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Dryout Modeling in Support of the Organic Tank Safety Project

C. S. Simmons

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Richland, Washington 99352

Summary

This work was performed for the Organic Tank Safety Project to evaluate the moisture condition of the waste surface in certain organic-nitrate bearing tanks that are classified as being conditionally safe because sufficient water is present. This report describes the predictive modeling procedure used to predict the moisture content of waste in the future, after it has been subjected to dryout caused by water vapor loss through passive ventilation.

This report describes a simplified procedure for modeling the drying out of tank waste. Dryout occurs as moisture evaporates from the waste into the headspace and then exits the tank through ventilation. In a passively ventilated tank, the rate of water loss through ventilation is controlled by the breathing rate as well as the temperature and humidity of the ventilation air. Evaporation from the waste is controlled by diffusion of water vapor through the waste surface. Thus, the concentration gradient of water vapor between the subsurface waste and the tank headspace determines the evaporation rate. This rate may be impeded by any dry crust present at the surface. The water vapor concentration within the waste or the headspace is determined by the vapor-liquid equilibrium, which depends on the waste's moisture content and temperature. This equilibrium has been measured experimentally for a variety of waste samples and is described by a curve called the "water vapor partial pressure isotherm." This curve describes the lowering of the partial pressure of water vapor in equilibrium with the waste relative to pure water due to the waste's chemical composition and hygroscopic nature.

The modeling has been kept simple to avoid complicated calculations that require detailed physical characterization of the waste, which is not available. Liquid flow in the waste is neglected, and moisture loss is treated as caused entirely by surface evaporation. These assumptions permit modeling without hydraulic information about the waste.

Saltcake and sludge are described by two distinct calculations that emphasize the particular physical behavior of each. A simple, steady-state model is devised for each type to obtain the approximate drying behavior.

The report shows the application of the model to Tanks AX-102, C-104, and U-105.^(a) Waste in Tanks C-104 and U-105 are, respectively, deep sludge and saltcake, which are both substantially wet and would resist being dried out by evaporation and ventilation even over 50 years. However, the shallow waste contained by AX-102 could potentially dry out over decades. For both AX-102 and C-104, the report shows that the past decline of the liquid level may be consistent with evaporative water loss. The model is used to test for signs of a crust that may restrict or limit evaporation in the future.

(a) Hanford waste tanks are designated by the prefix 241- followed by the tank farm indicator and actual tank number. In this report the prefix is omitted, as it is in common usage.

The humidity in the headspace of AX-102 and U-105 appears to be in equilibrium with the waste's moisture content at the surface, whereas C-104 may have a crust that impedes evaporation and reduces the humidity below that of equilibrium. However, the water vapor concentration in the C-104 headspace could also be reduced by condensation rather than by a crust, limiting the diffusion of water vapor in response to high ventilation rate.

Waste modeled in Tank AX-102 showed a slight re-wetting over time as cooling occurs. However, the waste dried from 25 wt% to 14 wt% over 30 years before re-wetting to 18 wt%. This re-wetting behavior is a manifestation of the waste's hygroscopic properties, as described by the water vapor isotherm, which depends on temperature. The behavior indicates, in this case, the importance of accounting for waste cooling when predicting the future moisture content subject to drying.

Contents

Summary	iii
1.0 Introduction	1.1
1.1 Conceptual Model	1.1
1.2 Applications	1.5
2.0 Waste Dryout Model	2.1
2.1 Model Assumptions	2.1
2.1.1 One-Dimensionality	2.1
2.1.2 Uniform Moisture	2.2
2.1.3 Steady State	2.2
2.1.4 No Replenishment	2.2
2.1.5 Uniform Water Vapor Concentration	2.2
2.1.6 Water Loss by Ventilation	2.3
2.1.7 Constant Ventilation Rate	2.3
2.1.8 A Single Water Vapor Isotherm	2.3
2.1.9 Fixed Yearly Climate Cycle	2.3
2.1.10 Tanks Not Connected	2.3
2.1.11 No Condensation of Water Vapor	2.4
2.2 Model Formulation	2.4
2.3 Solving the Water Loss Equation	2.6
2.3.1 The Waste Physical Types	2.7
2.3.2 Deep Sludge-Type Waste	2.9
2.3.3 Shallow Waste with Constant Temperatures	2.9
2.3.4 Deep Saltcake-Type Waste	2.11
2.4 Shallow Waste Drying Example	2.13
3.0 Waste Moisture - Water Vapor Equilibrium	3.1
3.1 Water Vapor Isotherm in Terms of Partial Pressure	3.1
3.2 The Temperature Dependence of the Isotherm	3.3
3.2.1 Adjusted Isotherm for Another Temperature	3.3
3.2.2 Water Vapor Concentration Beneath the Waste Surface	3.4
3.2.3 Confirming the Isotherm Adjustment Method	3.5
3.3 Relating Headspace Humidity to Waste Moisture	3.5
4.0 Tank Temperature Trends	4.1
5.0 Modeling Examples of Dryout	5.1
5.1 Tank AX-102	5.1
5.2 Tank U-105	5.4

5.3 Tank C-104	5.6
5.3.1 Tank C-104 Waste as Sludge	5.8
5.3.2 Tank C-104 Waste as Saltcake	5.10
5.4 Bounding the Dryout	5.12
6.0 Conclusions	6.15
7.0 References	7.16

Figures

1.1	Diagram of Water Loss for a Single-Shell Waste Tank	1.2
2.1	Dryout for Tank AX-102 Waste	2.14
2.2	Depth of Air-Dry Layer in AX-102	2.14
2.3	Relative Humidity in the Headspace of AX-102 for Waste Drying	2.15
3.1	Water Partial Pressure Isotherm of Tank U-105 Waste	3.2
3.2	Water Vapor Isotherm Adjustment Confirmed for Tank A-102 Waste	3.6
3.3	Predicted Water Content of Tank U-105 Waste Depending on Surface Temperature ..	3.8
4.1	Tank U-105 Headspace Temperature Fit to Measurements	4.2
5.1	Waste Water Content in Tank AX-102. Modeled with and Without a Surface Crust ...	5.3
5.2	Predicted Headspace Water Vapor Concentration in Tank AX-102	5.3
5.3	Predicted Water Content of Waste Surface Layer in Tank U-105	5.5
5.4	Headspace Relative Humidity Predicted for Tank U-105	5.5
5.5	Water Vapor Isotherms for Waste in Tank C-104	5.7
5.6	Surface Moisture Content in Tank C-104 in Equilibrium with Headspace RH	5.7
5.7	Moisture Content below Crust in Tank C-104	5.9
5.8	Dryout of Waste in Tank C-104 with Surface Crust	5.9
5.9	Relative Humidity in Headspace of Tank C-104	5.10
5.10	Drying Depth of Surface Crust in C-104 Waste as Saltcake	5.11
5.11	Dryout of Waste in Tank C-104 as Saltcake	5.11
5.12	Moisture Content of Surface Crust for Waste in Tank C-104	5.12
5.13	Relative Humidity in the Headspace of Tank C-104	5.13
5.14	Dryout for the Three Example Tanks	5.14

Tables

4.1	Temperature Correlation Parameters for Ambient and Selected Tanks	4.2
5.1	Waste Characteristics for Tanks AX-102, U-105, and C-104	5.1
5.2	Breathing Rates Used for Bounding the Dryout Curves	5.13

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1.0 Introduction

The water content of waste is recognized as a key factor in determining potential reaction hazards in the Hanford Site organic-bearing high-level radioactive waste tanks (Webb et al. 1995; Hunter et al. 1997). The Organic Tank Safety Project has shown specifically that water is effective in preventing combustion propagation reactions in organic-nitrite/nitrate salt waste (Webb et al. 1995, Meacham et al. 1997). Waste that is classified as "conditionally safe" (Webb et al. 1995) because it has a high water content may not remain safe if a significant amount of water is lost from the waste in the future. Water loss from a tank that is not leaking occurs primarily by evaporation into the tank headspace, with subsequent removal by the ventilation system via "breathing." Water loss by evaporation may also be preceded by pumping and leakage in some tanks that now contain stabilized waste. Evaporative water loss is examined here through modeling for selected tanks of interest to the Organic Tank Safety Project.

1.1 Conceptual Model

A conceptually simplified modeling procedure is employed to estimate the worst-case dryout of surface waste resulting from water evaporation. The modeling approach is referred to as simplified because it focuses on the overall loss of water from a surface layer of waste (which is expected to be the driest and therefore of greatest concern to the Organic Tank Safety Issue), and it does not attempt to predict the distribution of water content with depth in the waste. Simmons et al. (1997) modeled and studied upward water migration through stabilized porous saltcake waste, including wicking of moisture to the waste surface as it dried. Predicting the detailed moisture distribution in tank waste is hindered by the spatial variability of physical properties and by a lack of hydraulic characterization for the two primary waste types, saltcake and sludge. Neglecting replenishment from moisture deeper within the waste by excluding liquid flow lessens the computational complexity of the model but results in an exaggerated (conservative) estimate of evaporative drying. Thus, the simplified modeling provides a worst-case estimate of the moisture content of waste near its surface. The model is also simplified because it relies on empirical information about the most important physical factors that affect the rate of evaporative water loss.

Figure 1.1 is a diagram of the dryout model. Water is lost from a tank by movement of water vapor from the headspace to the outside air. The rate of loss is determined by the breathing rate, v , which is the volumetric rate of air flow into and out of a vent, and by the difference between the concentrations of water vapor inside and outside the tank. Water vapor is exhaled at the existing concentration inside the headspace, C , and inhaled at the ambient concentration, C_A .

A basic assumption in this modeling is that the water loss rate by ventilation is always equal to the evaporation rate from the waste surface. This is the supposition of (quasi) steady-state flow of water vapor, essentially that water vapor neither builds up rapidly nor becomes depleted in the headspace. Such dynamical reservoir capacity effects for water vapor entering

Figure 1.1. Diagram of Dryout for a Single-Shell Waste Tank

and leaving the headspace are not evaluated, and details of the flow behavior are beyond the scope of this modeling effort. However, quasi-steady-state conditions do not mean that moisture loss or headspace water vapor concentration are constant over time. Rather, such changes are gradual, and it is reasonable to describe the transfer of water vapor from the waste into the headspace and into the outside air as steady state, given the lack of data to the contrary.

Generally, the temperature in the headspace above the waste surface is cooler than the waste, and the water partial pressure in the headspace will therefore be less than that at or below the warmer surface, driving a diffusive flux. A crust, if present, may limit the evaporation rate by imposing a diffusion resistance, or it may not if the interstitial liquid level is currently up to or above the crust surface. A stagnant boundary layer of air over the surface may also offer resistance to the transfer of water vapor from the waste into the headspace. These mass-transfer limitations are included in the conceptual model, although they may not be operating in every

case. When diffusion does not limit the overall rate of water vapor loss, the model implies that the concentration in the headspace is nearly the same as that at or below the crust surface, wherever the water vapor originates.

The water vapor within the drained waste interstices is assumed to be in equilibrium with the moisture in the waste. The equilibrium water vapor concentration is determined by the moisture content, temperature, and chemical composition of the waste (Scheele et al. 1996). The model relies on measurements of the water vapor partial pressure in equilibrium with actual waste samples to specify the water vapor concentration at or below the crust surface for the prevailing thermal and chemical conditions. Because the equilibrium partial pressure of water vapor over various tank wastes has been found to vary significantly, waste samples have been obtained and tested for specific tanks of concern to the Organic Tank Safety Project (Scheele et al. 1997). Generally, these measurements are lower than the saturation value of partial pressure for water vapor over pure water. The lower partial pressure is a reflection of the dissolved salts and all other mechanisms of water absorption and adsorption in the waste. The waste's chemical composition causes the relative humidity in the headspace to be lower.

The relationship between the equilibrium water vapor partial pressure and moisture content of the waste for a particular temperature is called a water vapor isotherm. Measurements for a particular waste sample are performed at a specific controlled reference temperature in the laboratory (Scheele et al. 1997). To make an isotherm applicable to tank conditions, the model must adjust for the different (and changing) temperature of the actual waste. This adjustment yields the equilibrium water vapor concentration for a specific waste with a given water content at a given temperature.

The water vapor partial pressure is strongly affected by temperature, which varies seasonally and diminishes over time as the rate of radioactive decay decreases. A simple empirical model fit to actual tank temperature data is used to describe the yearly cycle of variation and decline over time. A similar equation in the model tracks the temperature and humidity of the outside air as well. Thus, the important influence of temperature variations outside, in the headspace, and below the waste surface is accounted for in the modeling.

Breathing rate ultimately determines how rapidly water vapor can be removed by ventilation. Only a single estimate of breathing rate based on tracer gas studies is usually available for most tanks (Huckaby et al. 1997). That estimate may be based on the average of multiple measurements taken over a number of different days, but usually the data do not span the seasonal variation of ventilation. Used in conjunction with the transfer coefficient for diffusion-limited evaporation, the breathing rate is a key modeling parameter. Unfortunately, the variation of breathing rate throughout the year is not available; only this single value for a particular period is available. This imposes on the modeling the simplifying requirement that the breathing rate is a constant equal to a single estimated value. However, a range of breathing rates can nevertheless be applied to assess the consequences of the uncertainty in this parameter. An alternative

approach, estimating the breathing rate indirectly from observations of liquid level decline, is possible for a few cases. In this approach, one assumes that the liquid level falls due to evaporative water loss and that the tank did not leak.

The modeling is intended to focus attention on the drying of a single arbitrary surface layer of specified depth, L , as shown in Figure 1.1. This is the weakest conceptual aspect of the modeling, because the layer must be chosen to reflect the assumptions that drying is concentrated there and that it is thick enough that replenishment of water from below can be reasonably disregarded. If the waste is shallow, this "layer" could reasonably extend to the tank bottom and include the entire profile. If the waste is deep, however, treating the waste as having a uniform moisture content and removing moisture from its entire depth will probably not yield any meaningful estimates of the dryness of the surface of the waste. In the model, the length of a core segment (19 in.) is generally selected as the layer thickness, L . Because a core segment is usually the shallowest sample unit of waste taken from a tank, only moisture changes within such a unit are detectable by current waste characterization sampling practices. (In some cases, the sample is divided into the upper and lower halves, or even quarter segments. For such cases, a shallower layer could be selected.)

In the model, if the specified layer becomes severely dried, that is, dried below the water content that would be established by equilibrium with a typical headspace water vapor concentration, the layer thickness is increased to be consistent with the assumption that replenishment would not occur. In this way, the model also answers the question of how dry a certain sample depth measured by core segments (or subsegments) might become over time.

Calculating spatial gradients of moisture content with depth are avoided by this conceptual approach; only the average moisture content in the layer is tracked. This is consistent with the measurement of water content in a homogenized core sample, which typically yields only one value of average moisture content. In the presence of a diffusion-limiting crust, the crust of thickness, Z , may have a different water content than the waste below it because it is in equilibrium with the significantly lower headspace water vapor concentration. This diffusion depth, Z , may or may not change over time, depending on the presumed nature of the waste type. (The treatment of the crust is explained further in the Section 2 discussion of solving the moisture loss equation.)

Another justification for focusing the dryout on an arbitrary layer based on core segments is that measurements of moisture content at the resolution of whole- or half-segments have not displayed any trend with depth as would be anticipated in an ideal homogeneous waste. That is, the typical core segment or fractional segments have not displayed any indication of a drying front that would be expected in a homogeneous porous material. In particular, the typical heterogeneity of the waste produces unpredictable variability in moisture with the depth. Therefore, no model of the moisture distribution can be justified or confirmed on the basis of core segment sample resolution of waste. The typical heterogeneity of waste properties on a core segment resolution makes it unrealistic to treat the moisture distribution as anything but uniform.

Thus, in the modeling, the spatial dependence of water content with depth is averaged conceptually within the imposed drying layer.

Just as multiple core samples from different riser locations generally yield variable measurements of moisture content, so each sample tested for partial pressure equilibrium may exhibit a different water vapor isotherm. Scheele et al. (1997) found this variability in the isotherms for wastes from certain tanks. The implication is that waste in different parts of a tank equilibrated to the same well-mixed water vapor concentration in the headspace may exhibit different moisture contents. In the modeling, therefore, the calculation of moisture content as it varies in time is only one possible realization of the drying layer's behavior. Each distinct water vapor isotherm can produce a different projection of the dryout behavior, i.e., wt% water versus time. Uncertainty in dryout, of course, can also be due to uncertainty in the other controlling parameters, such as the initial water content and breathing rate. However, the model's simplicity makes it computationally easy to examine the impact of uncertainty in the controlling parameters.

Other simplifying assumptions are introduced in Section 2, including one-dimensionality. The problem of simulating detailed (three-dimensional) water migration in stabilized waste was treated in Simmons et al. (1997) before more specific data became available that directly link surface wetness with water vapor concentration in the headspace. The newly available data facilitate this more direct and simplified modeling approach, which will hopefully elucidate the factors that control surface drying.

1.2 Applications

Although the dryout model will be applied for a number of different tanks of concern to the Organic Tank Safety Issue (Meacham et al. 1998), this report describes only three (AX-102, C-104, and U-105) as examples of the application of the model. Each tank contains a different waste type and presents a somewhat unique problem in solving the water loss equation. For instance, AX-102 contains a shallow waste profile; waste in U-105 (not yet stabilized saltcake) is wet and deep; waste in C-104 is a sludge type with a crust that might be limiting evaporation. This demonstrates another value of the dryout modeling: it can help examine the present condition of the waste as well as attempt to predict the future moisture condition.

The remainder of this report shows the steps for determining the dryout potential of the example tank wastes. Section 2 puts the waste dryout model, as conceptualized in Figure 1.1, into a mathematical context, shows various ways of solving the water loss equation for dryout, and summarizes the basic assumptions. The relationship between the waste moisture content and the partial pressure of water vapor in the headspace in equilibrium is discussed in Section 3, as is the method for deriving the temperature adjustment of a water vapor isotherm for each waste. Section 4 gives the equation that describes how the temperature trend and yearly cycle are calculated. Example applications are described in Section 5, and bounding dryout curves are provided for each tank. Section 6 contains the conclusions and Section 7 the cited references.

2.0 Waste Dryout Model

2.1 Model Assumptions

As explained in Section 1, the model is designed to provide estimates for worst-case drying of the waste surface given specified system temperatures and ventilation rates. The model is based on the following simplifying assumptions:

- One-dimensional, vertical waste profile, neglecting horizontal variability of waste properties
- quasi-steady-state moisture transfer
- uniform water content and uniform chemical/physical properties within the surface layer
- no upward movement of liquid to replace water lost from the surface layer
- a well-mixed tank headspace, i.e. uniform headspace water vapor concentration
- water loss by ventilation only, no drainage
- constant ventilation rate
- water vapor isotherms may be based on only a few equilibrium measurements
- ambient air temperature and humidity follow the same fixed, yearly cycle
- ventilation air originates from outside, not from connected tanks
- no condensation of water vapor takes place on the dome or within the ventilation system.

The justifications for these special assumptions are given before deriving their implications in the form of a water loss rate equation. These assumptions are intended to facilitate reducing the dryout problem to its most fundamental aspects and to eliminate the need for predicting complicated patterns of moisture distribution that cannot be confirmed with current tank data. The intent is to keep the modeling compatible with available data and to avoid nonconservative conclusions about the wetness of the surface waste. Many of these assumptions were discussed in Section 1.

2.1.1 One-Dimensionality

The model takes the same vertical perspective provided by a single or average core sample of a waste profile. The horizontal variability apparent in duplicate, separated core samples is not adequate to describe the three-dimensional spatial structure of waste and its impact on the horizontal variation of water content. That is, the layering and spreading of tank waste is not well evaluated for specific tanks, and a model that would attempt to incorporate these three-dimensional unknown patterns with the associated radial transfer of water would be even more uncertain in its predictions. The model, therefore, lumps the entire drying region into a layer with uniform properties. Detailed variation of moisture content across the horizontal, or radial, dimension (e.g., as a result of the temperature decreasing toward the tank wall) is not included.

2.1.2 Uniform Moisture

A single value of moisture content (as would be obtained from averaging measurements from the first or top core segments, including the surface) is used to describe the entire drying layer. (While an average provides a general estimate for a tank, a minimum of the moisture content values could be used to represent the driest portion of the waste and to emphasize the worst-case impact of further drying over time.) As explained in Section 1, the model is not intended to estimate the vertical distribution of water in the drying layer; water is lost from the drying surface layer as a whole.

2.1.3 Steady State

The rate of water transfer across the waste surface and the rate at which it exits through the ventilation system are equal from moment to moment. At any instant, this state is likely not to hold exactly but seems reasonable over a monthly or yearly time scale. However, the water loss rate is variable on a time scale of hours—not constant over time. It varies according to the temperature's time-dependence, which influences the water vapor concentrations in the headspace and waste. Thus steady state, as used here, does not mean that constant conditions hold.

2.1.4 No Replenishment

A construct of the model is that the drying surface layer is large enough to neglect replenishment of water from below. This leads to overestimating the dryout of the hypothesized layer. This imposed condition is intended to yield a more conservative (i.e., lower) estimate of the moisture content in the surface waste. This assumption may also yield an underestimate of the total water loss over time because, as the surface layer dries, the equilibrium headspace concentration may be less than it actually would be if the surface layer were re-wetted from below. Increasing the size of the layer can reduce the error of underestimating the total water loss but may result in an average moisture content that does not indicate potentially severe surface drying.

2.1.5 Uniform Water Vapor Concentration

The model assumes (reasonably) that, on the time scale of interest, the headspace air is well mixed. Studies of tank headspaces support this condition of uniformity (Huckaby et al. 1997). The temperature of the headspace is presumed uniform as well. This assumption is consistent with a one-dimensional evaluation of evaporation over the waste surface. Also, water vapor concentration in the waste drying layer is assumed described by a single value. The variability of waste chemical properties across the surface would likely produce corresponding variations in the water vapor concentration within drained interstices of the waste surface. Water vapor concentration at the surface would be influenced by temperature differences as well. In particular, the fact that the temperature generally decreases radially in the waste with heat loss through the tank sides is disregarded. Thus, single temperatures for each region, headspace and waste surface, are assumed to describe a tank system.

2.1.6 Water Loss by Ventilation

The model does not account for drainage by pumping or leakage. Water moves only by evaporation and loss through the tank ventilation system, assumed to be connected only to the outside atmosphere (ambient conditions).

2.1.7 Constant Ventilation Rate

This assumption is not necessarily accurate but is imposed to be consistent with available information about tank breathing, which is based on only a single estimate derived from, at most, a few measurements taken over a limited time period. This is not a necessary or fundamental construct of the modeling. A time-dependent breathing rate could be readily implemented into the water loss equation solution. However, the assumption is believed to have a minor impact on dryout predictions unless variations in breathing rate were somehow correlated with variations in water vapor concentration in the headspace. Such correlations, however, have not been demonstrated. Therefore, a single, constant breathing rate is employed to be consistent with current knowledge about tank ventilation.

2.1.8 A Single Water Vapor Isotherm

Each waste sample may produce a somewhat different isotherm, depending on its specific chemical composition and physical condition. The isotherm is often based on relatively few (five to six) measurements; consequently, the entire range of drying may fall between only two data points. For lack of more complete data, the isotherm is treated as linear between measurements. Only if duplicate measurements are available can the impact of the variability on the overall dryout be evaluated. However, one can test the consistency of the measured isotherm with in-tank conditions using the model and appropriate initial conditions (e.g., measured values of the headspace partial pressure and temperature and waste surface temperature and water content). Given the water vapor isotherm's variability from sample to sample, the trend in the partial pressure deduced from a few measurements of each particular waste sample seems adequate to describe the range of moisture change during dryout.

2.1.9 Fixed Yearly Climate Cycle

In the model, ambient temperature and relative humidity follow a fixed seasonal cycle with no daily fluctuations. While daily fluctuations do, in reality, occur, they are both rapid on the time scale of the model and small compared with annual fluctuations. Again, this assumption is not absolutely necessary but greatly simplifies calculation.

2.1.10 Tanks Not Connected

The model assumes that the incoming ventilation stream always reflects the temperature and humidity of the outside air. The possibility of moisture entering a tank's headspace from

another (wetter) tank is not considered. If the incoming water vapor concentration were generally greater than the ambient, then the rate of water loss would decrease. This is not a fundamental restriction on the model. Water vapor concentration from a connected tank could be readily considered, but assuming ambient incoming air should always yield an overestimation of drying. This condition increases the estimated cumulative water loss by drying.

2.1.11 No Condensation of Water Vapor

This is a fundamental limitation on the modeling construct. The coupling of evaporation with heat transfer is not considered. Coupling has been examined by Simmons et al. (1997). Condensation on the walls or absorption in the waste of water vapor would reduce the actual water vapor concentration in a tank's headspace. The actual evaporation rate could then be much greater than the breathing loss rate if water is returned to the waste by condensation on and absorption by cooler regions. The transfer coefficient used in the current model only describes the portion of evaporative flux that exits the tank through breathing.

2.2 Model Formulation

These assumptions and modeling constructs are the basis for the following equations, which result in a water loss equation for the drying layer at the waste surface. The model has two parts: 1) diffusion of water vapor from a waste drying layer passing through a combined surface crust and an air boundary layer into the headspace, and 2) removal of water vapor from the headspace by ventilation. Loss of water through the tank vent is considered first, and then secondly the evaporation of water vapor governed by diffusion is described. Figure 1.1 is the conceptual diagram for the model, where the key symbols are defined.

The rate at which the mass of water vapor (in the headspace) is removed by ventilation,

$\dot{m}_{vent}$, is given by

$$\dot{m}_{vent} = v(C - C_A) \quad (2.1)$$

where v is the volumetric ventilation (breathing) rate of the tank headspace, C is the water vapor concentration in the headspace, and C_A is the mass concentration of water vapor in the ambient air.

The net rate at which water evaporates from the waste and enters the headspace is given by

$$\dot{m}_{evap} = k(C_0 - C) \quad (2.2)$$

where $\dot{m}_{evap}$ is the net mass of water (in the drying surface layer) per unit time transported across the surface boundary into the headspace per unit time, k is a mass transfer coefficient that describes diffusion of water vapor through air-filled pores (if present) and the boundary layer for the entire cross-sectional area, A , of the tank; and C_0 is the mass concentration of water vapor in equilibrium with the waste at some depth at or below the waste surface.

At steady state, the rate at which water is evaporated and diffuses into the headspace is equal to the rate at which it is removed by ventilation:

$$\dot{m}_{vent} = \dot{m}_{evap} \quad (2.3)$$

Combining equations (2.1) through (2.3) yields the following expression for the headspace water vapor concentration:

$$C = \frac{vC_A + kC_0}{v + k} \quad (2.4)$$

and the following expression for the time rate of change of water mass, m , in the drying layer:

$$\dot{m} = \frac{-kv}{k + v}(C_0 - C_A) \quad (2.5)$$

The overall water mass transfer coefficient, k , can be obtained theoretically from the two mass-transfer resistances, diffusion through the drained waste followed by transport across a boundary layer over the waste. When these two resistances are in series, the overall transfer coefficient is found by

$$\frac{1}{k} = \frac{1}{k_e} + \frac{Z}{AD} \quad (2.6)$$

where D is the "effective" diffusion coefficient for water vapor in air in the drained porous material, and k_e is an eddy transfer coefficient for passage of water vapor through a boundary layer of air over the waste surface area, A . Employing an approach used in soil physics for flow of gases in a porous medium, D can be taken as the diffusion coefficient of water vapor in air at the appropriate temperature multiplied by the drained porosity and by tortuosity (Marshall and Holmes 1979). (Tortuosity, unknown for tank waste, is here taken as unity.) The characteristic

diffusion distance is defined as depth Z , or the crust thickness. The eddy transfer coefficient k_e was employed by Heard (1993) to model the drying of an actively ventilated tank. The same formula is used here.

Alternatively, the transfer coefficient, k , can be estimated by using equation (2.4) with the measured moisture content of the waste, the ventilation rate, and the measured headspace water partial pressure. This approach was applied to Tank AX-102 to describe the likelihood of a crust forming in shallow waste as drying occurs.

For passively ventilated tanks with wet waste surfaces, the mass transfer coefficient, k , is large compared with the ventilation rate, v . That is, diffusion does not limit vapor loss, and equation (2.5) can be simplified to

$$\dot{m} = v(C_0 - C_A) \quad (2.7)$$

Similarly, in passively ventilated tanks with a liquid surface below the waste surface, the eddy transfer coefficient, k_e , is large compared with the product AD , and equation (2.6) can be reduced to

$$\frac{1}{k} \approx \frac{Z}{AD} \quad (2.8)$$

Not enough is known about the development of a surface crust as drying occurs to model its diffusion-limiting influence on moisture loss over a long time. Heard (1993) employed a diffusion coefficient for water vapor similar to that for water diffusing through concrete to explain the low rate of water loss in an actively ventilated tank.

Equation (2.5) constitutes the model for waste dryout. To perform the dryout calculations, the rate equation (2.5) for water loss is solved in different ways, depending on the type of waste and how it is expected to dry out. The water lost by the waste is assumed to come from some as-yet unspecified depth below the surface.

2.3 Solving the Water Loss Equation

Solving the differential equation (2.5) with specified initial waste conditions gives the mass of water, m , in the drying surface layer as a function of time, t . The concentration C_0 depends on T_0 , the temperature of the surface waste, which depends on time, t , as the waste cools and cycles over the seasons. It also depends (implicitly, through the water vapor isotherm) on the moisture (water) content in the layer, which dries over time.

The water vapor isotherm measured for the particular waste determines the functional dependence of C_0 on T_0 and on the water content w , given by $w = m/M$ where M is the dry mass of the layer, a fixed quantity. Note that wt% water = $100 w/(w + 1)$. Dividing equation (2.5) by the constant M makes equation (2.5) a rate equation for w . At this point, the construct that a single value of w describes the layer is imposed. The water vapor isotherm required at this point is a measured relationship between wt% water and the equilibrium partial pressure for a specific reference temperature (Scheele et al. 1997). An example is shown in Figure 3.1 for waste from Tank U-105. The isotherm must be continually adjusted for the applicable temperature, T_0 , which varies in time. (This adjustment procedure is discussed later.) The ambient water vapor concentration in equation (2.5) depends on time also, through its dependence on T_A . Let $C_s(T_A)$ be the saturation water vapor concentration and RH_A the relative humidity of outside air. Then $C_A = RH_A C_s(T_A)$, which is simply a definition of ambient relative humidity.

Equations that model the time dependence of T_0 and T_A will be described in more detail later. These are empirical relations fitted to actual in-tank and atmospheric measurements. The discussion will return to the isotherm adjustment and temperature cycle models after first considering how the water loss equation is solved for various kinds of waste.

2.3.1 The Waste Physical Types

There are three possible waste cases, and each requires a different tactic for solving equation (2.5): 1) sludge, 2) shallow waste of either sludge or saltcake type, or 3) saltcake, with substantial depth so that the drying layer is only part of the waste. For the special shallow case (2), the drying layer is the entire waste. For most tanks of concern to the Organic Tank Safety Issue, the waste has not been stabilized and is expected to behave as a sludge (i.e., the surface has not been drained). Therefore, case (1) was usually the most appropriate viewpoint. However, some of the organic issue tanks with higher organic chemical concentrations are shallow, and the dryout analysis gives that circumstance a special evaluation. In the current situation, no tanks of concern seem to belong to the case (3). In the future, when more organic safety issue tanks are pumped to stabilize them (e.g., U-105 and U-106), case (3) would then become more relevant. This section further describes the waste character before considering the solution steps for each of the cases (1–3).

Waste is generally described as either a saltcake or sludge type. Saltcake waste, which is typically crystalline with significant amounts of sodium nitrate and nitrite, can be drained, leaving a solid matrix of liquid-emptied interstices through which air and water vapor can diffuse. By contrast, sludge, which typically consists of amorphous metal hydroxides, is consolidated by draining, and its volume shrinks without allowing interstices to empty (at least until a shrinkage limit is attained where it is severely dry and becomes saltcake-like). Commonly, a saltcake does not exhibit the physical characteristics of such material until it is drained, although chemically, based on nitrate/nitrite content, it can be identified as such. That is, saltcake waste may not have a rigid porous matrix until after it is drained or stabilized and may behave as sludge before being drained.

The chemical compositions characteristic of saltcake and sludge waste types are not of direct use to the physical modeling discussed here. Interpretation of chemical characterization information and observations of physical appearance generally are used to decide whether a waste is sludge or saltcake, and no special physical tests are performed to determine whether it is best classified as one or the other. Nor do we use the classification of waste based on processing history to for modeling water loss. The chemical characteristics are reflected entirely in the water vapor equilibrium isotherm to be described later.

Evaporation of water may alter the waste character (in particular, its porous structure) near the surface by transporting dissolved chemicals that subsequently precipitate there. This model, however, assumes that evaporation removes liquid from the waste just as draining would. The precipitated porous matrix that would be formed by evaporation cannot be considered because liquid transport is not included in this modeling. The only transport property for the waste that the model needs is the apparent diffusion coefficient for water vapor in the dried waste material (i.e., crust). Even in sludge waste tanks, a dry crust often covers the surface. Just below such a crust, core samples of sludge generally show high moisture content. The subsections below discuss how this usually unknown transfer coefficient can be determined to be consistent with tank conditions.

Following are the physical conceptualizations of the waste cases used to solve equation (2.5):

- 1) For tanks with the sludge waste type, a crust layer of fixed depth, Z , is presumed to control evaporation from the waste below it. Below this crust, the water content w decreases as water is lost, and this in turn changes C_0 over time. When no crust is present, the loss of moisture from the waste is not limited by diffusion, C and C_0 are equal, and equation (2.7) applies. In this case, the moisture content below the crust may change only slightly from year to year (assuming a sufficiently deep sludge), allowing a simple numerical solution, presented in equation (2.9), below.
- 2) For tanks with a shallow waste of either type, the entire waste (including the dry crust) determines C_0 . The surface crust is assumed to have reached air-dry conditions, and the diffusion depth, Z , increases with time. In solving this case, the temperatures (waste, headspace, and ambient) are taken as constant average values by supposing that the water loss is rapid enough to disregard long-term cooling or annual temperature cycles. Imposing constant temperatures allows an easy solution for the water loss that gives a bounding estimate of dryout.
- 3) For tanks with saltcake-type waste, water loss results in the formation of a dry surface layer of depth $Z(t)$ that continually increases as water is removed. At and below the interstitial liquid level, the water content is assumed to be constant. Above the interstitial liquid level, the water content of the waste is assumed to be in equilibrium with the prevailing water vapor concentration in the headspace. In this model, C decreases as the interstitial liquid level recedes deeper. C is determined from C_0 and C_A by assuming steady loss of vapor.

2.3.2. Deep Sludge-Type Waste

For tanks with deep sludge-type waste, the water content w changes little each year. Because the mass transfer coefficient and ventilation rate are assumed constant, equation (2.5) can be integrated to obtain the change in $w = m/M$, in terms of yearly averages:

$$\Delta w = \frac{-v/M}{1 + \frac{v}{k}} (\hat{C}_0 - \hat{C}_A) \Delta t \quad (2.9)$$

where $\hat{C}_0$ and $\hat{C}_A$ are averages of the headspace and ambient air water vapor concentrations over the time period $t = 1$ yr. Specifically, the average $\hat{C}_0$ is the integral of $C_0(w, T_0(t))$ over the interval t to $t + \Delta t$ divided by Δt . In the integration, w is held constant. A similar integral is applied to C_A , which depends on time through T_A . Note that the time increment Δt need not be a whole year if w should decrease too rapidly to maintain an accurate solution. In general, equation (2.5) is a first-order differential equation in w and t that would be solved by standard numerical methods (e.g., Runge-Kutta).

2.3.3. Shallow Waste with Constant Temperatures

To solve the water loss equation (2.5) for shallow waste, case (2), constant temperature is imposed on the solution as a condition to facilitate a closed-form solution. Although constant temperature is not a realistic trend over a long period (a decade or longer), the condition can be imposed to examine the dry-out behavior of a shallow waste over a shorter period. In fact, the dry-out solution, when restricted to constant temperature, should produce a lower bound (worst case) for the final moisture content. This would be so because the waste is treated as remaining hotter without cooling, and evaporation loss would be held at a greater rate than the actual when cooling occurs. Moreover, this solution scheme could be applied repeatedly to intervals of decreasing temperature to resolve a time-dependent case.

Dividing equation (2.5) by the dry mass, M , gives

$$\dot{w} = -B (C_0/C_A - 1), \text{ with } B = vk C_A / (v + k)M \quad (2.10)$$

where C_0 is defined as before and is a function of both w and T_0 . The ambient concentration, C_A is a function of T_A , which is taken as the yearly mean. Explicitly, C_0 is given in terms of the water vapor isotherm equation. (This equation is derived later in Section 3 as equation 3.8.) The details of incorporating the water vapor isotherm are not required at this juncture to

understand the solution of (2.5) and will be discussed later. When the diffusion depth, Z , is constant, then B is a constant too. But if Z increases, say as drying occurs, then B is a function of Z , by its dependence on k , which may then depend on w for the waste. First, the simple case of constant B is considered, and then the solution for the more complicated case with a drying crust is considered.

When Z is constant, one can rearrange and integrate equation (2.10) to give a solution of the form:

$$\int_w^{w_0} \frac{1}{g(w) - 1} dw = B \cdot t \quad (2.11)$$

where B is the constant defined in equation (2.10) and $g(w) = C_0/C_A$. The solution (2.11) determines the time t over which the water content falls from an initial value, w_0 , to w (where $w < w_0$). Moreover, the water content, w'' , in equilibrium with the ambient water vapor concentration satisfies $g(w'')$ equal to 1 (the denominator of the integrand in equation (2.11) becomes zero). In other words, when the water content ceases to decrease, the water vapor concentration in the waste must be the same as the ambient vapor concentration. This condition defines the air-dry state, the driest the waste can become at a given temperature when in equilibrium with the ambient water vapor concentration. However, the air-dry state may not be reached until an infinite time.

When a crust is forming and becoming thicker, Z now depends on the amount of water removed. The total mass of water, m , is

$$m = A (L - Z) D_{\text{wet}} w_0 + A Z D_{\text{dry}} w_{\text{dry}} \quad (2.12)$$

where D_{wet} and D_{dry} are the wet and dry density of the waste. The initial water content is w_0 , and this value is assumed to describe the waste at all times below the crust depth, Z . The air-dry water content is w_{dry} , determined by setting $g(w_{\text{dry}}) = 1$. Using equation (2.12), Z is found as a function of w :

$$Z = (w - c L)/(d - c) \quad (2.13)$$

with $c = (A D_{\text{wet}}/M) w_0$ and $d = (A D_{\text{dry}}/M) w_{\text{dry}}$.

Substituting equation (2.13) for Z in the expression for the transfer coefficient, equation (2.6), gives k as a function of w and $B(w)$ as defined by equation (2.10). A small initial depth, Z_0 , may need to be added to this estimate of Z so that water vapor initially comes from below a slightly drained surface. With B depending on w (not constant), the solution of (2.10) is now found by replacing the integrand in the integral of equation (2.11) by $1/(B(w)(g(w) - 1))$. The integral that results now equals t .

An inherent requirement of this constant temperature solution is that the water vapor concentration, C_0 , below the crust must be in equilibrium with the entire average water content of waste depth L , including the crust. This assumption is reasonable for a shallow waste but would not apply for a deep waste profile.

Equation (2.11) can be solved for a number of values of w to produce a drying curve of water content w versus time. Given the changing C_0 as a function of w and equation (2.4) for C , the relative humidity in the headspace can be determined (see equation (3.11)), and the crust depth given by equation (2.13) can be calculated.

2.3.4. Deep Saltcake-Type Waste

In case (3), the waste may be any depth and temperatures will depend on yearly cycles (see Section 4). Equation (2.5) must be solved as a general first-order differential equation in terms of w and t . Now Z depends on time explicitly as water is removed from above the interstitial liquid level and below the crust. To solve this case, the moisture content for the entire waste is first expressed in terms of the same variable for the crust and for the waste below the crust. The moisture in the crust is treated as being in equilibrium with the headspace water vapor concentration, which is being determined by the prevailing evaporation and ventilation rates.

First, let m_z and m_o be the masses of water in the surface crust to depth Z and in the remaining waste from Z to the maximum depth L . The total water mass, m , is the sum of the water in the crust and below the interstitial liquid level. Let M_z and M_o be the dry masses of these same two regions, with sum M . The water contents are w_z and w_o , which are the masses of water divided by the respective dry masses. Now $M_z = (Z/L) M$ and $M_o = (1 - Z/L) M$. Letting W be the water content of the total waste, then

$$W = (Z/L) w_z + (1 - Z/L) w_o \quad (2.14)$$

For a saltcake waste, the water content, w_o , below Z does not change and is taken as constant. Above depth Z , the water content in the crust is changing and is determined by the equilibrium with the water vapor concentration given by equation (2.4), diffusing into the headspace.

To solve the water loss equation (2.5), first note that the water vapor concentration beneath the surface, C_0 , depends on w_o and T_o and is obtained by using the adjusted water vapor isotherm. The calculation is given in Section 3.2.2; in brief, the partial pressure beneath the waste surface for the applicable water content is obtained by adjusting the water vapor isotherm measured at the reference temperature to the waste surface temperature. Then the ideal gas law is applied to convert partial pressure to the required concentration. (Equation 3.8, derived in Section 3.2.2, provides the explicit formula for obtaining C_0 .)

The headspace concentration, equation (2.4), is related to the water vapor concentration in the waste as

$$C = \frac{C_0 + (\alpha\eta + \mu)C_A}{\alpha\eta + \mu + 1} \quad (2.16)$$

where

$$\eta = Z/L \quad \alpha = vL/AD \quad \mu = v/k_e$$

The water loss equation (2.5) can be expressed as

$$dW/dt = -\lambda (C_0 - C_A)/(\alpha\eta + \mu + 1) \quad (2.17)$$

with $\lambda = v/M$. Equation (2.14) is rearranged to yield an expression for the dimensionless crust depth, h ,

$$\eta = (W - w_o)/(w_z - w_o) \quad (2.18)$$

The unknown, w_z , in equation (2.18) is found by determining the water content in equilibrium with the headspace water vapor concentration given by equation (2.16) for temperature T . For this calculation, methods described in Section 3 must be employed once again for adjusting the water vapor isotherm for varying temperature. A reader may return to consider this computational detail after considering Section 3.2.1. The specific equation for w_z , however, is

$$p_{ref}(w_z) = p_{sat}(T_{ref}) \left(\frac{C}{C_s(T)} \right)^{T/T_{ref}} \quad (2.19)$$

where $C_s(T)$ is the saturation water vapor concentration for T , and p_{sat} is the saturation partial pressure evaluated at the reference temperature, T_{ref} , in equation (2.19). The reference partial pressure, p_{ref} , appearing on the left side of equation (2.19) is then inverted, giving the water content, w , as a function of the partial pressure given by the right side of (2.19). Note that this inverted curve for $p_{ref}(w)$ is the same as the original water vapor isotherm: the equilibrium w , or equivalent wt% water, as a function of the reference partial pressure to which a waste sample was exposed.

Equations (2.16) and (2.18) together imply that the dimensionless crust depth is implicitly a function of W and t . Equation (2.17) for the water loss is then solved for W subject to equations (2.16) and (2.18) using (2.19). A Mathcad (MathSoft, Inc.) program is used to solve (2.18) simultaneously in terms of W and t and to integrate (2.17) with a Runge-Kutta solution.

Certain mathematical approximations were made to simplify the calculation of salt-cake drying. In particular, the detailed spatial gradient of the water vapor concentration in the dry crust region is replaced by a single value. The whole crust, which is forced to have a single uniform moisture content, is presumed equilibrated with the partial pressure in the headspace. The moisture content below the liquid level is uniform. Finally, the evaporation rate is made to follow the temperature cycle steadily during the year. In view of the unknown variability of waste properties with depth, it is expected that this modeling approach for saltcake is sufficiently accurate and describes the dryout appropriately.

2.4. Shallow Waste Drying Example

Waste in Tank AX-102 is an example of a shallow waste. Before performing a more detailed analysis, including the declining temperature trend with yearly cycle, this section illustrates the results of a drying estimate as calculated according to the method described in Section 2.3.3. The results can be contrasted with those discussed in Section 5.1, which incorporates the consequences of waste cooling. This example calculation is intended to demonstrate that the essential aspects of dryout, subject to moisture equilibrium described by a laboratory-measured water vapor isotherm, is captured in this simple, although approximate, equation (2.11), which is basically an analytical answer depending only on the evaluation accuracy of the integral.

The objective of this dry-out analysis when based on equation (2.11) is an estimate of the drying depth and the resulting decrease of relative humidity in the headspace over time. Relative humidity as depending on time may provide an important quantity for monitoring the waste dryout when direct measurements of moisture content are not obtainable.

Figure 2.1 shows the typical drying curves for AX-102 waste starting from two different initial moisture contents. Under the imposed constant temperatures for the headspace, waste, and ambient, these curves should reflect the fastest possible drying.

The curves in Figure 2.1 show a continually decreasing moisture content that approaches the air-dry value. For this model that imposes constant temperatures, the waste does not re-wet, as will be shown in Section 5 when cooling is taken into account. Moreover, notice that the difference in moisture content for the two initial values is increasing slightly with time. This behavior is a reflection of the nonlinear dependence of drying on time, as expressed by equation (2.11). These drying curves are for a crust depth that depends on the remaining water content (i.e., equation 2.13 is applied).

Figure 2.2 shows the depth of the air-dry crust over time. The crust reaches deeper, sooner for the waste with the lower initial moisture. In general, Figure 2.2 shows that dryout occurs more rapidly and to greater depth when the starting moisture content is less. The solution for constant temperatures thus has the value of providing an easy estimate of the impact of different initial moisture contents on the dryout and a time for which a certain dryness (wt% water) is likely going to be reached.

Figure 2.1. Dryout for Tank AX-102 Waste. Wt% moisture of the waste is based on measured water vapor partial pressure.

Figure 2.2. Depth of Air-Dry Layer in AX-102. Squares indicate the case with initial 25 wt% water.

The decreasing relative humidity in the headspace as drying occurs is shown in Figure 2.3. Both simulations for differing initial moisture begin with the same relative humidity, but the drier waste shows a more rapid decline in relative humidity with time. Notice that there is a difference of nearly 10% in the relative humidity after about 30 years for the two starting moisture contents of 25 and 30 wt%. Thus, relative humidity in the headspace appears to be a very sensitive indicator of the dryness condition of a shallow waste after drying has begun.

An estimate of the relative humidity as it depends on drying time is an important prediction because it would be the main measurable physical quantity that would be readily available to test the accuracy of the model's projections. This presumes that a time series of direct measurements of moisture content would not be available from repeated (expensive) core samples. That is, once the isotherm describing the particular surface waste is known, measurements of relative humidity in the headspace are the most effective way to track the drying trend. Such measurements could be applied to re-estimate the operable transfer coefficient, presuming the breathing rate is known and temperatures are available. Such a re-estimated transfer coefficient could then be used to improve projections of future drying rate. Thus equation (2.11) could be used to estimate dryout parameters by matching its predictions with actual measurements of moisture content or relative humidity. Using relative humidity to estimate the transfer coefficient for modeling dryout is discussed further in Section 3.3.

Head Space Temp = 23.5C
 Air Dry Wt% = 11.6
 Outside Temp = 12 C
 Outside RH% = 54

Figure 2.3. Relative Humidity in the Headspace of AX-102 for Waste Drying. The curves (same symbols) correspond to those of Figure 2.1.

3.0 Waste Moisture - Water Vapor Equilibrium

As previously discussed, the relationship between the water content of the waste surface and the water vapor concentration in equilibrium with it is expressed by a water vapor isotherm. This section explains how the water vapor concentration at or beneath the surface crust is obtained from a water vapor isotherm.

3.1 Water Vapor Isotherm in Terms of Partial Pressure

A water vapor isotherm is a functional relationship between the partial pressure of water vapor in equilibrium with waste having a specific water content at a fixed reference temperature. Such a curve is obtained by allowing a waste sample to equilibrate with an imposed water vapor partial pressure. Scheele et al. (1996) discuss the method of measuring the water vapor isotherm for waste tank samples. Usually, a waste sample is placed in a closed container holding a saturated solution of a certain salt that has a known equilibrium partial pressure. The samples are then allowed to equilibrate for a sufficient amount of time until a fixed (no longer changing) moisture content is reached (Scheele et al. 1996). Because the time required to obtain each equilibration measurement is substantial, generally only five or six points are obtained for the entire isotherm.

Generally, the equilibrium moisture content for a particular partial pressure exposure is attained by either drying the sample from its initial value or re-wetting it. A sample exposed to a partial pressure greater than its equilibrium value will become wetter; the opposite occurs if the partial pressure is less than the equilibrium value. Usually, the equilibrium moisture content is approached asymptotically as either a minimum (drying) or maximum (wetting) value.

How quickly a sample reaches its final moisture equilibrium depends on its mass (size) and the rate of water vapor diffusion (transfer) through the exposed surfaces. The isotherm also quantifies how strongly the moisture is held in the waste by chemical and physical forces.

The simple drying model for constant temperatures, equation (2.11), is directly applicable as a means to estimate the laboratory-scale diffusion coefficient or to determine the isotherm that is consistent with the drying dynamics (provided the diffusion coefficient is already known). Thus, an isotherm is obtained from a series of dryout curves that would be predicted by the model for drying a shallow waste (Section 2.3.3). Each curve is associated with exposure to a different outside partial pressure or ambient water vapor concentration. In the laboratory, however, the chamber holding the waste sample is closed, and it does not connect to the water vapor source or sink through ventilation.

Figure 3.1 is an example of an isotherm curve measured for a waste sample from the surface of Tank U-105. The curve includes only five measurements. In order to define the entire isotherm, linear interpolation or another appropriate interpolation scheme is employed to obtain a

Figure 3.1. Water Partial Pressure Isotherm of Tank U-105 Waste Measured at Reference Temperature 33°C and Adjusted to 23.3°C. Data are for core 131 segment 2U waste sample.

continuous relationship between the variables. The linear interpolation shown in Figure 3.1 constitutes an approximation of what the actual isotherm curve might be. Denoting p_{ref} as the partial pressure at the reference temperature, T_{ref} , the isotherm curve is expressed as

$$p_{ref} = p_{ref}(w; T_{ref}) \quad (3.1)$$

This is the reference partial pressure in equilibrium with waste having a moisture content, w . In the laboratory, waste water content w is typically reported in terms of the wt% water. The two are related as

$$wt\% \text{ water} = 100w/(1 + w) \quad (3.2)$$

Figure 3.1 also shows the adjusted isotherm estimated for another temperature, i.e., one for which the curve was not directly measured. Such an adjustment is necessary to convert isotherms at laboratory conditions to the actual conditions at the waste surface, which evolve over time in the model. The next section discusses the adjustment procedure.

3.2 The Temperature Dependence of the Isotherm

This section demonstrates how a water vapor isotherm is adjusted to a temperature other than the reference value for which it was originally measured. This adjustment step is necessary to obtain the water vapor concentration at or below the waste surface in equilibrium with the existing waste moisture content at a particular temperature. Waste is continually cooling in a tank, lowering the water vapor concentration in the headspace, so the isotherm must be continually adjusted over the dryout time.

3.2.1 Adjusted Isotherm for Another Temperature

To adjust the isotherm from the reference temperature to another temperature, a relationship is derived based on postulating that the potential energy (also, the chemical free energy) of water in waste is constant over an applicable range of temperature (Perry et al. 1984). The range of temperature must encompass the range of waste cooling over the calculated time period. The validity of the isotherm adjustment based on imposing constant potential energy has been confirmed directly for only a few waste samples (see Section 3.2.3), so it must be viewed as an approximation at best.

However, relationships derived in a later section (Section 3.3) and applied to cases where both the relative humidity in the headspace and the surface moisture content are measured can be used to test the isotherm adjustment. The agreement between the calculated and measured values of moisture content for the temperature of the waste surface (Section 3.3) confirms the isotherm adjustment method described below.

The potential energy of water in waste, ψ , is expressed as

$$\psi = \frac{RT}{M_w} \ln \left(\frac{p}{p_{sat}} \right) \quad (3.3)$$

where R is the gas law constant (8.314 Joule/mole-K), M_w is the molecular weight of water (0.018 kg/mole), p is the partial pressure of water above the waste, and p_{sat} the vapor pressure of pure water (called the saturation value) at the absolute temperature T . In the model, the saturation vapor pressure of water, in torr, is calculated from the following empirical relation adapted from Hammel et al. (1981):

$$p_{sat} = 4.585 \exp \left(\frac{17.27(T - 273.16)}{T - 35.86} \right) \quad (3.4)$$

The potential energy, as expressed by equation (3.3), includes all factors (e.g., solution ionic strength, adsorption of water by solid matrix, etc.) that affect the partial pressure of water above a waste sample. The concept of water potential energy for porous material with osmotic effects is discussed by Marshall and Holmes (1979). Applying the assumption that the potential energy (equation (3.3)) is constant over a temperature range gives $\psi = \psi_{ref}$ or (rearranging)

$$T \ln \left(\frac{p}{p_{sat}} \right) = T_{ref} \ln \left(\frac{p_{ref}}{p_{sat}(T_{ref})} \right) \quad (3.5)$$

which can also be stated as

$$\frac{p}{p_{sat}} = \left(\frac{p_{ref}}{p_{sat}(T_{ref})} \right)^{\frac{T_{ref}}{T}} \quad (3.6)$$

Because $p_{ref}(w; T_{ref})$ is a known function (it is the measured water vapor isotherm), as is $p_{sat}(T)$, the two expressions can be substituted into equation (3.6) to yield an expression for $p(w; T)$. In other words, for any given waste water content w , equation (3.6) gives the partial pressure p of water vapor in the waste at any temperature T , based on the reference (isotherm) values of the same variables at that value of w .

3.2.2 Water Vapor Concentration Beneath the Waste Surface

The water vapor isotherm adjusted for the waste surface temperature can now be used to obtain the water vapor concentration in equilibrium with the waste moisture content. Using the ideal gas law, the partial pressure of water vapor in the waste, p_o , is converted to the water vapor concentration at the waste temperature, T_o , by the following:

$$C_o = \frac{M_w}{RT_o} p_o \quad (3.7)$$

Since water vapor concentration is often expressed in terms of relative humidity, the definition of relative humidity, RH_o , at the waste temperature T_o gives

$$C_o = C_s(T_o) RH_o \quad (3.8)$$

where the saturation water vapor concentration, C_s , is given by

$$C_s(T_o) = \frac{M_w}{RT_o} P_{sat}(T_o) \quad (3.9)$$

By applying equation (3.6) and noting that $p_o/p_{sat} = C_o/C_s$, the relative humidity (in the waste beneath the crust), RH_o , is given by

$$RH_o = \left(\frac{P_{ref}}{P_{sat}(T_{ref})} \right)^{\frac{T_{ref}}{T_o}} \quad (3.10)$$

Again, the water vapor concentration of equation (3.8) based on equation (3.10) is a function of w as well as T_o through equations (3.1) and (3.2), which define the reference isotherm. Equation (3.10) is used in Section 3.3 to relate the headspace relative humidity, which does not equal that below the waste surface, to the moisture content of the surface.

3.2.3 Confirming the Isotherm Adjustment Method

The adjusted isotherm appearing in Figure 3.1 is obtained from equation (3.6). For each measured partial pressure at the reference temperature corresponding to a particular w , the adjusted p is found by substituting the new temperature (in degrees Kelvin) into equation (3.6). Note that only the actual measurements are adjusted this way. The curve between measurements remains defined by linear interpolation for each isotherm.

Figure 3.2 demonstrates an explicit confirmation of the adjustment procedure for a waste sample from Tank A-102. Three points measured at 32°C are compared with predictions from an adjusted isotherm based on a reference temperature of 24°C. The measured values fall nearly on the adjusted isotherm. The agreement can also be verified by applying the reverse adjustment, projecting the 32°C isotherm to 24°C (not shown). These points also deviate little from the actual measurements for 24°C.

3.3 Relating Headspace Humidity to Waste Moisture

Section 3.2 discussed how the equilibrium water vapor concentration is related to waste's water content. This section relates the *headspace* water vapor concentration (in terms of relative humidity) at its temperature T to the water content below the crust. This water content and the temperature of the waste, T_o , determine the water vapor concentration, C_o , that drives

Figure 3.2. Water Vapor Isotherm Adjustment Confirmed for Tank A-102 Waste. Water partial pressure measured at 24°C is adjusted and compared with the isotherm measured for 32°C. The curve defined by triangles was generated by applying equation (3.6) to each point of curve defined by solid square.

evaporation by diffusion through the crust into the headspace. The emphasis is on relative humidity because this parameter is typically measured in the headspace of breathing tanks. Note, however, that this parameter must be reported in combination with the prevailing temperature. The equations derived here are used to further test the validity of the isotherm adjustment and are the basis for estimating the transfer coefficient in situ for actual tank conditions, as reflected in common measurements of relative humidity and temperature.

The relative humidity in the headspace, which can be measured, is, by definition,

$$RH = \frac{C}{C_s(T)} \quad (3.11)$$

where the saturation water vapor concentration, $C_s(T)$, is defined as in equation (3.9). Using equation (2.4) for the steady-state water vapor concentration in the headspace gives

$$RH = \frac{\frac{b \cdot C_a}{C_s(T)} + RH_o \cdot \frac{C_s(T_o)}{C_s(T)}}{1 + b} \quad (3.12)$$

where $b = v/k$.

Solving for RH_o in this equation (3.12) and using equation (3.10) and then solving for p_{ref} gives

$$p_{ref}(wt\% \text{ water}) = p_{sat}(T_{ref}) \cdot \left[\frac{(1+b) \cdot RH \cdot C_s(T) - b \cdot RH_a \cdot C_s(T_a)}{C_s(T_o)} \right]^{\frac{T_o}{T_{ref}}} \quad (3.13)$$

Here, subscript a refers to ambient. The left side of equation (3.13) is the isotherm equation (3.1) expressed in terms of wt% water instead of water content. At a given value of RH , then, everything in equation (3.13) is known except for wt% water. Simply inverting the isotherm from p_{ref} as a function of wt% to yield wt% as a function of p_{ref} and solving the resulting expression gives the wt% water of the waste. In turn, wt% water is related to w by equation (3.2). In this way, equation (3.13) gives the water content, w , in terms of headspace and outside conditions (temperatures and relative humidities) and the reference temperature.

In the special situation where water vapor transfer from the waste surface is not limited by diffusion, or when the breathing rate is comparatively small, k is much greater than v , so b approaches zero. In this situation, C approximates C_o , and the term in brackets on the right side of equation (3.13) reduces considerably to yield the following expression:

$$p_{ref}(wt\% \text{ water}) = p_{sat}(T_{ref}) \left(RH \frac{C_s(T)}{C_s(T_o)} \right)^{\frac{T_o}{T_{ref}}} \quad (3.14)$$

Thus, when the concentration of water vapor in the headspace is in balance with that beneath the surface, equation (3.14) predicts the water content from the temperatures and the relative humidity of the headspace, RH .

With these expressions, the water partial pressure isotherm and the method for adjusting it for a different temperature can be shown to be consistent with tank headspace humidity measurements and tank temperatures. In Tank U-105, for example, the partial pressure of water in the headspace is expected to be essentially the equilibrium partial pressure of water over the waste surface, because the waste surface is covered with supernatant liquid and the ventilation rate is relatively low. The water partial pressure isotherm for the core 131 segment 2 sample from U-105 (Figure 3.1) can be used to evaluate equation (3.14) for a headspace partial pressure of 13 torr with $RH = 64\%$ and $T = 22.3^\circ\text{C}$. The unknown surface temperature, T_o , ranges between the headspace and subsurface waste temperatures. This is plotted in Figure 3.3 as an isobar (i.e., constant RH and T). A horizontal line is also drawn at 37 wt% water, corresponding to the actual water content measured in the core 131 segment 2 waste sample. The isobar graph and horizontal line intersect at about 22.7°C . This is the calculated value for the waste surface temperature when waste having 37 wt% water exhibits a water partial pressure of 13 torr in the headspace. This calculated value is slightly higher than the expected 22.3°C temperature of the headspace measured at the time the headspace humidity was determined. This comparison indicates that the measured quantities and the isotherm adjustment method are consistent with the premise that the Tank U-105 headspace humidity and waste moisture content are essentially in equilibrium.

Equation (3.13), which is general for any transfer coefficient and breathing rate, can be used to determine k when the relative humidity and temperature in the headspace are measured and the surface temperature is known. To find $k = v/b$, one solves for b in this equation using the known breathing rate. In this way, a mass transfer coefficient consistent with initial conditions in a tank can be determined. This equation (3.13) is used in Section 5 to examine Tank C-104.

Figure 3.3. Predicted Water Content of U-105 Waste Depending on Surface Temperature. Curve is for constant water partial pressure of 13 torr (64% RH and 22.3°C) in the headspace. The dashed line is the expected water content.

4.0 Tank Temperature Trends

The temperatures of the waste, headspace, and ambient air are assumed to cycle with seasonal meteorological changes. The waste and headspace temperatures are also assumed to decrease with time as the heat produced by radioactive decay diminishes. The equation derived to describe these temperature cycles is

$$T = \hat{T}_{final} + (\hat{T}_{initial} - \hat{T}_{final})e^{-at} + (G + (E - G)e^{-at})\cos(2\pi(t+h)) \quad (4.1)$$

Here $\hat{T}_{initial}$ is the initial mean temperature, $\hat{T}_{final}$ is the final mean temperature, t is time in years, E and G are initial and final amplitudes of the temperature cycle, h is a phase for synchronizing the equation with the seasonal cycle, and a is the decay constant for decline of the yearly mean temperature. The decay constant a (obtained by fitting) is approximately the decay constant for ^{137}Cs or for ^{90}Sr radioactive decay, since the heat load and temperature are directly related to the amount of these radionuclides present. Constants E , G and h were determined by fitting the available data to equation (4.1).

In each simulated tank, there are three versions of equation (4.1): one for ambient conditions, one for the headspace, and one for the waste. In the ambient atmosphere, $\hat{T}_{initial}$ is equal to

$\hat{T}_{final}$ and E is equal to G , so equation (3.16) reduces to

$$T = \hat{T} + G\cos(2\pi(t+h)) \quad (4.2)$$

Table 4.1 lists parameter values obtained for ambient air and several selected tanks. Figure 4.1 demonstrates the fit of the temperature correlation to the thermocouple measurements made in the headspace of Tank U-105. The parameters in Table 4.1 will be used to evaluate the dryout behavior of these three tanks in the next section.

Table 4.1. Temperature Correlation Parameters for Ambient Air and Selected Tanks

Tank	Date of $t = 0$	$\hat{T}_{initial}$ (°F)	$\hat{T}_{final}$ (°F)	a (yr ⁻¹)	E (°F)	G (°F)	h (yr)
Ambient		56.3	56.3	0	0	0	0.541
AX-102 Headspace	9/14/94	75	56.3	0.023	3.1	1	0.26
AX-102 Waste	9/14/94	75	55	0.023	3.1	1	0.23
U-105 Headspace	1/3/91	78	60	0.021	5.2	1	0.24
U-105 Waste	1/3/91	80.2	60	0.021	5.2	1	0.23
C-104 Headspace	4/4/94	89	60	0.027	5.4	1	0.244
C-104 Waste	4/4/94	98	60	0.027	2.8	1	0.168

Figure 4.1. Tank U-105 Headspace Temperature Fit to Measurements. Individual data points are fit to equation (4.1) (smooth curve). See Table 4.1 for the start date of time.

5.0 Modeling Examples of Dryout

In this section, the dryout model is applied to three example tanks, AX-102, C-104, and U-105. These examples are typical of other organic safety issue tanks that will require evaluation (Meacham et al. 1997). The tank applications discussed here are sufficient to demonstrate typical results for the various waste types. Table 5.1 provides general descriptions of the waste in the example tanks and gives the relative humidity measured for the headspace on a particular day.

Table 5.1. Waste Characteristics for Tanks AX-102, U-105, and C-104

	AX-102	U-105	C-104
Waste type	saltcake	saltcake	sludge
Waste volume (kgal)	39	418	295
Waste depth (m)	0.254 (10 in.)	3.96 (156 in.)	2.16 (85 in.)
Interstitial liquid volume (kgal)	17	170	11
Supernate volume (kgal)	3	37	0
Ventilation rate (m ³ /h)	28	8.5	102
Current wt% water (%)	25	34	50
Headspace RH and date measured	57% on 6/27/95	64% on 2/24/95	45% on 3/3/94
Waste surface temperature (°C)	23.5	23.3	33.7

5.1 Tank AX-102

Tank AX-102 is a shallow sludge waste tank that has been interim stabilized (i.e., drainable liquids have been pumped). The tank was found to have a high ventilation rate (Huckaby et al. 1997), which may account for the 0.27 in./yr (0.686 cm/yr) drop in liquid level observed between 1981 and 1988. Two waste samples analyzed for water content gave significantly different results; an auger sample collected in 1995 was reported to be 30.5 wt% water (Sederburg et al. 1995), but a sample collected in 1998 was found to have only 25 wt% water (Scheele et al. 1998). For this modeling example, it was presumed that the waste currently has 25 wt% water.

The water content of waste in equilibrium with the measured headspace humidity was calculated to be 25 wt% using the partial pressure isotherm. This agrees very well with the water content of the second sample. It suggests that, despite the relatively high ventilation rate, water

vapor in the headspace is nearly in equilibrium with waste moisture. Resistances to transport of water from the waste into the headspace are relatively small, and loss of water from the waste is determined primarily by the ventilation rate. The measured headspace humidity, water partial pressure isotherm, and water content of the waste do not indicate the presence of a water vapor diffusion limitation in the waste (i.e., a dry surface crust).

When the temperature trends both inside and outside the tank are taken into account, the model predicts that the waste will reach a minimum water content of about 14.5% in 40 years, then increase gradually as the waste continues to cool and begins to reabsorb water vapor. The predicted wt% water in the waste for the next 100 years is shown by the dashed curve in Figure 5.1. Figure 5.2 shows how the vapor concentration in the headspace behaves over time. Note also that during the simulated drying period, the headspace relative humidity (no figure provided) begins at about 56% and drops to about 37%, before increasing again to about 42% at 100 years.

The model for Tank AX-102 assumes that all incoming air has the water vapor concentration of ambient air, but much of the air introduced to Tank AX-102 may actually come from the other humid tanks in AX Tank Farm. This may be true of many tanks but particularly in AX Tank Farm, where large underground vent pipes connect the tank headspaces and are associated with the relatively high ventilation rates observed there.

If a crust does form on the surface of the waste that significantly impedes water transport, then water loss from Tank AX-102 would occur more slowly. This situation has been modeled by assuming that a 5.1-mm- (2-in.-) thick porous crust forms. Assuming the air-filled pore structure has a porosity of 10%, the diffusion coefficient for transport through the crust, D , becomes

$$D = 0.1D_{H_2O} \quad (5.1)$$

where D_{H_2O} is the diffusion coefficient for water in air. In conjunction with the eddy transfer coefficient, this gives an overall mass transfer coefficient of about $k = 70 \text{ m}^3/\text{h}$. The water content of the waste predicted by the model under these assumptions is given by the solid curve in Figure 5.1. As is expected, the waste water content decreases less slowly and does not become as dry as it does in the absence of a crust.

Figure 5.1. Waste Water Content in Tank AX-102, Modeled with and without a Surface Crust

Figure 5.2. Predicted Headspace Water Vapor Concentration in Tank AX-102

5.2 Tank U-105

The waste in Tank U-105 is a relatively deep, wet saltcake. Though records indicate the presence of about 37 kgal of supernatant liquid (equivalent to a 34-cm-thick layer across the surface), two of the three core samples from this tank did not contain supernatant liquid. It is assumed here that core 131, segment 2U (which did not contain supernatant liquid) is representative of the waste near the surface. This core was the most central of the three (Brown 1996). The waste has not been stabilized by pumping and is likely to undergo some consolidation (i.e., shrink like sludge) as water is removed by evaporation (Simmons et al. 1997). Only after the waste is partially drained and a rigid saltcake matrix has formed would evaporation via a porous saltcake crust be expected to occur. Thus the waste was treated as a sludge type for this drying analysis.

Because the waste profile is about 4 m deep and believed to be saturated with liquid, it qualifies as a "deep" waste. Because we are considering it to behave as a sludge type, it is treated as described for case (1). We therefore specify a drying layer of thickness 48 cm, corresponding to the first 19-in. core segment. As discussed in Section 2, this assumption should provide a bounding estimate of the surface moisture loss.

The average water content of the waste near the surface was taken to be 34 wt%. Calculations indicate that the water vapor concentration of Tank U-105 waste agrees very well with the measured headspace humidity (see Figure 3.3). This indicates that, as in the case of Tank AX-102, the rate of water loss is determined by the ventilation rate of the tank and not by the rate water is transported from the waste into the headspace. It was therefore assumed that diffusion resistance associated with the waste and headspace boundary layer was negligible.

The calculated water content of the uppermost 48-cm layer of waste in U-105 is plotted in Figure 5.3 as a function of time. The water vapor isotherm of Figure 3.1 is used for this dryout calculation. As indicated in the figure, the water content of this thin layer of waste decreases only slightly to about 29 wt% after 50 years. Figure 5.4 shows the predicted yearly average headspace relative humidity in U-105. The simulation begins in 1991 and roughly agrees with the single measurement of 64% relative humidity made in early 1995.

Another way of expressing the model results is to consider the depth of waste that dries to a particular wt% water. Assuming no replenishment of water from below and neglecting diffusional resistance associated with the formation of a porous layer, the model predicts that the top 10 cm of waste could be dried to about 10 wt% water. Assuming the average ventilation rate doubled in the model (i.e., $v = 17 \text{ m}^3/\text{h}$), the model predicts that a 19-cm top layer could be dried to 10 wt% water in 25 years.

Figure 5.3. Predicted Water Content of Waste Surface Layer in Tank U-105. Layer is 48 cm deep, one core sample segment.

Figure 5.4. Headspace Relative Humidity Predicted for Tank U-105.

5.3 Tank C-104

Waste in Tank C-104 is a sludge type (Baldwin 1997). It is about 216 cm (85 in.) deep and mostly wet. In photos taken in 1990, a crust with extensive cracks and plates is seen covering the surface. The liquid level decline (0.75 in./yr) over an eight-year period indicates a breathing rate of 102 m³/hr (60 cfm) in the absence of leakage. This breathing estimate is obtained by calculating the water loss due to ventilation using the current water vapor concentration measured in the headspace. Huckaby et al. (1998) measured approximately the same breathing rate (66 to 68 cfm) by independent means. Such relatively high breathing rates are attributed to pipe connections with other C Farm tanks, which are being actively ventilated, and the breathing rate is expected to be reduced in the future when ventilation becomes entirely passive. However, the estimated past rate of 60 cfm is presumed to continue into the future for calculating dryout under worst-case conditions.

For the current tank temperatures, 27.3°C in the headspace and 33.7°C just below the waste surface, the partial pressure of water vapor in the headspace is substantially lower than the value that would reflect equilibrium with the present waste moisture. Figure 5.5 provides the water vapor isotherms measured for C-104 waste obtained from the surface (core 162, segment 1 and core 165, segment 2, upper halves). Figure 5.6 shows the water content that is expected at the surface if equilibrium held. Waste at the surface should have a water content in the range of 7 to 10 wt% for equilibrium with the 45% relative humidity measured in the headspace at 27.3°C. This condition is consistent with the presence of the observed crust, which covers the waste and has a bulk moisture of around 40 to 50 wt%. Core segments including the surface indicated about 40 wt% water. If the headspace water vapor concentration were in equilibrium with 40 wt% water, then the relative humidity would have to be about 81%, which would reflect a partial pressure of 22.1 torr instead of the 13.4 torr actually measured.

Thus, for this waste surface, it appears that the steady exhausting of water vapor is potentially diffusion-limited, and the high breathing rate depresses the headspace water vapor concentration much below what should prevail below the crust in the waste with 40 wt% water. Note that an alternative explanation is that water vapor is also being removed by condensation and absorption on the cooler waste along the tank wall. Moreover, the single measurement of relative humidity may not always be representative of the headspace. Nevertheless, the water vapor concentration in the headspace is effectively reduced below the value that would result by equilibrium with the wet bulk waste.

The next two subsections analyze Tank C-104 first as a sludge (the apparent waste type) and then as saltcake to better estimate the potential depth of surface drying if the crust thickens during drying.

Figure 5.5. Water vapor isotherms for waste in Tank C-104. Reference temperature is 36°C and subsurface temperature is 33.7°C (adjusted curve). (Average of isotherms for core samples 162 seg 1 and 165 seg 2, upper halves.)

Figure 5.6. Surface Moisture Content in Tank C-104 in Equilibrium with Headspace Relative Humidity. Headspace RH is 45% at 27.3°C. No crust limits evaporation into the headspace.

5.3.1 Tank C-104 Waste as Sludge

To model a crust limiting diffusion of water vapor into the headspace, a transfer coefficient was estimated to be consistent with the observed relative humidity. Figure 5.7 uses equation (3.13) with $b = 2.4$ to relate the subcrust moisture to a range of temperatures there. Figure 5.7 shows that 40 wt% is associated with a sub-crust temperature of 31.4°C . This temperature is midway between values measured in the headspace and deep waste. The crust thickness was taken to be 14 cm (5.5 in.), and the void space porosity is 15%. This gives 0.104 m/hr for the transfer coefficient per unit area, i.e., k/A , and an eddy transfer coefficient, k_e/A , of 2.3 m/hr. Therefore, the overall transfer coefficient is determined mainly by the diffusion resistance through the crust (see equation 2.8). This yielded a transfer rate of $k = 42.6 \text{ m}^3/\text{hr}$ relative to $v = 102 \text{ m}^3/\text{hr}$. As a result, the water vapor concentration in the headspace is midway between that below the crust and the ambient value, according to equation (2.4).

Figure 5.8 shows the drying of the bulk waste and the surface crust, treated as a sludge problem. (A waste depth of 115 in., corresponding to the reported volume of 295 kgal, was used instead of the present 85 in. determined by manual tape level.) With these modeling parameters, the beginning relative humidity in Figure 5.9 is comparable with the actual value of 45% in 1994. Figure 5.9 shows that the relative humidity would actually increase over time with drying. The relative humidity given is the yearly average, though it actually varies over the yearly temperature cycle. Notice that the surface crust in equilibrium with the headspace water vapor becomes wetter, corresponding to the increasing relative humidity. Apparently, the relative humidity increases even though the headspace is cooling, because water vapor concentration produced by the modeled evaporation rate is still increasing relative to the saturation value. The modeled water vapor concentration on a yearly average basis, however, continually decreases with time in the headspace.

In 50 years, the bulk waste (115 in. deep) below the imposed fixed 5.5-in.-thick crust would dry to from 50 to 44 wt%. In the crust, which remains equilibrated with the headspace water vapor concentration, the water content is initially about 10 wt% and rises to 12 wt% in 50 years. (Note that the 85-in.-deep waste would dry to 41.5 wt% in 50 years, with the same surface drying trend.)

A calculation of moisture loss without accounting for tank cooling and assuming a constant relative humidity of 45%, produces a steady water loss of about 8500 kg/yr. This loss rate would reduce the water content of the waste to about 35 wt% in 50 years and to less than 20 wt% in 100 years. Thus, it is clearly important in this case to account for tank cooling to estimate the dryout behavior appropriately. Note also that this large sludge mass is exceedingly resistant to being dried out even at the high ventilation rate.

Figure 5.7. Moisture Content below Crust in Tank C-104. A crust with transfer coefficient $k/A = 0.104$ m/hr with $b = 2.4$ limits evaporation into the headspace. Breathing rate is $102 \text{ m}^3/\text{hr}$; graph is based on equation (3.13).

Figure 5.8. Dryout of Waste in Tank C-104 with a Surface Crust. Drying takes place with $b = 2.4$ for breathing rate of $102 \text{ m}^3/\text{hr}$.

Figure 5.9. Relative Humidity in Headspace of Tank C-104. Drying occurs through a crust with $b = 2.4$ in equation (3.13).

5.3.2 Tank C-104 Waste as Saltcake

To better estimate the potential depth of surface drying if the crust thickens, the waste in Tank C-104 was also modeled as a saltcake. The same water vapor isotherm was employed, giving the waste the same properties relative to water vapor equilibrium. As a saltcake, however, the water content of the waste below the thickening crust remains constant. The bulk waste, which includes the crust, does exhibit an overall decline in water content, since that value is based on the volume-weighted average of moisture remaining in the crust and that below the declining interstitial liquid level.

When modeling a saltcake waste, the increasing crust depth causes the diffusive flux of water vapor to fall with time compared with an idealized sludge with a constant-depth crust. Figure 5.10 shows the crust depth as a function of time. The crust begins with about a 5-in. thickness to produce the initial 45% relative humidity. Recall that without a crust the relative humidity in equilibrium with the surface moisture would need to be much greater. The average water content of the waste shown in Figure 5.11 decreases only from 50% to about 47 wt% in 50 years, but the dry crust thickness reaches about 20 inches, with a minimum moisture content of about 7.5 wt% (Figure 5.12). Recall that the sludge-type analysis yielded a final water content of about 44%. This 3 wt% greater loss of water resulting with a crust of fixed thickness represents a substantial amount of water in the 115 in. of waste.

Figure 5.10. Drying Depth of Surface Crust in C-104 Waste as Saltcake

Figure 5.11. Dryout of Waste in Tank C-104 as Saltcake. Wt% water is for the bulk waste, including crust.

Figure 5.12. Moisture Content of the Surface Crust for Waste in Tank C-104

Figure 5.13 shows that the behavior of relative humidity in the headspace is entirely different for the saltcake. The relative humidity decreases to a minimum and then increases again. The behavior is caused by the cooling of the waste surface, which becomes wetter as a result.

5.4 Bounding the Dryout

This section evaluates the sensitivity of the dryout modeling results to changes in the initial moisture content and breathing rate. These control parameters have the most influence on the predictions and are the most uncertain. Moisture content uncertainty generally reflects the variability of waste properties found in many tanks. Breathing rate is generally obtained only as a single value for a single day, by means of a tracer gas test.

While the water vapor isotherm and temperature trends are presumed to be measured with minor error, a particular waste may have many different isotherms, depending on the sample used to represent it. A single isotherm or average of two samples for material taken near the waste surface is presumed to represent the hygroscopic behavior in each tank for estimating dryout.

Figure 5.13. Relative Humidity in the Headspace of Tank C-104. Waste is treated as saltcake with a crust.

Table 5.2 lists the breathing rates in cubic feet per minute (cfm) for the three bounding cases. Figure 5.14 shows bounding curves for the dryout of the three example waste tanks. The initial moisture was set to represent the likely extremes found in each tank. This initial value is seen as the starting value for each curve. The “high” bound in Figure 5.14 is obtained by combining the low breathing rate with the high moisture content, while the “low” bound uses the high breathing rate and low initial moisture. Thus, the initial moisture and breathing rate are correlated to achieve the largest possible increase and decrease around the best estimates.

Table 5.2. Breathing Rates Used for the Bounding Dryout Curves*

Tank	High	Best	Low
AX-102	24 cfm	16 cfm	8 cfm
C-104	90 cfm	60 cfm	30 cfm
U-105	10 cfm	5 cfm	5 cfm
*cfm = cubic feet per minute (multiply by 1.7 to find m ³ /hr)			

The low and high bounding breathing rates for AX-102 and C-104 do not represent actual uncertainty or likely variability. The fluctuation of breathing rate is generally unknown (Huckaby et al. 1997). However, the best estimates for these tanks were supported by observed past declines in the interstitial liquid levels of each. The best and low bound breathing rates are the same for Tank U-105, because the breathing rate is presumed likely not to be lower than 5 cfm for the current conditions.

Figure 5.14. Dryout for the Three Example Tanks. “Low” cases were subject to high estimates of breathing rate; “high” cases were subject to lower breathing rates.

6.0 Conclusions

A model was devised to estimate the future dryout of waste tanks subject to water loss by ventilation. Sampling the moisture content of the waste and the relative humidity in the headspace tends to support the initial conditions that determine future drying.

According to the model, the waste (at the surface) in Tanks C-104 and U-105 would not dry to less than 20 wt% water in 50 years. Tank AX-102, however, is potentially subject to severe drying, possibly dropping to less than 20 wt% water in less than 10 years. The shallowness and low moisture content make AX-102 vulnerable to drying out.

The dryout modeling presented in this document represents the best possible estimates (within the scope of the assumptions made) based on measured waste hygroscopic behavior, temperature trends, breathing rates, and initial moisture contents. The impact of a crust on evaporation can be accounted for, provided that measurements of relative humidity in the headspace over a sufficient period are available to calibrate the evaporation rate. There are no long-term monitoring data available for tank waste drying that could be applied to evaluate the model accuracy and to refine its conceptual and mathematical foundations. More advanced predictions should take into consideration waste variability along with the actual tank geometrical shape. The one-dimensional perspective as presumed here may not be accurate enough. Consideration of heat transfer and water vapor condensation, however, should nevertheless yield reduced water vapor concentrations subject to breathing loss. Therefore, the present modeling approach should overestimate the dryout and provide a reasonable evaluation of waste safety.

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