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**OAK RIDGE
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**Characterization of the BVEST
Waste Tanks
Located at ORNL**

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MASTER



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Chemical and Analytical Sciences Division

Characterization of the BVEST Waste Tanks Located at ORNL

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TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
ACKNOWLEDGMENTS	v
ABBREVIATIONS AND ACRONYMS	vi
EXECUTIVE SUMMARY	vii
1.0 Introduction	1
2.0 Sample Collection Activities	5
3.0 Analytical Methodology	5
3.1 <u>Sample Preparation</u>	6
3.2 <u>Metal Analysis</u>	7
3.3 <u>Anion Analysis</u>	9
3.4 <u>Radiochemical Analysis</u>	11
3.5 <u>Criticality Controls</u>	13
3.6 <u>Organic Analysis</u>	15
3.6.1 Non-halogenated Volatile Organic Analysis (NHVOA)	15
3.6.2 Volatile Organic Analysis (VOA)	15
3.6.3 Semivolatile Organic Analysis	16
3.6.4 Polychlorinated Biphenyls	16
4.0 Quality Assurance	17
5.0 Summary of Inorganic and Radiochemical Analytical Results	19
5.1 <u>Description of Data Tables</u>	19
5.2 <u>Discussion of BVEST Supernatant Characteristics</u>	31
5.3 <u>Discussion of BVEST Sludge Characteristics</u>	35
5.4 <u>RCRA Characteristics for the BVEST System</u>	41
5.5 <u>TRU Classifications for LLLW System</u>	42
5.6 <u>Distribution of Fissile Material in LLLW System</u>	43
5.7 <u>Discussion of the Total Anion Content in the Sludge</u>	47
5.7.1 Nitrate/Nitrite	47
5.7.2 Halides (fluoride, chloride, bromide)	48
5.7.3 Phosphate	48
5.7.4 Sulfate	49
5.7.5 Summary	49

5.8	<u>Solubility of BVEST Sludge in Water</u>	50
5.9	<u>Estimates for Compliance with WIPP WAC, Rev. 5 for BVEST Sludge</u>	51
6.0	Summary of Organic Analytical Results	57
6.1	<u>Discussion of Organic Analysis</u>	62
7.0	Summary of Rheometry Measurements	63
7.1	<u>Rheometry Tests</u>	63
7.2	<u>Shear Strength Measurements</u>	64
7.3	<u>Viscosity and Flow Curves</u>	72
REFERENCES		79
APPENDIX A		A-1
	QC Acceptance Criteria for Radioactive Liquid/Solid Waste Samples	A-1
	Volatile Organic Analyses QC Limits	A-4
	Nonhalogenated Volatile Organic Analyses QC Limits	A-5
	Semivolatile Organic Analyses QC Limits	A-5
APPENDIX B		B-1
Table B1	Total Mass and Activity for Selected Species of Interest in Sludge ...	B-2
Table B2	Dose Measurements on Liquid Samples	B-3
Table B3	Dose Measurements on Sludge Samples	B-3

LIST OF TABLES

<u>Table</u>		<u>Page</u>
Table 1	Summary of Tanks in the Active ORNL LLLW System	2
Table 2	Volume Estimates for Liquid and Sludge in the LLLW System	3
Table 3	Analytical Data for Liquids in Tanks W-21, W-22, and W-23	23
Table 4	Analytical Data for Sludge in Tanks W-21, W-22, and W-23	27
Table 5	Summary of Quality Checks for BVEST Supernatant Data	33
Table 6	Distribution of Beta Activity in Supernatant	35
Table 7	Assumption Used for Major Compounds in BVEST Sludge	36
Table 8	Summary of Quality Checks for BVEST Sludge Data	36
Table 9	Distribution of Beta Activity in BVEST Sludge	39
Table 10	Summary of Actinide Elements in BVEST Sludge	40
Table 11	Summary of RCRA Regulatory Limits	41
Table 12	Summary of Denature Ratios for BVEST Supernatant	44
Table 13	Summary of Denature Ratios for BVEST Sludge	44
Table 14	Example of Converting Atom % to Weight % for Typical Sludge	45
Table 15	Summary of Total Anion Data for BVEST Sludge	47
Table 16	Recovery of Selected Species in Water Leach of BVEST Sludge	50
Table 17	Estimates for ²³⁹ Pu FGE with the BVEST Sludge	52
Table 18	Estimates for ²³⁹ Pu Equivalent Activity with the BVEST Sludge	53
Table 19	Isotopes that Contribute to the Decay Heat in the BVEST Sludge	54
Table 20	Distribution of Decay Heat in BVEST Sludge	54
Table 21	Summary of Relative Decay Heat in BVEST Sludge	55
Table 22	Analytical Organic Data for BVEST Liquid Samples	58
Table 23	Analytical Organic Data for BVEST Sludge Samples	60
Table 24	W-21 Shear Strength Test Measurements	66
Table 25	W-22 Shear Strength Test Measurements	67
Table 26	W-23 Shear Strength Test Measurements	67

LIST OF FIGURES

Figure		Page
Figure 1	Distribution of Major Cations and Anions in Liquid Phase	32
Figure 2	Distribution of Selected Ionic Species in Liquid Phase	32
Figure 3	Distribution of Major Compounds in BVEST Sludge	38
Figure 4	Distribution of Uranium and Thorium in BVEST Sludge	38
Figure 5	Distribution of Plutonium by Alpha Activity in BVEST Sludge	46
Figure 6	Distribution of Plutonium by Concentration in BVEST Sludge	46
Figure 7	Distribution of Beta Decay Heat in BVEST Sludge	56
Figure 8	Distribution of Alpha Decay Heat in BVEST Sludge	56
Figure 9	Shear Strength Curves for Top Core from W-21 Sludge	68
Figure 10	Shear Strength Curves for Bottom Core from W-21 Sludge	68
Figure 11	Shear Strength Curves for Composite Core from W-21 Sludge	69
Figure 12	Expanded View for W-21 Composite Sludge Curve	69
Figure 13	Shear Strength Curves for Top Core from W-22 Sludge	70
Figure 14	Shear Strength Curves for Bottom Core from W-22 Sludge	70
Figure 15	Shear Strength Curves for Top Core from W-23 Sludge	71
Figure 16	Shear Strength Curves for Bottom Core from W-23 Sludge	71
Figure 17	Viscosity vs. Shear Rate for W-21 Sludge	74
Figure 18	Shear Stress vs. Shear Rate for W-21 Sludge	74
Figure 19	Viscosity vs. Shear Rate for W-22 Sludge	75
Figure 20	Shear Stress vs. Shear Rate for W-22 Sludge	75
Figure 21	Viscosity vs. Shear Rate for W-22 Sludge (Duplicate)	76
Figure 22	Shear Stress vs. Shear Rate for W-22 Sludge (Duplicate)	76
Figure 23	Viscosity vs Shear Rate for W-22 Sludge (Static)	77
Figure 24	Shear Stress vs. Shear Rate for W-22 Sludge (Static)	77
Figure 25	Viscosity vs. Shear Rate for W-23 Sludge	78
Figure 26	Shear Stress vs. Shear Rate for W-23 Sludge	78

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ABBREVIATIONS AND ACRONYMS

ALARA	As Low As Reasonably Achievable
BVEST	Bethel Valley Evaporator Service Tanks
CAO	Carlsbad Area Office
CASD	Chemical and Analytical Sciences Division
CVAA	Cold Vapor Atomic Absorption
DOT	Department of Transportation
DQO	Data Quality Objective
EPA	Environmental Protection Agency
GC/MS	Gas Chromatography/Mass Spectrometry
GC	Gas Chromatography
GFAA	Graphite Furnace Atomic Absorption
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
LLLW	Liquid Low-Level Waste
LMER	Lockheed Martin Energy Research, Corp.
LMES	Lockheed Martin Energy Systems, Inc.
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MVST	Melton Valley Storage Tanks
NHVOA	Non-halogenated Volatile Organic Analysis
NTS	Nevada Test Site
ORNL	Oak Ridge National Laboratory
PCB	Polychlorinated Biphenyls
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan
QAPP	Quality Assurance Program Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RMAL	Radioactive Materials Analytical Laboratory (Building 2026)
SVOA	Semivolatile Organic Analysis
TC	Total Carbon
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
TIC	Total Inorganic Carbon or Tentatively Identified Compounds
TIMS	Thermal Ionization Mass Spectrometry
TOC	Total Organic Carbon
TRU	Transuranic
TWCP	Transuranic Waste Characterization Program
VOA	Volatile Organic Analysis
WAC	Waste Acceptance Criteria
WIPP	Waste Isolation Pilot Plant

EXECUTIVE SUMMARY

During the fall of 1996 there was a major effort to sample and analyze the Active Liquid Low-Level Waste (LLLW) tanks at ORNL which include the Melton Valley Storage Tanks (MVST) and the Bethel Valley Evaporator Service Tanks (BVEST). The characterization data summarized in this report was needed to address waste processing options, address concerns dealing with the performance assessment (PA) data for the Waste Isolation Pilot Plant (WIPP), evaluate the waste characteristics with respect to the waste acceptance criteria (WAC) for WIPP and Nevada Test Site (NTS), address criticality concerns, and meet DOT requirements for transporting the waste. This report discusses the analytical characterization data for the supernatant and sludge in the BVEST waste tanks W-21, W-22, and W-23. Two of the Bethel Valley tanks, C-1 and C-2, are not discussed in this report because there is no access to these tanks for taking samples. There is a companion report on the MVST waste tanks (ORNL/TM-13357) that includes the analytical data and the results on the MVST supernatant and sludge.

The isotopic data presented in this report supports the position that fissile isotopes of uranium (^{233}U and ^{235}U) and plutonium (^{239}Pu and ^{241}Pu) were "denatured" as required by the administrative controls stated in the ORNL LLLW waste acceptance criteria (WAC). In general, the BVEST sludge was found to be hazardous based on RCRA characteristics and the transuranic alpha activity was well above the 100 nCi/g limit for TRU waste. The characteristics of the BVEST sludge relative to the WIPP WAC limits for fissile gram equivalent, plutonium equivalent activity, and thermal power from decay heat were estimated from the data in this report and found to be far below the upper boundary for any of the remote-handled transuranic waste (RH-TRU) requirements for disposal of the waste in WIPP.

Characterization of the BVEST Waste Tanks Located at ORNL

J. M. Keller, J. M. Giaquinto, A. M. Meeks

1.0 Introduction

The active ORNL Liquid Low Level Waste (LLLW) system consists of the set of waste tanks summarized in Table 1. As indicated in Table 1, this report discusses the analytical characterization data for the supernatant and sludge in the BVEST waste tanks W-21, W-22, and W-23. The BVEST tanks C-1 and C-2 were not sampled for this project because there is currently no access available from which samples can be taken from these tanks. There is a companion report¹ that includes the characterization data for the MVST waste tanks. The characterization data summarized in this report was needed to address waste processing options, examine concerns from the performance assessment (PA) for the Waste Isolation Pilot Plant (WIPP), evaluate the waste characteristics with respect to the waste acceptance criteria (WAC) for WIPP and Nevada Test Site (NTS), deal with criticality concerns, and to meet DOT requirements for transporting the waste.

The data was collected during a sampling and analysis campaign performed during the late summer and fall of 1996. The sampling and waste characterization requirements were documented in a Sampling and Analysis Plan² (SAP). The level of quality assurance approximates that required for regulatory measurements with the understanding that, when needed, sample size requirements were reduced, and steps were taken to reduce sample handling to ensure radiation exposures were as-low-as-reasonably-achievable (ALARA). Some procedure modifications were required to handle chemical matrix problems due to the high levels of sodium nitrate, uranium, and thorium present. Any deviations from procedures or problems observed with the tank samples were documented in the data files maintained by the laboratory. The regulatory holding time requirements for mercury and the organic measurements were complied with unless noted differently in the data tables. The Quality Control (QC) Acceptance Criteria for measurements used on this project are summarized in Appendix A. Total tank inventory for selected species and the dose measurements on the sludge and supernatant samples are discussed in Appendix B.

Table 1 Summary of Tanks in the Active ORNL LLLW System

Tanks	Data Presented in this report	
	Liquid	Sludge
BVEST TANKS		
C-1 (HLW)	none	none
C-2 (HLW)	none	none
W-21 (PWTP)	✓	✓
W-22 (BVCT)	✓	✓
W-23 (LLLW)	✓	✓
MVST TANKS		
W-24	none	none
W-25	none	none
W-26	none	none
W-27	none	none
W-28	none	none
W-29	none	none
W-30	none	none
W-31	none	none

Earlier waste tank characterization work performed in 1985 by Peretz³ et al. and 1990 by Sears⁴ et al. did not specifically address criticality concerns. There was limited radiochemical data on ²³³U, ²³⁵U and ²³⁹Pu; which was taken from gross radiochemical screening measurements. This previous data for fissile actinide elements in the LLLW waste tanks had relatively large analytical errors and should be used with caution. More recent data reported by Keller⁵ et al. and Sears⁶, which was collected in early 1996, addresses some of the criticality concerns but did not deal with all the tanks of interest. The analytical data for fissile isotopes in this report are based on mass spectrometry measurements, similar to the data collected in early 1996, but includes a more complete set of LLLW waste tanks. The uranium and plutonium were each chemically separated from the waste matrix

prior to measurement of the isotopic ratios by mass spectrometry. The mass spectrometry measurements yield more detailed and accurate information than radiochemical measurements for the major fissile isotopes present. The isotopic mass ratio measurements on the sludge samples may not represent the average isotopic ratios due to the heterogeneous nature of the sludge. Based on intermittent mixing of the supernatant the isotopic data for liquid samples should be more representative of the overall supernatant present than comparable measurements for the sludge. Physical observations indicate that the sludge in each tank tends to be segregated into vertical layers which demonstrates minimal mixing of the sludge material as it was either added to the tanks or precipitated from the liquid layer. At the time the samples were collected for this project there was only a single access manhole to each of the waste tanks; consequently, there is no analytical data available to evaluate lateral segregation across the tank.

An inventory of radioactive liquid waste and sludge stored in each tank are shown in Table 2 and includes estimates for the volumes through October 1996. The volume data is based on estimates⁷ provided by the Chemical Technology Division (CTD).

Table 2 Volume Estimates for Liquid and Sludge in the LLLW System

Tank	Total Waste Volume		Sludge Volume		Supernatant Volume	
	(gal)	(L)	(gal)	(L)	(gal)	(L)
W-21	23100	87500	6500	24600	16600	62900
W-22	13100	49600	6800	25800	6300	23800
W-23	21800	82600	10600	40100	11200	42400
W-24	22300	84400	8700	32900	13600	51500
W-25	44100	167000	17300	65500	26800	101500
W-26	44600	168900	11800	44700	32800	124200
W-27	26000	98500	16000	60600	10000	37900
W-28	44200	167400	4500	17000	39700	150300
W-29	44300	167800	11000	41700	33300	126100
W-30	41200	156000	11000	41700	30200	114300
W-31	43900	166200	10600	40100	33300	126100

2.0 Sample Collection Activities

A detailed description on the background, operation of the LLLW system, and the sample collection techniques has been presented in previous reports and will not be discussed here (see Sections 2 and 3 of Reference 3). The staff from the Liquid and Gaseous Waste Operations (LGWO) Department provided all sample collection support and delivered the samples to the analytical laboratory. A good description of the sampling procedures is provided in Appendix A of the Sampling and Analysis Plan²; a current copy of these procedures are available from the LGWO Department. The documentation for chain-of-custody was prepared, maintained for each sample collected, and stored with the data files by the analytical laboratory.

3.0 Analytical Methodology

The information and data collected from these studies are used to support various activities. The activities include demonstration of regulatory compliance, measurements to support future processing options, and to meet data needs for risk assessments and other safety related assessments such as criticality. Standardized analytical procedures are used to the extent possible to ensure broad acceptance of the data generated. Unless stated otherwise, the U. S. Environmental Protection Agency (EPA) methods were used for the analyses of constituents listed as hazardous under the Resource Conservation and Recovery Act (RCRA), which includes all the inorganic and organic measurements presented in this report. In general the EPA Guidance Manual, *Test Methods for Evaluating Solid Waste*⁸ (SW-846), was used for inorganic and organic methods. Some modifications of the standard procedures were necessary to handle the high radiation levels and the high salt/solids content of the samples. Some procedure modifications were required to generate valid data; these changes were usually needed to correct for chemical or other matrix related interferences common to DOE generated liquid waste from nuclear processes. All deviations from the standard procedures are documented in the raw data files and can be provided upon request to data users.

3.1 Sample Preparation

The aqueous supernatant samples from the waste tanks were filtered or centrifuged to remove suspended particles. The clarified liquids were then digested by the SW-846 Method 3015, *Microwave Assisted Acid Digestion of Aqueous Samples and Extracts*. This sample preparation for aqueous samples was then used for all subsequent metal analyses by ICP-AES and GFAA and most of the radiochemical analyses. Results from a collaborative study⁹ with Argonne National Laboratory - East (ANL-E) demonstrated Method 3015/3051 provided excellent recovery for mercury and was, therefore, used to prepare the tank samples for this project for mercury determination.

The primary method for digesting the sludge samples was SW-846 Method 3051, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*. This sample preparation is considered to be a total digestion for metals and radionuclides by regulatory agencies and yields good results for most metals and radionuclides of interest. This digestion gave poor performance on two of the metals of interest, silver and silicon. Although nitric acid is excellent for dissolving silver compounds, there is usually enough chloride present in waste samples to form an insoluble silver chloride (AgCl) precipitate. If the chloride concentration is increased sufficiently, a silver chloride complex (AgCl_3^{-2}) forms which is soluble in the aqueous environment. Improved matrix spike recovery and defensible data for silver were obtained using a separate sample digestion discussed later in this report.

If the total silicon content in the sludge must be known to develop waste treatment options such as vitrification, another sample digestion is required. A simple nitric acid treatment will not dissolve most siliceous materials. The SW-846 Method 3052, *Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices*, provides the necessary digestion chemistry to yield good silicon data. Sludge samples were prepared for measurement of total silicon, by taking approximately 0.5 g of sludge and mixing with 7 mL of concentrated nitric acid and 3 mL of hydrofluoric acid in a fluorocarbon microwave vessel. The samples were digested for 10 minutes at 95% full power (570 watts) and then cooled to room temperature. The acid solution was then treated with excess boric acid and heated to 80°C for ten minutes to complex any free fluoride. This

digestion mixture is cooled, filtered into a 50 mL volumetric flask, and diluted to volume with ASTM Type II water. Care must be exercised to ensure the digestion solution is cooled to room temperature prior to opening the sealed microwave vessel or there may be a significant loss of the volatile SiF_4 . The free fluoride is complexed with the boron to protect the sample introduction system to the ICP-AES and to prevent a high silicon background from the instrument glassware. This sample digestion with hydrofluoric acid should not be used for radiochemical measurements, especially for measurement of lanthanides or actinides.

Most of the metal and radionuclide data presented in this report are based upon a Method 3051 digestion with approximately a 0.5 gram sludge sample and 10 mL of concentrated nitric acid. After the microwave digestion is completed and the solution cooled to room temperature, the sample is filtered into a volumetric flask and diluted to 50 mL with ASTM Type II water or better. To ensure valid silver and antimony data, samples were digested in a similar manner except the 10 mL of nitric acid was replaced with 6 mL of concentrated nitric acid plus 4 mL of concentrated hydrochloric acid. Any residue remaining after the nitric acid or nitric-hydrochloric acid digestion consisted of mostly SiO_2 and was discarded.

3.2 Metal Analysis

Three analytical measurement methods were used to determine all of the metals included in this report. Most of the metals are first determined by SW-846 Method 6010A, *Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)*. There are several elements of interest for which the ICP-AES has insufficient detection limits, and these elements must be determined by Method 7000A, *Atomic Absorption Methods*. The Radioactive Materials Analytical Laboratory (RMAL) uses a Graphite Furnace Atomic Absorption (GFAA) Spectrometer for elements that require better sensitivity. The elements that usually require GFAA were antimony (Method 7041), arsenic (Method 7060A), lead (Method 7421), selenium (Method 7740), and thallium (Method 7841). All the mercury measurements are done by either Method 7470A, *Mercury in Liquid Waste (Manual Cold-Vapor Technique)*, or Method 7471A, *Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)*. The samples discussed in this report were prepared for mercury analysis by the

microwave technique discussed in section 3.1, the sample preparation specified in the mercury methods (7470A and 7471A) were not used.

The level of radioactivity in most LLLW tank samples required that the analytical systems used for metal measurements be modified for operation in a radiochemical hood or glove box. Custom instrument configurations are necessary to ensure contamination control and worker safety. All work was performed in radiochemical laboratories which are operated under strict radiation protection programs, with the use of protective clothing and routine contamination monitoring. Both an ICP-AES system and a GFAA system can generate dry, dusty particles which are difficult to contain and are highly hazardous when radioactive. A detailed description of the RMAL setup for these instruments are given in Appendix B of Reference 4.

The instrument detection limits (IDL) for various metals with undiluted aqueous samples are listed in data tables along with the results. For sludge samples, these detection limits must be increased by a factor that represents the dilution that results from the sample preparation. For all the BVEST sludge samples approximately 0.5 g of sample was digested and then diluted to 50 mL which results in about a 100 fold dilution for the sample, and thus a 100 fold increase in the detection limits.

The analytical error for the metal measurements depends upon the analytical method, the concentration level, and the chemical matrix. Inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) are both multi-element measurement techniques that are designed for the best average performance for all elements analyzed. In general, these measurement techniques are not optimized for any single element. The sample introduction system for ICP instruments adds additional variability due to changes in sample density, viscosity, and solids content between samples and/or calibration standards. Overall, the expected analytical error for ICP measurements range from $\pm 4-6\%$ at concentrations above 10 times the detection limit to $\pm 20-50\%$ near the detection limit. These error estimates are typical for both ICP-AES and ICP-MS measurements.

Graphite Furnace AA instruments are generally optimized for a specific element and usually provide lower detection limits and better precision. The expected analytical error for GFAA measurements

range from 3-5% for concentrations greater than 10 times the detection limit to 20-40% near the detection limit. One advantage of GFAA analysis is that the measurements are normally well above the method's detection limits. The mercury measurements were done by Cold Vapor Atomic Absorption (CVAA), which is very selective and sensitive for mercury. The analytical errors for CVAA measurements are similar to GFAA work.

3.3 Anion Analysis

The determination of the inorganic anions was needed for the development of process treatment options, to provide information to explain the distribution and chemical behaviors observed in the waste tanks, and to ensure the major chemical constituents were identified in the waste for which data was used to calculate the mass and charge balance for each sample. The common inorganic anions; including fluoride, chloride, bromide, phosphate, nitrate, nitrite, and sulfate; were measured by ion chromatography (IC) with a Dionex Model 4500i system. In addition, several water soluble organic acids were measured along with the inorganic anions. These organic acids were measured in their ionized form and included formate, acetate, citrate, and oxalate. Both the citrate and the oxalate can form strong complexes with many metals and change the solution chemistry of these metals in the waste. The ion chromatography system used for measurements on these radioactive samples was configured such that the components that come into contact with radioactivity were isolated in a radiochemical hood for contamination control.

From past observations, the nitrate content usually dominates both the mass and charge balance calculations with both the supernatant and sludge samples taken from the active LLLW tanks. There are many other anions present in the waste, some of which are measured directly by ion chromatography and others which can be estimated from the metal data such as chromate, dichromate, permanganate, and others. The carbonate is estimated from the total inorganic carbon measurement.

The liquid samples were always analyzed directly by ion chromatography after an appropriate dilution with water. Accounting for the mass and charge balance with the aqueous samples requires less assumptions about the solution chemistry compared to the precipitation chemistry for

the sludge samples. The mass/charge balance checks for aqueous samples should agree within the analytical error (approximately $\pm 10\%$) of the measurements. The performance of balance checks for sludge samples is not expected to be as good as the liquid samples because of the large content of mixed oxides, hydrated hydroxides (heavy metals and actinides), and insoluble carbonates (calcium carbonate, etc.) present in the sludge. The complex precipitation chemistry of the sludge complicates the measurements of total anions and makes estimates for the mass and charge balance more difficult. Analytical techniques such as x-ray fluorescence (XRF) are useful for solid samples but are limited to total element measurements (total sulfur vs. sulfate, total phosphorus vs. phosphate). Another technique, x-ray diffraction (XRD), is useful for the identification of compounds present but only provides qualitative information such as the determination of crystal structures. For this report, the primary sludge anion data is based on a water leach which represents the sum of the anions in the interstitial liquid and the water soluble anions from the solids. For these measurements the sludge samples were prepared by adding approximately 1 gram of sludge to 10 mL of water, mixing for several minutes at room temperature on a vortex mixer, and separating the solids. The resulting solution was analyzed by ion chromatography and the anion concentration was normalized back to the wet weight of the sludge.

Based on conversations with chemists from the Savannah River Site (SRS) and the Hanford site, who have been involved with similar waste characterization work and the experience over the past five years by the RMAL laboratory, the water leach preparation of the caustic sludge samples provides the best total anion data for the halides, nitrites, nitrates, and fair data for sulfate. To resolve questions concerning the total anion content of the sludge an additional sample preparation method was tested on the BVEST sludge samples. The preparation method used was the Parr bomb combustion of the sludge.

Method for Parr Bomb Combustion of Sludges

The procedure used for the bomb combustion is outlined below.

1. Approximately 0.25 g of sludge was weighed into the combustion crucible.
2. 0.5 mL of mineral oil was added to the crucible with the sample.

3. 1 mL of 1 M sodium hydroxide was placed on the bottom of the bomb.
4. The bomb was assembled, charged to 30 atm. with UHP (ultra-high purity) oxygen, and vented. This flush was repeated two more times to remove the nitrogen contribution from air. The bomb was charged to a final pressure of 30 atm with UHP oxygen, placed into a water bath and then the sample was ignited with an electronic spark.
5. The bomb was allowed to stand in the water bath for 4 min. to condense combustion gases.
6. The bomb condensate was rinsed three times into a flask and diluted to 50 mL with water.

The resulting solution was analyzed by ion chromatography for anions.

It is important to note that a bomb combustion preparation of the BVEST sludge samples yields total concentrations of the element measured. An example would be sulfate analysis. A water leach of the sludge will yield a sulfate concentration due to water soluble compounds containing sulfate while a bomb preparation of the sludge would yield a sulfate concentration due not only to the compounds containing sulfates (both water soluble and insoluble) but any compound containing sulfur. In other words the bomb preparations yield a total sulfur concentration rather than a total sulfate concentration. In theory, the same principle applies to any anion determined using the bomb or total dissolution preparation method.

The final anion measurement technique was ion chromatography, no matter which sample preparation method was used. For simple water samples, without complex chemical matrix problems, the empirical analytical error for ion chromatography measurements ranges from 4-6% for concentrations above 10 times the detection limits to 20-40% near the detection limit. The measurement of anions present at concentrations much lower ($< 1/25$) than other anionic species present may increase the overall error of the measurement.

3.4 Radiochemical Analysis

The only standard radiochemical methods useful for radioactive waste characterization are EPA Method 600/900.0, *Gross Alpha and Beta Radioactivity in Drinking Water*, and EPA Method

600/901.1: *Gamma Emitting Radionuclides in Drinking Water*. The EPA Method 600/905.0, *Radioactive Strontium in Drinking Water*, gave poor performance with the chemical matrix found in ORNL LLLW supernatant and sludge samples. The EPA method for gross alpha/beta measurements uses gas-flow proportional counting. In general, this counting technique requires drying a sample at elevated temperatures onto a metal (usually stainless steel) plate, which resulted in the loss of cesium chloride and other volatile radionuclides such as ^3H , ^{14}C , ^{99}Tc , ^{106}Ru , and ^{129}I , which resulted in poor gross beta measurements for the ORNL waste samples. To avoid this problem, all gross beta measurements reported are based on measurements by liquid scintillation counting. Other than the gamma spectroscopy measurements, all of the radionuclide measurements were done with in-house procedures. The method detection limits for radiochemical measurements are dependent on both sample matrix and count time and are not listed here. In general, the radiochemical measurements used count times to yield at least 1% (10,000 counts) counting statistics. The expected errors for the radiochemical data range from $\pm 5\text{-}10\%$ for gross alpha/beta and gamma emitter measurements to $\pm 10\text{-}20\%$ for radionuclides that require chemical separations before counting (i.e. ^{99}Tc , ^{90}Sr , ^{129}I , and ^{237}Np).

The long-lived fission products are typically more difficult and expensive to measure than short-lived fission products. Many of these long-lived radionuclides are either pure beta emitters or have weak, low energy, and/or low yield gamma-rays which are not very useful for accurate analytical measurements. In general, good radiochemical data requires that each of these isotopes be chemically separated from all other radioactivity prior to measurement. These chemical separations and measurements are currently being done routinely for ^{99}Tc and ^{129}I because both can exist as anionic species (TcO_4^- , I^- , and IO_3^-) in the waste, and these anions would be highly mobile in the environment. The ^{99}Tc is currently being separated by extraction chromatography and measured by ICP-MS which is much more sensitive than counting techniques for radionuclides with a low specific activity. The ^{129}I is first extracted into carbon tetrachloride as iodine (I_2), then reduced to iodide (I^-), back-extracted into an aqueous matrix, and loaded onto an anion exchange resin. The ^{129}I is then determined by neutron activation analysis. Typically the level of ^{99}Tc and ^{129}I in the waste is lower than expected from the fission yields, and one possible explanation is that both isotopes may have been volatilized as HTcO_4 , HI , and I_2 when exposed to either acid and/or heat in the past.

The long-lived fission products are a very small fraction of the overall activity present in the waste, and there has been little interest in the measurement of these radionuclides in the past. The determination of these isotopes are less routine and are frequently more expensive methods to perform. The judgement of most waste characterization teams has been that the measurement of these radionuclides, with the exception of ^{99}Tc , would be interesting but there is insufficient risk to justify the analytical cost.

3.5 Criticality Controls

At the time samples were collected for this project, the ORNL waste acceptance criteria (WAC) for liquid-low level waste required that the fissile isotopes of uranium and plutonium be isotopically diluted with ^{238}U and ^{232}Th , respectively. These administrative controls also required that the ratio of the ^{238}U mass divided by the fissile equivalent mass (FEM) for uranium be greater than 100. The ^{235}U FEM is a useful scale for criticality calculations that normalizes the fission probability for each fissile isotope to ^{235}U . These FEM factors, designated as f_{35} for ^{235}U mass factors, are discussed and listed in the Appendix A, Table 1 of ORNL Procedure NCS-1.0, *Nuclear Criticality Safety Program*.

The major fissile isotopes of concern in the ORNL waste tanks are ^{233}U , ^{235}U , and ^{239}Pu . The fissile isotope ^{241}Pu is also present in the waste, but the mass is usually several orders of magnitude lower and below a level that would influence the isotopic dilution ratio for plutonium. Other fissile isotopes present in the ORNL waste include isotopes of neptunium, americium, and curium, but the actual mass present in the waste has been too low for major concern, and the low concentration would make it difficult and expensive to measure by mass spectrometry.

The data presented in this report for isotopic dilution ratios (also referred to as denature ratios) reflect both the past and current ORNL standard practices for disposal of fissile isotopes of uranium and plutonium. The administrative controls which were in effect when the waste was generated, required that the ^{233}U and ^{235}U be diluted with depleted uranium such that the following condition was true,

$$\frac{(^{238}\text{U})}{(1.35)(^{233}\text{U}) + (^{235}\text{U})} \geq 100 \quad (1)$$

Because thorium chemistry is more similar to plutonium than uranium chemistry, the administrative procedures required that the ^{239}Pu be diluted with ^{232}Th as follows,

$$\frac{(^{232}\text{Th})}{(^{239}\text{Pu})} \geq 100 \quad (2)$$

All calculations dealing with isotopic dilution for criticality safety are based on isotope mass ratios and must not be confused with activity ratios. For any data discussed in this report that uses ^{232}Th relative to isotopic mass ratios, the total thorium concentration and the ^{232}Th concentration are the same value.

The new requirements for administrative criticality control, which were scheduled to be in effect by the end of 1996, are more conservative and require that the following conditions be satisfied for uranium,

$$\frac{(^{238}\text{U}) - 200(^{233}\text{U})}{(^{235}\text{U})} \geq 110 \quad (3)$$

$$\frac{(^{238}\text{U}) - 100(^{235}\text{U})}{(^{233}\text{U})} \geq 200 \quad (4)$$

The new administrative controls also change requirements for plutonium by increasing the ratio of thorium to plutonium, as given in eq. 2, from a dilution ratio of 100 to a ratio of 200.

3.6 Organic Analysis

The organic sample preparation and analysis methods were based on SW-846 methods which had been adapted for radioactive samples. The performance of these methods had been demonstrated according to the Transuranic Waste Characterization Program (TWCP) Quality Assurance Program Plan (QAPP)¹⁰ requirements. The amounts of sample extracted and analyzed for this project were limited to ensure contamination control and good ALARA practices. In general, it was not necessary to reduce the sensitivities of the volatile organic compound analysis (VOA), the non-halogenated volatile organic compound analysis (NHVOA), the semivolatile organic compound analysis (SVOA), or the polychlorinated biphenyls (PCB) analysis to meet sampling handling requirements due to the radioactivity.

3.6.1 Non-halogenated Volatile Organic Analysis (NHVOA)

The NHVOA measurements were done by SW-846 Method 8015A, *Nonhalogenated Volatile Organics by Gas Chromatography*. One gram of sludge or one milliliter of supernatant was extracted by shaking with 1 mL of water. This extraction was reduced two-fold from the method used in the TWCP, but it retained the same method detection limit (MDL) because the relative proportions of sample and solvent were not changed. A volume of 0.001 mL of the extract was injected onto each of two gas chromatography columns, and the organic compounds were detected by flame ionization and quantified using the method of external standards. A surrogate standard was added to all samples and quality control samples. The latter included a laboratory blank, matrix spike (MS) and spike duplicate (MSD) samples, and a laboratory control sample (LCS).

3.6.2 Volatile Organic Analysis (VOA)

The VOA measurements were done by SW-846 Method 8260A, *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique*. For sludge samples 1 g of solids was extracted by shaking with 1 mL of methanol. A 0.05 mL aliquot of the extract was added to 5 mL of water and was subjected to purge and trap gas chromatography-mass spectrometry (GC-MS). For the supernatant samples, the purge and trap GC-MS was done directly on 5 mL of each sample. Quantitation was by the method of internal standards. Surrogate standards

were added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

3.6.3 Semivolatile Organic Analysis

The SVOA measurements included SW-846 Method 3550A, *Ultrasonic Extraction*, for sample preparation, and SW-846 Method 8270B, *Semivolatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS): Capillary Column Technique*, for sample analysis. For sludge samples, 10 g of solids were mixed with sodium sulfate until a free-flowing matrix was obtained, and the mixture was extracted with 100 mL of methylene chloride using an ultrasonic bath. For supernatant samples, 200 mL of liquid was extracted with 100 mL of methylene chloride according to SW-846 Method 3510, *Separatory Funnel Liquid-Liquid Extraction*. The methylene chloride was concentrated to 1 mL, and the extract was analyzed by GC-MS using the method of internal standards. Surrogate standards were added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

3.6.4 Polychlorinated Biphenyls

The PCB measurements included SW-846 Method 3550A, *Ultrasonic Extraction* and Method 3665, *Sulfuric Acid/Permanganate Cleanup*, for sample preparation, and Method 8081, *Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique*, for sample analysis. A fraction of the SVOA methylene chloride extract was used for the PCB sample preparation. The extract was concentrated and solvent-exchanged into hexane, washed with sulfuric acid until the acid washes were colorless and did not contain precipitates, washed with water to remove excess acid, combined with a hexane back-extract of the acid washes, and then were concentrated to 1 mL. Analysis was conducted on a dual capillary column GC equipped with dual electron capture detectors using the method of external standards. A surrogate standard was added to all samples and quality control samples. The latter included a laboratory blank, MS and MSD, and a LCS.

4.0 Quality Assurance

Both the inorganic and organic chemical characterization of the BVEST samples followed the method requirements and Data Quality Objectives (DQO) of the TWCP QAPP. The RMAL implements the TWCP QAPP with a flow down RMAL Quality Assurance Project Plan (QAPjP)¹¹ and implementation procedures. The list of metals determined was expanded from the TWCP requirements to meet ORNL needs. Although the organic target compounds were those listed in the TWCP QAPP, the full set of semivolatile and volatile organic compounds for the EPA Contract Laboratory Program Target Compound List (TCL) were reported as Tentatively Identified Compounds (TIC), if they were detected in the samples.

Quality assurance during the sampling activities was primarily addressed by the use of approved procedures for sampling both the liquid and sludge phase found in each waste tank. These procedures provide detailed instructions for the collection, labeling, and shipping of each sample. Chain-of-custody forms were used to track individual samples from their collection point to the analytical laboratory.

The RMAL also operates under a Radioactive Waste Characterization QA Plan¹² which, in conjunction with the TWCP QAPjP, defines the basis for quality assurance and quality control used for the analysis of the waste tank samples. The QA plans discuss staff qualification requirements, laboratory participation in performance demonstration programs, quality control acceptance criteria for analytical methods, sample management, and most other laboratory operations. The set of QA plans implemented for RMAL waste characterization meet both the WIPP and the Nevada Test Site (NTS) QA requirements for inorganic, organic, and radiochemical measurements.

5.0 Summary of Inorganic and Radiochemical Analytical Results

5.1 Description of Data Tables

A summary of the inorganic and radiochemical analytical results are presented in Table 3 for the BVEST supernatant samples, and the data for BVEST sludge samples are presented in Table 4. These tables are arranged in a similar format to facilitate comparing data from different tanks and to group information into useful units. The analytical data presented in these tables are the consolidation of data from a single project which had a fixed set of analytical requirements. Any parameter reported with a dash ("-") indicates that the data was not measured for that sample.

The first section, "Physical properties and miscellaneous data", includes information that does not fit well into other table groups. The first parameters entered in a column include the RMAL request and sample numbers, which are laboratory filing codes used to track sample information. The next set of data includes information on the moisture or water content and the solids content of the sample. The group is completed with data on the inorganic and organic carbon content. For BVEST waste tank samples the inorganic carbon can be assumed to be all carbonate and bicarbonate. The Total Organic Carbon (TOC) provides an upper limit on the organic content in the tank waste and current methods include volatile organic compounds. Most of the liquid waste in the active system has been through an evaporator which removes the highly volatile organic compounds from the waste. It should be noted that W-22 is the collection tank for all LLLW generated in the plant and is the feed to the evaporator. Therefore, it is likely the liquid waste in W-22 has not been through an evaporator.

The next two sections include groups of metals; the "RCRA metals" are separated out for quick reference. The regulatory limit for the concentrations are listed in parentheses next to each RCRA metal. For the liquid samples, the RCRA regulatory limits are used directly, since the supernatant would be defined as the TCLP leachate in the determination of waste characteristics for hazardous waste. The RCRA metal sludge data represents total metal measurements, as defined by EPA. Exceeding the RCRA regulatory limits listed for the sludge samples only indicates that the waste has

the potential to be classified as hazardous. The sludge waste should only be classified as RCRA waste if the final waste form fails the TCLP leaching test.

The remaining metals are grouped under "Process metals", which includes the common Group IA & IIA metals along with elements that could effect chemical processing, criticality concerns, and stabilization techniques such as grouting or vitrification. For the sludge data, all the metals are reported on an "as received" (wet weight) basis.

The section "Semi-quantitative metals by ICP-MS" includes additional metals identified in a full mass range scan by inductively coupled plasma - mass spectrometry. This measurement helps ensure all major elements have been identified in the waste. Each element reported is quantified based upon a response factor from a curve generated from a few elements across the mass range, verses quantification based upon calibration with each element of interest. Therefore, these elemental concentrations are listed as estimates only.

The "Calculated Alkalinity" and the "Anions by ion chromatography" sections are separate for the supernatant samples, but are combined for the sludge samples. For supernatant samples the pH is measured directly, and the anions are determined on the liquid samples after dilution with water. The pH and anions reported for the sludge samples are based on a water wash of the sludge, as discussed in section 3.3. Along with the inorganic anions, several water soluble organic acids are reported, which includes compounds classified as complexing agents such as citrate and oxalate.

The "Beta/gamma emitters" section summarizes the radionuclides that emit gamma-rays and beta particles. This section includes the gross beta activity, radionuclides identified by gamma spectrometry, and several "pure" beta emitters of interest. Many of the "pure" beta emitters (^3H , ^{14}C , and ^{90}Sr) require radiochemical separations prior to measurement by either liquid scintillation or gas-flow proportional counting. The ^{99}Tc was measured by ICP-MS without any prior chemical separation, and the ^{151}Sm was estimated by ICP-MS after a lanthanide group separation.

The "Alpha emitters" section summarize the actinide elements in the waste. These section includes the gross alpha activity, an estimate of the activity for each alpha emitter identified in a gross alpha spectrum, and plutonium isotopes determined by alpha spectrometry after a radiochemical separation. For supernatant samples, an estimate of the $^{232}\text{Th}/^{239}\text{Pu}$ mass ratio is included in this section to address criticality concerns if enough thorium is present to calculate the ratio. For the sludge samples, this mass ratio is included with the plutonium mass spectrometry data.

The remaining sections include "Uranium isotopes by TIMS", "Plutonium isotopes by TIMS", and "Uranium isotopes by ICP-MS". These sections summarize the uranium and plutonium data measured by thermal ionization mass spectrometry and for comparison to the uranium isotopes measured by ICP-MS. Also, included in these sections are the isotopic mass dilution or "denature" ratios for uranium and plutonium based on the requirements in place when the waste was generated (see section 3.5). The plutonium section for the sludge samples also includes the activity for each plutonium isotope, which was calculated from the mass spectrometry data.

Table 3 Analytical Data for Liquids in Tanks W-21, W-22, and W-23

Characteristic (Analysis)	W-21 L	W-22 L	W-23 L	IDL ⁱ
Physical properties and miscellaneous data				
Request number	7772B	7772C	7772A	-
Sample number	960923-013	960923-014	960905-167	-
TDS ^a (mg/mL)	410	3.5	530	-
TSS ^b (mg/mL)	< 1	< 1	< 1	-
Density (g/mL)	1.27	1.01	1.34	-
TC ^c (mg/L)	544	481	11700	15
TIC ^d (mg/L)	11.5	414	9390	15
TOC ^e (mg/L)	533	67.0	2310	15
RCRA Metals ($\pm 10\%$)				
Ag ^f (5) ^g (mg/L)	< 0.2	< 0.2	< 0.2	0.005
As (5) (mg/L)	< 0.09	< 0.09	0.676	0.005
Ba (100) (mg/L)	60.3	< 0.02	0.461	0.001
Cd (1) (mg/L)	7.78	< 0.02	8.77	0.006
Cr (5) (mg/L)	57.0	0.100	12.4	0.004
Hg (0.2) (mg/L)	1.30	-	0.312	0.0002
Ni (50) (mg/L)	21.8	1.05	13.7	0.009
Pb (5) (mg/L)	43.2	< 0.09	11.4	0.005
Se (1) (mg/L)	< 0.09	< 0.09	< 0.092	0.005
Tl (0.9) (mg/L)	< 0.09	< 0.09	< 0.092	0.005
Process metals ($\pm 10\%$)				
Al (mg/L)	299	< 0.3	5.74	0.02
B (mg/L)	2.01	0.351	8.65	0.012
Be (mg/L)	0.481	< 0.01	0.0601	0.0009
Ca (mg/L)	34500	32.3	111	0.01
Co (mg/L)	0.291	< 0.19	0.551	0.007
Cs ^h (mg/L)	0.525	-	0.452	0.005
Cu (mg/L)	11.6	0.140	13.7	0.002
Fe (mg/L)	532	< 0.04	< 0.04	0.003
K (mg/L)	6810	180	51300	0.08
Mg (mg/L)	3560	10.0	0.471	0.020
Mn (mg/L)	31.9	1.03	0.0701	0.0009
Na (mg/L)	52200	665	126000	0.02
P (mg/L)	239	58.4	567	0.02
Sb (mg/L)	< 2	< 2	12.3	0.13
Si ⁱ (mg/L)	52.3	4.40	25.1	0.013
Sr (mg/L)	235	0.220	1.00	0.0003
Th (mg/L)	507	0.591	< 0.5	0.04
U (mg/L)	4030	67.0	148	0.07
V (mg/L)	0.501	< 0.1	0.130	0.02
Zn (mg/L)	168	1.29	78.7	0.02

Characteristic (Analysis)	W-21 L	W-22 L	W-23 L	IDL ¹
Semi-quantitative metals by ICP-MS (±30-50 %)				
Bi, bismuth (mg/L)	2.8	1.3	0.14	-
Ce, cerium (mg/L)	2.8	< 0.001	0.43	-
Ga, gallium (mg/L)	1.3	< 0.001	0.09	-
I, iodine (mg/L)	8.9	2.7	50	-
La, lanthanum (mg/L)	0.35	< 0.001	0.005	-
Li, lithium (mg/L)	18	8.1	140	-
Mo, molybdenum (mg/L)	1.5	< 0.001	8.22	-
Nb, niobium (mg/L)	0.007	< 0.001	0.001	-
Rb, rubidium (mg/L)	0.97	0.06	4.6	-
Sn, tin (mg/L)	0.070	< 0.001	0.67	-
Ti, titanium (mg/L)	0.32	0.05	0.92	-
W, tungsten (mg/L)	0.16	0.06	2.1	-
Y, yttrium (mg/L)	0.29	< 0.001	< 0.001	-
Zr, zirconium (mg/L)	0.051	< 0.001	< 0.001	-
Calculated Alkalinity				
pH (pH)	0.93	8.92	12.7	-
Hydroxide (mM)	-	-	50.1	-
Carbonate (mM)	-	6.9	157	-
Bicarbonate (mM)	-	-	-	-
Anions by ion chromatography (±10%)				
<u>Inorganic</u>				
Bromide (mg/L)	109	< 12	1390	0.05
Chloride (mg/L)	1170	168	8830	0.05
Chromate (mg/L)	< 50	< 25	< 50	0.01
Fluoride (mg/L)	236	57.9	1210	0.05
Nitrate (mg/L)	204000	< 25	225000	0.10
Nitrate (M)	3.29	< 0.001	3.63	-
Nitrite (mg/L)	< 31	< 12	17300	0.10
Phosphate (mg/L)	< 50	169	675	0.20
Sulphate (mg/L)	1400	153	10600	0.10
<u>Organic</u>				
Acetate (mg/L)	127	< 12	303	-
Citrate (mg/L)	< 50	< 25	1480	-
Formate (mg/L)	< 25	< 12	643	-
Oxalate (mg/L)	34	< 12	1120	-
Phthalate (mg/L)	< 50	< 25	< 50	-
Beta/gamma emitters (±10%)				
Gross beta (Bq/mL)	6.1e+05	1.9e+04	1.4e+06	-
⁶⁰ Co (Bq/mL)	7.9e+03	3.2e+02	2.2e+03	-
⁹⁰ Sr/ ⁹⁰ Y (Bq/mL)	8.7e+04	3.2e+02	4.1e+03	-
⁹⁹ Tc (Bq/mL)	4.9e+02	< 1.2e+01	3.7e+03	-
¹⁰⁶ Ru/ ¹⁰⁶ Rh (Bq/mL)	-	5.8e+03	-	-
¹²⁹ I (Bq/mL)	-	-	-	-
¹³⁴ Cs (Bq/mL)	3.2e+03	2.3e+03	3.1e+04	-
¹³⁷ Cs (Bq/mL)	9.5e+04	3.6e+03	1.1e+06	-
¹⁵² Eu (Bq/mL)	1.9e+05	< 5.7e+01	< 8.9e+02	-
¹⁵⁴ Eu (Bq/mL)	7.7e+04	< 1.8e+01	< 5.3e+02	-
¹⁵⁵ Eu (Bq/mL)	2.1e+04	< 6.4e+01	< 1.9e+03	-

Characteristic (Analysis)		W-21 L	W-22 L	W-23 L	IDL ⁱ
Alpha emitters (±10%)					
<u>Gross alpha</u> (Bq/mL)		21000	52	430	-
²⁴⁴ Cm (Bq/mL)		18000	41	360	-
²⁴¹ Am (Bq/mL)		1500	-	-	-
<u>Total Pu alpha</u> (Bq/mL)		180	0.13	25	-
²³⁸ Pu (Bq/mL)		99	-	19	-
²³⁹ Pu/ ²⁴⁰ Pu (Bq/mL)		69	-	6	-
²⁴² Pu (Bq/mL)		6.9	-	< 0.1	-
Uranium isotopics by TIMS (±0.5%)					
²³³ U (atom %)		0.128	0.042	0.073	0.01
²³⁴ U (atom %)		0.003	0.005	0.004	0.01
²³⁵ U (atom %)		0.254	0.604	0.481	0.01
²³⁶ U (atom %)		0.006	0.005	0.005	0.01
²³⁸ U (atom %)		99.609	99.344	99.437	0.01
²³³ U/MS (ng/mL)		5.05	0.028	0.11	-
²³⁵ U/MS (ng/mL)		10.1	0.40	0.70	-
²³⁸ U/ ²³⁵ U FEM		237	152	174	-
U activity					
²³³ U (Bq/mL)		1800	9.8	38	-
²³⁴ U (Bq/mL)		27	0.8	1.3	-
²³⁵ U (Bq/mL)		0.7	< 0.1	< 0.1	-
²³⁶ U (Bq/mL)		0.6	< 0.1	< 0.1	-
²³⁸ U (Bq/mL)		50	0.8	1.8	-
Plutonium isotopics by TIMS (±1%)					
²³⁸ Pu (atom %)		< 0.716	-	< 2.068	-
²³⁹ Pu (atom %)		76.736	-	76.773	-
²⁴⁰ Pu (atom %)		21.012	-	19.252	-
²⁴¹ Pu (atom %)		0.687	-	0.823	-
²⁴² Pu (atom %)		0.848	-	1.084	-
²⁴⁴ Pu (atom %)		< 0.001	-	< 0.001	-
Pu activity					
²³⁸ Pu (Bq/mL)		100	-	20	-
²³⁹ Pu (Bq/mL)		39	-	2.7	-
²⁴⁰ Pu (Bq/mL)		40	-	2.5	-
²⁴¹ Pu (Bq/mL)		590	-	48	-
²⁴² Pu (Bq/mL)		< 0.1	-	< 0.1	-
²⁴⁴ Pu (Bq/mL)		< 0.1	-	< 0.1	-
(²³⁹ Pu) (ng/mL)		17.2	< 1.5	1.17	-
²³² Th/ ²³⁹ Pu		29600	10400	428	-
(a) Total solids, (b) TSS is zero because suspended solids were removed prior to analysis, (c) Total carbon, (d) Total inorganic carbon, (e) Total organic carbon, (f) nitric-hydrochloric acid prep., (g) RCRA regulatory limits, (h) measured by ICP-MS, (i) nitric-hydrofluoric acid prep., (j) Instrument detection limits.					

Table 4 Analytical Data for Sludge in Tanks W-21, W-22, and W-23

Characteristic (Analysis)	W-21 S	W-22 S	W-23 S	IDLJ
Physical properties and miscellaneous data				
Request number	7835A	7835B	7835C	-
Sample number	960930-015	961008-056	961011-016	-
pH	7.7	11.3	12.3	-
Water ^a (%)	50.9	71.0	44.8	-
TS ^b (mg/g)	491	290	552	-
Bulk density (g/mL)	1.36	1.16	1.57	-
TC ^c (mg/Kg)	25000	40500	21700	15
TIC ^d (mg/Kg)	7400	8000	17000	15
TOC ^e (mg/Kg)	17600	32500	4700	15
RCRA Metals (±10%)				
Ag ^f (100) ^g (mg/Kg)	22.4	31.7	19.9	0.005
As (100) (mg/Kg)	< 4.8	< 5.4	< 5.5	0.005
Ba (2000) (mg/Kg)	82.2	80.4	77.3	0.001
Cd (20) (mg/Kg)	38.0	28.9	33.3	0.006
Cr (100) (mg/Kg)	229	132	194	0.004
Hg (4) (mg/Kg)	23.8	72.4	25.7	0.0002
Ni (1000) (mg/Kg)	104	49.8	142	0.009
Pb (100) (mg/Kg)	394	427	1200	0.005
Se (20) (mg/Kg)	< 4.8	< 5.4	< 5.5	0.005
Tl (18) (mg/Kg)	< 4.8	< 5.4	< 5.5	0.005
Process metals (±10%)				
Al (mg/Kg)	1230	2100	1740	0.02
B (mg/Kg)	20.0	4.78	5.98	0.012
Be (mg/Kg)	2.19	3.80	2.79	0.0009
Ca (mg/Kg)	68300	43500	63200	0.01
Co (mg/Kg)	4.30	3.80	9.77	0.007
Cu (mg/Kg)	83.0	31.3	37.8	0.002
Cs ^h (mg/Kg)	< 0.53	< 0.59	1.01	0.005
Fe (mg/Kg)	2980	3090	2020	0.003
K (mg/Kg)	11500	3260	20500	0.08
Mg (mg/Kg)	11500	5110	14500	0.020
Mn (mg/Kg)	173	784	937	0.0009
Na (mg/Kg)	44000	10000	75500	0.02
P (mg/Kg)	3550	10400	3570	0.02
Sb (mg/Kg)	< 4.8	< 5.4	< 5.5	0.13
Si ⁱ (mg/Kg)	3900	5290	3530	0.013
Sr (mg/Kg)	266	175	473	0.0003
Th (mg/Kg)	8650	9580	29600	0.04
U (mg/Kg)	26300	35600	7990	0.07
V (mg/Kg)	3.51	3.61	2.99	0.02
Zn (mg/Kg)	801	1060	588	0.02

Characteristic (Analysis)	W-21 S	W-22 S	W-23 S	IDU
Semi-quantitative metals by ICP-MS (±30-50 %, * indicates data from water leach)				
Au, gold (mg/Kg)	0.70	< 0.001	0.25	-
Bi, bismuth (mg/Kg)	4.6	53	13	-
Ce, cerium (mg/Kg)	1.0	59	13	-
Er, erbium (mg/Kg)	< 0.001	0.34	0.29	-
Eu, europium (mg/Kg)	0.44	1.8	1.4	-
Ga, gallium (mg/Kg)	0.56	3.2	5.2	-
Gd, gadolinium (mg/Kg)	2.7	8.9	5.4	-
Ho, holmium (mg/Kg)	0.31	0.41	0.11	-
I, iodine (mg/Kg)	< 0.001	< 0.001	< 0.001	-
La, lanthanum (mg/Kg)	0.54	3.5	3.3	-
Li, lithium (mg/Kg)	230	37	260	-
Mo, molybdenum (mg/Kg)	* 49	* 7.8	* 0.54	-
Nb, niobium (mg/Kg)	0.077	0.90	0.42	-
Rb, rubidium (mg/Kg)	* 34	* 8.8	* 5.1	-
Sn, tin (mg/Kg)	4.1	25	13	-
Ti, titanium (mg/Kg)	< 0.001	< 0.001	< 0.001	-
W, tungsten (mg/Kg)	0.97	3.0	1.5	-
Zr, zirconium (mg/Kg)	1.3	10	7.1	-
Anions by ion chromatography in water wash of sludge (±10%)				
Inorganic				
Bromide (mg/Kg)	96.8	25.2	362	0.05
Chloride (mg/Kg)	1370	249	3420	0.05
Chromate (mg/Kg)	< 10	12.6	16.2	0.01
Fluoride (mg/Kg)	23.3	20.5	149	0.05
Nitrate (mg/Kg)	158000	6930	109000	0.10
Nitrite (mg/Kg)	1180	480	6290	0.10
Phosphate (mg/Kg)	< 10	< 10	< 10	0.20
Sulphate (mg/Kg)	6030	191	3850	0.10
Organic				
Acetate (mg/Kg)	67.3	26.7	386	-
Citrate (mg/Kg)	< 10	36.8	61.9	-
Formate (mg/Kg)	123	48.3	215	-
Oxalate (mg/Kg)	21.3	92.5	5510	-
Phthalate (mg/Kg)	< 10	< 10	< 10	-
Beta/gamma emitters (±10%)				
Gross beta				
⁵⁹ Ni (Bq/g)	3.1e+06	3.9e+06	1.1e+07	-
⁶³ Ni (Bq/g)	< 1.0e+02	< 5.1e+01	< 6.6e+01	-
⁶³ Ni (Bq/g)	1.3e+04	6.7e+03	8.6e+03	-
⁶⁰ Co (Bq/g)	5.1e+04	3.8e+04	3.0e+04	-
⁹⁰ Sr/ ⁹⁰ Y (Bq/g)	5.8e+05	8.6e+05	4.6e+06	-
⁹⁹ Tc (Bq/g)	2.9e+02	3.4e+01	1.5e+03	-
¹⁰⁶ Ru/ ¹⁰⁶ Rh (Bq/g)	-	3.7e+04	-	-
¹²⁹ I (Bq/g)	-	-	-	-
¹³⁴ Cs (Bq/g)	< 3.0e+03	7.2e+03	5.6e+03	-
¹³⁷ Cs (Bq/g)	1.6e+05	2.7e+05	4.0e+05	-
¹⁵¹ Sm (Bq/g)	-	-	-	-
¹⁵² Eu (Bq/g)	9.3e+05	9.0e+05	2.2e+05	-
¹⁵⁴ Eu (Bq/g)	3.3e+05	3.3e+05	9.9e+04	-
¹⁵⁵ Eu (Bq/g)	9.0e+04	7.4e+04	2.9e+04	-
²²⁷ Ac (Bq/g)	< 1.7e+04	< 1.9e+04	< 1.4e+04	-
²⁴¹ Pu (Bq/g)	1.0e+05	7.7e+04	1.6e+05	-

Characteristic (Analysis)		W-21 S	W-22 S	W-23 S	IDL
Alpha emitters (±10%)					
<u>Gross alpha</u>	(Bq/g)	150000	150000	440000	-
²³² Th	(Bq/g)	35	39	120	-
²³³ U	(Bq/g)	8500	5600	7300	-
²³⁴ U	(Bq/g)	120	160	130	-
²³⁵ U	(Bq/g)	4.7	6.4	2.5	-
²³⁸ U	(Bq/g)	330	440	99	-
²³⁷ Np	(Bq/g)	56	4	8	-
²⁴¹ Am	(Bq/g)	12000	12000	33000	-
²⁴⁴ Cm	(Bq/g)	100000	100000	330000	-
²⁵⁰ Cf	(Bq/g)	< 100	< 100	< 100	-
²⁵² Cf	(Bq/g)	< 100	< 100	< 100	-
<u>Total Pu alpha</u>	(Bq/g)	26000	30000	67000	-
²³⁸ Pu	(Bq/g)	15000	19000	49000	-
²³⁹ Pu/ ²⁴⁰ Pu	(Bq/g)	11000	11000	18000	-
²⁴² Pu	(Bq/g)	-	-	-	-
<u>TRU activity</u>					
Pu+Am (3700)	(Bq/g)	38000	42000	100000	-
Uranium isotopics by TIMS (±0.5%)					
²³³ U	(atom %)	0.093	0.045	0.261	0.001
²³⁴ U	(atom %)	0.002	0.002	0.007	0.001
²³⁵ U	(atom %)	0.253	0.255	0.448	0.001
²³⁶ U	(atom %)	0.005	0.005	0.018	0.001
²³⁸ U	(atom %)	99.647	99.693	99.266	0.001
²³³ U/MS	(mg/Kg)	23.9	15.7	20.4	-
²³⁵ U/MS	(mg/Kg)	65.7	89.6	35.3	-
²³⁸ U/ ²³⁵ U FEM	-	267	320	126	-
Uranium isotopics by ICP-MS (±2%)					
²³³ U	(atom %)	0.106	0.051	0.291	0.001
²³⁴ U	(atom %)	0.003	0.002	0.007	0.001
²³⁵ U	(atom %)	0.288	0.286	0.481	0.001
²³⁶ U	(atom %)	0.006	0.005	0.020	0.001
²³⁸ U	(atom %)	99.598	99.656	99.202	0.001
²³³ U/MS	(mg/Kg)	27.2	17.7	22.8	-
²³⁵ U/MS	(mg/Kg)	74.8	101	38.0	-
²³⁸ U/ ²³⁵ U FEM	-	235	285	116	-

Characteristic (Analysis)	W-21 S	W-22 S	W-23 S	IDL ^j
Plutonium isotopics by TIMS ($\pm 1\%$)				
²³⁸ Pu (atom %)	< 0.684	< 0.884	< 1.335	-
²³⁹ Pu (atom %)	80.888	79.733	81.168	-
²⁴⁰ Pu (atom %)	16.750	17.696	15.918	-
²⁴¹ Pu (atom %)	0.759	0.592	0.711	-
²⁴² Pu (atom %)	0.917	1.094	0.868	-
²⁴⁴ Pu (atom %)	< 0.002	< 0.001	< 0.001	-
Pu activity				
²³⁸ Pu (Bq/g)	15000	19000	49000	-
²³⁹ Pu (Bq/g)	6400	6200	11000	-
²⁴⁰ Pu (Bq/g)	4800	5000	7700	-
²⁴¹ Pu (Bq/g)	100000	77000	160000	-
²⁴² Pu (Bq/g)	4.6	5.4	7.4	-
²⁴⁴ Pu (Bq/g)	< 0.1	< 0.1	< 0.1	-
(²³⁹ Pu) (ng/g)	2770	2690	4680	-
²³² Th/ ²³⁹ Pu	3120	3564	6329	-
(a) Free water content of sludge, (b) Total solids, (c) Total carbon, (d) Total inorganic carbon, (e) Total organic carbon, (f) nitric-hydrochloric acid prep., (g) RCRA regulatory limits, (h) measured by ICP-MS, (i) nitric-hydrofluoric acid prep., (j) Instrument detection limits.				

5.2 Discussion of BVEST Supernatant Characteristics

The analytical data for the BVEST supernatant samples are presented in Table 3. This data is based on samples that were first clarified by centrifugation and then stabilized with nitric acid. Extra care was taken to remove suspended particles from the liquid samples because the particulate material was an artifact of the sampling technique and could bias the liquid phase data. At high pH most of the thorium, uranium and other actinide elements in the ORNL waste tanks form an insoluble hydroxide precipitate. This chemical behavior is usually apparent with the supernatant when the pH is compared to the uranium concentration and the alpha activity.

The Group IA elements, sodium and potassium, are very soluble in the supernatant at any pH. In general, the concentration of Group IIA metals such as calcium and strontium will increase in the supernatant as the pH decreases. These Group IIA metals remain mostly soluble in the liquid phase at high pH, but as carbon dioxide is absorbed into the supernatant from the air, both calcium and strontium form insoluble carbonate compounds. The general distribution of radioactivity in the waste tanks is a function of the pH, where at higher pH the ^{137}Cs dominates the beta activity in the liquid phase and the $^{90}\text{Sr}/^{90}\text{Y}$ is the predominate source of the beta activity in the sludge phase. At high pH, the actinide elements are mostly insoluble which corresponds to most of the alpha activity being concentrated in the sludge phase.

As expected, the concentration of silicon compounds increases in the supernatant as the pH increases. Many of the other common metals found in the waste, such as iron and magnesium, are less soluble as the pH increases. In general, as the pH decreases, the total dissolved solids in the supernatant increases. Figures 1 and 2 illustrate the distribution of major cations and anions in the BVEST liquid samples. Figure 2 is similar to Fig. 1, but with the sodium and nitrate removed to show more detail for species present at lower concentrations.

Figure 1 Distribution of Major Cations and Anions in Liquid Phase

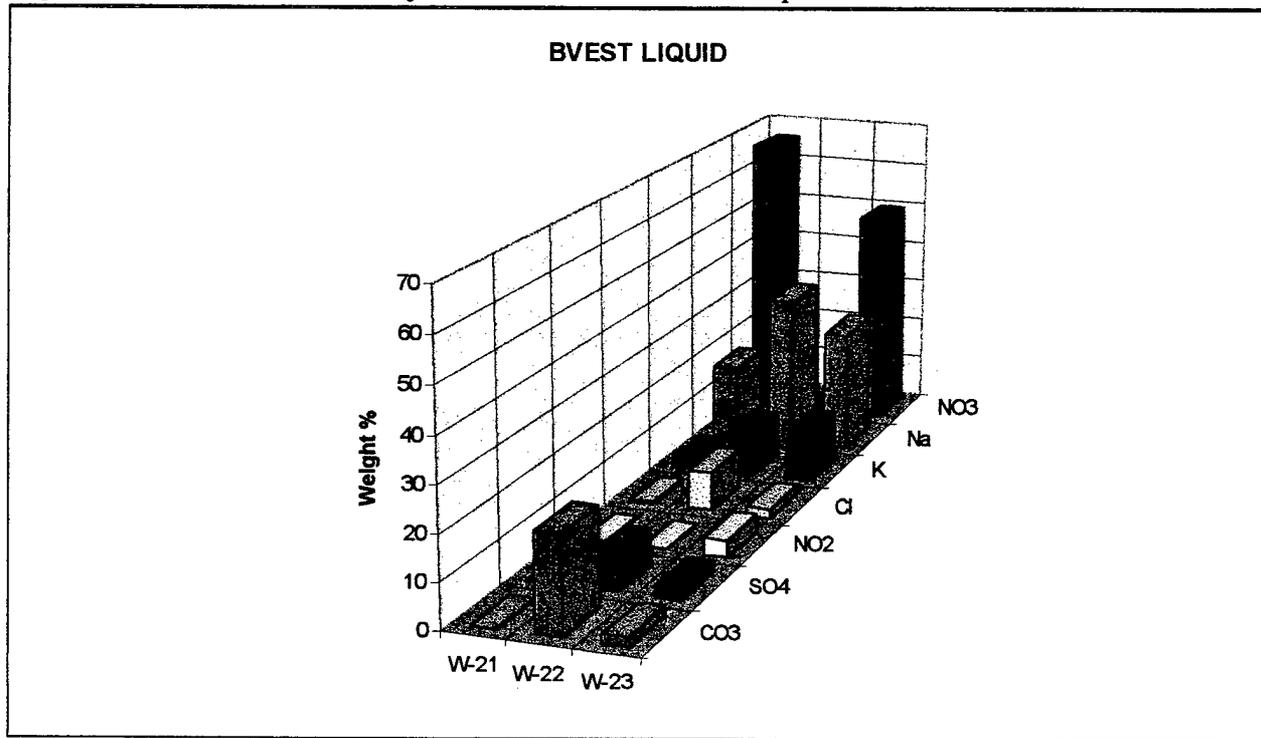
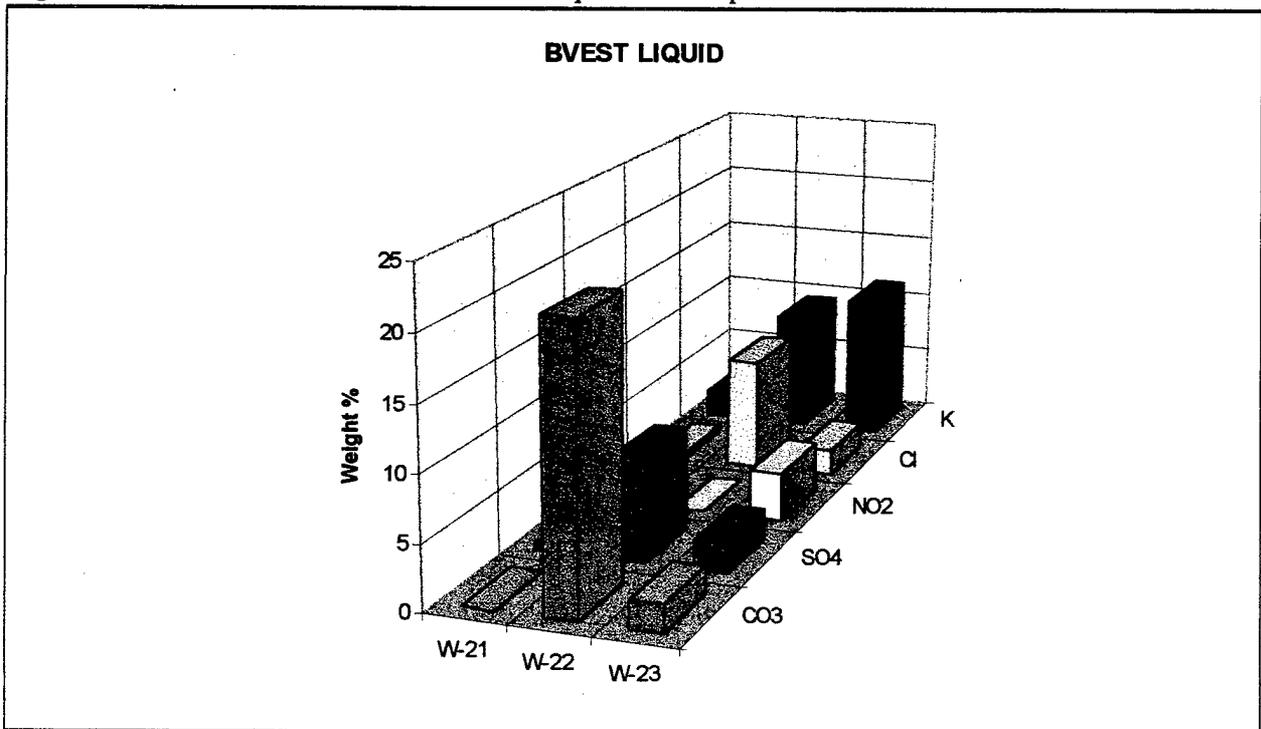


Figure 2 Distribution of Selected Ionic Species in Liquid Phase



The sludge layers in the ORNL waste tanks are typically high in several RCRA metals, including chromium, mercury, and lead. At high pH these RCRA metals are generally below the hazard limits in the supernatant, but as the pH decreases the concentration of these RCRA metals can increase to the point where the regulatory limits are exceeded in the liquid phase.

The mass and charge balance data for the BVEST supernatant samples are summarized in Table 5, and provide a good check for data completeness. The mass balance checks are based on the summation of cation and anion concentrations divided by the total solids concentration. The total solids concentration is measured directly by weighing a known volume of sample that has been dried to a constant weight. The mass balance data indicates a low bias of 15-25% for the liquid samples from W-21 and W-23. The total solids content for W-22 supernatant was very low at the time the sample was collected, which resulted in a large relative error for the mass balance calculation for this tank. In general, the charge balance checks are less accurate than the mass balance check because one must make an assumption about the chemical form and oxidation state for each species present in solution. The charge balance data is based on the summation of the molar cation charge divided by the summation of the molar anion charge. The charge balance data shows fair agreement but with a negative bias ranging from 18-28% for the BVEST liquid samples. The charge balance data is acceptable considering the assumptions required for the calculation.

Table 5 Summary of Quality Checks for BVEST Supernatant Data

Tank	Mass Balance (TS_{calc.}/TS_{meas.})	Charge Balance (M⁺/A⁻)	pH	¹³⁴Cs+¹³⁷Cs (%)	⁹⁰Sr/⁹⁰Y (%)	Beta Recovery (%)
W-21	0.755	0.737	0.9	19.16	29.21	100.63
W-22	0.548	0.823	8.9	34.24	3.35	100.81
W-23	0.853	0.719	12.7	98.93	0.62	94.99

The beta recovery listed in Table 5 is based on the summation of the activity for the known beta emitters divided by the gross beta activity. Considering the typical analytical errors associated with radiochemical measurements, the beta recoveries listed in Table 5 are excellent. The gross

beta data reported is based on a total activity measurement by liquid scintillation counting which includes contributions from the conversion and Auger electrons. To determine the beta recovery, the total activity measurement minus the alpha activity is the gross beta value that is compared to the summation of the individual radionuclides identified. Also, one must take into account the large effect that analytical error for the radioactive strontium activity can have on the value of the beta recovery. Since the ^{90}Sr is in secular equilibrium with the ^{90}Y , any error on the ^{90}Sr activity would be counted twice when calculating the error on the beta recovery. In general, the distribution of ^{137}Cs in the liquid waste is independent of pH, and the ^{90}Sr activity is a function of both pH and carbonate concentration.

If the waste tank chemistry approaches the conditions where the pH is high and the carbonate concentration is low, it is possible for the ^{90}Sr to remain soluble and the ^{90}Y to precipitate as the hydroxide and disrupt the secular equilibrium. It is important to understand any conditions that could disrupt this equilibrium because some radiochemical screening techniques and the interpretation of beta dose assume that the ^{90}Y activity is equal to the ^{90}Sr activity. The separation of the strontium from the yttrium is frequently observed with ^{90}Sr contaminated water moving through soil. The soluble ^{90}Sr moves with the water and the ^{90}Y is absorbed to the soil by an ion exchange process. Past practices used clay based materials as a mobilizing agent for pumping sludge. Therefore, the sludge may have an ion exchange affinity for yttrium or other radionuclides, which could interfere with the expected behavior for some radionuclides or other chemical species.

In general, the beta/gamma emitters found in the BVEST supernatant represent what would be expected for fission product waste that had been aged for 5-10 years for tanks W-21 and W-23, whereas tank W-22 had a less aged fission product mixture present (comparatively more $^{106}\text{Ru}/^{106}\text{Rh}$ and ^{134}Cs present). The relative distribution of the beta activity in the BVEST supernatant is summarized in Table 6. The ORNL liquid waste is normally stored at a caustic pH and the radioactive cesium dominates the activity such as was observed with tank W-23. The pH of the supernatant in tank W-21 is much lower than most ORNL liquid waste storage tanks and there is a corresponding increase in the strontium, uranium, and many other caustic insoluble metals in the liquid phase.

Table 6 **Distribution of Beta Activity in Supernatant**

Tank	pH	Percent of Total Beta Activity					U (mg/L)
		⁹⁰ Sr/ ⁹⁰ Y (%)	⁹⁹ Tc (%)	¹⁰⁶ Ru (%)	¹³⁴ Cs (%)	¹³⁷ Cs (%)	
W-21	0.9	29.21	0.08	-	0.55	18.61	4030
W-22	8.9	3.35	< 0.01	60.73	12.25	21.99	67
W-23	12.7	0.62	0.28	-	2.37	96.56	148

The alpha activity is usually low in the supernatant, as would be expected with a caustic pH such as the W-23 tank. If the hydroxide concentration in the supernatant is less than about 0.1 M, the uranium can form a complex with the carbonate present and become more soluble. As shown in Table 6 the uranium concentration is generally low at the higher pH, but in tank W-21 where the supernatant is acidic the uranium concentration increases significantly. Based on past experience, the alpha activity observed in the supernatant from W-22 and W-23 is likely due to suspended particles and the activity is dominated by the ²⁴⁴Cm present. The uranium contribution to the total alpha activity is typically minor relative to the ²⁴⁴Cm activity present in ORNL waste.

5.3 **Discussion of BVEST Sludge Characteristics**

Determination of the mass and charge balance for the sludge samples are more difficult than for the supernatant samples. Not only are there assumptions required about the chemical form and the oxidation state of the species present in the sludge, but many of the compounds in the sludge are mixed oxides which are not directly measured. Also, the sludge is actually a compressed slurry with a high water content. The interstitial liquid is in close contact with the sludge, and there are many ionic solubility equilibria. The anion data for the sludge samples are based on the water soluble anions that would be available to a water wash. The water wash would not account for the insoluble hydroxides, carbonates, and mixed oxides present. The insoluble species do not contribute to the charge balance, and the cation charge is not used in the calculation, as indicated in Table 7. Most of the nitrate reported for the sludge is due to the interstitial liquid. Considering these limitations, the compounds listed in Table 7 were used to estimate the mass and charge balance.

Table 7 Assumption Used for Major Compounds in BVEST Sludge

Cation	Chemical Form	Cation Charge Used	Gravimetric Factors
Al ³⁺	Al ₂ O ₃	0	1.890
Ca ²⁺	CaCO ₃	0	2.497
Fe ³⁺	Fe ₂ O ₃	0	1.430
K ⁺	K ⁺ NO ₃ ⁻	+1	2.586
Mg ²⁺	Mg(OH) ₂	0	2.399
Mn ²⁺	Mn(OH) ₂	0	1.619
Na ⁺	Na ⁺ NO ₃ ⁻	+1	3.697
Th ⁴⁺	Th(OH) ₄	0	1.293
UO ₂ ²⁺	UO ₂ ((OH) ₂ -H ₂ O	0	1.353

Table 8 summarizes the mass and charge balance for the BVEST tank sludge samples. Considering the limitations of these calculations, the mass balance is within the analytical error ($\pm 20\%$) for these sludge samples. The charge balance is more influenced by the chemical form assumptions, and the results have a larger corresponding error range.

Table 8 Summary of Quality Checks for BVEST Sludge Data

Tank	Mass Balance (TS _{calc.} /TS _{meas.})	Charge Balance (M ⁺ /A ⁻)	pH	¹³⁴ Cs+ ¹³⁷ Cs (%)	⁹⁰ Sr/ ⁹⁰ Y (%)	Beta Recovery (%)
W-21	0.984	0.739	7.7	6.47	40.22	97.8
W-22	1.163	1.292	11.3	9.02	48.12	95.3
W-23	1.123	1.437	12.3	4.60	89.50	97.3

The beta recovery results are listed in Table 8 for the BVEST sludge samples. As discussed for the supernatant samples there is some variability for the beta recovery which is probably due to the analytical error on the ^{90}Sr measurement. Any measurement error for the ^{90}Sr activity would be doubled when considering the beta recovery calculation. Considering the potential for propagated error, the comparison of the gross beta to the summation of the identified radionuclides was excellent for the BVEST sludge samples.

The distribution of the major compounds (listed in Table 7) by weight percent are illustrated in Fig. 3 for each BVEST sludge sample. The BVEST sludge is similar to most ORNL waste in that the sodium/potassium nitrate and calcium carbonate accounts for most of the sludge mass and volume. The balance of the sludge mass is dominated by the uranium and thorium content. The distribution of the total uranium and thorium concentration for each BVEST sludge sample are shown in Fig. 4.

Figure 3 Distribution of Major Compounds in BVEST Sludge

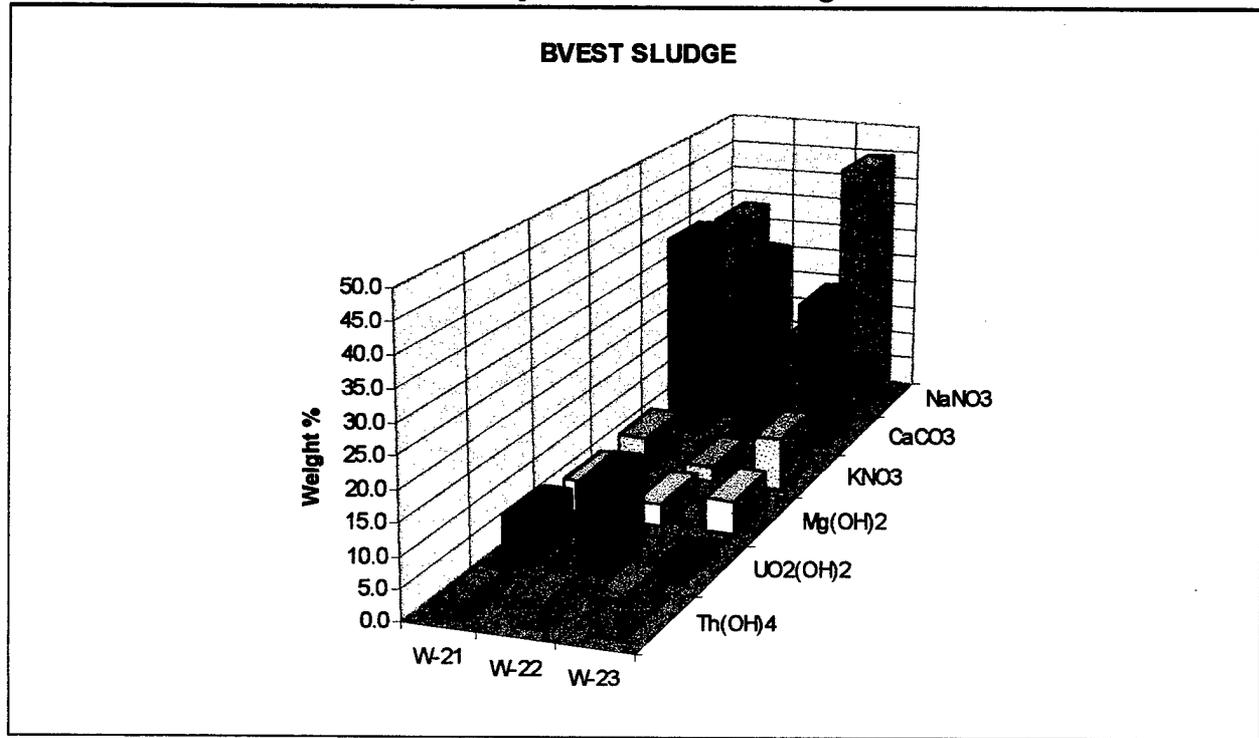
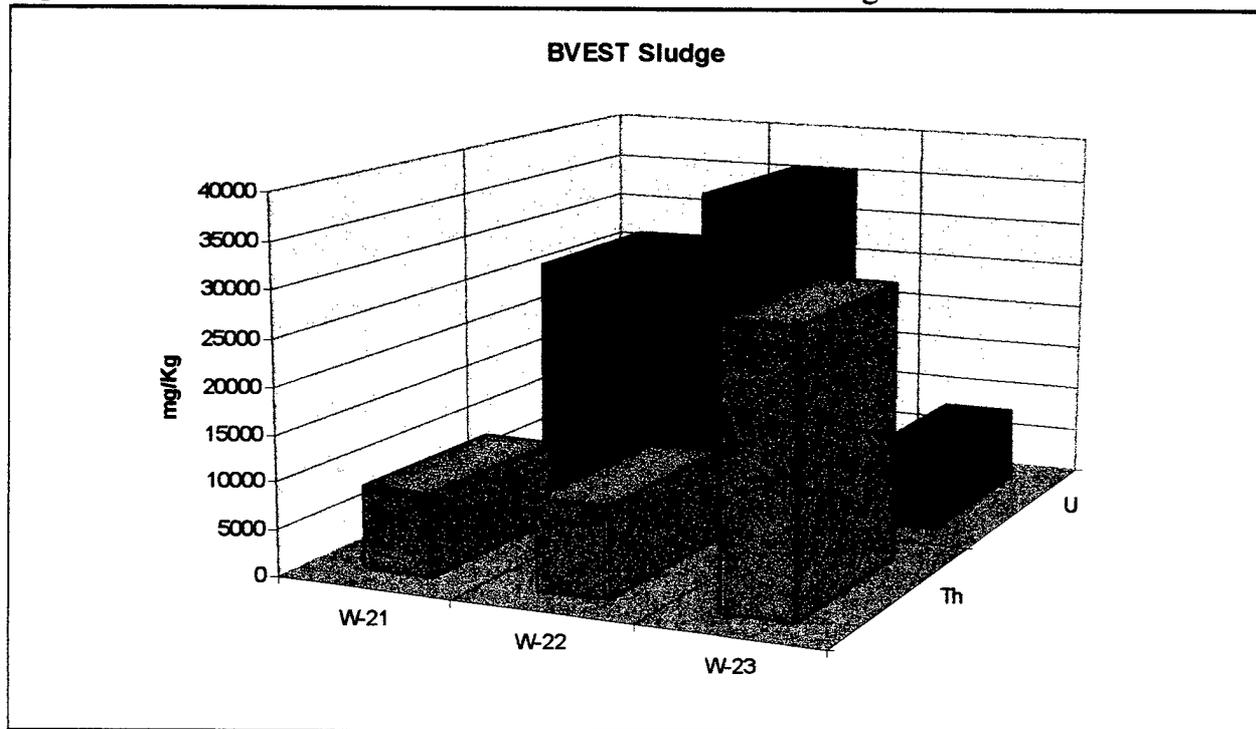


Figure 4 Distribution of Uranium and Thorium in BVEST Sludge



The distribution of the beta emitters found in the BVEST sludge samples are summarized in Table 9. The distributions of the beta activity are shown to be dependent upon the radionuclides present, which is a function of the age of the radioactive waste, and the pH of the supernatant found over the sludge. Under the typical basic conditions for ORNL waste tanks, the major difference in the beta distribution between the supernatant and the sludge is that the distribution of the longer lived fission products (^{90}Sr and ^{137}Cs) are reversed due to the differences in solubility. The Group IA metals (^{134}Cs and ^{137}Cs) and the radionuclides that form anionic species ($^{99}\text{TcO}_4^-$, $^{129}\text{I}^-$, and $^{129}\text{IO}_3^-$) are more soluble in the supernatant. The solubility of the Group IIA metals (^{90}Sr) in the supernatant are a function of both pH and carbonate concentration. At high pH most of the other metals, lanthanides, and actinide elements form insoluble hydroxides and mixed oxides, which are found in the sludge. If present, the ^{99}Tc activity would be higher in the supernatant than the sludge. The source of most of the ^{99}Tc found in ORNL sludge samples was the interstitial liquid, and not insoluble forms of technetium. The shorter lived radionuclides observed include the europium (^{152}Eu , ^{154}Eu , and ^{155}Eu) isotopes and to some extent ^{134}Cs . Although not shown in Table 9, the radionuclide pair $^{106}\text{Ru}/^{106}\text{Rh}$ was observed in the W-22 sludge at a level of about 2% of the total beta activity.

Table 9 Distribution of Beta Activity in BVEST Sludge

Tank	pH	Percent of Total Beta Activity					
		$^{90}\text{Sr}/^{90}\text{Y}$ (%)	$^{134}\text{Cs}+^{137}\text{Cs}$ (%)	^{60}Co (%)	^{99}Tc (%)	$^{152,154,155}\text{Eu}$ (%)	^{241}Pu (%)
W-21	7.7	40.22	6.47	1.77	0.01	47.13	3.47
W-22	11.3	48.12	9.02	1.06	< 0.01	37.00	2.15
W-23	12.3	89.50	4.60	0.33	0.01	3.58	1.53

The distribution of beta activity observed in W-23 is typical of the sludge found in the ORNL active waste system. The significance of the low pH found in the supernatant and sludge from W-21 is a more even distribution of the ^{90}Sr activity between the liquid and sludge phase. The percentage of ^{90}Sr activity in W-22 appears low considering the high pH, but the relative activity is misleading because of the higher percentage of short-lived radionuclides present in the W-22 tank.

Table 10 Summary of Actinide Elements in BVEST Sludge

Actinide	W-21	W-22	W-23
	(% α)	(% α)	(% α)
^{232}Th	0.02	0.03	0.03
^{233}U	5.81	3.77	1.66
^{234}U	0.08	0.11	0.03
^{235}U	< 0.01	< 0.01	< 0.01
^{238}U	0.22	0.30	0.02
^{237}Np	0.04	< 0.01	< 0.01
^{238}Pu	10.05	12.68	11.09
^{239}Pu	4.33	4.16	2.45
^{240}Pu	3.29	3.39	1.77
$^{241}\text{Am}^a$	8.16	8.09	7.54
^{244}Cm	67.99	67.46	75.41
Gross α (Bq/g)	150000	150000	440000

^a The ^{241}Am data is based on subtracting the ^{238}Pu by TIMS from the alpha peak measured at 5.15 MeV ($^{238}\text{Pu} + ^{241}\text{Am}$) in the alpha spectrum.

The distribution of the alpha activity for each BVEST sludge sample are summarized in Table 10 by radionuclide as the relative percent alpha . In general, the alpha activity in the BVEST system is strongly weighted by the ^{244}Cm which has a high specific activity. The list of actinides in Table 10 required several radiochemical and inorganic analytical measurements to generate the best estimates for each of the alpha activities. The ^{232}Th activity was calculated from the total thorium measured by ICP-AES. The other thorium isotopes (^{228}Th , ^{229}Th , and ^{230}Th) are present in the ORNL sludge waste at such low mass, their presence would not effect the ICP-AES measurements. The uranium isotopes were measured by TIMS. The atom % results were then converted to weight % and used to calculate the concentration of each uranium isotope from the total uranium results obtained by ICP-AES. The activity for each uranium radionuclide is then calculated from the specific activity for each isotope. The plutonium isotopes were first measured by TIMS, and then along with the total plutonium alpha activity measured after a chemical separation was used to calculate the activity for each plutonium isotope. The ^{244}Cm was measured directly by alpha

spectrometry without any chemical separation. The ^{241}Am activity was determined by subtracting the ^{238}Pu activity from the sum of the $^{238}\text{Pu} + ^{241}\text{Am}$ measured by alpha spectrometry. Both ^{238}Pu and ^{241}Am have an alpha energy of about 5.50 MeV and can not be resolved by alpha spectrometry. There was no chemical separation of the plutonium and americium for this project because of cost concerns.

5.4 RCRA Characteristics for the BVEST System

The RCRA regulatory limits are listed in Table 11, which also includes the limits for the EPA Toxicity Characteristic Leaching Protocol (TCLP) extract and the functional total metal limits for a solid or sludge waste. Because of the 1:20 dilution used for the TCLP extraction procedure, the total metal limits for sludge samples are twenty times higher than the TCLP extraction limits.

Table 11 Summary of RCRA Regulatory Limits

Metals		TCLP Extract and Liquids (mg/L)	Solid/Sludge Total Metal (mg/Kg)
Silver	(Ag)	5	100
Arsenic	(As)	5	100
Barium	(Ba)	100	2000
Cadmium	(Cd)	1	20
Chromium	(Cr)	5	100
Mercury	(Hg)	0.2	4
Nickel	(Ni)	50	1000
Lead	(Pb)	5	100
Selenium	(Se)	1	20
Thallium	(Tl)	0.9	18

If the RCRA metal concentrations are found to be below the total metal limits, the solid waste can not fail the TCLP leach test. If the RCRA metal concentrations exceed the total metal limits, the

TCLP leach test must be done to determine if the solid waste is hazardous. For solid samples, the TCLP leach test is only valid for the final waste form ready for disposal. The total metal concentration data can be used as acceptable process knowledge if the final waste form only results in a dilution of the RCRA metal concentrations. Examples of waste forms that result in a dilution of a solid waste includes grouting (2 fold dilution) and vitrification (3 fold dilution). If the total metal limit is exceeded after stabilizing the waste, the TCLP leach test would be required for only the metals that had the potential to exceed the regulatory limits.

Only the supernatant sample from the W-22 tank did not exceed the RCRA regulatory limits. The supernatant from both the BVEST waste tanks W-21 and W-23 exceeded the regulatory limits for cadmium, chromium, mercury, and lead. The current technology used for long term storage of the liquid waste is a solidification process that usually results in a final waste form that passes the TCLP leach test. The nickel and thallium are proposed RCRA metals and are included in the data for future waste management decisions.

All of the BVEST tank sludge samples exceed the total metal limits for cadmium, chromium, lead, and mercury. Most of the ORNL radioactive waste sludge samples characterized to date have exceeded the total metal limits for these RCRA metals. Based on past experience, it is expected that solidification of the most ORNL sludge would fix these RCRA metals such that the final waste form would pass a TCLP leach test.

5.5 TRU Classifications for LLLW System

The DOE definition for Transuranic (TRU) Waste includes the following conditions,

- TRU activity ≥ 3700 Bq/g (100 nCi/g),
- TRU isotopes must be alpha emitting actinides with $Z > 92$ (uranium),
- TRU isotopes must have a half life ≥ 20 years.

This definition excludes all thorium and uranium isotopes. The short lived actinide ^{244}Cm ($t_{1/2} = 18.1$ years), which is common to ORNL waste, falls outside the TRU definition. Also, the plutonium isotope, ^{241}Pu , would be excluded from calculation of the TRU activity because it is a pure beta

emitter. The primary actinide elements common to ORNL waste, that are present at sufficient levels to meet the TRU definition, include ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{241}Am . There is some current work at the Radiochemical Engineering Development Center (Mark-42 fuel assembly processing) that could generate enough ^{243}Am to make a significant contribution to TRU alpha content of the waste. The remaining actinide elements present in ORNL waste are generally not available at high enough activity, and/or do not have a long enough half-life to meet the TRU definition.

None of the BVEST supernatant samples discussed in this report had enough alpha activity to be considered as TRU waste, however, the pH in tank W-21 needs to be raised before enough sludge is dissolved to make the liquid phase TRU waste. All of the BVEST sludge samples characterized for this project were classified as TRU waste based on only the plutonium and americium activity. The alpha activity reported is based on wet weight and if adjusted for dry weight the TRU activity would almost double. The BVEST sludge samples contained enough plutonium and americium activity to easily satisfy the WIPP waste acceptance criteria¹³ for transuranic waste. Based on the TRU activity, any dilution of the sludge that would result from a solidification process such as grouting or vitrification would most likely not effect the TRU classification.

5.6 Distribution of Fissile Material in LLLW System

The ORNL LLLW waste acceptance criteria (WAC) requires the fissile isotopes of uranium and plutonium to be diluted with ^{238}U and ^{232}Th , respectively. Table 12 summarizes the dilution or "denature" ratios for the BVEST supernatant samples. All the dilution ratios for the BVEST liquid samples were well above the required dilution factors for criticality safety. A summary of the dilution ratios for fissile material in the BVEST sludge samples are provided in Table 13. All the dilution ratios for the BVEST sludge samples well exceeded the required dilution factors for the fissile isotopes of uranium and plutonium except for the W-23 uranium ratios which were just at the limit. All the dilution ratios listed in Table 12 and 13 are based on equations discussed in section 3.5 of this report.

Table 12 Summary of Denature Ratios for BVEST Supernatant

Tank	$^{238}\text{U}/^{235}\text{U} f_{35}$ (eq. 1)	$^{238}\text{U}/^{235}\text{U}$ (eq. 3)	$^{238}\text{U}/^{233}\text{U}$ (eq. 4)	$^{232}\text{Th}/^{239}\text{Pu}$ (eq. 2)	pH
W-21	237	297	575	33200	0.9
W-22	152	153	821	10400	8.9
W-23	174	179	660	428	12.7

^a Concentration of thorium and plutonium to low to calculate ratio.

Table 13 Summary of Denature Ratios for BVEST Sludge

Tank	$^{238}\text{U}/^{235}\text{U} f_{35}$ (eq. 1)	$^{238}\text{U}/^{235}\text{U}$ (eq. 3)	$^{238}\text{U}/^{233}\text{U}$ (eq. 4)	$^{232}\text{Th}/^{239}\text{Pu}$ (eq. 2)	pH
W-21	267	326	793	3120	7.7
W-22	320	361	1630	3560	11.3
W-23	126	109	198	6330	12.3

The dilution ratios listed in Tables 12 and 13 are based on the ratio of weight %, not the ratio of atom % given in the data tables. There is a small difference between atom %, reported for the uranium and plutonium, and weight %, which is needed for many calculations performed with the analytical data. To convert from atom % to weight %, we used the following equation,

$$W_i = \frac{a_i M_i}{\sum_i^n a_i M_i} \times 100\%$$

where, W_i = weight %,
 M_i = nuclidic mass
 a_i = atom %.

An example of this calculation is provided in Table 14, which shows there is not much difference between the atom % and the weight %.

Table 14 Example of Converting Atom % to Weight % for Typical Sludge

Isotope	Nuclidic mass (g/mol)	atom %	($a_i M_i$)	weight %
²³³ U	233.039629	0.056	13.0502	0.0548
²³⁴ U	234.040947	0.004	0.9362	0.0039
²³⁵ U	235.043924	0.621	145.9623	0.6132
²³⁶ U	236.045563	0.002	0.4721	0.0020
²³⁸ U	238.050785	99.316	23642.2518	99.3260
Total		99.999	23802.6726	99.9999

The distribution of plutonium isotopes by alpha activity are illustrated in Fig. 5 for each of the BVEST samples. For comparison, Fig. 6 shows the distribution of the plutonium isotopes by concentration for each of the BVEST sludge samples. One should note that the ²³⁸Pu dominates the alpha activity and the ²³⁹Pu is the major isotope by weight or concentration.

Figure 5 Distribution of Plutonium by Alpha Activity in BVEST Sludge

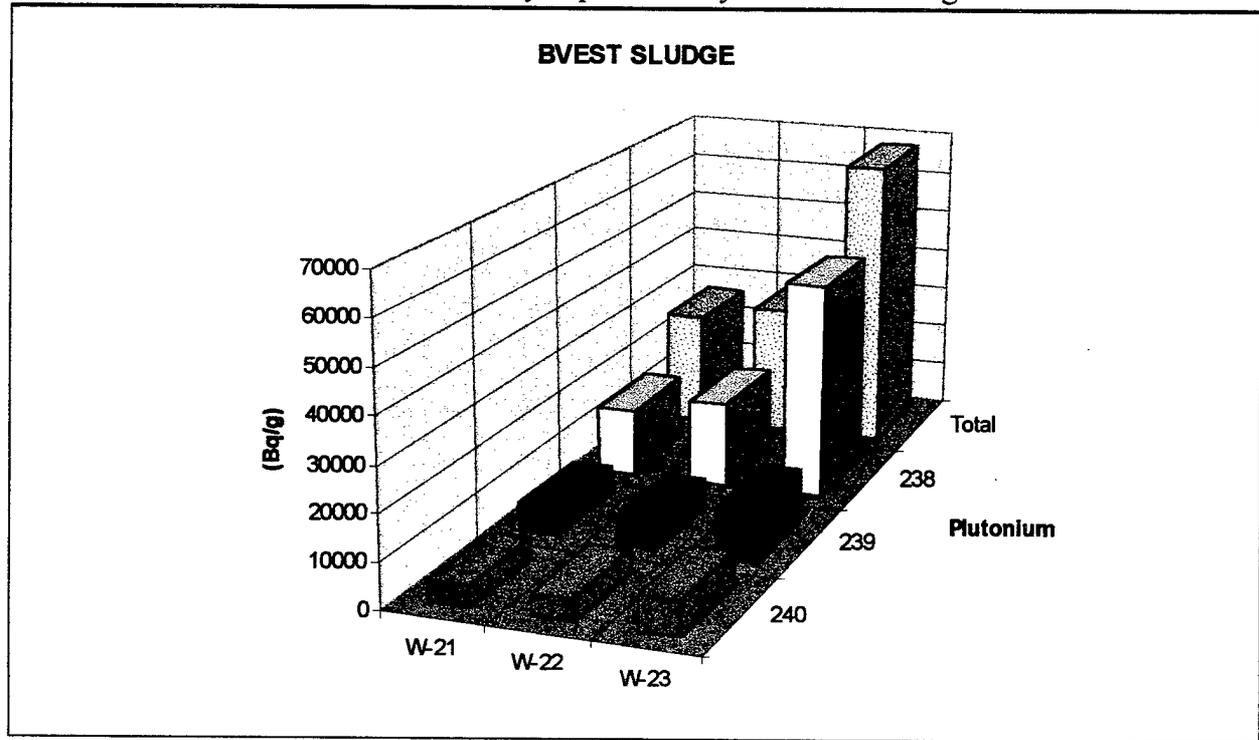
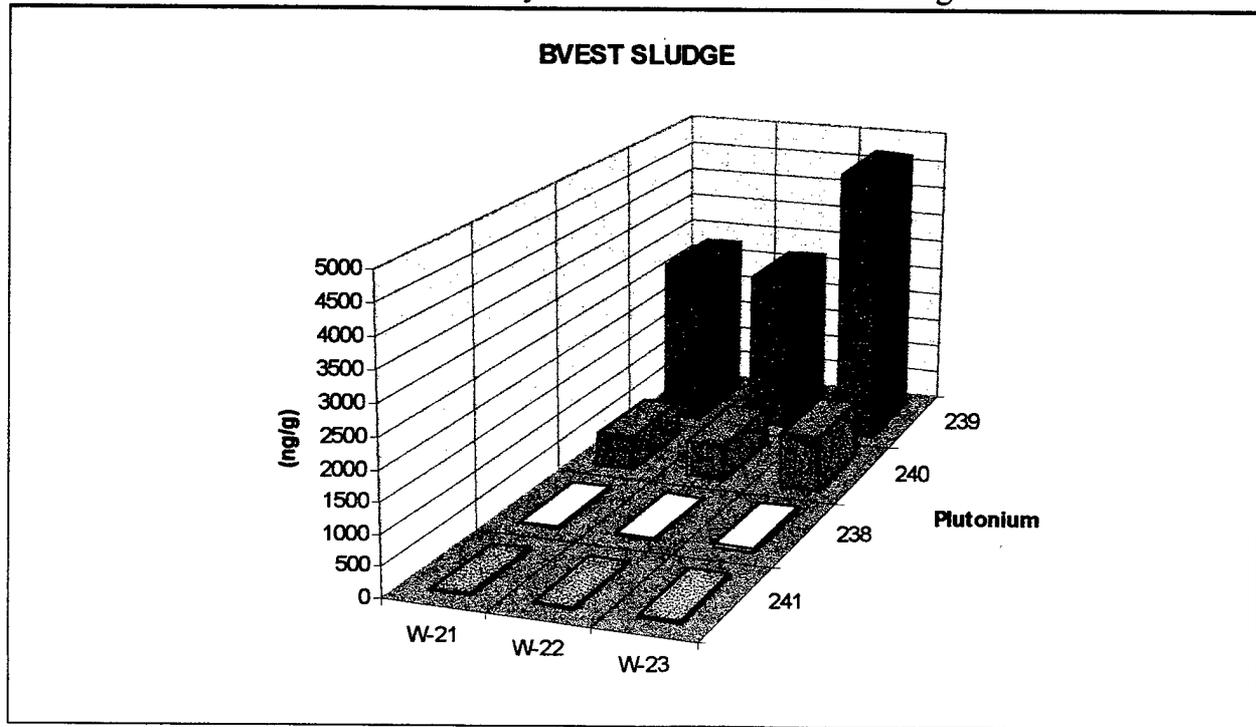


Figure 6 Distribution of Plutonium by Concentration in BVEST Sludge



5.7 Discussion of the Total Anion Content in the Sludge

As discussed in section 3.3, there were two sample preparation methods used to investigate the total anion content of the BVEST sludge samples, which included (1) water leach and (2) oxygen bomb combustion. A summary and comparison of these sludge preparation methods are given in Table 15.

Table 15 Summary of Total Anion Data for BVEST Sludge

Anion	Method	(mg/Kg)		
		W-21	W-22	W-23
Bromide	Water Leach Bomb	96.8	25.2	362
		70.2	33.3	246
Chloride	Water Leach Bomb	1370	249	3420
		798	186	2010
Fluoride	Water Leach Bomb	23.3	20.5	149
		14.3	25.6	21.4
Nitrate	Water Leach Bomb	158000	6930	109000
		68000	2220	41900
Nitrite	Water Leach Bomb	1180	480	6290
		1680	333	7150
Phosphate	Water Leach Bomb	< 10	< 10	< 10
		< 26	< 38	130
	ICP-AES	3550	10400	3570
Sulfate	Water Leach Bomb	6030	191	3850
		1620	5920	2100

5.7.1 Nitrate/Nitrite

It is difficult to compare the yield for these two anions between the two preparation methods. The majority of the compounds present in the BVEST waste system that contain nitrate and nitrite readily dissolve in water and are accounted for in the water leaches. This can be argued by looking at the cation/anion charge balance calculations for the sludge analysis. These calculations show acceptable agreement between the anionic species and the cationic species (which are accurately determined by conventional methods) present in the sludges. The majority of the anion contribution is by far due to the nitrate ion with the other anions contributing just a fraction of the total negative molar charge.

Based on this calculated charge balance it is believed that the majority of the nitrates are accounted for in the water leaches. When the sludge is prepared using the bomb method the sample is subject to an oxidizing environment which will not only change the nitrate/nitrite ratio in the sample but will also oxidize any other nitrogen containing compounds present in the sample to nitrate or nitrite. The ratio of the nitrate/nitrite measured after the bomb method does not represent the ratio in the original sample.

5.7.2 Halides (fluoride, chloride, bromide)

The data in Table 15 shows that there is no benefit for using a bomb combustion over a water leach of the BVEST sludges for fluoride and chloride. For the bromide results the water leach was analyzed using a Dionex AS4A ion exchange column while the bomb combustion results were determined using a new Dionex AS14 ion exchange column. The older AS4A column separation of the bromide and nitrate peaks is not as good as the AS14 and due to the high levels of nitrate present in the sludges the bromide peak could not be resolved from the nitrate peak using the AS4A column. Therefore, a comparison could not be made between the water leaches and the other methods for bromide.

5.7.3 Phosphate

It is believed that a large fraction of the phosphate in the BVEST sludge is present as tributyl phosphate and degradation products dibutyl- and monobutyl phosphate. The tributyl phosphate has low solubility in water and would not be seen in the water leach, which is illustrated in Table 15 where phosphate values are below the detection limit of the instrument. When the sludges were prepared using the Parr bomb some phosphate was detected but still at low levels. The explanation for this could be due to poor combustion of the sludge. In order to obtain an adequate combustion, 5000 calories of heat must be produced in the bomb. Since the BVEST sludges are not comprised of combustible material all of the heat must be generated by the combustion aid (mineral oil). Using the heat of combustion for mineral oil, 0.5 mL was determined to be able to produce greater than 5000 calories and therefore provide for an adequate combustion. After a material undergoes complete combustion it should have an ash like appearance. By visual observation after the sludge

was combusted it appears to be just dried out sludge with a crusty appearance. Based on this and the fact that only low levels of phosphates were detected it is felt that the bomb is a poor choice for preparation of the sludge for phosphate determination.

Also shown in the Table 15 are the phosphate results by ICP-AES measurements. These phosphate values are calculated results based on the analysis of total phosphorus by the ICP-AES method after a closed vessel microwave acid digestion of the sludge. The ICP-AES values are currently considered to be the best results for the total phosphorus in the sludge. The water leach and bomb combustion methods both yielded phosphate results much lower than the ICP-AES measurements after an acid digestion.

5.7.4 Sulfate

The analysis of sulfate between the water leaches and the bomb combustion do not show good agreement. The poor agreement may be due to both non-water soluble sulfate compounds in the sludge and incomplete combustion by the bomb procedure due to the problems discussed earlier.

5.7.5 Summary

There is no ideal method to obtain a total anion content on the BVEST sludges. The water leaches are considered to be adequate for nitrate, nitrite, and the halides. The total phosphate and sulfate content however will not be obtained by a water leach and any method used that oxidizes the sample would be considered to be a total phosphorus or sulfur. The best preparation method for total phosphorus or sulfur appears to be closed vessel microwave digestion followed by analysis by ICP-AES or ICP-MS. Other DOE sites that have experience with caustic high nitrate sludge samples and have worked with the bomb combustion method, have related similar observations which include poor yields and heavy matrix interferences associated with these preparation methods.

5.8 Solubility of BVEST Sludge in Water

The BVEST sludge samples were taken through a water wash to determine the water soluble anions and measure the effect of the sludge on pH. Since this water leach solution was available, several of the lower cost analytical measurements, including the metals by ICP-AES, gross alpha/beta, and gamma emitters, were measured on the wash solution to evaluate the relative solubility of the sludge in water. The water wash experiment consisted of taking 5 grams of wet sludge and diluting the sample to 50 mL with deionized water. The sludge was leached with the water on a vortex mixer for several minutes and the clarified liquid was then removed for analysis. Results from the water leaching experiment are summarized in Table 16.

Table 16 Recovery of Selected Species in Water Leach of BVEST Sludge

Analytical Measurement	% Recovery in Water Leach of Sludge		
	W-21	W-22	W-23
Selected metals			
pH of water wash	7.7	11.3	12.3
Al	< 0.01	1.6	6.7
Ca	31	0.049	0.042
Cr	0.059	2.2	2.5
Fe	< 0.01	0.081	< 0.01
K	71	16	83
Mg	7.2	0.21	0.027
Na	88	45	90
Th	0.013	0.11	0.031
U	0.017	0.15	0.11
Selected radionuclides			
Gross alpha	0.051	0.058	0.005
Gross beta	8.1	1.7	4.4
⁶⁰ Co	1.1	1.2	4.2
¹³⁷ Cs	75	19	93
¹⁵² Eu	0.13	0.053	0.17

The water leach appears to remove more of the sodium and potassium than the total digestion with nitric acid, however, the high recovery is more likely due to the difference in sample size used for each sample preparation. Only 0.5 g of sample was used for the nitric acid digestion as compared to the 5 g used for the water leach. The larger sample size would be more representative of the overall sludge and introduces less sampling error. The water wash does not remove many of the metals (i.e. uranium) that cause spectral interference problems. Therefore, both analytical and sampling errors most likely contribute to the high bias for the sodium and potassium recovery. In general, the lighter alkali metals are quantitatively removed from the sludge along with the nitrate. Some of the cesium (see ^{137}Cs recovery) appears to be bound to the sludge, which could be due to differences in ion exchange properties between the cesium and the lighter alkali metals. The incomplete removal of ^{137}Cs from the sludge with water, caustic, and low acid washing has been observed in past experiments with the ORNL sludge samples.

As expected, the actinide and lanthanide elements are not significantly removed by the water wash and this behavior is illustrated by the uranium, thorium, ^{152}Eu , and gross alpha recovery listed in Table 16. The water solubility of the alkaline earth elements, represented by calcium in Table 16, are a function of both the pH and the carbonate concentration. The recovery of the calcium ranges from < 1% to about 33 % for the BVEST sludge samples, and this behavior would also be expected for the ^{90}Sr activity. Most of the other major metals are usually insoluble in a water wash except for the chromium which is probably present as the chromate anion, and many anionic species tend to be soluble in water.

5.9 Estimates for Compliance with WIPP WAC, Rev. 5 for BVEST Sludge

The purpose of this section is to establish upper boundary estimates, based upon a 55-gal. drum shipping container, for several of the preliminary nuclear properties criteria and requirements for RH-TRU waste as specified in the WIPP WAC, Revision 5. Specifically, this section will develop estimates for the ^{239}Pu Fissile Gram Equivalent (FGE), ^{239}Pu Equivalent Activity, and Thermal Power or decay heat limits per RH-TRU canister. The preliminary RH-TRU limits per waste canister for each of these nuclear criteria are listed as follows,

- ^{239}Pu FGE < 325 g
- ^{239}Pu Equivalent Activity < 1000 Ci
- Thermal Power < 300 watts.

For the BVEST sludge, the ^{239}Pu FGE can be estimated by the summation of the gram-equivalents for ^{233}U , ^{235}U , and ^{239}Pu . As shown in Table 17, the ^{235}U dominates the total ^{239}Pu FGE for the BVEST sludge samples and the ^{239}Pu is less than 5% of the total fissile gram equivalent. Based on packaging the wet sludge in 55-gal. drums, none of the BVEST sludge would approach the RH-TRU limit of 325 g per canister for the ^{239}Pu FGE. Estimates for the total weight (Kg) of sludge in a 55 gal. drum, for each BVEST sludge sample, are listed in Table 20.

Table 17 Estimates for ^{239}Pu FGE with the BVEST Sludge

Isotope	^{239}Pu FGE factor	W-21 (mg/Kg)	W-22 (mg/Kg)	W-23 (mg/Kg)
^{233}U	0.865	23.9	15.7	20.4
^{235}U	0.641	65.7	89.6	35.3
^{239}Pu	1.000	2.77	2.69	4.68
^{239}Pu FGE (mg/Kg)		65.6	73.7	45.0
^{239}Pu FGE in 55 gal. (g)		18.6	17.8	14.7

Estimates for the total ^{239}Pu equivalent activity (Ci) in a 55-gal. drum for each of the BVEST sludge samples are listed in Table 18. The ^{239}Pu equivalent activity is based on following calculation,

$$^{239}\text{Pu Equivalent Activity} = \sum_{i=1} \frac{A_i}{F_i} \quad (6)$$

where A_i is the activity of radionuclide i , and F_i is the ^{239}Pu equivalent activity weighting factor for radionuclide i . The weighting factors for the major radionuclides found in the BVEST sludge are listed in Table 17. As shown in the last row of Table 18, all of the BVEST sludge estimates for ^{239}Pu Equivalent activity would be less than 3 Ci per 55 gal. drum, which is well below the RH-TRU limits. The BVEST sludge is well below the CH-TRU limit of 80 Ci of plutonium equivalent activity for untreated waste in a 55-gal. drum and will not approach the 1000 Ci WAC limit for a RH-TRU canister, which holds three 55-gal. drums.

Table 18 Estimates for ²³⁹Pu Equivalent Activity with the BVEST Sludge

Isotope	²³⁹ Pu wt. factor ^a	W-21 (Bq/g)	W-22 (Bq/g)	W-23 (Bq/g)
²³³ U	3.9	8500	5600	7300
²³⁸ Pu	1.1	15000	19000	49000
²³⁹ Pu	1.0	64000	62000	11000
²⁴⁰ Pu	1.0	48000	5000	7700
²⁴¹ Pu	52.0	100000	77000	160000
²⁴¹ Am	1.0	12000	12000	33000
²⁴⁴ Cm	1.9	100000	100000	330000
²³⁹ Pu Eqv. (Bq/g)		194370	151821	274878
²³⁹ Pu Eqv. in 55 gal. (Ci)		1.49	0.99	2.43

^a Radionuclide-specific weighting factors for the ²³⁹Pu equivalent activity taken from Appendix A of DOE/WIPP-069, Rev.5

There is concern about the thermal power from the decay heat of the radionuclides present in waste packages prepared for WIPP disposal. These concerns are addressed in Revision 5 of the WIPP WAC, with limits of 40 watts for a TRUPACT-II container for CH-TRU waste and a limit of 300 watts for a RH-TRU canister. High decay heat is also an indicator for potential problems with hydrogen gas generation. The major radionuclides found in the BVEST sludge are listed in Table 19 along with the "Q" values needed to calculate the decay heat for each isotope.

An estimate of the decay heat distribution by radionuclide for the BVEST sludge samples are listed in Table 20 along with an estimate for an upper boundary for total decay heat that would be in a 55 gal. drum full of wet sludge. These estimates indicate that the decay heat from BVEST sludge is far below any of the WIPP WAC limits for thermal power and should have no impact on packaging requirements. For general interest, the relative percent distributions of the decay heat by radionuclide, beta activity, and alpha activity are listed in Table 21. The distribution of decay heat as a function of BVEST tank and radionuclide is illustrated in Fig. 7 for beta decay, and in Fig. 8 for alpha decay. It is interesting to note that the beta activity accounts for most of the decay heat output and that the heat from alpha decay is generally less than 30% of the total thermal power.

Table 19 Isotopes that Contribute to the Decay Heat in the BVEST Sludge

Isotope	"Q" value (W/Ci)	"Q" value (W/Bq)	W-21 (Bq/g)	W-22 (Bq/g)	W-23 (Bq/g)
⁶⁰ Co	1.54E-02	4.16E-13	5.10E+04	3.80E+04	3.00E+04
⁹⁰ Sr	1.16E-03	3.14E-14	5.80E+05	8.60E+05	4.60E+06
⁹⁰ Y	5.54E-03	1.50E-13	5.80E+05	8.60E+05	4.60E+06
¹³⁷ Cs	1.01E-03	2.73E-14	1.60E+05	2.70E+05	4.00E+05
^{137m} Ba	3.94E-03	1.06E-13	1.51E+05	2.55E+05	3.78E+05
¹⁵² Eu	7.65E-03	2.07E-13	9.30E+05	9.00E+05	2.20E+05
¹⁵⁴ Eu	9.08E-03	2.45E-13	3.30E+05	3.30E+05	9.90E+04
¹⁵⁵ Eu	7.59E-04	2.05E-14	9.00E+04	7.40E+04	2.90E+04
²⁴¹ Pu	3.20E-05	8.65E-16	1.00E+05	7.70E+04	1.60E+05
Total beta (Ci/Kg)			8.03E-02	9.74E-02	2.94E-01
²³³ U	2.86E-02	7.72E-13	8.50E+03	5.60E+03	7.30E+03
²³⁸ Pu	3.26E-02	8.81E-13	1.50E+04	1.90E+04	4.90E+04
²³⁹ Pu	3.02E-02	8.17E-13	6.40E+03	6.20E+03	1.10E+04
²⁴⁰ Pu	3.06E-02	8.26E-13	4.80E+03	5.00E+03	7.70E+03
²⁴¹ Am	3.28E-02	8.87E-13	1.20E+04	1.20E+04	3.30E+04
²⁴⁴ Cm	3.44E-02	9.29E-13	1.00E+05	1.00E+05	3.30E+05
Total alpha (Ci/Kg)			3.96E-03	3.99E-03	1.18E-02
Total beta in 55 gal. drum (Ci):			22.74	23.92	92.90
Total alpha in 55 gal. drum (Ci):			1.12	0.96	3.87

Table 20 Distribution of Decay Heat in BVEST Sludge

Isotope	"Q" value (W/Ci)	"Q" value (W/Bq)	W-21 (W/Kg)	W-22 (W/Kg)	W-23 (W/Kg)
⁶⁰ Co	1.54E-02	4.16E-13	2.12E-05	1.58E-05	1.25E-05
⁹⁰ Sr	1.16E-03	3.14E-14	1.82E-05	2.70E-05	1.44E-04
⁹⁰ Y	5.54E-03	1.50E-13	8.68E-05	1.29E-04	6.89E-04
¹³⁷ Cs	1.01E-03	2.73E-14	4.37E-06	7.37E-06	1.09E-05
^{137m} Ba	3.94E-03	1.06E-13	1.61E-05	2.72E-05	4.03E-05
¹⁵² Eu	7.65E-03	2.07E-13	1.92E-04	1.86E-04	4.55E-05
¹⁵⁴ Eu	9.08E-03	2.45E-13	8.10E-05	8.10E-05	2.43E-05
¹⁵⁵ Eu	7.59E-04	2.05E-14	1.85E-06	1.52E-06	5.95E+07
²⁴¹ Pu	3.20E-05	8.65E-16	8.65E-08	6.66E-08	1.38E-07
²³³ U	2.86E-02	7.72E-13	6.56E-06	4.32E-06	5.64E-06
²³⁸ Pu	3.26E-02	8.81E-13	1.32E-05	1.67E-05	4.32E-05
²³⁹ Pu	3.02E-02	8.17E-13	5.23E-06	5.07E-06	8.99E-06
²⁴⁰ Pu	3.06E-02	8.26E-13	3.96E-06	4.13E-06	6.36E-06
²⁴¹ Am	3.28E-02	8.87E-13	1.06E-05	1.06E-05	2.93E-05
²⁴⁴ Cm	3.44E-02	9.29E-13	9.29E-05	9.29E-05	3.07E-04
Total (W/Kg)			5.54E-04	6.07E-04	1.37E-03
Density (Kg/L):			1.36	1.16	1.57
Total in 55 gal drum (Kg):			283	241	327
Total in 55 gal drum (Watt):			0.157	0.147	0.447

Table 21 Summary of Relative Decay Heat in BVEST Sludge

Isotope	"Q" value (W/Ci)	"Q" value (W/Bq)	W-21 (% Watt)	W-22 (% Watt)	W-33 (% Watt)
⁶⁰ Co	1.54E-02	4.16E-13	3.83%	2.60%	0.91%
⁹⁰ Sr	1.16E-03	3.14E-14	3.28%	4.43%	10.55%
⁹⁰ Y	5.54E-03	1.50E-13	15.67%	21.16%	50.38%
¹³⁷ Cs	1.01E-03	2.73E-14	0.79%	1.21%	0.80%
^{137m} Ba	3.94E-03	1.06E-13	2.91%	4.47%	2.95%
¹⁵² Eu	7.65E-03	2.07E-13	34.67%	30.57%	3.33%
¹⁵⁴ Eu	9.08E-03	2.45E-13	14.61%	13.31%	1.78%
¹⁵⁵ Eu	7.59E-04	2.05E-14	0.33%	0.25%	0.04%
²⁴¹ Pu	3.20E-05	8.65E-16	0.02%	0.01%	0.01%
Total beta heat (%):			76.10%	78.01%	70.74%
²³³ U	2.86E-02	7.72E-13	1.18%	0.71%	0.41%
²³⁸ Pu	3.26E-02	8.81E-13	2.38%	2.75%	3.15%
²³⁹ Pu	3.02E-02	8.17E-13	0.94%	0.83%	0.66%
²⁴⁰ Pu	3.06E-02	8.26E-13	0.72%	0.68%	0.46%
²⁴¹ Am	3.28E-02	8.87E-13	1.92%	1.75%	2.14%
²⁴⁴ Cm	3.44E-02	9.29E-13	16.76%	15.27%	22.39%
Total alpha heat (%):			23.90%	21.99%	29.26%

Figure 7 Distribution of Beta Decay Heat in BVEST Sludge

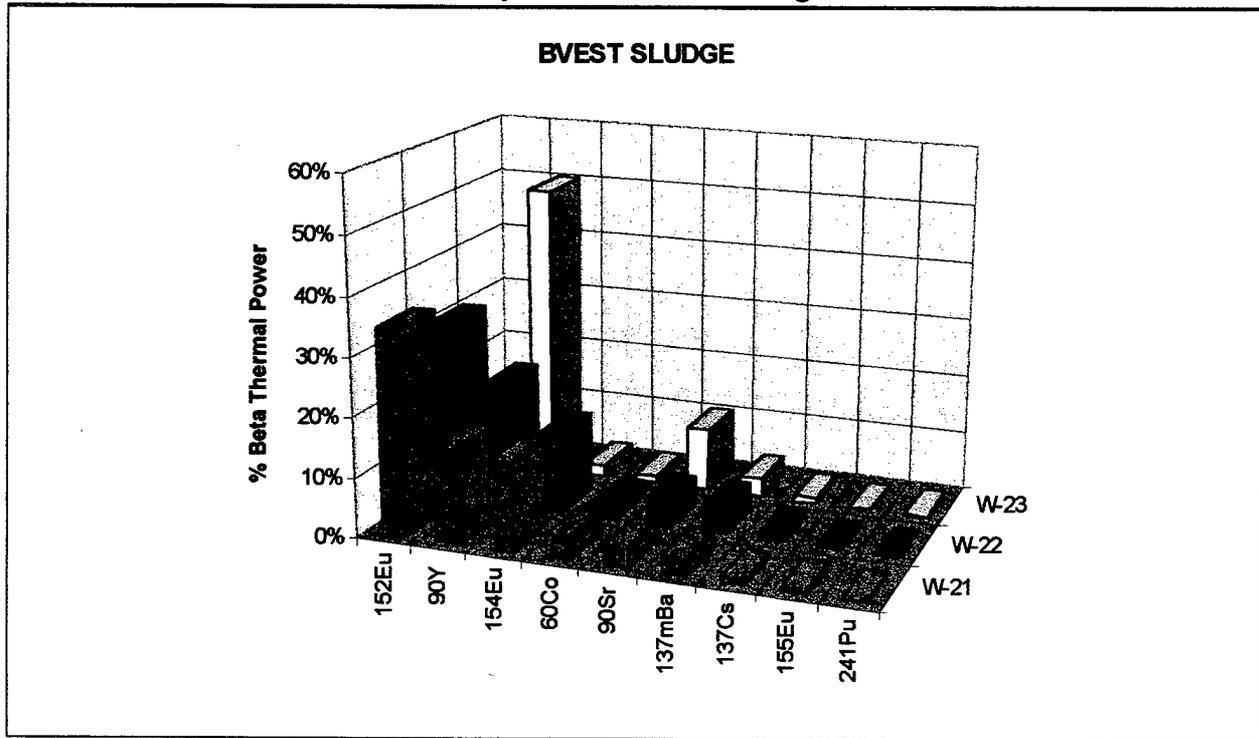
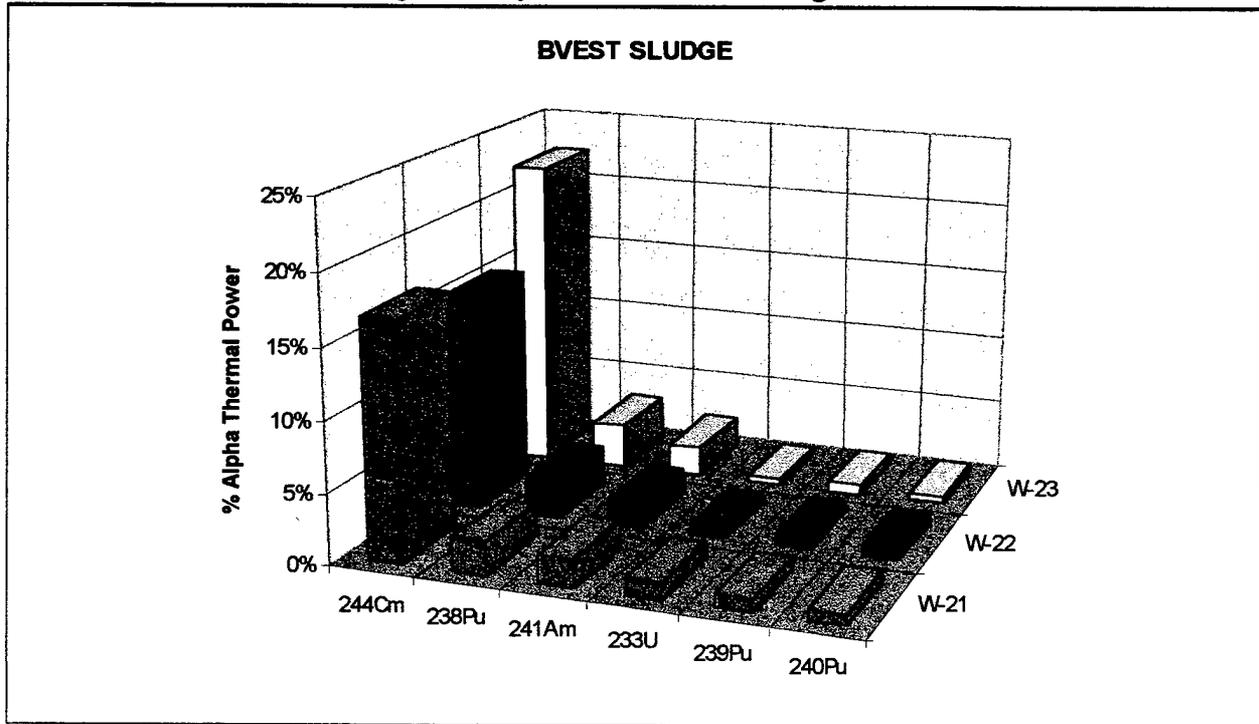


Figure 8 Distribution of Alpha Decay Heat in BVEST Sludge



6.0 Summary of Organic Analytical Results

The organic content of the BVEST samples was very low, with almost nothing above the detection limits observed in the supernatant and only trace amounts observed in the sludge samples. The few organic compounds observed consisted of products from the Purex and other actinide separation processes used by past chemical processing plants within ORNL. The target compound list (TCL) hits and the tentatively identified compounds (TIC) from the GC-MS analyses are listed in Table 22 for the supernatant samples and Table 23 for the sludge samples. For the organic chemical characterization results the following reporting conventions are used:

Reporting limits	The reporting limits are the concentrations above which the response of the instrument for the calibrated range of concentrations is linear.
B	Data qualifier meaning that the compound was also found in the accompanying laboratory blank sample.
D	Data qualifier meaning sample dilution was required.
E	Data qualifier indicating that the reported concentration of the compound exceeded the calibration range of the instrument.
J	Data qualifier meaning that the compound was estimated at a concentration below the reporting limit; also used to indicate that the concentrations for tentatively identified compounds (TICs) are estimates.
U	Data qualifier meaning compound was not detected and method detection limits was reported.
TIC	Tentatively identified compound. The identification is based upon mass spectral data only, and the quantitation is based upon the response factor of the nearest eluting internal standard. All TIC values are estimates and are flagged with the "J" qualifier.

Table 22 Analytical Organic Data for BVEST Liquid Samples

Target Compound	Concentration in Liquid, mg/L		
	W-21	W-22	W-23
Non-halogenated Volatile Organic Compounds (NH-VOA)			
Methanol	2 U	na	2 U
Acetone	2 U	na	2 U
Methyl Ethyl Ketone	2 U	na	2 U
Isobutanol	2 U	na	2 U
Butanol	2 U	na	2 U
Pyridine	2 U	na	2 U
Volatile Organic Compounds (VOA)			
Vinyl Chloride	1 U	na	1 U
Trichlorofluoromethane	1 U	na	1 U
Ethyl Ether	1 U	na	1 U
1,1,2-Trichloro-1,2,2-trifluoroethane	1 U	na	1 U
1,2-Dichloroethylene	1 U	na	1 U
Methylene Chloride	1 U	na	1 U
Chloroform	1 U	na	1 U
1,2-Dichloroethane	1 U	na	1 U
1,1,1-Trichloroethane	1 U	na	1 U
Carbon Tetrachloride	1 U	na	1 U
Benzene	1 U	na	1 U
Trichloroethylene	1 U	na	1 U
1,1,2-Trichloroethane	1 U	na	1 U
Bromoform	1 U	na	1 U
Toluene	1 U	na	1 U
Tetrachloroethylene	1 U	na	1 U
Chlorobenzene	1 U	na	1 U
Ethylbenzene	1 U	na	1 U
m&p-Xylenes	1 U	na	1 U
o-Xylene	1 U	na	1 U
1,1,2,2-Tetrachloroethane	1 U	na	1 U
1,4-Dichlorobenzene	1 U	na	1 U
Ortho-Dichlorobenzene	1 U	na	1 U

Target Compound	Concentration in Liquid, mg/L		
	W-21	W-22	W-23
Tentatively Identified Volatile Organic Compounds			
Acetone	0.12 J	na	0.01 J
2-Butanone	-	na	0.01 J
methane, chloro-	0.33 J	na	-
methane, bromo-	0.10 J	na	-
Unknown	0.32 J (4) ^a	na	-
Semivolatile Organic Compounds (SVOA)			
2-Methyl Phenol	0.1 UD	na	0.05 U
Hexachloroethane	0.1 UD	na	0.05 U
4-Methyl Phenol	0.1 UD	na	0.05 U
Nitrobenzene	0.1 UD	na	0.05 U
2,4-Dinitrotoluene	0.1 UD	na	0.05 U
2,4-Dinitrophenol	0.1 UD	na	0.05 U
Hexachlorobenzene	0.1 UD	na	0.05 U
Pentachlorophenol	0.1 UD	na	0.05 U
Tentatively Identified Semivolatile Organic Compounds			
1-Hexanol, 2-ethyl-	0.06 J	na	-
Tributylphosphate (TBP)	0.13 J	na	1.2 J
Unknown	0.06 J (1) ^a	na	2.5 J (19) ^a

^a Number of compounds grouped together listed in parenthesis.

Table 23 Analytical Organic Data for BVEST Sludge Samples

Target Compound	Concentration in Sludge, mg/Kg		
	W-21	W-22	W-23
Semivolatile Organic Compounds (SVOA)			
2-Methyl Phenol	10 UD	10 UD	10 UD
Hexachloroethane	10 UD	10 UD	10 UD
4-Methyl Phenol	10 UD	10 UD	10 UD
Nitrobenzene	10 UD	10 UD	10 UD
2,4-Dinitrotoluene	0.6 UD	0.6 UD	0.6 UD
2,4-Dinitrophenol	10 UD	10 UD	10 UD
Hexachlorobenzene	0.6 UD	0.6 UD	0.6 UD
Pentachlorophenol	10 UD	10 UD	10 UD
Tentatively Identified Semivolatile Organic Compounds			
Benzene, diethyl-	7.3 JD (2)	27 JD	2.8 JD
Benzene, (1-butyloctyl)-	-	10 JD	-
Benzene, (1-methyldecyl)-	-	20 JD	-
Benzene, (1-methylundecyl)-	-	15 JD	-
Decane, -trimethyl-	-	11 JD	-
1- Decanol	-	-	4.5 JD
Dibutyl phthalate	-	-	6 JD
Dodecane	15 JD	64 JD	5.8 JD
Ethanone, 1-(2,3,4- trimethylphenyl)-	3 JD	22 JD	-
Ethanone, 1-(4- ethylphenyl)-	4.2 JD	-	-
1-Hexanol, 2-ethyl	6 JD	23 JD	24 JD
1- Nonadecanol	-	-	3.4 JD
Pentadecane	-	-	3.8 JD
Phosphoric acid, tris- (2-ethylhexyl)-	8.9 JD	41 JD	11 JD
Tetradecane	37 JD	56 JD	13 JD
Tributylphosphate (TBP)	17 JD	72 JD	-
Tridecane	52 JD	120 JD	17 JD

Target Compound	Concentration in Sludge, mg/Kg		
	W-21	W-22	W-23
Undecane	-	32 JD	3.6 JD
Unknown Hydrocarbons	-	47 JD (3) ^a	-
Unknown	78 JD (9) ^a	64 JD (4) ^a	54 JD (9) ^a
Polychlorinated Biphenyls (PCB) Analysis			
Aroclor-1016	nd ^b	nd ^b	nd ^b
Aroclor-1221	nd ^b	nd ^b	nd ^b
Aroclor-1232	nd ^b	nd ^b	nd ^b
Aroclor-1242	0.05 U	0.05 U	0.05 U
Aroclor-1248	nd ^b	nd ^b	nd ^b
Aroclor-1254	0.05 U	1.0 J	0.05 U
Aroclor-1260	nd ^b	nd ^b	nd ^b

^a Number of compounds grouped together listed in parenthesis.

^b Compounds not detected and calibration was not available to calculate detection limit, but concentration was well below 0.1 ppm.

6.1 Discussion of Organic Analysis

There was no measurement or separation problems encountered during the organic analysis of the BVEST sludge samples. However, some problems were experienced with the BVEST supernatant samples from W-21 and W-23 (no organic measurements were requested for the W-22 liquid phase) with the methylene chloride extractions. These extraction problems were also observed with the MVST liquid samples. The high salt content and the reactivity of the concentrated nitrate causes phase separation problems during the extraction operations along with the evolution of a mixture of nitrogen oxide gases. Both the phase separation problems and the gas generation complicate the handling of these radioactive solutions and tend to increase the overall measurement error due to poor recovery and loss of extraction solvents. Some of the supernatant samples with the high nitrate content can result in large volumes of gas to be released which can pressurize sealed extraction vessels and create both safety and contamination control hazards. In general, it is recommended for future work that aqueous waste samples with nitrate concentrations in excess of 3 M be diluted 1:1 prior to any extraction with methylene chloride or other organic solvents. This sample dilution ensures both the phase separation and gas generation problem are minimized.

7.0 Summary of Rheometry Measurements

7.1 Rheometry Tests

The rheometry data presented here was collected for the purpose of obtaining a simple and rapid estimate of flow properties for the BVEST sludges. The sludge samples used for these tests were highly heterogeneous and contained coarse particles, both of these sample characteristics would degrade the rheometry measurements. The interpretation of the data presented in this section is left to the user of this document. No data reduction was performed nor were any mathematical corrections or curve fitting/smoothing parameters applied to the data. The data is presented as measured directly from the instrument with the parameters listed in this document. All of the data presented here is on file at the RMAL and is available for further study and analysis for those readers who desire more information.

Shear strength and viscosity data were collected for each of the BVEST sludges utilizing a Rotovisco RV30 Searle type rotational CR (controlled rate) rheometer, available from Gebrueder HAAKE GmbH, Karlsruhe or HAAKE (USA). The Searle type measuring system is comprised of a calibrated spring whose deflection is proportional to the torque and converted by a transducer to an electronic signal. The system is close to friction free and provides an instantaneous response. Two types of sensors were used for the tests. A HAAKE FL100 shear vane rotor was used to determine shear strengths. This rotor is comprised of six vanes that are 16 mm high and has a diameter of 22 mm. Viscosity and flow curves were generated using an immersion system comprised of an immersion tube and a modified HAAKE MV DIN rotor. The modified rotor has a smaller diameter than the original (36.4 mm vs. 38.7 mm) and a height of 58.08 mm.

All tests were conducted in a hot cell. The sensors and measuring system were located in the cell and connected to a control unit outside of the cell. A personal computer connected to the control unit was used to run the rheometer software, set test parameters, and collect data. Samples for viscosity measurements were kept at a constant temperature during the tests utilizing a plexiglass bath located in the cell with cooling coils that were supplied from a temperature controlled water bath located outside of the cell.

7.2 Shear Strength Measurements

The shear strength of a fluid provides information of the shear conditions needed to overcome a substance's resistance to flow. It is measured using a constant shear rate and determined from the peak shear stress on a shear stress versus time curve. In theory, a sludge begins as an elastic solid with a specific shear strength. Once this shear strength is surpassed the sludge, if it demonstrates thixotropic properties (the potential to reform its gel structure), becomes a thixotropic fluid that with sufficient time to reach steady state flow conditions may exhibit a yield stress. The yield stress is measured as the residual torque on the shear vane after its rotation has been stopped in the fluid. If a yield stress is present the stored "flow energy" in the sludge at steady state conditions will clamp the vane at a fixed torque value and would be measured as a constant shear stress. As can be seen on the shear stress versus time curves, there was an attempt to measure the yield stress for these sludges. However, in most cases there was an initial drop off in shear stress but it jumped right back up to the steady state value or continued to increase versus maintaining a lower constant shear stress as would be expected. There is no explanation presented here for these observations and the yield stress measurements are considered to be inconclusive. Many of the problems encountered during the laboratory measurements with the shear vane would have been avoided if the shear vane analysis was done directly in the tank.

Shear strength was measured for each individual core sample received. Core samples were transferred to the test containers so as to minimize any disturbance to the samples and to reduce the amount of air that was trapped in the sludge as it was poured into the container. To ensure that there was no influence from the walls of the container a distance of at least three times the diameter of the shear vane was maintained between the shear vane and the sample container walls. When this distance was not satisfied it is noted on the data graphs. Once in the containers, the sludges were not mixed or stirred in any way. The shear tests were performed on these raw sample portions at in-cell temperatures. The data collected on these raw sample portions are not considered to be reproducible and are unique to each sample core collected. There are many variables that can affect the shear stress data that can not be reproduced. Some examples are the physical disturbances on the sludge during the sampling and transfer to the test containers which can result in the formation of random air pockets within the test sample. The placement of the shear vane in the sludge sample, relative to air pockets, large particles, sample beaker walls, etc., can have a significant impact on the overall

shear stress measured. For comparison a non-steady-state shear strength measurement was obtained on a composite of W-21. This composite was mixed and allowed to stand for 48 hours with a layer of supernatant before being tested. The sample mixing and addition of a supernatant layer removed any air/liquid interfaces that were present in the sample and the 48 hour stand period allowed the gel structure to reform prior to the measurement. This non steady state shear strength data is presented for comparison purposes with the original undisturbed sludge core data.

During the actual measurements, the FL100 six vane rotor was rotated at a speed to allow the vanes to cut through the sludge at a rate of one sixth of a revolution in a two minute period. This allowed for sufficient data to be collected before the elasticity of the sludge was broken. The shear rate used was determined to be 0.016 s^{-1} by visually observing the rotation of the shear vane over a two minute period. A number of measurements were conducted at an erroneously high shear rate of 0.16 s^{-1} (as designated on the respective graphs). For these tests the maximum shear stress is measured as a sharper peak versus a broader peak that is seen on the tests conducted at the lower shear rate. The W-21 composite sample shear strength was measured at both shear rates to determine if the shear strength value was affected by the higher shear rate. As can be seen on the graphs, it is believed that this higher shear rate only resulted in the shear strength value being reached in a shorter time period, thus the sharper peak, and the magnitude was not affected for this sample. The shear strength was measured at varying depths in the samples. The different shear vane depths are noted on the curves.

Fluctuations in the data can be seen on the shear stress versus time curves. As mentioned earlier, the measuring system is nearly friction free providing for an instantaneous and smooth response. The fluctuations during measurements are believed to be due to a combination of the samples' heterogeneous matrix, air bubbles and particles. As mentioned earlier for shear strength measurements, minimal disturbance of the sample was emphasized. During the transfer from the field sample tube to the test container, some of the sludges flowed into the test containers and held their shape forming obvious air pockets. The only way to break those air pockets would be to agitate the samples in some manner. This was not an option. Video footage of the sample transfers are on file at the RMAL documenting the sample appearance and flow characteristics as the samples were transferred from the field sample collection tubes into the laboratory sample containers.

Table 24 W-21 Shear Strength Test Measurements

Curve ID	Measurement Description
TSV1	Shear Rate = 0.016 s^{-1} for 4 minutes, then 0.0 s^{-1} for 2 minutes. Shear vane just below sample surface. There were many air pockets observed in sample and the shear vane may not have been covered sufficiently.
TSV2	Shear Rate = 0.016 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. Top of shear vane submerged about one and one half inch into sample.
TSV4	Shear Rate = 0.016 s^{-1} for 16 minutes, then 0.0 s^{-1} for 8 minutes. Shear vane removed from sample for zero adjust then re-submerged one inch from beaker bottom.
BSV1	Shear Rate = 0.016 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. Shear vane just under sample surface. Air gaps in sample by visual observation.
BSV2	Shear Rate = 0.016 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. Top of shear vane about two inches below sample surface
CSV1	Shear Rate = 0.16 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. (Note higher shear rate) Mixed sludge and added layer of supernatant. Let stand for 48 hours. First test - Top of shear vane just below sludge surface.
CSV3	Shear Rate = 0.16 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. (Note higher shear rate) Mixed sludge and added layer of supernatant. Let stand for 48 hours. Second test - Shear vane just above container bottom.
CSV4	Shear Rate = 0.016 s^{-1} for 8 minutes, then 0.0 s^{-1} for 8 minutes. Mixed sludge and added layer of supernatant. Mixture stood for 48 hours then was tested at 0.16 s^{-1} . Ten days later the sample was tested again at 0.016 s^{-1} . Shear vane just off bottom of the sample jar.

Table 25 W-22 Shear Strength Test Measurements

Curve ID	Measurement Description
TSV1	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. First test - Only three quarters of the shear vane was in the sample (could not see because of a hump in sample). Air gaps present in the sample.
TSV2	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. Second test - Top of shear vane about one inch below sample surface. Air gaps present in the sample.
BSV1	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. First test - Top of shear vane about 1/4 inch below sample surface. Air gaps present in the sample.
BSV226	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. Second test - Top of shear vane about 2 inches below sample surface. Air gaps present in the sample. Communication problem between the rheometer and the control system during test. Although data shows spikes at baseline, the shear strength can still be approximated from the curve.

Table 26 W-23 Shear Strength Test Measurements

Curve ID	Measurement Description
TSV1	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. First test - Top of shear vane about 1/4 inch below sample surface. Air gaps present in the sample.
TSV2	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. Second test - Top of shear vane about 2 inches below sample surface. Air gaps present in the sample.
BSV1	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. First test - Top of shear vane about 1/4 inch below sample surface. A few air gaps present in the sample.
BSV2	Shear Rate = 0.16 s ⁻¹ for 8 minutes, then 0.0 s ⁻¹ for 8 minutes. Second test - Top of shear vane about 2 inches below sample surface. Few air gaps present in the sample.

Figure 9 Shear Strength Curves for Top Core from W-21 Sludge

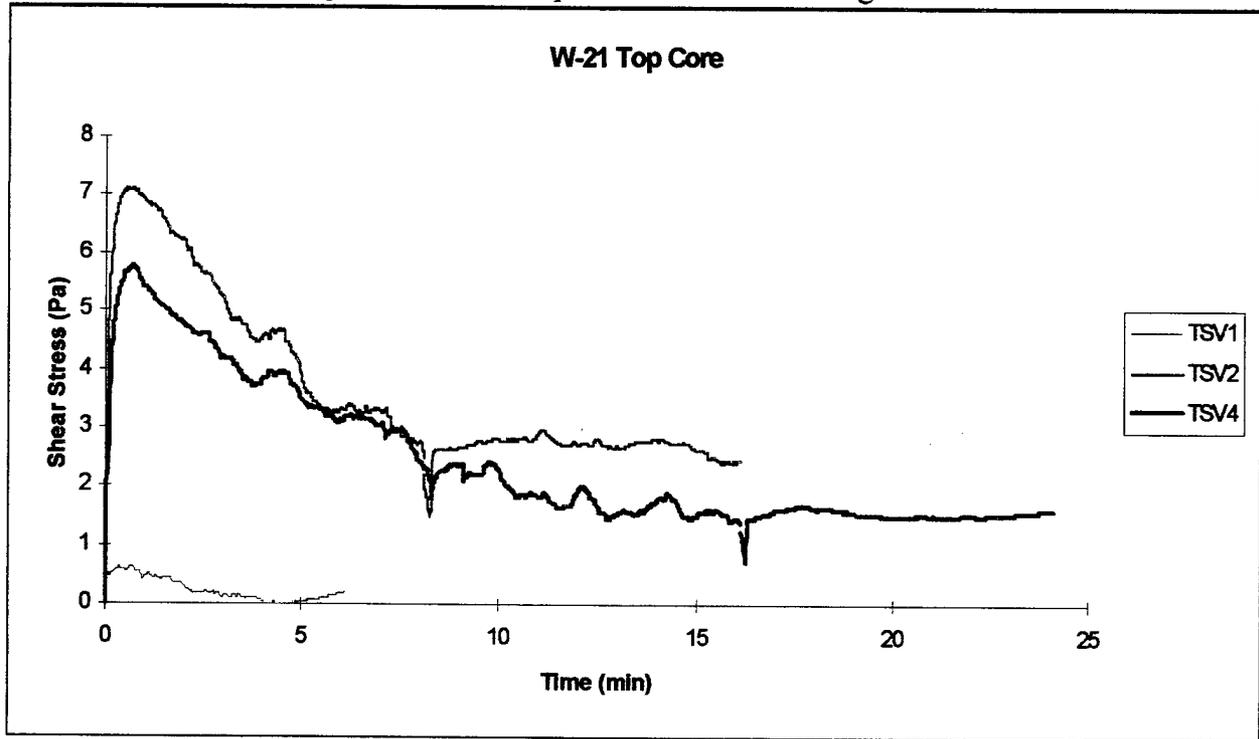


Figure 10 Shear Strength Curves for Bottom Core from W-21 Sludge

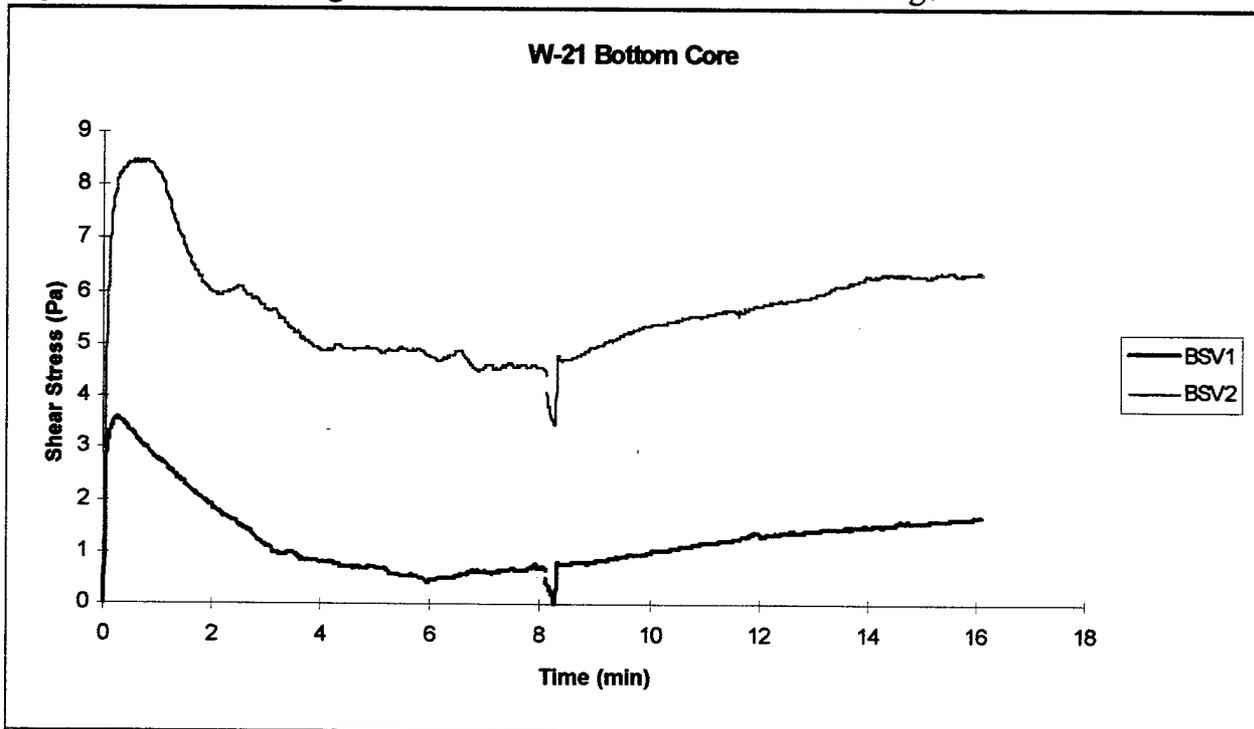


Figure 11 Shear Strength Curves for Composite Core from W-21 Sludge

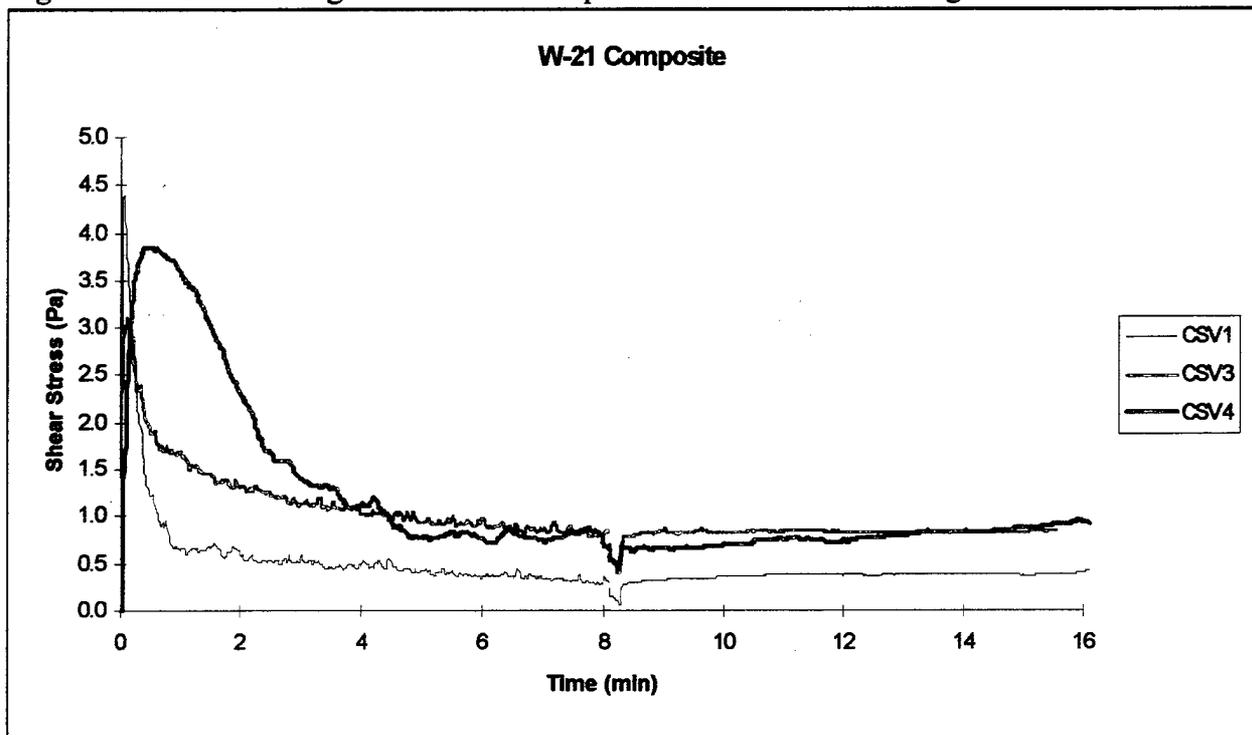


Figure 12 Expanded View for W-21 Composite Sludge Curve

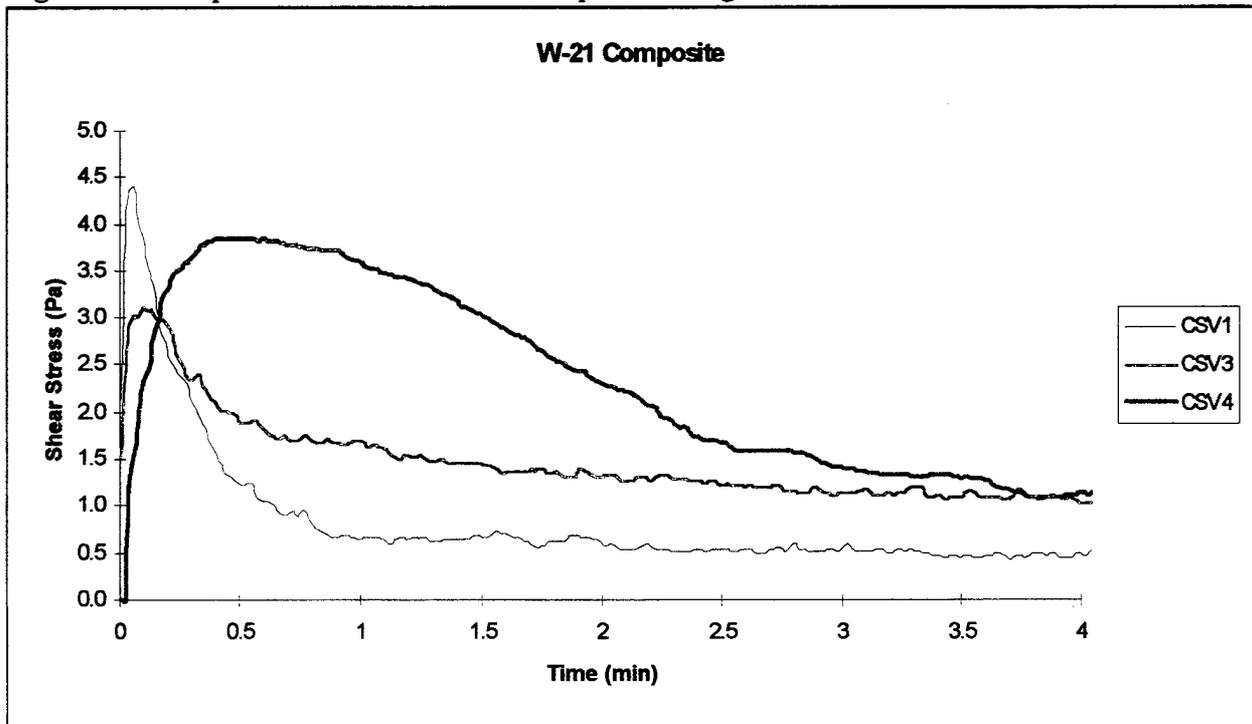


Figure 13 Shear Strength Curves for Top Core from W-22 Sludge

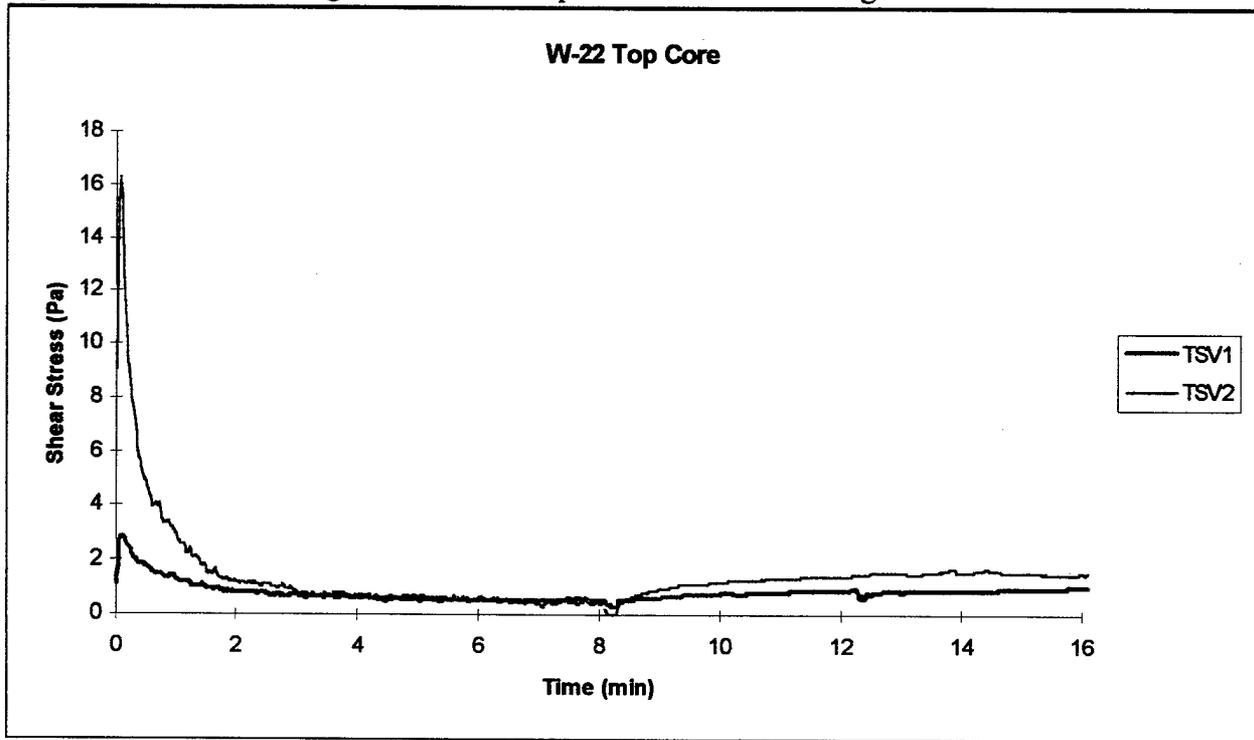


Figure 14 Shear Strength Curves for Bottom Core from W-22 Sludge

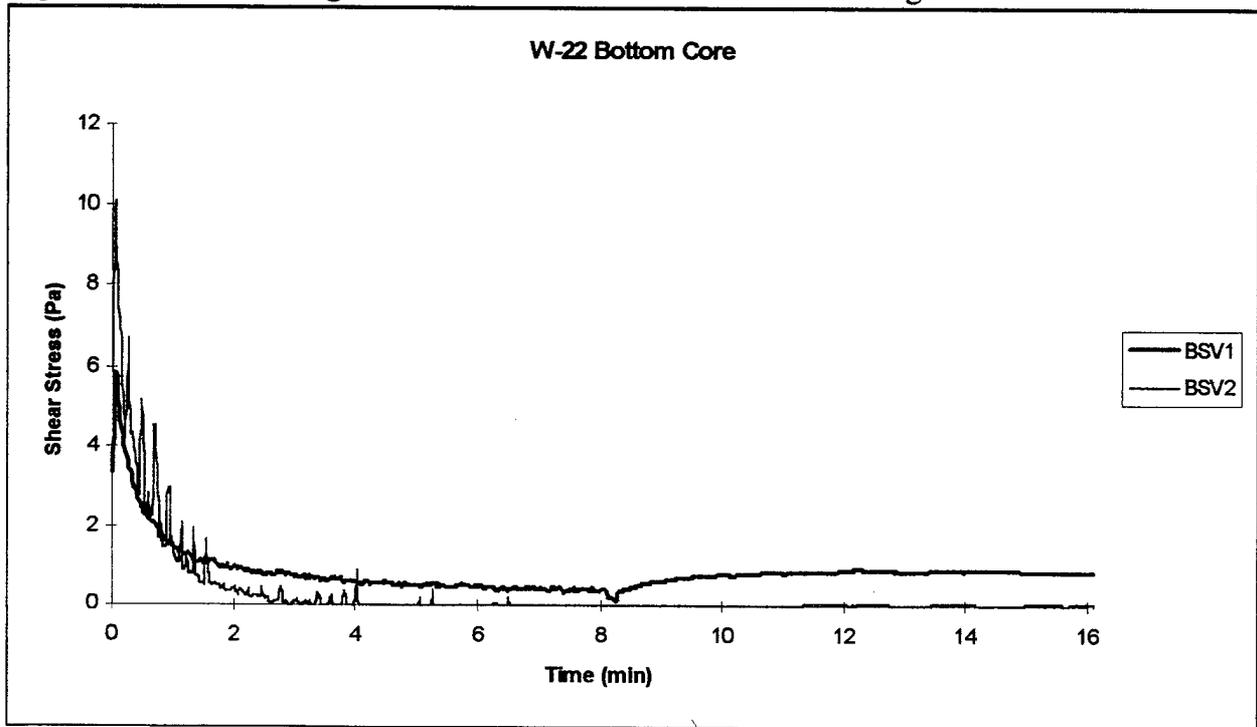


Figure 15 Shear Strength Curves for Top Core from W-23 Sludge

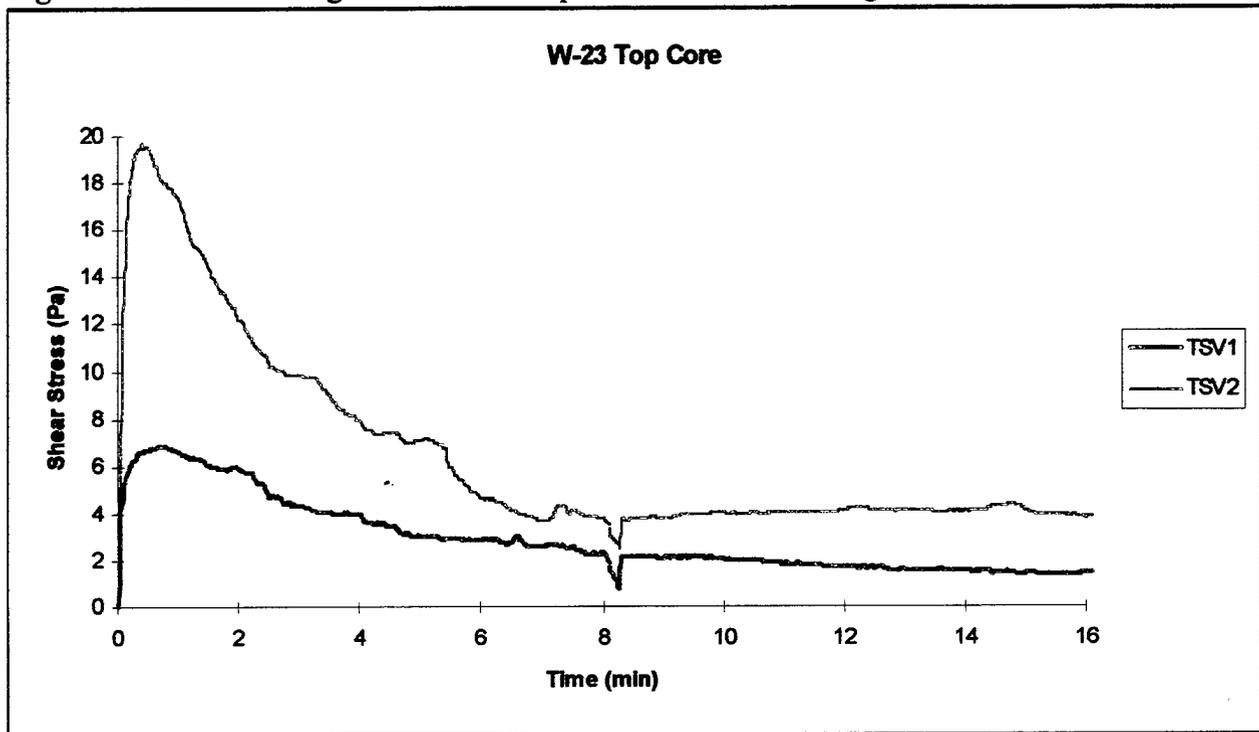
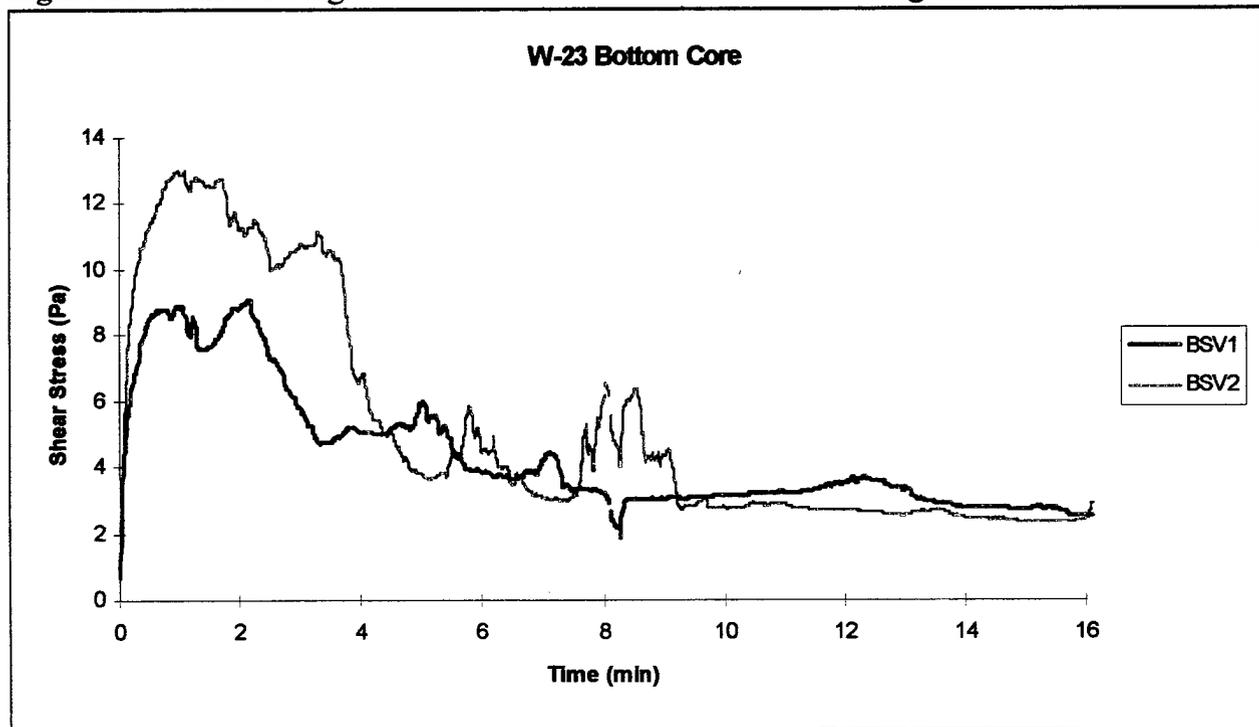


Figure 16 Shear Strength Curves for Bottom Core from W-23 Sludge



7.3 Viscosity and Flow Curves

After the completion of the shear strength tests the two cores from each tank were composited, mixed, and diluted with their respective tank supernatant at an approximate ratio of 1:1. From this mixed dilution, an aliquot was removed for total solids and undissolved solids determination. Subsequently, the viscosity and flow characteristics were measured over a range of increasing (0.0 s^{-1} to 450 s^{-1}) to decreasing (450 s^{-1} to 0.0 s^{-1}) shear rates. A time interval of three minutes was chosen for both the increasing and decreasing shear rate steps, for a total of six minutes per test. The temperature throughout the tests was maintained at $25 \text{ }^{\circ}\text{C} \pm 1 \text{ }^{\circ}\text{C}$ unless otherwise noted on the curves. The tests were performed using the HAAKE immersion sensor system. The system is comprised of a hollow immersion tube with an inner diameter of 42 mm and a modified cylindrical MV DIN rotor with a diameter of 36.8 mm that is placed within the tube. This leaves an annular distance of 5.2 mm between the rotor and tube wall for the sample to flow during the test. Without the modification to the rotor this annular distance would have only been 3.3 mm. The annular distance was enlarged to minimize the bias due to the enactment of large particles within the sludges on the flow measurements.

Prior to the start of all tests, the samples were stabilized at a temperature of $25 \text{ }^{\circ}\text{C} \pm 1 \text{ }^{\circ}\text{C}$ with a circulating water bath. During the temperature stabilization process each sample was stirred to suspend the slurry for the test. Typically this process took approximately 10 min. to complete. Once at temperature, the sensor was lowered into the sample and the measurements were begun. The samples were stirred throughout the tests to ensure that the particles were maintained in suspension. Tests were conducted to compare the measured viscosity with and without sample stirring during the measurement cycle. These test were done on both standards and the W-22 sludge sample. The viscosities obtained on the standard solutions were comparable with and without stirring. The “no mixing” results on W-22 are presented along with the stirred results for comparison purposes. It does appear that both tests are comparable.

As indicated in the shear stress versus time curves, fluctuations in the data can be seen on the viscosity and flow curves. The fluctuations during measurements are believed to be due to a combination of the samples' heterogeneous matrix and the presence of significant particles in the samples. Also, the sensitive measurement scale used (mPa) for the y-axis on the viscosity curves

would amplify those fluctuations. These fluctuations are most pronounced for the W-21 and W-23 curves. The increasing shear rate or “Up curve” data (0.0 s^{-1} to 450 s^{-1} shear rates in three minutes) is depicted as a thin blue line on the graphs. The decreasing shear rate or “Down curve” data (450 s^{-1} to 0.0 s^{-1} shear rates in three minutes) as a thick red line.

Figure 17 Viscosity vs. Shear Rate for W-21 Sludge

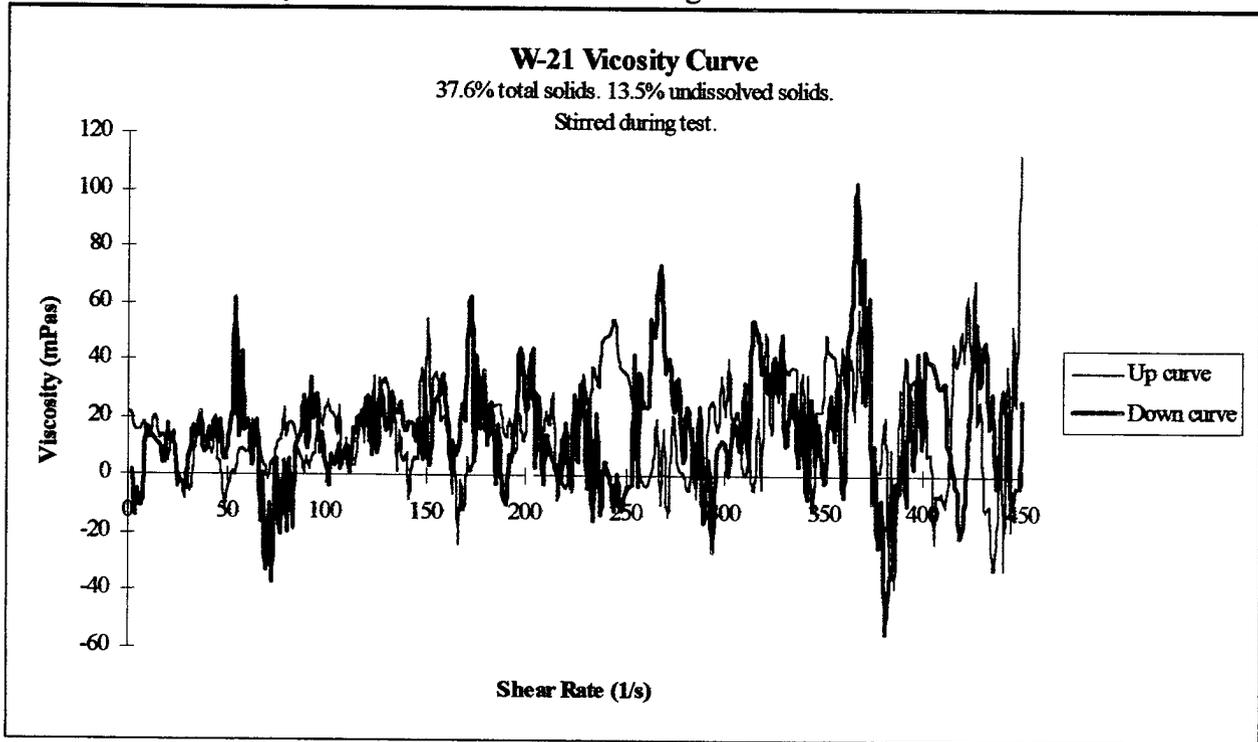


Figure 18 Shear Stress vs. Shear Rate for W-21 Sludge

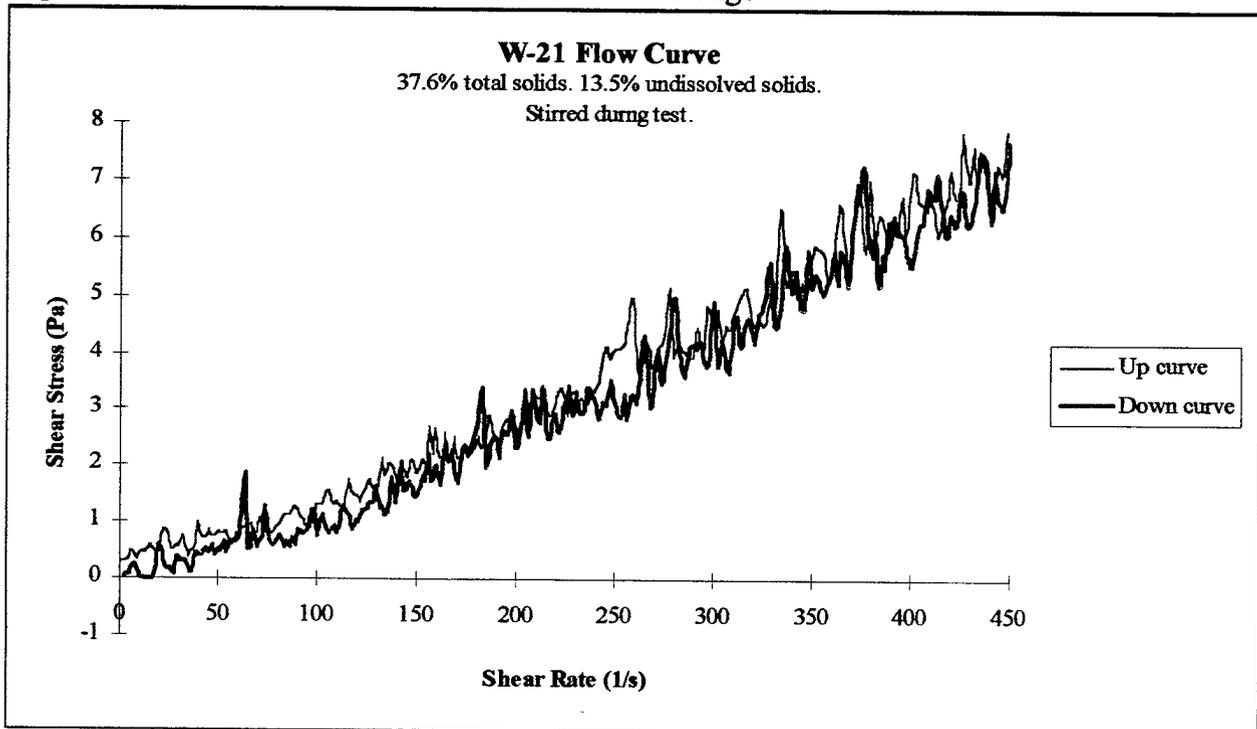


Figure 19 Viscosity vs. Shear Rate for W-22 Sludge

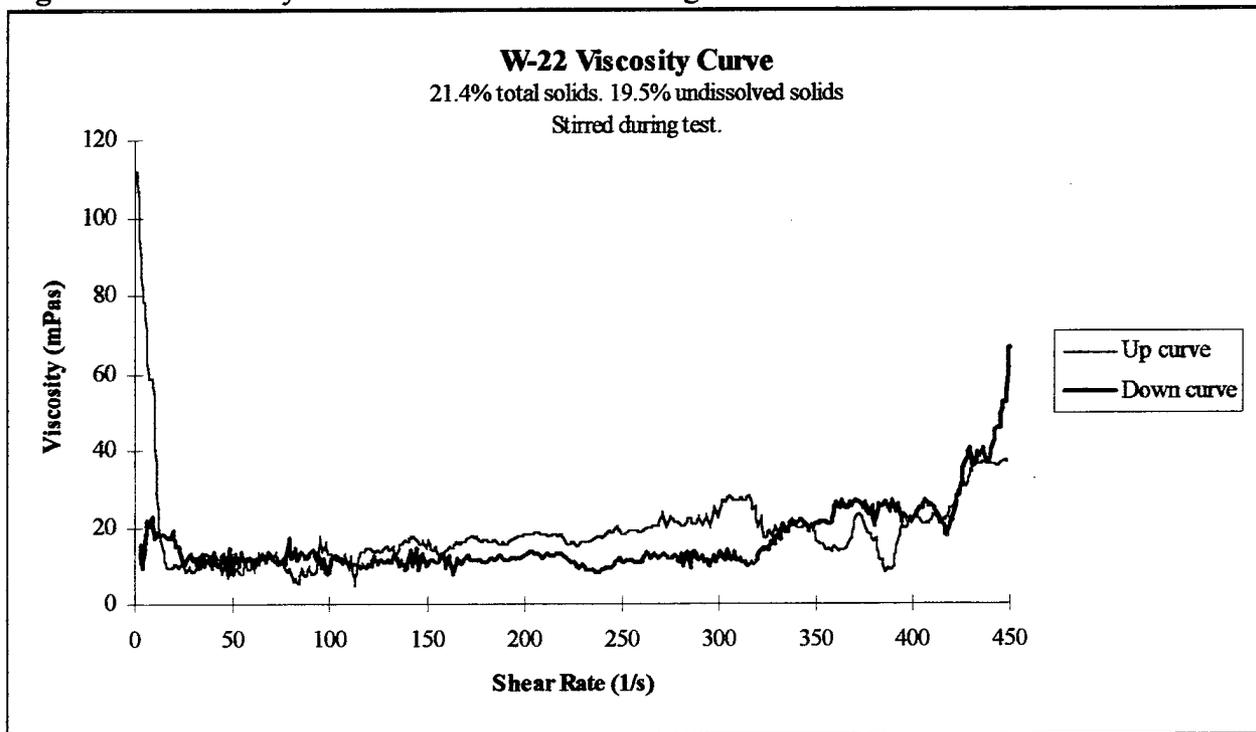


Figure 20 Shear Stress vs. Shear Rate for W-22 Sludge

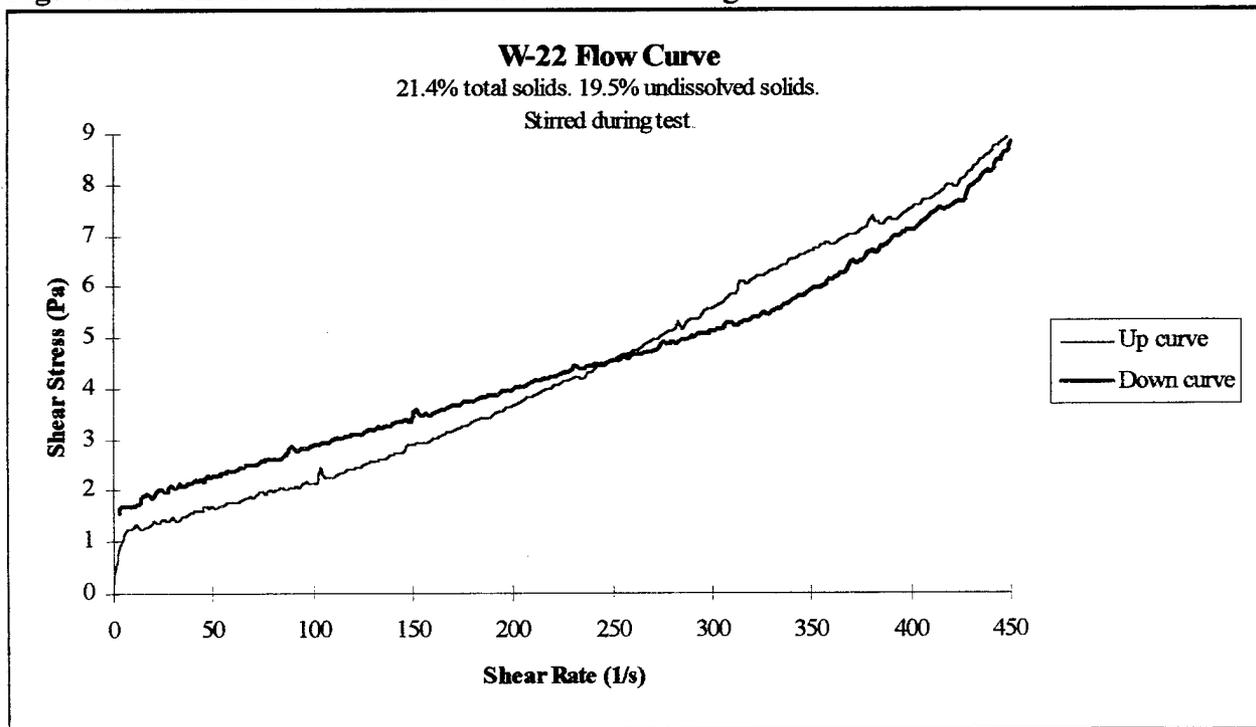


Figure 21 Viscosity vs. Shear Rate for W-22 Sludge (Duplicate)

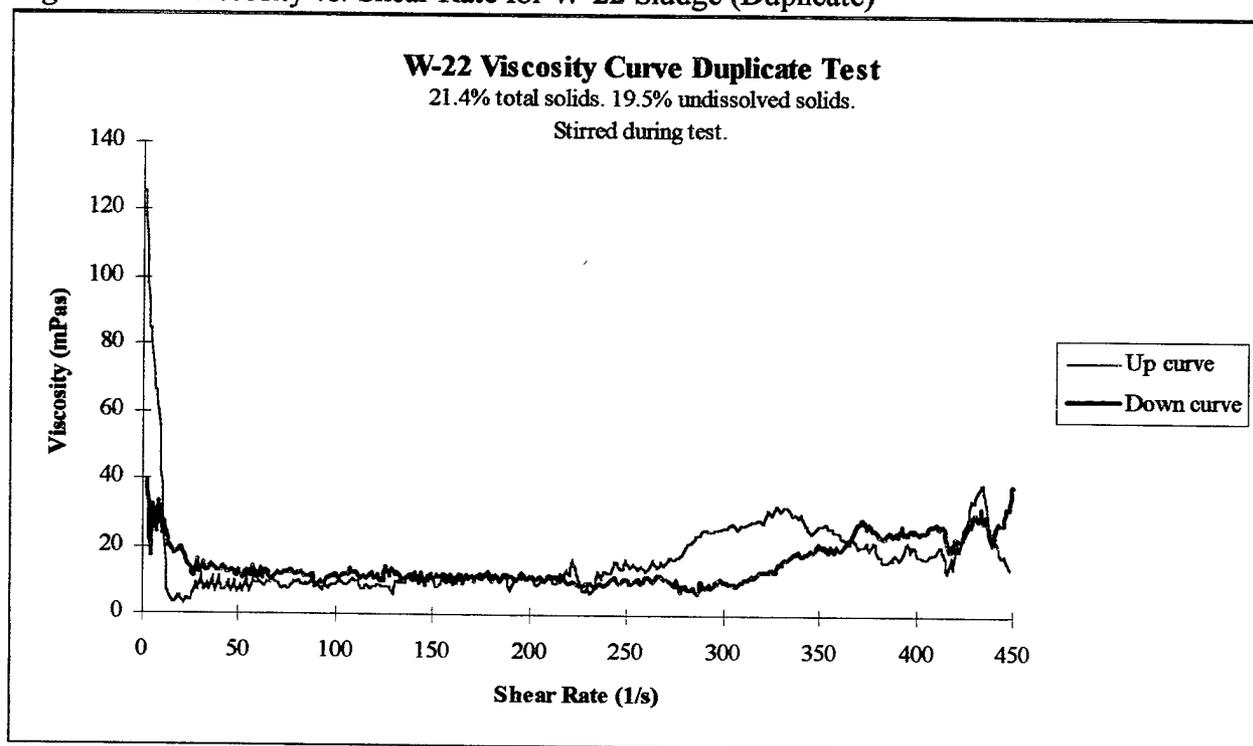


Figure 22 Shear Stress vs. Shear Rate for W-22 Sludge (Duplicate)

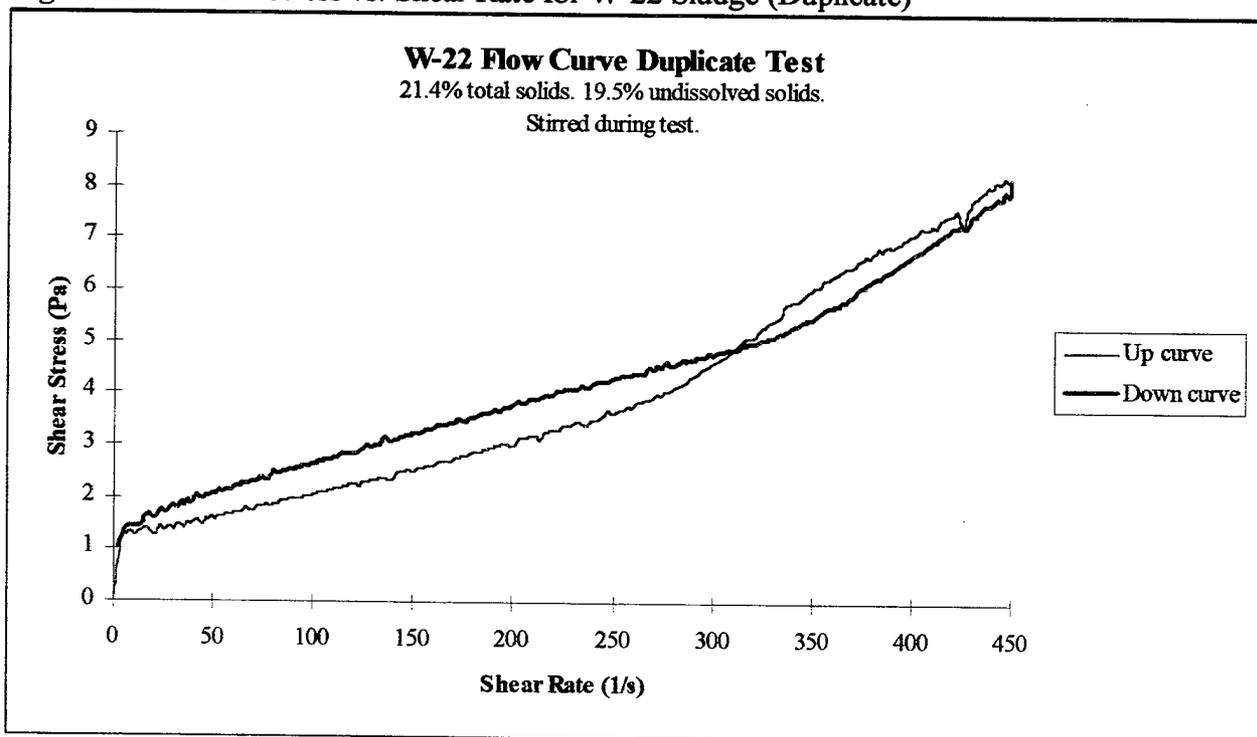


Figure 23 Viscosity vs Shear Rate for W-22 Sludge (Static)

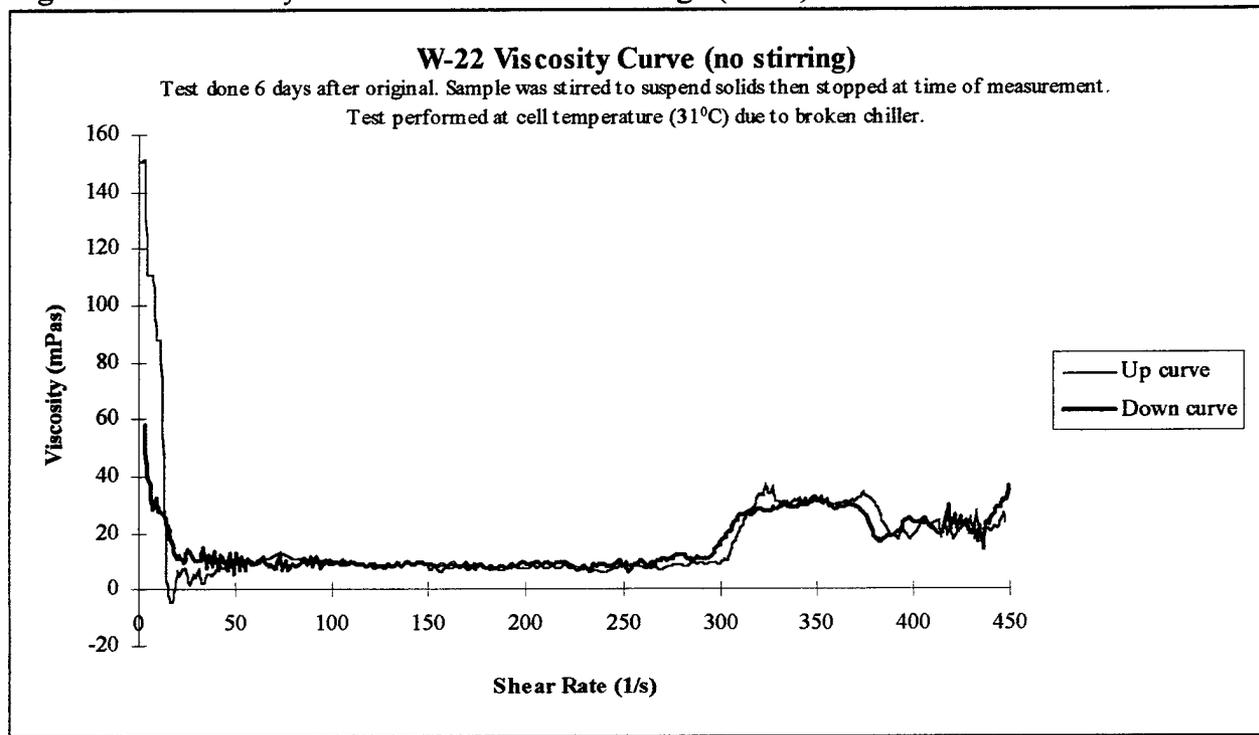


Figure 24 Shear Stress vs. Shear Rate for W-22 Sludge (Static)

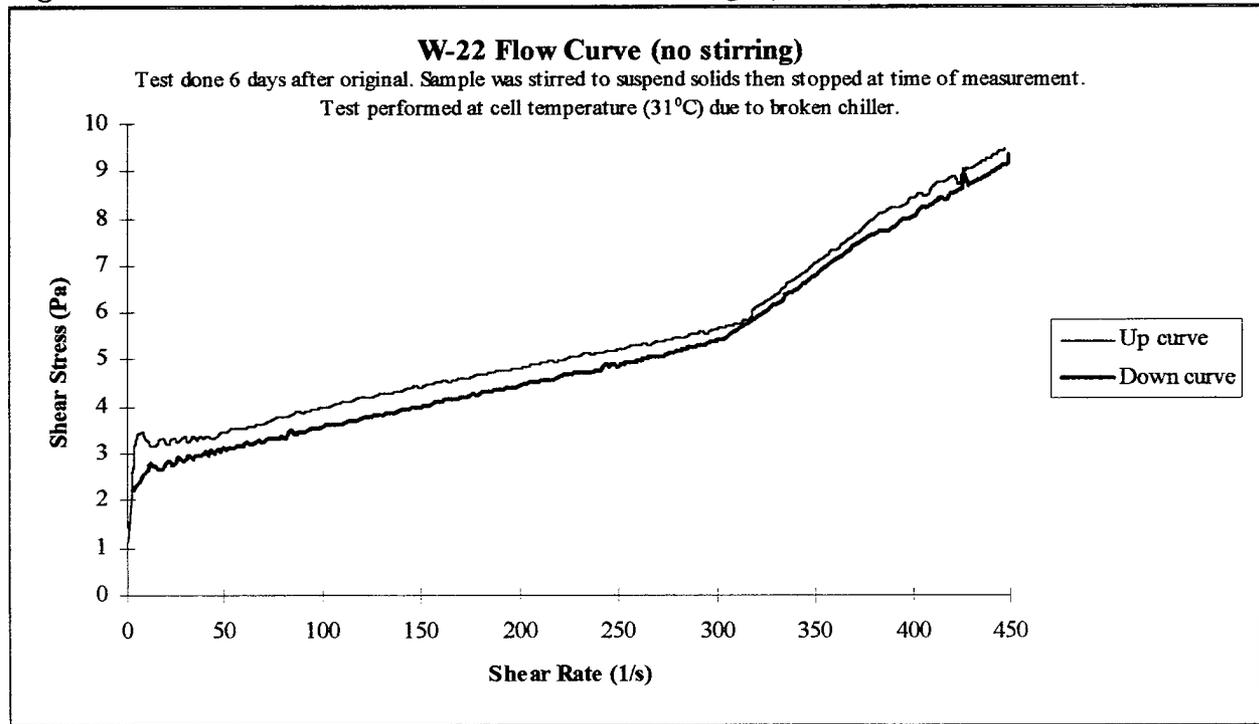


Figure 25 Viscosity vs. Shear Rate for W-23 Sludge

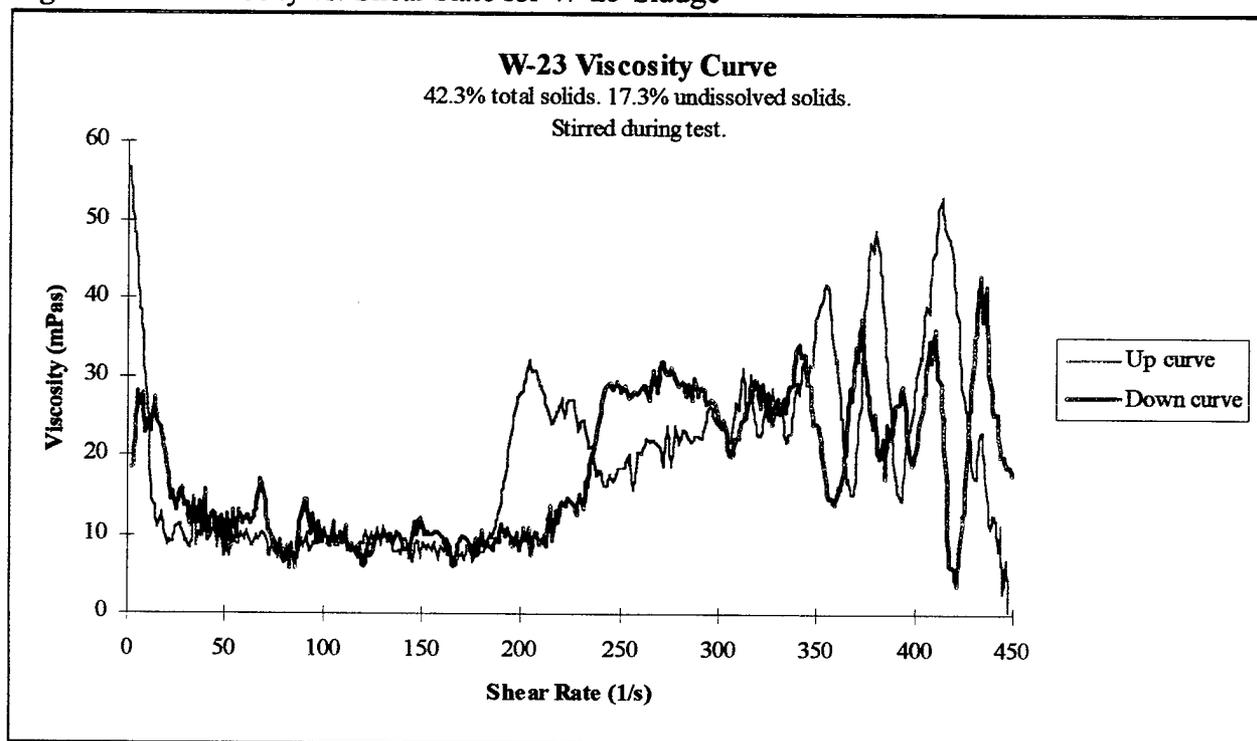
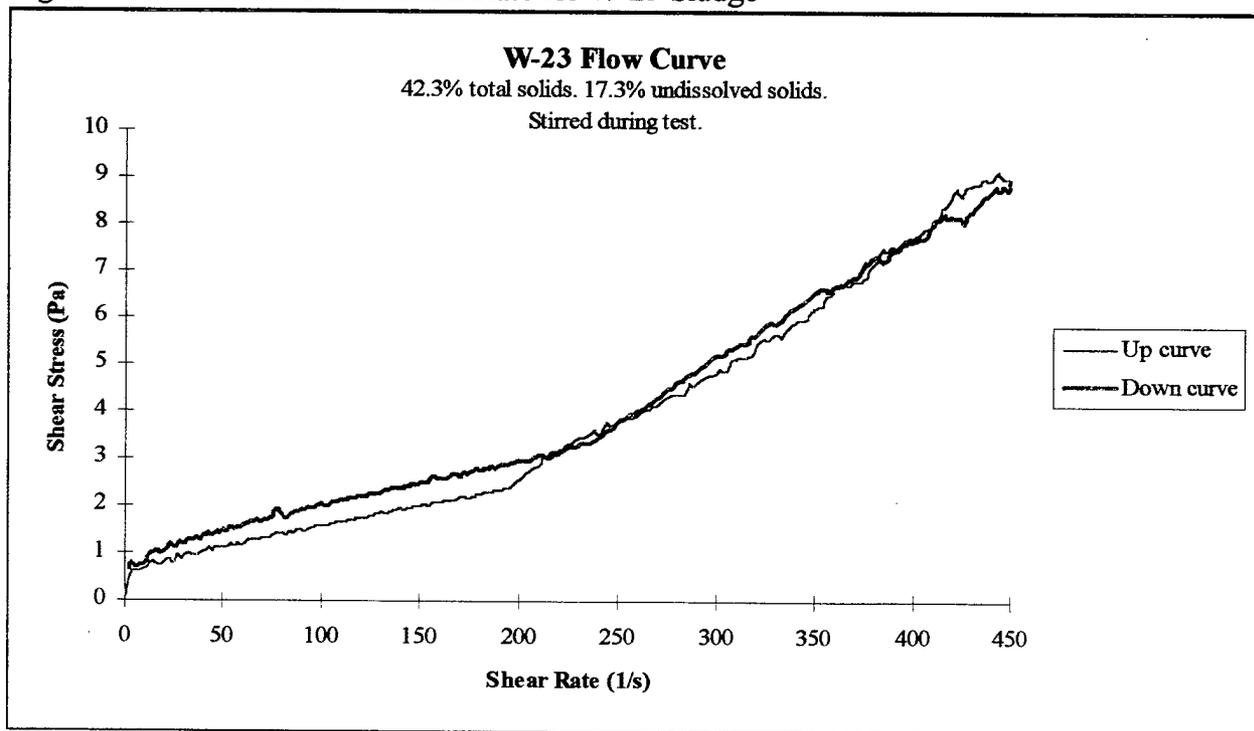


Figure 26 Shear Stress vs. Shear Rate for W-23 Sludge



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13. *Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, WIPP-DOE-069, Rev. 5.0, April 1996.

APPENDIX A

Radioactive Materials Analytical Laboratory QC Acceptance Criteria for Radioactive Liquid/Solid Waste Samples

Analysis	Method (s) CASD-AM-	Quality Control Check (per batch)	SW-846 Acceptance Criteria (%D, %R, RPD) ^e	RMAL Acceptance Criteria (%D, %R, RPD) ^e
Metals by ICP-AES (inductively coupled plasma atomic emission spectroscopy)	SW846-6010A	high standard calibration verifications (ICV & CCV) ^a calibration blank & checks (ICB & CCB) ^a method blank (sample prep) ^a matrix spike matrix spike duplicate or sample duplicate laboratory control sample (sample prep) ^a serial dilution (if interference suspected) post digestion spike ^a	±5%D ±10%D <3 x IDL <3 x IDL ±20%D ±20 RPD none specified ±10%R ±20%D	±5%D ±10%D <3 x IDL <3 x IDL ±25%D (liq.), ±30%D (solid) ±20 RPD (liq.), ±30 RPD (solid) ±20%D ±10%R ±25%D (liq.), ±30%D (solid)
Metals by ICP-MS (inductively coupled plasma- mass spectrometry, fully quantitative method)	SW846-6020	calibration verifications (ICV & CCV) ^a calibration blank & blank checks (CCB) ^a method blank (sample prep) ^a matrix spike matrix spike duplicate or sample duplicate laboratory control sample (sample prep) ^a internal standard post digestion spike ^a	±10%D <3 x IDL none specified none specified ±20 RPD none specified 30-120% R ±10%D	±10%D <3 x IDL <10 x IDL ±25%D (liq.), ±30%D (solid) ±20 RPD (liq.), ±30 RPD (solid) ±20%D ±30%D ±20%D
Metals by GFAA (graphite furnace atomic absorption)	SW846-7000A	high standard calibration verifications (ICV & CCV) ^a method blank (sample prep) ^a matrix spike matrix spike duplicate laboratory control sample (sample prep) ^a serial dilution (if interference suspected) post digestion spike ^a	not required ±10%D (ICV), ±20%D (CCV) none specified none specified none specified none specified ±10%R ±15%D	±5%D ±10%D (ICV), ±20%D (CCV) <3 x IDL ±25%D (liq.), ±30%D (solid) ±20 RPD (liq.), ±30 RPD (solid) ±25%D ±10%R ±25%D (liq.), ±30%D (solid)
Mercury by CVAA (cold vapor atomic absorption)	SW846-7471A SW846-7470	instrument blank calibration verification (ICV & CCV) ^a method blank (sample prep) ^a laboratory control sample (sample prep) ^a matrix spike matrix spike duplicate or sample duplicate post digestion spike ^a	none specified none specified none specified none specified none specified none specified none specified none specified	<5 x IDL ±10%D <5 x IDL ±25%D ±25%D (liq.), ±30%D (solid) ±20 RPD (liq.), ±30 RPD (solid) ±25%D (liq.), ±30%D (solid)
Carbon (total organic carbon, total carbon, total inorganic carbon)	SW846-9060	instrument blank calibration verification (ICV & CCV) ^a matrix spike matrix spike duplicate	none specified none specified none specified none specified	<3 x IDL ±10%D (ICV), ±20%D (CCV) ±25%D (liq.), ±30%D (solid) ±20 RPD (liq.), ±30 RPD (solid)
Anions by Ion Chromatography (IC)	SW846-9056	calibration verification (ICV & CCV) ^a matrix spike sample duplicate	±10%D (ICV), ±5%D (CCV) none specified none specified	±10%D (ICV), ±15%D (CCV) ±25%D ±20 RPD
pH measurement	SW846-9040A SW846-9045B	check standard sample duplicate	none specified none specified	±10%D ±20%D
Total and dissolved solids (TS & TDS)	EPA600-160.2 EPA600-160.3	sample duplicate check standard	none specified none specified	±10 mg/ 10mL sample ±10%D
Carbonate and bicarbonate titration	AC-MM-1 003105	sample duplicate check standard	none specified none specified	±20 RPD ±20%D
Gross alpha/beta	EPA-900.0 RML-RA02 RML-RA12	background check calibration verification method blank (optional) ^a sample duplicate matrix spike	none specified none specified none specified none specified none specified	< 3sigma daily change ±10%D evaluated for contamination ±25 RPD (liq.), ±30 RPD (solid) ±25%D (liq.) & ±30%D (solid)
Nuclides by gamma spectrometry	EPA-901.1	background check calibration verification sample duplicate	none specified none specified none specified	< 3sigma daily change ±10%D ±25%D (liq.) & ±30%D (solid)

Analysis	Method (s) CASD-AM-	Quality Control Check (per batch)	SW-846 Acceptance Criteria (%D, %R, RPD) ^e	RMAL Acceptance Criteria (%D, %R, RPD) ^e
Sr-90 determination	RML-RA13 EPA-905.0	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gross alpha/beta criteria
Tc-99 determination	DOE Compendium RP550 RML-RA05	method blank (optional) laboratory control sample matrix spike matrix spike or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	< 3 x IDL 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see ICP-MS criteria
H-3 determination	EPA-906.0	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gross alpha/beta criteria
Cm-244	RML-RA06	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gross alpha/beta criteria
Pu-238,239/240	RML-RA11 RML-RA08	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gross alpha/beta criteria
U-233/234	RML-RA10	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gross alpha/beta criteria
Th Determination	EPA-901.1 RML-RA09	method blank (optional) laboratory control sample matrix spike matrix spike duplicate or sample duplicate associated instrument QC	none specified none specified none specified none specified none specified	evaluated for contamination ^d 20%D ±25%D (liq.) & ±30%D (solid) ±25 RPD (liq.), ±30 RPD (solid) see gamma spectrometry criteria
PCBs (polychlorinated- biphenyls)	SW846-8080	calibration verification (ICV & CCV) ^a method blank (sample prep) ^a surrogate standard matrix spike matrix spike duplicate sample duplicate laboratory control sample (sample prep) ^a	refer to method 8080 none specified none specified none specified none specified none specified none specified	to be specified ^b < regulatory limit (2ppm) ± 50-150%R ± 50-150%R ± 50-150%R to be specified ^b to be specified ^b
Volatile organics	SW846-8260	calibration verification (ICV & CCV) ^a method blank (sample prep) ^a surrogate standard matrix spike matrix spike duplicate sample duplicate laboratory control sample (sample prep) ^a	see SW846 8260, Sept. '86 " " " " "	± 20% D 3 X MDL refer to supplement Table A refer to supplement Table A refer to supplement Table A refer to supplement Table A
Nonhalogenated volatile organics	SW846-8015	calibration verification (ICV & CCV) ^a method blank (sample prep) ^a surrogate standard matrix spike matrix spike duplicate sample duplicate laboratory control sample (sample prep) ^a	see SW846-8015, Sept. '86 " " " " "	± 15% D 3 X MDL refer to supplement Table B refer to supplement Table B refer to supplement Table B refer to supplement Table B
Semivolatile organics	SW846-8270	calibration verification (ICV & CCV) ^a method blank (sample prep) ^a surrogate standard matrix spike matrix spike duplicate sample duplicate laboratory control sample (sample prep) ^a	see SW846-8270, Sept. '86 " " " " "	± 20% D 3 X MDL refer to supplement Table C refer to supplement Table C refer to supplement Table C refer to supplement Table C

- a Initial calibration verification (ICV) is typically performed at the beginning of a run to check the calibration and must be independent of the calibration standards. The continuing calibration verification (CCV) must also be independent of the calibration standards, but may be the same standard as the ICV. The CCV is typically analyzed every 10 samples and at the end of the run for metals analysis or every 12 samples for organic analysis.
- b The calibration blank is an instrument blank used in the calibration to initially determine the blank value and therefore used as blank subtraction. The continuing calibration blank (CCB) is also an instrument blank which is analyzed every 10 samples and at the end of the run, but is not used in blank subtraction, but only to monitor instrument contamination.
- c Method blanks and laboratory control samples are only required if a sample preparation is performed before analysis. Sample preparation does not include dilutions or transfers to containers.
- d Post digestion spikes are not necessary if the pre-digestion spike is in control. If this control does not meet the QC acceptance criteria, the post digestion spike should be performed.
- e Acceptance criteria:
%D = % deviation from true value
%R = % recovery of true value
RPD = relative percent difference between two compared values
- f Method blanks for radiochemical analysis are used to monitor cross contamination. However, due to the levels of radioactivity present in samples at the RMAL, the effect of contamination may be insignificant in most cases. Therefore, the requirement to analyze a method blank for radiochemical analysis is optional (i.e. at the discretion of the chemist or supervisor).
- g Acceptance criteria for the method blanks performed for radiochemical analysis varies based upon the level of activity in the samples and the amount of background activity. A qualified chemist reviews the data from method blanks to determine if significant contamination is present.
- h The acceptance criteria for PCB analyses which are not identified in this table, shall be specified at a later date. Currently, the Analytical Methods Group group leader specifies the QC criteria if different from SW846 and if not specified by the sample generator.

SUPPLEMENT TABLE A
Volatile Organic Analyses QC Limits

CAS #	Compound	Precision (RPD)	Accuracy (% R)	MDL (mg/Kg)	PRQL (mg/Kg)	LCS (% R)
75-01-4	Vinyl Chloride	≤ 200	D-251	1	4	34-100
75-69-4	Trichlorofluoromethane	≤ 110	17-181	1	10	47-103
76-13-1	1,1,2-Trichloro-1,2,2-Trifluoroethane	≤ 50	60-150	1	10	49-105
75-35-4	1,1-Dichloroethylene	≤ 250	D-234	1	10	43-100
75-9-2	Methylene Chloride	≤ 50	D-221	1	10	67-108
75-15-0	Carbon Disulfide	≤ 50	60-150	1	10	36-100
67-66-3	Chloroform	≤ 44	51-138	1	10	72-111
107-6-2	1,2-Dichloroethane	≤ 42	49-155	1	10	76-112
71-55-6	1,1,1-Trichloroethane	≤ 33	52-162	1	10	71-110
56-23-5	Carbon Tetrachloride	≤ 30	70-140	1	10	54-115
71-43-2	Benzene	≤ 45	37-151	1	10	70-109
79-1-6	Trichloroethylene	≤ 36	71-157	1	10	80-120
79-0-5	1,1,2-Trichloroethane	≤ 38	52-150	1	10	80-120
75-25-2	Bromoform	≤ 47	45-169	1	10	61-115
108-88-3	Toluene	≤ 29	47-150	1	10	80-120
127-18-4	Tetrachloroethylene	≤ 29	64-148	1	10	80-120
108-90-7	Chlorobenzene	≤ 38	37-160	1	10	80-120
100-41-4	Ethylbenzene	≤ 43	37-162	1	10	80-120
1330-20-7	Xylenes	≤ 50	60-150	1	10	80-120
79-34-5	1,1,2,2-Tetrachloroethane	≤ 55	46-157	1	10	67-117
106-46-7	1,4-Dichlorobenzene	≤ 60	18-190	1	10	80-120
95-50-1	ortho-Dichlorobenzene	≤ 60	18-190	1	10	80-112
60-29-7	Ethyl Ether	≤ 50	60-150	1	10	54-100
Surrogates						
	1,2-Dichloroethane-d ₂		61-129			
	Toluene-d ₈		89-118			
	4-Bromofluorobenzene		93-107			

SUPPLEMENT TABLE B
Nonhalogenated Volatile Organic Analyses QC Limits

CAS #	Compound	Precision (RPD)	Accuracy (% R)	MDL (mg/Kg)	PRQL (mg/Kg)	LCS (% R)
67-56-1	Methanol	≤ 50	60-150	10	100	49-145
67-64-1	Acetone	≤ 50	60-150	10	100	61-136
78-93-3	Methyl Ethyl Ketone	≤ 50	60-150	10	100	62-134
78-83-1	Isobutanol	≤ 50	60-150	10	100	52-126
71-36-3	Butanol	≤ 50	60-150	10	100	50-110
110-86-1	Pyridine	≤ 50	60-150	10	100	64-122
Surrogate						
71-23-8	n-Propanol		60-150			

SUPPLEMENT TABLE C
Semivolatile Organic Analyses QC Limits

CAS #	Compound	Precision (RPD)	Accuracy (% R)	MDL (mg/Kg)	PRQL (mg/Kg)	LCS (% R)
95-48-7	2-Methylphenol	≤ 50	60-150	5	40	46-104
67-72-1	Hexachloroethane	≤ 44	40-113	5	40	38-100
106-44-5	4-Methylphenol	≤ 50	60-150	5	40	46-114
98-95-3	Nitrobenzene	≤ 72	35-180	5	40	46-100
121-14-2	2,4-Dinitrotoluene	≤ 46	39-139	0.3	2.6	54-146
118-74-1	Hexachlorobenzene	≤ 319	D-152	0.3	2.6	52-115
87-86-5	Pentachlorophenol	≤ 128	14-176	5	40	54-130
51-28-5	2,4-Dinitrophenol	≤ 119	D-172	5	40	47-100
Surrogates						
367-12-4	2-Fluorophenol		D-107			
	Phenol-d ₅		8-142			
	Nitrobenzene-d ₅		28-117			
321-60-8	2-Fluorobiphenyl		24-144			
	2,4,6-Tribromophenol		D-100			
	Terphenyl-d ₁₄		D-226			

APPENDIX B

This section includes three tables of information and measurements that may be of value to the data users. The first Table B1, includes the field measurements taken from the top of the tank to each phase change (air/liquid, liquid/sludge, and bottom of the tank). Table B1 also includes the total mass and/or activity for some of the major species in the sludge of general interest to the data users.

The dose measurement taken in during the field sampling for the liquid and sludge samples are included in Table B2 and Table B3. The dose measurements were taken at contact with the sampling container (250 mL I-Chem jar) for the liquids and at contact with the one inch core sludge sampling device.

Table B1 Total Mass and Activity for Selected Species of Interest in Sludge

Measurement		W-21	W-22	W-23	
Depth to top of liquid	(in.)	165	180	171	
Depth to top of sludge	(in.)	200	193	192	
Depth to top of hard sludge	(in.)	227	227	228	
Depth to bottom of tank	(in.)	227	227	230	
Depth of supernatant	(in.)	35	13	21	
Depth of soft Sludge	(in.)	27	34	36	
Depth of hard Sludge	(in.)	0	0	2	
Total depth of Sludge	(in.)	27	34	38	
Summary of tank volumes and sludge mass					Total
Volume of Supernatant	(L)	62900	23800	42400	129100
Volume of Sludge	(L)	24600	25800	40100	90500
Density of Sludge	(Kg/L)	1.36	1.16	1.57	
Mass of Sludge	(Kg)	33456	29928	62957	126341
Concentration of selected species of interest in sludge					
Thorium	(mg/Kg)	8650	9580	29600	
Uranium	(mg/Kg)	26300	35600	7990	
Plutonium	(mg/Kg)	3.43	3.37	5.77	
²³³ U	(mg/Kg)	23.9	15.7	20.4	
²³⁵ U	(mg/Kg)	65.7	89.6	35.3	
²³⁹ Pu	(mg/Kg)	2.77	2.69	4.68	
Activity for selected species of interest in sludge					
⁹⁰ Sr	(Bq/g)	580000	860000	4600000	
¹³⁷ Cs	(Bq/g)	160000	270000	400000	
²³³ U	(Bq/g)	8500	5600	7300	
²³⁸ Pu	(Bq/g)	15000	19000	49000	
²⁴¹ Am	(Bq/g)	12000	12000	33000	
²⁴⁴ Cm	(Bq/g)	100000	100000	330000	
Total mass for selected species of interest in sludge					Total
Thorium	(Kg)	289.4	286.7	1863.5	2439.6
Uranium	(Kg)	879.9	1065.4	503.0	2448.4
Plutonium	(Kg)	0.115	0.101	0.363	0.579
²³³ U	(Kg)	0.800	0.470	1.284	2.554
²³⁵ U	(Kg)	2.198	2.682	2.222	7.102
²³⁹ Pu	(Kg)	0.093	0.081	0.295	0.468
Total activity for selected species of interest in sludge					Total
⁹⁰ Sr	(Ci)	524.45	695.62	7827.09	9047.2
¹³⁷ Cs	(Ci)	144.67	218.39	680.62	1043.7
²³³ U	(Ci)	7.69	4.53	12.42	24.6
²³⁸ Pu	(Ci)	13.56	15.37	83.38	112.3
²⁴¹ Am	(Ci)	10.85	9.71	56.15	76.7
²⁴⁴ Cm	(Ci)	90.42	80.89	561.51	732.8

Table B2 Dose Measurements on Liquid Samples

Tank	Supernatant (mR/hr)				Color	Date sampled
	L1	L2	L3	L4		
W-21	1100	1000	1000	1100	dark yel.	09/18/96
W-22	90	80	80	60		09/18/96
W-23	1600	1600	1600	1600	dark yel.	09/05/96
W-24	420	440	none	none	yellow	08/05/96
W-25	440	450	none	none		08/05/96
W-26	600	600	none	none		07/24/96
W-27	130	125	none	none		07/24/96
W-28	220	240	none	none	yellow	07/10/96
W-31	180	200	none	none	yellow	07/10/96

Table B3 Dose Measurements on Sludge Samples

Tank	Sludge (mR/hr)			Color	Date sampled
	S1	S2	S3		
W-21	1200	1100	none	brown-tan	09/26/96
W-22	?	?	none		
W-23	2400	1300	none	brown-tan	10/10/96
W-24	600	650	none	tan	08/06/96
W-25	350	400	800		08/22/96
W-26	500	700	none		08/30/96
W-27	150	250	250		09/04/96
W-28	1100	2900	none	brown	07/24/96
W-31	1400	1500	none	lt. brown	07/16/96

Note: All dose measurements measured on contact with sampling device.

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