Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

Organic Tank Safety Project: Effect of Water Partial Pressure on the Equilibrium Water Content of Waste Samples from Hanford Tank 241-U-105

R. D. Scheele
P. R. Bredt
R. L. Sell

RECEIVED
DEC 18 1997
OSTI

September 1997

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

This document was printed on recycled paper.

(9/97)

**Organic Tank Safety Project: Effect of
Water Partial Pressure on the Equilibrium
Water Content of Waste Samples from
Hanford Tank 241-U-105**

R. D. Scheele
P. R. Bredt
R. L. Sell

September 1997

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Pacific Northwest National Laboratory
Richland, Washington 99352

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

Summary

Water content plays a crucial role in the strategy developed by Webb et al. (1995) to prevent propagating or sustainable chemical reactions in the organic-bearing wastes stored in the 20 Organic Tank Watch List tanks at the U. S. Department of Energy's Hanford Site. Because of water's importance in ensuring that the organic-bearing wastes continue to be stored safely, Duke Engineering and Services Hanford commissioned the Pacific Northwest National Laboratory to investigate the effect of water partial pressure (P_{H_2O}) on the water content of organic-bearing or representative wastes. Of the various interrelated controlling factors affecting the water content in wastes, P_{H_2O} is the most susceptible to being controlled by the arid Hanford Site's environmental conditions and, if necessary, could be managed to maintain the water content at an acceptable level or could be used to adjust the water content back to an acceptable level.

Of the various waste types resulting from weapons production and waste-management operations at the Hanford Site, Webb et al. (1995) determined that saltcake wastes are the most likely to require active management to maintain the wastes in a Conditionally Safe condition. Webb et al. identified Tank U-105 as a Conditionally Safe saltcake tank. A Conditionally Safe waste is one that is currently safe based on waste classification criteria but could, if dried, be classified as "Unsafe." To provide information on the behavior of organic-bearing wastes, the Westinghouse Hanford Company provided us with four waste samples taken from Tank 241-U-105 (U-105) to determine the effect of P_{H_2O} on their equilibrium water content.

In these U-105 studies, PNNL exposed waste obtained by Core 131 from the two uppermost 48-cm-segment samples (Segments 2U and 3U), by Core 133 from its uppermost 48-cm-segment sample (Segment 3), and by Core 136 from its uppermost 48-cm-segment sample (Segment 3U) to water partial pressures of 2.7, 8.7, 23, 33, and 37 torr at 34°C, the highest temperature observed in the solid waste in U-105. These water partial pressures encompass the minimum P_{H_2O} observed in the atmosphere at the Hanford Site between 1985 and 1995 and the higher water partial pressures that may exist in the tank. The water content was monitored until stabilized or appeared to be approaching a stable level, at which time the samples exposed to 2.7 and 37 torr were exchanged between humidity baths to determine whether hydration and dehydration had an effect on the retentive capabilities of these wastes and whether the samples had achieved a true equilibrium water content. The water contents of the equilibrated samples were determined gravimetrically by drying in a 105°C oven until a stable mass was reached.

Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U have similar, although slightly different, equilibrium water contents after exposure to water vapor pressures ranging from 2.7 torr, near the Hanford minimum P_{H_2O} between 1989 and 1995, and 37 torr. For water partial pressures of 2.7, 8.7, 23, 33, and 37 torr, the average equilibrium or terminal water contents for Core 131 Segment 2U are 8, 12, 33, 69, and 75 wt%, respectively. The waste sample obtained by Core 131 Segment 3U had equilibrium water contents of 5, 7, 26, 67, and 74 wt% at the same water partial pressures, respectively. The physical appearances of these samples at the end of testing are provided in

Table 4.2. For each sample, the samples exposed to the two lower water partial pressures were dry solids, those exposed to 23 torr were moist solids, and the upper two water partial pressures were primarily liquid with some solids.

Our studies indicate that, as expected, the equilibrium water content of these saltcake and sludge wastes depends on the P_{H_2O} . Exposure to water partial pressures ranging from 2.7 to 37 torr resulted in water contents in the samples ranging from 5 to 76 wt% water, respectively. The equilibrium or terminal water contents for these waste samples from the different cores and segments were similar, ranging from 5 to 8 wt% at 2.7 torr, 7 to 12 wt% at 8.7 torr, 26 to 37 wt% at 23 torr, 66 to 69 wt% at 33 torr, and 73 to 76 wt% at 37 torr. The waste samples were all primarily sodium nitrate and nitrite, which could explain the similarities at higher water partial pressures. However, no consistent differences in the reported chemical compositions provide any explanation for the observed similarities and differences at the lower water partial pressures where past work (Scheele, Bredt, and Sell 1996) found that sodium nitrate and nitrite did not sorb water at low water partial pressures below 12 torr at 22°C and 90 torr at 65°C. Aluminum and sodium sulfate and phosphate or the unmeasured hydroxide may be the controlling chemical constituents at the lower water partial pressures because they are hydrophillic, retaining many waters of hydration. These materials or other minor constituents may control in combination with the nitrate/nitrite the wastes' water content. We have not studied the behavior of sodium sulfate and phosphate, and our studies of sodium aluminate yielded anomalous results.

The results of these studies also indicate that if the uppermost wastes in U-105 are allowed to equilibrate with the ambient Hanford atmospheric water partial pressures ranging from monthly averages of 3.5 to 8 torr at current waste temperatures (about 30°C), their water contents will range from 5 to 12 wt%. These water contents are less than the 20 wt% water content, guaranteeing that an organic-bearing waste will not support a propagating reaction (Webb et al. 1995). Thus, it will be necessary to rely on the combined moisture and total organic carbon or energetics criteria to ensure that the wastes remain Conditionally Safe. At the average Hanford P_{H_2O} of 5.5 torr, based on interpolation, the equilibrium water content of the uppermost 96 cm in U-105 will range from 6 to 10 wt% water.

The observed reversibility of the water loss/gain displayed by all four samples shows that water content in these wastes can be controlled or increased by controlling the P_{H_2O} in the tank's headspace. This indicates that it may be possible to rehydrate the U-105 organic-bearing wastes at 20 wt% water using air with a controlled P_{H_2O} near 20 torr.

Acknowledgments

We thank the following people for their invaluable support in developing a method for measuring the equilibrium water content of Hanford wastes and for helping with this report: L. L. Burger was our scientific sounding board, consultant, and technical peer reviewer as we attempted to understand the behavior of the different materials as they were exposed to water vapor; K. W. Burke provided the Hanford Site environmental water partial pressures; W. C. Cosby provided editorial review and assistance in publishing this report; Duke Engineering and Services Hanford, Inc. and the U.S. Department of Energy provided funding for the project.

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

Glossary

DESH	Duke Engineering and Services Hanford
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DTA	differential thermal analyzer
DTG	differential TGA
P_{H_2O}	water partial pressure
PNNL	Pacific Northwest National Laboratory
RPD	relative percent difference
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
WHC	Westinghouse Hanford Company

Contents

Summary	iii
Acknowledgments	v
Glossary	vii
1.0 Introduction	1.1
2.0 Experimental Approach and Method	2.1
3.0 Background Information on U-105 and Its Wastes	3.1
3.1 Fill History	3.1
3.2 Temperature	3.3
3.3 Core Sampling Event	3.3
3.4 Composition	3.4
4.0 Water Retention of U-105 Waste	4.1
4.1 Water Sorption/Desorption with Time	4.1
4.1.1 Behavior of Core 131 Segment 2U Waste	4.2
4.1.2 Behavior of Core 131 Segment 3U Waste	4.5
4.1.3 Behavior of Core 133 Segment 3 Waste	4.8
4.1.4 Behavior of Core 136 Segment 3U Waste	4.12
4.1.5 Summary of Sorption/Desorption Studies	4.16
4.2 Effect of P_{H_2O} on Equilibrium Water Content	4.18
5.0 Conclusions	5.1
6.0 References	6.1

Figures

1.1 Average Hanford Monthly P_{H_2O} 1980-1995	1.2
2.1 Schematic of Constant Humidity Chambers Used for Testing	2.1
3.1 Schematic of U-105	3.2
3.2 U-105 RMCS Core Profile 04/04/96 Reproduced with Permission of Characterization Equipment Engineering	3.5
4.1 Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Samples Obtained by Core 131 Segment 2U from U-105	4.2
4.2 Thermal Behavior as Measured by TGA and DTA of Waste Obtained by Core 131 Segment 2U from U-105	4.4
4.3 Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 2U Waste after Equilibrating with a final P_{H_2O} of 37 torr	4.4
4.4 Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 2U Waste after Equilibrating with a final P_{H_2O} of 2.7 torr	4.5
4.5 Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Waste Samples Obtained by Core 131 Segment 3U from U-105	4.6
4.6 Thermal Behavior as Measured by TGA and DTA of As-Received Core 131 Segment 3U Waste Obtained from U-105	4.7
4.7 Thermal Behavior As-Measured by TGA and DTA of Tank U-105 Core 131 Segment 3U Waste Equilibrated with a Final P_{H_2O} of 37 torr	4.7
4.8 Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 3U Waste Obtained from U-105 after Equilibrating with a P_{H_2O} of 2.7 torr	4.8
4.9 Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Waste Samples Obtained by Core 133 Segment 3 from U-105	4.9
4.10 Thermal Behavior as Measured by TGA and DTA of As-Received Tank U-105 Core 133 Segment 3 Waste	4.10
4.11 Thermal Behavior as Measured by TGA and DTA of Tank U-105 Core 133 Segment 3 Waste Equilibrated with a Final P_{H_2O} of 37 torr	4.11

4.12 Thermal Behavior as Measured by TGA and DTA of As-Received Tank U-105 Core 136 Segment 3U Waste Equilibrated with a Final P_{H_2O} of 2.7 torr	4.12
4.13 Effect of Exposure Time on the Water Content of Core 136 Segment 3U Waste Obtained from U-105	4.13
4.14 Thermal Behavior as Measured by TGA and DTA of As-Received Core 136 Segment 3U Waste Obtained from U-105	4.14
4.15 Core 136 Segment 3U Thermal Behavior as Measured by TGA and DTA after Equilibrating with a Final P_{H_2O} of 3.7 torr	4.15
4.16 Core 136 Segment 3U Thermal Behavior as Measured by TGA and DTA after Equilibrating with a Final P_{H_2O} of 2.7 torr	4.15
4.17 Equilibrium or Terminal Water Contents of Waste Samples Obtained from U-105 by Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U at 34°C	4.19

Tables

3.1 Concentration ($\mu\text{mol/g}$) of Major Chemical Components in Tested U-105 Samples on a Wet Basis	3.6
3.2 Concentration of Major Chemical Components in Tested U-105 Samples on a Dry Basis	3.7
4.1 Equilibrium or Terminal Water Contents of Tested U-105 Waste Samples at 33°C	4.18
4.2 Appearance of U-105 Samples after Exposure to Selected Water Partial Pressures at 34°C	4.19

1.0 Introduction

Twenty of the 177 underground high level radioactive waste storage tanks at the U. S. Department of Energy's (DOE) Hanford Site have been identified as tanks that contain wastes that originally included or are suspected of containing potentially reactive combinations of organics and oxidants. Because these potentially hazardous chemical reactions could release radioactive materials to the environment, the following 20 tanks have been placed on the Organic Tanks Watch List (Hanlon 1997) to ensure that special precautions and controls are used for all activities involving the tanks and the wastes stored in these tanks:

241-A-101	241-S-102	241-TX-105	241-U-106
241-AX-102	241-S-111	241-TX-118	241-U-107
241-B-103	241-SX-103	241-TY-104	241-U-111
241-C-102	241-SX-106	241-U-103	241-U-203
241-C-103	241-T-111	241-U-105	241-U-204

Note: Waste storage tanks will be referred to hereafter without the 241- prefix.

Several interrelated factors control the potential for and the consequences of hazardous chemical reactions between the organics and the oxidants nitrate and nitrite present in the Hanford Site's stored radioactive wastes. These factors include the identities and concentrations of the organic fuel(s), the identities and concentrations of the oxidant(s), and the heat absorption and heat transfer properties of the waste, the tank, and its surrounding environment.

Water's heat-absorption and heat-transfer properties make it one of the primary common waste components that control whether hazardous self-sustaining reactions (Scheele et al. 1995) or propagating reactions (Fauske et al. 1995) can occur in an organic-bearing waste (Burger 1995; Fauske et al. 1995); Fauske et al. found that mixtures of organics and nitrate and/or nitrite would not support a propagating reaction if the water content exceeded 20 wt%. The lower the water content, the greater the potential that energetic and vigorous reactions can occur. Because of water's efficiency for preventing propagating reactions, Webb et al. (1995) used water content as one of the bases for the criteria used to assess the potential chemical reactivity hazard of a Hanford Site's stored waste. These criteria are based on 1) water content alone, 2) a combination of water content and total organic carbon (TOC), or 3) a combination of water content and reaction energetics.

Applying the Webb et al. criteria classifies wastes into the three waste safety categories of "Safe," "Conditionally Safe," and "Unsafe." For a waste to be classified as Safe, not even minimal control of tank configuration is required to maintain the water content at or above 20 wt% or to satisfy the energetics or TOC criteria (Webb et al. 1995). If minimal controls are required to maintain the waste in

a condition that satisfies the criteria, then the waste is classified as Conditionally Safe. If the waste does not satisfy the criteria, the waste is classified as Unsafe in its current condition.

Because of water's importance in determining the hazard level of an organic-bearing waste, it is important to understand the factors that control the water content in the waste and whether it is necessary to actively control any of these factors to continue to ensure safe storage or to mitigate a future "unsafe" situation. Several factors control the waste's water content, including the water partial pressure (P_{H_2O}) in the tank's headspace, the temperature of the waste, the temperature of the surrounding soil, the exchange rate of air within the tank with the outside air, the outside air's P_{H_2O} , and the strength of the chemical bond(s) between the waste and the retained water. For example, higher water contents will occur at higher water partial pressures and lower waste temperatures. Conversely, lower water contents will occur at lower water partial pressures and higher waste temperatures. In the long term, if the storage system is allowed to reach equilibrium with the ambient arid Hanford environment, the waste's water content will be determined by the P_{H_2O} in the tank's head space, which will be equivalent to or nearly equal to the ambient Hanford P_{H_2O} provided in Figure 1.1.

In 1996 as part of Pacific Northwest National Laboratory's (PNNL's) Organic Tank Safety Project, building on established methods to measure water potential in materials such as described by Campbell and Gee (1986), we developed and demonstrated a method to determine the effect of P_{H_2O} on the

Figure 1.1. Average Hanford Monthly P_{H_2O} 1980-1995 (Data Provided by KW Burk of PNNL's Meteorological Group)

equilibrium water content of Hanford's stored radioactive wastes, providing a means to predict a waste's future safety status or category. As a result of our development and demonstration effort, we determined the effect of P_{H_2O} on selected potential waste components, surrogate waste mixtures made of those components, a simulated Hanford waste, and waste from T-111 (Scheele, Brecht, and Sell 1996). These studies showed that the water content of Hanford wastes will depend on the individual waste components' identities and concentrations, temperature, and P_{H_2O} . Before these studies and the development effort, little was known about the response of actual Hanford wastes and their major components to P_{H_2O} , nor did the capability exist to measure accurately the effect of water partial pressures on the water content of radioactive Hanford wastes; Armstrong, Freeman, and Kovach (Postma et al. 1994) studied the response of simulated ferrocyanide wastes to different water vapor pressures at 25°C.

Later in 1996, we applied the method to determine the equilibrium water content of waste samples obtained from BY-108 (Scheele, Brecht, and Sell 1997). The BY-108 study found water contents ranging from 1 to 16 wt% when exposed to the Hanford site monthly average water partial pressures. The equilibrium water contents were less than the 20 wt% water content criteria (Webb et al. 1995).

In continuing support of the Duke Engineering and Services Hanford (DESH) effort to ensure continued safe storage of Hanford's organic-bearing radioactive wastes, we at PNNL applied the developed method to determine the effect of P_{H_2O} on the water content of waste samples obtained from the Organic Watch List Tank U-105. This report provides the results of studies on the effect of P_{H_2O} on the water content of four waste samples taken from the uppermost 50-cm layer in U-105 by core samplings 131, 133, and 136 taken in February and March 1996. These studies provide the water content of these samples as a function of time and the equilibrium moisture content as a function of P_{H_2O} . These results can be used to determine whether these wastes and similar wastes will require active management to ensure that they will retain sufficient water to be classified as "Conditionally Safe" when allowed to equilibrate with ambient Hanford air. In addition, these studies provide general guidance on the P_{H_2O} required to maintain or achieve the desired water content in a waste.

2.0 Experimental Approach and Method

We used the general experimental approach and procedure provided by Scheele, Bredt, and Sell (1996) to measure the equilibrium water content of waste samples taken from U-105 when exposed to a range of water partial pressures that it might experience during storage as it awaits final disposal at the solid waste's measured maximum temperature of 34°C (Hanlon 1996). The P_{H_2O} used for the experiments ranged from 2.7 to 36 torr. These water partial pressures encompass the minimum P_{H_2O} observed at the Hanford Site between 1985 and 1995, 3.5 torr, and the higher water partial pressures that may exist in the tank.

To determine the equilibrium water content of U-105 waste, samples of waste were exposed to a controlled P_{H_2O} , and the samples' masses were monitored until they stabilized. The water content was determined by drying the samples at 105°C to a stable mass and by using thermogravimetric analysis (TGA) for selected samples. The procedure follows:

- Duplicate 1-g samples are placed in 20-mL glass vials, then placed in 500-mL sealed desiccators containing saturated solutions to control the P_{H_2O} at particular levels, and then placed in a constant-temperature oven. The salts used in the saturated solutions to control P_{H_2O} were NaOH (2.7 torr), $CaCl_2$ (8.7 torr), NaBr (23 torr), KCl (33 torr), and KNO_3 (36 torr). A schematic of this system is shown in Figure 2.1.

Figure 2.1. Schematic of Constant Humidity Chambers Used for Testing

- The samples' masses are monitored frequently at first, with the frequency lessening to weekly intervals until the mass appears to be stabilizing. Then the frequency is increased to 3-day intervals until the mass changes are less than 3 mg for a 3-day interval.
- Once the masses have stabilized over three successive 3-day intervals, samples exposed to the highest P_{H_2O} and the lowest P_{H_2O} are exchanged to investigate the reversibility of the water absorption and desorption. The samples' masses are monitored again until they stabilize, based on the same criteria used before. Subsamples are then taken from the highest P_{H_2O} and the lowest P_{H_2O} for TGA.
- The final equilibrium water contents are determined gravimetrically by drying at 105°C to a stable mass, and TGA is repeated on 105°C dried subsamples taken from the highest P_{H_2O} and the lowest P_{H_2O} .

3.0 Background Information on U-105 and Its Wastes

The single shell tank U-105 is listed on both the "Hydrogen Tank" and the "Organic Tank" Watch Lists. Tank U-105 was added first to the Hydrogen Tank Watch List in January 1991 and later to the "Organic Tank Watch List" in May 1994 (Hanlon 1997). Inclusion on the Organic Tank Watch List was based on historical records that indicated the waste stored in U-105 contained >3 wt% TOC (Babad and Turner 1993).

Tank U-105, which was constructed during 1943 and 1944, is a concrete tank with a primary mild steel liner. Tank U-105 has a 2010-kL (530-kgal) capacity, a diameter of 23 m (75 ft), and an operating depth of 5.18 m (17 ft). The tank has a dished bottom with a 1.2-m (4-ft) radius knuckle. Tank U-105 was the second tank in a cascade of three where overflow wastes from one tank could flow into and from another tank. For U-105, waste flowed from U-104 to U-105 and then to U-106. The tank was designed to store non-boiling waste with a maximum temperature of 100°C (220°F) (Brown and Franklin 1996). Figure 3.1 provides a schematic of U-105's configuration (Brevick, Stroup, and Funk 1997).

The waste types currently stored in U-105 include, listed from most recent to earliest, 1041 kL of 242-S evaporator waste (72 vol%), 280 kL of 242-T evaporator waste (19 vol%), and 121 kL of metal waste (8 vol%) (Brown and Franklin 1996). The tank contains 140 kL (37 kgal) of supernate and an estimated 538 kL (142 kgal) of drainable interstitial liquid (Hanlon 1997). Agnew (1997) provides compositions and descriptions of these waste types. During its lifetime, U-105 received metal waste, high-level REDOX waste, cladding waste, evaporator bottoms waste, evaporator waste, evaporator feed, and residual evaporator liquor.

3.1 Fill History

As Brown and Franklin (1996) describe, Tank U-105 was placed into service in the fourth quarter of 1947 when it first received metal waste cascading from Tank U-104. Tank U-105 continued to receive metal waste until the 3rd quarter of 1948 when the added metal waste cascaded into U-106.

In the first quarter of 1953, the stored metal waste was flushed with water to U-106. This waste was later sent to U Plant to recover uranium. In the 4th quarter of 1954, metal waste again cascaded into U-105 from U-104, filling the tank. In the first quarter of 1956, the operating contractor sluiced the metal waste in U-104 into U-105. This waste in U-105 was periodically transferred to U-Plant for uranium recovery. After the final sluicing in 1957 and a subsequent water flush, U-105 was declared empty.

Tank U-105 remained inactive until the first quarter of 1961 when high level REDOX waste was cascaded from U-104 into U-105. During the last quarter of 1961, cladding waste stored in U-108 was transferred to U-105. The next period of recorded activity occurred in the first quarter of 1974 when waste was sent to S-110.

TANK RISER LOCATION

Figure 3.1. Schematic of U-105 (Brevick, Stroup, and Funk 1997)

In the 2d quarter of 1975, U-105 began receiving evaporator wastes. The first evaporator waste was evaporator bottoms waste from TX-106. During the 3rd and 4th quarters of 1975 and the first quarter of 1976, evaporator waste from TX-118 arrived. During this same period, the remainder of 1976, and the first quarter of 1977, waste was sent from U-105 to U-111. Beginning in the 2d quarter of 1976, U-105 received wastes from S-102 through the first quarter of 1977. During 1977 and 1978, U-105 received waste from and sent waste to SY-102. The operating contractor placed U-105 on inactive status in 1979 and partially interim stabilized the tank in 1982. The tank is currently considered sound (Hanlon 1997).

3.2 Temperature

The single thermocouple tree used to measure the temperatures in U-105 at 11 different heights is located in Riser 1. Riser 1 is located approximately 2 m from the edge of the tank. Brevick et al. (1997) postulate, based on historical tank-temperature profiles, that thermocouple probes 1 through 7 are located in or near the surface of the solids, and probes 8 through 11 are located in the tank's vapor space.

Between January 1991 and May 1997, temperatures in Tank U-105 waste solids ranged from 34 to 23°C bottom to top, depending on depth and season. Temperatures varied seasonally with maximum temperatures occurring in August or September and the minimum temperatures occurring in February and March. The variability in temperature is less at the lower depths.

The temperatures in U-105's vapor space ranged from 19 to 31°C between January 1991 and May 1997 with temperatures again depending on the season and the thermocouple height. The thermocouple in the vapor space nearest the waste, thermocouple 8, measured temperatures ranging from 23 to 31°C. The highest thermocouple, thermocouple 11, recorded temperatures ranging from 19 to 28°C between January 1991 and June 1995. Tank U-105 is passively ventilated with no active circulation of vapor, which probably explains the temperature differences at different heights.

3.3 Core Sampling Event

Three core samples were collected from U-105 in February and March 1996 using the push mode sampling truck. These core samples are referred to as Core 131, Core 133, and Core 136. Core 131 was taken from Riser #20 located in the SW quadrant of the tank, nominally 6 m from the center of the tank, and 5 m from the outside wall (see Figure 3.1 for riser locations); we estimated the distances using the schematic presented in Figure 3.1, assuming the drawing is roughly to scale, although the drawing does contain a warning that the drawing is not to scale. The Westinghouse Hanford Company (WHC) took Core 133 through Riser #2 located in the NW quadrant of the tank nominally 9 m from the center of the tank and 2 m from the outside wall. WHC took Core 136 through Riser #7 located in the SW quadrant of U-105 nominally 9 m from the center of the tank or 2 m from the outside wall. Risers #7 and #20 are on the same radial line from center. The 222-S laboratory, operated by WHC, extruded and analyzed all three cores.

As Brown and Franklin (1996) report and Figure 3.2 shows, Core 131 consisted of nine segments. A full segment is 48 cm in length. Segments are numbered starting from the top of the waste, so Segment 1 will contain material from the uppermost layer of the waste. The Segment 1, 2, 3, 5, and 6 samplings yielded less than a full segment of material and were subdivided into upper-half segments only. WHC provided PNNL with waste samples obtained by Segments 2 and 3 for studies to determine their equilibrium moisture content. WHC obtained no drainable liquid in this sampling. Brown and Franklin (1996) and Figure 3.2 describe the uppermost recovered solids (Segment 1) as a dark-brown sludge and the Segment 2 and 3 samples as a dark-brown crystalline saltcake and a dark-brown, crumbly saltcake, respectively.

The 222S laboratory received nine segments from the Core Sampling 133 (Brown and Franklin 1996). Figure 3.2 shows that Segment 1 yielded liner liquid and drainable liquid only. Segments 2, 3, 4, 5, and 6 provided small amounts of material ranging from 4 to 140 g and were identified as whole segments. Segment 7 yielded no material. Segments 8 and 9 each provided 350-g samples. WHC provided PNNL with material from Segment 3. Brown and Franklin describe the material obtained by Segment 3 as a brown damp sludge.

Core Sampling 136 produced ten segment samples with two Segment 9 samples obtained (Brown and Franklin 1996). Segments 1, 2, and 8 yielded no material (see Figure 3.2). The Segment 3, 4, 5, 6, and 7 samplings recovered between 70 and 450 g of a black sludge. The first Segment 9 sampling recovered 314 g of a dark-brown sludge, and the second Segment 9 recovered 370 g of a dark-brown sludge and 50 g of yellow sludge. WHC provided PNNL with a sample of Segment 3 for equilibrium moisture testing.

3.4 Composition

As Fauske et al. (1995) and we have demonstrated (Scheele, Bredt, and Sell 1996), the equilibrium water content of a waste or compound-water mixture at different water partial pressures depends on the chemical composition. Fauske et al. studied NaOH and NaNO₃. We studied the effects of P_{H_2O} on the equilibrium moisture content of several potential Hanford organic-bearing waste constituents, surrogate wastes, a simulated organic-bearing waste, T-111 waste, and BY-108 waste. Tables 3.1 through 3.4 show that the four U-105 waste samples tested vary in their chemical composition although they are all from the 242-S Evaporator. We recognize that the U-105 wastes at different levels arose from different waste feeds to the evaporator.

Table 3.1 provides the concentrations on a weight and molar basis of the major chemical constituents measured as reported by the Hanford Tank Waste Characterization Program for the wet samples that we tested (Brown and Franklin 1996). Table 3.2 provides the concentrations on a dry basis. WHC measured some elements after preparing the sample either by acid digestion or fusing the sample. The concentrations reported in Tables 3.1 and 3.2 are the higher of the two reported values unless the quality control check found significant variability between duplicate analyses. WHC did not measure sodium hydroxide, a species observed by Fauske (1995) and ourselves (Scheele, Bredt, and Sell 1996) to have a significant effect on equilibrium water content.

Profiles below indicate primary constituent in sampler and are intended to reflect tank waste conditions. In some instances, extrusion information may be adjusted knowing other key information such as previous water additions.

Figure 3.2. U-105 RMCS Core Profile 04/04/96 Reproduced with Permission of Characterization Equipment Engineering

Table 3.1. Concentration ($\mu\text{mol/g}$) of Major Chemical Components in Tested U-105 Samples on a Wet Basis (Brown and Franklin 1996)

Chemical Component	U-105 Sample							
	Core 131 Segment 2U		Core 131 Segment 3U		Core 133 Segment 3		Core 136 Segment 3U	
	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$
Al	11900	440	8995	330	16900	640	12850	480
Ca	420	11	380	10	240	6	310	8
Cr	3500	67	1900	36	3400	65	3300	63
Fe	1000	18	400	7	960	17	1500	28
Mn	320	6	140	3	340	6	320	6
Ni	150	3	150	3	150	3	140	2
P	1100	36	980	31	2100	67	2800	91
K	1500	38	1200	32	1600	41	1700	44
Si	1200	43	<1000	<36	<1100	<40	1100	40
Na	210000	9100	220000	9500	200000	8800	200000	8800
S	7600	240	4000	120	3700	160	3800	190
Cl ⁻	4400	120	4000	110	3700	104	3800	108
F ⁻	610	32	260	<14	870	46	940	50
NO ₃ ⁻	150000	2500	380000	6200	250000	4000	180000	3000
NO ₂ ⁻	51000	1100	42000	900	44000	950	45000	980
PO ₄ ³⁻	3600	38	9700	102	6500	69	11000	110
SO ₄ ²⁻	25000	260	16000	170	13000	130	19000	200
C ₂ O ₄ ²⁻	10000	110	8200	93	6600	74	6900	79
TOC	11000	940	8800	740	12000	970	9500	790
TIC	19000	1600	9400	780	32000	2600	11000	880
H ₂ O, wt%	37		31		36		45	

Table 3.2. Concentration of Major Chemical Components in Tested U-105 Samples on a Dry Basis (Brown and Franklin 1996)

Chemical Component	U-105 Sample							
	Core 131 Segment 2U		Core 131 Segment 3U		Core 133 Segment 3		Core 136 Segment 3U	
	µg/g	µmol/g	µg/g	µmol/g	µg/g	µmol/g	µg/g	µmol/g
Al	19000	700	13000	480	27000	1000	24000	870
Ca	680	17	560	14	380	10	560	14
Cr	5600	110	2800	50	5300	100	5900	110
Fe	1600	29	580	10	1500	27	2800	42
Mn	510	9	210	4	540	10	580	11
Ni	240	4	220	4	240	4	250	4
P	1800	57	1400	46	3200	100	5100	160
K	2400	61	1800	46	2500	64	3100	79
Si	1900	69	1500	53	<1800	62	<2000	72
Na	330000	15000	320000	14000	320000	14000	360000	16000
S	12000	380	5800	180	8200	250	11000	340
Cl ⁻	7000	200	5800	160	5800	160	6900	200
F ⁻	970	51	380	20	1400	72	1700	90
NO ₃ ⁻	240000	3900	560000	9000	390000	6300	330000	5400
NO ₂ ⁻	81000	1800	61000	1300	68000	1500	82000	1800
PO ₄ ³⁻	5800	61	14000	150	10000	110	19000	200
SO ₄ ²⁻	40000	420	24000	250	20000	210	34000	360
C ₂ O ₄ ²⁻	16000	180	12000	140	10000	120	12000	140
TOC	18000	1500	13000	1100	18000	1500	17000	1400
TIC	30000	2500	14000	1100	50000	4100	19000	1600

As shown in Tables 3.1 and 3.2, the principle elements, anions, and other measured constituents, excluding water, in each of the samples are aluminum, sodium, chromium, nitrate, nitrite, phosphate, sulfate, chloride, organic carbon including oxalate, and inorganic carbon (carbonate or bicarbonate depending on pH); note that phosphate and sulfate are components of the measured phosphorous and sulfur with anions determined using ion chromatography (IC) and the elements determined independently using inductively coupled argon plasma spectroscopy (ICP). It is beyond the scope of this work to explain the difference between the reported P and PO_4^{3-} concentrations observed for Core 131 Segment 3U. In general and on a dry basis, these samples have similar compositions, although some compositional differences exist between the four segments. The aluminum concentrations vary from 480 to 1000 $\mu\text{mol/g}$. The nitrate + nitrite varies from 5700 to 10300 $\mu\text{mol/g}$. The total inorganic carbon (TIC) varies from 1100 to 4100 $\mu\text{mol/g}$; it is important to note that the amount of TIC in these potentially high pH samples will depend on their exposure to carbon dioxide in the air.

4.0 Water Retention of U-105 Waste

Several different chemical forms or types of water can be retained by wastes. As we discussed in our 1996 report (Scheele, Bredt, and Sell 1996), water may be present in tank wastes in a variety of conditions. It may exist as hydrates of differing stabilities; in a hydrate water is a ligand chemically bound or coordinated with a central atom typically a transition metal. It may be chemisorbed via hydrogen bonding, or physically adsorbed or retained in capillary-like interstices. It may exist in bulk aqueous solution having widely different partial pressures depending on the solute and the concentration. The different thermodynamic activities of these water forms translate into water vapor pressure, and conversely, the water vapor pressure will determine the nature of the water in the waste.

To determine the amount of water retained by waste in U-105, samples taken from Segments 2U and 3U of the Core 131 sampling event, Segment 3 of the Core 133 sampling event, and from Segment 3U of the Core 136 sampling event from U-105 were exposed to partial pressures of water of 2.7, 8.7, 23, 33, and 37 torr at 34°C, the solid wastes' maximum temperature, to determine the equilibrium water contents of the uppermost wastes. The water partial pressures used encompass those observed at the arid Hanford site and others that the waste may experience during its storage lifetime.

After the samples reached stable masses, the samples in the 2.7- and 37-torr vessels were exchanged and their masses were monitored until stable or deliquescent and forming a drainable liquid. Samples in the 2.7- and 37-torr water vapor baths were then analyzed by simultaneous TGA and differential thermal analysis (DTA) before being exchanged. These two samples were chosen for TGA/DTA to assess the difference in thermal behavior between the extremes in water content and to determine if different types of water are present in U-105 waste.

The exchanged samples previously in the 2.7- and 37-torr vessels were then reanalyzed by TGA/DTA at the end of the experiments. All water contents used in the following discussion are based on the water content determined gravimetrically after drying at 105°C. Thermogravimetric and DTA analyses of the U-105 wastes equilibrated at a final 37 torr after drying at 105°C indicated that drying at 105°C effectively removed retained water.

This section provides the measured water content of these samples during the duration of the experiments, the TGAs and DTAs of the as-received waste samples and the samples exposed to final water partial pressures of 2.7 and 37 torr, and the equilibrium or terminal water contents that these wastes will achieve if allowed to equilibrate with potential water partial pressures.

4.1 Water Sorption/Desorption with Time

To determine the effect of P_{H_2O} on the equilibrium water content of the waste in U-105, samples of waste from Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U taken from U-105 were exposed to selected water partial pressures. Their masses were monitored until they stabilized or were beginning to approach a stable mass. In addition to the final equilibrium water content,

the water sorption and desorption behavior as a function of time provides information on the nature of the wastes and the types of water retained by these two waste samples. The water content of these four samples during the course of the experiment is given here in addition to the TGA/DTA analyses after the experiments were completed.

The reader is reminded that although we are providing water sorption or desorption as a function of time, differences in surface area, particle size, and particle shape between the tested samples and the waste in the tank will cause differences in the kinetics of water sorption and desorption. Because of potential differences in sorption/desorption kinetics, the absolute kinetic results presented here must be applied cautiously to the behavior of actual wastes. Another limit on the ability to use these data for predicting rates in the actual tank is the small sample size used for this testing. The equilibration time should be shorter for these small samples because of the shorter transport distances.

4.1.1 Behavior of Core 131 Segment 2U Waste

As shown in Figure 4.1, the Core 131 Segment 2U samples, which contained about 36 wt% water when testing began, exposed to 2.7, 8.7, and 23 torr water reached their average equilibrium water contents of 8, 12, and 34 wt% within the first 400 h, respectively; most of the sorbed water in the original

Figure 4.1. Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Samples Obtained by Core 131 Segment 2U from U-105

sample was lost by 200 h. The samples exposed to 33 torr water deliquesced reaching an equilibrium water content of 68 wt% by 800 h. At the time that the samples exposed to 37 torr water were transferred to the 2.7-torr bath at 1080 h, they were continuing to deliquesce, slowly absorbing small amounts of water in the 37-torr bath; however, it does appear that they were near equilibrium. Water contents of the duplicate samples had relative percent differences (RPD) of approximately 13, 1, 1, 1, and 1% at 2.7, 8.7, 23, 33, and 36 torr water, respectively.

The behaviors observed for the exchanged samples in the 2.7 torr and 37 torr vessels after stable or near-stable masses were reached after 1080 h suggest that the observed water contents are a true equilibrium and that the sorption and desorption of water is reversible. As shown in Figure 4.1, Core 131 Segment 2U samples initially equilibrated with 37 torr water when exposed to 2.7 torr water reached their equilibrium water content of 8 wt% within 280 h. The samples originally exposed to 2.7 torr reached their as-received water content of 36 wt% within 40 h and then reached 72 wt% water in another 640 h. This roughly corresponds to the 620 h required for the samples originally exposed to 37 torr to reach 72 wt% water, suggesting equivalent behavior of the two sample sets. This nearly identical behavior indicates that these samples previously exposed to 2.7 torr would continue to deliquesce, absorbing water until reaching the same equilibrium water content as its as-received siblings originally exposed to 37 torr water.

The TGA, the differential of the TGA (DTG), and the DTA analyses of the as-received Core 131 Segment 2U samples indicate that two major types of water are present in the waste stored in U-105 (Figure 4.2) and that thermally initiated exothermic reactions can occur in this waste. The DTA and TGA detected two major endothermic mass losses below 150°C, resulting in a 38-wt% loss corresponding closely to the gravimetrically determined 37 wt% water. The mass loss with a DTG minimum and DTA maximum at 60°C is likely due to free or loosely bound water. The mass loss with a DTG minimum and DTA maximum at 110°C is due to a more tightly bound water.

The DTA of the as-received waste also indicates that an exothermic reaction begins near 200°C. This initiation temperature is lower than the 400°C or 350°C initiation temperatures observed by Turner and Miron (1994) and by this laboratory for exothermic reactions between oxalate and nitrate or nitrate/nitrite or nitrite; PNNL did differential scanning calorimetric (DSC) and DTA/TGA analyses of 6-wt% TOC oxalate and nitrate or nitrite mixtures in support of efforts to determine if spectrophotometric analyses of organic functional groups could be used to identify energetic wastes (Wahl et al. 1996).

The single endothermic events characterized by a DTG minimum at 75°C for the samples exposed to first to 2.7 torr and later 37 torr (Figure 4.3) and the samples exposed first to 37 torr and later 2.7 torr (Figure 4.4) indicate that a single type of water exists in these treated samples. This is in contrast to the TGA/DTA observed water behavior for the as-received Core 131 Segment 2U waste. This water is likely free or loosely bound water. This change in the nature of water in this U-105 waste shows that the more strongly bound water also has a significant vapor pressure at tank temperatures.

These differences in thermal behavior between the as-received and the samples exposed to different water vapor pressures indicate that the waters of rehydration return as free or loosely bound water rather

Figure 4.2. Thermal Behavior as Measured by TGA and DTA of Waste Obtained by Core 131 Segment 2U from U-105

Figure 4.3. Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 2U Waste after Equilibrating with a final P_{H_2O} of 37 torr. The sample was first equilibrated with 2.7 torr.

Figure 4.4. Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 2U Waste after Equilibrating with a final P_{H_2O} of 2.7 torr. The sample was first equilibrated with 37 torr.

than a more tightly bound water. This difference suggests that stronger bonds may form between sorbed water and this U-105 waste with time and that, although the sorption curves suggest reversibility, the nature of the new sorbed water is different than in the aged wastes.

4.1.2 Behavior of Core 131 Segment 3U Waste

As shown in Figure 4.5, the Core 131 Segment 3U samples, which began at about 25 wt% water, exposed to 2.7, 8.7, 23, 33, and 37 torr reached equilibrium or terminal water contents averaging 8, 11, 37, 68, and 76 wt%, respectively. Core 131 Segment 3U samples exposed to 2.7, 8.7, and 23 torr reached equilibrium masses within the first 300 h; they essentially reached their equilibrium water contents within the first 200 h. The samples exposed to 33 and 37 torr continued to deliquesce and gain water for 1080 h when the samples exposed to 2.7 and 37 torr were exchanged. Duplicate samples had RPDs of approximately 6, 6, 7, 2, and 1% at 2.7, 8.7, 23, 33, and 37 torr, respectively.

Once changed from the 37-torr water vapor bath to the 2.7-torr bath, these Core 131 Segment 3U samples lost most of their absorbed water within 300 h and reached an equilibrium water content of 5 wt% after another 300 h. This behavior was very similar to that observed for the Core 131 Segment 2U samples treated in the same fashion.

The samples originally equilibrated with 2.7 torr water and then changed to a 37-torr water vapor bath returned to their original water content of 25 wt% within 40 h and then reached 71 wt% water after

Figure 4.5. Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Waste Samples Obtained by Core 131 Segment 3U from U-105

another 630 h. This behavior was comparable to the 680 h required for the as-received sample to reach 71 wt% water. This behavior was very similar to that observed for the Core 131 Segment 2U samples treated in the same fashion.

The TGA, the DTG, and the DTA analyses of the as-received Core 131 Segment 3U samples indicate that three major types of water or possibly four types are present in this waste stored in U-105 (Figure 4.6), assuming that all mass losses below 200°C are due to water. The DTA also indicates that a thermally initiated exothermic reaction can occur in this waste beginning near 200°C. The DTA and TGA detected three major endothermic mass losses below 180°C, resulting in a 25 wt% loss corresponding closely to the gravimetrically determined 25-wt% water. The mass loss with a DTG minimum and DTA maximum at 60°C is likely due to free or loosely bound water while the mass loss with a DTG minimum and DTA maximum at 110°C is due to a more tightly bound water. The mass loss with a DTG minimum and DTA maximum at 140°C may be due to waters of hydration. Close inspection of the DTG curve at 130°C suggests that a fourth type of water is present, again likely a water of hydration.

The TGAs and DTAs of the Core 131 Segment 3U samples equilibrated first with 37 torr and then exposed to a final 2.7 torr water (Figure 4.7) indicate that adding large amounts of water followed by removing water by drying at a low P_{H_2O} alters the nature of the water in the waste. The predominant form of water in the as-received material characterized by a DTG minimum at 140°C is absent from the

Figure 4.6. Thermal Behavior as Measured by TGA and DTA of As-Received Core 131 Segment 3U Waste Obtained from U-105

Figure 4.7. Thermal Behavior As-Measured by TGA and DTA of Tank U-105 Core 131 Segment 3U Waste Equilibrated with a Final P_{H_2O} of 37 torr. Sample first was Equilibrated with 2.7 torr.

37 torr/2.7 torr exposed waste. The two water types present in this dry sample are characterized by DTG minimums at 30 and 85°C and do not appear to correspond to any of the water types in the as-received material, although DTG minimums can shift, depending on the amount of the volatilizing material in the sample. Based on the peak shape, it appears that the water characterized by the 85°C DTG minimum is the same type as observed for the Core 131 Segment 2U sample.

The TGAs and DTAs of this predominately liquid Core 131 Segment 3U sample exposed to a final 37 torr (Figure 4.8) indicate that loosely bound water characterized by a DTG minimum and DTA maximum at 85°C becomes the predominate type of water as this waste deliquesces. It appears that additional water characterized by a DTG minimum at 140°C is also sorbed by this waste or forms as the sample dries in the TGA/DTA. Some water characterized by a DTG minimum at 110°C appears to be present.

4.1.3 Behavior of Core 133 Segment 3 Waste

As shown in Figure 4.9, the Core 133 Segment 3 samples, which contained between 20 and 32 wt% water when testing began, exposed to 2.7, 8.7, and 23 torr water, reached their average equilibrium water contents of 6, 9, and 29 wt% within the first 300 h; these samples were essentially at equilibrium within 100 h with only small changes occurring afterwards. The samples exposed to 33 torr water deliquesced, reaching a near-equilibrium water content of 65 wt% by 1080 h; the duplicate samples were still sorbing

Figure 4.8. Thermal Behavior as Measured by TGA and DTA of Core 131 Segment 3U Waste Obtained from U-105 after Equilibrating with a P_{H_2O} of 2.7 torr. The sample was first equilibrated with 37 torr.

Figure 4.9. Effect of Exposure Time to Selected Partial Pressures of Water at 34°C on the Water Content of Waste Samples Obtained by Core 133 Segment 3 from U-105

water slowly when the experiments were terminated. When the samples exposed to 37 torr water were switched to the 2.7-torr bath at 1080 h, they contained 73 wt% water and were continuing to deliquesce, slowly absorbing small amounts of water; however, it does appear that they were approaching equilibrium with little prospect of gaining significant amounts of additional water. Water contents of the duplicate samples had RPDs of 4, 2, 6, 2, and 0.3% at 2.7, 8.7, 23, 33, and 36 torr water, respectively.

Once changed from the 37-torr water vapor bath to the 2.7-torr bath, these Core 133 Segment 3 samples lost most of their absorbed water within 300 h, reaching an equilibrium water content of 5 wt% after another 300 h. This behavior was very similar to that observed for the two Core 131 Segments treated similarly.

The samples originally equilibrated with 2.7 torr water and then changed to a 37-torr water vapor bath recovered to a water content of 20 wt% within 20 h and then reached 72.5 wt% water after another 650 h. This 650 h to reach 72.5 wt% water is significantly faster than the 1000 h required for the as-received sample (beginning at 20 wt% water) originally exposed to 37 torr to reach 72.5 wt% water. The Core 131 Segment samples originally exposed to 2.7 torr and then rehydrated at 37 torr water sorbed water similar to the as-received Core 131 samples exposed to 37 torr. We offer two possible explanations for the more rapid sorption of water by the dried sample than by the as-received sample. The first is that the samples

were chemically different and the second is that drying by exposure to 2.7 torr increased the surface area of the solid crystals by causing the particles to fracture or form small, high surface area to volume crystals.

The TGA, the DTG, and the DTA analyses of the as-received Core 133 Segment 3 samples indicate that three major types of water or possibly four types are present in this waste stored in U-105 (Figure 4.10), assuming that all mass losses below 200°C are due to water. In contrast to the two Core 131 Segment samples, the DTA for the Core 133 Segment 3 sample does not indicate that a thermally initiated exothermic reaction can occur in this waste beginning near 200°C; rather, the observed reaction above 200°C is endothermic.

The DTA and TGA detected three or possibly five endothermic mass losses from the as-received material below 180°C, resulting in an 18-wt% loss. This 18-wt% mass loss corresponds closely to the gravimetrically determined 20 wt% water for the two samples exposed to 37 torr (see Figure 4.9); based on the initial water content of the tested samples and the order that they were prepared, this parent sample dried as we transferred the test samples to their individual containers. This differed from the Core 131 samples in which the parent samples did not dry when transferred to their individual containers. The 7 wt% mass loss occurring between 30 and 95°C is likely due to free or loosely bound water; two types of water characterized by DTG minimums at 30 and 60°C appear to compose this mass loss. The 1 wt%

Figure 4.10. Thermal Behavior as Measured by TGA and DTA of As-Received Tank U-105 Core 133 Segment 3 Waste

mass loss with a DTA maximum at 110°C is due to a more tightly bound water. The 9-wt% mass loss with a DTG minimum and DTA maximum at 130°C may be due to waters of hydration; note the shoulder with a DTG minimum at 150°C, which suggests that a fourth type of water is present, again likely a water of hydration.

The TGAs and DTAs of the Core 131 Segment 3U samples exposed to a final 37 torr (Figure 4.11) indicate that the loosely bound water characterized by the DTG minimum at 70°C in the as-received material becomes the predominate type of water as this waste deliquesces. This water appears to be the same type of water, characterized by an 85°C DTG minimum, as observed for the sample exposed to a final 2.7 torr. It appears that additional water characterized by the DTG minimum at 140°C in the as-received waste is also sorbed by this waste or forms as the sample dries in the TGA/DTA. Some water characterized by the DTG minimum at 110°C appears to be present.

The TGAs and DTAs of the Core 133 Segment 3 samples equilibrated first with 37 torr and then exposed to a final 2.7 torr water (Figure 4.12) indicate that adding large relative amounts of water followed by drying at 2.7 torr alters the nature of the water in the waste. The predominant form of water in the as-received material characterized by a DTG minimum at 130°C is absent from the 37-torr/2.7-torr exposed waste. It appears that only the two water types characterized by DTG minimums at 40 and 80°C

Figure 4.11. Thermal Behavior as Measured by TGA and DTA of Tank U-105 Core 133 Segment 3 Waste Equilibrated with a Final P_{H_2O} of 37 torr. Sample was first equilibrated with 2.7 torr.

Figure 4.12. Thermal Behavior as Measured by TGA and DTA of As-Received Tank U-105 Core 136 Segment 3U Waste Equilibrated with a Final P_{H_2O} of 2.7 torr. Sample was first equilibrated with 37 torr.

in the as-received material remained in this material, which was exposed initially to a very high humidity and then to a very dry environment; the shift in the DTG minimums to 35 and 90°C, respectively, could be due to smaller amounts of water in the treated sample. Alternatively, the shapes of the DTG and DTA curves for these two types of water suggest different types of water than observed in the as-received sample.

4.1.4 Behavior of Core 136 Segment 3U Waste

The Core 136 Segment 3U samples contained 36 wt% water when testing began. When exposed to 2.7, 8.7, and 23 torr water, they reached their average equilibrium water contents of 8, 12, and 37 wt% within the first 350 h (Figure 4.13); these samples were essentially at equilibrium within 100 h with only small changes occurring afterwards. The samples exposed to 33 torr water deliquesced, reaching a near-equilibrium water content of 68 wt% by 1080 h; these duplicate samples were sorbing water slowly when the experiments were terminated. When the samples exposed to 37 torr water were switched to the 2.7-torr bath at 1080 h, they contained 76 wt% water and were continuing to deliquesce slowly, absorbing small amounts of water; however, it does appear that they were near equilibrium with little prospect of gaining significant amounts of additional water. Water contents of the duplicate samples had RPDs of 12, 4, 4, 2, and 1% at 2.7, 8.7, 23, 33, and 36 torr water, respectively.

Figure 4.13. Effect of Exposure Time on the Water Content of Core 136 Segment 3U Waste Obtained from U-105

The two samples exchanged between the 2.7 and 37 torr baths behaved differently than the as-received material when exposed to the same water partial pressures. Once changed from the 37-torr water vapor bath to the 2.7-torr bath, the Core 133 Segment 3 samples needed 200 h to return to their original water content of 36 wt%. They then needed another 200 h, compared to 100 h for the as-received sample to reach the equilibrium water content of 8 wt%. The samples originally equilibrated with 2.7 torr water and then changed to a 37-torr water vapor bath recovered to their starting water content of 36 wt% within 50 h and then reached 73 wt% water after another 630 h. This rehydration took much less time to reach 73 wt% from 36 wt% water than the 840 h required for the as-received sample to reach 73 wt% water.

The TGA, the DTG, and the DTA analyses of the as-received Core 136 Segment 3U samples indicate that two major types of water and a third less significant type are present in this waste stored in U-105 (Figure 4.14), assuming that all mass losses below 200°C are due to water, and losses above 200°C are due to other reactions. As with the two Core 131 Segment samples and in contrast to the Core 133 Segment 3 sample, the DTA indicates that a thermally initiated exothermic reaction can occur in this waste beginning near 200°C.

The DTA and TGA detected three endothermic mass losses from the as-received Core 136 Segment 3U sample below 180°C, resulting in a 35-wt% loss. This 35-wt% mass loss corresponds closely to the gravimetrically determined 36 wt% water for all of the test samples. The 14-wt% mass loss occurring

Figure 4.14. Thermal Behavior as Measured by TGA and DTA of As-Received Core 136 Segment 3U Waste Obtained from U-105

between 30 and 80°C and characterized by a DTG minimum at 60°C is likely due to free or loosely bound water. The 21-wt% mass loss with DTA maximums and DTG minimums at 115 and 130°C is due to two types of more tightly bound water. These higher temperature mass losses may be due to waters of hydration.

The TGAs and DTAs of the predominately liquid Core 131 Segment 3U sample exposed to a final 37 torr (Figure 4.15) indicates that the added water is different than any of the water types in the as-received material. This added water is characterized by a DTG minimum and DTA maximum at 85°C while the waters in the as-received sample are characterized by DTG minimums and DTA maximums at 60, 110, and 130°C. This added water in the sample exposed to 2.7 torr first and later 37 torr appears to be the same type as exists in the sample exposed to 37 torr and later to 2.7 torr.

The TGAs and DTAs of the Core 136 Segment 3U samples equilibrated first with 37 torr and then exposed to a final 2.7 torr water (Figure 4.16) indicate that adding large relative amounts of water followed by drying at a low P_{H_2O} alters the nature of the water in the waste. The predominant form of water in the as-received material characterized by a DTG minimum at 130°C is absent from the 37-torr/2.7-torr exposed waste. It appears that either two new water types characterized by DTG minimums at 40 and 85°C are present or that the two water types characterized by DTG minimums at 60 and 110°C in the as-received material are the two water types remaining in this material exposed initially to a very high

Figure 4.15. Core 136 Segment 3U Thermal Behavior as Measured by TGA and DTA after Equilibrating with a Final P_{H_2O} of 37 torr. The sample was first equilibrated with 2.7 torr.

Figure 4.16. Core 136 Segment 3U Thermal Behavior as Measured by TGA and DTA after Equilibrating with a Final P_{H_2O} of 2.7 torr. The sample was first equilibrated with 37 torr.

humidity and then to a very dry environment; the shift in the DTG minimums to 40 and 85°C, respectively, could be due to smaller amounts of water in the treated sample.

4.1.5 Summary of Sorption/Desorption Studies

The water sorption and desorption behavior and thermal analyses of the as-received and water vapor-equilibrated U-105 wastes obtained by the two Core 131 Segments, Core 133 Segment 3, and Core 136 Segment 3 indicate that the waste in the uppermost 50 cm of U-105 is not homogeneous but similar. The water sorption and desorption curves indicate that these four waste samples sorb and lose water similarly in the testing environment, although subtle differences exist. The thermal analyses of the as-received wastes found 3 to 5 types of water depending on the sample. The thermal analyses of the samples exposed to combinations of 2.7 and 37 torr water found one predominant water type not characteristic of the as-received wastes. Depending on the exposure vapor pressure and the source of the sample, a second type of water could be present in the sample.

In general, the sorption/desorption behaviors presented in Figures 4.1, 4.5, 4.9, and 4.13 for the four different U-105 waste samples show similar sorption/desorption behavior of all of the waste samples that we tested. The similarity of the shape and magnitude of the sorption/desorption behaviors of the different samples at the various water vapor pressures suggests similar chemical and physical properties. The samples exposed to 2.7, 8.7, and 23 torr reached their equilibrium water contents within 200 hours. The samples exposed to 33 and 37 torr were continuing to deliquesce slowly at 1100 hours. The wastes have similar chemical compositions with small differences, such as Core 136 Segment 3U and Core 133 Segment 3 having more aluminum than either of the two Core 131 Segments. Given the significant water content at the lower vapor pressures (unexpected for nitrate and nitrite [Scheele, Bredt, and Sell 1996]) and the differences in the nitrate and nitrite contents (see Tables 3.1 and 3.2), chemical constituents other than nitrate and nitrite control or help control symbiotically with nitrate and nitrite the water content of the U-105 wastes.

The rehydration behavior of the four samples shows similarities and differences between the samples. The Core 133 Segment 3 Core 136 Segment 3U samples originally exposed to 2.7 torr and then rehydrated at 37 torr rehydrated more rapidly than the as-received materials. In contrast, the Core 131 Segment 2U and 3U samples behaved similarly to the as-received Core 131 samples exposed to 37 torr. Two possible explanations may account for the more rapid sorption of water by the dried sample than by the as-received sample. The first is that the samples were chemically different and the second is that drying by exposure to 2.7 torr increased the surface area of the solid crystals by causing the particles to fracture or form small, high surface area to volume crystals.

The sorption/desorption reversibility shows that for these four samples of U-105 waste on a chemical basis, it may be possible to mitigate a lower than acceptable waste water content (Webb et al. 1995) by treating this waste or other similar wastes with a controlled P_{H_2O} to rehydrate or control the water content of the waste. However, some caution should be used when applying the equilibrium water content results for the high P_{H_2O} exposures when planning a remediation strategy. The sample size and vial geometry used in this testing prevent free flowing liquid from draining, as is possible in the actual tank. As a result, the high P_{H_2O} test samples could have a higher water content than that in a similarly exposed tank. In

addition, samples used for this work were homogenized (stirred), so the crystal sizes, crystal shapes, and resulting pore sizes and volumes could differ from that of the actual tank waste. As a result of the potential differences in these physical parameters, the retention of pore water could be different for actual in-tank waste at high P_{H_2O} where drainable liquids could be present. However, the water contained in the lower P_{H_2O} (2.7, 8.7, and 23 torr) samples is most likely contained in or on the solid particles and should be very similar to the values that would be achieved in the actual tank; e.g., the water content could be raised to > 20 wt% without the formation of drainable liquid.

The thermal analyses of the as-received wastes also indicate similarities and differences between the different U-105 waste samples. Each of the waste samples appear to contain two principle types of water; however, the nature of these two principle types of water differ by sample. The materials also contain up to three additional types of water. Each waste contains a water that is characterized by a DTA and DTG peak maximum or minimum nominally at 65°C. The other principle water type in Core 131 Segment 2U is characterized by a peak at 110°C. The second principle water type in the three Segment 3 samples was a more strongly bound type characterized by DTA and DTG peaks between 130 and 140°C. Only one minor water type was observed in the Core 131 Segment 2U sample characterized by a DTA and DTG peak at 135°C; each of the Segment 3 samples had up to three additional types of water. Common to each Segment 3 sample as a minor type of water was the principle water type found in the Core 131 Segment 2U sample characterized by the nominal 110°C peak; this water type was the only secondary type found in the Core 136 Segment 3U sample. The Core 131 Segment 3U and the Core 133 Segment 3 samples had two additional secondary water peaks at 125 and 135°C and at 115 and 150°C, respectively. The thermal analyses of the as-received wastes indicate that the types of water in the upper 50 cm of U-105 range from the loosely bound free water characterized by the DTA and DTG peak at 65°C to the more strongly bound characterized by a peak at 150°C.

It is valuable to note that the two Core 131 Segment samples and the Core 136 Segment 3U sample exhibited thermally initiated exothermic reactions beginning near 200°C. In contrast, the DTA observed an endothermic reaction at about 250°C for the Core 133 Segment 3 sample.

The chemical compositions (Tables 3.1 and 3.2) provide few clues why these differences and similarities exist. Hydroxide, a hydrophilic substance and a common ingredient in Hanford wastes, was not measured. Core 133 Segment 3 has more aluminum than the other two, more nitrate/nitrite than Core 131 Segment 2U, less nitrate/nitrite than Core 131 Segment 3U, less sulfate than Core 131 Segment 2U, roughly the same sulfate as Core 131 Segment 3U, more phosphate than Core 131 Segment 2U, and less phosphate than Core 131 Segment 3U. Identifying the chemical factors controlling the nature of water in these wastes might be accomplished using statistical pattern-recognition methods. Our earlier studies (Scheele, Bredt, and Sell 1996) did not investigate the behavior of sulfates and phosphates, both of which can have up to 12 waters of hydration—e.g., sodium phosphate.

The TGAs and DTAs of the U-105 materials 1) dried at 2.7 torr and rehydrated at 37 torr or 2) hydrated at 37 torr and then dried at 2.7 torr indicate that, in general, hydration or dehydration in the time frame of our experiments changes the nature of the water. The predominant form of water observed for all of these samples is characterized by DTA and DTG peaks with maxima and minima at nominally 85°C; this is apparently a different type of water than observed in any of the as-received samples because

it is observed independent of the water concentration in the sample analyzed. The DTAs and TGAs of the Core 131 Segment 3U and the Core 133 Segment 3 composite samples dried at 2.7 torr and rehydrated at 37 torr indicate that some of the waters of rehydration are the strongly bound water characterized by peaks at 135°C; in contrast to its other Segment 3 siblings, the rehydrated Core 136 Segment 3U did not reabsorb this type of water after drying at 2.7 torr.

4.2 Effect of P_{H_2O} on Equilibrium Water Content

The equilibrium water content of waste samples taken from the upper levels of the stored waste in U-105 is sensitive to P_{H_2O} (Table 4.1 and Figure 4.17). The amount of retained water depends on P_{H_2O} and to a lesser extent the location where the waste sample was obtained. The amount of equilibrium water retained by each of the different U-105 samples tested increases gradually as P_{H_2O} increases. The amount of equilibrium water present in each of the different samples is similar, although small differences exist.

Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U have similar, although slightly different, equilibrium water contents after exposure to water vapor pressures ranging from 2.7 torr, near the Hanford minimum P_{H_2O} between 1989 and 1995, and 37 torr. For water partial pressures of 2.7, 8.7, 23, 33, and 37 torr, the average equilibrium or terminal water contents for Core 131 Segment 2U are 8, 12, 33, 69, and 75 wt%, respectively. The waste sample obtained by Core 131 Segment 3U had equilibrium water contents of 5, 7, 26, 67, and 74 wt% at the same water partial pressures, respectively. The physical appearances of these samples at the end of testing are provided in Table 4.2. For each sample, the samples exposed to the two lower water partial pressures were dry solids, those exposed to 23 torr were moist solids, and the upper two water partial pressures were primarily liquid with some solids.

Differences exist between the equilibrium water contents in the four U-105 waste samples tested. No clear consistent differences in the chemical compositions are readily apparent to explain these differences

Table 4.1. Equilibrium or Terminal Water Contents of Tested U-105 Waste Samples at 33°C

P_{H_2O} , torr	Water Content, wt%			
	Core 131 Segment 2U	Core 131 Segment 3U	Core 133 Segment 3	Core 136 Segment 3U
2.7	7.8	4.6	6.1	7.8
8.7	12	7.3	8.6	11
23	33	26	28	37
33	69	67	66	68
37	75	74	73	76

Figure 4.17. Equilibrium or Terminal Water Contents of Waste Samples Obtained from U-105 by Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U at 34 °C

Table 4.2. Appearance of U-105 Samples after Exposure to Selected Water Partial Pressures at 34 °C

Sample	Description				
	P_{H_2O} , torr				
	2.7	8.7	23	33	37
Core 131 Segment 2U	Dry Solids	Dry Solids	Wet Solids	Liquid/Solids	Liquid/Solids
Core 131 Segment 3U	Dry Solids	Dry Solids	Wet Solids	Liquid/Solids	Liquid/Solids
Core 133 Segment 3	Dry Solids	Dry Solids	Wet Solids	Liquid/Solids	Liquid/Solids
Core 136 Segment 3U	Dry Solids	Dry Solids	Wet Solids	Liquid/Solids	Liquid/Solids

in equilibrium moisture content. For example, consistent with the observed behavior for equimolar sodium nitrate and nitrite at 22 and 65°C in our earlier studies, the two wastes having the highest total sodium nitrate and nitrite contents (10.3 and 7.8 mmol/g) had the lowest water contents of the four wastes at water partial pressures below 23 torr. However, the other two waste samples having total nitrate and nitrite contents of 7.2 and 5.7 mmol/g behaved similarly at 2.7 and 8.7 torr and at 23 torr the Core 131 Segment 2U sample with the lowest nitrate and nitrite content contained less water than the Core 136 Segment 3U sample containing 7.2 mmol/g. Similar cursory analyses for aluminum, phosphate, and sulfate do not identify a single constituent that accounts for the observed differences. The behavior presented in Figure 4.18 appears to be a blend of the behaviors of the simulated organic-bearing waste PAS94 and sodium nitrate and nitrite (Scheele, Brecht, and Sell 1996). Phosphate, sulfate, and aluminum content (Tables 3.1 and 3.2) could explain the significant water content at the lower partial pressures. Our studies (Scheele, Brecht, and Sell 1996) found anomalous behavior for sodium aluminate and did not determine the responses of sodium phosphate and sulfate, both hydrophilic salts, to varying water partial pressures.

Because of temperature differences between our pure potential waste component studies and the U-105 studies, we were unable to develop a simple linear model based on the individual waste components' behavior (Scheele, Brecht, and Sell 1996) to predict the behavior of U-105 waste; such a model would take the form

$$\text{wt\% H}_2\text{O} = a_1[X_1] + a_2[X_2] + \dots + a_n[X_n] \quad (4.1)$$

where wt% H₂O is the water content, X₁ is component 1 such as NaOH, and a_n is the coefficient. The studies of the pure potential waste constituents were done at 20 and 65°C. The U-105 studies were performed at 34°C. A model based on measured chemical composition could be useful to predict the equilibrium water content of waste equilibrated with ambient Hanford air.

Comparing the expected P_{H₂O} in the tank's head space based on our studies and Brown and Franklin's (1996) reported 31 to 45 wt% water contents in these waste samples with the measured P_{H₂O} in U-105's vapor space provides some insight into the dynamics within U-105. Pool et al. (1995) reported a P_{H₂O} of 13.2 torr at 22.3°C in U-105's vapor space on February 24, 1995. At 13.2 torr, the equilibrium water contents, based on this work, should be 18 wt% for Core 131 Segment 2U, 12 wt% for Core 131 Segment 3U, 15 wt% for Core 133 Segment 3, and 19 wt% for Core 136 Segment 3U. These predicted water contents are much lower than the measured 31 to 45 wt%. The higher than expected water content is likely due to complex chemical and physical interactions between the waste, the tank walls, and the outside Hanford environment.

Tank U-105 was not interim stabilized at the time of sampling and, as evidenced by the photograph of U-105 provided by Brevick, Stroup, and Funk (1997), U-105 contained free-standing liquid in 1988. The presence of free standing liquid indicates that interstitial solution should also be present in the solid waste, which would explain the higher than expected water content. Assuming that the composition of the free standing liquid is similar to a saturated solution of one of the U-105 waste samples tested, the expected vapor pressure in the tank's head space should be near saturation (20.2 torr at 22.3°C [Weast, Astle, and Beyer 1984]) rather than the observed 13.2 torr. Figure 4.17 shows that at existing water contents,

> 25 wt% water, the P_{H_2O} for any of the wastes is greater than 22 torr, thus, as the temperature decreases with rising elevation in the tank, water in excess of the water saturation level will condense, leaving the P_{H_2O} at saturation for pure water. This difference suggests that another factor is controlling the P_{H_2O} in U-105's head space.

The factor that is likely controlling P_{H_2O} in the tank's head space is the temperature of the tank's walls, which should be at or near the surrounding soil's temperature. Barney (1976) reports that the average soil temperature at a tank's depth is 17°C. At 17°C, water's vapor pressure is 14.5 torr (Weast, Astle, and Beyer 1984) or very near that of the observed 13.2 torr. The small difference between the measured 13.2 torr and 14.5 torr could be explained by a 1.5°C reduction in the soil's temperature to 15.5°C; such a reduction in soil temperature is reasonable, given the time of year (February). Another factor affecting P_{H_2O} in the head space is the exchange of dry air from the arid Hanford environment and the moist tank air to the environment; the exchange contribution will depend on the rate at which the passively ventilated tank breaths.

Consistent with the model that Simmons et al. (1997) developed to predict the water content in saltcake type wastes, it thus appears that an evaporation/condensation cycle is currently controlling the water content in the waste in this non-interim stabilized tank. In this hypothesized scenario, water evaporates from the nominal 35°C waste, condenses on the walls, and returns to the waste. Some gaseous water would be lost during the tank's breathing cycle, depending on the tank's breathing rate.

In general, exposing the U-105 saltcake wastes to ambient Hanford water partial pressures will dry the surface waste from its nominal 36 wt% water to between 5 and 12 wt%, depending on the waste's temperature. The average Hanford P_{H_2O} is approximately 5.5 torr with monthly highs up to 9 torr in the summer and lows down to 2.5 torr in the winter (Figure 1.1). The equilibrium water contents for the different samples at 2.7 and 8.7 torr range between 5 and 12 respectively. Therefore, at all current ambient Hanford partial pressures of water, the waste in the uppermost part of the waste stored in U-105 will dry to below the current TOC and energetics independent safety criterion of 20 wt% water (Webb et al. 1995). Additional evaluation is required to determine if the equilibrated wastes will satisfy the combined water and TOC/energetics criteria. It should be noted that currently these wastes are above the 20 wt% water safety criterion.

To maintain the upper 50 to 100 cm of waste in U-105 above the safety limit of 20 wt% water, the material would have to be exposed to pressure near or above 20 torr of water vapor. At current temperatures, at an average ambient Hanford water vapor pressure of 5.5 torr, these wastes should dry to an equilibrium water content between 6 and 9 wt%.

5.0 Conclusions

PNNL investigated the effect of P_{H_2O} on the equilibrium water content of the uppermost retrieved solid waste samples taken by Core 131 Segment 2U (sampling from uppermost 48 cm of solids; Segment 1 contained minimal [3 g] solids) and Segment 3U (next 48 cm sampling), Core 133 Segment 3 (Segment 1 retrieved no solids, and Segment 2 contained minimal [5 g] solids), and Core 136 Segment 3U (Segments 1 and 2 retrieved no solids) of the waste stored in U-105. These studies of U-105 waste found that, as expected, the equilibrium water content of these mixed saltcake and sludge wastes depends on the P_{H_2O} . Exposure to water partial pressures ranging from 2.7 to 37 torr resulted in water contents in these homogenized uppermost segment samples ranging from 5 to 76 wt% water.

In general, the study of the uppermost solid wastes stored in U-105 indicates that the equilibrium water contents of these wastes at 34°C.

- are largely independent of differences in the wastes' reported chemical compositions. Small differences do exist between the measured equilibrium or terminal water contents and the rates at which these wastes sorbed and lost water during testing. The behavior of these U-105 wastes is consistent with the behavior of complex mixtures such as the simulated organic-bearing waste PAS94 (Scheele, Bredt, and Sell 1996)
- can be achieved within 1 to 2 months for high surface area wastes
- will be less than the 20 wt% water needed to guarantee that a propagating reaction cannot occur when exposed to ambient Hanford Site water partial pressures. This indicates that active management of water content or water content monitoring may be required to maintain "Conditionally Safe" conditions depending on TOC or waste energetics (Webb et al. 1995) if the waste is allowed to equilibrate with ambient Hanford air
- can be controlled at levels satisfying Webb et al. (1995) "Conditionally Safe" criteria based on TOC or waste energetics by controlling P_{H_2O}
- can be rehydrated by controlling P_{H_2O} , thus providing a potentially effective means to mitigate an "Unsafe" (Webb et al. 1995) waste
- will be controlled by a complex evaporation/condensation cycle where water evaporates from the elevated temperature waste, condenses on the walls, and returns to the waste. Some gaseous water would be lost during the tank's breathing cycle depending on the tank's breathing rate.

6.0 References

- Agnew, S. F. 1997. *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*, LAUR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Babad, H., and D. A. Turner. 1993. *Interim Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Barney, G. S. 1976. *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*. ARH-ST-113, Atlantic Richfield Hanford Company, Richland, Washington.
- Brown, T. M., and J. Franklin. 1996. *Tank Characterization Report for Single-Shell Tank 241-U-105*. WHC-SD-WM-ER-617, Westinghouse Hanford Company, Richland Washington.
- Brevick, C. H., J. L. Stroup, and J. W. Funk. 1994. *Historical Tank Content Estimate for the Southwest Quadrant of the Hanford 200 West Area*. HNF-SD-WM-ER-352, Lockheed Martin Hanford Corporation, Richland, Washington.
- Burger, L. L. 1995. *Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*. PNL-8557, Rev. 1, Pacific Northwest Laboratory, Richland, Washington.
- Campbell, G. S., and G. W. Gee. 1986. "Water potential: Miscellaneous methods" in *Methods of Soil Analysis. Part I*, 2d ed., Agron. Monogr. 9. A. Klute, Ed., ASA and SSA, Madison, WI.
- Fauske, H. K., M. Epstein, D. R. Dickenson, R. J. Cash, and J. E. Meacham. 1995. *The Contact Temperature Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*. WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Hanlon, B. M. 1996. *Waste Tank Summary Report for Month Ending January 31, 1996*. WHC-EP-0182-94, Westinghouse Hanford Company, Richland, Washington.
- Hanlon, B. M. 1997. *Waste Tank Summary Report for Month Ending February 28, 1997*. HNF-EP-0182-107, Lockheed Martin Hanford Company, Richland, Washington.
- Pool, K. H., M. W. Ligothe, G. S. Klinger, O. P. Bredt, S. C. Goheen, T. W. Clauss, B. D. McVeety, K. B. Olsen, and J. S. Fruchter. 1995. *Vapor Space Characterization of Waste Tank 241-U-105: Results from Samples Collected on 2/24/95*. PNL-10702, Pacific Northwest Laboratory, Richland, Washington.
- Postma, A. K., J. E. Meacham, G. S. Barney, G. L. Borsheim, R. J. Cash, M. D. Crippen, D. R. Dickenson, J. M. Grigsby, D. W. Jeppson, M. Kummerer, J. M. McLaren, C. S. Simmons, and B. C. Simpson. 1994. *Ferrocyanide safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*. WHC-EP-0691.

Postma, A. K., J. E. Meacham, G. S. Barney, G. L. Borsheim, R. J. Cash, M. D. Crippen, D. R. Dickenson, J. M. Grigsby, D. W. Jeppson, M. Kummerer, J. M. McLaren, C. S. Simmons, and B. C. Simpson. 1994. *Ferrocyanide safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*. WHC-EP-0691. Westinghouse Hanford Company, Richland, Washington.

Scheele, R. D., P. R. Bredt, and R. L. Sell. 1996. *Organic Tank Safety Project: Development of a Method to Measure the Equilibrium Water Content of Hanford Organic Tank Wastes and Demonstration of Method on Actual Waste*. PNNL-11227, Pacific Northwest National Laboratory, Richland, Washington.

Scheele, R. D., J. L. Sobolik, R. L. Sell, and L. L. Burger. 1995. *Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste*. PNL-10213, Pacific Northwest Laboratory, Richland, Washington.

Scheele, R. D., P. R. Bredt, and R. L. Sell. 1996. *Organic Tank Safety Project: Development of a Method to Measure the Equilibrium Water Content of Hanford Organic Tank Wastes and Demonstration of Method on Actual Waste*. PNNL-11227, Pacific Northwest National Laboratory, Richland, Washington.

Scheele, R. D., P. R. Bredt, and R. L. Sell. 1997. *Organic Tank Safety Project: Effect of Water Partial Pressure on the Equilibrium Water Content of Waste Samples from Hanford Tank 241-BY-108*. PNNL-11401, Pacific Northwest National Laboratory, Richland, Washington.

Simmons, C. S., N. Aimo, M. J. Fayer, and M. D. White. 1997. *Developing a Model for Moisture in saltcake Waste Tanks: Progress Report*. PNNL-11595, Pacific Northwest National Laboratory, Richland, Washington.

Turner, D. A. and Y. Miron. 1994. *Testing of Organic Waste Surrogate Material in Support of the Hanford Organic Tank Program - Final Report*. WHC-MR-0455, Westinghouse Hanford Company, Richland, Washington.

Wahl, K. L., J. A. Campbell, I. E. Burgeson, S. A. Bryan, D. M. Camaioni, R. T. Hallen, B. D. Lerner, and R. D. Scheele. 1996. *Use of Organic Functional Group Concentrations as a Means of Screening for Energetics*. PNNL-10883, Pacific Northwest National Laboratory, Richland, Washington.

Weast, R. C., M. J. Astle, and W. H. Beyer. 1984. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida.

Webb, A. B., J. L. Stewart, D. A. Turner, M. G. Plys, B. Malinovic, J. M. Grigsby, D. M. Camaioni, P. G. Heasler, W. D. Samuels, and J. J. Toth. 1995. *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*. WHC-SD-WM-SARR-033 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Distribution

No. of Copies

OFFSITE

- 2 DOE/Office of Scientific and
Technical Information

S. F. Agnew
Los Alamos National Laboratory
P. O. Box 1663
Los Alamos, NM 87545

H. Babad
2540 Cordoba Court
Richland, WA 99352

K. K. Bandyopadhyay
Brookhaven National Laboratory
Upton, NY 11973

D. Campbell
102 Windham Road
Oak Ridge, TN 37830

S. J. Eberlein
Westinghouse Savannah River Co.
241-121H
Aiken, SC 29802

M. Epstein
Fauske and Associates, Inc.
16W070 W. 83rd St.
Burr Ridge, IL 60521

H. K. Fauske
Fauske and Associates, Inc.
16W070 W. 83rd St.
Burr Ridge, IL 60521

No. of Copies

B. C. Hudson
202 Northridge Court
Lindsborg, KA 67456

T. S. Kress
102-B Newridge Road
Oak Ridge, TN 37839

J. L. Kovach
Nuclear Consulting Services, Inc.
P. O. Box 29151
Columbus, OH 43229-0151

T. E. Larson
2711 Walnut Street
Los Alamos, NM 87544

D. A. Powers
MS-0744
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185

S. E. Slezak
MS-0741
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185

ONSITE

8 DOE Richland Operations Office

S. O. Branch	S7-54
W. F. Hendrickson	S7-54
D. H. Irby (2)	S7-54
Public Reading Room	H2-53
RL Docket File (2)	B1-17

**No. of
Copies****No. of
Copies****FAI**

M. G. Plys H4-62

MACTEC

M. H. Campbell S7-73

Los Alamos National Laboratory

J. R. White K5-12

Babcock & Wilcox Hanford Company

G. S. Barney T5-12

Duke Engineering and Services Hanford

R. J. Cash S7-14

J. E. Meacham (2) S7-14

A. B. Webb H4-65

Independent

J. M. Grigsby H4-62

L. M. Stock S7-14

Lockheed Martin Hanford Company

N. W. Kirch R2-11

D. A. Reynolds R2-11

45 Pacific Northwest National Laboratory

P. R. Bredt (3) P7-25

J. W. Brothers (2) K5-22

S. A. Bryan P7-25

L. L. Burger P7-25

D. M. Camaioni K2-38

C. D. Carlson P7-25

T. J. DeForest K7-97

P. G. Heasler K5-12

J. L. Huckaby K6-80

V. L. Hunter K7-97

R. T. Hallen P8-38

W. D. Samuels K2-44

R. D. Scheele (5) P7-25

R. L. Sell P7-25

C. S. Simmons K9-33

C. W. Stewart K7-15

J. M. Tingey P7-25

J. J. Toth K7-94

Technical Report Files (5)

Organic Tank Project File (4) P8-08