross alpha/beta	N/A	Method CASD-AM-EPA-900.0
	Gamma scan	N/A	Method CASD-AM-EPA-901.1
	Total Th	N/A	Method 7010A
	Radioactive strontium	N/A	Extraction Chromatography Method (AE-MM-2-21807)
4. Evaluate those physical properties of tank contents that would affect design of sludge mobilization system	Density	N/A	Method AC-MM-11011
	Total suspended solids	N/A	Method 160.2
	Total dissolved solids	N/A	Method 160.1
	pH	N/A	Method 9040 (liquids) and Method 9045A (solids)
	Shear stress versus shear rate	N/A	Procedure OHF-1 ^b
	Settleability	N/A	Procedure OHF-2 ^b
	Percent suspended solids versus density	N/A	Procedure OHF-3 ^b
	Moisture content	N/A	Procedure OHF-4 ^b

^aSource: ORNL RAP/LTR-88/24, Addendum 2 (Energy Systems 1995).

^bIncluded in Appendix A of ORNL RAP/LTR-88/24, Addendum 2 (Energy Systems 1995).

N/A - not applicable

2. DETERMINE WHETHER NUCLEAR CRITICALITY SAFETY IS A CONCERN

2.1 URANIUM

For purposes of evaluating compliance with the nuclear criticality safety requirements of the waste acceptance criteria, it is important to consider both total uranium and the ratios of the fissile uranium isotopes (^{233}U and ^{235}U) to ^{238}U (uranium denature ratios). Table 2.1 presents a summary of the results of uranium analysis of the tank contents. Sections 2.1.1 and 2.1.2 discuss the measurement of total uranium and calculation of uranium denature ratios, respectively.

2.1.1 Total Uranium

If Total U > 250 Grams, Then a Further Assessment Is Needed

The total concentration of uranium in any single tank is significantly greater than 250 g. For example, approximately 21.3, 21.8, 59.5, 54.7, and 6.8 kg of uranium are contained in Tanks 1, 2, 3, 4, and 9, respectively. In Tank 3, greater than 99% of the uranium is associated with the sludge, while in Tanks 1, 2, 4, and 9, the sludge contains 45, 58, 87, and 78%, respectively, of the total uranium. The concentration of uranium in the liquid phase of Tank 3 is very low (0.39 mg/L) as compared to uranium concentrations in the other four tanks (i.e., concentrations of 281, 219, 195, and 303 mg/L in Tanks 1, 2, 4, and 9, respectively. See Table 2.2). The low concentration of uranium in Tank 3 is most likely due to the high pH (pH of 11.5). As the pH of the liquid phase becomes >11, the uranium is rapidly precipitated from the system. This is especially the case in the presence of calcium and magnesium concentrations. The high pH of the liquid phase in Tank 3 (11.5) is sufficiently high compared to the other tanks (9.57, 9.64, 10.4, and 9.3 for Tanks 1, 2, 4, and 5, respectively) for precipitation of uranium from the liquid phase.

2.1.2 Uranium Denature Ratios

If Uranium Denature Ratios Calculated as $^{238}\text{U}/(^{233}\text{U} + ^{235}\text{U})$ Are < 100, Then Nuclear Criticality Safety Is a Concern

Current Oak Ridge National Laboratory (ORNL) waste acceptance criteria for liquid-low level (LLLW) waste requires that the fissile isotopes of uranium and plutonium be isotopically diluted with ^{238}U and ^{232}Th , respectively. For the fissile isotopes of uranium (^{233}U and ^{235}U), the ratio of the ^{238}U divided by the fissile equivalent mass (FEM) for uranium should be >100. This uranium denature ratio is calculated as follows:

$$\frac{(^{238}\text{U})}{(1.35)(^{233}\text{U}) + (^{235}\text{U})} \geq 100$$

Table 2.1. Uranium in OHF tanks

	Tank number				
	1	2	3	4	9
Volume of sludge (gal)	791	1,205	2,029	1,328	481
Volume of liquid (gal)	11,047	11,048	2,063	9,341	1,290
Total volume (gal)	11,838	12,253	4,092	10,669	1,771
Total tank volume (gal)	15,000	15,000	25,000	25,000	13,000
Liters of sludge	2,990	4,555	7,670	5,020	1,818
Liters of liquid	41,758	41,761	7,798	35,309	4,876
Bulk density (sludge)	1.33	1.33	1.31	1.21	1.16
Kilograms of sludge	3,977	6,058	10,047	6,074	2,109
U in sludge (mg/kg)	2,420	2,090	5,920	7,870	2,510
Total U in sludge (g)	9,624	12,661	59,479	47,802	5,294
U in liquid (mg/L)	281	219	0.39	195	303
Total U in liquid (g)	11,734	9,146	3	6,885	1,477
Total U in tank (g)	21,357	21,807	59,482	54,688	6,771
Percentage of U in sludge	45	58	99.99	87	78
Wt% U-233 in sludge	0.9107	1.0478	0.7246	0.8715	0.7148
U-233 in sludge (g)	88	133	431	417	38
Wt% U-235 in sludge	0.4247	0.3457	0.395	0.3753	0.4938
U-235 in sludge (g)	41	44	235	179	26
Wt% U-233 in liquid	0.3427	0.3427	0.2154	0.3427	0.4308
U-233 in liquid (g)	40	31	0	24	6
Wt% U-235 in liquid	0.553	0.474	0.5629	0.5234	0.5135
U-235 in liquid (g)	65	43	0	36	8
Total U-233 in tank (g)	128	164	431	440	44
Total U-235 in tank (g)	106	87	235	215	34

Table 2.2. Characteristics of liquid contained in the OHF tanks

Tank		1	2	3	4	9
<i>Physical properties and miscellaneous data</i>						
Total Suspended Solids	(mg/mL)	0.02	0.03	1.46	0.07	0.08
Total Dissolved Solids	(mg/mL)	8.44	13.5	54.2	17.2	15.9
Total Solids	(mg/mL)	8.58	13.7	56.5	17.5	16.1
Density	(g/mL)	1.010	1.022	1.052	1.023	1.021
Total Inorganic Carbon	(mg/L)	572	1060	800	392	413
Total Carbon	(mg/L)	1050	1880	2930	942	475
Total Organic Carbon	(mg/L)	478	820	2130	550	62
<i>RCRA metals</i>						
Ag	(5) ^a	(mg/L)	< 0.02	< 0.02	< 0.02	< 0.02
As	(5)	(mg/L)	0.01	0.009	0.298	< 0.008
Ba	(100)	(mg/L)	< 0.002	< 0.002	< 0.002	< 0.002
Cd	(1)	(mg/L)	< 0.04	< 0.04	< 0.04	< 0.04
Cr	(5)	(mg/L)	1.52	1.46	16.6	8.41
Hg	(0.2)	(mg/L)	0.544	0.273	12.8	1.98
Ni	(5)	(mg/L)	< 0.04	< 0.04	0.0718	< 0.04
Pb	(5)	(mg/L)	< 0.008	0.0167	< 0.008	< 0.008
Se	(1)	(mg/L)	< 0.008	< 0.008	0.0279	< 0.008
Tl	(0.9)	(mg/L)	< 0.008	< 0.008	< 0.008	< 0.008

Table 2.2 (continued)

Tank		1	2	3	4	9
<i>Process metals</i>						
Al	(mg/L)	0.419	0.713	0.549	5.17	0.249
B	(mg/L)	0.643	1.81	4.97	1.49	0.656
Be	(mg/L)	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
Ca	(mg/L)	5.78	8.98	2.81	1.53	14.2
Co	(mg/L)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Cu	(mg/L)	0.199	0.476	0.0468	0.0351	0.0902
Cs	(mg/L)	0.269	19.6	0.569	4.41	0.716
Fe	(mg/L)	0.010	0.0752	0.0217	< 0.006	< 0.006
K	(mg/L)	847	1380	3420	1320	695
Mg	(mg/L)	1.11	4.86	< 0.03	0.0651	2.97
Mn	(mg/L)	< 0.002	< 0.003	< 0.003	< 0.003	< 0.003
Na	(mg/L)	2210	3590	14800	4550	4830
P	(mg/L)	48.6	33.4	129	30.1	25.6
Sb	(mg/L)	< 0.37	< 0.39	< 0.37	< 0.37	< 0.37
Si	(mg/L)	103	118	317	167	46.8
Sr	(mg/L)	0.195	0.139	0.0418	0.0351	1.02
Th	(mg/L)	0.237	1.95	< 0.081	0.142	0.239
U	(mg/L)	281	219	0.386	195	303
V	(mg/L)	< 0.007	< 0.007	0.424	< 0.007	< 0.007
Zn	(mg/L)	< 0.05	0.105	0.0551	< 0.049	< 0.049
<i>Alkalinity</i>						
pH	(pH)	9.33	9.47	11.55	10.43	9.08

Table 2.2 (continued)

Tank		1	2	3	4	9
<i>Anions by ion chromatography</i>						
Bromide	(mg/L)	< 5.0	10.4	25.5	11.8	50.9
Chloride	(mg/L)	464	737	1630	650	5490
Fluoride	(mg/L)	37.5	53.4	283	59.2	19.5
Nitrite	(mg/L)	948	975	6300	1680	8.0
Nitrate	(mg/L)	141	95.2	7140	3010	2100
Phosphate	(mg/L)	< 20	< 20	< 20	< 20	< 20
Sulphate	(mg/L)	557	1380	4890	1580	821
<i>Beta/gamma emitters</i>						
<u>Gross beta</u>	(Bq/mL)	86000	150000	230000	220000	120000
⁶⁰ Co	(Bq/mL)	21	67	120	< 17	28
¹³⁴ Cs	(Bq/mL)	< 49	< 67	< 82	< 81	< 59
¹³⁷ Cs/ ^{137m} Ba	(Bq/mL)	64000	120000	190000	180000	92000
¹⁵² Eu	(Bq/mL)	< 35	< 39	< 35	< 35	< 11
¹⁵⁴ Eu	(Bq/mL)	< 31	< 31	< 50	< 44	< 35
¹⁵⁵ Eu	(Bq/mL)	< 140	< 190	< 240	< 240	< 170
⁹⁰ Sr/ ⁹⁰ Y	(Bq/mL)	3500	2800	240	1700	10000
⁹⁹ Tc	(Bq/mL)	13	20	29	24	9.0

Table 2.2 (continued)

Tank		1	2	3	4	9
<i>Alpha emitters by alpha spectrometry</i>						
<u>Gross alpha</u>	(Bq/mL)	340	300	3.1	270	500
²³³ U	(Bq/mL)	340	270	0.3	240	470
²³⁴ U	(Bq/mL)	6.4	5	0	4.4	6.9
²³⁵ U	(Bq/mL)	0.1	0.1	0	0.1	0.1
²³⁸ U	(Bq/mL)	3.5	2.7	0	2.4	3.7
<u>Total Pu alpha</u>	(Bq/mL)	2.3	5.7	0.43	6.1	1.3
²³⁸ Pu	(Bq/mL)	1.9	3.3	-	3.7	0.88
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/mL)	0.4	2.4	-	2.4	0.42
²⁴² Pu	(Bq/mL)	-	-	-	-	-
[²³⁹ Pu]	(ng/mL)	1.00	2.48	0.19	1.05	0.18
²³² Th/ ²³⁹ Pu ^b	(200)	237	785	-	136	1310
<i>Uranium isotopics by mass spectrometry</i>						
²³³ U	(atom %)	0.35	0.35	0.22	0.35	0.44
²³⁴ U	(atom %)	0.01	0.01	0.01	0.01	0.01
²³⁵ U	(atom %)	0.56	0.48	0.57	0.53	0.52
²³⁶ U	(atom %)	0.01	0.01	0.01	0.01	0.01
²³⁸ U	(atom %)	99.07	99.15	99.19	99.10	99.02
²³⁸ U/ ²³⁵ U FEM ^c	(100)	98	106	116	101	90
²³⁵ U/MS ^d	(mg/L)	1.55	1.04	0.002	1.02	1.56
²³⁵ U/NAA ^e	(mg/L)	2.15	1.60	0.0037	1.57	2.53

^aRCRA regulatory limits, concentrations in bold exceed regulatory limit.

^bDenature ratio for plutonium, ²³²Th/²³⁹Pu (200 is lower limit for criticality safety).

^cDenature ratios for uranium, ²³⁸U/²³⁵U FEM (100 is lower limit for criticality safety).

^dConcentration of ²³⁵U calculated from the MS and ICP data.

^eGross fissile content by delayed neutron counting, units are ²³⁵U equivalent.

Because of differences in uranium and plutonium chemistry, the plutonium denature ratio should be diluted with ^{232}Th and calculated as follows:

$$\frac{(^{232}\text{Th})}{(^{239}\text{Pu})} \geq 100$$

Keep in mind that all of the isotopic denature ratios are based on isotopic mass and not activity ratios. There have also been discussions of raising the dilution ratio limits, and some of the suggested ratios include $^{238}\text{U}/^{235}\text{U} > 104$, $^{238}\text{U}/^{233}\text{U} > 140$, and $^{232}\text{Th}/^{239}\text{Pu} > 200$ (Keller et al. 1996). As a consequence, these ratios will also be used in some of the data tables.

The average uranium denature ratios expressed as $^{238}\text{U}/^{235}\text{U}$ -FEM ratios for the sludge and liquid in the OHF tanks are 64 and 100, respectively (Fig. 2.1). The low ratios are primarily due to the high concentrations of ^{233}U . This is especially true for concentrations of ^{233}U in the sludges (Table 2.3). ^{233}U concentrations in the liquids are generally 0.2 to 0.4 wt% while concentrations in the sludges are 4 to 5 times higher (0.7 to 1.0 wt%). The $^{238}\text{U}/^{233}\text{U}$ denature ratios for the sludges were all below the proposed limit of 140 indicating a nuclear criticality concern. The same ratios for the liquids sampled from the tanks were all > 140 .

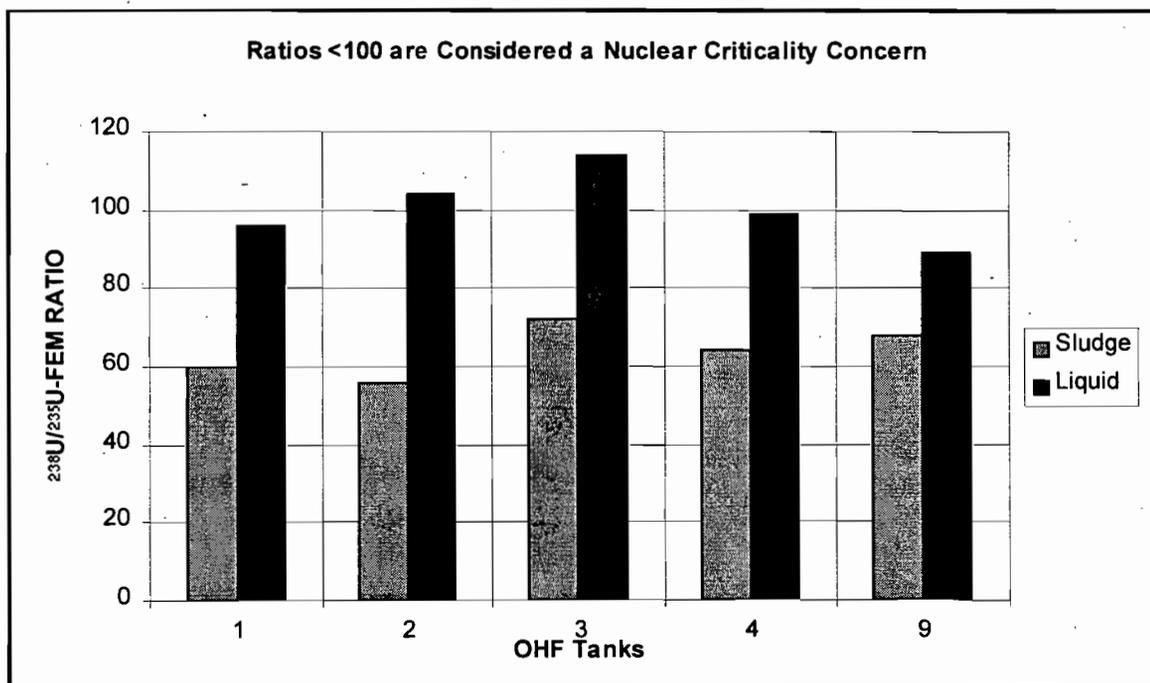


Fig. 2.1. Uranium $^{238}\text{U}/^{235}\text{U}$ -FEM denature ratios in sludge and liquid of OHF tanks.

It is not clear why the concentrations of ^{233}U in the sludge fraction are in excess of that measured in the liquid fraction. A likely explanation is that each represents a different source of uranium. For example, fine particulate (water-insoluble) highly enriched in ^{233}U and/or ^{235}U in a tetravalent state may have been disposed. Any ^{238}U added as the uranyl ion would tend to remain in the soluble phase as a uranyl carbonate complex due to the readily available carbonate in the pH

Table 2.3. Comparison of ²³³U concentrations in sludges and liquids sampled from the OHF tanks

	Tank									
	1		2		3		4		9	
	Liquid	Sludge								
²³³ U (wt%) ^a	0.34	0.91	0.34	1.04	0.21	0.72	0.34	0.87	0.43	0.71
²³⁸ U/ ²³³ U ratio ^b	283	108	283	94	451	136	283	113	225	138

^aWeight fraction of total isotopic uranium.

^bUranium denature ratios <140 are considered a nuclear criticality concern.

ranges of 8 to 10. If the ²³⁸U added to the waste stream (to denature the ²³³U) is not in a similar valence state or same physical/mineralogical state, a differential distribution of the two isotopes into the liquid and sludge phase may occur in the waste tanks. These waste tanks become carbonate-based systems due to sorption of carbon dioxide from the atmosphere (note that concentrations of inorganic carbon in the liquid phase of the tanks ranged from approximately 400 to 1000 mg/L). Another source of carbonate in the OHF tanks may be due to bionitrification of nitrate; note the high concentrations of nitrite (>6000 mg/L in Tank 3). Bionitrification likely occurs because of the high concentrations of tributyl phosphate added to the tanks as a defoamer. Tributyl phosphate (TBP) can serve as a carbon as well as a phosphorous source in bionitrification.

High levels of ²³³U in the sludge could have also resulted as a consequence of disposing highly enriched ²³³U solutions containing reduced uranium forms, such as tetravalent uranium. In a reducing condition, such as that present in a system where bionitrification prevails, the tetravalent uranium will not be oxidized to the uranyl (VI) form. Tetravalent uranium does not complex with carbonate as does the uranyl form, but rather hydrolyzes and forms insoluble hydroxides in the pH range of 8 to 10, thus enriching the sludge with ²³³U.

2.2 PLUTONIUM DENATURE RATIOS

If ²³²Th/²³⁹Pu < 100, Then Nuclear Criticality Safety Is a Concern

Extremely large concentrations of ²³²Th are present in the OHF sludge (average concentration in the five tanks is >88,000 mg/kg, appreciably greater than the average quantities of iron or aluminum, ca. 31,000 and 20,000 mg/kg, respectively). Concentrations of the major process metals in sludges of the five OHF tanks are illustrated graphically in Fig. 2.2. The exceptionally high concentration of ²³²Th results in an average ²³²Th/²³⁹Pu ratio of 43,625 for the sludge, much greater than a ratio of <100 or proposed 200, which are considered to indicate the possibility of a nuclear criticality safety concern. Average ²³²Th/²³⁹Pu concentration in the liquid component of four of the five OHF tanks is 386, again appreciably greater than the ratio of 200 considered to be a nuclear criticality safety concern. The ratio in the liquid phase of Tank 3 could not be calculated because the concentration of ²³²Th was below detection.

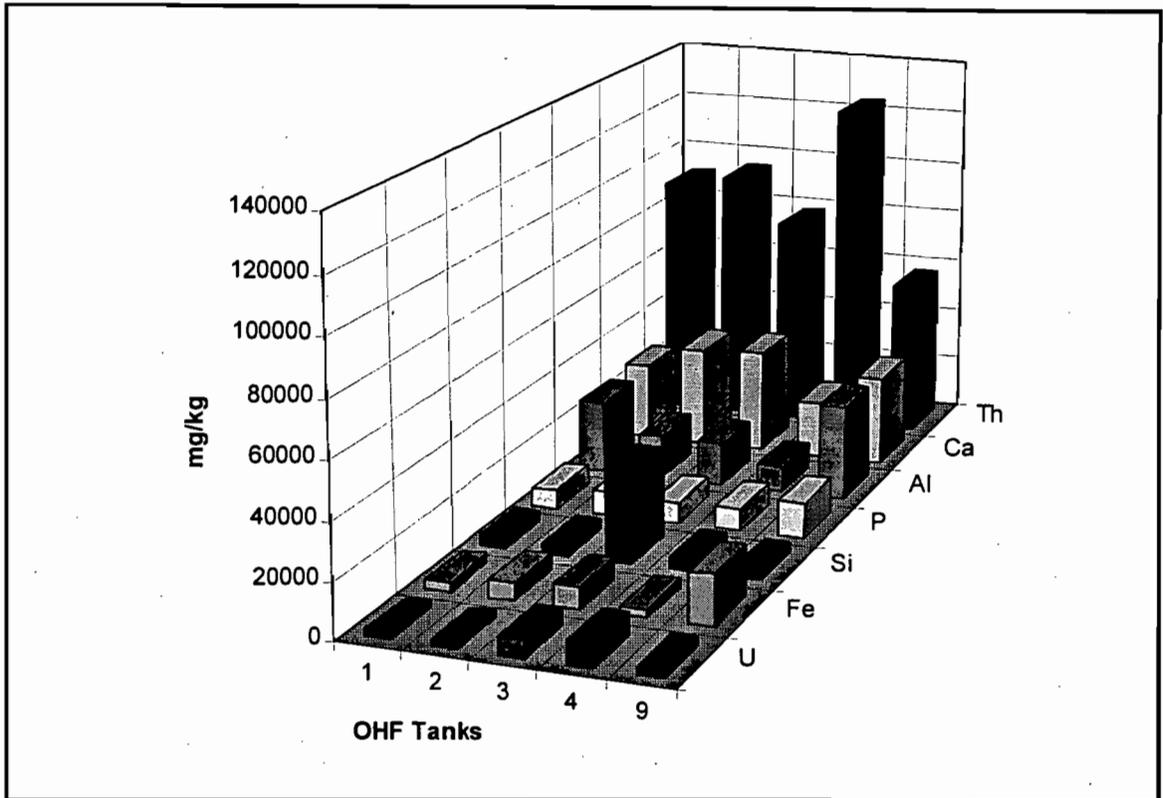


Fig. 2.2. Relative concentration of Th and U to other process metals contained in sludge of the OHF tanks.

3. DETERMINE WHETHER ORNL LLLW ACCEPTANCE CRITERIA ARE MET

3.1 TOTAL RADIONUCLIDE ACTIVITY

If Total Radionuclide Activity $\geq 2 \times 10^{10}$ Bq/L, Then Further Assessment Is Needed

Gross beta activity in the liquid contained in the OHF tanks ranged from 8.6×10^7 to 2.3×10^8 Bq/L. Most of the activity appears to be ^{137}Cs (activity from 6.4×10^7 to 1.9×10^8 Bq/L). Alpha activity in the liquid phase is relatively low ($<5.0 \times 10^5$ Bq/L). Thus, these data indicate that the liquid phase of the OHF tanks appear to contain activity levels $<2 \times 10^{10}$ Bq/L. However, the sludge component may contain activities in excess of 2×10^{10} Bq/L (i.e., assuming densities of 1.1 to 1.3 g/mL, sludges in all the tanks exhibit a gross beta in excess of 2×10^{10} Bq/L). Much of the activity in the sludges is associated with $^{90}\text{Sr}/^{90}\text{Y}$ and $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$, approximately 10^{10} and 10^8 Bq/L, respectively. The sludge also contains significant levels of alpha emitters $\sim 10^8$ Bq/L. Most of the alpha activity in the sludge fraction is associated with ^{241}Am and ^{244}Cm , approximately 10^7 and 10^8 Bq/L, respectively. Tanks 3 and 4 also contain ^{233}U activities on the order of 10^7 Bq/L.

3.2 TRANSURANIC ISOTOPES

If Transuranic (TRU) Isotopes or ^{233}U Contribute Total Specific Activity $\geq 3.7 \times 10^6$ Bq/kg, Then the Material Is Considered TRU and Further Assessment Is Needed

The liquid phase of all OHF tanks does not contain activities of TRU isotopes or ^{233}U in excess of 3.7×10^6 Bq/kg; thus, the liquid phase is not considered to be a TRU material. However, the sludge fraction of all tanks does contain TRU activities significantly greater than 3.7×10^6 Bq/kg making the sludge potential TRU wastes. Keep in mind that TRU criteria would require removal of free water for disposal practices; thus, on a dry weight basis, TRU activities would be on the order of 2.5 times the activities on a wet weight basis since most of the sludges contain at least 60% water.

3.3 RCRA METALS

Resource Conservation and Recovery Act (RCRA) Metals—If RCRA Limits Are Exceeded, Then Further Assessment Is Needed

Limits for RCRA metals are determined by conducting the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP is a waste leaching procedure that uses acetic acid to extract RCRA components from waste. Its intent is to simulate the leaching of a waste co-disposed in a municipal waste landfill. Rather than conducting the TCLP per se, total concentrations of RCRA metals were determined in the liquid and sludge fractions in the OHF tanks. Under the TCLP guidelines, the total concentrations of a constituent can be used to determine if the waste contains sufficient concentrations to exceed the TCLP regulatory limit. The TCLP regulatory limit is the concentration of the hazardous constituent in the final extract of the TCLP extraction test—not the concentration in the waste. The TCLP procedure uses a 20:1 ratio in the waste extraction procedure (100 g of filtered waste extracted by 2000 mL of extractant); thus, the total concentration of a hazardous constituent in the filtered waste must be at least 20 times the regulatory limit to fail the TCLP. For

liquid wastes (those containing <0.5% solids) the TCLP regulatory limit is determined by the total concentrations of the RCRA hazardous constituents in the liquid.

The liquid fraction of the OHF tanks contain concentrations of mercury and chromium in excess of the RCRA limits. Mercury levels in the liquid of all five tanks exceed the RCRA limit (0.2 mg/L). Tank 3 contains an extremely high mercury concentration (12.8 mg/L), greater than 60 times the RCRA limit. Tanks 3 and 4 contain concentrations of chromium (16.6 and 8.41 mg/L, respectively) in excess of the RCRA limit (5 mg/L). Concentrations of the other RCRA metals in the liquids contained in the OHF tanks were below regulatory concern.

The sludge in the OHF tanks also appear to contain concentrations of RCRA metals in excess of the regulatory limit based on total concentrations. To estimate potential excessive concentrations of RCRA metals in these sludges, the regulatory limit was taken to be 20 times the regulatory limit as determined by the TCLP extract. Keep in mind that these are simple estimates of potential concerns relating to the RCRA metals in the sludge. The sludge as sampled does not constitute a final waste form; thus, the analyses at this time do not represent an attempt to characterize them with respect to RCRA disposal criteria. To do so would require extraction of the final waste form using the TCLP protocol. The TCLP protocol removes only the extractable fraction of the RCRA metal. The fraction extracted varies significantly depending on waste form and RCRA metal. For chromium, mercury, and lead in OHF sludges, the percent extracted seldom exceeds 5% of the total concentration.¹

Total analyses of the OHF sludges for RCRA metals indicate mercury, chromium, and lead to be potential concerns (see Table 3.1). Mercury concentrations in the sludge of Tanks 1 and 2 are especially high ~200 mg/kg (closer to 400 mg/kg on a dry weight basis); that is, extraction of ~1% of the mercury in these sludges by the TCLP would characterize these sludges as toxic under RCRA. Sludges in Tanks 3 and 4 would probably not exceed mercury TCLP limits, assuming <15% of the mercury could be extracted by the TCLP. Sludges in all five tanks contained high concentrations of lead (four of the five sludges contained lead concentration >500 mg/kg, see Table 3.1). If the TCLP extracted >10% of the total lead from these sludges, these sludges would likely be classified as toxic wastes under RCRA. Sludges from Tanks 2 and 4 contained total chromium concentrations >100 mg/kg. If the TCLP extracted >20% of the chromium from these sludges, these sludges would likely be considered toxic under RCRA. The important point here is to realize that these sludges can only be characterized under RCRA by using the TCLP on the final waste form. Presently, one can only speculate which sludge might be suspect using the information available. It is conceivable that only two of the sludges (sludges from Tanks 1 and 2 because of elevated mercury levels) might be classified as toxic under RCRA. Any treatment resulting in the precipitation of the RCRA metals into insoluble waste forms in the sludge fraction would likely render all the wastes (liquids as well as the sludges) as non-toxic using the TCLP to determine the toxicity characterization under RCRA.

¹ Based on extraction of chromium, lead, and mercury from the OHF sludges by the EP-TOX (see Table 4.12, ORNL/ER-13, Autrey et al. 1990).

Table 3.1. OHF tanks sludge characteristics --- dissolution using nitric acid

Tank		1	2	3	4	9	
<i>Physical properties and miscellaneous data</i>							
Water	(%)	68.3	61.9	60.4	72.2	70.2	
Bulk density	(g/mL)	1.33	1.33	1.31	1.21	1.16	
Total Inorganic Carbon	(mg/kg)	8900	16000	12000	5200	16000	
Total Carbon	(mg/kg)	13000	29000	16000	15000	16000	
Total Organic Carbon	(mg/kg)	4100	13000	4000	9800	< 100	
<i>RCRA metals</i>							
Ag	(100) ^a	(mg/kg)	< 1.0	< 1.0	< 1.1	< 1.0	< 1.2
As	(100)	(mg/kg)	< 1.2	< 1.2	< 1.3	< 1.2	< 1.4
Ba	(2000)	(mg/kg)	51.9	52.3	69.6	26.5	81.3
Cd	(20)	(mg/kg)	14.4	14.4	10.2	16.4	10.9
Cr	(100)	(mg/kg)	79.4	241	51.8	118	85.1
Hg	(4)	(mg/kg)	187	196	7.89	15.1	1.80
Ni	(1000)	(mg/kg)	373	173	50.0	134	452
Pb	(100)	(mg/kg)	568	654	229	598	521
Se	(20)	(mg/kg)	< 1.2	< 1.2	< 1.3	< 1.2	< 1.4
Tl	(18)	(mg/kg)	1.18	1.4	< 1.3	< 1.2	< 1.4
<i>Process metals</i>							
Al		(mg/kg)	26200	15900	15600	9320	34500
B		(mg/kg)	43.7	43.9	31.8	49.7	41.6
Be		(mg/kg)	24.3	19.6	< 2.9	< 2.7	45.4
Ca		(mg/kg)	27900	36600	37900	20600	32800
Co		(mg/kg)	4.24	14.2	5.53	11.0	9.54
Cu		(mg/kg)	156	126	64.3	293	117
Cs		(mg/kg)	1.48	22.5	5.66	5.53	1.43
Fe		(mg/kg)	3440	6240	7790	3150	17900
K		(mg/kg)	1680	2130	6140	2080	974

Table 3.1 (continued)

Tank		1	2	3	4	9
Mg	(mg/kg)	3460	3170	3570	1730	5140
Mn	(mg/kg)	318	336	199	472	337
Na	(mg/kg)	4040	5060	18800	7400	6640
P	(mg/kg)	6940	8340	7510	8080	12600
Sb	(mg/kg)	< 17	< 17	< 19	< 17	< 20
Si (HF)	(mg/kg)	4010	3950	32500	4570	3640
Sr	(mg/kg)	946	992	282	334	908
Th	(mg/kg)	90500	94300	77500	124000	56800
U	(mg/kg)	2420	2090	5920	7870	2510
V	(mg/kg)	< 6.6	< 6.7	< 7.3	< 6.8	< 7.8
Zn	(mg/kg)	178	236	151	183	149
<i>Anions by ion chromatography (water wash)</i>						
pH		9.57	9.64	11.5	10.4	9.3
Bromide	(mg/kg)	< 4.63	< 5.20	< 43	< 41	70
Chloride	(mg/kg)	247	366	947	401	3760
Fluoride	(mg/kg)	176	233	257	272	140
Nitrate	(mg/kg)	52.6	27.9	4250	1470	869
Nitrite	(mg/kg)	629	576	4670	1460	219
Phosphate	(mg/kg)	< 18.5	< 20.8	< 174	< 165	< 195
Sulphate	(mg/kg)	339	726	2960	1210	616
<i>Beta/gamma emitters</i>						
<u>Gross beta</u>	(Bq/g)	4.5e+07	4.4e+07	2.3e+07	4.1e+07	5.0e+07
¹⁴ C	(Bq/g)					
⁶⁰ Co	(Bq/g)	6.7e+04	7.7e+04	1.0e+05	1.6e+05	4.9e+04
⁹⁰ Sr/ ⁹⁰ Y	(Bq/g)	2.0e+07	1.8e+07	8.5e+06	1.6e+07	2.0e+07
⁹⁹ Tc	(Bq/g)	1.3e+01	4.7e+01	3.3e+01	2.8e+01	1.4e+02
¹³⁴ Cs	(Bq/g)	< 4.9e+02	< 5.1e+02	< 7.1e+02	< 5.9e+02	< 4.8e+02

Table 3.1 (continued)

Tank		1	2	3	4	9
¹³⁷ Cs/ ^{137m} Ba	(Bq/g)	3.9e+05	3.5e+05	1.6e+06	3.4e+05	2.6e+05
¹⁵² Eu	(Bq/g)	6.3e+04	7.3e+04	5.6e+04	1.2e+05	4.3e+04
¹⁵⁴ Eu	(Bq/g)	4.3e+04	5.2e+04	3.4e+04	7.5e+04	3.1e+04
¹⁵⁵ Eu	(Bq/g)	< 2.7e+03	< 2.7e+03	5.9e+03	1.1e+04	6.9e+03
²⁴¹ Pu	(Bq/g)	2.9e+04	5.0e+04	1.1e+04	2.9e+04	3.0e+04
<i>Alpha emitters by alpha spectrometry</i>						
<u>Gross alpha</u>	(Bq/g)	4.6e+05	5.3e+05	3.0e+05	6.0e+05	3.5e+05
²³² Th	(Bq/g)	3.7e+02	3.8e+02	3.2e+02	5.0e+02	2.3e+02
²³³ U	(Bq/g)	7.9e+03	7.8e+03	1.5e+04	2.4e+04	6.4e+03
²³⁴ U	(Bq/g)	1.1e+02	9.5e+01	1.3e+02	1.8e+02	5.7e+01
²³⁵ U	(Bq/g)	0.7e+00	0.5e+00	1.7e+00	2.1e+00	0.9e+00
²³⁸ U	(Bq/g)	3.0e+01	2.6e+01	7.3e+01	9.7e+01	3.1e+01
²³⁷ Np	(Bq/g)	9.0e+00	1.2e+01	8.9e+00	1.9e+01	1.2e+01
²⁴¹ Am	(Bq/g)	5.2e+04	2.6e+04	1.5e+04	8.0e+03	1.3e+04
²⁴⁴ Cm	(Bq/g)	3.5e+05	4.6e+05	2.5e+05	5.3e+05	2.7e+05
²⁵² Cf	(Bq/g)	< 4.6e+02	< 5.0e+02	< 3.0e+02		< 3.5e+02
<u>Total Pu alpha</u>	(Bq/g)	4.0e+04	3.4e+04	1.7e+04	3.5e+04	5.8e+04
²³⁸ Pu	(Bq/g)	2.9e+04	2.3e+04	1.1e+04	2.2e+04	4.8e+04
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)	1.1e+04	1.0e+04	6.5e+03	1.3e+04	9.2e+03
²⁴² Pu	(Bq/g)	-	-	-	-	-

Table 3.1 (continued)

Tank		1	2	3	4	9
<i>Uranium isotopics by mass spectrometry</i>						
²³³ U	(atom %)	0.93	1.07	0.74	0.89	0.73
²³⁴ U	(atom %)	0.02	0.02	0.01	0.01	0.01
²³⁵ U	(atom %)	0.43	0.35	0.40	0.38	0.50
²³⁶ U	(atom %)	0.01	0.01	0.01	0.01	0.01
²³⁸ U	(atom %)	98.61	98.55	98.84	98.71	98.75
²³⁸ U/ ²³⁵ U FEM ^b		60	56	72	64	68
²³⁵ U/MS ^c	(mg/kg)	10.3	7.2	23.4	29.5	12.4
²³⁵ U/NAA ^d	(mg/kg)	27.3	25.2	57.1	80.9	27.5
<i>Plutonium isotopics by mass spectrometry</i>						
²³⁸ Pu	(atom %)	1.45	1.00	0.68	0.78	2.45
²³⁹ Pu	(atom %)	75.24	71.12	69.02	69.73	77.60
²⁴⁰ Pu	(atom %)	19.89	23.61	26.86	25.89	17.04
²⁴¹ Pu	(atom %)	0.24	0.38	0.14	0.19	0.25
²⁴² Pu	(atom %)	3.17	3.86	3.30	3.37	2.66
²⁴⁴ Pu	(atom %)	< 0.01	< 0.01	< 0.01	0.03	< 0.01
<u>Pu activity^e</u>						
²³⁸ Pu	(Bq/g)	2.9e+04	2.2e+04	8.9e+03	2.0e+04	4.8e+04
²³⁹ Pu	(Bq/g)	5.5e+03	5.6e+03	3.3e+03	6.4e+03	5.5e+03
²⁴⁰ Pu	(Bq/g)	5.3e+03	6.8e+03	4.7e+03	8.8e+03	4.5e+03
²⁴¹ Pu	(Bq/g)	2.9e+04	5.0e+04	1.1e+04	2.9e+04	3.0e+04
²⁴² Pu	(Bq/g)	1.5e+01	1.9e+01	1.0e+01	2.0e+01	1.2e+01
²⁴⁴ Pu	(Bq/g)	< 1.0e+00				
²³⁹ Pu	(ng/g)	2400	2400	1440	2800	2410
²³² Th/ ²³⁹ Pu ^f (200)		37700	38800	53800	44200	23600

(a) RCRA regulatory limits based on 20 times the concentration of the TCLP extract regulatory concentration, (b) Denature ratios for uranium, ²³⁸U/²³⁵U FEM, (c) Concentration of ²³⁵U calculated from the MS and ICP data, (d) Gross fissile content by delayed neutron counting, units are ²³⁵U equivalent, (e) Calculated from mass spec. and total Pu alpha data, (f) Denature ratio for plutonium, ²³²Th/²³⁹Pu.

3.4 RCRA ORGANIC COMPOUNDS

RCRA Organic Compounds—If RCRA Limits Are Exceeded, Then Further Assessment is Needed

If RCRA organic compounds in a waste exceed concentration limits established by the TCLP, then the waste needs to be managed as a RCRA hazardous waste. Wastes in the OHF tanks are not considered to be in their final waste form; thus, these analyses should be viewed as a screening effort to evaluate the potential of these wastes to be a RCRA waste. Concentrations of RCRA organic compounds measured in the liquid and sludge fractions of the OHF tanks have been summarized in Tables 3.2 and 3.3. Based on the concentration of RCRA organic compounds regulated by the TCLP, neither the liquid or the sludge fraction is in excess of the TCLP regulatory limits.

3.4.1 RCRA Volatile Organic Compounds

RCRA Volatile Organic Compounds—If RCRA Limits Are Exceeded, Then Further Assessment Is Needed

Volatile organic compounds (VOCs) detected in at least one supernatant and/or sludge are summarized in Table 3.4. The principal VOCs detected in supernatant were acetone (up to 1300 µg/L), chloroform (up to 440 µg/L), and 2-butanone (up to 510 µg/L). Other VOCs, including cis-1,2-dichloroethene, 2-hexanone, 4-methyl-2-pentanone, toluene, and m&p-xylene were detected in at least one tank at concentrations in the low µg/L range. Bromomethane, 1,1-dichloroethene, and 1,1,1-trichloroethane were similarly detected at low µg/L levels, but were also found in blanks; the reported levels in supernatants may therefore be artifacts. Tentatively identified compounds (TICs) detected at levels below 100 µg/L included 2-methyl-1-propene (Tank 9), 4,4-dimethyl-2-pentanone (Tanks 3 and 4), 2-hexanone (Tanks 3 and 4), and 2-heptanone (Tank 4).

3.4.2 RCRA Semivolatile Organic Compounds

RCRA Semivolatile Organic Compounds—If RCRA Limits Are Exceeded, Then Further Assessment Is Needed

Semivolatile organic compounds (SVOCs) detected in at least one supernatant and/or sludge are summarized in Table 3.5. The only positively identified SVOCs detected in supernatants were benzyl alcohol (126 µg/L in Tank 3); 2-nitrophenol (up to 132 µg/L); 2,4-dimethylphenol (56 µg/L in Tank 3); 2,4-dinitrophenol (458 µg/L in Tank 4); and bis(2-ethylhexyl)phthalate (94 µg/L in Tank 2). Chloriodomethane was detected in Tank 9 (240 µg/L) but was found in the blank analysis as well; this analysis is therefore suspect.

Phosphoric acid tributyl ester, or TBP, was tentatively identified in the supernatant from each tank at levels of up to 3200 µg/L (Tank 2). N-butylbenzenesulfonamide was tentatively identified in four of the tank supernatants at levels up to 1000 µg/L (Tank 9). Tris(2-ethoxy) phosphoric acid was also detected in four tank supernatants at levels from 230 µg/L to 480 µg/L. Several additional TICs were detected in single tanks at levels below 500 µg/L.

Sludges contained several phthlates, including di-n-butylphthalate, bis(2-ethylhexyl)phthalate, and di-n-octylphthalate, at total phthlate concentrations of up to 13,600 µg/kg. The only other

Table 3.2. Summary of RCRA organic compounds in liquid phase

Contaminant	CAS No.	TCLP regulatory level (mg/L)	Tank				
			1	2	3	4	9
Carbon tetrachloride	56-23-5	0.5	<0.005	<0.005	<0.005	<0.005	<0.005
Chlorobenzene	108-90-7	100	<0.005	<0.005	<0.005	<0.005	<0.005
Chloroform	67-66-3	6.0	0.063	0.440	<0.005	0.047	0.065
o-Cresol	95-48-7	200	<0.050	<0.050	<0.050	<0.050	<0.050
p-Cresol	106-44-5	200	<0.050	<0.050	<0.050	<0.050	<0.050
Total Cresol		200	<0.100	<0.100	<0.100	<0.100	<0.100
1,4-Dichlorobenzene	106-46-7	7.5	<0.005	<0.005	<0.005	<0.005	<0.005
1,2-Dichloroethane	107-06-2	0.5	<0.005	<0.005	<0.005	<0.005	<0.005
1,1-Dichloroethylene	75-35-4	0.7	0.013	<0.005	<0.005	<0.005	0.006
2,4-Dinitrotoluene	121-14-2	0.13	<0.050	<0.050	<0.050	<0.050	<0.050
Hexachlorobenzene	118-74-1	0.13	<0.050	<0.050	<0.050	<0.050	<0.050
Hexachlorobutadiene	87-68-3	0.5	<0.050	<0.050	<0.050	<0.050	<0.050
Hexachloroethane	67-72-1	3.0	<0.050	<0.050	<0.050	<0.050	<0.050
Methyl ethyl ketone	78-93-3	200	0.009	<0.005	0.310	0.510	<0.005
Nitrobenzene	98-95-3	2.0	<0.050	<0.050	<0.050	<0.050	<0.050
Pentachlorophenol	87-86-5	100	<0.125	<0.125	<0.125	<0.125	<0.125

Table 3.2 (continued)

Contaminant	CAS No.	TCLP regulatory level (mg/L)	Tank				
			1	2	3	4	9
Pyridine	110-86-1	5.0	NQ	NQ	NQ	NQ	NQ
Tetrachloroethylene	127-18-4	0.7	<0.005	<0.005	<0.005	<0.005	<0.005
Trichloroethylene	79-01-6	0.5	<0.005	<0.005	<0.005	<0.005	<0.005
2,4,5-Trichlorophenol	95-95-4	400	<0.125	<0.125	<0.125	<0.125	<0.125
2,4,6-Trichlorophenol	88-06-2	2.0	<0.050	<0.050	<0.050	<0.050	<0.050
Vinyl chloride	75-01-4	0.2	<0.005	<0.005	<0.005	<0.005	<0.005

NQ - Not quantified because pyridine is not normally determined using Methods 8270 and 8260; however, if present at a regulatory level (5 ppm) it would have been detected by the volatile organics procedure (Method 8260)—Personal correspondence, May 30, 1996, Wayne H. Griest, Chemical and Analytical Research Division, Oak Ridge National Laboratory.

Table 3.3. Summary of RCRA organic compounds in sludge phase

Contaminant	CAS No.	TCLP regulatory level ^a (mg/L)	Tank				
			1	2	3	4	9
			(mg/kg)				
Carbon tetrachloride	56-23-5	10	<1	<1	<1	<1	<1
Chlorobenzene	108-90-70	2000	<1	<1	<1	<1	<1
Chloroform	67-66-3	120	<1	<1	<1	<1	<1
o-Cresol	95-48-7	4000	<2	<2	<2	<2	<2
p-Cresol	106-44-5	4000	<2	<2	<2	<2	<2
Total Cresol		4000	<4	<4	<4	<4	<4
1,4-Dichlorobenzene	106-46-7	15	<1	<1	<1	<1	<1
1,2-Dichloroethane	107-06-2	10	<1	<1	<1	<1	<1
1,1-Dichloroethylene	75-35-4	14	<1	<1	<1	<1	<1
2,4-Dinitrotoluene	121-14-2	2.6	<2	<2	<2	<2	<2
Hexachlorobenzene	118-74-1	2.6	<2	<2	<2	<2	<2
Hexachlorobutadiene	87-68-3	10	<2	<2	<2	<2	<2
Hexachloroethane	67-72-1	60	<2	<2	<2	<2	<2
Methyl ethyl ketone	78-93-3	4000	<1	<1	<1	<1	<1
Nitrobenzene	98-95-3	40	<2	<2	<2	<2	<2

Contaminant	CAS No.	TCLP regulatory level ^a (mg/L)	Tank				
			1	2	3	4	9
			(mg/kg)				
Pentachlorophenol	87-86-5	2000	<2	<2	<2	<2	<2
Pyridine	110-86-1	100	NQ	NQ	NQ	NQ	NQ
Tetrachloroethylene	127-18-4	14	<1	<1	<1	<1	<1
Trichloroethylene	79-01-6	10	<1	<1	<1	<1	<1
2,4,5-Trichlorophenol	95-95-4	8000	<2	<2	<2	<2	<2
2,4,6-Trichlorophenol	88-06-2	40	<2	<2	<2	<2	<2
Vinyl chloride	75-01-4	4	<1	<1	<1	<1	<1

^aMaximum total concentration allowable in sludge based on a 20:1 dilution based on liquid:solid ratio in the TCLP and regulatory limits in TCLP extract.
NQ - Not quantified because pyridine is not normally determined using methods 8270 and 8260; however, if present at a regulatory level (5 ppm) it would have been detected by the volatile organics procedure (Method 8260)—Personal correspondence, May 30, 1996, Wayne H. Griest, Chemical and Analytical Research Division, Oak Ridge National Laboratory.

Table 3.4. Volatile organic compounds in OHF liquid supernatant and sludges

Compound	OHF Tank ^a									
	1		2		3		4		9	
	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge
Bromomethane	23 ^b	<1000	<5	<1000	57 ^b	<1000	41 ^b	<1000	32 ^b	<1000
Acetone	65	<1000	<5	<1000	1300 ^c	<1000	1100 ^c	<1000	13	<1000
1,1-Dichloroethene	13 ^b	<1000	<5	<1000	<5	<1000	<5	<1000	6 ^b	<1000
cis-1,2-Dichloroethene	<5	<1000	10	<1000	<5	<1000	<5	<1000	<5	<1000
Chloroform	63	<1000	440 ^c	<1000	5	<1000	47	<1000	65	<1000
2-Butanone	9	<1000	<5	<1000	310 ^c	<1000	510 ^c	<1000	<2	<1000
1,1,1-Trichloroethane	12 ^b	<1000	<5	<1000	6 ^b	<1000	13 ^b	<1000	<5	<1000
2-Hexanone	<5	<1000	<5	<1000	13	<1000	27	<1000	<5	<1000
4-Methyl-2-pentanone	<5	<1000	<5	<1000	12	<1000	27	<1000	<5	<1000
Toluene	<5	<1000	<5	<1000	<5	<1000	6	<1000	<5	<1000
m&p-Xylene	<5	<1000	<5	<1000	<5	<1000	6	<1000	<5	<1000
2-Methyl-1-propene ^d	—	—	—	—	—	—	—	—	45	—
4,4-Dimethyl-2-pentanone ^d	—	—	—	—	39	—	86	—	—	—
2-Hexanone ^d	—	—	—	—	28	—	75	—	—	—
2-Heptanone ^d	—	—	—	—	—	—	66	—	—	—
Diethylbenzene isomer ^d	—	630	—	—	—	—	—	2300	—	—

^aLiquid concentrations expressed in µg/L and sludge concentrations expressed in µg/kg.

^bConcentration estimated (found in blank).

^cConcentration estimated (exceeded calibration range).

^dTentative identification; concentration estimated.

— = not detected.

Table 3.5. Semivolatile organic compounds in OHF liquid supernatant and sludge

Compound	Tank ^a									
	1		2		3		4		9	
	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge
Benzyl alcohol	<50	<2000	<50	<2000	126	<2000	<50	<2000	<50	<2000
2-Nitrophenol	<50	<2000	114	<2000	66	<2000	132	<2000	<50	<2000
2,4-Dimethylphenol	<50	<2000	<50	<2000	56	<2000	<50	<2000	<50	<2000
2,4-Dinitrophenol	<50	<2000	<50	<2000	<50	<2000	458	<2000	<50	<2000
Di-n-butylphthalate	<50	9100 ^b	<50	6700 ^b	<50	3900 ^b	<50	8200 ^b	<50	13000 ^b
bis(2-Ethylhexyl)phthalate	<50	<2000	94	4000	<50	<2000	<50	<2000	<50	<2000
Di-n-octylphthalate	<50	3000	<50	2900	<50	<2000	<50	<2000	<50	<2000
Chloroiodomethane	<50	3000	<50	2900	<50	<2000	<50	<2000	240 ^b	<2000
2-Ethylhexanal ^c	280	—	—	—	—	—	—	—	—	—
Acetophenone ^c	—	—	—	—	—	—	180	—	—	—
2-Fluoro-6-nitrophenol ^c	—	—	—	—	—	—	—	—	190	—
Iodomethylmercury ^c	—	—	—	—	180	—	—	—	—	—
Bromomethylbenzene ^c	73	—	—	—	—	—	—	—	—	—
Iodomethylbenzene	230	—	290	—	—	—	—	—	—	—
Ethylbenzoic acid ^c	—	—	—	—	140	—	—	—	—	—
Dodecanoic acid ^c	—	—	—	—	420	—	—	—	—	—
Phosphoric acid tributyl ester ^c	1200	29000	3200	210000	740	16000	460	25000	150	15000
N-Butylbenzenesulfonamide ^c	—	—	230	—	480	—	420	—	1000	—
Phosphoric acid, tris(2-ethy) ^c	370	—	450	—	230	—	380	—	—	—

^aLiquid concentrations expressed in µg/L and sludge concentrations expressed in µg/kg.

^cConcentration estimated (found in blank).

^bTentative identification; concentration estimated.

— = Not detected.

SVOC consistently detected in sludges was TBP, which was measured at levels as high as 210,000 $\mu\text{g}/\text{kg}$ (Tank 2). Levels of TBP in supernatants ranged from 1.0% to 4.6% of the concentrations in sludge, on a weight basis, reflective of the partitioning of TBP between solid and liquid phases in the tanks.

3.4.3 RCRA Nonhalogenated Volatile Organic Compounds

RCRA Nonhalogenated Volatile Organic Compounds—If RCRA Limits Are Exceeded, Then Further Assessment Is Needed

Analyses for six nonhalogenated VOCs are summarized in Table 3.6. No compounds were detected in supernatants from Tanks 1, 2, or 9. Acetone was measured in the supernatant of Tanks 3 and 4 at concentrations of 3.3 mg/L and 5.9 mg/L, respectively. These levels exceed by several-fold those measured by the VOC procedure (note that concentrations in Table 3.6 are reported in mg/L and mg/kg whereas the concentrations in Table 3.4 for VOCs are reported in $\mu\text{g}/\text{L}$ and $\mu\text{g}/\text{kg}$ levels). Thus, the values reported in Table 3.6 should be considered the more accurate. Methanol (up to 22 mg/L) and butanol (up to 28 mg/L) were also detected in supernatants from Tanks 3 and 4.

The only nonhalogenated VOC detected in any sludge sample was butanol in Tank 3 (18 mg/L), corresponding to the relatively high concentration measured in the supernatant also.

3.5 POLYCHLORINATED BIPHENYLS

PCBs—If PCB Levels >2 ppm, Then Further Assessment Is Needed

Results of analyses for polychlorinated biphenyls (PCBs) in supernatants and sludges for the five OHF tanks are summarized in Table 3.7. No PCBs were detected in any tank supernatant. Only Aroclor-1248 was detected in any tank sludge; levels ranged from 69 $\mu\text{g}/\text{kg}$ to 164 $\mu\text{g}/\text{kg}$. No tank sludge contained a PCB concentration that exceeded the Toxic Substances Control Act-based action level of 2 ppm (2000 $\mu\text{g}/\text{kg}$).

Table 3.6. Nonhalogenated volatile organic compounds in OHF liquid supernatant and sludge

Compound	Tank ^a									
	1		2		3		4		9	
	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge
Methanol	<2	<10	<2	<10	20	<10	22	<10	<2	<10
Acetone	<2	<10	<2	<10	3.3	<10	5.9	<10	<2	<10
Methyl ethyl ketone	<2	<10	<2	<10	<2	<10	<2	<10	<2	<10
Isobutanol	<2	<10	<2	<10	<2	<10	<2	<10	<2	<10
Butanol	<2	<10	<2	<10	28	18	3	<10	<2	<10
Pyridine	<2	<10	<2	<10	<2	<10	<2	<10	<2	<10

^aLiquid concentrations expressed in mg/L and sludge concentrations expressed in mg/kg.

Table 3.7. Polychlorinated biphenyls in OHF liquid supernatant and sludge

PCB Aroclor No.	Tank ^a									
	1		2		3		4		9	
	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge	Liquid	Sludge
1016	<10	<25	<10	<25	<10	<25	<10	<25	<10	<25
1221	<20	<50	<20	<50	<20	<50	<20	<50	<20	<50
1232	<10	<25	<10	<25	<10	<25	<10	<25	<10	<25
1242	<10	<25	<10	<25	<10	<25	<10	<25	<10	<25
1248	<10	111	<10	164	<10	69	<10	85	<10	121
1254	<10	<25	<10	<25	<10	<25	<10	<25	<10	<25
1260	<10	<25	<10	<25	<10	<25	<10	<25	<10	<25

^aLiquid concentrations expressed in µg/L and sludge concentrations expressed in µg/kg.

4. COMPARISON OF 1996 ANALYTICAL DATA WITH 1988 DATA

The intent here is to make some comparison of data recently obtained to that generated in the 1988 sampling period and reported in September 1990, ORNL/ER-13 (Autrey et al. 1990). It is important to keep in mind that the sophistication in sample preparation, preservation, and general analytical protocol in the recent work is at a considerably higher level than some of that conducted in the 1990 report. Thus, generally speaking, more credence should be reflected in the recent program.

4.1 RCRA METALS

For the liquid fraction contained in the OHF tanks, the 1996 sampling and analyses also revealed that mercury concentrations were in excess of the RCRA limits. The liquids contained in Tanks 3 and 4 also contained excessive levels of chromium. Similar results were observed in the 1988 samples. Mercury concentrations in the liquid of Tanks 1, 2, and 3 appear to higher in 1996 compared to 1988 (see Table 4.1). However, for tanks 4 and 9, mercury concentrations were higher in 1988 than 1996. The limits of detection for As, Ba, Pb, Se, and Tl in the 1996 work were considerable lower than those in the 1988 work. For example, in 1988 the limits of detection for lead varied between 0.5 and 1 mg/L. In 1996, the limit of detection was 0.008 mg/L. Probably the most significant factor in comparison of the two data sets is that both data sets revealed levels of mercury in the liquid fraction of these tanks were in excess of the RCRA limits. Both data sets also showed that the levels of chromium in Tanks 3 and 4 were in excess of the RCRA limits (16.6 and 14.0 mg/L in Tank 3 in 1996 and 1988, respectively, while Tank 4 contained concentrations of 8.4 and 12.1 for 1996 and 1988, respectively).

RCRA metals in the sludge fraction sampled from the OHF tanks are difficult to determine. For example, the lead and chromium data from the 1988 work were suspect. For barium and cadmium, there appears to be a very good agreement between 1996 and 1988 analyses (see Table 4.2). Mercury concentrations in the sludges taken from Tanks 1 and 2 for the 1996 work were considerably higher than the 1988 work (e.g., 187 and 196 mg/kg were measured in 1996 from Tanks 1 and 2 as compared to 74 and 70 mg/kg measured in 1988). The opposite appeared to hold true for sludge in Tanks 3, 4, and 9; viz, 7.8, 15, and 1.8 mg/kg measured in 1996 compared to 40, 585, and 39 mg/kg measured in 1988. The 585 mg/kg of mercury measured in sludge taken from Tank 4 in 1988 is likely a statistical outlier or a sample highly enriched in mercury for some unknown reason. It is important to keep in mind that the sampling strategy utilized does not constitute a "representative" sample. Considering all of the potential errors involved (sampling, analyses of a complex matrix for trace contaminants) agreement between the 1996 and 1988 databases is relatively good. The major difference between the 1996 and 1988 work is that the 1996 analyses verifies the potential for these sludges to be characterized as toxic under RCRA because of the high lead concentrations. As stated earlier, if the TCLP extracted >10% of the lead from these sludges, these sludges would likely be classified as toxic under RCRA.

Table 4.1. Concentrations of RCRA metals in liquid contained in the OHF tanks (1988 and 1996 samplings)

RCRA Metal	Tank ^a									
	1		2		3		4		9	
	1996	1988	1996	1988	1996	1988	1996	1988	1996	1988
Ag	< 0.02	0.01	0.02	<0.01	< 0.02	<0.01	< 0.02	0.02	<0.02	0.01
As	0.01	<0.8	0.01	<0.8	0.30	0.40	< 0.008	<0.04	< 0.008	<0.8
Ba	< 0.002	0.05	< 0.002	0.06	< 0.002	<0.02	< 0.002	<0.04	< 0.002	0.12
Cd	< 0.04	<0.02	< 0.04	<0.02	< 0.04	<0.01	< 0.04	<0.02	< 0.04	<0.02
Cr	1.52	0.24	1.46	0.44	16.60	14.00	8.41	12.13	0.02	0.40
Hg	0.54	0.07	0.27	0.10	12.80	5.70	1.98	3.90	0.90	3.40
Ni	< 0.04	<0.2	< 0.04	<0.2	0.07	<0.1	< 0.04	<0.2	< 0.04	<0.2
Pb	< 0.008	<1	0.02	<1	< 0.008	<0.5	< 0.008	<1	< 0.008	<1
Se	< 0.008	<0.2	< 0.008	<0.09	0.03	<0.5	< 0.008	<0.09	< 0.008	<0.09
Tl	< 0.008	<0.2	< 0.008	<0.09	< 0.008	<0.5	< 0.008	<0.09	< 0.008	<0.09

^aConcentrations are in mg/L; bold print represents concentrations in excess of the RCRA limits.

Table 4.2. Concentrations of RCRA metals in sludge contained in the OHF tanks (1988 and 1996 samplings)

RCRA metals	Tank ^a									
	1		2		3		4		9	
	1996	1988	1996	1988	1996	1988	1996	1988	1996	1988
Ag	<1.0	2.1	< 1.0	2.9	1.1	0.15	< 1.0	(1.7)	< 1.2	0.21
As	< 1.2	<2	< 1.2	<1	< 1.3	<3	< 1.2	<4	< 1.4	<2
Ba	51.9	88	52.3	33	69.6	76	26.5	<50	81.3	115
Cd	14.4	12.9	14.4	6.6	10.2	8.5	16.4	10	10.9	7.8
Cr	79.4	(130)	241	(180)	51.8	(69)	118	(102)	85.1	(<10)
Hg	187	74	196	70	7.89	40	15.1	585	1.8	39
Ni	373	190	173	7	50	57	134	160	452	380
Pb	568	(860)	654	(350)	229	-300	598	(510)	521	(540)
Se	< 1.2	(<2)	< 1.2	(<1)	< 1.3	(0.74)	< 1.2	(1.5)	< 1.4	(<2)
Tl	1.18	1.7	1.4	<1	< 1.3	<0.6	< 1.2	0.73	< 1.4	<2

^aConcentrations in sludge are expressed in mg/kg on the wet weight basis; 1988 values in parentheses () represent suspect data.

4.2 COMPARISON OF URANIUM IN LIQUID AND SLUDGE FRACTIONS—1996 AND 1988

There appears to be some major differences between 1996 and 1988 measured concentrations of uranium in the liquid fractions. For example, 195 mg/L of uranium was measured in Tank 4 in 1996 compared to 25 mg/L in 1998 (Fig. 4.1). The trend was reversed in Tank 9; viz, 852 mg/L in 1998 and 303 mg/L in 1996. No major differences in uranium 1996 and 1988 concentrations were observed (Table 4.3).

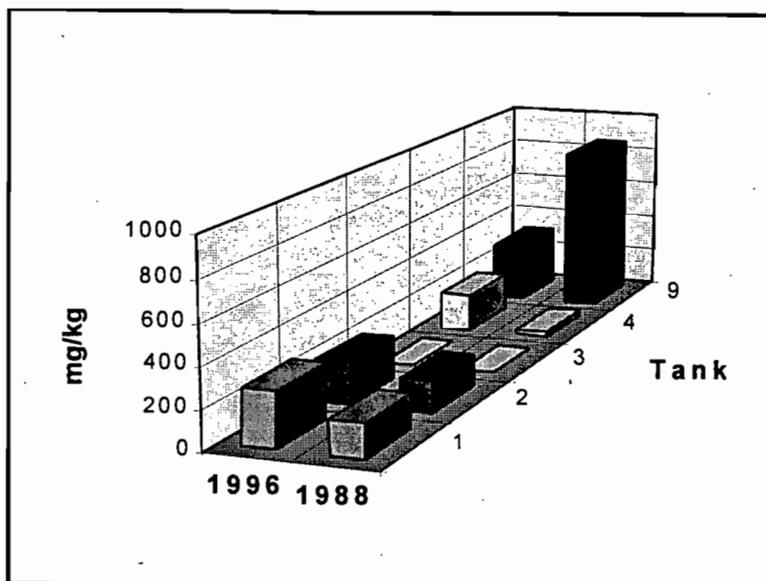


Fig. 4.1. Uranium concentration in the liquid fraction of the OHF tanks—1996 and 1988.

The very low concentrations of uranium observed in Tank 3 (1996 and 1988) were due to the higher pH of the liquid in this tank as compared to liquid in the other tanks. The concentration of uranium in the liquid of the tanks is very dependent on pH of the liquid. As the pH increases the concentration of uranium decreases exponentially (Fig. 4.2). Measurements of pH in 1996 were lower than 1988 measurements in each of the tanks (Table 4.4). Average pH (across all tanks) in 1996 was 9.97 compared to 10.62 in 1988.

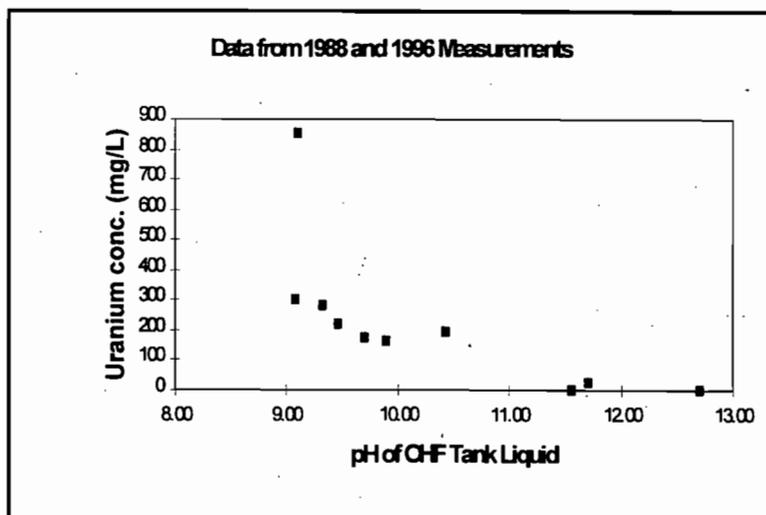


Fig. 4.2. Uranium concentration in the liquid fraction of the OHF tanks as a function of pH.

4.3 VOLATILE ORGANIC COMPOUNDS

Comparison of 1988 results for VOCs with the 1996 results is made more difficult by the large number of earlier analytes which were detected in blanks, as well as samples; these results must therefore be considered suspect. Methylene chloride, in particular, was found at elevated levels in Tanks 1, 2, and 9, which were analyzed as a batch in 1988. Benzene was detected in Tanks 1 and 9

Table 4.3. Comparison of uranium in liquid and sludge fractions—1996 and 1988

Tank	Liquid (mg/L)		Sludge (mg/kg)	
	1996	1988	1996	1988
1	281	173.5	2420	2800
2	219	163.5	2090	1000
3	0.386	0.2	5920	3060
4	195	25.5	7870	1850
9	303	852	2510	2930

Table 4.4. Comparison of pH of liquid in OHF tanks — 1996 and 1988

Tank	1996	1988
1	9.33	9.70
2	9.47	9.90
3	11.55	12.70
4	10.43	11.70
9	9.08	9.10
Mean	9.97	10.62

(130 µg/L and 11 µg/L, respectively) in 1988, but not in 1996. Carbon disulfide was also detected in Tanks 1 and 9 (130 µg/L and 4 µg/L, respectively) in 1988, but not in 1996.

Comparison of analyses conducted in 1988 with those conducted in 1996 showed relatively little change in the organic constituents of Tank 4, the tank with the highest overall concentrations of VOCs. In 1988 the supernatant contained acetone (mean of three samples: 7.3 mg/L), methanol (38 mg/L), ethanol (37 mg/L), 1-propanol (3 mg/L), and n-butanol (4 mg/L). Measured values in 1996 for acetone, methanol, and n-butanol are between 58% and 81% of those measured 8 years earlier. Levels of 2-hexanone and 4-methyl-2-pentanone, 20 and 10 µg/L, respectively, in 1988, were both measured at 27 µg/L in 1996. Benzene, detected earlier at levels of 7–10 µg/L, was not detected in 1996 (<5 µg/L). Total xylenes, measured at 36 µg/L and 170 µg/L in two Tank 4 samples in 1988, was 6 µg/L in 1996. Heptanone, tentatively identified and measured at 80 µg/L in 1988, was measured at 66 µg/L in 1996.

Comparison of the VOC data suggests that the more volatile compounds, such as the chlorinated solvents, benzene, and toluene, have been reduced to nondetectable levels in most of the tanks since 1988. The mechanism for reduction is probably slow volatilization and leakage of vapors from the tanks. The more water-soluble compounds, such as alcohols and ketones, have remained, although their levels have dropped considerably.

4.4 SEMIVOLATILE ORGANIC COMPOUNDS

More SVOCs were detected in Tank 2 in 1988 than in the other tanks. The concentration of 2-nitrophenol, reported at 185 µg/L (mean of three analyses) in 1988, was 114 µg/L in 1996. This compound was speculated in the 1990 report to be a result of reactions under way in the tank; if so, it appears that this process is no longer active. Both 2-nitrophenol and 2,4-dinitrophenol were measured (132 µg/L and 458 µg/L, respectively) in supernatant from Tank 4 in 1996 but had not been detected in 1988, which suggests that nitration reactions may be still under way in this tank.

Benzyl alcohol was reported in Tank 3 supernatant at nearly identical levels in both 1988 (120 µg/L) and 1996 (126 µg/L). In Tank 9 both benzoic acid and benzyl alcohol concentrations dropped from 1988 levels (340 µg/L and 160 µg/L, respectively) in 1988 to below detection (<50 µg/L) in 1996, suggesting that slow reactions may still be under way. The more nearly neutral pH of this tank (9.08) may permit microbial activity in Tank 9 that might explain the disappearance of these compounds.

The principal constituents in tank sludges in 1988, as in 1996, were phthalates. The principal compound detected in Tank 1 sludge, di-n-butylphthalate, was 3500 µg/kg in 1988, compared to a measured level of 9100 µg/kg in 1996. Similar ratios between 1988 and 1996 levels were observed for Tanks 2 (4600, 6700), 3 (3100, 3900), 4 (3400, 8200), and 9 (3700, 13,000). Phthalates are not likely to be generated by any processes occurring in the tanks. It seems most likely that the compounds have not changed in actual concentration, and that the higher levels observed in 1996 reflect more thorough extraction techniques or other increases in the accuracy of the analytical procedure.

4.5 TRIBUTYL PHOSPHATE

Although TBP is not on the SVOC Target Compound List, it has been tentatively identified in sample analyses both in 1988 and in 1996. Interpretation of changes in TBP levels reported for the tank sludges and supernatants, however, is not clear. In the 1988 analyses TBP was reported in tank supernatants at concentrations ranging from 2000 µg/L (Tank 3) to 40,000 µg/L (Tank 1). These levels significantly exceed those reported in 1996: concentrations measured recently, reported as a percentage of the 1988 value, are: Tank 1, 3–4%; Tank 3, 37%; Tank 4, 15%; Tank 9, 0.5% (no value was reported for Tank 2 in 1988). Comparison of reported values for sludges, however, shows a reverse trend: for the two tanks for which 1988 levels were reported, levels measured in 1996 exceed those measured in 1988 by factors of 750% (Tank 9) and 1450% (Tank 1).

Differences in compound levels observed in both supernatant and sludge may be due to changes in analytical procedures, rather than real changes in constituents. However, the analysis of aqueous supernatants would be expected to be reasonably similar in precision in 1996 as in 1988, even if the sludge extraction and analysis was not sufficiently effective to give accurate results in 1988. If this were the case, then the decline in the supernatant levels may be real, and may reflect processes in the tanks that have reduced the aqueous concentrations, such as hydrolysis or microbial degradation. The high pH of Tanks 3 and 4 (~10 and 11, respectively) would argue against microbial activity in these tanks; however, bionitrification is known to occur at the lower pH values measured in Tanks 1 and 9 (~9). This could also be the reason much lower concentrations of TBP were observed in these two tanks in 1996 as compared to 1988 (3–4% in Tank 1 and 0.5% in Tank 9) as compared to the reductions in TBP in Tanks 3 and 4 over the same period (37% in Tank 3 and 15% in Tank 9).

The relatively high concentration of nitrite in all the tanks imply that biodenitrification may be occurring.

An alternative explanation is that changes in both supernatant and sludge are real, and that TBP has largely precipitated from solution during the intervening 8 years, thus reducing levels in the supernatant and increasing them in the sludge by a comparable factor.

4.6 RCRA ORGANIC COMPOUNDS

No organic contaminant was detected in the 1996 analyses, in the supernatant or sludge of any of the five tanks, that exceeds the RCRA Toxicity Characteristic regulatory level (40 CFR 261.24).

In the ORNL/ER-13 report (Autrey et al. 1990), Tank 9 was identified as one of 10 inactive tanks containing volatile organic RCRA constituents above the regulatory threshold. The exceedance was based on the analyzed concentration of methylene chloride (600 µg/L), which exceeded the specified regulatory criterion of 200 µg/L. The 1996 data do not confirm the earlier analysis; the level of methylene chloride reported was below detection (<5 µg/L). The supernatant in Tank 9 would therefore no longer exceed the criterion identified in the ORNL/ER-13 report for categorization as RCRA hazardous waste on the basis of VOC content.

5. SUMMARY AND CONCLUSIONS

The major issue relating to the chemical characterization of the liquid and sludge contained in the OHF tanks is the nuclear criticality concern. Present waste acceptance criteria require that "solutions containing ^{233}U , ^{235}U , ^{239}Pu , or ^{241}Pu must be mixed with either depleted uranium or natural thorium (according to chemical similarity) so that the resultant solution will contain at least 100 parts by weight of ^{238}U or ^{232}Th per part by weight of the fissile isotope (s)" (Parrott et al. 1991). Uranium denature ratios expressed as $^{238}\text{U}/^{235}\text{U}$ -FEM ratios should be in excess of 100; if they are less than 100 then there is concern relative to nuclear criticality. Average $^{238}\text{U}/^{235}\text{U}$ -FEM ratios for the sludge and liquid in the OHF tanks are 64 and 100, respectively. The low ratios are primarily due to the high concentrations of ^{233}U . Thus, the sludge contains ratios that are of concern. More recently proposed ratios call for higher ratios of ^{238}U ; for example, ratios of $^{238}\text{U}/^{235}\text{U}$ of 104 and $^{238}\text{U}/^{233}\text{U}$ ratios of 140. The $^{238}\text{U}/^{233}\text{U}$ ratios for sludges were all well below the proposed 140 limit indicating a nuclear criticality concern. However, the same ratios for the liquids sampled from the tanks were well over 140. These data indicate that it is important to add additional ^{238}U to these tanks so that the uranium denature ratios meet waste acceptance criteria. Simple addition of needed ^{238}U (depleted uranium) and elevation of the pH in the waste tanks in excess of 11.5 will ensure precipitation of the ^{238}U into the sludge phase, thus raising the uranium denature ratios to acceptable levels.

Waste acceptance criteria also require ratios of ^{232}Th to ^{239}Pu or ^{232}Th to ^{241}Pu to be in excess of 100 (or proposed ratio of 200). Extremely large concentrations of ^{232}Th are present in the OHF sludge (average concentration in the five tanks is $>88,000$ mg/kg, appreciably greater than the average quantities of iron or aluminum, ca. 31,000 and 20,000 mg/kg, respectively). The exceptionally high concentration of ^{232}Th results in an average $^{232}\text{Th}/^{239}\text{Pu}$ ratio of 43,625 for the sludge, much greater than the ratio of 100 or proposed 200. Average $^{232}\text{Th}/^{239}\text{Pu}$ concentration in the liquid component of four of the five OHF tanks is 386; thus, the thorium to plutonium ratios are not a nuclear criticality concern. In fact, the large quantities of ^{232}Th will act as a denaturing agent for the fissile-uranium isotopes. It is generally accepted that no mixture of ^{235}U and water can be made critical at a ^{235}U concentration less than 5 g/L (Bigelow 1996). Thus, these tanks are a long way from criticality concern; however, if either the liquid or sludge fractions is evaporated, this could become a concern. This also could be a significant concern in any engineering effort to solidify/stabilize either the liquid or sludge fractions of the waste contained in any of the OHF tanks.

The chemical characterization data also indicate that wastes contained in the OHF tanks may also be in excess of two other waste acceptance criteria. Both may be due to the separation of the waste stream into liquid and sludge fractions. Waste acceptance criteria require "liquid radioactive wastes added to the LLW system must not have a total radionuclide activity concentration exceeding 2×10^{10} Bq/L (2 Ci/gal) ^{90}Sr equivalent."²² The radiological analyses indicate that the liquid fraction of the OHF tanks contain activity levels $<2 \times 10^{10}$ Bq/L; however, the sludge component may contain activities in excess of the 2×10^{10} Bq/L criterion. For example, if one assumes bulk densities of 1.1 to 1.3 g/mL, sludges in the OHF tanks appear to contain on the order of 10^{10} Bq/L of $^{90}\text{Sr}/^{90}\text{Y}$. Sludges also appear to contain excessive levels of TRU isotopes. For example, the waste acceptance criteria require solutions containing TRU isotopes or ^{233}U which are added to the LLLW system must not have a total specific activity from those nuclides greater than 3.7×10^6 Bq/kg (100 nCi/g). The activity level (100 nCi/g) is the basis of the U.S. Department of Energy definition of TRU wastes. TRU isotopes must be alpha-emitting actinides with $Z > 92$ (uranium). TRU isotopes must also have a half-life ≥ 20 years. This definition excludes all thorium and uranium isotopes. The primary TRU isotopes in the OHF tanks include ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Am . Concentrations of these isotopes in the liquid fraction of the OHF tanks are all well below the 3.7×10^6 Bq/kg criterion; however,

sludges in all OHF tanks contain TRU activities significantly greater than the TRU criteria. Keep in mind that TRU criteria would require removal of free water for disposal practices; thus, on a dry weight basis TRU activities would be on the order of 2.5 times the activities on a wet weight basis since most of the sludges contain at least 60% water. These characterization data strongly indicate that sludge in the OHF would be TRU wastes if processed accordingly.

Analyses of the liquid and sludge fractions for RCRA metals revealed that the OHF tanks contain RCRA wastes. For example, mercury levels in the liquid fraction of all five tanks exceed the RCRA limit (0.2 mg/L). Tank 3 contains an extremely high mercury concentration (12.8 mg/L), greater than 60 times the RCRA limit. Liquid waste in two of the tanks (Tanks 3 and 4) contain concentrations of chromium (16.6 and 8.4 mg/L, respectively) in excess of the RCRA limit (5 mg/L). Based on total concentrations of RCRA metals in the sludge fraction, it appears that the sludge in the OHF tanks will also be in excess of regulatory limits. However, this can only be determined by characterization of the final waste form using the TCLP. Since the TCLP removes only the extractable fraction of RCRA metals from the waste form, it is impossible to determine their regulatory status until the final waste form is characterized using this test. Analyses of TCLP/RCRA organic compounds in the liquid and sludge fractions contained in the OHF tanks showed concentrations below regulatory levels indicating the wastes are not a concern with respect to their concentrations of TCLP/RCRA organic compounds.

The above assessment of the chemical characteristics of the liquid and sludge contained in the OHF tanks is based on the samples collected. The representativeness of these samples has not been verified. The ORNL/ER-13 report (Autrey et al. 1990) showed that the analyses of liquid samples taken from varying depths in the OHF tanks were not appreciably different, indicating that liquid samples are likely representative samples of the liquid phase. However, the sludge samples were taken from only one location within the individual tank and are probably not representative. However, there were similar characteristics in the chemical make-up of sludge from all OHF tanks. This was especially true for radionuclides; for example, gross beta and gross alpha activity (expressed in Bq/g) were in the 10^7 and 10^5 range, respectively, across all five tanks. The $^{238}\text{U}/^{235}\text{U}$ FEM ratios in the sludges from all tanks were relatively uniform (ranging from 56 to 72, a mean of 64 ± 5.6 , and a coefficient of variance of 8.8%) indicating that the variability in the chemical/radionuclide composition of the sludge fraction within each tank may not be as significant as one might think. Regardless, it would be prudent to collect additional sludge samples to verify the range in chemical/radionuclide compositions. Possibly more important is to investigate differences in physical properties of sludge within the tanks. These data will be needed before suitable engineering efforts can be developed for treatment and disposal of these wastes.

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