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Organic Tank Safety Project: Equilibrium Moisture Determination Task FY 1997 Annual Progress Report

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September 1997

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**Organic Tank Safety Project:
Equilibrium Moisture Determination Task
Fiscal Year 1997 Progress Report**

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

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Pacific Northwest National Laboratory
Richland, Washington 99352

Abstract

Twenty waste storage tanks at the U.S. Department of Energy's Hanford Site are included in the Organic Tank Watch List. The water content in the wastes plays a significant role in preventing propagating or sustainable chemical reactions, and the fuel and energetics independent safety criterion has been determined to be 20 wt % water. To ensure 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. If necessary, the P_{H_2O} could be managed to maintain the water content at an acceptable level or adjust the water content back to an acceptable level.

During fiscal year 1997, the effect of P_{H_2O} was tested to determine how organic-bearing wastes will respond if exposed to environmental Hanford water partial pressures or other potential water partial pressures. The samples tested were obtained from Organic Watch List Tanks, tanks that D.A. Reynolds of Lockheed Martin Hanford suspects may contain wastes having significant organic content, or wastes characteristic of organic-bearing wastes. Temperatures at or near maximum tank waste surface temperatures were used in the tests. At 26°C, the lowest temperature used, the water partial pressures used in the tests ranged from 2 to 22 torr. At 41°C, the highest temperature used, the water partial pressures used ranged from 3.5 to 48 torr.

Samples from the following tanks were studied:

- BY-108: When samples were exposed to the range of Hanford environmental vapor pressures, the equilibrium water contents ranged between 1 and 16 wt%. A variety of constituents appears to control the equilibrium water contents. Unfortunately, the amount of hydroxide, a significant water sorbent, is unmeasured.
- U-105: At Hanford water partial pressures, each of the samples had water contents between 5 and 12 wt%. No one particular constituent appears to be controlling the samples' equilibrium water contents; rather, the behavior appears to be a combination of behaviors.
- S-102: At Hanford water partial pressures, each of the samples had water contents between 3 and 6 wt%. The equilibrium water contents appear to be controlled by sodium nitrate, although below 29 torr, the lesser constituents appear to cause the waste to retain water.
- U-107: The equilibrium water contents in the solid sample ranged from 2 wt% at 2 torr to 72 wt% at 22 torr. At Hanford water partial pressures, at the average Hanford P_{H_2O} of 5.5 torr, the supernate's equilibrium water content will be about 15 wt%. However, it will be greater than 20 wt% at pressures exceeding 7 torr.
- A-101, A-102, & BY-110: The testing of waste samples from these tanks are at the time of this writing incomplete. The results to date indicate that each of the samples tested will have equilibrium water contents below 20 wt% at Hanford water partial pressures.

In general, it appears that the equilibrium water contents in these wastes will dry to below the 20 wt% safety criterion if allowed to equilibrate with Hanford water partial pressures. The water content in all samples can be increased or decreased by controlling the P_{H_2O} , so it may be possible to rehydrate organic-bearing wastes to 20 wt% water using air with a controlled P_{H_2O} .

Summary

Water content plays a significant 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 (PNNL) 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 water partial pressures (2.8 to 9 torr) 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.

During fiscal year 1997, PNNL investigated the effect of water partial pressure at or near maximum tank waste surface temperatures on the equilibrium water content of selected Hanford waste samples to determine how organic-bearing wastes will respond if exposed to environmental Hanford water partial pressures or other potential water partial pressures. The samples tested were obtained from Organic Watch List Tanks, tanks that D. A. Reynolds of Lockheed Martin Hanford suspects may contain wastes having significant organic content, or wastes having characteristics of organic-bearing wastes. The wastes studied or partially studied during FY 1997 were obtained from 241-A-101, 241-A-102, 241-BY-108, 241-BY-110, 241-S-102, 241-U-105, and 241-U-107; hereafter the "241-" will not be used for the tank designation. At 26°C, the lowest temperature used, the water partial pressures used ranged from 2 to 22 torr. At 41°C, the highest temperature used, the water partial pressures used ranged from 3.5 to 48 torr.

In general, the experimental method consisted of exposing, at a selected temperature, duplicate 1-g samples of waste to water partial pressures controlled by saturated salt solutions contained in sealed dessicators. The mass of the samples was monitored until stabilized or for the high vapor pressures monitored until they appeared to be approaching a constant mass. At this time, the samples exposed to the high and low partial pressures were exchanged and their masses monitored until stable. Water content was then determined by drying at 105°C, assuming that all mass loss was due to water loss (Scheele, Bredt, and Sell 1996).

In the BY-108 studies, PNNL exposed waste obtained by Core 99 from the uppermost 48-cm-segment sample (Segment 1) and from the lower quarter portion of the next 48-cm-segment sample (Subsegment 2D) to water partial pressures of 2.2, 7.6, 18, 27, and 29 torr at 30°C, the nominal temperature of the uppermost waste in BY-108. The two samples exhibited different behaviors. Exposure to these water partial pressures resulted in water contents in the homogenized Segment 1 sample ranging for the low and high P_{H_2O} from 1 to 48 wt% water, respectively. Exposure of homogenized Subsegment 2D to water partial pressures ranging for 2.2 to 29 torr resulted in water contents ranging from 1 to 62 wt% water. When exposed to the range of Hanford environmental vapor pressures, the equilibrium water content for both samples was below the 20 wt% water energetics and total organic carbon independent safety criterion established by Webb et al. (1995). No one particular waste constituent appears to be controlling the equilibrium water contents; rather, it appears to be a

combination of a variety of constituents. Unfortunately, the amount of hydroxide, a significant water sorbent, has in general not been measured.

In the U-105 studies, four samples of 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) were exposed 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. In general, all of the U-105 samples exhibited similar behavior with a steady increase in equilibrium water content with increasing water partial pressure. The equilibrium water contents ranged from 5 wt% at 2.7 torr to 75 wt% at 37 torr. At Hanford atmospheric water partial pressures, each of the samples had water contents less than the 20 wt% water content that guarantees that an organic-bearing waste will not support a propagating reaction. No one particular waste constituent appears to be controlling the samples' equilibrium water contents; rather, the behavior appears to result from a combination of the constituents' behavior.

In the S-102 studies, two samples of waste obtained by Core 125 Segment 3 and Core 130 Segment 3 samples were exposed to water partial pressures of 3.5, 11, 29, 44, and 48 torr at 41°C, the highest temperature observed in the solid waste's surface. In general, the S-102 samples exhibited identical behavior qualitatively characteristic of sodium nitrate and/or nitrite. The equilibrium water content remained low until a particular P_{H_2O} is exceeded, after which significant amounts of water are retained. The S-102 wastes did exhibit a slight steady increase in equilibrium water content up to 29 torr. The equilibrium water contents ranged from 5 wt% at 2.7 torr to 75 wt% at 37 torr. At Hanford water partial pressures, each of the samples had water contents below 5 wt%, significantly less than the 20 wt% water content that guarantees that an organic-bearing waste will not support a propagating reaction. The equilibrium water contents of the S-102 samples appear to be controlled by sodium nitrate, although below 29 torr, the lesser constituents appear to cause the waste to retain water.

In the U-107 studies, a supernate sample obtained by the Cores 129 Segment 1 sampling and a solid sample obtained by the Core 134 Segment 2 sampling were exposed to water partial pressures of 2, 7, 15, 21, and 22 torr at 26°C, the highest temperature observed in the solid waste's surface. The U-107 samples exhibited significantly different behaviors over this range of water partial pressures. The amount of water retained by the supernate, which contains significant hydroxide, steadily increases with increasing P_{H_2O} . The equilibrium water content in the supernate sample ranges from 6 wt% at 2 torr to 79 wt% at 22 torr. In contrast, the solid sample qualitatively exhibits the characteristics of sodium nitrate and/or nitrite retaining little water (<7 wt%) at water partial pressures up to 15 torr and significant amounts of water beginning at a P_{H_2O} above 15 torr. The U-107 solid waste did exhibit a slight steady increase in equilibrium water content up to 15 torr with increasing P_{H_2O} . The equilibrium water content in the solid U-107 sample ranged from 2 wt% at 2 torr to 72 wt% at 22 torr. At Hanford water partial pressures, at the average Hanford P_{H_2O} of 5.5 torr, the supernate's equilibrium water content will be below the 20 wt% water safety criterion; however, at Hanford water pressures exceeding 7 torr, the equilibrium water content will be greater than the 20 wt% water criterion. The solid will always have a water content of <6 wt% at Hanford water partial pressures (2.8 to 9 torr).

The A-101, A-102, and BY-110 studies are as yet incomplete, however, the results to date indicate that these wastes at current temperatures will retain < 20 wt% water at Hanford atmospheric water partial pressures. It appears that the three A-101 waste samples and the two A-102 waste samples

will retain < 14 wt% water at Hanford partial pressures. The two BY-110 waste samples appear to be approaching maximum water contents of < 10 wt% water at Hanford atmospheric vapor pressures.

The observed reversibility of the water loss/gain displayed by all samples tested indicates 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 is possible to rehydrate organic-bearing wastes to 20 wt% water using air with a controlled P_{H_2O} depending on the composition of the waste.

In general, these studies indicate that the equilibrium water content of wastes stored in A-101, A-102, BY-108, BY-110, U-105, and U-107 will, if allowed to equilibrate with Hanford water partial pressures, dry to below the desired 20 wt% water content (Webb et al. 1995). How far below 20 wt% water safety criterion depends on the waste and its composition. At this time, we have too little information to predict the contribution of all of the individual major waste constituents found in Hanford wastes or their interactions. Most of the studied wastes are primarily sodium nitrate and/or nitrite, although the concentration of the lesser constituents varies with the waste. Some of the solid wastes studied exhibit the qualitative characteristics of sodium nitrate and nitrite, retaining small amounts of water (< 20 wt%) at relative humidities less than 50% and retaining significant amounts when exposed to relative humidities of 90% or more. 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 (Webb et al. 1995).

References

Scheele RD, PR Bredt, and RL 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.

Webb AB, JL Stewart, DA Turner, MG Plys, B Malinovic, JM Grigsby, DM Camaioni, PG Heasler, WD Samuels, and JJ 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.

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Glossary

DESH Duke Engineering and Services Hanford

GEA gamma energy analysis

IC ion chromatography

ICP inductively coupled argon plasma spectroscopy

ICP/AES inductively coupled plasma/atomic emission spectroscopy

P_{H_2O} water partial pressure

PNNL Pacific Northwest National Laboratory

PUREX Plutonium Uranium Extraction

RH relative humidity

TGA thermogravimetric analysis

TIC total inorganic carbon

TOC total organic carbon

WHC Westinghouse Hanford Company

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1.0 Introduction

Twenty of the 177 underground high level radioactive waste storage tanks at the U. S. Department of Energy's 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 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 or vice versa will occur with lower water contents resulting from low 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 the ambient Hanford P_{H_2O} provided in Figure 1.1.

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

In 1996, we adapted and demonstrated a method to determine the effect of P_{H_2O} on the equilibrium water content of Hanford's stored radioactive wastes, providing a means to predict a waste's future safety status or category. We built on established methods to measure water potential in materials such as described by Campbell and Gee (1986) or used by Armstrong, Freeman, and Kovach (Postma et al. 1994). This was done as part of Pacific Northwest National Laboratory's (PNNL's) Organic Tank Safety Project. As a result of this 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, Bredt, and Sell 1996).

Our earlier 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.

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 investigated the effect of P_{H_2O} on the equilibrium water content of waste samples obtained from Organic Watch List Tanks or wastes suspected by D. A. Reynolds of Lockheed Martin Hanford of having significant organic content or wastes characteristic of organic-bearing wastes. This report provides for BY-108, U-105, U-107, S-102, A-101, A-102, and BY-110

- historical information on the types of Hanford wastes present in the tanks
- the measured chemical compositions of the waste samples tested
- existing temperatures and water partial pressures in these tanks
- the effect of P_{H_2O} on the equilibrium water content of tested waste samples
- discussions on the effect of chemical compositions on the equilibrium water contents and
- comparisons of the measured P_{H_2O} in the tanks' headspace and the expected P_{H_2O} based on our results.

More comprehensive reports are available for BY-108 and U-105 (Scheele, Bredt, and Sell 1997a; 1997b). The studies of the wastes from A-101, A-102, and BY-110 are incomplete, so the results to date are provided.

2.0 Experimental Approach and Method

We used a several experimental methods and procedures to measure selected physical properties and the effect of P_{H_2O} on the equilibrium water content of selected and available Hanford wastes. The physical properties were measured to support C. S. Simmons of PNNL in his efforts to model moisture behavior in Hanford organic-bearing wastes (Simmons 1996; Simmons et al. 1997). This section describes the methods used to measure the equilibrium water content of wastes and various physical properties related to water behavior, such as water content.

2.1 Determination of Equilibrium Moisture Content

We used the adapted experimental approach and procedure described in an earlier report (Scheele, Bredt, and Sell 1996) to measure the equilibrium water content of Hanford waste samples when exposed to a range of water partial pressures. In this approach, waste samples were exposed to known water partial pressures at the tank's reported maximum surface temperature, and their mass was monitored until stabilized or appeared to be approaching a stable water content. The water partial pressures encompassed or were near the minimum P_{H_2O} observed at the Hanford Site between 1985 and 1995, 3.5 torr (see Figure 1.1), and the higher water partial pressures that may exist in the tank. The temperatures are from tank characterization reports, the tank characterization database, or from Hanlon's summary reports on Hanford tank wastes status (Hanlon 1996; 1997).

To determine the equilibrium water content of a waste, nominal 1-g aliquots of waste were exposed to a P_{H_2O} controlled by a saturated salt solution, 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 as well as using thermogravimetric analysis (TGA) for selected samples. The procedure follows:

1. 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 reagent grade NaOH, $CaCl_2$, NaBr, KCl, and KNO_3 . A schematic of this system is shown in Figure 2.1.
2. 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.
3. 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.
4. 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} .

The temperatures and the water partial pressures used for the different waste samples are presented in Table 2.1. The maximum temperatures in the tested tank's surface wastes range from 26 to 41°C. In some tanks, the maximum temperature in some locations within the waste is significantly higher

than the surface waste's temperature; e.g. A-101 has a maximum waste temperature of 65°C deep in the waste. With time, the tank waste temperatures will decline because the heat-producing radionuclides are decaying. Over time, the equilibrium moisture content should increase because of the drop in temperature.

Figure 2.1. Schematic of Constant Humidity Chamber

Table 2.1. Experimental Test Conditions

Tank	Temperature, °C	Water Partial Pressures, torr
A-101	41	3.5, 11, 30, 44, 48
A-102	32	2, 8, 20, 30, 32
BY-108	30	2, 8, 18, 27, 29
BY-110	35	3, 9, 23, 34, 37
S-102	41	3.5, 11, 30, 44, 48
U-105	34	3, 9, 23, 33, 37
U-107	26	2, 7, 15, 21, 22

The effect of declining waste temperatures and the corresponding effect of P_{H_2O} on the equilibrium water content can be estimated using the results of our testing and the Clausius–Clapeyron relationship presented in Equation 2.1. In the equation, ΔH_v is the heat of vaporization, P_1° is the equilibrium vapor pressure at temperature 1, P_2° is the equilibrium vapor pressure at temperature 2, R is the gas constant, and T is temperature in Kelvin.

$$\ln \frac{P_2^\circ}{P_1^\circ} = \frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Eq 2.1.}$$

Without additional studies to obtain a true ΔH_v for each waste, a first estimate of temperature effects for a particular waste-water mixture could be calculated using the results of these studies, the Clausius-Clapeyron equation, and the ΔH_v for pure water, 43.6 kJ/mole. It must be assumed that ΔH_v is constant as a function of temperature for all combinations of waste and water. This assumption is probably not true since the number of phases could change as temperature changes.

2.2 Determination of Physical Properties

To determine the density of the as-received material, centrifuged solids density, supernate density, the wt% and vol% centrifuged solids, the wt% solids in the as-received material, the wt% solids in the centrifuged solids, and the wt% dissolved solids in the supernate, a nominal 1-g sample was first centrifuged 1 h at 1860 g in a graduated centrifuge cone. The mass and volume of the centrifuged solids and supernate were determined by weighing duplicate samples before and after the supernate was decanted. The centrifuged solids and the supernate were air dried at room temperature until sufficient water had evaporated to prevent splattering and loss of sample during drying at 105°C. The wt% and vol% interstitial solution are calculated values based on the assumption that the water in the sample is an interstitial solution having the composition of the recovered supernate or the supernate in the tank.

All of the waste's physical properties are calculated from measured masses and volumes. The density of the as-received sample equals the total mass divided by the total volume after centrifuging; in all cases, the volumes did not change measurably as a result of centrifuging. The densities of the centrifuged solids and centrifuged supernate equals the respective masses of the centrifuged solids or centrifuged supernate divided by their respective volumes. We calculated the vol% and wt% centrifuged solids by dividing the respective volume or mass of the centrifuged solids by the total volume or mass of the centrifuged sample. The wt% solids or wt% dissolved solids in the centrifuged solids and supernate is the mass of the dried solids divided by the mass of the undried centrifuged solids or supernate, respectively. Because of the shortage of sample, we calculated the wt% solids in the as-received material by multiplying the wt% solids in the centrifuged solids by the wt% centrifuged solids and added the product of the wt% centrifuged supernate and wt% dissolved solids.

The wt% and vol% of interstitial solution are derived properties calculated using the measured water content, the dissolved solids content in the supernate, and the as-received solids and the supernates' densities. The wt% interstitial solution is calculated by adding the wt% water in the as-received material to the wt% solids associated with that water, assuming the water is in the as-received solids as interstitial solution. The vol% interstitial solution is calculated by multiplying the wt% interstitial solution by the ratio of the solids density and supernate (interstitial solution) density.

3.0 Background Information on Tanks and Their Wastes

The equilibrium water content of Hanford's organic-bearing wastes at a particular P_{H_2O} will be controlled by temperature, the chemical composition, and several physical factors such as the ability of water to migrate through waste and other factors beyond the scope of this work. Our work focused on empirically determining the response of selected Hanford wastes to the range of water partial pressures that the organic-bearing wastes may be exposed to during storage and supplying physical properties for C. S. Simmons efforts to model water behavior in wastes.

The importance of chemical composition and temperature were demonstrated by previous studies by Fauske et al. (1995) and this laboratory (Scheele, Bredt, and Sell 1996). These studies demonstrated that the equilibrium water content of a waste or compound-water mixture at different water partial pressures depends on the chemical composition. Both Fauske et al. and our laboratory found sodium hydroxide to be quite hydrophilic and sodium nitrate and/or nitrite to sorb water only at very high (>70%) relative humidities. Mixtures of potential waste constituents exhibited the qualitative behavior of the primary constituent, however, the mixture behaved as a blend of the ingredients, as would be expected. The chemical composition of the stored wastes depends on the processes that produced the wastes and any additional processing that the waste encountered during its lifetime. As Scheele, Sobolik, Burger, and Sell (1996) and Agnew (1997) discuss, strontium removal from Plutonium Uranium Extraction (PUREX) wastes produced most of the Hanford organic-bearing wastes.

This section provides the reader with some of the key background information necessary to understand the response of the tested Hanford wastes to different water partial pressures. The background information provided in this section includes 1) a brief history of the wastes stored in the tanks, 2) the temperatures and water partial pressures found in the tanks, 3) the history of the sampling event that yielded the samples studied, and 4) the major measured chemical constituents found in the wastes studied. It should be noted that for all but one waste studied, the hydroxide content was unmeasured.

3.1 Background on BY-108 and Its Contents

Tank BY-108 was classed as a "Ferrocyanide Watch List Tank" based on historical records that indicated the waste stored in BY-108 contained >8 wt% sodium nickel ferrocyanide on an energy equivalent basis (Hanlon 1996); this did not take into account any aging of the ferrocyanide that may have occurred during the years of storage (Lilga et al. 1992; 1993; 1994; 1995; 1996). The Hanford Site operating contractor used the ferrocyanide scavenging process to remove radiocesium and to a lesser extent radiostrontium from aqueous wastes, thus allowing disposal of the decontaminated wastes to a soil column.

Although BY-108 is not currently on the Organic Watch List, the waste stored in BY-108 is a saltcake type waste and should be representative of some of the organic-bearing saltcake wastes stored in the Hanford Site's tanks that have been identified by Webb et al. (1995) as the wastes of greatest concern. We studied samples of waste taken by Core 99 segments 1 and 2D from BY-108 because they were in the form of saltcake and were readily available to us. We determined the equilibrium water content after exposure to a range of water partial pressures that it might experience during its storage as a result of environmental conditions or waste-management operations.

3.1.1 BY-108 Fill History

Tank BY-108 was placed into service in March of 1951 and has been used to receive and store many different Hanford Site waste types. Tank BY-108 was the second tank in a cascade of three where overflow wastes from one tank could flow into and from another tank with waste flowing from BY-107 to BY-108 and then to BY-109. Much of the supernate was removed and disposed of in soil columns.

Baldwin et al. (1996) list many transfers in and out of the tank between 1951 and 1982. From 1951 to 1954, the initial waste stream was 5500 kL of first-cycle decontamination waste from the bismuth-phosphate process. Between 1954 and 1957, BY-108 was the primary settling tank for 33000 kL of U-Plant ferrocyanide-scavenged uranium recovery waste (Stedwell 1954). The resulting radiocesium decontaminated supernate was disposed of in soil columns. In 1957, 1900 kL of ferrocyanide-decontaminated supernate was transferred to BY-108 from C-112. In 1959, 1900 kL of combined uranium recovery waste, cladding waste, and PUREX cladding removal waste were transferred from C-105 to BY-108. Between 1969 and 1974, 3300 kL of waste, including evaporator bottoms waste, cladding waste, and organic wash waste, were transferred from BY-109. Approximately 1400 kL of in-tank solidification waste were transferred into BY-108 from BY-111 during 1968, and 2300 kL of in-tank solidification waste were transferred from BY-112 between 1970 and 1971. Between 1972 and 1975, approximately 100 kL of water were added to the tank.

Tank BY-108 was classified as an assumed leaker in 1972 with an estimated leak of less than 20 kL. While the reported tank volume has remained constant since 1982 at approximately 860 kL (Hanlon 1996; Baldwin et al. 1996), Baldwin et al. (1996) report that drywell measurements indicate that "significant (radioactivity) was observed in the past (as expected from an assumed leaker)." Tank BY-108 has seven drywells located in the ground around the tank to monitor for leaks. The tank was interim stabilized in February 1985 by removing drainable liquid.

3.1.2 BY-108 Temperatures and P_{H_2O}

Temperatures in Tank BY-108 range from 40 to 26°C bottom to top as measured by the one properly functioning thermocouple tree. This tree with 13 thermocouples is located in Riser 8. Riser 8 is located approximately 2 m north of the tank's center and is 18 cm in diameter. Thermocouple numbers 1 through 5 are located 15.2 cm, 76.2 cm, 137.2 cm, 198.2 cm, and 259.2 cm from the bottom of the tank, respectively. The waste height is measured by a manual tape in Riser 4, approximately 4 m north of the center of the tank and 2 m north of the thermocouple tree in Riser 8. On October 1, 1995, the surface level in Riser 4 was measured at 220 cm. This measured waste height places Thermocouples 1 through 4 in the waste and 5 in the headspace. Thermocouple readings on March 20, 1996, for Thermocouples 1 through 5 were 41°C (106°F), 38°C (100°F), 33°C (91°F), 26°C (79°F), and 25°C (77°F), respectively. From these temperature data, 30°C (86°F) was determined to be at or near the waste surface temperature and used for the water equilibrium testing of BY-108.

Pool et al. (1996) measured a P_{H_2O} of 14.8 torr on January 24, 1996 at a headspace temperature of 24°C. This corresponds to an RH of 65% at the headspace temperature.

3.1.3 BY-108 Core Sampling Events

Three core samples were collected from BY-108 in July and August of 1995 using the rotary mode sampling truck. These core samples are referred to as Core 98, Core 99, and Core 104. Cores 98 and 99

were taken from Riser 12A and Core 104 from Riser 7. Riser 12A is 18 cm dia and approximately 8 meters north of the center of the tank. Cores 98 and 104 were extruded and analyzed at Westinghouse Hanford Company's (WHC) 222-S laboratory. Core 99 was extruded at WHC's 222-S laboratory and shipped to PNNL's 325 building Analytical Chemistry Laboratory for analysis.

Core 99 consisted of 4 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 surface of the waste. Segment 1 in Core 99 contained approximately 5 cm of solids and no drainable liquid. Baldwin et al. (1996) described the material as a dirty white saltcake. Segment 2 contained 230 mL of an opaque yellow-green drainable liquid and approximately 5 cm of solids. The solids were divided into two 2.5-cm subsamples referred to as Quarter Segment 2A and Quarter Segment 2D. Quarter Segment 2A was described as a dirty-white saltcake, and Quarter Segment 2D as a cream-colored sludge; the subsequent 2D sample tested was a light brown moist grainy material. Segment 3 contained 25 mL of tan-colored opaque drainable liquid and 2.5 cm of grainy cream-colored saltcake. Segment 4 contained 48 cm of a brown sludge with embedded saltcake and no drainable liquid. The material in Segment 4 was divided into four quarter segments labeled 4A through 4D.

All samples were homogenized at PNNL using a mortar and pestle before any analysis and before removing subsamples for moisture equilibrium testing reported here. Given the limited volume of material, PNNL's high-shear blender, which is normally used for homogenization, could not be used for this homogenization. Elemental contents as measured by inductively coupled argon plasma coupled with atomic emission spectroscopy (ICP/AES) and gamma energy analysis (GEA) in duplicate subsamples from Segment 1 and Quarter Segment 4B were compared to determine if the homogenization was effective. The results reported by Silvers et al.⁽¹⁾ showed inhomogeneity between duplicates. The highest relative percent difference between duplicates, 42%, was seen for iron.

3.1.4 Compositions of the Tested BY-108 Wastes

Selected compositional data collected on Segments 1 and 2D from Core 99 used in our equilibrium-water-content studies were taken from Baldwin et al. (1996) and Silvers et al.⁽¹⁾ Their references include data collected for Cores 98, 99, and 104.

The water content in Segments 1 and 2D, the samples used for our moisture testing, was 29 wt% and 17 wt% water, respectively, as measured by TGA. The mass losses observed between ambient and approximately 150°C for Segment 1 and from ambient to approximately 200°C for Segment 2D were assigned to water loss.

As shown in Tables 3.1 and 3.2, the major elements, anions, and other measured constituents in Segments 1 and 2D are aluminum, sodium, phosphorous, principally as phosphate, nitrate, nitrite, sulfate, and fluoride, although significant compositional differences exist between the two segments. Both segments have traces of carbonate and/or bicarbonate (total inorganic carbon [TIC]) and TOC; the TOC is in excess of the carbon associated with the cyanide. The elemental concentrations provided in Table 3.1 on a dry basis were determined by ICP/AES of acidic solutions prepared from both KOH-KNO₃ fusions and Na₂O₂-NaOH fusions. Table 3.1 provides the cyanide, TOC, TIC, and anion concentrations on a dry

(1)K. L. Silvers, L. R. Greenwood, R. T. Steele, J. M. Tingey, and M. W. Urie. 1995. *Single Shell Tank Waste Characterization Project, Core 99, Revision 1*. A letter report to Westinghouse Hanford Company. Pacific Northwest National Laboratory, Richland, Washington.

basis; the anion concentrations were measured using ion chromatography (IC). None of the samples from BY-108 were analyzed for $[\text{OH}]$, a major water absorbing waste constituent (Scheele, Bredt, and Sell 1996; Fauske et al. 1995; Barney 1976).

Table 3.1. Elemental Concentrations ($\mu\text{g/g}$ dry) Measured by ICP/AES for BY-108 Core 99 Segment 1 and Subsegment 2D Waste Samples (Baldwin et al. 1996).

Element	KOH-KNO ₃ Fusion		Na ₂ O ₂ -NaOH Fusion	
	Segment 1	Subsegment 2D	Segment 1	Subsegment 2D
Al	200,000	83,000	160,000	73,000
Ca	1,000	1,100	4,900 ^(a)	3,100 ^(a)
Fe	2,100	1,100	1,700	650
K	(b)	(b)	8,900	5,300
Na	140,000	170,000	(b)	(b)
P	35,000	2,900	5,400 ^(c)	280 ^(c)
Si	10,000	1,400	4,800	1,300
(a) 3,700 $\mu\text{g/g}$ detected in process blank.				
(b) Not measured due to fusion technique.				
(c) Zirconium crucibles used, so low results due to precipitation of zirconium phosphate.				

Table 3.2. Anions, Total Organic and Inorganic Carbon, and Cyanide Content ($\mu\text{g/g}$ dry) in BY-108 Core 99 Segment 1 and Subsegment 2D Waste Samples (Baldwin et al. 1996).

Analyte	Segment 1	Subsegment 2D
CN ⁻	130	170
TOC	1,500	2,800
TIC	1,700	2,900
F ⁻	8,500	4,700
Cl ⁻	990	1,400
NO ₂ ⁻	11,000	24,000
NO ₃ ⁻	86,000	300,000
PO ₄ ³⁻	82,000	17,000
SO ₄ ²⁻	1,700	12,000

3.2 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).

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.

3.2.1 U-105 Temperatures and P_{H_2O}

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. Ewer 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.

Pool et al. (1995) reported a P_{H_2O} of 13.2 torr at 22.3°C in U-105's vapor space on February 24, 1995. This vapor pressure corresponds to an RH of 65% at the headspace temperature.

3.2.2 U-105 Core Sampling Events

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. 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 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) 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). Brown and Franklin report 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. 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.

3.2.3 Compositions of Tested U-105 Waste

Table 3.3 provides the measured concentrations on a weight and molar basis of the major chemical constituents as reported by the Hanford Tank Waste Characterization Program for the wet samples that we tested (Brown and Franklin 1996). Table 3.4 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 Table 3.3 and Table 3.4 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 et al. (1995) and ourselves (Scheele, Bredt, and Sell 1996) to have a significant effect on equilibrium water content.

As shown in Table 3.3 and Table 3.4, 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 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^- 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 plus nitrite varies from 5700 to 10300 $\mu\text{mol/g}$. The 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.

Table 3.3. Concentration 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
$\text{C}_2\text{O}_4^{2-}$	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_2O , wt%	37		31		36		45	

Table 3.4. 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

3.3 Background Information on S-102 and its Wastes

The single shell Tank S-102 is listed on both the "Hydrogen Tank" and the "Organic Tank" Watch Lists. Tank S-102 was added to both the Hydrogen Tank Watch List and the "Organic Tank Watch List" in January of 1991 (Hanlon 1997). Inclusion on the Organic Tank Watch List was based on historical records that indicated the waste stored in S-102 contained >3 wt% TOC (Babad and Turner 1993).

Tank S-102, which was constructed during 1950 and 1951, is a concrete tank with a primary mild steel liner. The dome is concrete with 12 risers between 10 cm (4 in.) and 1.1 m (42 in.) in diameter, providing access to the waste. Tank S-102 has a 2869-kL (758-kgal) capacity, a diameter of 23 m (75 ft), and an operating depth of 7.0 m (23 ft). The tank has a dished bottom with a 1.2 m (4 ft) radius knuckle. Tank S-102 was the second tank in a cascade of three where overflow wastes from one tank could flow into and from another tank. For S-102, waste flowed from S-101 to S-102 and then to S-103. The tank was designed to store non-boiling waste with a maximum temperature of 104°C (220°F).

3.3.1 S-102 Fill History

Hanford Tank 241-S-102 was placed into service in the fourth quarter of 1953 (Brager 1994). From 1953 to approximately 1955, the tank received 1,630 kL of high level waste from the REDOX process. This stream included salt waste, lab waste, and hot condensate (Ewer et al 1997b). Waste from the REDOX process flowed into the three-tank cascade from S-101 to S-102 and then to S-103. Much of the supernate was removed and disposed of in soil columns. The next series of major changes in waste inventory began in 1973 when S-102 waste was transferred to evaporator 242-S, and the tank started receiving evaporator bottoms. Between 1976 and 1977, S-102 began receiving a combination of non-complexed waste, partially neutralized waste, and double-shell slurry feed.

The waste level fluctuated between 1973 and 1980 with a high of approximately 691 cm, the height of the cascade overflow, and a low of 183 cm. The tank was removed from service in 1980 with a total waste height of approximately 569 cm. This was followed by a drop in level ending in December of 1982. Level data show that the waste height has been increasing slowly since 1982 from approximately 502 cm in the first quarter of 1982 to 518 cm in mid 1993 (Brager 1994). This level growth is attributed to gas retention within the waste and not liquid intrusion (Gauglitz et al. 1996). The tank is currently considered sound (Hanlon 1997).

3.3.2 S-102 Temperatures and P_{H_2O}

The single thermocouple tree used to measure the temperatures in S-102 at six different heights is located in Riser 3. Riser 3 is located approximately 5 m from the center of the tank. According to level data provided in Ewer et al. (1997a), the thermocouple probes are numbered sequentially with elevation. Probes 1 through 5 are located in the solids with Probe 1 located approximately 15 cm (6 in.) from the bottom of the tank, and Probe 6 located in the tank's vapor space. All six thermocouple probes indicate that the waste has cooled from between 43 to 49°C (110 to 120°F) in 1988 to between 38 to 43°C (100 to 110°F) in August of 1996. Thermocouple Probe 5, located approximately 262 cm below the waste surface, ranges from 39 to 40°C (102 to 104°F).

The temperatures in S-102's vapor space ranged from 24°C (75°F) to 29°C (85°F) between 1990 and 1997. The vapor space temperatures peak in November and reach a minimum in early May. The P_{H_2O} measured by Pool et al. (1995) on March 14, 1995 was 16.5 torr at a temperature of 24°C. This P_{H_2O} corresponds to an RH of 74% at the vapor space's temperature.

3.3.3 S-102 Core Sampling Events

Two core samples were collected from S-102 between January and March 1996 using the push mode sampling truck. These core samples are referred to as Core 125 and Core 130. Core 125 was taken from Riser 11 located on the west side of the tank, roughly 2.5 m from the outer wall of the tank; we estimated the distances using the schematic presented in Ewer et al. (1997b), assuming the drawing is roughly to scale, although the drawing does contain a warning that the drawing is not to scale. WHC took Core 130 through Riser #14 located in the NE quadrant of the tank roughly 5 m from the outside wall. The 222-S laboratory, operated by WHC, extruded and analyzed all three cores.

As Eggers (1996) reports, Core 125 consisted of 11 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. Due to sampling problems, Core 130 had three duplicate segments in the entire core of 11 segments (14 total segment samples). Extrusion of these segments indicates stratification of waste (Eggers, 1996). Both cores contained saltcake in Segments 2 through 8, sludge-like material in Segments 9 and 10, with more salt cake in Segment 11. Segment 1 in both cores contained one gram or less of sample. Since segments are numbered from the top of the waste down, Segment 11 contains material near the bottom of the tank. Tank S-102 appears to contain a thin heel of salt cake, approximately 48 cm (19 in.), covered by a thick layer of sludge, approximately 96 cm (38 in.), covered with a thicker layer of salt cake, approximately 338 cm (133 in.).

Segments from Cores 125 and 130 were extruded at WHC's 222-S laboratory facility in the 200 West Area. Segments 7 and 11 of Core 125 and Segments 5, 6A, and 10 of Core 130 contained drainable liquid. Drainable liquids were separated from the solids and handled as unique samples. Solids were subsampled into half segments or quarter segments based on general appearance. The subsamples were then homogenized by hand mixing. Samples from Core 125 Segment 3 and Core 130 Segment 3 were used for testing at PNNL.

3.3.4 Compositions of Tested S-102 Samples

Table 3.5 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 from Tank S-102 that we tested (Eggers 1996). Table 3.6 provides the concentrations on a dry basis. WHC measured elements after preparing the sample by acid digestion. 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.

As shown in Table 3.5 and Table 3.6, the principle elements, anions, and other measured constituents, excluding water, in both of the samples are sodium, nitrate, and nitrite. The samples also contain less than 20,000 $\mu\text{g/g}$ of aluminum, phosphate, sulfate, chromium, phosphorous, potassium, sulfur, 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 ICP. Constituents with measured concentrations below 500 $\mu\text{g/g}$ were not included in Table 3.5 and Table 3.6. In general, these samples have similar compositions with the exception of phosphorus, which is 2400 $\mu\text{g/g}$ in Core 125 Segment 3U, and only 370 $\mu\text{g/g}$ in Core 130 Segment 3U. Sulfur is roughly twice as high in the Core 130 sample compared to the Core 125 sample, 900 $\mu\text{g/g}$ and 510 $\mu\text{g/g}$ respectively. However, neither phosphorus nor sulphur are at high concentrations in either sample. 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.

3.4 Background Information on U-107 and its Wastes

The single shell Tank U-107 is listed on both the "Hydrogen Tank" and the "Organic Tank" Watch Lists. Tank U-107 was added first to the "Organic Tank Watch List" in January 1991 and later to the Hydrogen Tank Watch List in December 1993 (Hanlon 1997). Inclusion on the Organic Tank Watch List

Table 3.5. Concentration of Major Chemical Components in Tested S-102 Samples on a Wet Basis (Eggers 1996)

Chemical Component	Core 125 Segment 3U ^(a)		Core 130 Segment 3U ^(a)	
	µg/g	µmol/g	µg/g	µmol/g
Al	4500	170	4300	160
Cr	1400	28	1500	29
P	2400	77	370	12
K	500	13	590	15
Na	210000	9100	220000	9600
S	510	16	900	28
Cl ⁻	1900	54	3000	85
NO ₃ ⁻	640000	10000	620000	10000
NO ₂ ⁻	20000	440	17000	370
PO ₄ ³⁻	15000	160	ND	ND
SO ₄ ²⁻	6700	70	11000	120
C ₂ O ₄ ²⁻	2300	26	3300	38
TOC	1000	83	1100	92
TIC	2300	190	4300	360
H ₂ O, wt%	81000	4500	58000	3200

a) U designates the upper half of the segment

Table 3.6. Concentration of Major Chemical Components in Tested S-102 Samples on a Dry Basis

Chemical Component	Core 125 Segment 3U		Core 130 Segment 3U	
	µg/g	µmol/g	µg/g	µmol/g
Al	4900	200	4600	180
Cr	1579	34	1600	33
P	2600	94	390	14
K	550	16	630	17
Na	230000	11000	230000	11000
S	560	19	960	32
Cl ⁻	2100	65	3200	98
NO ₃ ⁻	700000	13000	660000	12000
NO ₂ ⁻	22000	530	18000	395
PO ₄ ³⁻	16000	190	ND	ND
SO ₄ ²⁻	7300	85	12000	130
C ₂ O ₄ ²⁻	2500	32	3500	43
TOC	1100	100	1200	110
TIC	2500	230	4600	410

a) U designates the upper half of the segment

was based on historical records that indicated the waste stored in U-107 contained >3 wt% TOC (Babad and Turner 1993).

Tank U-107, which was constructed during 1943 and 1944, is a concrete tank with a primary mild steel liner. Tank U-107 has a 2010-kL capacity, a diameter of 23 m, and an operating depth of 5.18 m. The tank has a dished bottom with a 1.2-m radius knuckle. Tank U-107 was the first tank in a cascade of three tanks where overflow wastes from U-107 could flow into U-108 and then U-109. The overflow line is approximately 4.9 m from the bottom of the tank. The tank was designed to store non-boiling waste with a maximum temperature of 104°C (220°F) (Jo, Morris, and Tran 1996). Jo et al. provide detailed drawings of U-107's configuration.

Tank U-107 became operational in September 1948 when it received metal waste from T Plant and remained in service until November 1980. Tank U-107 currently contains 1540 kL (2450 Mgal) of waste. The solid waste types currently stored in U-107 include, listed from most recent to earliest, 1079 kL (280 kgal) of 242-S evaporator waste (76 vol%), 53 kL (14 kgal) of 242-T evaporator waste (4 vol%), and 288 kL (76 kgal) of Type I REDOX coating waste (20 vol%) (Jo, Morris, and Tran 1996). The tank contains 117 kL (31 kgal) of supernate and an estimated 558 kL (147 kgal) of drainable interstitial liquid (Hanlon 1997). Agnew (1997) provides compositions and descriptions of these waste types. During its lifetime, U-107 received metal waste, REDOX coating waste, miscellaneous laboratory wastes, N-Reactor decontamination waste, T-Plant decontamination waste, and evaporator wastes.

3.4.1 U-107 Temperatures and P_{H_2O}

The single thermocouple tree used to measure the temperatures in U-107 at 11 different heights is located in Riser 1. Riser 1 is located approximately 2 m from the edge of the tank. Ewer et al. (1997b) 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 July 1987 and August 1997, temperatures in Tank U-107 waste solids ranged from 32 to 17°C, depending on depth and season. Temperatures varied seasonally with maximum temperatures occurring in October to November and the minimum temperatures occurring in March and April. The variability in temperature is less at the lower depths. Based on Ewer et al.'s (1997a) reported 396-cm surface level, thermocouple 6 is the last thermocouple in the waste. The temperature in the surface waste ranges from 20 to 26°C with occasional temperature spikes up to 30°C.

The temperatures in U-107's vapor space ranged from 20 to 28°C between January 1993 and October 1996 with temperatures again depending on the season, but in general independent of location. The thermocouple in the vapor space nearest the waste, thermocouple 7, measured temperatures ranging from 20 to 30°C. Tank U-107 is passively ventilated with no active circulation of vapor.

The measured P_{H_2O} observed in U-107's vapor space on February 17, 1996, as reported in the Tank Characterization Database, was 12.2 torr at a tank headspace temperature of 21°C. This P_{H_2O} corresponds to an RH of 65% at the headspace temperature.

3.4.2 U-107 Core Sampling Events

Three core samples were collected from U-107 in February and March 1996 using the push mode sampling truck (Jo, Morris, and Tran 1996). These core samples are referred to as Core 129, Core 134, and Core 135. Core 129 was taken from Riser 9 located in the SE quadrant of the tank, nominally 3 m from the center of the tank and 8.5 m from the outside wall assuming that Jo et al.'s (1996) Figure 2.1 is roughly to scale. WHC took Core 134 through Riser 7 located in the SW quadrant of the tank nominally 9 m from the center of the tank and 2 m from the outside wall. WHC took Core 135 through Riser 2 located in the NE quadrant of U-107 nominally 9 m from the center of the tank or 2 m from the outside wall. The 222-S laboratory, operated then by WHC, extruded and analyzed all three cores.

As Jo et al. (1996) report, eight segments were expected for each core; however, because hard surfaces were encountered at various levels, fewer segments were retrieved. Core 129 consisted of three 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. Core 129 Segment 1 was liquid, Segment 2 was a dark brown to black wet saltcake, and Segment 3 was a moist saltcake. No additional samples were obtained from Riser 9 because the waste could not be penetrated. Six segments were obtained by Core 134. The uppermost segment was liquid, Segment 2 was a dry salt, Segment 3 and the upper half of Segment 4 was a moist salt, the bottom half of Segment 4 and the upper third of Segment 5 was a wet sludge, Segment 5A was a moist salt, Segment 5B was liquid, the upper third of Segment 6 contained no material, Segment 6A was moist salt, and Segment 6B was empty. Only two segments were retrieved from Riser 2 by Core 135. Segment 1 was liquid and Segment 2 was a moist salt. WHC provided PNNL with waste samples obtained by Core 129 Segment 1 and Core 134 Segment 2 for our studies to determine their equilibrium moisture content at various water partial pressures.

3.4.3 U-107 Tested Wastes Compositions

Table 3.7 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 (Jo, Morris, and Tran 1996). Table 3.8 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 Table 3.7 and Table 3.8 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 for the Core 134 Segment 2 sample, a species observed by Fauske (1995) and ourselves (Scheele, Bredt, and Sell 1996) to have a significant effect on equilibrium water content.

As shown in Table 3.7 and Table 3.8, the principle ($>1000 \mu\text{mol/g}$ dry) elements, anions, and other measured constituents, excluding water, in the supernate sample are aluminum, sodium, nitrate, nitrite, and hydroxide. Potassium, chloride, sulfur primarily as sulfate, organic carbon including oxalate, and inorganic carbon (likely carbonate at this hydroxide concentration) are the major secondary constituents; the nearly identical phosphate and phosphorous concentrations indicate that in the supernate, phosphorous is phosphate. The supernate is 53 wt% water (Jo, Morris, and Tran 1996).

Table 3.7. Concentration of Major Chemical Components in Tested U-107 Samples on a Wet Basis (Jo, Morris, and Tran 1996)

Constituent	Core 129 Segment 1 (Supernate)		Core 134 Segment 2 (Solids)	
	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$
Al	17700	650	3000	110
Ca	90	2	200	5
Cr	590	10	670	10
Fe	<40	<0.6	1240	22
Mn	<7	<0.1	30	1
Ni	20	<0.3	<15	<0.3
P	920	30	1400	45
K	2100	50	530	10
Si	<59	<2	200	7
Na	165000	7200	212000	9200
S	1800	60	660	20
Cl ⁻	5300	150	1400	40
F ⁻	330	20	<240	<10
OH ⁻	20507	1200	NM	NM
NO ₃ ⁻	150000	2400	650000	10400
NO ₂ ⁻	64000	1400	16000	350
PO ₄ ³⁻	2600	30	12000	120
SO ₄ ²⁻	4400	50	6300	70
C ₂ O ₄ ²⁻	450	5	2300	30
TOC	2300	190	770	60
TIC	3400	290	3600	300

NM = Not Measured

Table 3.7 and Table 3.8 show that the principle elements, anions, and other measured constituents, excluding water, in the solid sample tested are sodium and nitrate. Other analytes above 100 $\mu\text{mol/g}$ dry are aluminum, nitrite, phosphate, and inorganic carbon (either carbonate or bicarbonate depending on pH). The IC-measured phosphate and sulfate concentrations are unexplainably more than twice the ICP/AES-measured phosphorous and sulfur concentrations. The solids contained 7 wt% water (Jo, Morris, and Tran 1996).

3.5 Background Information on A-101 and its Wastes

The single shell Tank A-101 is listed on both the "Hydrogen Tank" and the "Organic Tank" Watch Lists. Tank A-101 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). The waste has been partially interim stabilized. The tank is passively ventilated (Field, Place, and Cromar 1997).

Tank A-101, which was constructed during 1954 and 1955, is a concrete tank with a primary mild steel liner. Tank A-101 has a 3785-kL capacity, a diameter of 23 m, and an operating depth of 9.5 m. The tank has a flat bottom. Tank A-101 was the first tank in a cascade of four tanks where overflow

Table 3.8. Concentration of Major Chemical Components in Tested U-107 Samples on a Dry Basis (Jo, Morris, and Tran 1996).

Constituent	Core 129 Segment 1 (Supernate)		Core 134 Segment 2 (Solids)	
	μg/g	μmol/g	μg/g	μmol/g
Al	38000	1400	3200	120
Ca	190	5	210	5
Cr	1300	20	720	14
Fe	<80	<1	1338	24
Mn	<15	<0.3	35	1
Ni	34	1	<20	<0.3
P	1966	63	1516	49
K	4500	115	570	15
Si	<130	<4	210	7
Na	353000	15300	23200	10000
S	3800	120	710	22
Cl ⁻	11200	320	1470	41
F	700	40	<260	<14
OH ⁻	43800	2600	NM	NM
NO ₃ ⁻	319000	5100	698000	11300
NO ₂ ⁻	137000	3000	17500	380
PO ₄ ³⁻	5600	59	12700	130
SO ₄ ²⁻	9400	98	6800	71
C ₂ O ₄ ²⁻	970	10	2400	28
TOC	4800	400	830	69
TIC	7300	610	3900	330

NM = Not Measured

wastes from A-101 could flow into A-102, then A-103, and then A-106. The overflow line is approximately 4.9 m from the bottom of the tank. The tank was designed to store self-boiling waste with a maximum temperature of 121°C (250°F) (Field, Place, and Cromar 1997). Field, Place, and Cromar's report (1997) for detailed drawings of A-101's configuration.

Tank A-101 became operational in the first quarter of 1956 when it received PUREX organic wash waste and was used until November 1980 when it last received residual waste from 81-1 evaporator campaign and was removed from service. Tank A-101 currently contains 3607 kL of waste. The solid waste types currently stored in A-101 are comprised of two types. The uppermost waste consists of 3596 kL of 242-A evaporator waste, and the bottom waste is a layer of 10 kL PUREX high level waste. Hanlon (1997) reports that A-101 contains no supernate in the tank; however, it does contain 1560 kL of drainable (interstitial) liquid. Agnew (1997) provides compositions and descriptions of these waste types. During its lifetime, A-101 received PUREX organic wash waste, PUREX high and low level wastes, evaporator flush water and dilute feed for the evaporators, flush water from miscellaneous sources, strontium recovery waste, and evaporator wastes.

3.5.1 A-101 Temperatures and P_{H2O}

3.5.1 A-101 Temperatures and P_{H_2O}

The thermocouple tree used to measure the temperatures in A-101 at 11 different heights is located in Riser 12 (Field, Place, and Cromar 1997). Riser 12 is located approximately 4 m north of the southernmost edge of the tank. Based on the surface data provided in the supporting documents provided by Consort et al. (1996a), thermocouples 1 through 16 should be in the waste and thermocouples 17 and 18 in the tank's head space. Thermocouple 15 is at 803 cm and thermocouple 16 is at 863 cm, about 6 cm below the reported surface of the waste.

Between June 1987 and June 1997, temperatures in Tank A-101 waste solids ranged from 70 to 26°C, depending on depth and season. Temperatures varied seasonally with maximum temperatures occurring in October to November and the minimum temperatures occurring in March and April. The variability in temperature is less at the lower depths. Thermocouple 16, the uppermost thermocouple in the waste, measured temperatures ranging from 26 to 42°C.

The temperatures in A-101's vapor space ranged from 30 to 40°C between March 1988 and June 1997 with temperatures again depending on the season, but in general independent of location. Tank A-101 is passively ventilated with no active circulation of vapor.

The observed P_{H_2O} in A-101's headspace on June 8, 1995, was 25 torr at a headspace temperature of 35°C (Huckaby and Bratzel 1995). This P_{H_2O} corresponds to an RH of 60% at 35°C.

3.5.2 A-101 Core Sampling Events

Two nineteen segment core samples were collected from A-101 in July 1996 using the push mode sampling truck (Field, Place, and Cromar 1997). These core samples are referred to as Core 154 and Core 156. Core 154 was taken from Riser 15 located in the SE quadrant of the tank, nominally 8 m from the center of the tank, and 3.5 m from the outside wall; assuming Field, Place, and Cromar's (1997) tank schematic is roughly to scale. Core 156 was taken through Riser 24 located and estimated 1.5 m from the westernmost wall and 9 m from the center of the tank. The 222-S laboratory analyzed all three cores.

As Field, Place, and Cromar (1997) report, both core samples obtained nineteen segments recovering 94% of the expected recovery. 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 upper half (U) of Core 154 Segment 1 recovered 28 cm of yellowish-brown solids with the upper 13 cm resembling a dry salt and the lower 15 cm resembling a moist salt. The lower half (L) of Segment 1 was 43 cm of a moist, dark gray salt. Segments 2 through 9 were similar in appearance to the lower half of Segment 1. Segment 10 yielded a light gray salt slurry and about 5 mL of a yellow liquid. Segment 11 contained only the hydraulic head fluid. Segments 13 through 16 and Segments 18 and 19 yielded principally an opaque yellow liquid and small amounts of a white salt slurry. Segment 17 was primarily an opaque white liquid with a very small amount of white solids. PNNL studied the behavior of the Segment 1U and Segment 1L.

The uppermost sample obtained by Core 156, Segment 1L, recovered 3 cm of green-brown solids and 5 mL of a green-brown opaque liquid. Segments 2 through 8 recovered moist dark gray salt solids.

Segment 10 yielded 18 cm of a white to gray salt slurry and 110 mL of a yellow opaque liquid. Segments 11 and 14 contained a white salt slurry and a yellow opaque liquid. Segments 12, 13, and 15 through 19 recovered white solids and an opaque green liquid. PNNL studied the drainable liquid from Segment 14.

3.5.3 A-101 Tested Wastes Compositions

Table 3.9 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 (Field, Place, and Cromar 1997). Table 3.10 provides the concentrations on a dry basis. Sodium hydroxide, a significant hydrophilic typical waste constituent, was not measured.

As shown in Table 3.9 and Table 3.10, the principle ($>1000 \mu\text{mol/g dry}$) elements, anions, and other measured constituents, excluding water, in the supernate sample are aluminum, sodium, hydroxide, nitrate, and nitrite. Potassium, chloride, sulfur primarily as sulfate, organic carbon including oxalate, and inorganic carbon (likely carbonate at this hydroxide concentration); the nearly identical phosphate and phosphorous concentrations indicate that in the supernate, phosphorous is phosphate. The supernate is 53 wt% water (Jo 1996).

Table 3.9 and Table 3.10 show that the principle ($>1000 \mu\text{mol/g dry}$) elements, anions, and other measured constituents, excluding water, in the two Segment 1 solid samples tested are sodium, nitrate, nitrite, aluminum, and TIC; significant potassium is also in the 1L sample. Other analytes above $100 \mu\text{mol/g dry}$ are potassium for the 1U sample, sulfate, chloride, and TOC including oxalate. The Segment 1U and 1L solids contained 29 and 32 wt% water, respectively (Field, Place, and Cromar 1997).

The principle waste constituents in the drainable liquid (DL) sample obtained by Core 156 Segment 14 are similar to those found in the two solid samples with the exception of TIC. The lesser constituents are nearly the same with the exception that no oxalate was found in the DL. The water content in the Core 156 Segment 14(DL) was 53 wt%.

3.6 Background Information on A-102 and its Wastes

The single shell tank A-102 is not listed on any Watch List; however, D. A. Reynolds of Lockheed Martin Hanford identified A-102 as a tank likely to contain a high concentration of organics. D. A. Reynolds evaluation is borne out by the dry basis 2.2 wt% TOC measured for the auger sample (Jo 1996). The drainable liquid has been removed from the waste or interim stabilized (Jo 1996). The tank is passively ventilated (Jo 1996).

Tank A-102, which was constructed during 1954 and 1955, is a concrete tank with a primary mild steel liner. Tank A-102 has a 3785-kL capacity, a diameter of 23 m, and an operating depth of 9.5 m. The tank has a flat bottom. Tank A-102 was the second tank in a cascade of four tanks where overflow wastes from A-101 could flow into A-102, then A-103, and then A-106. The overflow line is approximately 4.9 m from the bottom of the tank. The tank was designed to store self-boiling waste with a maximum temperature of 121°C (250°F). The reader is referred to Jo's report (1996) for detailed drawings of A-102's configuration.

Table 3.9. Concentration of Major Chemical Components in Tested A-101 Samples on a Wet Basis
(Field, Place, and Cromar 1997)

Constituent	Core 154 Segment 1U		Core 154 Segment 1L		Core 156 Segment 14DL	
	µg/g	µmol/g	µg/g	µmol/g	µg/g	µmol/g
Al	22400	830	27500	1020	37900	1400
B	<70	<7	<72	<7	40	4
Ca	507	13	325	8	<41	<1
Cr	1480	28	1850	36	39	1
Co	47	1	54	1	<8	<0.1
Fe	3010	54	160	3	<21	<0.4
Pb	<140	<1	<140	<1	88	0.4
Mn	78	1	42	1	<4	<0.1
Mo	<72	<1	<72	<1	97	1
Ni	76	1	70	1	<8	<0.1
P	2020	65	1590	51	950	31
K	2990	76	88700	2270	5430	140
Si	245	9	460	16	110	4
Na	220000	9570	214000	9304	172000	7500
S	7640	240	6500	200	320	10
Br ⁻	<530	<7	<530	<7	600	8
Cl ⁻	3860	110	4830	140	6400	180
F ⁻	250	13	245	13	<40	<2
NO ₃ ⁻	186000	3000	166000	2680	102000	1650
NO ₂ ⁻	62700	1360	81300	1770	107000	2300
PO ₄ ³⁻	5000	53	4640	49	2220	23
SO ₄ ²⁻	24800	260	20500	210	880	9
C ₂ O ₄ ²⁻	6760	77	10100	110	<300	<3
TOC	3670	310	5490	460	2470	210
TIC	22900	1900	15400	1280	1170	98

Tank A-102 became operational in the first quarter of 1956 when it received PUREX organic wash waste and was used until November 1980 when it last received PUREX high level waste and was removed from service. The pumpable, drainable liquor was removed from the tank in 1983. Tank A-102 currently contains 155 kL of waste. The top layer is comprised of 15 kL of supernate. The middle layer is comprised of 57 kL of 242-A evaporator saltslurry and 72 kL of 242-A evaporator saltcake waste. The bottom layer is believed to be 11 kL of strontium recovery sludge. Agnew (1997) provides compositions and descriptions of these waste types. During its lifetime, A-102 received PUREX organic wash waste, PUREX high level waste, supernate waste, slurried PUREX strontium sludge, strontium recovery waste, and B-Plant high-level waste.

Table 3.10. Concentration of Major Chemical Components in Tested A-101 Samples on a Dry Basis (Field, Place, and Cromar 1997).

Constituent	Core 154 Segment 1U		Core 154 Segment 1L		Core 156 Segment 14DL	
	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$
Al	31600	1170	40700	1500	80500	3000
B	<100	<9	<110	<10	80	8
Ca	720	18	480	12	<90	<2
Cr	2100	40	2740	50	80	2
Co	67	1	80	1	<20	<0.3
Fe	4250	80	240	4	<40	<1
Pb	<200	<1	<200	<1	190	1
Mn	110	2	60	1	<9	<0.2
Mo	<100	<1	<100	<1	200	2
Ni	108	2	100	2	<20	<0.3
P	2850	90	2350	80	2020	65
K	4220	110	131000	3400	11500	300
Si	350	10	680	20	240	9
Na	311000	13500	317000	13800	366000	15900
S	10800	340	9600	300	680	20
Br ⁻	<750	<9	<790	<10	1300	20
Cl ⁻	5450	150	7100	200	13700	380
F ⁻	350	20	360	20	<80	<4
NO ₃ ⁻	263000	4200	246000	4000	21700	3500
NO ₂ ⁻	88600	1900	120000	2600	227000	4900
PO ₄ ³⁻	7060	70	6900	70	4700	50
SO ₄ ²⁻	35000	360	30300	320	1900	20
C ₂ O ₄ ²⁻	9550	110	14900	170	<640	<7
TOC	5200	430	8100	680	5200	440
TIC	32300	2700	22800	1900	2500	210

3.6.1 A-102 Temperatures and P_{H2O}

The single functional thermocouple tree used to measure the temperatures in A-102 at 18 different heights is located in Riser 7. Riser 7 is located approximately 7.3 m north of the southernmost edge of the tank. Based on the surface data provided in the supporting documents provided by Consort et al. (1996a), Thermocouple 1, the only thermocouple in the 35.6 cm (14 in.) of waste at a height of 9 cm (3.6 in.), indicates that the waste temperature is a nominal 33°C. Thermocouple 2 located at 70 cm (28 in.) from the bottom of the tank indicates that the headspace temperature is also 33°C. The other thermocouples range from 32 to 33°C relatively independent of location.

Huckaby (1996) reports a P_{H2O} of 26 torr (73% relative humidity) in the head space in A-102 on November 10, 1995. Tank A-102 is passively ventilated with no active circulation of vapor

3.6.2 A-102 Core Sampling Events

Two auger samples were collected from A-102 in June 1995 and March 1996. These auger samples are referred to as Sample 95-AUG-033 and Sample 96-AUG-003. The March 1996 sample of A-102 waste provided for the equilibrium moisture testing studies was obtained using a 50.8-cm auger with 1.27-cm spaced flutes through Riser 5. Riser 5 is located approximately 7 m south of the northernmost edge of the tank. We estimated the distances using Jo's (1996) tank schematic providing riser locations, assuming the drawing is roughly to scale. The 222-S laboratory, operated then by WHC, extruded and analyzed both samples.

Jo (1996) reports that Sample 95-AUG-033 retrieved a total of 96 g of solids, and Sample 96-AUG-003 retrieved a total of 198 g of solids. Flutes 1 through 6 of Sample 95-AUG-033 contained a small amount of material on their edges and Flutes 7 through 19 provided a gritty sludge containing hard black pebbles throughout. Sample 96-AUG-003 provided a brown, runny, wet sludge with pebble-like material scattered throughout the gritty paste-like waste. Unlike the push or rotary drilling sampling methods, auger sampling is designed to recover only solid surface samples retaining no free liquid. Thus any samples obtained this way may not be representative of the surface waste with respect to total water content.

3.6.3 Composition of Tested A-102 Waste

Table 3.11 provides the concentrations on a mass and molar basis of the major chemical constituents ($> 100 \mu\text{g/g}$ wet) measured and reported by the Hanford Tank Waste Characterization Program (Jo 1996). Table 3.11 provides these concentrations both on wet and dry sample bases; the dry concentrations were calculated using the reported 34.5 wt% water. WHC did not measure sodium hydroxide for the Core 134 Segment 2 sample, a species observed by Fauske (1995) and ourselves (Scheele, Bredt, and Sell 1996) to have a significant effect on equilibrium water content.

As shown in Table 3.11, the principle ($>1000 \mu\text{mol/g}$ dry) elements, anions, and other measured constituents, excluding water, are aluminum, sodium, nitrate, nitrite, and organic carbon including oxalate. Other significant ($>100 \mu\text{mol/g}$ dry) constituents are chromium, iron, potassium, silicon, uranium, chloride, phosphate, and inorganic carbon (either carbonate or bicarbonate depending on the pH).

3.7 Background on BY-110 and Its Wastes

Tank BY-110 was one of the original tanks classed as a "Ferrocyanide Watch List Tank" based on historical records that indicated the waste stored in BY-110 contained $>8 \text{ wt}\%$ sodium nickel ferrocyanide on an energy equivalent basis (Hanlon 1996); this did not take into account any aging of the ferrocyanide that may have occurred during the years of storage (Lilga et al. 1992; 1993; 1994; 1995; 1996). The Hanford Site operating contractor used the Ferrocyanide Scavenging Process to remove radiocesium and to a lesser extent radiostrontium from aqueous wastes, thus allowing disposal of the decontaminated wastes to a soil column.

Table 3.11. Concentration of Major (>100 µg/g wet) Chemical Components in the Tested A-102 Sample on Wet (Jo 1996) and Dry Bases

Constituent	Sample 96-AUG-003 (wet)		Sample 96-AUG-003 (dry)	
	µg/g	µmol/g	µg/g	µmol/g
Al	31650	1170	48200	1780
Ba	140	1	210	2
Bi	340	2	510	2
Cd	690	20	1050	30
Ce	158	1	240	2
Cr	8800	170	13400	260
Fe	19600	350	29800	530
La	103	1	160	1
Pb	1410	7	2150	10
Mg	470	20	710	30
Mn	3380	60	5140	90
Nd	230	2	350	2
Ni	410	7	630	10
P	1600	50	2440	80
K	3080	80	4690	120
Si	3920	140	5970	210
Ag	370	3	560	5
Na	129000	5610	196000	8540
S	550	20	840	30
U	35300	150	53700	230
Zn	120	2	190	3
Zr	480	5	740	8
Cl ⁻	7970	225	12100	340
NO ₃ ⁻	90300	1460	137000	2220
NO ₂ ⁻	83200	1810	127000	2750
PO ₄ ³⁻	6300	66	9590	100
SO ₄ ²⁻	4480	47	6820	70
C ₂ O ₄ ²⁻	11900	140	18100	210
CN ⁻	30	1	50	2
TOC	14800	1240	22600	1880
TIC	4340	360	6610	550

Although BY-110 is not currently on the Organic Watch List, DA Reynolds of Lockheed Martin Hanford identified it as a characteristic saltcake waste of interest to the Organic Tank Safety Program. The majority of the waste stored in BY-110 is a saltcake type waste (Schreiber 1996b) and should be characteristic in many respects to some of the organic-bearing saltcake wastes stored in the Hanford Site's tanks identified by Webb et al. (1995) as the wastes of greatest concern.

3.7.1 BY-110 Fill History

Based on information provided by Schreiber (1996b) Tank BY-110 was built during 1948 and 1949. BY-110 was placed into service in the fourth quarter of 1951 and has been used to receive and store many different Hanford Site waste types. Tank BY-110 has a capacity of 2870 kL, a diameter of 23 m, a dished bottom with a 1.2 m radius knuckle, and an operating depth of 7 m. Tank BY-110 was the first tank in a cascade of three where over flow wastes from one tank could flow into and from another tank. The cascade was designed to allow waste to flow from BY-110 to BY-111 and then to BY-112. Much of the supernate was removed and disposed of in soil columns.

Tank BY-110 was put into service when it first received first-cycle decontamination waste in the fourth quarter of 1951 (Schreiber 1996b). Currently BY-110 contains a total of 1507 kL of waste. This 1507 kL is estimated to be comprised, bottom to top, of 140 kL of first cycle decontamination waste, 420 kL, 579 kL of in-plant ferrocyanide waste, and 787 kL of BY saltcake waste. No supernate has been in the tank since it was interim stabilized in January 1985; however, the waste is estimated to contain 34 kL of drainable interstitial liquid.

3.7.2 BY-110 Temperatures and P_{H_2O}

Tank BY-110 has two thermocouple trees with six thermocouples located at various heights in risers 1 and 10A. Riser 1 is near the center of BY-108 approximately 8 m from the easternmost edge of the tank and riser 10A is nearer the edge of the tank, approximately 3 m from the southernmost tank edge. Schreiber (1996b) reports a baseline waste height of 3.85 m and indicates that surface measurements of 245 cm measured since April 1995 are suspect because of faulty equipment.

During 1997, temperatures in BY-110 ranged from 45 to 20°C bottom to top in Riser 1 and from 40 to 20°C in Riser 10A (Ewer 1997a). Based on the baseline height provided by Schreiber (1996b), thermocouples 1 through 5 in both thermocouple trees reside in the waste and thermocouples 6 reside in the tank's headspace. Thermocouples 5 in Risers 1 and 10A, located at 270 cm and 338 cm, respectively, observed maximum temperatures during 1997 of 35 and 24°C, respectively. The thermocouples located in the upper reaches of the head space, nominally 760 cm (300 in.), both report a temperature of 20°C. Schreiber attributes the consistent difference between the two thermocouple tree readings to the difference in location of the two thermocouple trees. Because Riser 10A is closer to tank walls, heat transfer is better than near the interior center of the tank. We used 35°C for our experiments to ensure that we are imposing the most realistic rigorous conditions.

Huckaby and Bratzel (Schreiber 1996b) measured a P_{H_2O} of 8.3 torr in the headspace of BY-110 on November 11, 1994. This corresponds to a relative humidity of 31% at the headspace temperature of 27°C.

3.7.3 BY-110 Core Sampling Events

Nine core samples were collected from BY-110 between July and October (Schreiber 1996b). Both rotary and push mode were used to obtain the samples. The samples delivered to PNNL for the equilibrium moisture testing were obtained by Cores 103 and 113 taken from Risers 7 and 4, respectively. Core 103 was the second sampling taken from Riser 7. Core 113 was the only core sample taken from Riser 4. Riser 4 is located approximately 8 m (318 in.) from the northernmost edge of the tank, and Riser

7 is located approximately 9.4 m (370 in.) from the westernmost edge of the tank. Cores 98 and 104 were extruded and analyzed at Westinghouse Hanford Company's (WHC) 222-S laboratory.

Core 103 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 surface of the waste. Segment 1 in Core 103 contained approximately 25 cm of light yellow to white, dry crystalline material and no drainable liquid (Schreiber 1996b).

Core 113 consisted of eight segments. Segment 1 contained 15 cm of dry, crumbly, light brown to yellow solids. The solids did not retain the shape of the sampler when extruded (Schreiber 1996b).

3.7.4 Compositions of Tested BY-110 Samples

Table 3.12 and Table 3.13 provide the mass and molar concentrations of major ($>100 \mu\text{g/g}$ wet) constituents measured on both wet and dry bases, respectively (Schreiber 1996a). The concentrations on a dry basis were calculated using the reported Core 103 Segment 1U and Core 113 Segment 1 respective water contents of 28 and 18 wt. Hydroxide, a major water absorbing constituent was not measured.

Table 3.12. Concentration of Major ($>100 \mu\text{g/g}$ wet) Chemical Components in Tested BY-110 Samples on Wet Basis (Schreiber et al. 1996a)

Constituent	Core 103 Segment 1U		Core 113 Segment 1	
	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$
Al	14700	540	32700	1200
B	70	7	130	10
Ca	210	5	540	10
Cr	620	10	2400	40
Fe	1800	30	5200	90
Ni	100	2	260	4
P	31700	1000	10300	330
K	800	20	720	20
Si	640	20	530	20
Na	213000	9300	246000	10700
Sr	120	1	70	1
S	1900	60	10800	340
U	420	2	820	3
Cl ⁻	290	8	470	10
F ⁻	9000	470	10200	540
NO ₃ ⁻	278000	4500	24500	400
NO ₂ ⁻	6300	140	7200	160
PO ₄ ³⁻	74600	780	27400	290
SO ₄ ²⁻	5600	60	34100	360
C ₂ O ₄ ²⁻	8390	95	28100	320
TOC	2400	200	7600	640
TIC	11600	970	56900	4700

As shown in Table 3.12 and Table 3.13, the principal (>1000 $\mu\text{mol/g}$ dry) constituents in Core 103 Segment 1U are sodium, nitrate, phosphorous principally as phosphate, and inorganic carbon, either carbonate or bicarbonate depending on the pH. Other constituents present at significant levels (>100 $\mu\text{mol/g}$ dry) are aluminum, fluoride, organic carbon principally as oxalate, and nitrite. This waste sample appears to be nearly half sodium nitrate and nitrite with the remainder sodium phosphate and sodium carbonate or bicarbonate.

The principal (>1000 $\mu\text{mol/g}$ dry) constituents in Core 113 Segment 1 are sodium, inorganic carbon (carbonate or bicarbonate), and aluminum. Other constituents present at significant levels (>100 $\mu\text{mol/g}$ dry) are fluoride, organic carbon as oxalate, nitrate, sulfur as sulfate, phosphorous as phosphate, nitrite, and iron. This sample appears to be principally sodium carbonate with the remainder predominately sodium aluminate with smaller amounts of sodium oxalate, sodium fluoride, sodium nitrate, sodium sulfate, and sodium phosphate; crystal studies would be required to determine the true nature of the compounds in this sample.

Table 3.13. Concentration of Major (>100 $\mu\text{g/g}$ wet) Chemical Components in Tested BY-110 Samples on Dry Basis (Scheiber et al. 1996a)

Constituent	Core 103 Segment 1U		Core 113 Segment 1	
	$\mu\text{g/g}$	$\mu\text{mol/g}$	$\mu\text{g/g}$	$\mu\text{mol/g}$
Al	19000	700	39900	1500
B	90	9	160	15
Ca	270	7	650	16
Cr	800	15	2900	60
Fe	2400	40	6300	110
Ni	120	2	310	5
P	41000	1300	12600	400
K	1040	30	880	20
Si	830	30	650	20
Na	276000	12000	300000	13000
Sr	160	2	90	1
S	2400	80	13200	410
U	550	2	1000	4
Cl^-	380	10	580	20
F^-	11600	610	12400	660
NO_3^-	36000	5800	29900	480
NO_2^-	8190	180	8800	190
PO_4^{3-}	96600	1020	33400	350
SO_4^{2-}	7270	80	41600	430
$\text{C}_2\text{O}_4^{2-}$	10900	120	34300	390
TOC	3100	260	9300	780
TIC	15000	1250	69400	5780

4.0 Effect of P_{H_2O} on Wastes' Water Retention

The equilibrium water content in Hanford wastes at different water partial pressures depends on the chemical constituents in the wastes and their interactions. Depending on the nature of the chemical composition of the waste, several different chemical forms of water can be retained in wastes (Scheele, Bredt, and Sell 1996). 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 effect of water partial pressures on the equilibrium water content of Hanford wastes, we exposed wastes from selected Hanford underground storage tanks to a range of water vapor pressures at current tank temperatures. These pressures encompassed the water partial pressures extant at Hanford and others that the waste might experience during storage or mitigation activities. The wastes selected for testing are on the Organic Tanks Watchlist or have the potential to have a significant organic inventory based on an assessment by D. A. Reynolds of Lockheed Martin Hanford or are characteristic of an unsampled class of organic-bearing wastes. The Clausius-Clapeyron equation could be used to estimate the effect of P_{H_2O} on the water content; a first estimate could be made using the ΔH_v for pure water.

This section provides the results of our studies to determine the effect of P_{H_2O} on the equilibrium water content of waste samples from BY-108, U-105, S-102, U-107, A-101, A-102, and BY-110. The studies of BY-108, U-105, S-102, and U-107 were complete at the time this report was prepared, so we have provided the equilibrium water contents at different water vapor pressures. More detailed reports on the effect of P_{H_2O} on the equilibrium water content and the nature of water in BY-108 and U-105 wastes are available (Scheele, Bredt, and Sell 1997a; Scheele, Bredt, and Sell 1997b). The studies of A-101, A-102, and BY-110 are incomplete at this writing because these waste samples were received late in the fiscal year; therefore, we are providing our results to date as the response of these wastes to various vapor pressures over time.

4.1 Effect of P_{H_2O} on Equilibrium Water Content in BY-108 Wastes

Samples taken from Segment 1 and Subsegment 2D of the Core 99 sampling event from BY-108 were exposed to partial pressures of water of 2.2, 7.6, 18, 27, and 29 torr at 30°C to determine the equilibrium water contents of a characteristic saltcake waste. After stable masses were reached, samples in the 2.2 and 29 torr vessels were exchanged and their masses monitored until they were stable or very slowly changing. All water contents used in the following discussion are based on the water content determined gravimetrically after drying at 105°C.

The effect of P_{H_2O} on the equilibrium water content is presented in Figure 4.1 for Core 99 Segment 1 and Subsegment 2D waste samples taken from BY-108. The equilibrium water contents for Segment 1 are 1, 15, 17, 36, and 48 for water partial pressures of 2.2, 7.6, 18, 27, and 29 torr, respectively. Subsegment 2D had water contents of 1, 5, 12, 55, and 62 at the same water partial pressures. While Segment 1 has a higher equilibrium water content at water partial pressures below

Figure 4.1. Effect of P_{H_2O} on the Equilibrium Water Content of BY-108 Core 99 Segment 1 and Subsegment 2D at 30°C

18 torr, 15 wt% for Segment 1 versus 5 wt% for Subsegment 2D at 7.6 torr, the weight fraction water for Subsegment 2D exceeds that for Segment 1 at water partial pressures greater than approximately 20 torr.

The differences between the two waste samples likely arise from higher concentrations of phosphate and aluminum in Segment 1 and higher nitrate and nitrite concentrations in Subsegment 2D. The water content below 20 torr could be due to the higher concentration of PO_4^{3-} and Al in Segment 1, 82,000 $\mu\text{g/g}$ PO_4^{3-} in Segment 1 compared to 17,000 $\mu\text{g/g}$ in Subsegment 2D and 200,000 $\mu\text{g/g}$ Al in Segment 1 compared to 83,000 $\mu\text{g/g}$ in Subsegment 2D. Based on our earlier work at 22°C (Scheele, Bredt, and Sell 1996), the higher NO_3^- concentrations in Subsegment 2D, 300,000 $\mu\text{g/g}$ in Subsegment 2D compared to 86,000 $\mu\text{g/g}$ for Segment 1, probably cause the higher water content for Subsegment 2D material above 20 torr of water; our earlier studies showed that mixtures of $NaNO_3$ and $NaNO_2$ begin to absorb significant amounts of water between 14 and 17 torr. We can only postulate that these compositional differences caused the differences in water contents because our sodium aluminate studies yielded confounded results (Scheele, Bredt, and Sell 1996), and no reports were found on the effect of P_{H_2O} on water content of Al and PO_4^{3-} in the forms potentially present in Hanford waste tanks.

In general, exposing the BY-108 saltcake and sludge-like wastes to ambient Hanford water partial pressures will cause the waste to dry from Segment 1's 29 wt% water at the time of the original core analysis and Subsegment 2D's 16.7 wt% water (Baldwin et al. 1996). 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 Segment 1 are 1, 15, and 17 wt% at 2.2, 7.6, and 18 torr, respectively. Therefore, at all current ambient Hanford partial pressures of water, the waste in Segment 1 will dry below the current TOC and energetics independent safety criterion of 20 wt% water

(Webb et al. 1995). The same situation exists for Subsegment 2D, with equilibrium water contents of 0, 5, and 12 at 2.2, 7.6, and 18 torr, respectively. It should be noted that Subsegment 2D's 16.7 wt% water is already below this safety criterion but may satisfy the combined water and TOC criterion. For the top 100 cm of waste in BY-108 to remain above the safety limit of 20 wt% water, the material would have to be exposed to pressures near or above 20 torr of water vapor. Under current conditions, at an average ambient Hanford water vapor pressure of 5.5 torr, the waste in Segment 1 would dry to an equilibrium water content of approximately 10 wt%, and Subsegment 2D should dry to approximately 3 wt% water.

Based on the measured behavior of Segment 1 and its reported water content of 30 wt% (Baldwin et al. 1996), the equilibrium P_{H_2O} above the upper layer of material in BY-108 should be about 23 torr. The measured P_{H_2O} in the head space of BY-108 was 14.8 torr (Pool et al. 1996) on January 24, 1996, when the temperature in the head space measured in Riser 8 was 24°C. The equilibrium vapor pressure of pure water is 22.4 torr at 24°C (Weast, Astle, and Beyer 1984). At the average Hanford soil temperature of about 17°C (Barney 1976), water's P_{H_2O} is 14.5 torr (Weast, Astle, and Beyer 1984).

Because the measured P_{H_2O} in the head space is less than both the vapor pressure of water at the headspace temperature and the equilibrium P_{H_2O} for the uppermost segment, it appears that either the environment exchanges air significantly with BY-108 (breathing), or, alternatively, the water content in the head space is controlled by the temperature of the tank's wall and the surrounding soil with condensation of water on the wall's surface. If there is significant tank breathing, eventually the waste's water content should be controlled by the equilibrium with ambient Hanford air. Huckaby (1994) reports an average daily exchange of air equal to about 0.46% of each tank's headspace due to a diurnal cycle of barometric changes

4.2 Effect of P_{H_2O} on Equilibrium Water Content in U-105 Wastes

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 4.2). 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.

Table 4.1. Equilibrium Water Content of Tested U-105 Waste Samples

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

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 4.1. 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.

Figure 4.2. Effect of P_{H_2O} on the Equilibrium Water Content of U-105 Core 131 Segments 2U and 3U, Core 133 Segment 3, and Core 136 Segment 3U at 33°C

Table 4.2. Appearance of Equilibrated U-105 Waste Samples after Exposure to Selected Water Partial Pressures at 33°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

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 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 (Core 131 Segment 3U and Core 133 Segment 3) having the highest total sodium nitrate and nitrite contents (10.3 and 7.8 mmol/g dry) 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 dry 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 4.2 appears to be a blend of the behaviors of the simulated organic-bearing waste PAS94 and sodium nitrate and nitrite (Scheele, Bredt, and Sell 1996). Phosphate, sulfate, and aluminum content (Tables 3.3 and 3.4) could explain the significant water content at the lower partial pressures.

Comparing the expected P_{H_2O} in U-105'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_{H_2O} in U-105's vapor space provides some insight into the dynamics within U-105. Pool et al. (1995) reported a P_{H_2O} 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 U-105 contained free-standing liquid. For evidence of free liquid in U-105, see the photograph of U-105 provided by Brevick, Stroup, and Funk (1997) and the U-105 RMCS Core Profile (available from Characterization Equipment Engineering) that indicates that only liquid was obtained by the Core 133 Segment 1 sampling. 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.

Comparison of our results and the measured P_{H_2O} in the tank suggest that factors other than the water content in the surface wastes are controlling the P_{H_2O} in U-105's headspace. If the solids in the free-standing liquid in U-105 are similar to the solids in the surface solids 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. At existing water contents, >25 wt% water (see Figure 4.2), P_{H_2O} for any of the tested 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, reducing P_{H_2O} to that of pure water.

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 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). 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 pressures near or above 20 torr of water vapor.

4.3 Effect of P_{H_2O} on Equilibrium Water Content in S-102

Our studies to determine the equilibrium water content of S-102 wastes exposed to a range of water vapor pressures extant at the Hanford Site and potentially within the tank indicate that the two solid Segment 3 samples of waste taken by Cores 125 and 130 are sensitive to P_{H_2O} and will dry to less than the 20 wt% water energetics and fuel independent criterion guaranteeing that an organic-bearing waste cannot support a propagating reaction (Webb et. al. 1995; Fauske et. al. 1995). In addition these studies indicate that the response of S-102 waste at the Segment 3 level is independent of radial location within the tank (see Table 4.3 and Figure 4.3) and that the water content of the two wastes are controlled by sodium nitrate and nitrite but are influenced by other waste constituents.

Table 4.3. Equilibrium Water Content of Tested S-102 Waste Samples at 41°C

P_{H_2O} , torr	Water Content, wt%	
	Core 125 Segment 3	Core 130 Segment 3
3.5	3.1	3.2
11	4.5	5.6
30	10.8	10.5
44	67.7	68.0
48	77.7	77.0

The equilibrium water contents of these two S-102 wastes vary, depending on P_{H_2O} . Below 30 torr, the amount of water retained by both samples increases gradually to 11 wt% water. Above 30 torr, the two waste samples retain significant amounts of water (68 and 77 wt% water at 44 and 48 torr, respectively). Qualitatively, this response is similar to the behavior of sodium nitrate and/or nitrite (Fauske et. al. 1995; Scheele, Bredt, and Sell 1996) and consistent with the measured composition. Quantitatively, in contrast to sodium nitrate and/or nitrite, which do not retain water up to 60% relative humidity (RH) at 22°C or 47 % RH at 65°C, both S-102 samples retain small amounts (<11 wt%) of equilibrium water until P_{H_2O} exceeds a RH of 50%. This retention of small amounts of water at lower water partial pressures is likely due to the lesser constituents or the interaction between lesser constituents and sodium nitrate similar to the behavior of surrogate waste mixtures composed primarily of sodium nitrate and nitrite (Scheele, Bredt, and Sell 1996).

Figure 4.3. Effect of P_{H_2O} on the Equilibrium Water Content of S-102 Core 125 and Core 130 Segment 3 Waste Samples at 41°C

These studies indicate that at ambient Hanford water partial pressures (2.5 to 9 torr) these S-102 wastes will dry to between 3 and 6 wt% water, which is below the 20 wt% water content that ensures organic-bearing waste will not support a propagating reaction. This behavior would be predicted based on Fauske et al. (1995) and our earlier studies (Scheele, Bredt, and Sell 1996) of sodium nitrate and/or nitrite behavior, which found no water sorption at low water partial pressures, but significant water sorption above a critical level.

The identical responses of these two S-102 wastes to different water partial pressures suggests near homogeneity across the Segment 3 level in S-102. This similarity in behavior between the two samples is consistent with the reported chemical compositions of the two wastes (See Tables 3.5 and 3.6).

To maintain the water content above 20 wt% water, these wastes at their current temperature would have to be treated with a P_{H_2O} in excess of 30 torr.

The physical appearances of these two S-102 samples at the end of testing are provided in Table 4.4. The samples exposed to the lowest water partial pressure of 3.5 torr were mostly dry solids. The samples exposed to 11 torr appear to be slightly moist. The samples exposed to 29 torr were moist solids, and the remaining samples were mostly liquid.

Table 4.4. Appearance of Equilibrated S-102 Waste Samples after Exposure to Selected Water Partial Pressures at 41°C

Sample	Description				
	P_{H_2O} , torr				
	3.5	11	30	44	48
Core 125 Segment 3	Mostly Dry Solids	Slightly Moist Solids	Moist Solids	Mostly Liquid	Mostly Liquid
Core 130 Segment 3	Mostly Dry Solids	Slightly Moist Solids	Moist Solids	Mostly Liquid	Mostly Liquid

At the measured P_{H_2O} of 16.5 torr, the water content of these S-102 wastes should be between 4.5 and 11 wt% water or by interpolation 6 to 7 wt% water, which corresponds well with the measured water contents of 8 and 5 wt%. This suggests that these wastes may be in equilibrium with the P_{H_2O} in the tank's headspace.

In general, exposing the S-102 wastes to ambient Hanford water partial pressures will dry these wastes to between 3 and 4 wt% water. Therefore, the final equilibrium water content at all current ambient Hanford partial pressures of water will be below the current TOC and energetics independent safety criterion of 20 wt% water (Webb et al. 1995).

4.4 Effect of P_{H_2O} on Equilibrium Water Content in U-107 Wastes

The equilibrium water contents of the supernate and solid waste samples taken from the upper levels of the stored waste in U-107 are sensitive to P_{H_2O} (Table 4.5 and Figure 4.4). The amount of retained water by each depends on P_{H_2O} and the phase of the waste sample. The amount of equilibrium water retained by the supernate increases gradually as P_{H_2O} increases. In contrast, the amount of equilibrium water present in the solid sample is small up to 15 torr. Between 15 and 21 torr, the solid sample sorbs significant amounts of water.

Core 129 Segment 1 and Core 134 Segment 2 differ markedly in their response to water vapor pressures ranging from 2 torr, slightly below the 2.6-torr Hanford minimum P_{H_2O} between 1989 and 1995, and 22 torr. For water partial pressures of 2, 7, 15, 21, and 22 torr, the average equilibrium or terminal water contents for Core 129 Segment 1 (a sample of the tank's supernate) at the tank's upper waste maximum temperature of 26°C are 6, 21, 51, 71, and 79 wt%, respectively. The waste sample obtained by Core 134 Segment 2 (uppermost solid waste in the tank) had equilibrium water contents at 26°C of 2.3, 2, 6.2, 63, and 72 wt% at the same water partial pressures and temperature, respectively.

Table 4.5. Equilibrium Water Content of Tested U-107 Waste Samples at 26°C

P_{H_2O} , torr	Water Content, wt%	
	Core 129 Segment 1 (Supernate)	Core 134 Segment 2 (Solids)
2	6.1	2.3
7	21	2.0
15	51	6.2
21	71	63
22	79	72

Figure 4.4. Effect of P_{H_2O} on the Equilibrium Water Content of U-107 Core 129 Segment 1 and Core 134 Segment 2 Waste Samples at 26°C

Comparing the behavior of the U-107 solid sample at 26°C with respect to relative humidity (RH) with the behavior of sodium nitrate and nitrite at 22°C (Scheele, Bredt, and Sell 1996) shows nearly identical qualitative behavior with significant sorption of water beginning after about 60% RH. This suggests, since RH is a measure of the equilibrium constant and thus free energy for the vaporization reaction of water at a particular temperature, that the U-107 solid sample is controlled by sodium nitrate and nitrite. This is consistent also with the chemical composition.

In contrast, a similar comparison of the behavior of the supernate sample at 26°C with the pure compounds, surrogate wastes, and simulated waste at 22°C that we studied earlier indicates that the supernate's behavior is controlled by a blending of its constituents, sodium nitrate, nitrite, and hydroxide. Comparing the two response curves for the two U-107 samples indicates that the contained solids in the

supernate differ in composition from the solids in the upper level of the solid wastes in the tank, at least those represented by the Core 134 Segment 2 solids.

The physical appearances of these samples at the end of testing are provided in Table 4.6. The solid and supernate samples exposed to the lowest water partial pressure were dry solids as were the solids exposed to 7 torr. The supernate exposed to 7 torr and the solids exposed to 15 torr were moist solids. The two materials exposed to the remaining water partial pressures were all mixed solids and liquid. It is likely that given time, from the supernate would have become all liquid.

Table 4.6. Appearance of Equilibrated U-107 Waste Samples after Exposure to Selected Water Partial Pressures at 26°C

Sample	Description				
	P_{H_2O} , torr				
	2	7	15	21	22
Core 129 Segment 1	Dry Solids	Slightly Moist Solids	Liquid/Solids	Liquid/Solids	Liquid/Solids
Core 134 Segment 2	Dry Solids	Dry Solids	Moist Solids	Liquid/Solids	Liquid/Solids

The measured P_{H_2O} observed in U-107's vapor space on February 17, 1996, was 12.2 torr at a tank headspace temperature of 21°C. Thermocouple 6, which resides in the uppermost level of waste, reported a temperature of 23°C. Our studies indicate that at 26°C, the P_{H_2O} above the supernate at its reported 53 wt% water content (Jo, Morris, and Tran 1996) should be about 15 torr. Applying the Clausius-Clapeyron equation assuming the ΔH_v for water of 44 kJ/mole, the predicted P_{H_2O} for a 23°C supernate would be 12.5 torr, very close to the observed 12.2 torr; using the true ΔH_v for water retained by the supernate should reduce the predicted P_{H_2O} .

In general, exposing the U-107 wastes to ambient Hanford water partial pressures will dry the surface wastes to between 2 and 16 wt% water, depending on the waste. If the supernate remains and dries on the surface, the average water content should be about 16 wt% at the average Hanford P_{H_2O} of 5.5 torr; this assumes that the composition of the supernate remains unchanged. This is unlikely given the significant hydroxide concentration that should convert to carbonate when exposed to air. The upper solids tested are already at 7.2 wt% and will dry further to about 2 wt% water when exposed to ambient Hanford water partial pressures. Therefore, the final equilibrium water content at all current ambient Hanford partial pressures of water will be below the current TOC and energetics independent safety criterion of 20 wt% water (Webb et al. 1995).

Based on the supernate results, a P_{H_2O} of 7.5 torr would be required to maintain the upper waste in U-107 above the safety limit of 20 wt% water. Based on the Core 134 Segment 2 solids data, water partial pressures in excess of at least 15 torr would be required to maintain the water content above 20 wt%.

4.5 Effect of P_{H_2O} on Water Content in A-101 Wastes

At the time of this report, the A-101 samples had not all reached their equilibrium water content; therefore, we are presenting the water content in the samples versus time. The water content provided is based on our single TGA of the as-received material. When the experiments are complete, the samples will be dried at 105°C to a stable mass to determine their water contents. TGA can provide a lower than true water content because the high-surface area sample is placed in a stream of dry flowing gas for several seconds before the analysis begins; in addition, sample inhomogeneity can be a factor for such small samples. The three A-101 samples tested were the upper and lower half subsegments obtained by Core 154 Segment 1 and the drainable liquid obtained by the Core 156 Segment 14 sampling. These samples were exposed to 3.5, 11, 30, and 48 torr of water.

As Figure 4.5 shows, the upper half sample of the Core 154 Segment 1 exposed to water partial pressures ranging from 3.5 to 48 torr either gain or lose water. At water partial pressures of 3.5, 11, and 18 torr, the Segment 1U sample loses water from the TGA-measured 20 wt%. Exposure to 30 and 48 torr causes the material to gain water. The duplicate samples exposed to 3.5 torr appear to be approaching an equilibrium water content near 0 wt%. The samples exposed to 11 torr appear to be approaching an equilibrium moisture content near 10 wt% water. The duplicates exposed to 30 torr appear to be approaching 32 wt% water. The samples exposed to 48 torr are approaching 73 wt% water.

Figure 4.5. Effect of P_{H_2O} on the Water Content of A-101 Core 154 Segment 1U waste at 40°C

As Figure 4.6 shows, the lower half sample taken by the Core 154 Segment 1 sampling from A-101 gains or loses water when exposed to water partial pressures ranging from 3.5 to 48 torr. When exposed to 3.5 torr, the originally 30 wt% water sample loses water and appears to approach an

equilibrium water content near 10 wt%. When exposed to 11 torr, this material also loses water and appears to approach an equilibrium water content near 15 wt%. The duplicate samples exposed to 30 torr are gaining water, approaching a final water content of 42 wt%. The two samples exposed to 48 torr are approaching water contents near 78 wt%.

The behavior of the drainable liquid obtained by Core 156 Segment 14 from A-101 is very similar to that observed for the Segment 1L sample (compare Figures 4.5 and 4.6). The duplicates exposed to 3.5 torr appear to be approaching 10 wt% water. The samples exposed to 11 torr are approaching 12 wt% water. The samples exposed to 30 torr gained water and are approaching 40 wt% water. The waste exposed to 48 torr is deliquescent and is approaching 78 wt% water.

Figure 4.6. Effect of P_{H_2O} on the Water Content of A-101 Core 154 Segment 1L waste at 40°C

The behavior of the drainable liquid obtained by Core 156 Segment 14 from A-101 is very similar to that observed for the Segment 1L sample (compare Figures 4.6 and 4.7). The duplicates exposed to 3.5 torr appear to be approaching 10 wt% water. The samples exposed to 11 torr are approaching 12 wt% water. The samples exposed to 30 torr gained water and are approaching 40 wt% water. The waste exposed to 48 torr is deliquescent and is approaching 78 wt% water.

The two solid A-101 waste samples began as moist solids, and the drainable liquid began as a slurry. The two solid samples exposed to 3.5 torr and the Segment 1U sample exposed to 11 torr are now dry (See Table 4.7). The Segment 1L and the Segment 14 drainable liquid are mostly dry solids after exposure to 11 torr. All three samples exposed to 30 torr are wet solids. All three samples exposed to 48 torr are a combination of liquid and solids.

The observed P_{H_2O} in the tank's headspace on June 8, 1995, was 25 torr at a headspace temperature of 35°C (RH 60%). The water contents reported in the Tank Characterization Database for Segment 1U and Segment 1L were 29 and 32 wt%, respectively. These water contents are nominally consistent with the apparent equilibrium water contents predicted by our work for 25 torr. It should be noted that the temperature is higher than the surrounding soil's average temperature of 17°C (Barney 1976) and the reported P_{H_2O} is higher than would exist at 17°C. This indicates that the temperature of the surrounding soil is not controlling the tank's P_{H_2O} .

Figure 4.7. Effect of P_{H_2O} on the Water Content of A-101 Core 156 Segment 14DL waste at 40°C

In general, exposing the A-101 wastes to ambient Hanford water partial pressures will dry the surface waste from its nominal 30 wt% water to between 0 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). Therefore, if exposed to ambient Hanford partial pressures of water, the waste in the uppermost part of A-101 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.

Table 4.7. Appearance of A-101 Waste Samples after Exposure to Selected Water Partial Pressures at 40°C

Sample	Description			
	P_{H_2O} , torr			
	3.5	11	30	48
Core 154 Segment 1U	Dry Solids	Dry Solids	Wet Solids	Liquid/Solids
Core 154 Segment 1L	Dry Solids	Mostly Dry Solids	Wet Solids	Liquid/Solids
Core 154 Segment 14 DL	Dry Solids	Mostly Dry Solids	Wet Solids	Liquid/Solids

4.6 Effect of P_{H_2O} on the Water Content in A-102 Wastes

At the time of this report, the A-102 August 1996 auger surface sample exposed to vapor pressures ranging from 2 to 32 torr at 32°C had not reached its equilibrium water content at all the water vapor pressures. Therefore, we are presenting the water content in the samples versus time rather than the equilibrium moisture content versus P_{H_2O} . The water content is based on a single TGA of the as-received material. When the experiments are complete, the samples will be dried at 105°C to a stable mass to determine their water contents. TGA can provide a lower than true water content because the high-surface-area sample is placed in a stream of dry flowing gas for several seconds before the analysis begins.

As Figure 4.8 shows, the A-102 surface waste beginning at 36 wt% water dried when exposed to water partial pressures below 20 torr and gained water at water partial pressures of 20 torr and above. When exposed to 2 torr, the A-102 waste dropped to between 8 and 14 wt% water and is continuing to lose water after 1050 h. When exposed to 8 torr, the waste has dried to about 14 wt% water and is continuing to dry. After exposure to 20, 30, and 32 torr, the A-102 waste samples gained water to 40, 64, and 74 wt% water, respectively. The 20 torr sample appears to have stabilized; however, the aliquots exposed to 30 and 32 torr are continuing to sorb water.

The measured P_{H_2O} in A-102's headspace on November 10, 1995, was 26 torr at a nominal temperature of 32°C. The A-102 solid sample tested contained 36 wt% water (Jo 1996). Based on the results presented in Figure 4.8, the P_{H_2O} above the 32°C A-102 surface waste containing 36 wt% water would be about 20 torr instead of the measured 26 torr. The A-102 waste would need to contain about 60 wt% water for the P_{H_2O} to be 26 torr. Hanlon (1997) indicates that the A-102 waste is about 10% supernate and another 5% drainable liquid. The difference between the measured and expected P_{H_2O} based on Figure 4.8, indicates that unrecovered supernate liquid controls the tank's P_{H_2O} .

The current physical appearances of the A-102 waste samples exposed to the various water partial pressures are provided in Table 4.8. The A-102 waste began as a pasty dark brown lumpy sludge. After its exposure to 2 and 8 torr, it is now moist solids. Exposure to 20 and 30 torr has increased the A-102 materials water content, and it now appears wet. After exposure to 32 torr, the duplicates are now a combination of liquid and solids.

Figure 4.8. Effect of P_{H_2O} on the Water Content of the A-102 August 3, 1996 Auger Sample at 32°C

Table 4.8. Appearance of A-102 Waste Sample after Exposure to Selected Water Partial Pressures at 32°C

Sample	Description				
	P_{H_2O} , torr				
	2	8	20	30	32
August 3, 1996 Auger Sample	Moist Solids	Moist Solids	Wet Solids	Wet Solids	Liquid/Solids

In general, exposing the A-102 surface waste to ambient Hanford water partial pressures will dry the surface wastes to between 8 and 16 wt% water, assuming that exposure to 9 torr will not increase the equilibrium water content much above that observed for 8 torr. It appears that the final equilibrium water content at all current ambient Hanford partial pressures of water will be below the current TOC and energetics independent safety criterion of 20 wt% water (Webb et al. 1995).

4.7 Effect of P_{H_2O} on the Water Content in BY-110 Wastes

Two samples of waste obtained from the surface of BY-110 are currently being tested to determine their equilibrium water content when exposed to water vapor pressures existing at ambient Hanford conditions and at other vapor pressures that they might experience during their storage. The two Segment 1 samples were obtained by Cores 103 and 113. The experiments are, at the time of this writing not complete, although the samples do appear to be near their equilibrium water content.

The two samples at 35°C were exposed to four different water partial pressures ranging from 2.8 to 38 torr. The water contents of the Core 103 Segment 1 upper half sample during these exposure experiments are presented in Figure 4.9. The water content is based on a single TGA; TGA can provide a lower than actual measure of water because the sample is exposed to a flowing stream of dry gas for a few seconds before the temperature heating program begins. This material, beginning with about 13 wt% dries completely when exposed to 2.8 torr, near the lowest P_{H_2O} observed at Hanford between 1980 and 1995. Exposure to water partial pressures 9 and 23 torr have little effect on the original water content. When exposed to 34 and 37 torr, this BY-110 waste gains substantial amounts of water reaching 63 and 72 wt% water, respectively. These aliquots are continuing to sorb water after 1025 h of exposure.

Figure 4.9. Effect of P_{H_2O} on the Water Content of BY-110 Core 103 Segment 1U Waste Sample at 35°C

The second sample tested, Core 113 Segment 1, exhibited similar qualitative behavior to the other BY-110 sample Segment 1 sample tested drying when exposed to 2.8 torr, drying slightly when exposed to 9 and 23 torr, and gaining substantial water when exposed to 34 and 37 torr (see Figure 4.10). When exposed to 2.8 torr, the sample dried from its original 15 wt% water to 7 wt% water. When exposed to 9 and 23 torr, this BY-110 waste dried slightly to between 10 and 14 wt%.

Figure 4.10. Effect of P_{H_2O} on the Water Content of the BY-110 Core 113 Segment 1U Waste Sample at 35°C

At the measured P_{H_2O} of 9 torr in the BY-110's headspace on November 11, 1994, Figures 4.9 and 4.10 suggest that the 35°C surface waste should contain about 12 wt% water. The BY-110 solid samples tested contained 23 and 18 wt% water (Schreiber 1996a 1996) when analyzed at the 222S Laboratory indicating that these wastes have not yet equilibrated with the atmosphere in the tank or that other factors are contributing to the water content such as water migration from the lower depths in the tank

The current physical appearances of the BY-110 waste samples exposed to the various water partial pressures are provided in Table 4.9. Both BY-110 wastes tested began as slightly moist grainy solids containing some larger pieces. After exposure to 2.8 torr, both materials looked dry with few signs of moisture; the Core 113 sample exposed to 9 torr also looked dry. The Core 103 sample exposed to 9 torr appeared mostly dry with traces of water as did the Core 113 sample exposed to 23 torr. The Core 103 sample exposed to 23 torr appeared slightly moist. Both samples exposed to 34 and 37 torr were a combination of liquid and solids.

In general, exposing the BY-110 surface wastes to ambient Hanford water partial pressures will dry the surface wastes to between 0 and 15 wt% water. Based on our incomplete testing of these BY-110 materials, it appears that the final equilibrium water content at all current ambient Hanford partial pressures of water will be below the current TOC and energetics independent safety criterion of 20 wt% water (Webb et al. 1995).

Table 4.9. Appearance of BY-110 Surface Waste Samples after Exposure to Selected Water Partial Pressures at 32°C

Sample	Description				
	P _{H2O} , torr				
	2.8	9	23	34	37
Core 103 Segment 1U	Dry Crystalline Solids	Mostly Dry Crystalline Solids	Slightly Moist Crystalline Solids	Liquid/ Solids	Liquid/ Solids
Core 113 Segment 1	Dry Crystalline Solids	Dry Crystalline Solids	Mostly Dry Crystalline Solids	Liquid/ Solids	Liquid/ Solids

5.0 Physical Properties

In support of C. S. Simmons and coworkers' (1996; 1997) efforts to model the physical and physical/chemical behavior of water in Hanford tank wastes and predict the eventual water content of the organic-bearing wastes, we measured several physical properties of the waste samples that we received in FY 1997 or late FY1996. The materials characterized were primarily saltcake wastes from U-107, A-101, A-102, and BY-110. The physical properties determined were the densities of the as-received solids, supernate, and centrifuged solids, vol% and wt% centrifuged solids in the as-received sample, and wt% solids (dried) in the as-received solids, the supernate, and the centrifuged solids.

In addition to the measured quantities, we calculated wt% and vol% interstitial solution in the as-received solids based on the assumptions that 1) the water in the centrifuged solids is present in the waste as interstitial solution and 2) the interstitial solution has the same composition as the recovered centrifuged supernate or the as-received tank supernate. Such assumptions appear to be valid for sludges, based on the correspondence of predicted and measured compositions of actual and simulated ferrocyanide wastes (Scheele et al 1994) where discrete particles exist. However, solid saltcake wastes such as tested here that are crystalline or essentially a single continuous phase may be more analogous to saturated solution where water is the solute. The calculated values for wt% and vol% interstitial solution suggest that the latter is truly the case, and assumptions may not be valid.

The measured physical properties for wastes from U-107, A-101, A-102, and BY-110 are presented in Tables 5.1 through 5.7. The compacted densities of the as-received samples ranged from 1.2 g/mL for a BY-110 sample to 1.8 g/mL for an A-101 sample. The densities of the centrifuged solids ranged from a low of 1.2 g/mL for a BY-110 sample to a high of 2.0 g/mL for an A-101 sample. The vol% centrifuged solids ranged from 65 vol% in the A-102 sample to 100 vol% for the U-107 solids sample and the two BY-110 samples. The wt% centrifuged solids ranged from a low of 72 wt% in the A-102 sample to a high of 100 wt% for the samples from U-107 and BY-110. The wt% solids in the as-received samples ranged from 64 wt% in the A-102 sample to 99 wt% in the BY-110 Core 103 sample. The wt% solids in the centrifuged solids ranged from 68 wt%, again in the A-102 sample, to 99 wt% in the BY-110 Core 103 sample. The densities in the recovered supernates from A-101 samples and the U-107 supernate sample were 1.5 g/mL, and the A-102 recovered supernate was 1.4 g/mL; the drainable liquid sample obtained by Segment 14 from A-101 was received as a solid sample, differing little in appearance from its other A-101 delivered siblings. The wt% dissolved solids in these liquids ranged from 50 wt% for the U-107 supernate to 60 wt% for the A-101 Core 113 Segment 14 drainable liquid sample.

The derived wt% and vol% interstitial solution contents in the as-received solid samples are also presented in Tables 5.1 through 5.7. The wt% interstitial solution contents ranged from 18 wt% in the U-107 solid sample to 78 wt% for the A-102 grab sample. The vol% interstitial solution contents ranged from 19 vol% for the U-107 sample to 93 vol% for the A-102 sample. The high wt% and vol% interstitial solution contents in the A-102 and A-101 samples suggest that the model of solution occupying the space between the solid particles in the waste is not fully accurate for these solid saltcake wastes; rather, the model with non-recoverable water (by centrifuging) within the crystalline salt matrix may be more representative.

Table 5.1. Selected Properties of Wastes Obtained from Tank 241-U-107 by Cores 129 and 134

Property	Sample #1	Sample #2	Ave
As-Received Solids (Core 134 Segment 2)			
Density (After Centrifuging)	1.51	1.52	1.52
Centrifuged Solids Density, g/mL ^(a)	1.51	1.52	1.52
Vol% Centrifuged Solids	100	100	100
Wt% Centrifuged Solids	100	100	100
Wt% Solids (As-Received)	90.8	91.3	91.1
Wt% Solids (Centrifuged Solids)	90.8	91.3	91.1
Wt% Interstitial Solution ^(b)	18.3	17.3	17.8
Vol% Interstitial Solution ^(b)	19.3	18.0	18.6
Supernate (Core 129 Segment 1)			
Density, g/mL	1.4	1.5	1.5
Wt% Dissolved Solids	49.6	49.8	49.7

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

Table 5.2. Selected Properties of Wastes Obtained from Tank A-101 by Core 154 Segment 1UH

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Density (After Centrifuging), g/mL ^(a)	1.8	1.8	1.8
Centrifuged Solids Density, g/mL	1.9	1.9	1.9
Vol% Centrifuged Solids	85	84	84.5
Wt% Centrifuged Solids	89.3	90.4	89.85
Wt% Solids (As-Received)	76.2	76.0	76.1
Wt% Solids (Centrifuged Solids)	78.7	78.2	78.45
Wt% Interstitial Solution ^(b)	53.7	54.2	54.0
Vol% Interstitial Solution ^(b)	65.0	65.6	65.3
Centrifuged Supernate			
Density, g/mL	1.5	(c)	1.5
Wt% Dissolved Solids	55.8	(c)	55.8

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

c) Insufficient supernate recovered to perform second characterization

Table 5.3. Selected Properties of Wastes Obtained from Tank A-101 by Core 154 Segment 1LH

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Density (After Centrifuging), g/mL ^(a)	1.80	1.81	1.805
Centrifuged Solids Density, g/mL	2.0	2.0	2.0
Vol% Centrifuged Solids	80	80	80
Wt% Centrifuged Solids	86.8	87.1	87.0
Wt% Solids (As-Received)	71.6	72.0	71.8
Wt% Solids (Centrifuged Solids)	73.9	74.4	74.2
Wt% Interstitial Solution ^(b)	64.8	63.7	58.9
Vol% Interstitial Solution ^(b)	79.4	78.4	72.3
Centrifuged Supernate			
Density, g/mL	1.5	(c)	1.5
Wt% Dissolved Solids	56.1	(c)	56.1

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

c) Centrifuged supernate samples combined to provide sufficient material to determine dissolved solids

Table 5.4. Selected Properties of Wastes Obtained from Tank A-101 by Core 156 Segment 14DL

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Density (After Centrifuging), g/mL ^(a)	2.0	1.8	1.9
Centrifuged Solids Density, g/mL	2.0	1.9	2.0
Vol% Centrifuged Solids	84	86	85
Wt% Centrifuged Solids	89.4	89.8	89.6
Wt% Solids (As-Received)	75.9	76.7	76.3
Wt% Solids (Centrifuged Solids)	77.8	78.6	78.2
Wt% Interstitial Solution ^(b)	60.1	58.1	54.4
Vol% Interstitial Solution ^(b)	79.6	72.3	69.8
Centrifuged Supernate			
Density, g/mL	1.5	1.5	1.5
Wt% Dissolved Solids	59.9	(c)	59.9

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

c) Centrifuged supernate samples combined to provide sufficient material to determine dissolved solids

Table 5.5. Selected Properties of Wastes Obtained from Tank A-102 by 1996 Grab Sample

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Centrifuged Solids Density, g/mL ^(a)	1.7	1.6	1.65
Centrifuged Solids Density, g/mL	1.9	1.8	1.8
Vol% Centrifuged Solids	65	65	65
Wt% Centrifuged Solids	71.6	71.2	71.4
Wt% Solids (As-Received)	64.3	64.6	64.4
Wt% Solids (Centrifuged Solids)	68.3	68.8	68.55
Wt% Interstitial Solution ^(b)	78.0	77.3	77.6
Vol% Interstitial Solution ^(b)	93.3	86.5	89.9
Centrifuged Supernate			
Density, g/mL	1.4	1.4	1.4
Wt% Dissolved Solids	54.2	54.2	54.2

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

Table 5.6. Selected Properties of Wastes Obtained from Tank BY-110 by Core 103 Segment 1UH Sample

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Centrifuged Solids Density, g/mL ^(a)	1.2	1.2	1.2
Centrifuged Solids Density, g/mL	1.2	1.2	1.2
Vol% Centrifuged Solids	100	100	100
Wt% Centrifuged Solids	100	100	100
Wt% Solids (As-Received)	98.9	98.7	98.8
Wt% Solids (Centrifuged Solids)	98.9	98.7	98.8
Wt% Interstitial Solution ^(b)	(c)	(c)	(c)
Vol% Interstitial Solution ^(b)	(c)	(c)	(c)
Centrifuged Supernate			
Density, g/mL	(c)	(c)	(c)
Wt% Dissolved Solids	(c)	(c)	(c)

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

c) No supernate recovered by centrifuging

Table 5.7. Selected Properties of Wastes Obtained from Tank BY-110 by Core 113 Segment 1 Sample

Property	Sample #1	Sample #2	Ave
As-Received Solids			
Centrifuged Solids Density, g/mL ^(a)	1.3	1.1	1.2
Centrifuged Solids Density, g/mL	1.3	1.1	1.2
Vol% Centrifuged Solids	100	100	100
Wt% Centrifuged Solids	100	100	100
Wt% Solids (As-Received)	83.1	83.8	83.4
Wt% Solids (Centrifuged Solids)	83.1	83.8	83.4
Wt% Interstitial Solution ^(b)	(c)	(c)	(c)
Vol% Interstitial Solution ^(b)	(c)	(c)	(c)
Centrifuged Supernate			
Density, g/mL	(c)	(c)	(c)
Wt% Dissolved Solids	(c)	(c)	(c)

a) Sample centrifuged for 1 h at 1860 g

b) Assumes mass loss on drying is due to interstitial solution

c) No supernate recovered by centrifuging

6.0 Conclusions

Our studies indicate that the equilibrium water content of Hanford's organic-bearing wastes tested and those having similar chemical compositions will be controlled by a combination of P_{H_2O} and the chemical composition of the waste. The two chemical constituents whose influence is readily apparent from are sodium nitrate/nitrite and sodium hydroxide. The effects of other waste constituents such as aluminum, sulfate, and carbonate/bicarbonate are less obvious as are the interactions between all of the individual waste constituents. Based on the one sample, for which we have a measured hydroxide concentration, significant hydroxide content will cause these wastes to retain significant amounts of water at Hanford conditions. In contrast, sodium nitrate/nitrite has little affinity for water at Hanford conditions causing the waste to retain small amounts of water at Hanford conditions, however, the amount of water observed in the tested wastes is higher than expected based on the behavior of pure sodium nitrate/nitrite indicating that other constituents are causing the wastes to retain water.

Specifically, the wastes from BY-108, U-105, S-102, U-107, A-101, A-102, and BY-110 will, in general, equilibrate below the desired 20 wt% water content safety criterion (Webb et al. 1995) at Hanford water partial pressures ranging from 3 to 9 torr. The equilibrium water contents frequently were 10 wt% water or less at Hanford water vapor pressures. How far below 20 wt% depends on the waste and its composition. For example, the supernate from U-107 exposed to the Hanford Site average of 5.5 torr would be predicted to contain about 15 wt% water due, we believe, to its high hydroxide content; hydroxide was unmeasured in the other waste samples. Because of the low water content at Hanford water partial pressures, 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.

To understand the differences in behavior of these principally sodium nitrate Hanford wastes requires additional study to understand the contributions of all of the individual major waste constituents found in Hanford wastes and influence that each has on the aggregate behavior of the waste. Most of the studied wastes are primarily sodium nitrate and/or nitrite with concentrations of the lesser constituents varying from waste to waste. Some of the solid wastes studied qualitatively exhibit the characteristics of sodium nitrate and nitrite, retaining small amounts of water at relative humidities less than 50 wt% and retaining significant amounts when exposed to relative humidities of 90% or more. Other wastes such as those in U-105 indicate that other constituents have a significant influence on the equilibrium water content of the waste although it is unclear as to which constituent has the greatest secondary influence.

These studies also show that the water content in these wastes can be controlled by controlling P_{H_2O} . The observed reversibility of the water loss/gain displayed by all samples tested indicates 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 organic-bearing wastes to 20 wt% water or another acceptable level using air with a controlled P_{H_2O} .

7.0 References

- Agnew SF. 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 DA Turner. 1993. *Preliminary Criteria for Organic Watch List Tanks at the Hanford Site*. WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Baldwin JH, RJ Cash, L Amato, and T Tran. 1996. *Tank Characterization Report for Single-Shell Tank 241-BY-108*. WHC-SD-WM-ER-533, Westinghouse Hanford Company, Richland Washington.
- Barney GS. 1976. *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*. ARH-ST-113, Atlantic Richfield Hanford Company, Richland, Washington.
- Brager HR. 1994. *Summary of Information on Flammable Gas Watch List Tanks*, WHC-EP-0711, Westinghouse Hanford Company, Richland, Washington.
- Brown TM and J. Franklin. 1996. *Tank Characterization Report for Single-Shell Tank 241-U-105*. WHC-SD-WM-ER-617, Westinghouse Hanford Company, Richland Washington.
- Burger LL. 1995. *Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*. PNL-8557, Rev. 1, Pacific Northwest Laboratory, Richland, Washington.
- Campbell GS and GW. Gee. 1986. "Water potential: Miscellaneous methods" in *Methods of Soil Analysis. Part I*, 2nd ed., Agron. Monogr. 9. A. Klute, Ed., ASA and SSA, Madison, Wisconsin.
- Consort SD, KL Ewer, JW Funk, RG Hale, GA Lisle, and CV Salois. 1996a. *Supporting Document For The Historical Tank Content Estimate For A, AX, B, BX, BY, and C Tank Farms*. WHC-SD-WM-ER-308, Rev. 1b, Fluor Daniel Northwest, Richland, Washington.
- Consort SD, KL Ewer, JW Funk, RG Hale, GA Lisle, and CV Salois. 1996b. *Historical Tank Content Estimate For The Northeast Quadrant Of The Hanford 200 East Area*. WHC-SD-WM-ER-349, Rev. 1b, Fluor Daniel Northwest, Richland, Washington.
- Eggers RF. 1996. *Tank Characterization Report for Single-Shell Tank 241-S-102*. WHC-SD-WM-ER-611, Rev 0, Westinghouse Hanford Company, Richland, Washington.
- Ewer KL, JW Funk, RG Hale, GA Lisle, CV Salois, MR Umphrey. 1997a. *Supporting Document For The Historical Tank Content Estimate For S, SX, and U Tank Farms*. HNF-SD-WM-ER-323, Rev 1, Fluor Daniel Northwest, Richland, Washington.
- Ewer KL, JW Funk, RG Hale, GA Lisle, CV Salois, MR Umphrey.. 1997. *Historical Tank Content Estimate for the Southwest Quadrant of the Hanford 200 West Area*. HNF-SD-WM-ER-352, Rev 1, Fluor Daniel Northwest, Richland, Washington.

Fauske HK, M Epstein, DR Dickenson, RJ 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.

Field JG, DE Place, and RD Cromar. 1997. *Tank Characterization Report for Single-Shell Tank 241-A-101*. HNF-SD-WM-ER-673, Lockheed Martin Hanford Corporation, Richland Washington.

Gauglitz PA, SD Rassat, PR Bredt, JH Konynenbelt, SM Tingey, and DP Mendoza. 1996. *Mechanisms of Gas Retention and Release: Results for Hanford Waste Tanks 241-S-102 and 241-SY-103 and Single-Shell Tank Simulants*, PNNL-11298, Pacific Northwest National Laboratory, Richland, Washington.

Hanlon BM. 1996. *Waste Tank Summary Report for Month Ending January 31, 1996*. WHC-EP-0182-94, Westinghouse Hanford Company, Richland, Washington.

Hanlon BM. 1997. *Waste Tank Summary Report for Month Ending June 30, 1997*. HNF-EP-0182-111, Lockheed Martin Hanford Company, Richland, Washington.

Huckaby JL. 1994. *Tank 241-C-103 Headspace Flammability*, WHC-EP-0734 Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Huckaby JL and DR Bratzel. 1995. *Tank 241-A-101 Headspace Gas and Vapor Characterization Results for Samples Collected in June 1995*. WHC-SD-WM-ER-505 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Huckaby JL. 1996. *Headspace Vapor Characterization of Hanford Waste Tank 241-A-102: Results from Samples Collected on 11/10/95*. PNNL-11162, Pacific Northwest Laboratory, Richland, Washington.

Jo J, BJ Morris, and TT Tran. 1996. *Tank Characterization Report for Single-Shell Tank 241-U-107*. WHC-SD-WM-ER-614, Westinghouse Hanford Company, Richland Washington.

Jo J. 1996. *Tank Characterization Report for Single-Shell Tank 241-A-102*. WHC-SD-WM-ER-597, Westinghouse Hanford Company, Richland Washington.

Lilga MA, EV Alderson, DJ Kowalski, MR Lumetta, and GF Schiefelbein. 1994. *Ferrocyanide Safety Project: Task 3 Ferrocyanide Aging Studies FY1994 Annual Report*. PNL-10126, Pacific Northwest Laboratory, Richland, Washington.

Lilga MA, EV Alderson, RT Hallen, MO Hogan, TL Hubler, GL Jones, DJ Kowalski, MR Lumetta, GF Schiefelbein, and MR Telander. 1995. *Ferrocyanide Safety Project Ferrocyanide Aging Studies FY 1995 Annual Report*. PNNL-10713, Pacific Northwest Laboratory, Richland, Washington.

Lilga MA, MR Lumetta, and GF Schiefelbein. 1993. *Ferrocyanide Safety Project: Task 3 Ferrocyanide Aging Studies FY1993 Annual Report*. PNL-8888, Pacific Northwest Laboratory, Richland, Washington.

Lilga MA, MR Lumetta, WF Riemath, RA Romine, and GF Schiefelbein. 1992. *Ferrocyanide Safety Project: Subtask 3.4 Ferrocyanide Aging Studies FY1992 Annual Report*. PNL-8387, Pacific Northwest Laboratory, Richland, Washington.

Lilga MA, RT Hallen, EV Alderson, MO Hogan, TL Hubler, GL Jones, DJ Kowalski, MR Lumetta, WF Riemath, RA Romine, GF Schiefelbein, and MR Telander. 1996. *Ferrocyanide Safety Project Ferrocyanide Aging Studies Final Report*. PNNL-11211, Pacific Northwest National Laboratory, Richland, Washington.

Pool KH, et al., 1995, *Vapor Space Characterization of Waste Tank 241-S-102: Results from Samples Collected on 3/14/95*, PNL-10587, UC-606, Pacific Northwest Laboratory, Richland, Washington.

Pool KH, JC Evans, BL Thomas, KB Olsen, JS Fruchter, and KL Silvers. 1996. *Headspace Vapor Characterization of Hanford Waste Tank 241-BY-108: Comparison Study Results from Samples Collected on 1/23/96*. PNNL-11151, Pacific Northwest National Laboratory, Richland, Washington.

Pool KH, MW Ligothe, GS Klinger, OP Bredt, SC Goheen, TW Clauss, BD McVeety, KB Olsen, and JS 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 AK, JE Meacham, GS Barney, GL Borsheim, RJ Cash, MD Crippen, DR Dickenson, JM Grigsby, DW Jeppson, M Kummerer, JM McLaren, CS Simmons, and BC Simpson. 1994. *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*. WHC-EP-0691. Westinghouse Hanford Company, Richland, Washington.

Scheele RD, LL Burger, RL Sell, PR Bredt, and RJ Barrington. 1994. *Ferrocyanide Safety Project: Comparison of Actual and Simulated Ferrocyanide Waste Properties*. PNL-10175, Pacific Northwest Laboratory, Richland, Washington.

Scheele RD, PR Bredt, and RL 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 RD, PR Bredt, and RL Sell. 1997a. *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.

Scheele RD, PR Bredt, and RL Sell. 1997b. *Organic Tank Safety Project: Effect of Water Partial Pressure on the Equilibrium Water Content of Waste Samples from Hanford Tank 241-U-105*. PNNL-11638, Pacific Northwest National Laboratory, Richland, Washington.

Scheele RD., JL Sobolik, RL Sell, and LL 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.

Schreiber RD. 1996a. *Final Report for Tank 241-BY-110, Rotary Mode Cores 92, 95, 101, 103, 106, 107, 109, 96, & 113*. WHC-SD-WM-DP-153, Rev 1, Westinghouse Hanford Company, Richland, Washington.

Schreiber, RD. 1996b. *Tank Characterization Report For Single-Shell Tank 241-BY-110*. WHC-SD-WM-ER-591 Rev 0, Westinghouse Hanford Company, Richland, Washington.

Simmons CS, N Aimo, MJ Fayer, and MD White. 1997. *Developing a Model for Moisture in saltcake Waste Tanks: Progress Report*. PNNL-11595, Pacific Northwest National Laboratory, Richland, Washington.

Simmons CS. 1996. *Modeling Water Retention of Sludge Simulants and Actual Saltcake Tank Wastes*. PNNL-11831, Pacific Northwest National Laboratory, Richland, Washington.

Stedwell, M. J. 1954. *Evaluation of Nickel Ferrocyanide Scavenging of Uranium Recovery Plant Solvent Extraction Waste*. HW-31428, Hanford Atomic Works Operation, Richland, Washington.
Weast RC, MJ Astle, and WH Beyer. 1984. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Raton, Florida.

Webb AB, JL Stewart, DA Turner, MG Plys, B Malinovic, JM Grigsby, DM. Camaioni, PG Heasler, WD Samuels, and JJ 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

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