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**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**

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

September 1996

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

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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PNNL-11227

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**Organic Tank Safety Project:
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Abstract

Some of Hanford's underground waste storage tanks contain organic-bearing high level wastes that are high priority safety issues because of potentially hazardous chemical reactions of organics with inorganic oxidants in these wastes such as nitrates and nitrites. To ensure continued safe storage of these wastes, Westinghouse Hanford Company has placed affected tanks on the Organic Watch List and manages them under special rules.

Because water content has been identified as the most efficient agent for preventing a propagating reaction and is an integral part of the criteria developed to ensure continued safe storage of Hanford's organic-bearing radioactive tank wastes, as part of the Organic Tank Safety Program the Pacific Northwest National Laboratory developed and demonstrated a simple and easily implemented procedure to determine the equilibrium water content of these potentially reactive wastes exposed to the range of water vapor pressures that might be experienced during the wastes' future storage. This work focused on the equilibrium water content and did not investigate the various factors such as tank ventilation, tank surface area, and waste porosity that control the rate that the waste would come into equilibrium with either the average Hanford water partial pressure 5.5 torr or other possible water partial pressures.

The developed procedure exposes Hanford waste at a controlled temperature to an atmosphere with a partial pressure of water controlled by saturated salt solutions. To develop the procedure, we exposed several suspect waste constituents, three surrogate wastes (mixtures prepared from selected waste constituents), and a simulated organic-bearing waste, PAS94, characteristic of wastes resulting from radiocesium and radiostrontium removal operations to water partial pressures ranging from 1 to 16 torr at 20°C and 7 to 146 torr at 65°C controlled by saturated salt solutions. We used the procedure on waste samples from Tank 241-T-111 at 20°C to demonstrate its use on radioactive materials.

The results indicate that if a waste is allowed to come into equilibrium with the average Hanford partial pressure of water 5.5 torr the waste's water content will be below the 20 wt% water that allows classification as unconditionally Safe, however, the results also indicate that depending on the waste's composition and temperature, sufficient water may be present at equilibrium with the average Hanford partial pressure of water for the waste to be classified as Conditionally Safe based on the energetics or total organic carbon content criteria.

Each of the individual potential waste components had a unique behavior when exposed to different partial pressures of water. Although the surrogate can, in general, be approximated using the behavior of the individual components, the results of these studies indicate that interactions exist between the components that typically result in a typically small but sometimes significant underestimation of the equilibrium water content. The simulant and actual T-111 waste studies suggest that other unstudied waste components such as sodium phosphate and sodium sulfate contribute to the equilibrium water content. These studies also suggest that the water content of a waste can be controlled by controlling the water partial pressure in the inlet gas to the storage tank.

Summary

Years of producing and recovering nuclear-defense materials, decontaminating facilities, and managing wastes from chemical-recovery operations at the U.S. Department of Energy's Hanford Site have generated organic-bearing radioactive high-level waste (HLW). The organic-bearing HLWs, which could contain organic solvents, organic complexants, organic radiolytic and alkaline hydrolysis-degradation products, and the inorganic oxidants nitrate and nitrite, are stored in underground storage tanks at Hanford. The potential chemical reaction hazards associated with these organic-bearing radioactive wastes have been recognized as high priority safety issues, and as a result of these concerns, operational criteria and resolution plans have been developed to ensure continued safe storage of these wastes with tanks containing these wastes being placed on the Organic Watch List; the Organic Watch List is a set of tanks that are managed under special rules to ensure safety.

Because thermodynamic evaluations and experimental studies have shown that water in the wastes is the most effective agent for preventing the onset and propagation of a reaction between the organic fuels and inorganic oxidants in the Hanford organic-bearing wastes, water content was an integral element of the preliminary criteria developed to ensure continued safe storage of these Hanford wastes. Given the potential value and importance of water in preventing possible exothermic and energetic reactions, the Pacific Northwest National Laboratory has been assigned the task of developing and implementing a method to measure the equilibrium water content of stored radioactive wastes exposed to the range of relative humidities that might be experienced during the wastes' years of future storage, including the ambient Hanford environmental water partial pressures. This work is in continuing support of Westinghouse Hanford Company's efforts to ensure that the organic-bearing HLW stored in Hanford's single shell storage tanks continue to be stored safely.

While the equilibrium water content of wastes exposed to arid Hanford air will provide the conservative limiting case for developing management guidelines to ensure safe storage of the organic-bearing wastes, other factors that were not investigated in this study will control the rate at which a stored waste will reach its equilibrium water content. These factors include the surface area of the waste, the porosity of the waste, and whether the tank is passively or actively ventilated. The surface area and porosity of the waste can be affected by the drying of waste and reactions of the waste components with themselves or air; in the latter case, formation of sodium carbonate will occur, possibly reducing the porosity of the waste and thus the exchange of water between the headspace gases and the waste. The ventilation used will control how frequently the headspace gases are exchanged with environmental air.

As part of the Organic Tank Safety Program, we developed and demonstrated a simple and easily implemented procedure to determine the equilibrium water content of the potentially reactive organic-bearing wastes stored in some of Hanford's high level radioactive waste storage tanks; this procedure is an implementation of commonly used methods to expose materials to known partial pressures of water. The procedure was developed and equipment was tested by examining the behavior of several suspect waste constituents, three surrogate wastes (mixtures prepared from selected waste constituents), and a simulated organic-bearing waste, PAS94, characteristic of wastes resulting from radiocesium and

radiostrontium removal operations. We applied the method to wastes from Tank 241-T-111 (T-111) to demonstrate its use on radioactive materials.

In the developed procedure, wastes are exposed to water partial pressures controlled by saturated salt solutions contained in small-volume (250 mL) sealed containers. The saturated solution has a sufficient excess of water that the water partial pressure will not be affected by the sample's behavior. The method as implemented uses saturated solutions of sodium hydroxide, calcium chloride, sodium bromide, potassium chloride, and potassium nitrate to provide water partial pressures ranging from 1 to 16 torr at 20°C and 7 to 146 torr at 65°C. The partial pressures at 20°C bound the observed partial pressures for the Hanford Site that in their extreme range from 2.5 to 9.0 torr, based on atmospheric data from the last 15 years. The procedure is easily adaptable to provide additional water vapor pressures through the use of other saturated salt solutions or other materials that provide a known and constant partial pressure of water.

The observed behavior of selected potential waste components, mixtures containing these materials, and a complex simulated organic-bearing waste studied during the development effort provides insight into the chemical factors that control the water content of Hanford wastes. The potential waste constituents studied were ferric hydroxide, sodium hydroxide, a 2:1 mole ratio mixture of sodium nitrate and nitrite, sodium laurate, sodium glycolate, and sodium aluminate. The three surrogate wastes tested were selected combinations of these materials; one mixture contained all but laurate, a second contained all but the glycolate, and the third contained all but sodium hydroxide and laurate. The simulated waste PAS94 is a complexant-bearing waste characteristic of the waste resulting from the removal of radiocesium and radiostrontium from PUREX acid waste that had been made basic with sodium hydroxide.

Each of the individual potential waste components had a unique behavior when exposed to different partial pressures of water, absorbing different amounts of water at each respective water partial pressure. With sodium hydroxide, each increase in water vapor pressure resulted in an increase in the amount of associated water. Iron hydroxide, sodium nitrate/nitrite, and sodium glycolate appeared to have a threshold water vapor pressure level where they begin to absorb water. Sodium laurate, based on thermogravimetric analysis, has one water of hydration in the as-received salt, and it appears that it gains two additional waters of hydration at higher partial pressures of water. The behavior of sodium aluminate was complex, gaining mass initially upon exposure to the higher humidities and later losing mass, suggesting that reactions occurred between the aluminate and the absorbed water; the amount of water contained in the aluminate and water mixtures resulting from the testing was difficult to quantify because the final dried mass was greater than the initial dry mass.

Although the surrogate and simulant waste behavior can, in general, be approximated using the simple model based on independent behavior of the individual components, the results of these studies indicate that interactions exist between the components that result in a typically small but sometimes significant underestimation of the equilibrium water content. Each surrogate mixture began to absorb water at a lower water partial pressure than would be expected based on the behavior of the individual components. The simulated waste, which was about 30 wt% NaOH on a dry basis and contained unstudied compounds, had a water-absorption profile similar to that of sodium hydroxide, but contained more

water than would be predicted based on its sodium hydroxide, sodium nitrate, and sodium nitrite content. This finding indicates that constituents other than these three may also help control the water content of the simulant.

When the reactive waste obtained from T-111 by Core 33, Segment 2, was exposed to water partial pressures of 1.0, 5.4, 10.3, 15, and 16.3 torr, the final water content of the waste dropped from the original 62 wt% water (archived sample) to 4, 13, 20, and 44 wt% for the lowest four water partial pressures and remained unchanged at 16.3 torr. This indicates that if T-111 waste were to be exposed to average monthly environmental Hanford partial pressures of water (3.8 to 7.5 torr), the waste would have a water content less than the desired 20 wt% that would allow the waste to be placed unconditionally in the Safe category (Webb et al. 1995)^(a), therefore requiring that either the energetics or total organic carbon (TOC) criteria be applied; both are satisfied for all water contents of this waste. The T-111 studies also show that the waters predicted to be associated with sodium hydroxide, sodium nitrate, and sodium nitrite do not fully account for the measured water content. The T-111 waste contains significant amounts of sulfate and phosphate that could contribute to the water retained by the waste.

These studies show that at the monthly average, ambient environmental Hanford partial pressures of water ranging from 3.8 to 7.5 torr, sodium hydroxide and possibly sodium aluminate are the only components studied that absorb significant amounts of water that could help maintain the desired 20 wt% water content at 20°C (Webb et al.'s [1995] Safe Classification) or other acceptable water contents that allow the energetics and TOC criteria to be satisfied. At 65°C, only sodium hydroxide has sufficient attraction for water that the resulting mixture will have over 5 wt% water, thus requiring application of the energetics and TOC criteria to determine the waste's safety classification. The T-111 studies and the PAS94 studies indicate that other waste constituents may have sufficient water absorption capacity at these humidities to contribute significant enough amounts of water to a waste's water content to satisfy the safety energetics and TOC safety criteria (Webb et al. 1995) for Conditionally Safe Tanks.

In general, the ancillary studies indicate that the water content of a material is controlled by the individual constituents in a waste and the water vapor pressure above the waste. Comparing the observed water contents in the surrogate wastes with the predicted water contents, based on the concentration-weighted contributions of the individual constituents, indicates that the equilibrium water content can be approximately predicted by this simple model, although it fails at some conditions. The dependence of water content on water vapor pressure indicates that a waste's water content can be controlled by controlling the water partial pressure in the tank, offering a potential mitigation method.

Based on these studies, we recommend that studies be performed to 1) determine the response of actual wastes to a range of water partial pressures on the waste's equilibrium water content, 2) determine the behavior of additional major potential waste constituents, 3) determine the behavior of mixtures of the major waste constituents when exposed to a range of water partial pressures, 4) investigate controlling the water content of wastes at particular waste depths by controlling the water vapor pressure, and 5) explore the effect of atmospheric CO₂ on the hydroxide concentration in waste mixtures to better predict the water content and understand its effect on the porosity of the waste and the transfer of water.

(a) A revision of *Preliminary safety criteria for Organic Watch List Tanks at the Hanford Site* (Webb et al. 1995) is scheduled for publication in September 1996.

Acknowledgements

We thank the following people for their invaluable support in developing a method for measuring the equilibrium water content of Hanford wastes and for helping with this report: LL Burger was our scientific sounding board, consultant, and reviewer as we attempted to understand the behavior of the different materials as they were exposed to water vapor; KW Burke supplied the water partial pressure data; CD Carlson provided a technical peer review of the document; AM Fillion and WC Cosby provided editorial review and assistance in publishing this report. Westinghouse Hanford Company and the U.S. Department of Energy provided funding for the project.

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

Glossary

DBP	dibutyl phosphate
DSC	differential scanning calorimetry
DOE	U.S. Department of Energy
DTA	differential thermal analyzer
EDTA	ethylenediaminetetraacetate
EPA	U.S. Environmental Protection Agency
HEDTA	hydroxyethylethylenediamine-triacetate
HLW	high-level waste
IC	ion chromatography
ICP/AES	inductively coupled argon plasma atomic emission spectroscopy
IR	infrared spectroscopy
MBP	monobutyl phosphate
MS	mass spectrometry
NPH	normal paraffin hydrocarbon
P _{H₂O}	partial pressure of water (the plural is spelled out in the text to avoid the confusing P _{H₂O} s)
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium reduction and extraction (plant)
TBP	tributyl phosphate
TGA	thermogravimetric analysis
TOC	total organic carbon
UST	underground storage tank
WHC	Westinghouse Hanford Company

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1.0 Introduction

Years of producing and recovering nuclear defense materials, decontaminating facilities, and managing wastes from chemical recovery operations have resulted in organic- and oxidant-bearing radioactive high-level wastes (HLWs) that are stored in underground storage tanks (USTs) at the U.S. Department of Energy's (DOE) Hanford Site; the primary source of these organic-bearing wastes was the waste management operations to remove radiocesium and radiostrontium from the HLWs produced by the plutonium and uranium reduction and extraction (PUREX) plant (Strachan, Schulz, and Reynolds 1993). The organics in these wastes, which could include organic solvents, organic complexants, and organic radiolytic and alkaline hydrolysis degradation products, have the potential to react exothermically and vigorously with the inorganic oxidants nitrate and nitrite in the waste.

The DOE and the Hanford Site operating contractor Westinghouse Hanford Company (WHC) recognized this potential reactivity hazard as a high priority safety issue and as a result

- developed resolution plans to ensure continued safe storage of these wastes (Wilson and Reep 1991; Wodrich and Deichman 1992; Babad, Price, and Fulton 1993; Babad et al. 1993)
- commissioned studies to
 - assess chemical reactivity hazards (Turner and Miron 1994a and 1994b; Scheele et al. 1995; Burger 1995; Fauske et al. 1995)
 - determine the fate of these organics when exposed to high levels of radiation in a harsh chemical environment (Camaioni et al. 1994 and 1995; Campbell et al. 1995)
 - determine whether the organics could be concentrated under storage conditions (Gerber 1994)
 - estimate the water and fuel or total organic carbon (TOC) contents in tank wastes (Toth et al. 1995; Agnew 1996)
- developed operational criteria (Webb et al. 1995) to ensure continued safe storage of these wastes.

As part of WHC's continuing effort to ensure safe storage of these organic-bearing wastes, WHC gave the Pacific Northwest National Laboratory (PNNL) the task to develop and demonstrate a method for determining the equilibrium water content of waste exposed to the water partial pressures anticipated during storage in USTs at the Hanford Site.

Based on the theoretical evaluations of Burger (1995) and the experimental studies of Fauske et al. (1995), Webb et al. (1995) recognized the importance of water content in waste for preventing exothermic reactions in the organic-bearing wastes and used it as one of the major elements in the preliminary operational safety criteria developed to ensure continued safe storage of the organic-bearing wastes. The two developed criteria use combinations of water content and 1) measured energetics (energetics criterion) or 2) total organic carbon content (TOC criterion) to classify a particular stored waste as "Safe," "Conditionally Safe," or "Unsafe." For both criteria, if the water content is above 20 wt%, classification is independent of the TOC content and the energetics level; otherwise, the acceptable energetics or TOC level varies depending on the water content.

For a tank to be classified as Safe, no minimal control of tank configuration is required to maintain the water content at or above 20 wt% or to satisfy the energetics or the TOC criteria. If control of tank configuration is required to satisfy the safety criteria, then the waste is categorized as Conditionally Safe; 13 wastes were identified in this category. Such Conditionally Safe tanks require controls to ensure that fuel concentrations that would promote the onset of propagating exothermic reactions would be prevented. If the waste does not satisfy any of the criteria, the waste would be classified as Unsafe and action would be required to increase the water content or reduce the fuel (TOC) content and return the waste to the Conditionally Safe category; no wastes were identified in this category.

Water content in the stored Hanford wastes depends on a number of factors, including the chemical composition of the waste, the water partial pressure (P_{H_2O} [the plural is spelled out to avoid the confusing P_{H_2O} s]) in the tank's atmosphere, and the ability of gaseous water to migrate through the waste. The chemical composition is determined by the type of waste that was added to the tank and chemical reactions that have occurred between the waste components themselves and between the waste and the atmosphere to which it was exposed during storage. The ability of water to migrate throughout the waste can be affected by the reaction of the waste with carbon dioxide in the air to form sodium carbonate, which can reduce the permeability of the waste (Strachan 1975). The P_{H_2O} within the tank's atmosphere will be at least partially determined by whether the tank is passively or actively ventilated; the former will limit the exchange of air between the tank and the Hanford environment, but the latter will actively control the exchange. The ability of water to migrate throughout the waste can be determined by the chemical nature of the waste and its interaction with the atmosphere; reactions between components in the air and in the waste could result in crusts that could limit exchange of water between the waste and the tank's atmosphere.

Because of the importance of water for preventing or mitigating the hazards associated with an exothermic reaction in the organic-bearing wastes coupled with the recognition that exposure of these wastes to the arid Hanford air or the removal of drainable liquids from these wastes could result in wastes that do not satisfy the preliminary safe storage criteria (Webb et al. 1995), PNNL, in continuing support of WHC's efforts to ensure continued safe storage of these wastes, developed and demonstrated a method to measure the equilibrium water content of stored radioactive wastes exposed to the range of water partial pressures that these wastes might experience during their years of future storage. The developed method was adapted from the commonly employed procedure of exposing material to an atmosphere whose P_{H_2O} is controlled by aqueous saturated salt solutions at a controlled temperature and monitoring the water absorption or loss gravimetrically.

We used a two-step strategy to develop a method for determining the equilibrium water content of wastes stored in Hanford's high level radioactive waste storage tanks during their years of future storage. First, to develop the method and to gain an understanding of the various factors that control water content in Hanford wastes, we exposed 1) selected potential waste components, 2) surrogate wastes prepared from these potential components, and 3) a simulated Hanford organic-bearing waste to a range of water partial pressures controlled by saturated salt solutions at temperatures ranging from ambient ($\sim 20^\circ\text{C}$) up to 65°C and monitored their water content, assuming that changes in mass were due to water absorption or desorption. Secondly, we demonstrated the method using waste from the chemically reactive waste sample obtained from Organic Watch list Tank 241-T-111 (T-111) (Hanlon 1996).

This report provides the developed method, the results from the T-111 demonstration, and the ancillary results on the water retention behavior of potential waste components obtained during the development effort. Also discussed are the effects of exposure to arid Hanford air on the water content in wastes and the application of a simple model using the independent behaviors of measured chemical constituents to predict the equilibrium water content of Hanford wastes.

2.0 Background

The need to determine the effect of water content in the gas phase on the water content of the organic-bearing wastes arises from the nature of the organic-bearing wastes, the possibility that the waste constituents could react exothermically with each other, the role of water as an effective agent for preventing exothermic reactions in these wastes, and exposure to the arid Hanford environment, which could cause the waste to dry. The amount of water that will be retained by wastes depends on the nature of the chemical bonding between the waste constituents and water in addition to other factors. This section discusses briefly the nature of Hanford's organic-bearing wastes, the factors controlling chemical reactivity between organics and nitrates and/or nitrites, the nature of water that could be present in the waste, and the water content of the air at the Hanford Site.

2.1 Nature of Hanford Organic Wastes

The Hanford organic-bearing wastes in the USTs have diverse compositions (Strachan, Schulz, and Reynolds 1993; Klem 1990). The added organics include 1) the Plutonium Uranium Recovery by Extraction (plant) (PUREX) solvent and diluent (30 vol% tributyl phosphate [TBP] in normal paraffin hydrocarbon [NPH]); 2) TBP radiolytic and hydrolytic degradation products dibutyl phosphate (DBP), monobutyl phosphate (MBP), butanol, and phosphoric acid; and 3) organic complexants, such as ethylenediaminetetraacetate (EDTA), hydroxyethylethylenediamine-triacetate (HEDTA), hydroxyacetate (glycolate), citrate, and tartrate. As Delegard (1980; 1987), Camaioni et al. (1994; 1995), Barefield et al. (1995; 1996), Bryan et al. 1992, and Meisel et al. (1991a; 1991b; 1992; 1993) discovered in their studies using simulated wastes and Campbell et al. (1994) observed for the waste in SY-101, the organics originally present in the Hanford wastes are susceptible to degradation by radiolysis, oxidation by the inorganic oxidants nitrate and nitrite, and hydrolysis resulting in a plethora of other organics in the Hanford wastes; these reactions where the nature of the organic has been altered are commonly called "aging." In addition, the organic-bearing HLW usually contains inorganic constituents, including sodium hydroxide, that were added to neutralize the acidic wastes and to make the wastes chemically compatible with the carbon-steel USTs, metal fission products, other process additives, such as iron and nitrate, and nitrite that was added as a corrosion inhibitor or resulted from radiolysis of nitrate.

The wastes are also susceptible to reaction with environmental components such as CO_2 in the air. These reactions can affect the water content both by forming hygroscopic materials such as NaCO_3 that can form three different hydrates depending on temperature and by reducing the permeability of the waste (Strachan 1975). This reduced permeability could restrict gas flow and the ability of gaseous water to migrate throughout the waste.

With respect to water content in Hanford wastes, Toth and his coworkers (1995) estimated the moisture and organic contents of the wastes stored in all of the 149 Hanford single-shell storage tanks (SST) by statistically analyzing available moisture- and organic-content data for Hanford tanks based on the physical character of the stored wastes (liquid, sludge, or saltcake). Toth et al. found that the median moisture content in the liquid phase in the SSTs ranged from about 50 to about 85 wt% water, with the

concentration of the "worst 5%" of the liquid wastes ranging from about 30 to 70 wt% water; Toth et al. define the "worst 5%" as the 5% of the waste that has the highest total organic carbon and the lowest water contents. For the saltcake phase in SSTs, the median moisture content ranged from about 8 to about 50 wt%, with the water concentration in the worst 5% of the saltcake waste ranging from 6 to 35 wt%. For the sludge phase, the median moisture content in SSTs ranged from about 30 to about 65 wt%, with the water concentration in the worst 5% of the sludge waste ranging from 9 to 44 wt%. Toth and his coworker's analysis indicates a wide variability in the moisture contents in Hanford wastes stored in SSTs, some of which may be due to sampling and analytical artifacts.

2.2 Factors Controlling Chemical Reactivity Hazards

Chemical reactivity hazards are controlled by several thermochemical and physical factors, such as the amount of energy produced by a reaction, the rate at which energy is produced, and the rate at which heat is dissipated from the system (Sharkey et al. 1992). For the organic-bearing wastes, factors that will determine the energy produced include fuel concentration, the chemical nature of the organic fuel, oxidant concentration, the nature of the oxidant(s), and the chemical reaction mechanism. The rate at which energy is produced will be controlled by the fundamental reaction kinetics of the organic reaction with nitrate or nitrite or air for near-surface fuel, catalytic properties of waste constituents, catalytic properties of the containment vessel, and the temperature of the system. The heat capacities of the waste constituents (the heat required to raise the temperature one degree), the energy required for physical transitions of waste constituents, the thermal conductivity of the waste, its containment, and the surrounding soil will be among the factors controlling heat dissipation and the temperature of the system during a reaction.

Water, which is a common constituent of the Hanford wastes, is an effective agent for absorbing and transferring heat and thus can mitigate the consequences of an exothermic reaction (Burger 1995) or can effectively prevent propagation of an exothermic reaction (Fauske et al. 1995). Burger found that water, based on theoretical thermodynamic evaluations, was the most effective potential waste constituent for minimizing the temperature that would be reached due to exothermic reactions between various organics and nitrate and/or nitrite under adiabatic conditions. Experimentally, Fauske and his coworkers showed that mixtures of the organics sodium acetate or sodium HEDTA and sodium nitrate-sodium nitrite (4:1 mass ratio $\text{NaNO}_3:\text{NaNO}_2$) containing >20% water could not support a propagating reaction in their tube propagation test, independent of the organic's concentration. Fauske's results are consistent with earlier work by Beitel (1976b) that found that charcoal and sodium nitrate mixtures (1:4 ratio) having 22 wt% moisture would not support combustion; Beitel did report (1976c), when summarizing all of his studies on organic and nitrate reactivity (1976a; 1976b), that a stoichiometric charcoal and nitrate mixture containing up to 22 wt% moisture would support a combustion reaction.

2.3 Nature of Water in Wastes

The water in the Hanford wastes could be found in the waste as adsorbed water on the surfaces of the waste particles, or water in the interstices between the particles, or as waters of hydration. The first water type likely will be bound to the solid compounds in the waste by weak electrostatic bonding, such as hydrogen bonding or by Van der Waals bonding (Shoemaker and Garland 1967; Moore 1972). The second type of water is part of a saturated solution that will fill the free space between the waste particles;

the transition between the first two types of water will be gradual as additional water is adsorbed or is lost. The water of hydration is a ligand within a chemical complex and will experience full chemical bonding; because it is an integral part of a chemical complex, this water will usually be the most difficult to remove (require the most energy) and should contribute less to the P_{H_2O} above the waste than the more weakly bound types of water, unless the temperature exceeds the decomposition temperature of the complex. A thermogravimetric analysis (TGA) of a hydrated salt would indicate distinct regions of chemical stability where little or no water is lost, such as is illustrated by Duval's (1963) presentation of a TGA of $CuSO_4 \cdot 5H_2O$.

Figures 2.1 and 2.2, created using data from Adamson (1964) and Glasstone (1948), illustrate the effect that P_{H_2O} has on a typical hydrated metal salt-free water system ($CuSO_4 \cdot xH_2O$). Figure 2.1 shows

Figure 2.1. Effect of Water Content in Hydrated Copper Sulfate on Equilibrium P_{H_2O} at 25 and 50°C

Figure 2.2. Phase Diagram for Water Copper Sulfate System and an Example of the Effect of Adding Water at 40°C

how the P_{H_2O} would change as a solution of copper sulfate is evaporated at 25 and 50°C. Figure 2.2 provides a phase diagram for the water-copper sulfate system.

As Figure 2.1 shows, once the water content in a solution of copper sulfate has been reduced to the level corresponding to 5 waters, the P_{H_2O} above the hydrated salt remains constant as the waters of hydration are lost. For example, at 50°C, as the pentahydrate $[5(H_2O)]$ loses water and becomes the trihydrate $[3(H_2O)]$ —the $[5(H_2O)]$ to $[3(H_2O)]$ line—the P_{H_2O} remains constant at 42 torr or P/P^0 of 0.45, which is equivalent to the relative humidity (RH); P is partial pressure and P^0 is the pressure at temperature at a RH of 100% or saturation; it is important to recognize that P_{H_2O} is an absolute measure of water concentration that can easily be converted to other concentration units such as moles/L. As the trihydrate loses water to

become the monohydrate $[1(\text{H}_2\text{O})]$, the $P_{\text{H}_2\text{O}}$ remains constant at 24 torr. Similarly, the $P_{\text{H}_2\text{O}}$ over the monohydrate is 4.6 torr. If the temperature were much above 50°C where the pentahydrate is unstable (see Figure 2.2), the first plateau would be the $3(\text{H}_2\text{O})$ to $1(\text{H}_2\text{O})$ equilibrium.

Figure 2.2 presents the equilibrium relationships between the different phases of the water-copper sulfate system. Along any of the equilibrium lines, this two component system (water and CuSO_4) has three phases in equilibrium (solid, liquid $[l]$, and vapor $[V]$), which, based on the Gibbs phase rule, leaves one degree of freedom that can vary, temperature or pressure. For example, adding water to the system at a constant temperature of 40°C to the anhydrous salt would cause the $P_{\text{H}_2\text{O}}$ to increase until the $[1(\text{H}_2\text{O})]$ to $[0(\text{H}_2\text{O})]$ line (point a) is reached. The $P_{\text{H}_2\text{O}}$ would remain constant until sufficient water was added to convert the anhydrous copper sulfate to the monohydrate, at which time the pressure would begin to rise again. Adding more water would cause a similar behavior at each of the other equilibrium lines. When point (d) is reached, a solution phase appears that remains saturated until no more solid pentahydrate exists. The solution line $5(\text{H}_2\text{O})$ to Saturated Solution to V is approximated. Above a temperature in the vicinity of point (A), the pentahydrate no longer exists, and the trihydrate would dissolve. The same behavior would be shown by the lower hydrates, but at much higher temperatures. At some point below 0°C , the solution would solidify to a mixture of ice and the pentahydrate. Along the $5(\text{H}_2\text{O})$ to $3(\text{H}_2\text{O})$ to V line, the pentahydrate and trihydrate are in equilibrium with water vapor.

Absorbed water is the other expected form of water in the Hanford wastes. This water likely will be bound to the waste particles by hydrogen bonding. Figure 2.3 presents the partial pressure isotherms at various temperatures for the water-NaOH system where strong hydrogen bonding would be expected, but no distinct hydrate forms. As illustrated in this figure, increasing water content in the mixture results in a gradual increase in the water vapor pressure in contrast to the step-type relationship observed for the hydrate system presented in Figure 2.1.

Fauske and coworkers (1995), based on their experimental studies and theoretical evaluations of the effect of moisture on the capability of an organic-bearing mixture to support a propagating reaction, postulate that at moisture contents above 20 wt%, a water and nitrate solution will be the continuous phase. This implies that the temperature of the reaction front could not exceed the boiling point of the nitrate-saturated solution ($\sim 130^\circ\text{C}$), which is well below the temperature required to ignite an organic and nitrate mixture ($\sim 250^\circ\text{C}$). It should be noted that Scheele et al. (1995), using accelerating rate calorimetry, observed a self-supporting reaction under adiabatic conditions in dried simulated organic-bearing waste (PAS94) beginning near 150°C .

Fauske et al. (1995) also postulate that, based on their laboratory experiments with NaOH and NaNO_3 , the moisture content in wastes would be controlled by NaOH content at relative humidities $<75\%$ and by $\text{NaNO}_3/\text{NaNO}_2$ at relative humidities $>75\%$. This assumes that these constituents are the major waste components and that no interactions exist between these two materials and other constituents in the waste. Based on their work, Fauske et al. predict, using this simple model, that at the Hanford Site average RH of 55%, 7 wt% NaOH (presumably on a dry basis) in the waste would result in an equilibrium water content of about 20%, and at an RH of $>75\%$ in the tank's head space, the waste would contain an equilibrium moisture content equal to the mass of $\text{NaNO}_3/\text{NaNO}_2$. Our results for NaOH and a mixture of NaNO_3 and NaNO_2 are presented in Sections 4.2.2 and 4.2.3, respectively.

Figure 2.3. Effect of Water Content (Weight Fraction) on the P_{H_2O} over Mixtures of Sodium Hydroxide and Water

Other studies relating to the absorption of water by materials expected in Hanford wastes is limited; however, we found some reports discussing the absorption of water by molten nitrates. Although waste temperatures during storage should never reach those required to melt the nitrates in the wastes, these studies provide some insight into the chemistry of water absorption by nitrates.

Consistent with the Fauske et al. (1995) observation regarding the absorption of water by $NaNO_3$, others have observed the affinity of various nitrates for water, even in their molten state. In a study of the molten ammonium nitrate-water system, Keenan (1957) observed lower-than-expected water-vapor pressures and attributed them to weak hydrogen bonding between water and nitrate. Bertozzi (1967) found appreciable reversible water solubility in liquid $LiNO_3$ - $NaNO_3$ or $-KNO_3$ mixtures with no hydrolysis occurring; Bertozzi reported enthalpies (ΔH s) for water absorption at 265°C for lithium, sodium, and potassium nitrates of -52, -41, and -34 kJ/mole water, respectively, with those for the sodium and potassium salts being extrapolated values. Bertozzi concludes that the solubility of water vapor is much greater than that of non-polar gases in these same molten nitrates. Tripp and Braunsein (1969) found results consistent with those observed by Bertozzi for the lithium nitrate, potassium nitrate, and water system with an average ΔH of water vaporization of 43 kJ/mol in the temperature range 119 to 150°C; the enthalpy of vaporization for pure water at 135°C is 39 kJ/mol. This sampling of work on the interactions between water and nitrates indicates that water is capable of forming weak but stable bonds with nitrate salts.

In similar work in support of the Hanford effort to ensure that the ferrocyanide wastes are stored safely, Armstrong, Freeman, and Kovach (Postma et al. 1994) found that the amount of water absorbed by a simulated Hanford ferrocyanide waste was determined by the P_{H_2O} above the simulant. This simulated waste, which is composed principally of $NaNO_3$ and $NaNO_2$ and sodium nickel ferrocyanide (Jeppson and Wong 1993; Jeppson and Simpson 1994), when exposed to vapor pressures ranging from 7 to 21.4 torr at 25°C (30 to 90% RH), contained from 4 to 65 wt% water or 4 to 1.9 g H_2O /g dry solids. Their data indicate that a P_{H_2O} of 14 torr at 25°C (60% RH) would be required to achieve the 20 wt% water content in the waste postulated to preclude a propagating reaction.

In earlier experimental studies in support of waste management operations at Hanford, Barney (1976), found that the P_{H_2O} above solutions saturated in $NaNO_3$, $NaNO_2$, $NaAlO_2$, Na_2SO_4 , and Na_2CO_3 depended on the NaOH concentrations. Barney found equilibrium partial pressures of water ranging from 10 to 2.2 torr at 20°C and 140 to 10 torr at 80°C above solutions having NaOH concentrations ranging from 1.1 M to saturation (16 to 27 M depending on temperature), respectively. At the average ambient Hanford Site P_{H_2O} (calculated by Barney to be 4.5 torr, based on Stone, Jenne, and Thorp's [1972] reported average dew point), Barney's results indicate that a high sodium salt waste will at 17°C begin to deliquesce above a NaOH concentration of 6.4 M; it should be mentioned that conversion of an average dew point to P_{H_2O} will not provide the average P_{H_2O} because of the non-linear relationship between P_{H_2O} and dew point. At the P_{H_2O} for air in contact with the soil (15 torr at 17°C), Barney's work indicates that these waste solutions will deliquesce at all NaOH concentrations with the final water content depending on the waste temperature.

In other work of interest, Piekhokin and Bobrovskaya (1970) investigated the composition of the ternary systems of $NaNO_2$ -NaOH- H_2O and $NaNO_3$ -NaOH- H_2O on equilibrium water P_{H_2O} , and Dibrov, Mal'tsev, and Mashovets (1964) investigated the effect of NaOH and aluminate concentration on the P_{H_2O} above the solutions. Piekhokin and Bobrovskaya conclude that $NaNO_3$ and $NaNO_2$ have a similar dehydrating ability in relation to sodium hydroxide and that the two salts do not differ in their effect on the behavior of water in these two ternary systems. Dibrov, Mal'tsev, and Mashovets found complex behavior in effects of sodium hydroxide, sodium aluminate, and water concentrations on the equilibrium vapor pressure above these systems.

2.4 Hanford Environmental Conditions

One of the primary factors that will determine the water content of Hanford's organic-bearing wastes besides the chemical composition of the wastes themselves and the waste's temperature is the P_{H_2O} in the head space above the waste. The P_{H_2O} in the head space depends on the transfer of water between the waste and the head space, and the transfer of water from the external environment to the head space. The rate of transfer of gases from or to the tank's head space depends primarily on whether the tank is actively or passively ventilated. In the case of active ventilation, the gas above the waste is continuously replaced with Hanford ambient air. For the tanks that are passively ventilated, the exchange of arid Hanford environmental air with the air in the tank is more complex with the exchange dependent on the size of the ports or vents to the environment and the relative densities of the gases in the tank and the environment; Huckaby, Babad, and Story (1994) report that the atmospheric exchange rate for the passively ventilated

C-103 is on an average day about 0.46% of the headspace. Diffusion of gaseous water from or to the head space could also control or help control the transfer of gases to or from the waste.

In all likelihood, the largest reservoir of gaseous water and/or the driest air to which the waste will be exposed is the Hanford air. Thus in the long term, the water content in Hanford air will control the water content in Hanford organic wastes. We calculated the average monthly water partial pressures for 1980 to 1995 by converting the meteorological dewpoint records obtained from KW Burk of PNNL's Meteorological Group to water partial pressures (presented in Figure 2.4) to determine the average P_{H_2O} of the air to which the waste may be exposed. Figure 2.4 also provides the range of P_{H_2O} that occurs at Hanford during a particular month as error bars. The conversion to P_{H_2O} , which is an absolute measure of water concentration, was necessary because one cannot average dewpoints to obtain average water contents in air. The saturated water content is determined by a non-linear relationship with temperature. A similar problem exists with averaging RH since it depends on the saturated water content and temperature.

As can be seen by inspecting Figure 2.4, the average monthly P_{H_2O} varies from a minimum of about 3.5 torr in January and December to a maximum of about 7.5 in July and August. The minimum observed in this time frame is about 2.5 while the maximum is about 9 torr. Thus the P_{H_2O} that the waste will be exposed to at equilibrium will range from 2.5 to 9 torr, with the average being near 5.5 torr, depending on the transfer mechanisms for gas into and out of the tank.

Relative humidity is commonly used to express the water content of a gas; however, RH depends on the temperature of the water content relative to the saturation pressure of water. The temperature of the tank's head space will depend on a complex relationship between the temperature of the waste, the soil temperature, the temperature of the external air, the rate of mixing in the head space, and the rate of gas exchange between the head space and the environment. The amount and rate of exchange will be controlled by a number of factors, including gas pressure and temperature differentials between the head space and outside the tank.

In general, ambient Hanford air and the tank head space are at different temperatures with additional temperature variations within the head space itself. Therefore, the average Hanford RH is not the same average RH to which the waste is exposed. However, the air entering the tank head space does have the same P_{H_2O} as Hanford air. But, due to the non-linearity of RH with respect to P_{H_2O} , the average P_{H_2O} can not be calculated from the average Hanford RH. Therefore, P_{H_2O} (not RH) must be used when considering the transfer of water between the Hanford environment and the tank head space.

Figure 2.4. Average Hanford Monthly P_{H_2O} 1980-1995 (Data Provided by KW Burk of PNNL's Meteorological Group)

3.0 Experimental

This section presents and discusses the experimental approach used to develop the method for determining the equilibrium water content of wastes exposed to various partial pressures of water, the apparatus and the methods that we used to control the P_{H_2O} exposure level, the materials used for the development effort, and a brief history of the radioactive waste used to demonstrate the developed method on a radioactive waste sample.

3.1 Experimental Approach

In general, the approach taken to determine the equilibrium water content of Hanford wastes at potential storage conditions was to expose duplicate samples to a known P_{H_2O} at the surface temperature of the waste and to monitor the samples' masses until they stabilized; this approach relies on the assumption that the observed mass change is due to water absorption or desorption. This assumption should be valid because most Hanford tank wastes contain no more than trace quantities of volatile constituents; an exception is the waste stored in C-103 with its floating layer of liquid organic (Huckaby, Babad, and Story 1994). To eliminate the need for this assumption, the analytical methods would need to be refined to identify and quantify the volatile species.

The samples were placed in an airtight vessel that contained a saturated solution with a known P_{H_2O} . The samples were removed from the vessels and weighed at approximately 8, 24, 48, 72, 96, and 168 h and then every 3 to 4 days until their masses stabilized. When all of the samples' masses stabilized, the samples exposed to the highest and lowest water vapor pressures were switched to reverse conditions and weighed approximately every 3 days until a stable mass was reached.

To measure the water content of the starting and final materials after exposure to the water vapor, we used a slight modification of the primary method employed by the PNNL analytical laboratory^(a) to determine solids content in Hanford wastes. We supplemented it with TGA; the PNNL procedure is based on the U.S. Environmental Protection Agency (EPA 1989) procedure for solids determination. As our primary method to determine water content, we dried the samples at 105°C for 24 h as provided by the EPA procedure; however, we continued to monitor sample mass on a daily basis until the sample mass stabilized. Thermogravimetric analysis was used to determine water content only for samples exposed to the highest and lowest partial pressures of water after the initial exposures were complete and occasionally after drying at 105°C; the TGA of the dried material was to confirm that little or no free water remained in the sample and to determine whether hydrates were present. Our application of these two mass loss methods for determining water content assumes that all observed mass loss was due to water loss; analysis by infrared (IR) or mass spectroscopy (MS) of the thermally evolved gases during a TGA would

(a) The method used was Procedure PNL-ALO-504, "Percent Solids Determination of Soils/Sludges/Solids." This procedure is in PNL-MA-599, *Analytical Chemistry Laboratory (ACL) Procedure Compendium, Vol 6: Physical Testing*, Pacific Northwest National Laboratory, Richland, Washington.

confirm whether or not the mass loss is water loss. We did this for glycolate and laurate (discussed later in Section 3.4.1). We do not have the capability to monitor the evolved gases from radioactive samples.

3.2 Experimental Apparatus and Control of $P_{\text{H}_2\text{O}}$

Based on previous studies showing that saturated salt solutions can be used to control $P_{\text{H}_2\text{O}}$ in sealed systems (Wexler and Seinfeld 1991; Greenspan 1977; Broul 1981; Wagman 1982), we prepared five water vapor exposure chambers providing water partial pressures ranging from 1.7 to 21.8 torr at 25°C using saturated solutions of NaOH, CaCl_2 , NaBr, KCl, and KNO_3 . The duplicate, approximately 1-gram samples of each test material were weighed into each of ten 20-mL scintillation vials, placed in desiccators, and supported above the saturated salt solution by a plastic stand (Figure 3.1). To ensure that sufficient water was present and that the $P_{\text{H}_2\text{O}}$ remained at the desired level, we used an approximately 20:1 volume ratio of saturated solution to sample.

To control the temperature for measurements requiring temperatures above room temperature, we placed the sealed desiccators in a constant, controlled temperature oven. For measurements at room temperature (20 to 22°C), we used no special temperature controls nor did we use refrigeration to provide temperatures below room temperature; the lowest expected temperature of stored wastes is the ambient soil temperature of 17°C (Barney 1976).

Figure 3.1. Schematic of Constant Humidity Chambers Used for Testing

Most nonradioactive work was conducted in 3-L desiccators sealed on smooth glass joints with silicone grease. All actual waste testing and some nonradioactive testing was conducted in 500-mL screw-top desiccators with either Teflon® or paper seals.

Because the water partial pressures above these saturated salt solutions increase with temperature, and the referenced previous studies did not determine P_{H_2O} over the full temperature range of tank waste temperatures 17 to 65°C, we used the apparatus presented in Figure 3.2 to measure the water partial pressures above these saturated salt solutions to confirm and extend the temperature range from 25 to 65°C.

To quantify the effects of temperature on the P_{H_2O} over the temperature range of interest, the solutions were placed in 250-mL plastic jars with screw-top lids, holes were cut in the lids, a humidity sensor, a Vaisala HMP 233 HUMICAP H-sensor, was sealed in place over the saturated salt solutions with silicone rubber, and a thermocouple was used to monitor the solution temperature that was maintained within $\pm 1^\circ\text{C}$. The jars were placed in a laboratory oven, and an air-driven stirrer was used to mix the solutions; the air used to drive the stirrer was vented outside of the oven to prevent cooling the oven. The system was monitored until a stable solution temperature, headspace temperature, and RH were reached. Each increase in temperature, between 5 and 10°C, required approximately 2 h to reach the new equilibrium using the stirrers, compared to about 4 h in the absence of stirrers. Stirrers were not used for the waste components, surrogate wastes, simulated waste, and actual waste equilibrium water content determinations because the shortest sampling period was established at 8 h.

Figure 3.2. Schematic of System Used to Measure the Relative Humidities above Saturated Salt Solutions between 25°C and 65°C

Vaisala, the manufacturer of the humidity-measurement system, calibrated the HMP 233 temperature to $\pm 0.2^\circ\text{C}$ and the RH to $\pm 1\%$ between 0% and 90% RH, and $\pm 2\%$ between 90% and 100% RH. Relative humidity was then converted to vapor pressure of water using Equation 3.1 and the temperature measured by the HMP. Table 3.1 provides the reference (Lide 1993) and measured water partial pressures. Figure 3.3 provides the measured $P_{\text{H}_2\text{O}}$ over six saturated solutions as a function of temperature; the error bars in Figure 3.3 provide the variability associated with the instrument given above. The BaCl_2 saturated solution was not used for sample testing because it provided no advantage over KNO_3 solution. Comparison of the measured $P_{\text{H}_2\text{O}}$ over the KCl , NaOH , CaCl_2 , BaCl_2 , NaBr , and KNO_3 saturated solutions and those reported by Lide (1993) shows essentially the same partial pressures within the instrument's variability. For this report, we chose to use our measured water partial pressures, supplementing them with those provided by Lide below 25°C .

$$P_{\text{H}_2\text{O}} = \text{RH} \times P_{\text{T(H}_2\text{O)}}/100 \quad (3.1)$$

where

$P_{\text{H}_2\text{O}}$ is the partial pressure of water over the solution

RH is the measured relative humidity

$P_{\text{T(H}_2\text{O)}}$ is the vapor pressure of pure water at the respective temperature.

Table 3.1. Reference (Lide 1993) and Measured Partial Pressures of Water over Saturated Solutions Used for Constant Humidity Baths

Salt Solution	Data Source	$P_{\text{H}_2\text{O}}$, torr											
Temperature $^{\circ}\text{C}$		15	20	22	25	30	35	40	45	50	55	60	65
NaOH	Lide	0.77	1.05	1.19	1.43	1.91	2.52	3.31	4.29	5.52	7.03	8.88	
	This Work				1.71	2.2	2.83	3.54	4.32	5.18	6.03	6.73	7.13
CaCl_2	Lide	4.4	5.42	5.89	6.68	8.18	9.91						
	This Work				7.3	7.6	9.0	10.8	12.5	14.8	19.0	24.0	31.2
NaBr	Lide	7.63	10.3	11.5	13.7	18.0	23.5						
	This Work				14.1	18.3	23.3	29.2	36.3	44.9	6.4	71.3	89.3
KCl	Lide	11.0	4.9	16.8	20.0								
	This Work				20.2	26.6	34.5	44.4	56.5	71.6	89.7	112	138
BaCl_2	Lide	11.6	15.9	17.9	21.4								
	This Work				21	28	38	48	63	79	100	126	160
KNO_3	Lide	12.1	16.3	18.4	21.8	28.9	37.8	49.1	63	80.3			
	This Work				22	29	38	48	62	77	97	119	146

Figure 3.3. Measured Partial Pressures of Water above Saturated Salt Solutions of NaOH, CaCl₂, BaCl₂, KCl, and KNO₃

3.3 Determination of Water Content

To determine the water content in the ferric hydroxide, sodium hydroxide, sodium nitrate/nitrite, sodium laurate, sodium glycolate, the three surrogates, the simulant, and the waste sample taken from T-111 after exposure to the various partial pressures of water, we used two gravimetric methods and the assumption that the measured mass loss was due to water loss. The primary method was oven drying to a stable mass at 105°C and the supplementary method was TGA; in some cases the oven-dried material was analyzed using TGA. Interpretation of the results from both of these methods assumes that the mass lost below a certain temperature is water; this assumption is not always valid as observed for sodium laurate (discussed later in this section).

After the samples reached a stable mass in the water vapor exposure study, vials exposed to low humidity and high humidity were sub-sampled for TGA analysis. A combination TGA and differential thermal analyzer (DTA) was used for this analysis. The TGA measures mass changes as the temperature is changed at a known and constant rate, and the DTA measures temperature differences between the sample and a reference material as the temperature is changed at a known and constant rate.

The temperature calibration of the combination DTA/TGA was checked using the known melting point of an indium standard, and the balance calibration was checked with a 10 mg standard weight. The temperature and enthalpy calibration checks were all within 1°C or 0.4 J/g of their reported values, and the balance calibration was within 0.01 mg. Approximately 10 mg of each sample were placed in a

platinum pan and loaded into the instrument. The temperature was then increased from ambient to 350°C at a rate of 5°C/min and held at 350°C for 5 minutes using argon as the cover gas.

All samples were weighed and placed in a laboratory oven at 105°C, and the sample masses were monitored every 24 h until a stable mass was reached. The mass losses were assumed to be the result of changes in water content. For the experiment using waste from T-111, sub-samples were taken from samples exposed to the highest and lowest humidities and characterized using TGA.

Carbon dioxide absorption by NaOH containing mixtures is a potential source of experimental error that could lead to errors in measuring water content. Calculations show that mass changes resulting from the chemical absorption of CO₂ by the 1-g caustic samples should be just at or below the detection level in this experiment, 1 mg. The concentration of CO₂ in ambient air is approximately 350 parts per million by volume, and the volume of air in the headspace of the vessels is approximately 400 mL. Assuming that the headspace in the test vessel is completely replaced, 0.25 mg of CO₂ would be introduced into the vessel every time it is opened. Assuming two samples are in each vessel, as was the case for the T-111 testing, the vessels would need to be opened eight times with full exchange of the contained air for enough CO₂ to be introduced to cause a 1-mg change in the sample masses. In testing nonradioactive materials, each vessel contained four samples, and 16 openings would be required to produce a 1-mg increase in the sample masses.

3.4 Materials Used for Method Development and Demonstration

We developed the equilibrium water-content method using several nonradioactive potential waste components and surrogate and simulated wastes, and we demonstrated the method's use on a sample of waste stored in T-111. The potential waste components, the surrogate wastes, and the simulated organic waste used for the development effort were selected based roughly on postulated organic wastes developed by JL Sobolik and RD Scheele (Scheele et al. 1995). We used sodium laurate because of the potential that the NPH diluent in the PUREX solvent could be converted to a carboxylic acid.

3.4.1 Simulant, Surrogates, and Selected Potential Waste Components

The potential waste components used for the development effort were reagent-grade NaOH, sodium nitrate and nitrite (2:1 mole ratio), sodium glycolate (NaO₂CCH₂OH), sodium laurate (NaO₂CC₁₁H₂₃), and technical-grade sodium aluminate. We prepared the ferric hydroxide by precipitation from a 1 M Fe(NO₃)₃ solution by adjusting the pH to 11 with NaOH; TGA analysis of the dried precipitate suggests that FeO(OH) precipitated.

The simulated waste PAS94, developed by Sobolik and Scheele (Scheele et al. 1995) and based on waste management operations flowsheets to remove radiocesium and radiostrontium from PUREX acid-sludge wastes (Buckingham 1967), was used as the simulant for this work. Waste management operations to remove radiocesium and radiostrontium from PUREX wastes were a major source of the organic-bearing radioactive wastes at the Hanford Site (Strachan, Schulz, and Reynolds 1993).

The three surrogate mixtures (Mix 1, Mix 2, and Mix 3) used for this development effort contained the major inorganic PAS94 constituents (H_2O , NaOH , NaAlO_2 , ferric hydroxide, NaNO_3 , and NaNO_2) and sodium laurate or sodium glycolate. Tables 3.2 and 3.3 provide the make-up compositions of the PAS94 and surrogate mixtures, respectively. Sodium laurate, which could arise in Hanford wastes as a result of hydrolysis, oxidation, and radiolysis of the hydrocarbon diluent used at PUREX, was added to Mix 2. Sodium glycolate, which was one of the major complexants used during waste-management operations, was added to Mix 1 and Mix 3; no NaOH was added to Mix 3. The surrogate water content was adjusted to 50 wt% water by drying prepared slurries to a target mass that assumed that no chemical changes occurred during the drying process to the non-water components.

Table 3.2. Make-up Composition of Simulated Organic-Bearing Waste (PAS94)
Used for Method Development (Scheele et al. 1995)

Component	Concentration, wt%
NaOH	15.13
NaNO_3	7.40
NaNO_2	3.55
Na_2SO_4	4.19
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	2.20
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.04
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.06
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.11
$\text{Mn}(\text{NO}_3)_2$	0.03
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	0.07
$\text{Pb}(\text{NO}_3)_2$	0.20
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.23
$\text{NaAlO}_2 \cdot 0.21\text{NaOH} \cdot 1.33\text{H}_2\text{O}$	0.60
Zirconium Citrate	0.01
Sodium Glycolate	3.41
Na_3HEDTA	2.67
Na_4EDTA	1.64
Sodium Citrate $\cdot \text{H}_2\text{O}$	0.93
Sodium Tartrate $\cdot 2\text{H}_2\text{O}$	0.26
Sodium Di-2-Ethylhexylphosphate	0.34
Tributyl Phosphate	0.17
NPH	1.80
H_2O	54.98

Table 3.3. Composition of Nonradioactive Surrogate Wastes Used for Method Development

Component	Mix 1, wt%	Mix 2, wt%	Mix 3, wt%
H ₂ O ^(a)	50	50	50
NaOH	0.5	0.5	0
NaAlO ₂	0.5	0.5	0.5
FeO(OH)	0.5	0.5	0.5
NaNO ₃	24.3	30.6	24.7
NaNO ₂	9.9	12.5	10.0
Sodium Glycolate	14.3	0	14.3
odium Laurate	0	5.4	0

(a) Samples evaporated to approximately 50 wt% H₂O following homogenization

The PAS94, the three surrogate mixtures, and the selected potential waste components were studied at 22°C and 65°C. Although the non-radioactive testing was done to ensure that the method being developed would be applicable to materials in Hanford wastes, the studies of the behavior of components also provide information on the potential contribution of the waters associated with the component to the overall water content in wastes of concern. It is possible that the equilibrium water content of a particular waste could be determined using a simple model based on the individual components; a more complex model including interaction terms could be developed if necessary using a statistically based experimental design.

The results of duplicate differential scanning calorimetry (DSC) and single sample DTA/TGA analyses of sodium laurate and glycolate are presented in Figures 3.4 and 3.5 for laurate and glycolate, respectively. The results of the DTA/TGA for these two possible waste components are included here because the standard method for determining water content by drying at 105°C indicates that the sodium laurate is 25 wt% water. However, IR analysis of the gases evolved during heating found that carbon dioxide is also released, indicating that the laurate is unexpectedly decomposing. This indicates that our adaption of the standard method for determining solids content by drying at 105°C for measurement of water content does not provide an accurate measure of water content for laurate; to ensure that mass losses are properly assigned, the TGA method could be refined by analyzing the evolved gases using IR or mass spectroscopy.

The commercially-obtained sodium laurate used for our studies has several mass losses totaling 25 wt% as it is heated from room temperature up to 160°C as shown in Figure 3.4. The IR analysis of the evolved gases indicates that the gases are a combination of water and carbon dioxide. The gases lost during the decomposition observed beginning near 400°C are primarily hydrocarbons with traces of water. The 25 wt% mass loss is consistent with the loss of the carboxyl group and the loss of one water. Though not consistent with the reported melting of sodium laurate at 255 to 260°C (Bailar et al. 1973), we use a single water of hydration for the results reported and discussed in Section 4.0; possibly at the short times needed to measure the melting point, the decomposition is not observed.

Figure 3.4. Thermal Behavior of Sodium Laurate as Measured by DSC and Simultaneous TGA/DTA

Figure 3.5. Thermal Behavior of Sodium Glycolate as Measured by DSC and Simultaneous TGA/DTA (5°C/min, Ar purge)

In contrast to sodium laurate, the DTA/TGA and DSC analyses presented in Figure 3.5 indicate that sodium glycolate is stable up to beyond 225°C with no waters of hydration. We recognize that the DTA and the DSC analyses yielded conflicting results with the duplicate DSC analyses, indicating that the decomposition beginning near 250°C is endothermic while the single DTA analysis unexpectedly indicates this decomposition is exothermic; in principal, in the absence of oxidants, the decomposition of glycolate should be endothermic. We cannot explain this difference in observed energetics behavior nor do we plan to do the necessary experimental studies needed to understand the contradictory results obtained by the two instruments.

3.4.2 History of Actual Waste from Tank 241-T-111, Core 33, Segment 2

Because waste from T-111 is currently classed as an "Organic Watch List Tank" (Hanlon 1996) and the ready availability to us of the energetic waste sample obtained by Core 33, Segment 2, from T-111, we used it for our radioactive demonstration of the equilibrium water content method. The following provides a brief history of T-111.

Tank 241-T-111 was placed on the Organic Watch List in 1994 as a result of a series of DSC and TOC analyses by WHC and PNNL. Westinghouse Hanford Company found that the first three segments of Core 31 and the first two segments of Core 33 displayed exothermic events greater than 520 J/g (125 cal/g) on a dry weight basis (Simpson 1994), which exceeded the safety criteria. Additional work at PNNL during December 1993 using material from Segment 2 of Core 33 (McKinley et al. 1994) confirmed the high energetics with an enthalpy of approximately -870 J/g (210 cal/g) on a dry basis. Total organic carbon was measured as 3,500 µg/g, based on wet weight using a hot persulfate oxidation technique.

Tank T-111 was placed into service in 1945. Simpson (1994) indicates that waste was transferred in and out of the tank many times between 1945 and 1994. The initial waste stream was second-cycle decontamination waste from the bismuth-phosphate process. Tank T-111 was one tank in a cascade (Anderson 1990) where overflow wastes from one tank could flow into and from another tank. Much of the supernate was removed and disposed of in soil columns. From 1953 to 1955, lanthanum fluoride waste from the LaF₃ finishing process at T-Plant was added to the cascade. During 1952, drainage from cells 5 and 6 in B-Plant was also added to the cascade. In 1952, waste was also added to the tank from the plutonium purification-concentration processes at T Plant. Simpson (1994) points out that it is unclear if the cascade was in operation during all of these years. It is possible that some of these wastes were added directly to T-111. During the 1960s, decontamination chemicals, resulting from the T-Plant decontamination operations, were added to the tank.

Tank T-111 was removed from active service in 1974. The free, drainable liquid was removed from the bottom of the tank in 1976 during primary stabilization work. In 1984, the tank was declared an assumed leaker. Additional free liquid collected in the bottom of the tank was pumped from the tank again in 1994.

Simpson (1994) provides a detailed summary of the analytical results for Cores 31 and 33 taken from T-111. Tables 3.4 and 3.5 provide the elemental and anion concentrations as measured by inductively

Table 3.4. Elemental Concentrations in Core 33 as Measured by ICP/AES for Sample Prepared for Analysis by Acid Dissolution

Analyte	Core Composite 1, μg/g	Core Composite 2, μg/g	Segment 1, μg/g	Segment 3, μg/g
Al	472	405		
Sb	36	23		
Ca	1490	1350	4800	1100
Cr	2060	2140	490	1200
Fe	17500	17300	17300	11700
Mn	6710	6280	23900	3800
K	1210	1020		
Na	35000	36300	22400	25800
Bi	28500	28400	760	24200
La	4640	4890	3	3900
P	9860	11300	4400	4800
Si (fusion)	5460	5410		
S	1140	1220	800	720

Table 3.5. Anions in Core 33 as Measured by Ion Chromatography (IC)

Analyte	Core Composite 1, μg/g	Core Composite 2, μg/g
NO ₃ ⁻	36,900	40,100
PO ₄ ³⁻	13,600	15,100
SO ₄ ²⁻	3,290	3,470
Cl ⁻	401	432
F ⁻	1,370	1,630
NO ₂ ⁻	878	817

coupled argon plasma atomic emission spectroscopy (ICP/AES) and ion chromatography (IC), respectively, for Core 33. Core 33 composite samples 1 and 2 show that the predominant elements in T-111 waste include Fe, Mn, Na, Bi, and P. Major anions include NO_3^- , PO_4^{3-} , and SO_4^{2-} . The molar ratio of $\text{P}:\text{PO}_4^{3-}:\text{Bi}$ is approximately 1:0.45:0.43. The one-to-one ratio of Bi to PO_4^{3-} indicates that a BiPO_4 was a major component in the waste stream. As Rapko et al. suggested (1995), the ratio of P to PO_4^{3-} suggests that a major form of P in this waste is PO_4^{3-} .

The hydroxide concentration was measured by acid titration on liquid grab samples collected from T-111 in March 1994. The measured hydroxide concentration in the supernate was 3,000 $\mu\text{g/g}$ (0.18 M). We use this measurement to estimate the hydroxide concentration in the T-111 sample tested because at the measured 80 wt% water in the waste, the supernate should be a major if not the principal contributor in the sludge of free hydroxide.

4.0 Equilibrium Water Content Method and Results of Water Retention Studies

We developed and demonstrated a method to measure the equilibrium water content in wastes stored in tanks listed on Hanford's Organic Tank Watch list (Hanlon 1996) and other stored wastes having characteristics similar to the organic-bearing wastes. This section describes the developed method and discusses the effect of P_{H_2O} on water sorption and/or retention by 1) selected potential Hanford waste constituents, 2) surrogate wastes comprised of these potential waste constituents, 3) a simulated organic-bearing waste, PAS94A, and 4) a sample of waste taken from the Hanford Organic Watch List Tank T-111. The potential waste constituents used were ferric hydroxide, NaOH, a 2:1 mole ratio mixture of $NaNO_3$ and $NaNO_2$, sodium aluminate, sodium laurate, and sodium glycolate. The latter discussion on the behavior of the potential components and their mixtures, although supplemental to the objective to develop the method, provides insight into the factors that will control the water contents of Hanford wastes and could serve as a basis for a model to predict the water content of a chemically characterized waste.

4.1 Procedure for Determining the Equilibrium Water Content of Hanford Wastes

Appendix A describes in detail the method developed for measuring the equilibrium water content of Hanford wastes exposed to a range of water partial pressures that may be experienced during storage. The basic procedure is to expose duplicate 1-g samples to a range of water partial pressures at the waste's temperature by placing the sample in a sealed container whose P_{H_2O} is controlled by a saturated salt solution. The sample's mass is monitored by weighing the sample at selected times, frequently at first and less frequently with time, until the sample reaches a stable mass for three successive measurements. After reaching a stable mass, the four samples exposed to the highest and lowest partial pressures of water are switched after a subsample is removed to determine water content; the samples exposed to the highest humidity are exposed to the lowest humidity and vice versa for those samples exposed to the lowest humidity, and their masses are monitored as before. The samples' water content is determined by drying at 105°C until a stable mass is reached, using the assumption that the mass loss is due solely to water loss. The equilibrium water content of the samples is calculated based on the original samples' dry masses and the measured water loss.

The procedure only requires the following equipment: small (500 mL) commercially available screw-cap dessicators, an oven to control temperature, radiation-resistant vials to hold the samples, and a drying oven to determine the water content of the tested material as-received and after exposure to the range of water partial pressures. Although the radiation levels of the T-111 waste used for the demonstration were low enough to perform the demonstration in a laboratory fume hood, the concept and the equipment are sufficiently simple that the method could be easily adapted for use in a shielded high-level radiation facility.

4.2 Water Retention by Potential Waste Constituents, Surrogates, and Simulants

As part of the effort to develop a method to measure the equilibrium water content, we exposed several expected Hanford waste constituents, three surrogate wastes comprised of these potential Hanford waste constituents, and a simulated organic-bearing waste, PAS94, to a range of partial pressures of water. Although the goal of this work was to develop and test techniques and equipment necessary to measure the equilibrium water content, these results provide an opportunity to evaluate the simple model that assumes that each individual component will control the water content of a waste. A simple version of this model was provided by Fauske et al. (1995) when they postulated that the water of a waste could be predicted based on its NaOH, NaNO₃, and NaNO₂ contents.

The equilibrium water content reached by these materials after exposure to selected water partial pressures at 22°C and 65°C are presented, respectively, in Tables 4.1 and 4.2 and illustrated in Figures 4.1 and 4.2. Figures showing the behavior of these materials during the testing in weight-fraction water as a function of time are provided in Appendix B. The reader is reminded that the potential waste components were used as-received with no preparation, such as grinding to improve the kinetics of water transfer; the surrogate and simulant wastes began as moist materials containing nominally 50 wt% water.

Table 4.1. Average Equilibrium Water Contents of Potential Hanford Waste Components, Surrogate Wastes, and the Simulant Waste PAS94 at 22°C. Units are weight-fraction water.

Material	P _{H2O} , torr				
	1.2	5.9	11.5	16.8	18.4
FeO(OH)	0.001	0.038	0.070	0.389	0.413 ^(b)
NaOH	0.210	0.629	0.721	0.788	0.775 ^(b)
NO ₂ /NO ₃ (2:1 mole ratio)	0.000	0.000	0.000	0.593	0.640 ^(a)
Na Laurate	0.053	0.071	0.074	0.195	0.208
Na Glycolate	0.000	0.011	0.048	0.411 ^(b)	0.393 ^(b)
Mix 1	0.034	0.038	0.358	0.605	0.618 ^(b)
Mix 2	0.016	0.027	0.265	0.612	0.625 ^(b)
Mix 3	0.032	0.051	0.351	0.603	0.614 ^(b)
PAS94	0.161	0.401	0.548	0.703	0.711 ^(b)

(a) Samples did not reach equilibrium, extrapolated value.

(b) Samples did not reach equilibrium; this last measured value underestimates the final water content.

Table 4.2. Average Equilibrium Water Contents of Potential Hanford Waste Components, Surrogate Wastes, and Simulant Waste PAS94 at 65°C. Units are weight-fraction water.

Material	P_{H_2O} , torr				
	7.13	31.2	89.3	138	146
FeO(OH)	0.006	0.013	0.023	NM	0.529
NaOH	0.279	0.461	0.656	NM	0.807
NO ₂ /NO ₃ (2:1 mole ratio)	0.004	0.005	0.011	NM	0.633
Na Laurate Run 1	-0.236	-0.185	-0.009 ^(a)	0.072	0.054 ^(a)
Na Laurate Run 2			0.039 ^(a)		
Na Glycolate Run 1	0.006	0.010	0.040	0.596	0.598
Na Glycolate Run 2			0.036		
Mix 1	0.017	0.015	0.362	NM	0.709 ^(a)
Mix 2	0.002	0.012	0.264	NM	0.634 ^(a)
Mix 3	0.022	0.022	0.380	NM	0.746 ^(a)
PAS94 Run 1	0.025	0.261	0.403	NM	0.778 ^(a)
PAS94 Run 2	-0.015	0.218	0.304		

(a) Sample did not reach a stable mass.

NM = Not Measured

Figure 4.1. Effect of Water Partial Pressure at 22°C on the Water Contents of Water Mixtures of Selected Potential Hanford Waste Constituents, Surrogate Wastes, and Simulated Waste PAS94

Figure 4.2. Effect of Water Partial Pressure at 65°C on the Water Contents of Potential Hanford Waste Components, Surrogate Wastes, and the Simulated Waste PAS94

4.2.1 Behavior of Ferric Hydroxide During Exposure to Selected Water Partial Pressures

In general, as shown in Figures 4.1 and 4.2, water partial pressures in excess of those normally found at Hanford (maximum monthly average 7.5 torr) are required for ferric hydroxide to gain sufficient water for the ferric hydroxide and water mixture to exceed 10 wt% water, independent of temperature between 20 and 65°C. At 22°C, partial pressures of water exceeding 11.5 torr (58% RH) are required for the mixture to exceed 10 wt% water at equilibrium, and at 65°C, a P_{H_2O} of 146 torr (78% RH) is needed to exceed about 0.3 wt% water.

Ferric hydroxide reached equilibrium masses at 1.2, 5.9, and 11.5 torr P_{H_2O} within 900 hours, as seen in Figures B.1 and B.2. Although samples at 16.8 torr were still increasing slowly in weight-fraction water at 2200 hours, the change was less than 0.004 every 100 hours. Samples exposed to 18.4 torr did not reach a stable mass; the rate of water gain had not started to decrease when the samples were removed from the vessel at 1200 hours. At 65°C, all samples at all levels of P_{H_2O} reached stable masses within the 500 hours. Samples exposed to 7.1, 31.2, and 89.3 torr showed equilibrium weight-fractions of water below 0.03. A steep increase in the weight-fraction water was then seen with 0.529 weight-fraction water observed at 146 torr.

These results indicate that water associated with ferric hydroxide could contribute significantly to the overall water content of Hanford organic-bearing wastes, depending on the concentration of ferric

hydroxide and the P_{H_2O} in the tank's head space. But in order for the water associated with ferric hydroxide to contribute significantly to the waste's water content, the P_{H_2O} must exceed that of the normal maximum Hanford atmosphere.

4.2.2 Behavior of NaOH Exposed to Selected Water Partial Pressures

Sodium hydroxide can be one of the major components in Hanford's wastes; because of its hydrophilic nature, it could be one of the major factors that will control the equilibrium water content of the Hanford organic-bearing wastes. As discussed earlier, Fauske et al. (1995) suggest that NaOH will be one of the waste components that will dominate the factors that control the water content of these wastes. For these reasons, we decided to use NaOH during the method-development stage of our work.

In general, our studies, consistent with those of Barney (1976) and Fauske et al. (1995), indicate that waters associated with NaOH can be a significant contributor to the water content in the organic wastes, with its contribution depending on the NaOH concentration and temperature. Figures 4.1 and 4.2 show that of all of the materials studied, NaOH absorbs more water than any other material. At 22°C, a P_{H_2O} of 1 torr (lower than any measured P_{H_2O} at Hanford) will result in a water and NaOH mixture containing 20% water. At 65°C the maximum monthly average P_{H_2O} at Hanford will result in a mixture containing over 25% water.

The amounts of water that we measured that are associated with NaOH at various partial pressures of water at 22°C are comparable to those obtained by Fauske and coworkers (1995) (See Table 4.1). Our work shows that at equilibrium at 22°C, the NaOH and water mixtures had water weight-fractions of 0.210, 0.629, 0.721, 0.788, and 0.775 at partial pressures of 1.4, 6.9, 13.8, 20.0, and 21.9 torr, respectively, which compare favorably with Perry and Chilton's (1973) reported equilibrium water-fractions of 0.49, 0.65, 0.75, 0.86, and 0.93 at these same partial pressures of water. Values at 1.2 and 21.9 torr are lower in this work because the samples exposed to these two humidities did not reach equilibrium after 2200 h (see Figure B.3).

When we tested equipment and methods at 65°C, we exposed samples of NaOH for approximately 500 hours to a range of partial pressures of water. The measured moisture values (weight-fraction) after this time were 0.279, 0.461, 0.656, and 0.807 at water vapor pressures of 7.1, 31.2, 89.3, and 146 torr, respectively. Our values again compare well with interpolated values from Perry and Chilton's (1973) equilibrium weight-fraction water contents of 0.33, 0.55, 0.68, and 0.81, respectively. The plot of weight-fraction water as a function of time, presented in Figure B.4, suggests the samples exposed to 7.1 torr of water were not at equilibrium and still gaining water when the samples were removed from the vessels, explaining the lower-than-expected value at this pressure. A repeat of the 65°C experiments, using single samples and adding a 138-torr bath, presented in Figure B.5, is consistent with the results of the first experiments, with the possible exception that the sample exposed to 7.1 torr resulted in a 20 wt% water mixture compared to 28 wt% in the original experiment.

For a Hanford waste to contain 20 wt% water due to water associated with NaOH, the waste would need to contain significant quantities of NaOH. Using the results of our studies presented in Figures 4.1 and 4.2 for NaOH, a Hanford waste having a temperature between 22 and 65°C would require between

15 and 60 wt% NaOH on a dry basis for the waste to contain 20 wt% water at equilibrium, with the average Hanford atmosphere having 5.5 torr of water. At 22°C, the equilibrium NaOH and water mixture is about 56 wt% water (1.3 g H₂O/g NaOH); therefore, for the waste to contain 20 wt% water, the waste would need to be about 15 wt% NaOH on a dry basis. At 65°C, extrapolating the data presented in Figure 4.2, a mixture of NaOH and water exposed to 5.5 torr of water would be about 25 wt% water or 0.33 g H₂O/g NaOH. For a waste at 65°C to contain 20 wt% water due to its NaOH content, the waste would need to be 60 wt% NaOH on a dry basis, which, based on the postulated 30 wt% NaOH content of the saltcake waste PAS, shown in Table 3.4, is much higher than would be expected in most Hanford wastes. At higher waste temperatures, partial pressures of water greater than the average ambient Hanford P_{H₂O} of 5.5 torr would be required to maintain the 20 wt% water safety criterion.

The equilibrium water contents observed for NaOH indicate that water associated with NaOH could be one of the major contributors to the water content of Hanford's organic-bearing wastes, depending, of course, on the NaOH concentrations in the waste. These studies also indicate that the rate at which equilibrium is reached depends on the P_{H₂O} and temperature.

4.2.3 Behavior of a NaNO₃/NaNO₂ Mixture Exposed to Selected Partial Pressures of Water

As shown in Figures 4.1 and 4.2, the mixture of NaNO₃ and NaNO₂ did not absorb water at low partial pressures of water, but absorbed significant amounts of water when exposed to higher partial pressures of water. Partial pressures of water in excess of the maximum observed at Hanford are required before NaNO₃ and NaNO₂ begin to gain associated water.

In our experiments at 22°C, the sample mixture of NaNO₃ and NaNO₂ gained no water when exposed to 1.4, 5.9, and 13.8 torr of water at 22°C; however, when exposed to 16.8 torr, the equilibrium mixture reached 59.3 wt% water as shown in Figure B.6. This sharp rise in water content is similar to that reported by Fauske et al. (1995) for NaNO₃ at 25°C. The samples exposed to 18.4 torr did not reach equilibrium before being switched to the lowest-humidity vessel. The reported weight-fraction water value of 0.640 (listed in Table 4.1) for the 18.4 torr exposure was the lowest and, therefore, most conservative estimated water content obtained by fitting several different equations to the observed water content versus time behavior (Figure B.6).

The results obtained for the exposure experiments at 65°C indicate that NaNO₃ and NaNO₂ mixtures exhibit behavior similar to that observed at the lower temperatures, with little water absorption at lower partial pressures of water and a large absorption at higher partial pressures of water. At 65°C, the NaNO₃ and NaNO₂ mixture gained only to a 0.011 weight-fraction water when exposed to 89.3 torr of water. As at 22°C, 65°C also appears to have a threshold P_{H₂O}; the first indication of an increased affinity for water was observed at 146 torr of water, which yielded a mixture having 0.633 equilibrium weight-fraction water.

Our results indicate that at average Hanford environmental humidities and nominal waste temperatures, water associated with the NaNO₃ and NaNO₂ should contribute little to the water content of

Hanford wastes, assuming that no interactions exist among the different waste constituents. These results do indicate that if exposed to higher humidities, significant amounts of water will be associated with these two salts.

4.2.4 Behavior of Sodium Laurate Exposed to Selected Partial Pressures of Water

Sodium laurate (sodium dodecanate) resembles a class of organic compounds that may be formed by aging the PUREX hydrocarbon solvent. The determination of water in this organic salt is complicated by the thermal instability of the salt at temperatures normally used for water determination in Hanford waste samples. Because of this instability, we corrected the stable masses that are determined by drying at 105°C to account for the assumed total loss of CO₂ under these conditions.

As discussed earlier, the TGA results indicate that one water of hydration is associated with the sodium laurate at room temperature, provided that the water content is 7.5 wt%. At environmental water partial pressures observed at Hanford, pure sodium laurate will not gain additional waters of association. At higher temperatures that may be found in some wastes, the first water of hydration is lost, even at water vapor pressures exceeding ambient Hanford environmental conditions. At near-ambient temperatures, sodium laurate could contribute waters of association to the water content of a waste containing this organic salt.

The sodium laurate results at 22°C, presented in Tables 4.1 and 4.2 and Figures 4.1, 4.2, and B.8, show equilibrium weight-fraction waters of 0.071 and 0.074 at 5.89 and 11.5 torr, respectively. This is followed by a transition to 0.195 and 0.208 weight-fraction water at 16.8 and 18.4 torr. One water of hydration would calculate to 0.075 weight-fraction water, and three waters of hydration to 0.196 weight-fraction water. This stepped change indicates a transition from one water of hydration at 11.5 torr to three waters of hydration by 16.8 torr. Thermogravimetric data presented in Section 3.4.1 suggest that sodium laurate decomposes between 65°C and 160°C with the loss of one water and one CO₂.

The first data set collected for samples of sodium laurate exposed at 65°C, presented in Figure B.9, showed anomalous behavior with negative values at 89.3 torr and below. The weight-fraction waters of -0.236 and -0.185 at 7.1 and 31.2 torr, respectively, were reached after an onset period that differed from the two different pressures, but was similar for duplicates at the same pressure. This onset behavior suggests a complex decomposition mechanism that may depend on the water concentration in the surrounding air or suggests that the decomposition is self-catalyzed. Samples rerun at 89.3 torr (shown in Figure B.10) did not reproduce the result of the first data set, but both data sets at this pressure were not followed until a stable mass was reached.

The results of our studies indicate that sodium laurate, if present, could affect the water content in Hanford wastes exposed to ambient partial pressures of water at Hanford. If the waste's temperature exceeds the decomposition temperature of sodium laurate, waters associated with sodium laurate should contribute little to the waste's water content.

4.2.5 Behavior of Sodium Glycolate Exposed to Selected Partial Pressures of Water

In general, at Hanford environmental water vapor pressures, sodium glycolate absorbs little water (mixtures contain < 5 wt% water at equilibrium) independent of temperature. As with many of the other salts examined in this effort, significant water is absorbed only at partial pressures exceeding ambient Hanford conditions.

Sodium glycolate exposed to a $P_{\text{H}_2\text{O}}$ of 11.5 torr or less at 22°C resulted in mixtures with water contents less than 5 wt%. Sodium glycolate samples exposed to 18.4 and 16.8 torr at 22°C achieved 40 and 42 wt% water after 1200 hours and 2200 hours, respectively, as shown in Figure B.11. These two samples continued to gain water even after this exposure time. The sodium glycolate does not show the stable regions that indicated waters of hydration as seen with sodium laurate, with the exception that approximately 0.60 weight-fraction water was found for both 138 and 146 torr samples at 65°C. This value of 0.60 calculates to 8.17 water molecules for every sodium glycolate molecule.

The results indicate that if exposed to ambient Hanford air, sodium glycolate would not contribute significant amounts of associated water to the waste's overall water content. Further, if waste containing sodium glycolate were to be exposed to humidities equal to or exceeding 11.5 torr at near 20°C or at 138 torr or greater at 65°C, then sodium glycolate would absorb significant relative quantities of associated water.

4.2.6 Behavior of NaAlO_2 Exposed to Selected Water Partial Pressures

As illustrated by the results presented in Figures 4.1, 4.2, B.14, B.15, and B.16, the absorption of water by sodium aluminate is quite complex, possibly due to the hydrolysis of the aluminate as the water is absorbed (Parke 1939); the interpretation is complicated by the material after exposure to water having a greater mass after drying at 105°C than the starting material. Because the behavior of the sodium aluminate varied during the experiments, as shown in Figures B.14 through B.16, and the material never did appear to reach an equilibrium water content, no equilibrium water contents are reported in Tables 4.1 and 4.2 nor presented in Figures 4.1 and 4.2.

As shown in Figure B.14, sodium aluminate exposed to various partial pressures of water at 22°C showed large water weight gains during the first 200 hours, reaching stable masses after exposure to 1.2 and 5.9 torr. The indicated water contents in these mixtures were about 1 and 18 wt% water, respectively. The rate of water absorption in the remaining vessels slowed while their masses continued to increase. The indicated water content in the resulting mixture reached over 60% water for the samples exposed to 16.8 and 18.4 torr; these samples were still gaining weight at 2200 hours when the test was terminated.

At 65°C, all sodium aluminate samples in all of the vessels showed an initial rise in weight-fraction water followed by a decline, as shown in Figures B.15 and B.16. The indicated water content in the samples exposed to 7.1 torr of water was less than 0; however, exposure to water partial pressures ranging from 31.2 up to 146 torr caused the material to gain sufficient water to yield indicated water contents ranging from near 10 to near 60 wt%. The second set of tests at 65°C, which was performed for a longer time (over 1100 hours compared to 500 hours for the first set), indicated that water loss began after about

350 hours at all humidities except 7.1 torr. Although insufficient testing was conducted to determine the cause for the decline, it is likely that sodium aluminate is being converted to a mineral form, possibly gibbsite or bohemite.

With respect to sodium aluminate's influence on the waste's water content, our studies indicate that at nominal Hanford environmental humidities, sodium aluminate will absorb significant quantities of water at 20°C and will contribute to the overall water content of the waste. Significantly higher humidities are required at 65°C for sodium aluminate to absorb water. In addition, the results at 65°C suggest that over long periods of time, the amount of water associated with the sodium aluminate will decrease, even at 20°C, assuming that the same mechanism causing the mass loss observed at 65°C exists at 20°C, but is not observed due to a slow reaction rate.

4.2.7 Behavior of Surrogate Waste Mixtures Exposed to Selected Water Partial Pressures

In general, exposure of the surrogate wastes studied to humidities near ambient Hanford environmental humidities resulted in water contents of less than 10 wt%, independent of the temperature studied (see Tables 4.1 and 4.2 and Figures 4.1, 4.2, B.17, B.18, B.19, B.20, B.21, and B.22). At water partial pressures equal to or above 11.5 torr at 22°C for all three surrogates, ≥ 89.3 torr for Mix 1 and Mix 3, and 146 torr for Mix 2, the surrogates had equilibrium water contents in excess of 30 wt% water.

The surrogate waste mixtures, which originally contained 50 wt% water (see Table 3.3), as shown in Table 4.1, gained water at 22°C when exposed to 16.8 and 18.4 torr of water, and lost water at 11.5, 5.9, and 1.2 torr, resulting in equilibrium water contents ranging from 1.6 to about 60 wt% water, depending on the surrogate. As shown in Figures B.17 through B.22, samples exposed to 18.4 torr did not reach a stable mass within the 1200 hours they were left in the 18.4-torr vessel. Samples in the 1.2-, 5.9-, and 11.5-torr vessels reached stable masses within 1200 hours. Samples in the 16.8-torr bath reached a nearly stable mass by 2200 hours, although all samples appeared to be gaining some additional mass slowly. At 65°C, all except the 146-torr samples reached a stable mass within the first 500 hours.

The results obtained at both 22 and 65°C indicate that wastes having these compositions would contain less than the 20 wt% water safety criterion at the average Hanford P_{H_2O} of 5.5 torr. At 22°C, all three mixtures when exposed to 11.5-torr water pressure finished with large amounts of water of 36, 27, and 35 wt% water, respectively. Given that these surrogates are predominantly $NaNO_3$ and $NaNO_2$, it is unexpected that the equilibrium water content would be this high as inspection of Table 4.1 shows that the threshold for retention of water by $NaNO_3$ and $NaNO_2$ is above 11.5 torr water; this suggests that interactions occur between the surrogate waste constituents that reduce the water activity. The results obtained at 65°C also show a deviation from the observed behavior of $NaNO_3$ and $NaNO_2$ with the surrogate wastes achieving a higher water content at lower water partial pressures than the nitrate and $NaNO_2$ mixture (89 vs 146 torr, respectively). This is discussed in more detail later in Section 4.2.9.

Comparing the results for the different mixtures shows significant differences between Mix 2 and Mixes 1 and 3 at 11.5 torr at 25°C and 89.3 torr at 65°C; the behaviors are similar at the other water partial pressures. The difference between Mix 2 and Mix 1 is the nature of the organic salt with laurate in Mix 2 and glycolate in Mix 1; both have the same total organic carbon content, which introduces more

sodium into the glycolate mixtures. The difference between Mixes 1 and 3 is the presence of NaOH in Mix 1, although this difference does not appear to significantly affect the relative behavior of these two mixtures. These observed differences in behavior between the mixtures could be due to differences in the nature of the organic, interactions between the different components, and/or in the amount of sodium in the waste. Additional work would be required to understand the reasons for the difference in behavior.

In general, the results obtained for the waste surrogates indicate that the water content of a waste depends on its composition, and the water content cannot be predicted solely on the independent behavior of a waste component. The results also suggest that by controlling relative humidity in the head space by humidifying the inlet air, the water content of a complex mixture can be controlled.

4.2.8 Behavior of PAS94 Exposed to Selected Water Partial Pressures

The simulated organic-bearing waste PAS94 is a complex mixture of a variety of compounds (Table 2.2), some of which we did not examine in the method-development effort. Figures 4.1 and 4.2 suggest that the behavior of PAS94 is controlled by the NaOH, which is present in the simulant at about 30 wt% on a dry basis. The qualitative similarity is also observed by comparing Figure B.3 (NaOH) with Figure B.23 (PAS94) and Figure B.4 (NaOH) with Figures B.24 and B.25. As with NaOH, each P_{H_2O} resulted in a different water content, ranging from 16.5 up to 71 wt% water at 22°C and near zero to between 60 and 80 wt% water at 65°C. In general, this suggests that the NaOH in the simulant dominates the factors controlling the water content in the PAS94.

The indicated importance of NaOH in controlling the water content in Hanford wastes raises the importance of the consumption of NaOH by the absorption of carbon dioxide by wastes from the air. In our experiments, as mentioned earlier, the amount of carbon dioxide that was absorbed was minimized because of the use of sealed containers; however, Hanford wastes have been exposed to unlimited amounts of air during their years of storage, which could have neutralized the NaOH in the waste, limiting its importance in controlling water content. Because of this real and potential conversion, sodium carbonate and bicarbonate are additional waste components that could play a major role in controlling water content.

If the waters associated with the NaOH, $NaNO_3$, and $NaNO_2$ were the only materials controlling the water content of the PAS94, then the water contents at 22°C exposed to 1.2, 5.9, 11.5, and 16.8 torr would be, respectively, 6.7, 30, 35, and 42 wt%, which are less than the measured 16, 40, 55, and 70 wt% water. This comparison indicates that water associated with other components contributes significant amounts to the water content in the PAS94. A detailed description of the calculations used to predict the waters associated with NaOH, $NaNO_3$, and $NaNO_2$ is provided in Appendix C.

At 22°C, PAS94 behaved similarly to the surrogate mixtures, losing water from its original 55 wt% at 1.2, 5.9, and 11.5 torr and gaining water at 16.8 torr and 18.4 torr, as shown in Figure B.23. After 2200 hours, the water contents were 16.1, 40.1, 54.8, 70.3, and 71 wt%, respectively; the samples in the 16.8-torr bath reached a nearly stable mass by 2200 hours, although both duplicate samples appeared to be gaining some additional mass slowly.

At 65°C, PAS94 samples, with the exception of the 7.1- and 146-torr samples, reached a stable mass within the first 500 hours. The 65°C PAS94 samples were rerun because of the potential that the samples exposed to the highest and lowest partial pressures had not reached equilibrium; the results of these experiments are presented in Figure B.25. This re-analysis was performed with fresh samples and showed that although many of the samples in the first analysis appeared stable at 500 hours, samples at all partial pressures experienced additional water loss out to at least 1200 hours. The initial increase in water content at 146 torr followed by a drop indicates that components within the PAS94 could be reacting with each other. PAS94 is a complex mixture that was not formulated to be stable at 65°C. These "aging" concerns are not anticipated to be a problem in the actual waste testing, because actual wastes are tested at their in-tank temperatures where most significant self-reactions should have already occurred.

With respect to the long-term water content of Hanford wastes exposed to ambient Hanford humidities, the results obtained in this examination indicate that a waste with a composition similar to PAS94 having a substantial NaOH content (30 wt% dry basis) will contain significant quantities of water (>16 wt% water) if the temperature of the waste is near 20°C or less; however, the waste will dry out at temperatures approaching 65°C.

4.2.9 Comparison of Behaviors of Potential Waste Constituents and Surrogate Mixtures

A potential method to accurately predict the water content of a waste, based on its composition, is to assume that the water content will be determined by the water associated with each of the individual components at a particular P_{H_2O} . To assess the feasibility of using this simple model to predict water contents in waste, we calculated and compared the predicted water contents of the three surrogate wastes with the measured water contents. The step-wise results of the calculations are presented in Appendix C.

The data collected at 22°C for the individual components and the surrogate mixtures were compared to see how individual component data could be used to predict the behavior of more complex mixtures. This comparison was limited to the partial pressures 1.2, 5.9, 11.5, and 16.8 torr, at which most materials reached equilibrium water contents in our experiments.

For the comparison, the contributions of the individual components were calculated, assuming that no interactions existed between the different components that would affect the final water content. In the first step of the calculation, the wt% of the individual components in the surrogate mixtures was adjusted to account for water gained or lost during the equilibration process. The results of this calculation are listed in Tables C.1 through C.4 for 1.2, 5.9, 11.5, and 16.8 torr, respectively.

The weight-fraction water for each component at 22°C listed in Table 4.1 was then used to calculate the contribution of water to the three mixtures. The results for this calculation are listed in Tables C.5 through C.8. The final weight-fraction water is summarized in Table 4.3.

As shown in Table 4.4, in only one case does the predicted water content based on the expected contributions of the individual components match the measured water contents in the surrogate wastes. In all other cases, the measured water contents are greater than the predicted water contents. The differences are particularly striking for the mixtures exposed to 11.5 torr water. At 11.5 torr, the observed

Table 4.3. Observed and Calculated Equilibrium Water Content of Surrogate Waste Mixtures at 22°C. Units are in wt% water.

P_{H_2O}	Mix	Calculated	Observed
1.2	1	0.265	3.4
1.2	2	0.865	1.6
1.2	3	0.008	3.2
5.9	1	2.18	3.8
5.9	2	2.70	2.7
5.9	3	0.54	5.1
11.5	1	3.11	35.8
11.5	2	3.14	26.5
11.5	3	1.47	35.1
16.8	1	50.8	60.5
16.8	2	57.1	61.2
16.8	3	50.1	60.3

Table 4.4. Water Absorption by $NaNO_3$ and $NaOH$ as a Function of P_{H_2O}

Relative Humidity, %	P_{H_2O} , torr	Water Absorption (21°C), g H_2O ^a / g $NaNO_3/NaNO_2$	Water Absorption (20°C), g H_2O ^c / g $NaOH$
6	1.4	0	1.03
29	6.9	0	1.85
58	13.8	0	2.94
84	20.0	1.46	6.25
92	21.9	1.78 ^(b)	12.5

(a) Reported in this work.

(b) Extrapolated from incomplete data set.

(c) Calculated from data listed in Perry and Chilton (1973).

weight-fraction water is an order of magnitude higher than the calculated values. Since all components and mixtures were tested at the same temperatures in the same vessels, temperature effects and/or variations between vessels can be ruled out. This higher-than-calculated water content is most likely the result of interactions between the components within the surrogate mixtures. One interaction that may alter the water content is a common ion effect involving sodium. However, common ion effects would be expected to decrease the water content by reducing the solubility of the components. Increased solubility would increase the sodium concentration in solution and thus would be expected to reduce the water activity, increasing the equilibrium water content in the material.

This comparison of predicted with actual water contents suggests that a rough estimate of water content can be made based on the composition of the waste, provided detailed information on the individual components is known. However, as the results for the three surrogates at 11.5 torr indicate, significant errors can occur if no consideration is given to interactions between the individual components. Because of this one result, it is clear that the equilibrium water content of individual components, assuming independence of these components, can not be used to predict the water content of complex mixtures, although more refined models may provide more accurate data. For these mixtures, the interaction(s) typically resulted in an underestimation of the water content by shifting the absorption curve to lower partial pressures of water. Data in this work are insufficient, however, to say that underestimation will always be the case. In more concentrated salt solutions, common ion effects could result in overestimations.

4.3 Behavior of Waste from Tank T-111 Exposed to Selected Water Partial Pressures

We used waste from Core 33, Segment 2, taken from T-111, to demonstrate the procedure developed by this effort to determine the equilibrium water content of wastes stored in USTs listed on the Organic Tanks Watch List. This section provides the T-111 waste's water content as a function of time as it was exposed to a range of water partial pressures at room temperature and the equilibrium water content as a function of P_{H_2O} .

For this determination, the bulk sample was homogenized by hand stirring using a spatula. One-gram samples were weighed into ten 20-mL glass scintillation vials. Two sample vials were placed in each of the five 500-mL vessels containing approximately 75 mL of a particular saturated salt solution and sealed. The five saturated salt solutions, NaOH, $CaCl_2$, NaBr, KCl, and KNO_3 , have water vapor pressures at 20°C of 1.0, 5.4, 10.3, 14.9, and 16.3 torr, respectively; pure water has a vapor pressure of 18.1 torr, so these partial pressures of water correspond to 5.5, 29.9, 57.0, 82.3, and 90.1% RH at 20.5°C. The samples were placed in a fume hood and protected from drafts to equilibrate at room temperature ($20.5 \pm 0.5^\circ C$) because the maximum temperature measured in T-111 is 18°C (Hanlon 1996), near the ambient Hanford soil temperature (Barney 1976).

The samples were removed for 53 days at selected intervals from the controlled humidity chambers and weighed. The test's environmental temperature, measured each time the samples were weighed, varied between 20 and 21°C. The water content in the T-111 samples exposed to the different partial pressures of water as a function of time is shown in Figure 4.3. The T-111 waste samples exposed to

water partial pressures of 1.0, 5.4, and 10.3 torr reached stable masses within the first 500 hours, resulting in water contents after equilibration of 4, 13, and 20 wt%, respectively. The final equilibrium water contents are summarized in Figure 4.4. Samples exposed to 14.9 torr of water stabilized at 44 wt% water after 1200 hours. The samples exposed to 16.3 torr of water vapor remained at 62 wt% water, neither gaining nor losing water.

Figure 4.3. Effect of P_{H_2O} and Time on the Water Content of Waste Obtained from T-111 by Core 33 Segment 2

Figure 4.4. Effect of P_{H_2O} on the Equilibrium Water Content of Waste Taken from T-111 by Core 33 Segment 2

Based on our measured water absorption results for NaOH and NaNO₃/NaNO₂ (summarized in Table 4.4), we estimated the water contents in T-111 waste that should be associated with the 0.67 wt% NaOH and 5.1 wt% NaNO₃/NaNO₂ found in the T-111 waste (Simpson 1994) at the five water partial pressures used. The predicted water contents at these five water partial pressures due to absorption by NaOH and NaNO₃/NaNO₂ are 0.69, 1.2, 2.0, 11.6, and 17.5 wt%, respectively. These predicted water contents are well below the measured 4, 13, 20, 44, and 62 wt% water for the T-111 waste obtained by Core 33, Segment 2, indicating that some other chemical constituents or that interactions between the different waste constituents are controlling the equilibrium water content of the T-111 waste.

The results presented in Figure 4.4 indicate that at equilibrium with ambient Hanford environmental water partial pressures, the waste obtained by Segment 2 from T-111 will have a water content ranging from about 5 to about 19 wt%. At the average Hanford P_{H₂O} of 5.5 torr, the equilibrium water content should be 13 wt% water. This suggests that if the P_{H₂O} in the tank's head space is allowed to come into equilibrium with ambient Hanford conditions, the waste in the layer obtained by Segment 2 will dry from its current 80 wt% water to an average of 13 wt% water.

Other constituents that could affect the water absorption by Hanford wastes include hydrous metal oxides, such as the ferric hydroxide discussed earlier, sodium phosphate that forms stable hydrates with 10 or 12 waters, sodium sulfate that forms hydrates with 7 or 10 waters, and sodium carbonate that forms stable hydrates with 1, 7, or 10 waters. The T-111 waste sample taken by Core 33 contains about 1.4 wt% phosphate and 0.3 wt% sulfate. The hydrous metal oxides might be important because of possible complexation of the OH⁻ by metals in the waste that could reduce the OH⁻ activity and thus its capability to absorb and bind water. Alternatively, the organics in a waste could complex the transition metals, freeing OH⁻ and increasing the capability to absorb and bind water. This lack of correlation between the agents suspected of being the primary materials that would control water content in Hanford wastes (Fauske et al. 1995) and those that we selected for study indicates that other potential major waste ingredients, such as sodium sulfate, phosphate, carbonate, or bicarbonate, need to be studied.

As mentioned earlier, we used a simultaneous DTA/TGA to provide a second measure of water content in the samples after exposure to the high and low water partial pressures. The results of the TGA and DTA analyses (5°C/min, Ar purge) for the equilibrated T-111 waste samples are shown in Figures 4.5 and 4.6, respectively. The two figures also provide the differential of the TGA (DTG), which often helps the interpretation of the TGA and DTA results. The TGA and DTA results also provide some insight into the nature of the sorbed water as to whether it is water of hydration or is associated water.

The TGA and DTA results for the T-111 waste exposed to 16.3 torr of water (presented in Figure 4.5) indicate that the majority, if not all, of the water (the 50 wt% loss observed to 120°C) appears, because of the slow gradual mass loss and absence of stability plateaus in the TGA and DTA, to be associated water and not water(s) of hydration. An additional smaller mass loss occurs after 120°C; however, the nature of this mass loss is unknown and is also observed for the T-111 waste samples exposed to 1 torr of water (see Figure 4.6).

The gradual mass loss observed between 40 and 150°C by the TGA (presented in Figure 4.6) for the T-111 waste exposed to 1 torr of water suggests that the water in this sample is likely associated water

Figure 4.5. Thermal Behavior of T-111 Waste Obtained by Core 33, Segment 2, after Exposure to 16.3 torr H_2O as Measured by Simultaneous DTA and TGA ($5^\circ\text{C}/\text{min}$, Ar purge)

Figure 4.6. Thermal Behavior of T-111 Waste taken by Core 33, Segment 2, after Exposure to a 1 torr H_2O as Measured by DTA/TGA ($5^\circ\text{C}/\text{min}$, Ar purge)

and not water of hydration. As with the sample exposed to the high humidity, this material also loses mass above 120°C , and the nature of the mass loss is unknown. The DTA suggests that this mass loss could be due to the exothermic reaction reported between 110 and 390°C (McKinley and coworkers);^(a) interpretation of the DTA is difficult given the variability in the baseline for the method. The DTA suggests that an endothermic reaction begins near 250°C with no associated mass loss; mixtures of NaNO_3 and NaNO_2 melt between 225°C (eutectic) and 308°C (NaNO_3). Melting crystalline salts, such as NaNO_3 and NaNO_2 , which are in the waste, might be causing this reaction.

(a) *Tank 241-T-111 Core 33 Data Report*, by S.G. McKinley, R.T. Steele, J.M. Tingey, and M.W. Urie. Letter Report to Westinghouse Hanford Company, Richland, Washington, January 10, 1994.

5.0 Conclusions

A method that is simple in concept and implementation has been developed for determining the equilibrium water content of organic-bearing wastes stored in Hanford's HLW storage tanks. These wastes may be exposed to a range of different partial pressures of water during their years of future storage, either due to intrusion of ambient Hanford air into the tank or during potential waste-management operations. This method consists of exposing wastes to a controlled-humidity atmosphere at a controlled temperature in a sealed container. The P_{H_2O} in the container is controlled using a saturated salt solution that has a sufficient excess of water to preclude loss of humidity control. The method is easily adaptable to provide additional water vapor pressures by using other saturated salt solutions or other materials that provide a known and constant P_{H_2O} . This method was successfully demonstrated using a simulated Hanford waste, surrogate mixtures, and selected pure compounds that may be in Hanford tank wastes. The method was tested on one actual radioactive waste sample obtained from T-111 by Core 33, Segment 2.

Ancillary information gathered during the development effort indicates that at environmental Hanford humidities, most materials absorb and retain little water that would increase the water content of the waste to the desired 20 wt%. The results of the testing indicate that the water content of the waste can be controlled through controlling P_{H_2O} .

The studies of the pure potential waste constituents indicate that with the exception of NaOH and $NaAlO_2$, these tested materials, assuming no interactions between components, will have little water associated with them at ambient Hanford humidities. Should the P_{H_2O} in the tank's head space become equal to ambient Hanford humidities, these materials will contribute little to maintaining the water content of the wastes at 20 wt% or greater. The studies of $NaAlO_2$ indicate that the water content of the $NaAlO_2$ and water system is quite complex and unpredictable. As would be predicted, higher water vapor pressures are required at higher temperatures for these potential waste constituents to gather water.

Our studies of water partial pressure on the water content of the surrogate wastes, simulated waste PAS94, and T-111 waste found that materials other than NaOH, $NaNO_3$, and $NaNO_2$ can significantly affect the water content in Hanford wastes. The results of the T-111 demonstration test, when compared to predicted water contents arising from NaOH, $NaNO_3$, and $NaNO_2$ contents in the waste, indicate that the waters associated with these three materials will not necessarily dominate or be the sole controlling agents in Hanford's high-level radioactive wastes. The equilibrium water content of T-111 waste is approximately 15% percent higher than would be predicted if NaOH, $NaNO_3$, and $NaNO_2$ were the only species controlling the water content. The higher measured than predicted T-111 waste results suggest that interactions between the waste components or other constituents such as phosphate and sulfate that are principal waste constituents also affect the T-111 waste's water content. Additional studies would be required to identify the waste constituents that are major contributors to the water content of Hanford wastes.

The surrogate waste studies also indicate that humidities greater than those found at the Hanford site are required to achieve water contents in excess of 10 wt%. At the environmental humidities found at

Hanford, these surrogate wastes lost water. The surrogate testing also showed that in almost all cases, a simple model based on the known independent behavior of the neat component provides only an approximate and typically low estimate of the equilibrium water content of the waste. Unfortunately, these studies indicate that interactions occur between the independent materials, rendering the simple, independent factor inaccurate in some cases. A predictive model could be developed using a statistically based parametric study to investigate the predominant waste constituents that could be used to more accurately estimate water contents based on the chemical characterizations of a waste.

In contrast to the results obtained for the surrogate wastes that contained little NaOH, the results of the PAS94 test indicate that Hanford wastes similar to this simulant, which had a nominal NaOH content of 30 wt% on a dry basis, will gather sufficient water when exposed to ambient Hanford humidities to maintain a water content >16 wt% if the waste's temperature is near 20°C or less; however, at temperatures approaching 65°C, the waste will dry out when exposed to Hanford humidities. Given the short experimental time relative to the time that these wastes have been and will be stored and our control of air influx into the experimental vessels, it is not known how high-content NaOH wastes will behave in the long term with respect to affecting water content after years of exposure to atmospheric CO₂ and conversion to carbonate and/or bicarbonate.

These ancillary results show that each potential waste constituent has a unique effect on the amount of water that will be contained by wastes. For example, NaOH has an effect over the entire range of partial pressures studied, while NaNO₃ and NaNO₂ have a threshold P_{H₂O} above which they begin to gather waters of association. Other materials studied also exhibit this threshold behavior.

6.0 Recommended Future Work

Based on the results of our FY 1996 studies investigating the response of potential waste components, mixtures of potential waste components, a simulated waste, and waste from T-111, we are recommending that studies be performed to

- determine the responses of actual stored wastes to the partial pressures of water that the waste may experience during storage
- determine the behavior of additional major potential waste constituents
- determine the behavior of mixtures of the major waste constituents when exposed to a range of water partial pressures to support development of a more detailed predictive model
- investigate controlling the water content of wastes at particular waste depths by controlling the P_{H_2O}
- explore the effect of atmospheric CO_2 on the hydroxide concentration in waste mixtures to better predict the water content and to determine the effect of CO_2 absorption on the transfer of water vapor.

Continuing to determine the equilibrium water contents of actual individual wastes is important for understanding the potential consequences of exposure to Hanford humidities or how these wastes will react to varying partial pressures of water that they may experience during storage or potential mitigation activities. Knowing whether these wastes will retain sufficient water to preclude propagating reactions as defined by Fauske et al. (1995) will provide a basis for developing a strategy for each individual waste to ensure its continued safe storage.

Our FY 1996 studies indicated that the water content of a complex mixture totally or partially consisting of these materials could be conservatively (less than actual) estimated based on the individual component's concentration; however, these studies also indicated that the water content of complex mixtures is controlled by other unstudied potential waste constituents, such as sodium sulfate, sodium phosphate, sodium carbonate, sodium bicarbonate, and hydrous metal oxides or by interactions between the different components. Because these unstudied materials can be major waste components, we are recommending that studies be done to determine their individual potential effect on water content. In addition, we recommend that interactions among all the major waste components be investigated to provide a more refined and accurate predictive model for a waste's water content. Understanding the factors or materials that control the water contents of Hanford wastes will provide an estimate of the equilibrium water content of a waste based on the measured chemical composition of the waste obtained by waste characterization.

Because the equilibrium water contents in Hanford wastes are sensitive to the P_{H_2O} to which they are exposed, treating wastes with a controlled humidity gas is potentially an attractive and easy method for controlling the water content of the wastes while avoiding formation of free-flowing liquid; avoiding free-flowing liquid is desirable to prevent leakage of waste from the USTs that may be leakers. By controlling

the P_{H_2O} that a waste is exposed to, the water content can either be increased or decreased to a desired level, potentially without the formation of flowing water. We did not investigate the physical waste characteristics, such as particle size or porosity, that could affect the kinetics of water sorption or desorption or migration to depths below the waste's surface. We are recommending that studies be done to help assess whether treatment of wastes with controlled humidity atmospheres would be an effective method to control the water content in Hanford wastes.

With NaOH being the most absorbent potential waste constituent, its conversion to sodium carbonate or bicarbonate could play a significant role on the equilibrium water content of waste exposed to air for several years. This exposure could result in both chemical and physical changes that could affect how much water that an alkaline waste would contain. Investigating the effect of atmospheric CO_2 absorption on the water content of Hanford wastes is important for understanding the effect that years of storage exposed to air will have on the water content of a waste and the porosity of waste.

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Appendix A

Procedure for Determining the Equilibrium Water Content of Hanford Tank Waste as a Function of Water Vapor Pressure

Appendix A

Procedure for Determining the Equilibrium Water Content of Hanford Tank Waste as a Function of Water Vapor Pressure

A.1 Applicability

This method measures the water content of material by monitoring changes in sample mass during exposure to a constant water vapor pressure; as a result, this method cannot be applied to material containing volatile species or materials that are reactive with water or air. The equilibrium water content values determined under this procedure can be applied to the wastes as they are currently stored. Long-term processes including absorption of CO_2 from the dome space and self-reaction within the waste may result in a waste with a different equilibrium water content.

A.2 Materials

20-mL screw-cap vials (10)
500-mL screw-top desiccators (5)
Silicone grease
Saturated salt solutions (5)-NaOH, CaCl_2 , NaBr, KCl, and KNO_3
Laboratory oven
Laboratory Balance accurate to ± 0.001 g

A.3 Procedure

1. Add one of the five saturated salt solutions to each of five desiccators (NaOH, CaCl_2 , NaBr, KCl, and KNO_3). Be sure to add sufficient salt to maintain saturation at the temperature to be examined. The level of the solution should not reach the support tray in the desiccator.
2. Apply silicone grease to the threads on the desiccators. This will keep the threads clean and prevent the salt solution from freezing the desiccator shut.
3. Seal the desiccators and place them in a preheated laboratory oven. The temperature of the oven will depend on the temperature of interest for the study.
4. Check the desiccators at intervals to be sure they will remain saturated at the chosen temperature. The intervals will depend on the time required for the desiccators to preheat and the salts to reach the new solubility equilibrium.

5. Weigh ten uniquely labeled 20-mL screw-cap vials. Record the mass of the caps and vials separately. Record the mass to a milligram.
6. Weigh approximately 1.0 g of material into each of the 10 screw-cap vials. Record the masses to the nearest milligram. Be careful not to confuse the caps. Caps are to remain on the vials when the vials are not in the desiccators.

Alkaline wastes will react with CO_2 from the air and form carbonate. While the desiccators do not have sufficient headspace to trap enough CO_2 to cause a measurable mass change, samples left exposed to room air for extended time periods could be compromised.

7. Place two open vials in each of the desiccators and close the lids. Record which samples were placed in which desiccators. Place the desiccators in the preheated laboratory oven.
8. Place the vial lids in a storage location that will allow them to remain clean and dry.
9. At the following intervals, remove the samples from the desiccators, replace the lids, and record the mass (M_i), time and date: 8 hours, 1 day, 2 days, 4 days, 8 days, 10 days, and once a week until all eight samples reach a stable mass. Return the open samples to the desiccators and the lids to storage.

A stable mass is defined as a change of less than 3 mg in 3 days.

10. Once the samples have reached a stable mass (M_o), swap the samples between the NaOH and KNO_3 desiccators.
11. At the following intervals, remove the samples from the NaOH and KNO_3 desiccators, replace the lids, and record the weight, time, and date: 8 hours, 1 day, 2 days, 4 days, 8 days, 10 days, and once a week until all 4 samples reach a stable mass. Return the open samples to the desiccators and the lids to the jar.
12. Once the samples in the NaOH and KNO_3 desiccators have reached a stable mass, subsample them for TGA analysis. Record the mass of the vials before and after subsampling.
13. Reweigh all ten samples, remove the caps, and place them in a laboratory oven preheated to 65°C for approximately 3 hours; then raise the oven temperature to 105°C . If samples are taken directly from room temperature to 105°C , some sample could be lost because of boiling.
14. Every 24 hours, remove the samples from the oven, replace the lids, and record the mass, time, and date. Return the open samples to the oven until a stable mass (M_{dry}) is reached.

15. Once the samples in the oven reach a stable mass, subsample the samples that were in the NaOH and KNO₃ desiccators with TGA analysis. Record the mass of the vials before and after subsampling.
16. Analyze the eight subsamples collected for TGA analysis. The TGA analysis is to be conducted under an N₂ or argon cover gas in platinum pans. The oven should be programed to increase from ambient temperature to 350°C at a rate of 5°C per minute and hold at 350°C for 5 minutes.

A.4 Calculations

A.4.1 Samples in CaCl₂, NaBr, and KCl Desiccators

The equilibrium water content of the samples is determined by subtracting the oven dried mass from the equilibrium mass and dividing the result by the equilibrium mass. The resulting value is the equilibrium weight-fraction water.

$$\text{Weight-Fraction Water} = (M_o - M_{\text{dry}}) / M_o \quad (\text{A.1})$$

where

M_o = Stable mass (step 10)

M_{dry} = Oven dried mass (step 14)

This equation has been left in terms of M_o such that a plot of weight-fraction water versus time can be generated by replacing M_o with the M_t (the sample mass at time t , step 9).

A.4.2 Samples in NaOH and KNO₃ desiccators

The samples in the NaOH and KNO₃ desiccators were subsampled for TGA before oven drying; therefore, these masses need to be corrected for the material removed.

$$\text{Weight-Fraction Water} = (M_o - M_{\text{dry}} + [M_{\text{dry}}/M_{\text{wet}}] \times M_{\text{sub}}) / M_o \quad (\text{A.2})$$

where

M_o = Stable mass

M_{dry} = Oven dried mass

M_{wet} = Sample mass before oven drying

M_{sub} = Mass of subsample removed for TGA in Step#12

This equation has been left in terms of M_o such that a plot of weight-fraction water versus time can be generated by replacing M_o with the M_t (the sample mass at time t , step 9).

A.4.3 Plot of Equilibrium Weight-Fraction Water Versus Water Vapor Pressure

Average the duplicate samples to determine the average weight-fraction water for each of the desiccators. Use standard tables or the tables reported in this document to determine the water vapor

pressure for each saturated salt solution at the temperature of the study. Plot the average weight-fraction water on the Y-axis and the vapor pressure on the X-axis. An appropriate equation can be used to interpolate the values within the range; however, a simple curve smoothing can also be applied. Although a sample with no water should have no water vapor pressure, and a sample of pure water should have the vapor pressure of saturated air, these two points should not be added to the collected data and used to extrapolate to vapor pressures or weight fractions beyond the range of the analysis.

A.4.4 Analysis of TGA Data

The TGA data are used to quantify the amount of loosely and tightly bound water in the samples as a function of equilibrium vapor pressure. The cognizant scientist is to analyze the mass losses and determine which loss events can be quantified as water loss. The cognizant scientist then compares the samples, both between the high and low desiccators, as well as before and after oven drying. The resulting loosely bound water should compare well with the loss observed by oven drying. The resulting tightly bound water values are only an estimate because other mass losses are likely to occur at high temperatures.

Appendix B

Behavior of Selected Potential Hanford Organic Tank Waste Components, Surrogate Wastes, and the Simulated Organic Waste PAS94 During Exposure to Selected Water Partial Pressures

Appendix B

Behavior of Selected Potential Hanford Organic Tank Waste Components, Surrogate Wastes, and the Simulated Organic Waste PAS94 During Exposure to Selected Water Partial Pressures

Figure B.1. Effect of Exposure Time to Selected Partial Pressures of Water at 65°C on the Water Content of a Mixture of Ferric Hydroxide and Water

Figure B.2. Effect of Exposure Time to Selected Water Partial Pressures at 22°C on the Water Content of Mixtures of Water and Ferric Hydroxide

Figure B.3. Effect of Exposure to Selected Partial Pressures of Water at 22°C on the Water Content of Mixtures of Water and Sodium Hydroxide

Figure B.4. Effect of Exposure Time to Selected Partial Pressures of Water at 65°C on the Water Content of Mixtures of Sodium Hydroxide and Water

Figure B.5. Effect of Exposure Time to Selected Water Partial Pressures at 65°C of a Mixture of Sodium Hydroxide and Water (repeat of exposure experiment)

Figure B.6. Effect of Exposure Time to Selected Partial Pressures of Water at 22°C on the Water Content of Mixtures of a 2:1 Mole Ratio Mixture of Sodium Nitrate and Nitrite and Water

Figure B.7. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of Mixtures of a 2:1 Molar Ratio Mixture of Sodium Nitrate and Nitrite and Water

Figure B.8. Effect of Exposure Time to Selected Partial Pressures of Water at 22°C on the Water Content of Mixtures of Sodium Laurate and Water

Figure B.9. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of a Mixture of Sodium Laurate and Water

Figure B.10. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of Sodium Laurate and Water (repeat experiment)

Figure B.11. Effect of Exposure Time to Selected Partial Pressures of Water at 22°C on the Water Content of a Mixture of Sodium Glycolate and Water

Figure B.12. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of Mixtures of Sodium Glycolate and Water

Figure B.13. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of Mixtures of Sodium Glycolate and Water (repeat experiments)

Figure B.14. Effect of Exposure Time at Selected Water Partial Pressures at 22°C on the Water Content of Mixtures of Sodium Aluminate and Water

Figure B.15. Effect of Exposure Time to Selected Partial Pressures of Water at $65^\circ C$ on the Water Content of Mixtures of Sodium Aluminate and Water

Figure B.16. Effect of Exposure Time to Selected Partial Pressures of Water at $65^\circ C$ on the Water Content of Mixtures of Sodium Aluminate and Water (repeat experiments)

Figure B.17. Effect of exposure time to selected water vapor pressures at 22°C on the water content of the surrogate waste Mix 1

Figure B.18. Effect of exposure time to selected water partial pressures at 65°C on the water content of Mix 1

Figure B.19. Effect of exposure time to selected water partial pressures at 22°C on the water content of the surrogate waste Mix 2

Figure B.20. Effect of exposure time to selected water partial pressures at 65°C on the water content of mixtures of surrogate waste Mix 2 and water

Figure B.21. Effect of Exposure Time to Selected Partial Pressures of Water at 22°C on the Water Content of the Surrogate Waste Mix 3

Figure B.22. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of Surrogate Waste Mix 3

Figure B.23. Effect of Exposure Time at Selected Partial Pressures of Water at 22°C on the Water Content of the Simulated Waste PAS94

Figure B.24. Effect of Exposure Time to Selected Water Partial Pressures at 65°C on the Water Content of the Simulated Organic Waste PAS94

Figure B.25. Effect of Exposure Time to Selected Partial Pressures at 65°C on the Water Content of the Simulated Waste PAS94 (repeat experiments)

Appendix C

**Make-up Compositions and Predicted, Based on
Individual Components, of the Surrogate Wastes After
Exposure to Selected Water Partial Pressures at 20°C**

Appendix C

Make-up Compositions and Predictions, Based on Individual Components, of the Surrogate Wastes After Exposure to Selected Water Partial Pressures at 20°C

Table C.1. Composition of Surrogate Mixtures after Equilibration at 1.2 torr.
Units are in weight percent.

Material	Mix 1	Mix 2	Mix 3
H ₂ O	3.4	1.6	3.2
FeO(OH)	0.966	0.984	0.968
NaOH	0.966	0.984	0
NaNO ₃	46.9	60.2	47.8
NaNO ₂	19.1	24.6	19.4
Na Laurate	0	10.6	0
Na Glycolate	27.6	0	27.7
Na Aluminate	0.966	0.984	0.968

Table C.2. Composition of Surrogate Mixtures after Equilibration at 5.9 torr.
Units are in weight percent.

Material	Mix 1	Mix 2	Mix 3
H ₂ O	3.8	2.7	5.1
FeO(OH)	0.962	0.973	0.949
NaOH	0.962	0.973	0
NaNO ₃	46.8	59.5	46.9
NaNO ₂	19.0	24.3	19.0
Na Laurate	0	10.5	0
Na Glycolate	27.5	0	27.1
Na Aluminate	0.962	0.973	0.949

Table C.3. Composition of Surrogate Mixtures after Equilibration at 11.5 torr.
Units are in weight percent.

Material	Mix 1	Mix 2	Mix 3
H ₂ O	35.8	26.5	35.1
FeO(OH)	0.642	0.735	0.649
NaOH	0.642	0.735	0
NaNO ₃	31.2	45.0	32.1
NaNO ₂	12.7	18.4	13.0
Na Laurate	0	7.94	0
Na Glycolate	18.4	0	18.6
Na Aluminate	0.642	0.735	0.649

Table C.4. Composition of Surrogate Mixtures after Equilibration at 16.8 torr.
Units are in weight percent.

Material	Mix 1	Mix 2	Mix 3
H ₂ O	60.5	61.2	60.3
FeO(OH)	0.395	0.388	0.397
NaOH	0.395	0.388	0
NaNO ₃	19.2	23.7	19.6
NaNO ₂	7.82	9.70	7.94
Na Laurate	0	4.19	0
Na Glycolate	11.3	0	11.4
Na Aluminate	0.395	0.388	0.397

Table C.5. Predicted Water Content of Surrogate Mixtures after Equilibration at 1.2 torr,
Based on Individual Components. Units are in weight-percent water.

Material	Mix 1	Mix 2	Mix 3
FeO(OH)	0.001	0.001	0.001
NaOH	0.257	0.262	0
NaNO ₃ /NaNO ₂	0	0	0
Na Laurate	0	0.595	0
Na Glycolate	0	0	0
Na Aluminate	0.007	0.007	0.007
Total	0.265	0.865	0.008

Table C.6. Predicted Water Content of Surrogate Mixtures after Equilibration at 5.9 torr,
Based on Individual Components. Units are in weight-percent water.

Material	Mix 1	Mix 2	Mix 3
FeO(OH)	0.04	0.04	0.04
NaOH	1.63	1.65	0
NaNO ₃ /NaNO ₂	0	0	0
Na Laurate	0	0.80	0
Na Glycolate	0.31	0	0.30
Na Aluminate	0.20	0.21	0.20
Total	2.18	2.70	0.54

Table C.7. Predicted Water Content of Surrogate Mixtures after Equilibration at 11.5 torr,
Based on Individual Components. Units are in weight-percent water.

Material	Mix 1	Mix 2	Mix 3
FeO(OH)	0.05	0.06	0.05
NaOH	1.66	1.90	0
NaNO ₃ /NaNO ₂	0	0	0
Na Laurate	0	0.63	0
Na Glycolate	0.92	0	0.94
Na Aluminate	0.48	0.55	0.48
Total	3.11	3.14	1.47

Table C.8. Predicted Water Content of Surrogate Mixtures after Equilibration at 16.8 torr,
Based on Individual Components. Units are in weight-percent water.

Material	Mix 1	Mix 2	Mix 3
FeO(OH)	0.3	0.3	0.3
NaOH	1.5	1.4	0
NaNO ₃ /NaNO ₂	39.4	48.7	40.1
Na Laurate	0	1.0	0
Na Glycolate	8.9	0	9.0
Na Aluminate	0.7	0.7	0.7
Total	50.8	52.1	50.1

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