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7. Abstract

Condensed-phase, rapid reactions of organic salts with nitrates/nitrites in Hanford High Level Radioactive Waste single-shell tanks could lead to structural failure of the tanks resulting in significant releases of radionuclides and toxic materials. This report establishes appropriate preliminary safety criteria to ensure that tank wastes will be maintained safe. These criteria show that if actual dry wastes contain less than 1.2 MJ/Kg of reactants reaction energy or less than 4.5 wt % of total organic carbon, then the waste will be safe and will not propagate if ignited. Waste moisture helps to retard reactions; when waste moisture exceeds 20 wt %, rapid reactions are prevented, regardless of organic carbon concentrations.

Aging and degradation of waste materials has been considered to predict the types and amounts of organic compounds present in the waste. Using measurements of 3 waste phases (liquid, salt cake, and sludge) obtained from tank waste samples analyzed in the laboratory, analysis of variance (ANOVA) models were used to estimate waste states for unmeasured tanks.

The preliminary safety criteria are based upon calorimetry and propagation testing of likely organic compounds which represent actual tank wastes. These included sodium salts of citrate, formate, acetate and hydroxyethylethylenediaminetricetate (HEDTA). Hot cell tests of actual tank wastes are planned for the future to confirm propagation tests performed in the laboratory.

The effects of draining liquids from the tanks which would remove liquids and moisture were considered because reactive waste which is too dry may propagate. Evaporation effects which could remove moisture from the tanks were also calculated. The various ways that the waste could be heated or ignited by equipment failures or tank operations activities were considered and appropriate monitoring and controls were recommended.

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PRELIMINARY SAFETY CRITERIA FOR ORGANIC WATCH LIST TANKS AT THE HANFORD SITE

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LIST OF TERMS

ANOVA	analysis of variance
DBP	dibutyl phosphate
DOE	U.S. Department of Energy
ED3A	ethylenediaminetriacetic acid
EDDA	ethylenediaminediacetic acid
EDTA	ethylenediaminetetraacetic acid
FAI	Fauske and Associates, Inc.
FIC	Food Instrument Corporation
HEDTA	hydroxyethylethylenediaminetriacetic acid
HEPA	high-efficiency particulate air (filter)
HLW	high-level waste
IDA	iminodiacetic acid
IOSR	interim operational safety requirement
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PNL	Pacific Northwest Laboratory
PUREX	plutonium uranium reduction and extraction
REDOX	reduction and oxidation
RSST	reactive system screening tool
SORWT	sort on radioactive waste types
TBP	tributyl phosphate
TOC	total organic carbon
TSR	technical safety requirement
WHC	Westinghouse Hanford Company

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1.0 SUMMARY AND CONCLUSIONS

1.1 SUMMARY

Condensed-phase, rapid reactions of organic chemicals mixed with nitrate and/or nitrite in the Hanford Site single-shell tanks could lead to structural failure of the tanks with resulting significant releases of radionuclides and toxic materials. This report establishes preliminary safety criteria to ensure that tank wastes will be stored safely for the variety of tank conditions that might be experienced. The preliminary safety criteria replace the interim criteria provided in WHC-EP-0681, *Interim Criteria for Organic Watch List Tanks at the Hanford Site* (Babad and Turner 1993). The criteria and evaluation of wastes contained herein will be used to recommend changes to the organic tanks watch list.

The scope, objective, background, and approach for this document are discussed in Chapter 2. The relationship of the criteria to key safety questions is explored in Chapter 3. Aging and degradation of waste materials as evaluated by Pacific Northwest Laboratory (PNL) is discussed in Chapter 4. The development of preliminary safety criteria based upon work performed by Fauske and Associates, Inc. (FAI) is described in Chapter 5. PNL investigators have evaluated historical waste characterization data and used analysis of variance (ANOVA) models to estimate waste states for the 149 single-shell tanks as described in Chapter 6. FAI and G&P Consulting, Inc. have calculated the effects of loss of moisture from single-shell tank waste as discussed in Chapter 7. A supporting evaluation used solubilities of organic compounds, as determined by Barney (1994b) of Westinghouse Hanford Company (WHC), to assess the expected amounts of precipitated energetic organic materials in the waste for selected tanks. In Chapter 8, the various ways that the waste could be heated or ignited by equipment failures or tank operations activities are evaluated by G&P Consulting, Inc. In Chapter 9, WHC evaluators have integrated the foregoing information, compared the results to the preliminary safety criteria, and determined that there are no UNSAFE tanks at this time. However, changes in waste moisture content could cause 13 tanks to exceed the preliminary safety criteria, so these tanks have been categorized as CONDITIONALLY SAFE. These 13 tanks will require specific controls to ensure that safety is maintained as discussed in Chapter 9. Recommended refinements for improving understanding of safety issues and the state of waste in the tanks are provided in Chapter 10. References used in the development of this document are provided in Chapter 11.

1.2 CONCLUSIONS

As the waste ages, it becomes progressively less energetic, which means that it is less likely to support a condensed-phase, rapid reaction than the wastes originally deposited in the tanks.

Rapid propagation of reactions in organic chemical and nitrate/nitrite salt mixtures is precluded if the heat of reaction of the waste (or the amounts of total organic carbon [TOC] present in the waste) and waste moisture content are within specified limits. Where waste energetics information is available, the energy criterion is applied; where only TOC information is available, an equivalent TOC-based criterion is used. The preliminary safety criteria are represented by the following equations:

Energy: ΔH_{min} (J/g) < 1,200 + 45 (wt% free H_2O) when wt% free H_2O < 20%

or wt% free $H_2O \geq$ 20%.

TOC: TOC (wt%) < 4.5 + 0.17 (wt% free H_2O) when wt% free H_2O < 20%

or wt% free $H_2O \geq$ 20%.

Waste that satisfies either the energy or TOC criterion is SAFE. Waste that has energetics and moisture, or TOC and moisture values within these limits cannot sustain a condensed-phase, rapid reaction.

ANOVA models developed by PNL conservatively predict waste TOC and moisture concentrations for waste in the 149 single-shell tanks. Median values for TOC range from 0 to 10 wt% while moisture values range from 4 to 96 wt% for the waste phases. Worst 5% concentration values are also predicted using the ANOVA model. It is expected that most of the waste will be close to the median value. However, for conservatism, the worst 5% of the waste, which has high TOC and low moisture, has been estimated and compared to the preliminary safety criteria. The salt cake waste phase is generally the only phase with the potential to exceed the criteria; the liquid phase has too much moisture, and the sludge phase generally has both too little organic carbon and too much moisture.

Because the safety concern is focused on the salt cake phase, all salt cake tanks were evaluated for their dryout potential based upon their predicted conditions following draining. (Draining includes either loss of liquids as a result of leakage or deliberate removal of liquids by pumping.) Evaporation calculations show that the salt cakes in a few tanks have the potential to dry out so that their TOC/moisture condition exceeds the preliminary safety criteria some time within 50 years following draining. The conservative modeling for the draining effects did not take full advantage of the solubility of energetic organic compounds. In a future revision of this report, this effect is expected to show that most salt cakes will be very low in fuel as a result of draining. Alternate evaluations, which do account for this effect were performed for four selected tanks.

Comparison of conservatively estimated values for the worst 5% of the waste shows that 10 tanks would exceed the preliminary safety criteria if drained: A-102, BX-110, BY-102, TY-102, U-102, U-103, U-105, U-107, U-108, and U-109. These tanks have been categorized as CONDITIONALLY SAFE. It is recommended that priority be given to characterizing these tanks for waste energetics, TOC, and moisture concentrations before they are interim stabilized. The results from these analyses will be used to predict the conditions that would exist following jet-pumping. These conditions will be compared to the preliminary safety criteria to confirm that it would be safe to jet-pump these tanks. Further sampling following jet-pumping will be used to estimate the period of time during which the tanks would remain safe.

It is recommended that priority be given to characterizing CONDITIONALLY SAFE tanks and jet-pumped companion tanks.[1] The characterization program should evaluate the current state of CONDITIONALLY SAFE tanks and provide data to predict the post-jet-pumped condition. Before a CONDITIONALLY SAFE tank is interim stabilized by jet-pumping, it will be evaluated to establish that its post-jet-pumped state will be safe and will remain safe for a reasonable period of time. Examples of methods of evaluation that might be used include retrieval and analysis of samples from the same tanks that have not previously been sampled, detailed evaluations of available characterization and other data, comparisons of subject tanks with sibling tanks from the same sort on radioactive waste type (SORWT) groups, laboratory experiments performed on surrogates or actual waste samples, reruns of the ANOVA models with revised input data, or combinations of these approaches.

There are also three tanks that, if first drained and then allowed to dry out for up to 50 years, would exceed the preliminary safety criteria: B-102, BX-105, and BY-108. Tank B-102 is predicted to dry out within 15 years of draining; tank BX-105 is predicted to dry out within 7 years of draining; and tank BY-108 is predicted to dry out within 43 years of draining. Tank BY-108 was jet-pumped in February 1985, so it has started its drying cycle. The WHC-SD-WM-ER-349, *Historical Tank Content Estimate for the Northeast Quadrant of the Hanford 200 East Areas*, (Brevick et al. 1994a) shows the liquid level in tank BY-108 in 1993 to be the same as the top of the solids surface, so at that time it appeared not to have dried out appreciably.

The 13 tanks listed above are categorized as CONDITIONALLY SAFE and therefore require special consideration because they could become UNSAFE in the future. It is recommended that these tanks be given priority for characterization and evaluation to determine their energetics and actual TOC and moisture concentrations. Ignition controls should be emphasized during characterization activities for those tanks that might be low in moisture.

All remaining 136 single-shell tanks are predicted to remain SAFE under foreseeable conditions.

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[1] Jet-pumped companion tanks are tanks containing the same type of waste as the tanks in question, but which have already been jet-pumped. The waste conditions in the jet-pumped companion tanks are used to estimate waste conditions to be expected following jet-pumping of tanks not yet jet-pumped.

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2.0 INTRODUCTION

2.1 OBJECTIVE

This document contains preliminary safety criteria for Hanford Site single-shell waste tanks that contain potentially hazardous concentrations of organic chemicals mixed with nitrate and/or nitrite salts. These criteria supersede those previously issued by the Waste Tank Organic Safety Program (Fisher 1990; Babad and Turner 1993).

The preliminary criteria will be used to categorize the waste in each of the 149 single-shell tanks as "SAFE," "CONDITIONALLY SAFE," or "UNSAFE" (Christensen 1993). The categorization process requires key information on waste characteristics. This includes, as a minimum, the TOC and moisture contents of the waste. Waste characteristics are derived from a thorough review of historical waste characterization data.

Single-shell tanks with waste classified as SAFE will not be included on the organic tanks watch list (Gerton 1990). Tank monitoring will continue.

Single-shell tanks with waste classified as CONDITIONALLY SAFE will be treated as organic watch list tanks and/or recommended to the U.S. Department of Energy (DOE) as candidates for inclusion on the organic tanks watch list. Priority will be given to characterizing these tanks for energetics, TOC and moisture concentrations. Tank monitoring changes will be initiated in compliance with operating specifications for watch list tanks (Godfrey 1992). Technical activities supporting resolution of the organic tanks safety issue will continue.

Single-shell tanks with waste classified as UNSAFE will be recommended to the DOE for inclusion on the organic tanks watch list. Ignition source prevention controls will be instituted immediately. Priority will be given to characterizing these tanks for available combustion energy and moisture concentrations. Tank monitoring changes will be initiated in compliance with operating specifications for watch list tanks (Godfrey 1992). Near-term safety issue mitigation and/or remediation actions will be implemented as is technically feasible. "Mitigation" implies in-tank waste treatment to convert single-shell tank waste categorized as UNSAFE to waste categorized as CONDITIONALLY SAFE (or to a SAFE category if technically feasible). Mitigation actions might include adding water to a single-shell tank to increase waste moisture content, or adding water and force-ventilating a tank to reduce waste temperature. Mitigation may also consist of simply monitoring for water content to determine need for future actions. "Remediation" implies waste retrieval and out-of-tank treatment to achieve safety issue resolution.

2.2 SCOPE

The Waste Tank Organic Safety Program is addressing three safety issues, which are summarized in Table 2-1. This document presents preliminary safety criteria that address the first hazard shown in Table 2-1, a condensed-phase propagating chemical reaction.

Table 2-1. Waste Tank Organic Safety Program Safety Issues.

Potential hazard	Phenomenology	Organic chemicals of concern	Safety issue
Condensed-phase propagating chemical reaction	Nonvolatile organic nitrate/ nitrite mixtures could deflagrate if dry and heated to ≈200 °C (392 °F)	Complexants (salt cake)	Deflagration in dry salt cake waste caused by external ignition source
Vapor-phase combustion	Semi-volatile organics could ignite and burn if heated to their flash points	Process solvents (immiscible, floating organic layer)	Pool fire caused by external ignition source
Vapor-phase combustion followed by condensed-phase propagating chemical reaction	Semi-volatile organics could ignite and burn if heated to their flashpoints	Process solvents (entrained in salt cake)	Wick-stabilized fire caused by external ignition source Deflagration caused by heat from wick-stabilized fire

A condensed-phase propagating chemical reaction might occur if the organic chemicals in the tanks, mixed with sodium nitrate/nitrite salts, are dried and heated to approximately 200 °C (392 °F). The heat and pressure associated with the resultant deflagration could compromise tank integrity and release radioactive material to the environment.

The preliminary safety criteria presented in this document apply to Hanford Site single-shell waste tanks that may contain organic chemicals mixed with nitrate/nitrite salts in hazardous concentrations. The remaining two safety issues listed in Table 2-1 are not addressed in this report.

2.3 HAZARD BACKGROUND AND APPROACH

Radioactive waste from defense operations has been accumulating in underground waste tanks at the Hanford Site since the early 1940's. There are 177 waste tanks: 149 single-shell tanks and 28 double-shell tanks. Over the years, waste has been systematically disposed of among the various tanks. In this process, the two primary objectives were to ensure safe storage by segregating incompatible wastes and to conserve valuable tank space by reducing waste volumes. Volume reduction was accomplished by evaporation of waste liquids and by consolidation of compatible wastes.

In addition to fission products from irradiated fuel, the major constituents of the waste are sodium nitrate; sodium nitrite; metal silicates; aluminates; hydroxides; phosphates; sulfates; carbonates of iron, calcium, and other metals; a variety of organic materials; ferrocyanide; and uranium salts.

The presence of organic chemicals in the Hanford Site waste tanks became a significant safety issue needing reevaluation after information became available about the September 29, 1957, deflagration of a waste tank in Kyshtym, USSR (Fisher 1990). This event occurred because cooling was disrupted, the aqueous salts evaporated to dryness, and the mixture of oxidizing salts and organic chemical waste self-heated to reaction temperature (>250 °C), which caused an explosion of the waste materials. The constituents in the tank that caused this incident were sodium nitrate, sodium nitrite, and sodium acetate (mixed together).

The potential for reactions of nitrate with organic constituents stored in Hanford Site waste tanks has been studied. A paper published in April 1976 described some combustion screening studies with sodium nitrate (Beitel 1976a). However, in keeping with the concerns at that time, the work was directed toward the oxidative power of sodium nitrate rather than the reactivity of specific organic tank waste chemicals.

A screening study was conducted at the Hanford Site in 1989 (Fisher 1990). Twenty-six tests were performed to study the reactivity of mixtures containing various proportions of sodium acetate, sodium nitrate/sodium nitrite, and diluents. The results were used to define an upper limit for organic carbon constituents in the waste of 10 wt% organic calculated as sodium acetate on a dry basis. This corresponds to 3 wt% TOC on a dry basis. This figure represents the original Waste Tank Organic Safety Program safety criteria (Babad and Turner 1993). These safety criteria were updated in 1993 based on the results of a limited laboratory test program.

Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," required the DOE to identify Hanford Site radioactive waste storage tanks with the potential for release of high-level waste (HLW) resulting from uncontrolled increases in temperature or pressure and to develop plans to resolve the associated safety issues. These tanks, designated as watch list tanks, are identified in WHC-EP-0812-80, *Waste Tank Summary Report for Month Ending November 30, 1994* (Hanlon 1995). At the present time, 20 single-shell tanks are included on the organic watch list because they are believed to contain relatively high concentrations of organic chemicals (Payne 1994).

The preliminary safety criteria presented in this document will be used as the technical basis for assessing the organic chemical-nitrate/nitrite safety hazard in the future.

2.4 APPROACH

The technical approach used to develop the preliminary criteria relies upon an extensive series of adiabatic calorimetry tests to delineate the "fuel" concentrations and moisture contents of reactant mixtures that will, or will not, support a condensed-phase propagating chemical reaction. The reactant mixtures employ organic chemical surrogates (surrogates and simulants are described in Section 2.6), mixed with sodium nitrate/nitrite salts, that are believed to conservatively bound chemicals actually present in the single-shell waste tanks. The adopted approach permits the beneficial effect of waste moisture in suppressing condensed-phase propagating chemical reactions to be fully accounted for.

Specific conditions of fuel, moisture, and temperature are required to support a condensed-phase propagating chemical reaction. A minimum fuel concentration has been determined using a contact-temperature ignition model (FAI 1995). A necessary (but not sufficient) condition for a condensed-phase propagating chemical reaction is that the temperature at the interface between hot reacted material and cold unreacted material must be greater than the reaction initiation temperature. This criterion leads directly to a requirement for the minimum permissible heat of reaction that will permit propagation (refer to Chapter 5).

An intrinsic safety margin in the preliminary safety criteria exists because of waste "aging" (degradation). The solubilities of the fuel-rich organic chemical surrogates selected for testing include those believed to conservatively bound the energetics of the organic chemicals actually present in the tanks. However, as discussed in Chapter 4, the waste is known to have undergone significant aging during decades of storage to more highly oxidized and less energetic species. The preliminary criteria do not take credit for the significant safety margin attributable to waste aging.

2.5 PROCESS SEQUENCE

The following steps describe the process used to study this safety issue, develop preliminary safety criteria, assess the state of the waste, estimate moisture losses, and classify the waste in the 149 single-shell tanks.

1. Determined which species of organic salts might be present based on historical records of the organic chemicals originally disposed to the single-shell tanks and the subsequent aging (degradation) of these chemicals

2. Through theoretical development and testing of surrogate waste materials, determined key parameters and lower limits for a condensed-phase propagating chemical reaction

3. Provided preliminary safety criteria to prevent a condensed-phase propagating chemical reaction

4. Obtained documented laboratory results of samples taken from single-shell tanks to determine TOC and moisture levels in three waste phases: liquid, salt cake, and sludge

5. Utilized an ANOVA model to provide estimates of TOC and moisture for the three waste phases for all 149 single-shell tanks

6. Compared 95th quantile estimates with the preliminary safety criteria of step 3 to determine which tanks exceeded the safety criteria and the probability that each tank might exceed the safety criteria.

7. Classified as UNSAFE those tanks from step 6 that exceeded the preliminary safety criteria (there were no UNSAFE tanks) and tentatively classified as SAFE those tanks that currently do not exceed the preliminary safety criteria

8. Accounted for moisture losses resulting from drainage and sludge consolidation

9. Calculated the moisture content and TOC of the salt cake tanks, assuming all 65 had been jet-pumped

10. Compared post-jet-pumped moisture and TOC values from the salt cake tanks with the preliminary safety criteria

11. Provided evaporative moisture loss estimates for actively and passively ventilated tanks

12. Provided 50-year moisture and TOC values for all tanks assuming all 65 salt cake tanks had been jet-pumped

13. Compared results of step 12 to preliminary safety criteria in step 3

14. Provided sensitivity studies and dryout times for tanks exceeding the preliminary safety criteria during the 50-year mission

15. Recommended that tanks classified as UNSAFE be provided with more stringent operational controls (technical safety requirements [TSR]) and that they be recommended to DOE for inclusion on the organic watch list (no tanks fell into this category)

16. Recommended that tanks classified as CONDITIONALLY SAFE (i.e., currently below limits but predicted to eventually exceed the preliminary safety criteria) have controls appropriate to drainage or dryout hazards, that they be treated as organic watch list tanks, and that additional characterization be a high priority for these tanks

17. Recommended that tanks classified as SAFE not require additional operational controls other than conservatively controlling tank configuration to a passive mode (passively ventilated tanks only) and that tanks currently on the organic watch list that are categorized as SAFE according to this report be recommended to DOE for removal from the list.

2.6 SURROGATES AND SIMULANTS

A surrogate is a tank-related chemical used to measure some aspect of tank chemistry or physics without attempting to "simulate" the complexity of tank conditions. A simulant makes an attempt to replicate tank conditions in a radiologically cold or tracer-containing system. Both surrogates and simulants are designed to obtain experimental information that can be used to focus more expensive and time consuming tests on actual wastes or other radionuclide-containing mixtures.

The organic surrogate testing program conducted by FAI was designed to measure energetics of simple fuel-nitrate/nitrite hydroxide systems with fuel-rich mixtures based on chemicals known to have been added to the waste tanks. Such experiments, for the most part, did not accommodate known aging effects (radiological and chemical degradation of organic compounds to more oxidized and thus less fuel-rich forms). Nor did the experiments account for the effects of trace waste constituents on either accelerating or retarding reaction kinetics. The creation of an energy scale, namely, the determination of actual heats of reaction under adiabatic conditions provided a conservative boundary against which to judge reactivity of condensed phase reactions.

Use of surrogates in a program involving experimental testing is a more appropriately conservative method than simply making use of theoretical energies based on physical chemistry since one seldom can get more than 50 to 60% of theoretical energy from any reactive or propagating system without forcing optimization of experimental conditions. The surrogate testing program is an initial step that will help to prepare for simulant testing that is planned for fiscal year 1996.

3.0 FUEL-NITRATE WASTE SAFETY OBJECTIVE AND SAFETY CATEGORIES

3.1 SAFETY OBJECTIVE

The primary safety objective is to maintain organic compound-nitrate/nitrite waste in a state that prevents chemical reactions that have the potential for causing radiation doses or toxic exposures, either onsite or offsite, that are greater than allowed by applicable limits or guidelines (WHC-SD-WM-ISB-001, *Hanford Site Tank Farm Facilities Interim Safety Basis*, Chapter 2 [Sherwood 1994]).

This primary safety objective can be met by imposing a more stringent secondary objective that no rapid, condensed-phase propagating chemical reaction be possible. A propagating reaction is one that can spread beyond a local ignition source. A rapid reaction is one that generates heat faster than it can be removed by conduction; it excludes the slow aging (degradation) reactions believed to be occurring over a period of years.

3.2 SAFETY CATEGORIES FOR FUEL-NITRATE WASTES

3.2.1 Purpose of Safety Categories

Categorizing the organic compound-nitrate/nitrite waste hazard helps define the levels of assurance and control required to meet the stated safety objective. Using safety categories permits the use of a graded waste management approach to ensure that the hazard is controlled. At one extreme, where waste is nonreactive through inherent properties (e.g., low fuel content, low oxidizer content, high retained moisture), no organic compound-nitrate/nitrite hazard-related monitoring or controls would be required to meet the safety objective. At the other extreme, reactive waste (if any exists) would require mitigative action to meet the safety objective. In between these extremes, a graded set of waste management approaches ranging from monitoring to active controls is applied to ensure that organic compound-nitrate/nitrite hazards are controlled. The required waste management practices are defined and implemented through the tank farms interim operational safety requirements (IOSRs).

3.2.2 Key Safety Questions

Two key safety questions can be used to identify three safety categories. These questions were developed on the basis of the current understanding of the organic compound-nitrate/nitrite waste hazard and the graded IOSRs approach used for safe operation of the tank farms as described in Chapter 9.0.

> Question 1: Is a significant, rapid, condensed-phase propagating chemical reaction possible during interim storage with no, or only minimal, control of tank configuration?

The word significant in this question is defined by reference to the safety objective. A significant reaction would have consequences greater than permitted by the safety objective. The phrase "possible during interim storage" means conditions that could theoretically occur during long-term interim storage (e.g., 50 years) if only prudent waste management practices were placed on tank operations. This "prudent waste management practices only" stipulation means that no IOSR controls would be credited in the safety analysis. More specifically, no Safety Limits, Limiting Conditions for Operations, Surveillance Requirements, or Administrative Controls would be credited or imposed. Thus, analyzed waste conditions must consider possible but unlikely events such as dryout to minimum (equilibrium) levels and the introduction of local initiators. In the event that waste dryout to the minimum value is unacceptable but the dryout rate is significantly restrained by the tank ventilation configuration (i.e., the tank is passively ventilated rather than under forced ventilation), control of the tank configuration can be credited in the safety analysis and imposed via the Design Features portion of the IOSRs.

If the answer to question 1 is no (i.e., no reaction is possible), then the waste can be safely stored with, at most, only minimal control of the tank configuration to control waste moisture conditions. If the answer to question 1 is yes, then a second key question is posed as follows.

> Question 2: Is a significant, rapid, condensed-phase propagating chemical reaction possible under maintained conditions of waste moisture content?

If the answer to this question is no, then the safety objective can be met by imposing IOSRs to ensure that wastes maintain moisture content above a level that prevents significant, sustained, exothermic reactions.

If the answer to this question is yes (i.e., a reaction is possible), then the primary safety objective can be met only by imposing controls that prevent conditions that could initiate a reaction. If the secondary objective cannot be met, then ignition sources must be prevented and active measures to increase moisture or reduce fuel concentration may be pursued.

Answers to these two key safety questions lead to the definition of the three safety categories described in the following section.

3.2.3 Safety Categories

The three safety categories selected on the basis of answers to the key safety questions are SAFE, CONDITIONALLY SAFE, and UNSAFE. The categories are described in the following subsections.

3.2.3.1 SAFE. This category corresponds to a no answer to key safety question 1: a significant, rapid, condensed-phase propagating chemical reaction is not possible during interim storage, even when no, or only minimal, IOSR control is placed on the tank configuration. The safety objective can be met with a simple, prudent, waste management approach to operations without the need for required safety controls. Therefore, no IOSRs for monitoring and control of waste conditions (i.e., Safety Limits, Limiting

Conditions for Operation, Surveillance Requirements, or Administrative Controls) are imposed by the presence of fuel-nitrate waste hazards. The only control that is credited in this safety approach is control of the tank configuration, if required, to restrain waste dryout rate via the IOSRs Design Features.

In reaction phenomenology, the requirement is that reactions be self-extinguishing (i.e., that they could not continue to propagate at a measurable rate as the result of a localized initiator). Another key requirement is that decay heat can be dissipated passively without inducing a runaway reaction. Both requirements must be satisfied at all moisture concentrations that could occur within the allowed tank configurations.

3.2.3.2 CONDITIONALLY SAFE. This category corresponds to a yes answer to key safety question 1 followed by a no answer to key safety question 2: a significant, rapid, condensed-phase propagating chemical reaction is possible during interim storage when there is no, or only minimal, control of the tank configuration, but a significant, rapid, condensed-phase propagating chemical reaction is not possible under controlled conditions of high waste moisture content. The wastes in this category are safe on the condition that moisture content is maintained and verified to be above a definable critical level.

In reaction phenomenology, the requirements are the same as for the SAFE category except that the assurance that a significant, sustained exothermic reaction is prevented relies on the imposition of waste management safety controls (i.e., IOSRs) to maintain the waste moisture level above a critical level. Therefore, runaway and propagating reactions can be ruled out for this safety category as long as the IOSRs are met.

3.2.3.3 UNSAFE. This category corresponds to yes answers to both key safety questions: a significant, rapid, condensed-phase propagating chemical reaction is possible during interim storage as the waste has sufficient fuel, and moisture is insufficient to prevent a significant, rapid, condensed-phase propagating chemical reaction. For wastes in this category, a reaction initiated at a local site could propagate through a significant quantity of waste. Accidents would be prevented by taking action to prevent conditions that could initiate a reaction.

Storage of wastes in this category is inconsistent with the more stringent secondary safety objective because significant reactions cannot be ruled out. Action to increase waste moisture content or reduce the fuel concentration (i.e, by mitigative action) would be required to ensure that waste storage meets the level of safety required by the secondary safety objective.

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4.0 ORIGIN AND SUBSEQUENT AGING OF ORGANIC COMPOUNDS IN THE TANK FARMS

Knowledge of the TOC level in a particular tank waste is insufficient to bound the safety risk without knowing the kinds of organic compounds that are in the waste. Because nitrate/nitrite reaction energies vary widely for organic compounds, some information about the identity and functionality of the organic carbon is needed as well. For this reason, a discussion of the principal organic compounds that have been disposed to the tanks and the probable products of aging reactions is presented in this chapter. Sections 4.1 through 4.4 summarize what is known and believed to be the origin and fate of organic compounds stored in the HLW tanks. Tables 4-1 and 4-2 summarize this information.

Wastes containing organic compounds have been stored in Hanford Site underground storage tanks for tens of years. During that time the wastes have been exposed to radiation, temperatures of 20 °C to 140 °C (68 °F to 284 °F), and a reactive chemical environment having high concentrations of hydroxide, nitrate, nitrite, aluminate, and transition metal oxides including noble metals, radioactive elements (e.g., uranium, plutonium, cesium, strontium), and many other materials that could act as catalysts or reagents and thereby affect aging pathways or outcomes.

Each of the 177 waste tanks on the Hanford Site has a unique and largely unknown composition of organic and inorganic compounds and radioactive elements. A number of studies have been conducted to assess the inventory of compounds added to the tanks as a result of chemical processes (e.g., uranium recovery, reduction and oxidation [REDOX], plutonium uranium reduction and extraction [PUREX], and waste fractionation and strontium recovery encapsulation) (Allen 1976; Hall 1972; Jungfleisch 1984; Anderson 1990; Klem 1990; Agnew 1994). Some of these studies were summarized in PNL-8339, *Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford* (Gerber et al. 1992), which assessed the concentration mechanisms for organic compounds that were believed to have been added to the tanks.

The principal organic compounds that were disposed to the tanks are divided into two classes: extraction solvents and complexants for di-, tri-, and tetravalent cations. This division is maintained throughout this chapter and in Tables 4-1 and 4-2.

4.1 ORGANIC COMPLEXING AGENTS

The principal organic complexants that are believed to have been stored in the tanks are glycolic, citric, hydroxyethylethylenediaminetriacetic (HEDTA), and ethylenediaminetetraacetic acids (EDTA). Allen (1976) estimated the approximate quantities (listed here in kilograms and metric tons):

- Glycolic acid, 8.8×10^5 kg (880 t)
- Citric acid, 8.5×10^5 kg (850 t)
- HEDTA, 8.3×10^5 kg (830 t)
- EDTA, 2.2×10^5 kg (220 t).

Table 4-1. Organic Complexing Agents Disposed to Hanford Site Single-Shell Tanks.

Complexants disposed to Hanford Site single-shell tanks		Quantity (kg)	Inferred fate of constituent	Principal degradation products		Inferred fate of constituent
Name	Chemical formula			Name	Chemical formula	
Glycolic acid	$NaC_2H_3O_3$	8.8 E+05	Partially "aged" to more highly oxygenated and less energetic species (refer to degradation products). Remaining inventory probably present as solute in supernatant because of high solubility.	Sodium acetate	$NaC_2H_3O_2$	Inventory probably distributed between supernatant (as solute) and waste solids (as a precipitate) depending on solubility. Except for sodium oxalate, these chemicals are probably present largely as a solute. Sodium oxalate, because of its low solubility, is probably present largely as a precipitate.
Citric acid	$Na_3C_6H_5O_7$	8.5 E+05		Sodium formate	$NaCHO_2$	
HEDTA	$Na_3C_{10}H_{15}O_7N_2$	8.3 E+05		Sodium oxalate	$Na_2C_2O_4$	
EDTA	$Na_4C_{10}H_{12}O_8N_2$	2.2 E+05		Sodium succinate	$Na_2C_4H_4O_4$	
NTA	$Na_3C_6H_6NO_6$	Unknown		Disodium iminodiacetate	$Na_2C_4H_5O_4N$	
				Trisodium ethylenediamine triacetate	$Na_3C_8H_{10}O_6N_2$	

EDTA = ethylenediaminetetraacetic acid.
HEDTA = hydroxyethylethylenediaminetriacetic acid.
NTA = nitrilotriacetic acid.

Table 4-2. Organic Process Solvents Disposed to Hanford Site Single-Shell Tanks.

Solvents disposed to Hanford Site single-shell tanks		Quantity (kg)	Inferred fate of constituent	Principal degradation products		Inferred fate of constituent
Name	Chemical formula			Name	Chemical formula	
Tributyl phosphate	$C_{12}H_{27}PO_4$	7.2 E+05	Partially converted to salt of dibutyl phosphate. Remaining inventory present as immiscible phase floating on supernatant.	Sodium dibutyl phosphate	$NaC_8H_{18}PO_4$	Partially converted to salt of monobutyl phosphate. Remaining inventory probably present as solute because of high solubility of sodium salt. Present as a precipitate if calcium, aluminum, or iron salts stable in caustic.
				Butyl alcohol	$C_4H_{10}O$	Saponification product of tributyl phosphate with a very high vapor pressure.
Normal paraffin hydrocarbons	Mixture of C_{10} through C_{14} normal hydrocarbons	1.31 E+06	Major fraction of inventory probably lost to evaporation. Limited conversion to salts of long chain carboxylic acids.	Salts of long chain carboxylic acids (e.g., sodium dodecanoate)	$NaC_{12}H_{23}O_2$	If formed, probably present as a precipitate.
Methyl isobutyl ketone	$C_6H_{12}O$	Unknown	Essentially all solvent originally present lost to evaporation. Limited conversion to salts of isobutyric and acetic acids.	Salts of isobutyric acid (e.g., sodium isobutyrate)	$NaC_4H_7O_2$	Probably present largely as a solute in supernatant.
				Other hydrocarbons	C_nH_{2n+2}	If formed, probably present as a precipitate (depending upon carbon number, either volatizes or dissolves in NPH and reacts with it).
				Ketones	$C_nH_{2n}O$	Oxidizes to organic carboxylic acids.

NPH = normal paraffin hydrocarbon.

In addition to these complexants, lesser amounts of complexants such as nitrilotriacetic acid (NTA), di(2-ethylhexyl)phosphoric, and oxalic acids were used, but the amounts of these complexants that actually were disposed to the tanks are not known.

4.2 ORGANIC PROCESS SOLVENTS

Process solvents of concern that were used in Hanford Site chemical processes and disposed to the tanks are tributyl phosphate (TBP), normal paraffin hydrocarbons (NPHs), and methyl isobutyl ketone (hexone). A recent examination by Sederburg and Reddick (1994) of the PUREX Plant process solvent material balances[1] from 1951 to 1991 indicates that the quantities of TBP and NPH that were disposed to the tanks are 7.22 x 10^5 and 1.31 x 10^6 kg (720 and 1,310 t). Other processes also used organic solvents and organic phosphate extractants, but less is known about the quantities that were added to the tanks. Di(2-ethylhexyl)phosphate diluted with hydrocarbon solvent was used in the waste fractionation and encapsulation process. The reflux solvent extraction process used TBP/carbon tetrachloride and dibutyl butyl phosphonate/carbon tetrachloride for extraction solvents. Considerable quantities of hexone were used in the REDOX process as both extractant and solvent (Gerber et al. 1992). For example, 6.5 x 10^4 kg (65 t) of hexone were recently retrieved from one storage tank, treated, and disposed of.

The evidence suggests that the quantities of organic solvents added to the tanks rival the quantities of complexants. However, the fraction of organic solvents that have escaped the wastes via evaporation, or, in the case of phosphate esters, have been saponified in the alkaline wastes (Burger 1955) is not known. Sederburg and Reddick (1994) have pointed out that during early PUREX Plant operations, the organic wash waste was combined with HLWs that generated enough heat to cause the tank wastes to self-boil (Sederburg and Reddick 1994). Self-boiling temperatures ranged from 90 °C to 125 °C (200 to 260 °F). A typical self-boiling temperature was about 115 °C (240 °F). For reference, Table 4-3 lists boiling points of some organic compounds that were disposed to the tanks or that resulted from aging processes.

4.3 ORGANIC COMPOUND AGING PROCESSES

Chemical aging is chemical change. For organic compounds this requires breaking and making covalent bonds. Many chemical aging processes are at work in the tank wastes. However, in general, reactions may be classified according to the way in which bonds are broken and made.

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[1] The amount of organic entrained in PUREX organic wash waste disposed to the tanks is estimated to be 2,479 m^3 (655,000 gal). Assuming the composition of this waste was similar to the PUREX solvent (nominally 30 vol% TBP and 70 vol% NPH), then approximately 7.22 x 10^5 and 1.31 x 10^6 kg (722 and 1,310 t) of the respective solvents would have been disposed to the tanks.

Table 4-3. Boiling Points of Some Organic Compounds Disposed to Single-Shell Tanks.

Name	Boiling point °C[a]
Carbon tetrachloride	77
Methyl isobutyl ketone (hexone)	116
Butanol	117
i-Butyric acid[b]	153
Butyric acid[b]	165
Decane	174
Dodecane	214
Pentadecane	271
Tributyl phosphate	289[c]

[a] To convert temperature from °C to °F, multiply $T_{°C}$ by 1.8 and add 32.

[b] These compounds will be present in the tanks as sodium salts or acid anions.

[c] Decomposes.

Accordingly, two fundamental types of organic reactions are known: concerted and stepwise.

Concerted reactions convert reactants into products in one simultaneous step with bond breaking and bond making occurring in the same transition state complex. The most prevalent of this reaction type is the pericyclic reaction. In these reactions, bond reorganization occurs in a closed loop of interacting molecular orbitals. Reactions include molecular rearrangements, associations, and fragmentations.

Stepwise reactions occur in sequences involving reactant bond breaking to form metastable intermediates, which then react with other reactants or intermediates to make product bonds. Stepwise reactions are subdivided into heterolytic (ionic) and homolytic (radical) types. Heterolytic reactions involve the breaking and making of chemical bonds via charged intermediates. Homolytic reactions involve the breaking and making of chemical bonds by free radical intermediates (species having one or more unpaired electron).

Considering the chemical complexity of the tank wastes, all these reaction types probably occur in chemical aging processes. Furthermore, with the radiation fields to which the chemical wastes are exposed, radical reactions are expected to be important contributors to the aging process. Much of the radiolytic aging of organic compounds in the waste probably occurs by means of indirect radiation processes in which gamma and X rays and alpha and beta particles deposit energy into the wastes. The amount of energy absorbed by any component in the wastes is proportional to the electron fraction of that component. Thus, the radiation is largely absorbed by water, other highly concentrated solutes (i.e., alkali salts), and solids. Highly excited molecular and ionic species initially form and then fragment, thermalize, or react in very short times (10^{-14} seconds) to form reactive species, such as HO, H, e^-, NO, O^-, and O^{2-} that then diffuse and attack organic compounds with lifetimes of 10^{-9} seconds and longer (Bugaenko et al. 1993; Buxton et al. 1988). Organic compounds present in separate solid or liquid phases or adsorbed on solids could be aged via direct radiation processes. In that process, the radiation deposits energy directly in the bulk phases, which causes ionization and excited state reactions (Bugaenko et al. 1993) leading to reactive intermediates and products.

4.4 FATE OF CHEMICALS AND DEGRADATION PRODUCTS

This section reviews what is known about how the organics in the tank wastes are aging and identifies the principal aging products. The information derives from literature precedents, aging experiments with simulated wastes, and analyses of actual tank wastes. The discussion focuses first on complexants, then on solvents.

4.4.1 Complexants

Because of safety concerns about flammable gases evolved from complexant concentrate tanks, such as tank SY-101, a number of studies have been performed that address the fate of complexants in these tanks. These studies, which include both actual tank waste analyses (Campbell et al. 1994a and 1994b) and simulated aging studies (Delegard 1987; Ashby et al. 1994; Meisel et al. 1993), show that the complexants are degraded in varying degrees to chelator fragments and low molecular weight acids.

Organic analyses of tank SY-101 have been performed (Campbell et al. 1994a and 1994b). Accounting of the organic carbon from the various samples ranged from 73% to 93% of the TOC. Major components detected were EDTA, iminodiacetic acid (IDA) (detected as the N-nitroso derivative), NTA, citric acid, succinic acid, and ethylenediaminetriacetic acid (ED3A). Although HEDTA was one of the major complexants stored in the tanks, it was not observed in significant quantities in the samples retrieved from tank SY-101. Oxalic, formic, glycolic, and acetic acids were found to be the major low-molecular-weight acids (Campbell et al. 1994a and 1994b). NPH was found in many of the samples (Campbell et al. 1994a). Concentrations ranged from 20 to 1,440 ppm. While the NPH data improved the TOC accountabilities, the contribution to total TOC amounted to less than 5% except for the top-layer sample, which contained the largest concentration of NPH (Campbell et al. 1994a).

Several studies show that chelators decompose thermally in simulated nonradioactive wastes (Delegard 1987; Ashby et al. 1994; Meisel et al. 1993). An early study by Delegard (1987) reported HEDTA and glycolic acids degraded thermally in simulated waste producing H_2, N_2, N_2O, and NH_3 gases. Condensed-phase products were ED3A and oxalic acids from HEDTA, and oxalic acid from glycolic acid. Extensive studies of both thermal and radiolytic degradation reactions of chelators have since been performed and reported (Ashby et al. 1993 and 1994; Meisel et al. 1991a, 1991b, 1992, and 1993). Ashby et al. (1994) reported that HEDTA produced ethylenediaminediacetic acid (EDDA), IDA, glycine, and formate in addition to ED3A and oxalate. Glycolic acid produced formate as well as oxalate. Citric acid decomposed thermally in simulated waste producing formate, oxalate, and acetate. The reactivity order for thermal degradation of chelators is glycolate>HEDTA>>EDDA>EDTA, glycine, IDA, NTA. Thermal reaction mechanisms are proposed to involve air oxidation, heterolytic cleavage of nitrite esters, and hydride ion elimination from gem-diolate ions.

Studies of the effect of radiation on simulated wastes containing organic complexants have largely focused on gas production phenomena. Meisel et al. (1991b, 1992, 1993) have shown that radiation appreciably augments the production of H_2 gas from simulated wastes containing glycolic, EDTA, HEDTA, and citric acids. When simulated waste is preirradiated prior to thermal treatment, gas production is enhanced. Meisel et al. (1991b, 1992, 1993) explain that while H_2 is produced directly by water radiolysis and indirectly by H atom abstracting H from organic complexants, significantly greater yields of H_2 are obtained from radiolytic degradation of chelators to formaldehyde and glyoxylate, which produced H_2 thermally. Work at Georgia Institute of Technology, Argonne National Laboratory, and PNL has established that nitrogen-containing gases are largely a result of organic aging reactions involving organic compounds and nitrite ion in the simulated wastes (Meisel et al. 1993; Ashby et al. 1994; Bryan and Pederson 1994; Camaioni et al. 1994). Product and labelling studies of thermally and radiolytically aged simulated wastes clearly show that much of the nitrogen in the gases comes from nitrite ions. While both thermal and radiolysis conditions produce nitrogen-containing gases, radiation greatly enhances their production. Proposed mechanisms are complex multistep pathways involving both radical and ionic reaction steps. While the relative importance and exact details of the proposed pathways are not known, the evidence clearly indicates that organic carbon (C-H functionality) is oxidized while inorganic nitrogen (NO_2^-) is reduced.

Barney (1994b) investigated the solubilities of the sodium salts of the principal complexants and aging products in nitrate/nitrite/hydroxide solutions. Data for five compounds, Na_4EDTA, Na_3NTA, citrate, oxalate, and formate, show that solubilities are high except for oxalate (Barney 1994b). Accordingly, the complexants remaining in the tank wastes probably are present in the supernatant liquids, and low molecular weight acids are distributed between the supernatant and waste solids depending on the solubility of the carboxylate salts.

4.4.2 Solvents

Studies of the aging solvent constituents are less advanced, having just started in 1993 (Babad et al. 1993; Samuels et al. 1993; Camaioni et al. 1994). A literature review (Samuels et al. 1993) was performed in 1993 to gather precedent for aging reactions. Information pertinent to the aging of organic solvents is discussed in the following paragraphs and summarized in Table 4-2.

Viable thermal and radiolytic pathways exist for degrading TBP. Although TBP is only slightly soluble in water, when contacted with alkaline solutions, it hydrolyzes to dibutyl phosphate (DBP), which is soluble and stable in alkaline solutions (Burger 1955). Rates for alkaline hydrolysis of TBP are strongly dependent on temperature and hydroxide concentration. Undiluted TBP hydrolyzes in 1*M* sodium hydroxide with rates of 0.88, 4.4, and 283 mg/L/h at 30 °C, 50 °C, and 90 °C (86 °F, 122 °F, and 194 °F), respectively (Burger 1958; Kennedy and Grimley 1953). Direct radiolysis of undiluted TBP either by gamma rays or MeV electrons produced DBP acid and lesser amounts of monobutylphosphoric acid (Wilkinson and Williams 1961; Burger and McClanahan 1958; Burr 1958) as well as hydrogen and C1 through C4 hydrocarbon gases. In addition, polymers are formed but have not been identified. Irradiation of TBP diluted in hydrocarbon solvents produces DBP and monobutyl phosphate products (Barelko et al. 1966). Hydrogen atoms produced by radiolysis of water and hydrocarbons offer a radiation-induced path for cleaving alkyl phosphate esters (Camaioni et al. 1994; Bentrude 1973). In this path, the H atom adds to a P=O bond and an alkyl radical cleaves preferentially because a C-O bond is weaker than a H-O bond.

Rates of acid hydrolysis for mono and dialkyl phosphates have been determined (Stieglitz and Becker 1984 and 1985), but to the best of our knowledge, alkaline hydrolysis rates have not been measured. Burger (1958) reports that hydrolysis of TBP under alkaline conditions appears to stop after removing one butyl group. Accordingly, DBP may accumulate in the tank wastes that received PUREX Plant solvent wastes unless radiolytic degradation or metal-catalyzed hydrolysis reactions occur with significant reaction rates. Barney (1994b) has extended his organic waste solubilities studies to include DBP. Results show that mono- and DBPs have high solubilities in water. Calcium, aluminum, and iron salts are insoluble in water but partially soluble in 1*M* sodium hydroxide. Therefore, DBP will distribute between the solid and supernatant phases depending on the concentrations of sodium hydroxide and the availabilities of metal ions, such as calcium, aluminum, and iron in the tanks.

Radiolysis pathways for NPH aging are probably more important than thermal pathways. Lacking activated C-H bonds, even air oxidation requires elevated temperatures. Direct radiolysis produces saturated hydrocarbons of both higher and lower carbon numbers, olefins, and hydrogen (Bugaenko et al. 1993). Alkyl radicals and H atoms are transiently produced (Bugaenko et al. 1993). Hydrogen, HO, and NO_3 radicals, generated by supernatant radiolysis (Neta and Huie 1986; Buxton et al. 1988), also could attack hydrocarbons, generating alkyl radicals. The fate of radicals and resulting products depends on concentrations of trapping agents such as O_2, NO_x, and NO_2^-. Combination with O_2, NO_x, and NO_2^- may ultimately produce oxidized products (Ingold 1968; Camaioni et al. 1994; Meisel et al. 1991a and 1993). But, combination with other alkyl radicals could lead to higher molecular weight hydrocarbons.

Hexone, with activated C-H bonds located at tertiary and β-carbonyl positions, will be amenable to air oxidation and attack by radiolysis radicals. Plausible oxidation products are the salts of isobutyric and acetic acids that would form by oxidative scission of α-carbonyl bonds. Aldol condensation products are not expected to contribute significantly to hexone aging. In practice, the equilibrium between ketone and condensation product must be driven to obtain product in good yield. This can be accomplished under basic conditions by precipitating the condensation product with an alkaline earth metal (House 1972).

$$CH_3COR + HO^- \rightleftarrows CH_2 = C(O^-)R + H_2O$$

$$CH_2 = C(O^-)R + CH_3COR \rightleftarrows CH_3RC(O^-)CH_2COR$$

$$2\ CH_3RC(O^-)CH_2COR + Ca^{+2} \rightleftarrows [CH_3RC(O^-)CH_2COR]_2Ca.$$

Any hexone that hasn't evaporated or reacted by now will be distributed between aqueous and hydrocarbon phases. Hexone aging products, except for oxalic acid, will be soluble in the tank supernatant (Barney 1994b).

The floating organic layer in tank C-103 has been sampled and analyzed (Pool and Bean 1994; Campbell et al. 1994a). It consisted of NPH (25 wt% C12 through C15), TBP (47 wt%), and dibutyl butyl phosphonate (2 wt%). Approximately 25 wt% could not be analyzed by gas chromatography. Much of this material appeared to be inorganic. No polymeric or high molecular weight materials were identified. Alkaline hydrolysis of TBP is sluggish under the conditions in tank C-103: pH >10 (Poole and Bean 1994) and temperature ≥40 °C (≥104 °F).[1] Burger (1958) reports that a 20% TBP/kerosene mixture contacted with a 1*M* NaOH solution reacts at 50 °C (122 °F) with a rate of 2.2 mg/L/h. The rate is roughly doubled when undiluted TBP reacts. From this information the half-life for hydroxide is 9.2 years, assuming pseudo zero-order behavior for TBP (i.e., large excess is present). Thus, for a case analogous to tank C-103, in which the present aqueous concentration of HO^- is $10^{-4}M$, the aqueous phase DBP concentration will have increased by 0.03 g/L to 0.08 g/L over an 18-year reaction period, depending on whether the $[HO^-]$ was buffered at $10^{-4}M$ by tank constituents or started out higher and decreased with the extent of TBP hydrolysis.

The ratio of NPH to TBP used in PUREX Plant process solvent was 70/30 (v/v) compared to about 1/2 in tank C-103. The inverted ratio in C-103 suggests that a significant portion of NPH has evaporated. Early operations of PUREX combined the organic wash waste with HLWs that generated enough heat to cause the tank wastes to self-boil. In addition, concentration of tank wastes by pumping liquids through evaporators occurred in several campaigns to gain additional waste storage capacity. These campaigns, coupled with the fact that the tanks are vented to the atmosphere (through high-efficiency particulate air [HEPA] filters), foster the evaporation of volatile organic compounds.

Chemical and radiological aging studies of organic solvents are in progress at PNL. The studies involve irradiating a simulated waste containing organic solvent components (dodecane, TBP, DBP, and hexone) and complexants (EDTA and citrate) in an aqueous slurry of hydroxide, nitrate, nitrite, aluminum hydroxide, and a variety of alkali, alkaline earth, and transition metal cations, and monitoring the disappearance of reactants and appearance of products in both gas and condensed phases as a function of temperature

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[1] Tank C-103 headspace temperature is 38 °C (100.4 °F) (Huckaby and Story 1994).

(50 °C to 90 °C [122 °F to 194 °F]) and dose (0.20 MGy to 1.25 MGy [20 Mrad to 125 Mrad]). Preliminary results show that hydrogen, nitrous oxide, and nitrogen are produced while oxygen levels in the headspace fall to a steady-state level, even though the organic material present is sufficient to consume it entirely.

The apparent order of aging is TBP>>hexone, EDTA>>dodecane. Of these compounds, TBP is most readily degraded in the absence of radiolysis (Burger 1958). The decomposition of the other chemicals requires radiolysis. Dodecane and stearate degrade slowly under the applied conditions. Insolubility of dodecane and stearic acid in the aqueous phase probably contributes to their apparent stability. The water-soluble organics are much more effective in scavenging radicals generated by water radiolysis. DBP recovered from the irradiated simulant was at a much lower concentration than that initially present and the concentration of DBP showed little variation with dose. A conservative interpretation is that DBP was relatively unconverted, but the analysis method (Camaioni et al. 1994) extracted only a fraction of the material present. Recent analyses have identified isobutyric acid, heptadecane, and at least four dodecanones in extracts of the condensed phase. These probably derive from degradation of hexone, stearate, and dodecane.

4.5 RELATIONSHIP BETWEEN AGING AND NITRATE REACTION ENERGIES

Having described in the previous sections the principal organic compounds disposed to the tanks and the probable products of their aging reactions, this section discusses how waste aging phenomena affect the organic-nitrate reaction energies. As previously pointed out in this chapter, knowing TOC levels in the tank wastes is insufficient to bound the safety risk. The nitrate reaction energies of organic compounds vary greatly depending on carbon number and attached functional groups. This is clearly illustrated by Figures 4-1 and 4-2, which plot the heats of combustion per gram of carbon as a function of carbon number for functionalized hydrocarbons. Although the values are for heats of combustion and not heats of oxidation by nitrate, the heats of oxidation by nitrate correlate linearly with heats of combustion (see Figure 4-2). Thus, the trends for heats of combustion also apply for nitrate oxidations.

Chemicals with small carbon numbers show the widest variability. As the carbon number increases, the heats of combustion for all functional group classes asymptotically approach the heat of combustion of an alkane (limiting value is approximately 54 kJ/g carbon). The heats of combustion per gram of carbon for alkanes, alkenes, nitroalkanes, primary alcohols, and nitriles all exhibit an inverse dependence on carbon number. Limiting values (in kJ/g carbon) are methane, 39.3; methanol, 60.2; nitromethane 62.3; ethylene, 41.8; and acetonitrile, 9.4. With respect to the impact of aging on the "fuel" value of the organics in the tanks, this trend would be alarming, but the volatility of these compounds and/or their tendency to be oxidized should prevent their accumulation in the tank wastes. Evidence supporting this case

Figure 4-1. Heat of Combustion on a Per-Gram-of-Carbon Basis (Depends Greatly on Functional Group Content and Number of Carbons in an Organic Compound).

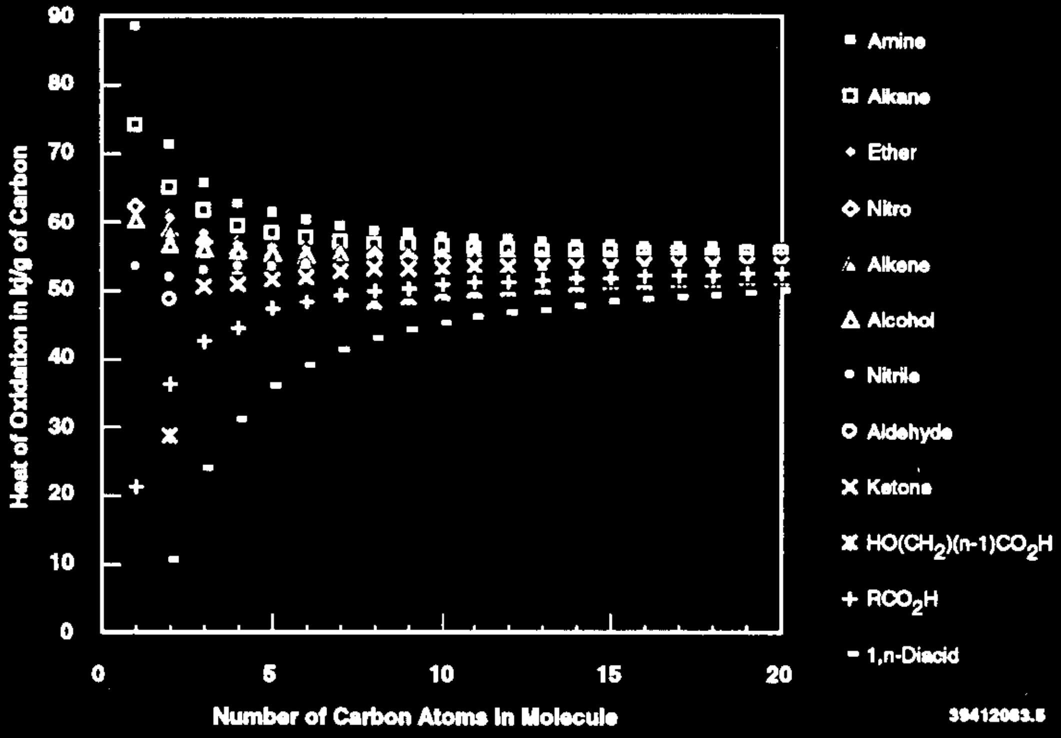
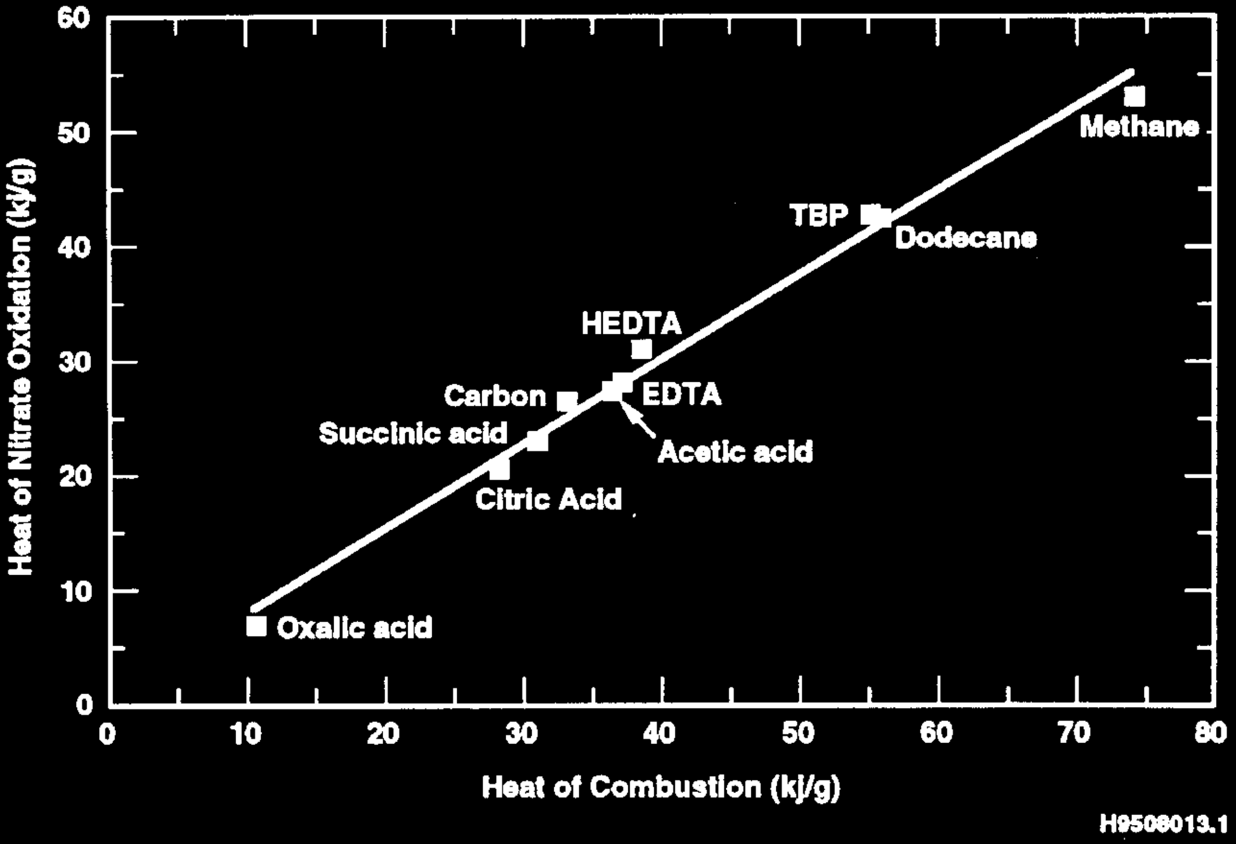


Figure 4-2. Heats of Combustion Correlate Linearly with Nitrate Heats of Oxidation (units in kJ/g carbon).



is being obtained by the Tank Vapor Sampling Program. Analyses reported for tank C-103 found that headspace gases contained small concentrations of hydrocarbons, butanol, nitriles, acetone, and other volatile organics (Huckaby 1994). Aldehydes, carboxylic acids, hydroxyacids, and diacids have heats of combustion per gram of carbon that increase with carbon number. Acetic acid has a value of 36.4 kJ/g carbon. The smallest value, 3.7 kJ/g carbon, is for oxalic acid. Although these low carbon number organic acids have lower energies than their parent compounds, being nonvolatile they may persist in the tanks.

4.6 AGING AND DEGRADATION CONCLUSIONS

There are large uncertainties about the composition of the wastes in the tanks. However, from process knowledge, a great deal is known about the types and gross amounts of waste disposed to the tanks, including substantial amounts of nitrate/nitrite salts, complexing agents, and process solvents.

Although precise rates and amounts of aging are not available for each of the waste tanks, the general process of aging and degradation is understood, and predictions have been made about the kinds and relative amounts of material that could now be found in the tanks. This knowledge allows prediction of which organic compounds are likely to be found in the tank, either by having been disposed to the tanks or having been produced by thermally activated and/or radiolytically induced aging of the original chemicals.

A research program has been undertaken to test candidate organic compounds to determine their ability to support condensed-phase propagating chemical reactions. A description of this program is included in Chapter 5.

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5.0 SUMMARY OF HAZARD PHENOMENOLOGY

Sodium salts of organic compounds disposed to the waste tanks, and their degradation products, are fuels that may potentially react with sodium nitrate/nitrite oxidizers also present in the tanks. Phenomena associated with these reactions are discussed here, and experimental data for waste surrogate materials are presented. The experimental data suggest conservative analytical criteria presented here for use as a safety basis. For more details, consult FAI/94-103, *The Contact-Temperature Ignition (CTI) Criterion for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste* (FAI 1995).

5.1 ORGANIC NITRATE/NITRITE REACTION PHENOMENA

Organic compounds disposed to the single-shell tanks include large quantities of hydroxyacetic acid, citric acid, EDTA, HEDTA, TBP, and NPH. The first four are expected to be present as soluble sodium salts in partially degraded forms, which thereby have lower energy values, last two are solvents used in the PUREX process and are believed to exist in partially degraded liquid forms insoluble in water.

In lieu of precise knowledge of the chemical forms of organic fuels actually in the single-shell tanks and the variety of possible mixtures, surrogate materials of known composition have been identified and tested that will exhibit similar chemical reaction characteristics and similar or greater reaction energies. Surrogate materials considered to date include a variety of organic compounds of diverse energy content (refer to Section 5.2).

The chemical reactivity characteristics sought generally include the character of the kinetic rate law at various temperatures, fuel compositions, the amounts of inert nonreactive constituents, and waste moisture content. The specific characteristic of interest is the ability of a reaction to propagate, or not, through a medium of average waste composition and temperature. This is because, as demonstrated by data in Section 5.3, the current waste temperature is too low for significant self-heating to occur, and in many cases, the moisture content of the waste is too high. Therefore, some reaction initiator must exist locally in a tank that causes the waste to dry out and heat up to the point at which a propagating chemical reaction occurs in that region. For this initiating event to be significant at all, the reaction must propagate through the waste outside the initiator region. Consequences of a propagating chemical reaction would be serious because tank failure may occur for reacting volumes on the order of several cubic meters.

A phenomenological basis to chemical reactivity safety in the waste tanks is therefore based upon determination of the fuel, oxidant, and moisture concentrations that could lead to propagating chemical reactions. The current experimental basis has been established with waste surrogates whose energetics are selected to bound those of compounds actually in the waste. For confirmation, additional tests with simulants and actual waste are planned in fiscal year 1996. The selection of representative organic waste surrogates is discussed in Section 5.2. The experimental method and results are discussed in Section 5.3.

5.2 REPRESENTATIVE ORGANIC WASTE SURROGATES

The information provided in Chapter 4 shows that a large number of often closely related (i.e., general structures) organic compounds make up the TOC in the tank wastes. Difficulties in statistically sampling a tank and making measurements on radioactive samples currently preclude basing safety criteria on actual tank waste measurements.

Tables 5-1 and 5-2 list a number of surrogate waste compounds along with values calculated for the energy released for stoichiometric oxidation by nitrate to produce Na_2CO_3, CO_2, H_2O, and N_2.

Table 5-1 specifically lists the key process solvents and their primary aging products. These process solvents and their aging products have some of the highest theoretical heats of reaction. Hexone, dodecane, and TBP are the most energetic, releasing approximately 5.02 x 10^6, 4.18 x 10^6, and 3.97 x 10^6 J/kg (1,200, 1,000, and 950 cal/g) of reactant mixture, respectively. However, studies show that when TBP and dodecane are mixed with nitrate and heated in a differential scanning calorimeter (Beitel 1976b, 1976c, 1977; Scheele et al. 1995) or reactive system screening tool (RSST) (FAI 1995), these compounds evaporate and leave the heated zone before nitrate reaction propagation temperatures are reached. Solvent aging products, such as sodium salts of dodecanoic, butyric and dibutyl phosphoric acids, with respective energy releases of approximately 4.14 x 10^6, 3.60 x 10^6, and 3.77 x 10^6 J/kg (990, 860, and 900 cal/g) of reactants, are nearly as energetic as their parent compounds. However, these compounds tend to decompose and leave the heated zone before nitrate reaction propagation temperatures are reached. The testing program described in Section 5.3 shows that these solvents and their aging products cannot support propagating chemical reactions, so they have not been chosen as surrogates for developing the preliminary safety criteria.

Table 5-2 lists the key complexants and their aging products. Of these complexing agents and their aging products, no compound has a higher theoretical energy of reaction than Na_3HEDTA (3.39 x 10^6 J/kg [810 cal/g]). The amount of energy it will theoretically release in reacting with nitrate is comparable to the theoretical releases of butyrates and DBP. Aging studies and analyses of actual samples from tank SY-101 suggest that Na_3HEDTA ages more rapidly than Na_4EDTA in wastes containing high concentrations of hydroxide and aluminate. Nonetheless, uncertainty about how rapidly Na_3HEDTA may have degraded in other tanks causes it to be included as a waste surrogate. Na_4EDTA is an important surrogate for testing purposes because its theoretical energy of reaction with nitrate (3.14 x 10^6 J/kg [750 cal/g]) is comparable to that of Na_3HEDTA.

Section 4.2 of the Contact-Temperature Ignition Report (FAI 1995) discusses the selection of sodium acetate as a representative organic waste surrogate. Sodium acetate (thermochemical energy of reaction with nitrate of 2.98 J/kg [713 cal/g]) is a good choice for estimating the energetics of tank waste and also for developing a conservative TOC envelope based on actual

Table 5-1. Process Solvent Organic Waste Surrogates.

Organic constituent		Energy[a] release (J/kg [cal/g] of mix)	Rationale
Name	Chemical formula		
Tributyl phosphate	$C_{12}H_{27}PO_4$	4.0 E+06 (950)	Process solvent. Partially converted to NaDBP. Remaining TBP present as immiscible floating phase with NPH.
Sodium dibutyl phosphate	$NaC_8H_{18}PO_4$	3.8 E+06 (900)[b]	Stoichiometric mixture of sodium dibutyl phosphate and sodium nitrate provides maximum theoretical energy release per gram of reactant.
Normal paraffin hydrocarbons	$C_{12}H_{26}$ (Dodecane)	4.3 E+06 (1,020)	Process solvent. Semivolatile organics do not react with sodium nitrate under laboratory conditions. When heated, semivolatile organics vaporize before reaching reaction propagation temperatures.
Sodium dodecanoate	$NaC_{12}H_{23}O_2$	4.4 E+06 (990)[c]	Representative hydrocarbon solvent oxidation product.
Methyl isobutyl ketone (Hexone)	$C_6H_{12}O$	4.2 E+06 (1,010)[c]	Process solvent. Much of the known inventory of hexone was retrieved, treated, and disposed of in 1990 and 1991.[d] Highly volatile; will vaporize from the waste mixture before reaching reaction propagation temperatures.
Sodium isobutyrate Sodium butyrate	$NaC_4H_7O_2$	3.6 E+06 (860)[c]	Decomposition products from hexone and TBP. Energy the same.

[a] Theoretical reaction enthalpy for a stoichiometric mixture of the organic compound and sodium nitrate, per gram of reactant (L. L. Burger, 1993, Calculation of Reaction Energies and Adiabatic Temperatures For Waste Tank Reactions, PNL-8557, Pacific Northwest Laboratory, Richland, Washington).

[b] Revised value.

[c] Estimated using heat of formation data.

[d] M. A. Gerber, L. L. Burger, D. A. Nelson, J. L. Ryan, and R. L. Zollars, 1992, Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford, PNL-8339, Pacific Northwest Laboratory, Richland, Washington.

DBP = dibutyl phosphate.
NPH = normal paraffin hydrocarbon.
TBP = tributyl phosphate.

Table 5-2. Complexing Agent Organic Waste Surrogates. (2 sheets)

Organic constituent		Energy[a] release (J/kg [cal/g] of mix)	Rationale
Name	Chemical formula		
Sodium glycolate	$NaC_2H_3O_3$	2.5 E+06 (600)	Process chemical.
Trisodium citrate	$Na_3C_6H_5O_7$	2.6 E+06 (620)	Process chemical.
Na_3HEDTA	$Na_3C_{10}H_{15}N_2O_7$	3.4 E+06 (810)	Process chemical. Only small amounts of Na_3HEDTA were found in tank SY-101. A stoichiometric mixture of sodium HEDTA and sodium nitrates provides maximum theoretical energy release per gram of reactant. Decomposition to ED3A(Na) thought to be the major aging pathway.[b]
Na_4EDTA	$Na_4C_{10}H_{12}N_2O_8$	3.2 E+06 (750)	Process chemical.
Na_3ED3A	$Na_3C_8H_{11}N_2O_6$	3.3 E+06 (780)[c]	Product of Na_3HEDTA and possibly Na_4EDTA.
Na_2EDDA	$Na_2C_6H_{10}N_2O_4$	3.4 E+06 (810)[c]	Product of Na_3HEDTA and possibly Na_4EDTA.
Na_3NTA	$Na_3C_6H_6NO_6$	2.8 E+06 (680)[c]	Process chemical; possible product of Na_4EDTA and Na_3HEDTA.
Na_2IDA	$Na_2C_4H_5NO_4$	2.9 E+06 (690)[c]	Product of Na_3HEDTA and possibly Na_4EDTA.
Sodium amino acetate	$NaC_2H_4NO_2$	3.0 E+06 (720)	Product of Na_3HEDTA and possibly Na_4EDTA.
Sodium succinate	$Na_2C_4H_4O_4$	2.7 E+06 (650)[c]	Product of both complexants and solvents.
Sodium acetate	$NaC_2H_3O_2$	3.0 E+06 (710)	Process chemical and possible product of both complexants and solvents.

Table 5-2. Complexing Agent Organic Waste Surrogates. (2 sheets)

Organic constituent		Energy[a] release (J/kg [cal/g] of mix)	Rationale
Name	Chemical formula		
Sodium formate	$NaCHO_2$	1.7 E+06 (410)	Product of both complexants and solvents.
Sodium oxalate	$Na_2C_2O_4$	9.62 E+05 (230)	Product of both complexants and solvents.

[a] Theoretical reaction enthalpy for a stoichiometric mixture of the organic compound and sodium nitrate, per gram of reactant (L. L. Burger, 1993, Calculation of Reaction Energies and Adiabatic Temperatures For Waste Tank Reactions, PNL-8557, Pacific Northwest Laboratory, Richland, Washington).

[b] E. C. Ashby, A. Annis, E. K. Barefield, D. Boatright, F. Doctorovich, C. L. Liotta, H. M. Neuman, A. Konda, C. F. Yao, K. Zhang, and N. G. McDuffie, 1994, Synthetic Waste Chemical Mechanism Studies, WHC-EP-0823, Westinghouse Hanford Company, Richland, Washington.

[c] Heats of formation of compounds estimated:

- $2\Delta H_f(Na_2EDDA) = \Delta H_f(Na_4EDTA) + \Delta H_f(\text{ethylenediamine})$
- $2\Delta H_f(Na_3ED3A) = \Delta H_f(Na_4EDTA) + \Delta H_f(Na_2EDDA)$
- $2\Delta H_f(Na_3IDA) = \Delta H_f(Na_3NTA) + \Delta H_f(\text{sodium amino acetate})$
- $\Delta H_f(Na_2\text{succinate}) = \Delta H_f(\text{succinic acid}) + \Delta H_f(Na_2\text{oxalate}) - \Delta H_f(\text{oxalic acid})$.

EDDA = ethylenediaminediacetic acid.
EDTA = ethylenediaminetetraacetic acid.
ED3A = ethylenediaminetriacetic acid.
HEDTA = hydroxyethylethylenediaminetriacetic acid.
IDA = iminodiacetic acid.
NTA = nitrilotriacetic acid.

laboratory tests. Results described in Section 5.3 show that the contact-temperature ignition criterion based on sodium acetate consistently and conservatively represents threshold nonpropagating mixtures, and it was therefore the basis for developing the preliminary safety criteria.[1] It is noted that experiments show that acetate propagates at lower TOC than HEDTA though acetate is theoretically somewhat less energetic than HEDTA.

5.3 ORGANIC NITRATE/NITRITE REACTION DATA

Two types of experimental apparatus, an adiabatic calorimeter and a propagation tube, are being used to explore the potential for propagating reactions in waste surrogates. The methods are briefly summarized in this section and data for surrogates are presented.

The RSST (Figures 5-1 and 5-2) is an adiabatic calorimeter used to screen the potential for propagating reactions of dry mixtures for various initial fuel concentrations. The RSST (previously described by Creed and Fauske [1990]) measures the temperature rise rate of a reacting sample as a function of temperature, which may be cast in an Arrhenius plot to visualize the kinetics (Figure 5-3). In the figure, the logarithm of the self-heating rate is zero while the sample is externally heated at 1 °C/min (1.8 °F/min) until the chemical reactions result in significant self-heating beginning at approximately 180 °C (356 °F). At about 230 °C (446 °F), an abrupt change in the self-heating rate is observed where the slope of the curve becomes essentially vertical. This is interpreted to be a propagating reaction wave passing by the thermocouple in the sample (which is offset from the center). The temperature at which such a rate change is observed is called the ignition temperature.

A set of RSST runs may be made to determine a pair of go/no-go fuel concentrations at which propagation is observed-not observed and thus to estimate the threshold concentration that could sustain a propagating reaction in a dry mixture. This estimate may be confirmed by placing a larger quantity of reacting material into a propagation tube, igniting the reaction at one end, and observing the temperature transient in thermocouples placed at various distances away from the initiating end (Figure 5-4). Figure 5-5 shows such a transient, which indicates the propagation of a reaction through the medium. The arrival time of the wave between thermocouples may be used to determine the propagation rate of the reaction. The advantage of the RSST is that a much smaller sample may be employed. The advantage of the propagation tube is that moisture may be present in the initial sample and the unreacted material emulates the bulk medium in a waste tank at some ambient temperature and moisture content.

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[1] In actual conditions, the achievable energetics of any fuel/oxidizer mixture are usually well below theoretical predictions. This is a result of incomplete reaction resulting from fuel and oxidizer dispersion, formation of lower energy combustion products, unfavorable reaction kinetics, and the absence of adiabatic conditions (heat escapes from the system instead of supporting propagation).

Figure 5-1. Reactive System Screening Tool
Reactor Vessel Cutaway.

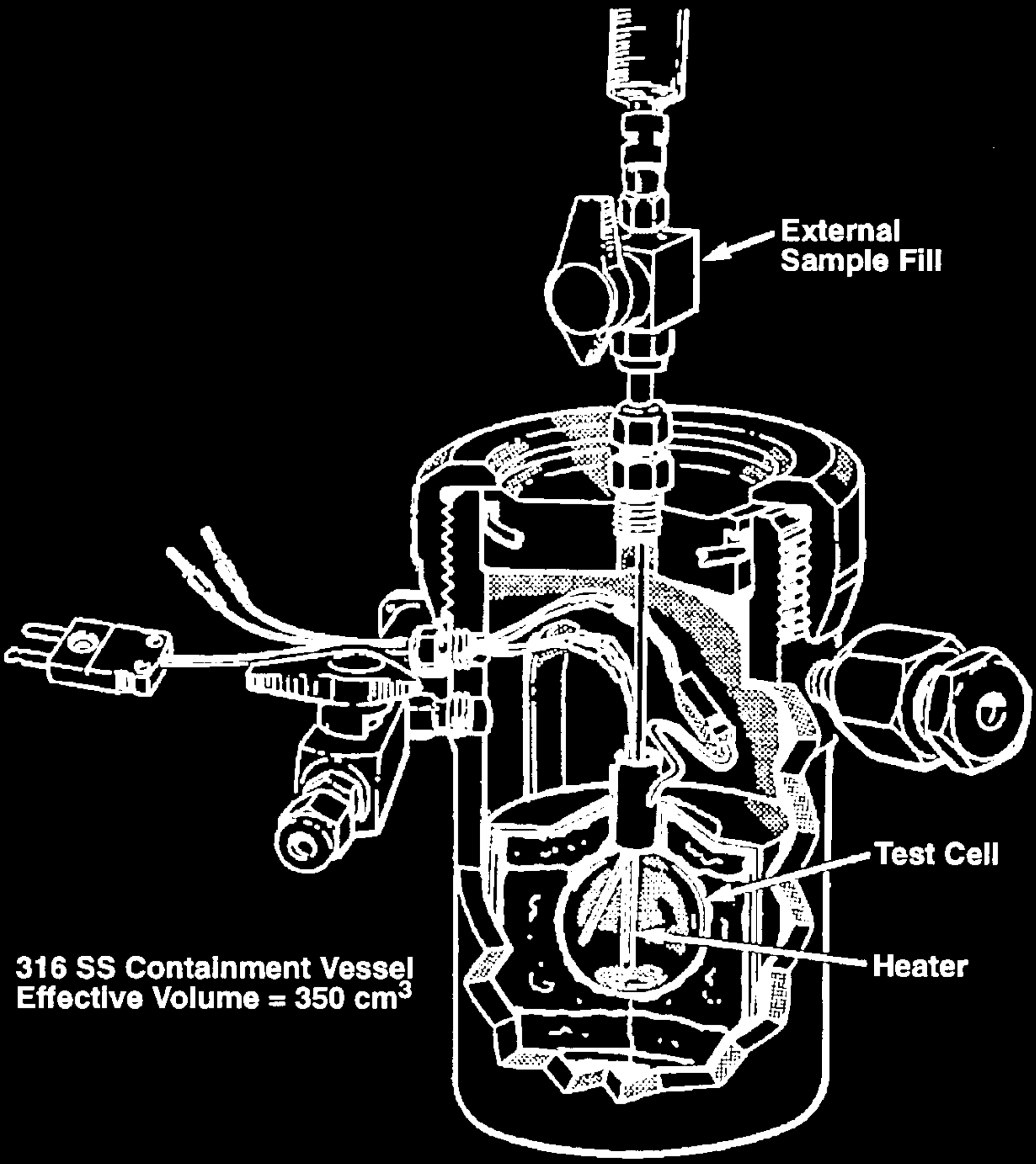


Figure 5-2. Reactive System Screening Tool Test Cell and Insulation and Instrument Detail.

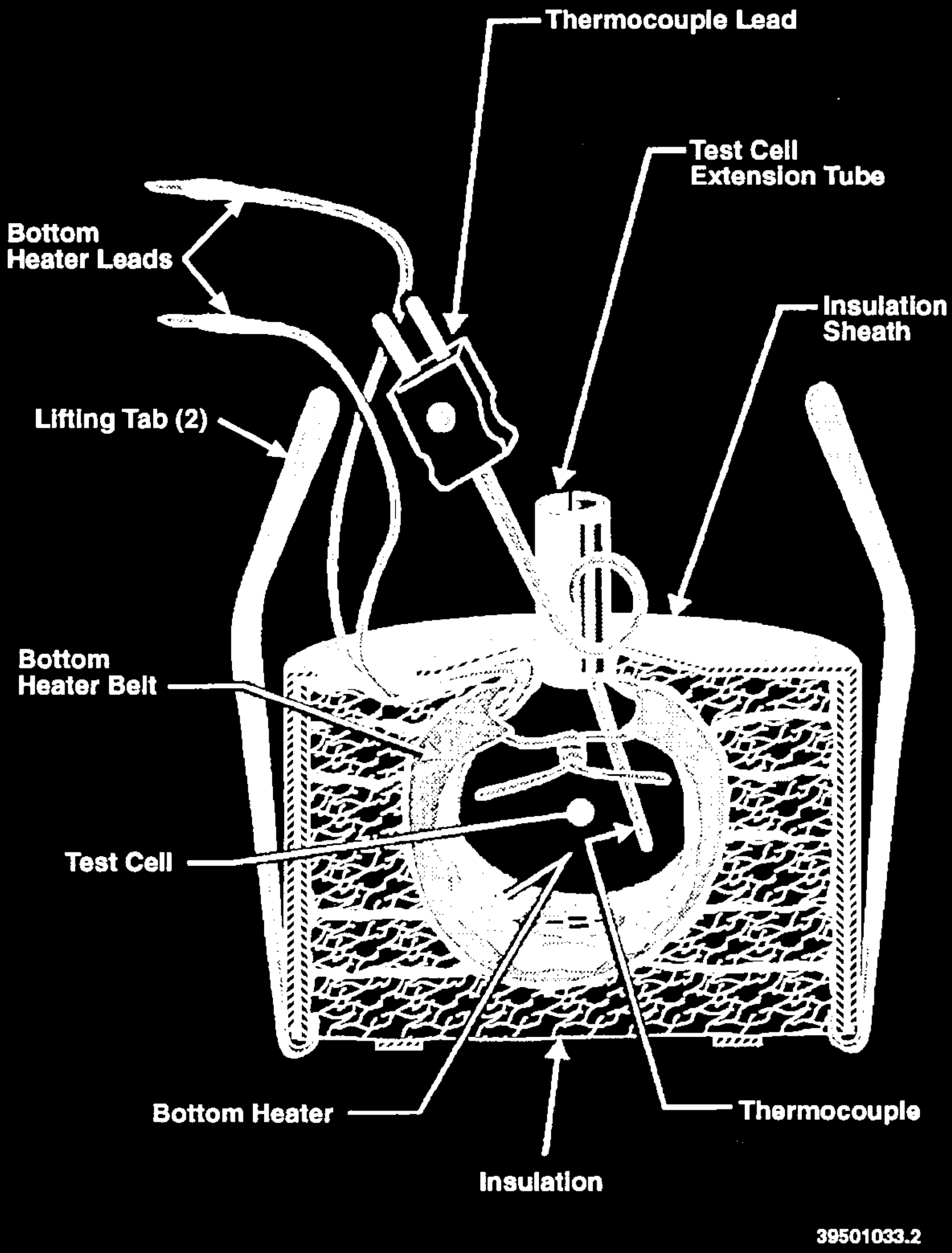
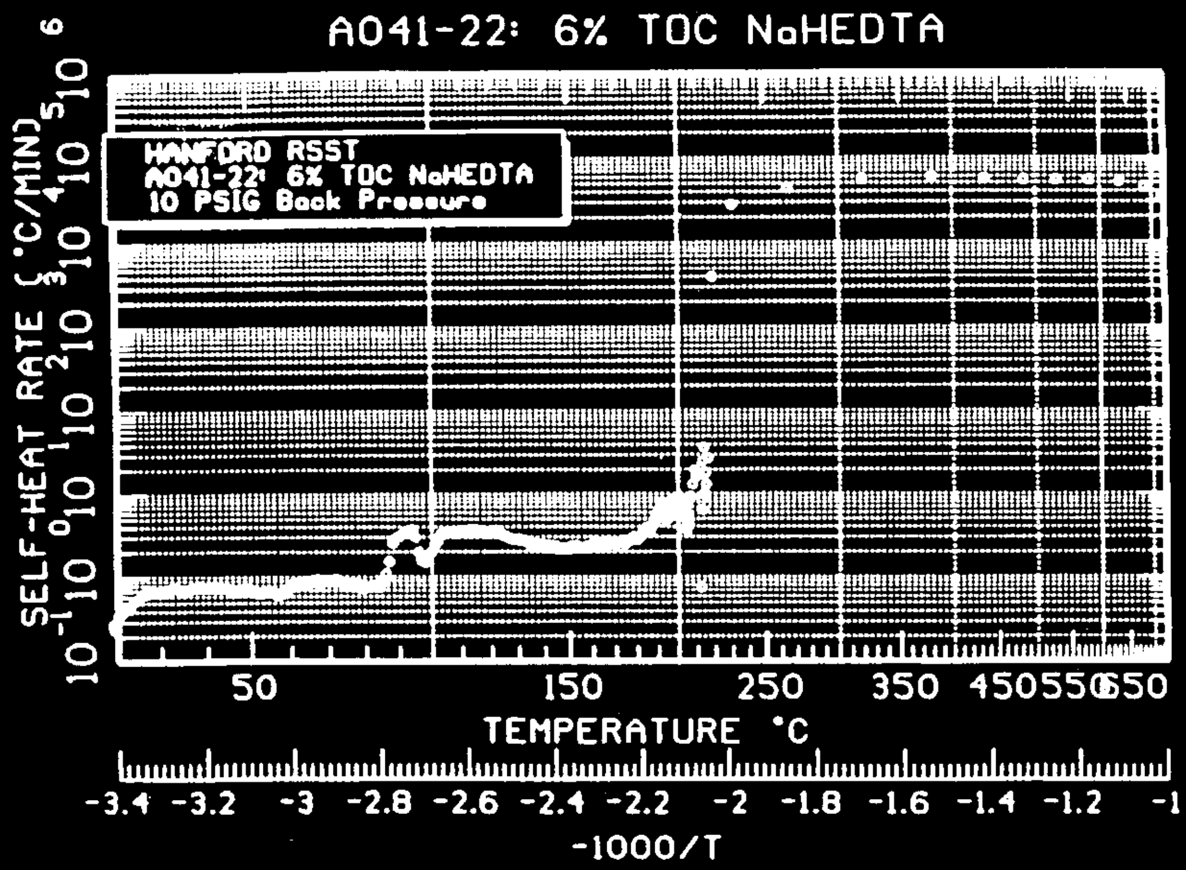


Figure 5-3. Arrhenius Plot of the Reactive System Screening Tool's Measurement for HEDTA that Exhibits Propagation.



HEDTA = hydroxyethylethylenediaminetriacetic acid.

Figure 5-4. Propagation Tube Test Cell.

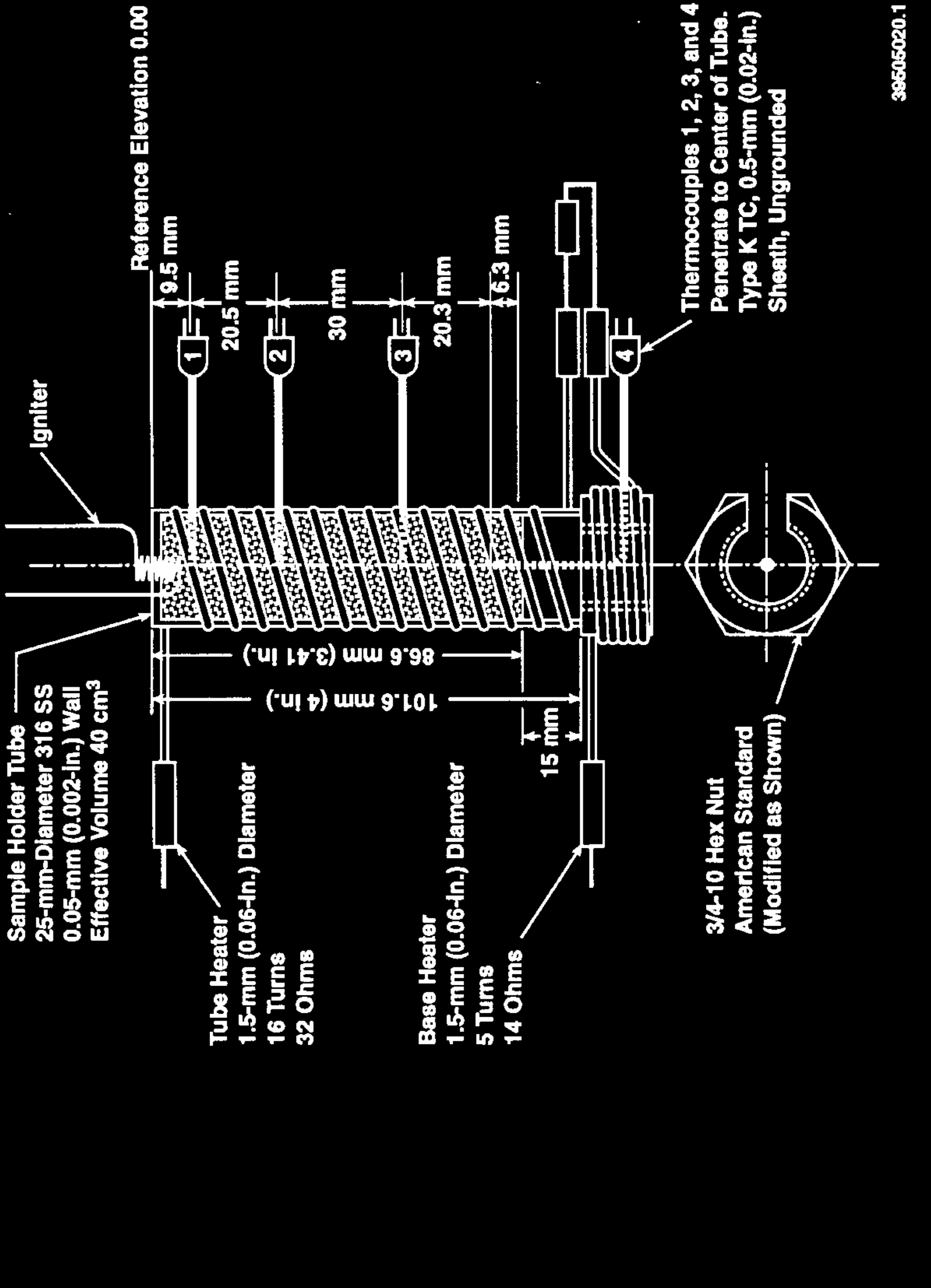
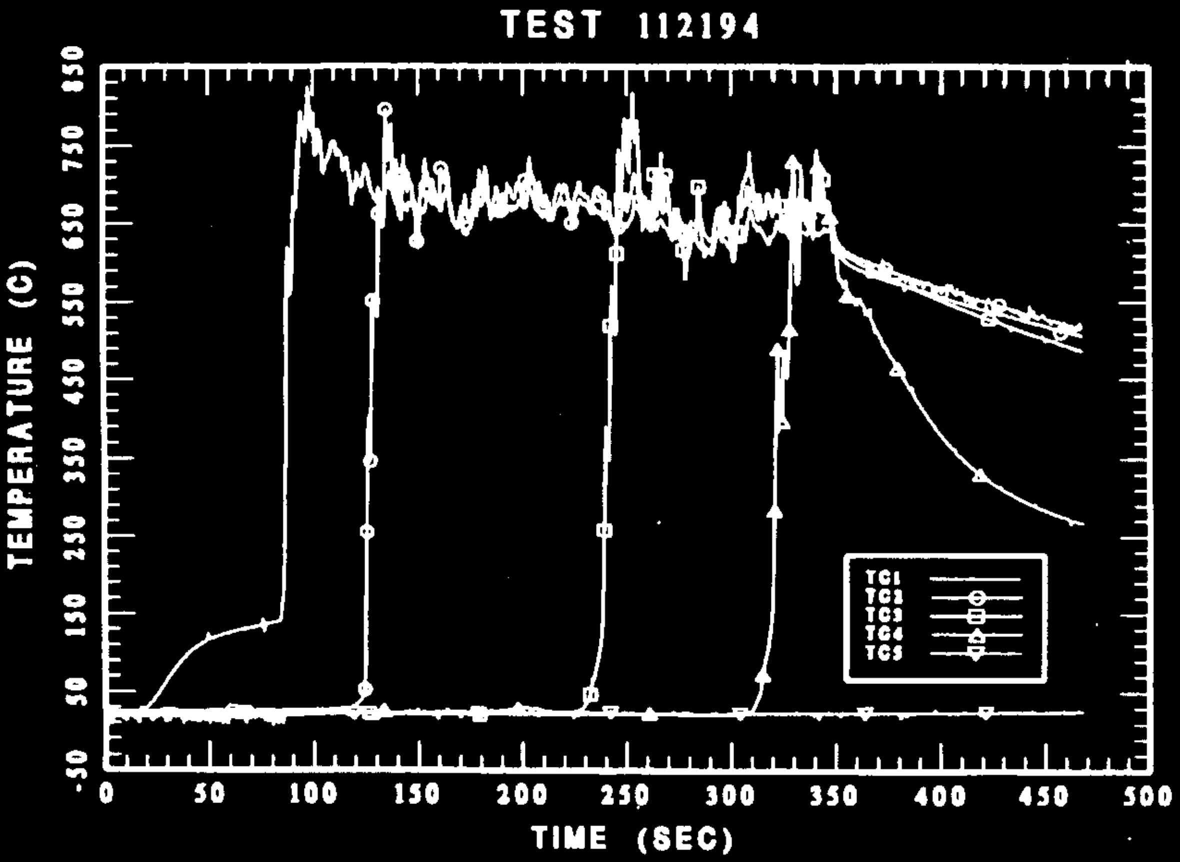


Figure 5-5. Propagation Tube Data for EDTA.



EDTA = ethylenediaminetetraacetic acid.

Propagation tube and RSST data for surrogate materials are summarized in Tables 5-3 and 5-4. There are two concerns: defining experimentally the

Table 5-3. Effect of Moisture Concentration and Propagation at 30 °C (86 °F) (Tube Propagation Tests).

Fuel	Dry basis fuel concentration wt% (TOC)	Free water concentration wt% (wet basis)	Propagation
Na acetate ($NaC_2H_3O_2$)	18.8 (5.5)	0	No
Na acetate	20.5 (6.0)	0	Yes
Na acetate	25.5 (7.5)	10	Yes
Na acetate	22.5 (6.6)	10	No
Na acetate	35.0 (10.2)	15	Yes
Na acetate	28.0 (8.2)	15	No
Na acetate	37.5 (11.0) (stoichiometric)	17	Yes
Na acetate	37.5 (11.0)	20	No
Na_3HEDTA ($Na_3C_{10}H_{15}O_7N_2$	15.5 (5.6)	0	No
Na_3HEDTA	17.2 (6.3)	0	Yes
Na_3HEDTA	28.0 (10.2)	10	Yes
Na_3HEDTA	31.5 (11.5) (stoichiometric)	13	Yes
Na_3HEDTA	31.5 (11.5)	15	No
Na_2EDTA[a] ($Na_2C_{10}H_{14}O_8N_2$)	19.8 (5)	0	No
Na_2EDTA[a]	23.8 (6)	0	Partial
30% TBP — 70% NPH	15.0 (11.3)	0	No
AlDBP[b]	18.2 (8.0)	0	No
Na butyrate	13.8 (6.0)	0	No
3% TOC Na citrate + 3% TOC AlDBP[b]	(6.0)	0	No
7% TOC Na citrate + 8.5% TOC dodecane	(15.5)	0	No

[a] Na_2EDTA was tested as a surrogate material. Hanford Site waste is espected to behave in a similar fashion though it is expected to contain Na_4EDTA with no appreciable Na_2EDTA present. Further testing will be conducted to confirm this.

[b] AlDBP = $Al[(C_4H_9)_2 PO_4]_3$, an insoluble salt.

DBP = dibutyl phosphate.
EDTA = ethylenediaminetetraacetic acid
HEDTA = hydroxyethylethylenediaminetriacetic acid.
NPH = normal paraffin hydrocarbon.
TBP = tributyl phosphate.
TOC = total organic carbon.

Table 5-4. Measured Lower Propagation Limit at 30 °C (86 °F) (Tube Propagation Tests) and Ignition Temperatures (Reactive System Screening Tool Tests) Oxidizer 4:1 $NaNO_3/NaNO_2$.

Fuel	Formula	LPL wt% (TOC)	Ignition temperature (°C [°F])
Na acetate	$NaC_2H_3O_2$	~ 20.5 (~ 6)	300 (572)
Na oxalate	$Na_2C_2O_4$	No burn	NA
Na dodecanoic acid	$NaC_{12}H_{23}O_2$	> 9.25 (> 6)	270 (518)
Nitrododecanoic acid	$C_{12}H_{23}O_2N$	~ 10.2 (~ 6)	260 (500)
Na stearate	$NaC_{18}H_{35}O_2$	> 12.75 (> 9)	260 (500)
Na_2EDTA	$Na_2C_{10}H_{14}O_8N_2$	~ 16.8 (~ 6)	250 (482)
Na_3HEDTA	$Na_3C_{10}H_{15}O_7N_2$	~ 17.2 (~ 6)	220 (428)
Na citrate	$Na_3C_6H_5O_7$	~ 28.9 (~ 8)	230 (446)

EDTA = ethylenediaminetetraacetic acid.
HEDTA = hydroxyethylethylenediaminetriacetic acid.
LPL = lower propagation limit.
NA = not applicable.
TOC = total organic carbon.

minimum amount of water that will prevent propagation of a stoichiometric mixture and the minimum amount of fuel at which propagation in a dry mixture is possible.

The effect of moisture on propagation in the propagation tube is shown in Table 5-3. The highest moisture concentration at which propagation was observed was for 17% moisture in an otherwise stoichiometric mixture with sodium acetate fuel; no propagation was observed at 20% water. For stoichiometric HEDTA, the propagation-no propagation fuel moisture pairs are 13% and 15%, respectively.

Propagation tube tests and RSST tests have also been conducted with selected organic solvents and their salts (FAI 1995). RSST tests with $TBP/NaNO_3$ at 28 wt% TOC and with $DBP/NaNO_3$ at 10 wt% TOC exhibited Arrhenius-type reaction kinetics above 170 and 150 °C, respectively, but did not exhibit step-change kinetics indicative of a propagating reaction. Propagation tube tests with organic solvents and salts in $NaNO_3$, listed in Table 5-3, yielded negative results as well. Note that the TBP-NPH mixture in Table 5-3 was the highest achievable TOC content without sample liquefaction and that AlDBP is an insoluble salt.

Further experiments were performed with mixtures of organic complexants and solvents whose TOC exceeded criteria as discussed in Section 5.4 below. As shown in Table 5-3, the lack of propagation indicates that addition of organic solvents or salts to salts of complexants does not make an otherwise unreactive waste (too little nonvolatile organic complexant) into a reactive one given an adequate ignition source.

Table 5-4 lists the lower propagation limit for a number of surrogates as determined by propagation tube experiments. Also listed are the ignition temperature data obtained for dry mixtures in the RSST. Note that the minimum TOC for propagation is about 6% and that the ignition temperature is 250 °C (482 °F) or above, (except for sodium HEDTA, which is thought to be virtually absent from tank waste as a result of waste aging [degradation] processes). The absence of HEDTA from HLW was observed in core samples taken from SY-101 and SY-103. These data are plotted in Figure 5-6 to illustrate the propagation/no propagation limits in terms of fuel and moisture content of the waste.

5.4 ORGANIC NITRATE PROPAGATION CRITERIA

The data in Figure 5-6 suggest criteria based on a combination of fuel and moisture content to judge the potential for propagating reactions. The physical basis and derivation of such criteria are provided by FAI (1995) and are summarized here.

During a propagating reaction, a reaction (temperature) wave front passes through the medium. Ahead of the wave, material is in its unreacted state at its initial temperature. Just as the wave passes, the material is in its reacted state at the adiabatic reaction temperature. For a propagating reaction to be possible, the contact temperature of the reaction zone must exceed or be equal to the ignition temperature. The ignition criteria were worked out by FAI (1995) and shown to correlate to experimental results. Using conduction theory, the contact temperature may be related to the adiabatic reaction temperature to yield the criteria for the combination of fuel and moisture that defines the propagation boundary.

When sodium acetate properties are used, the criterion is

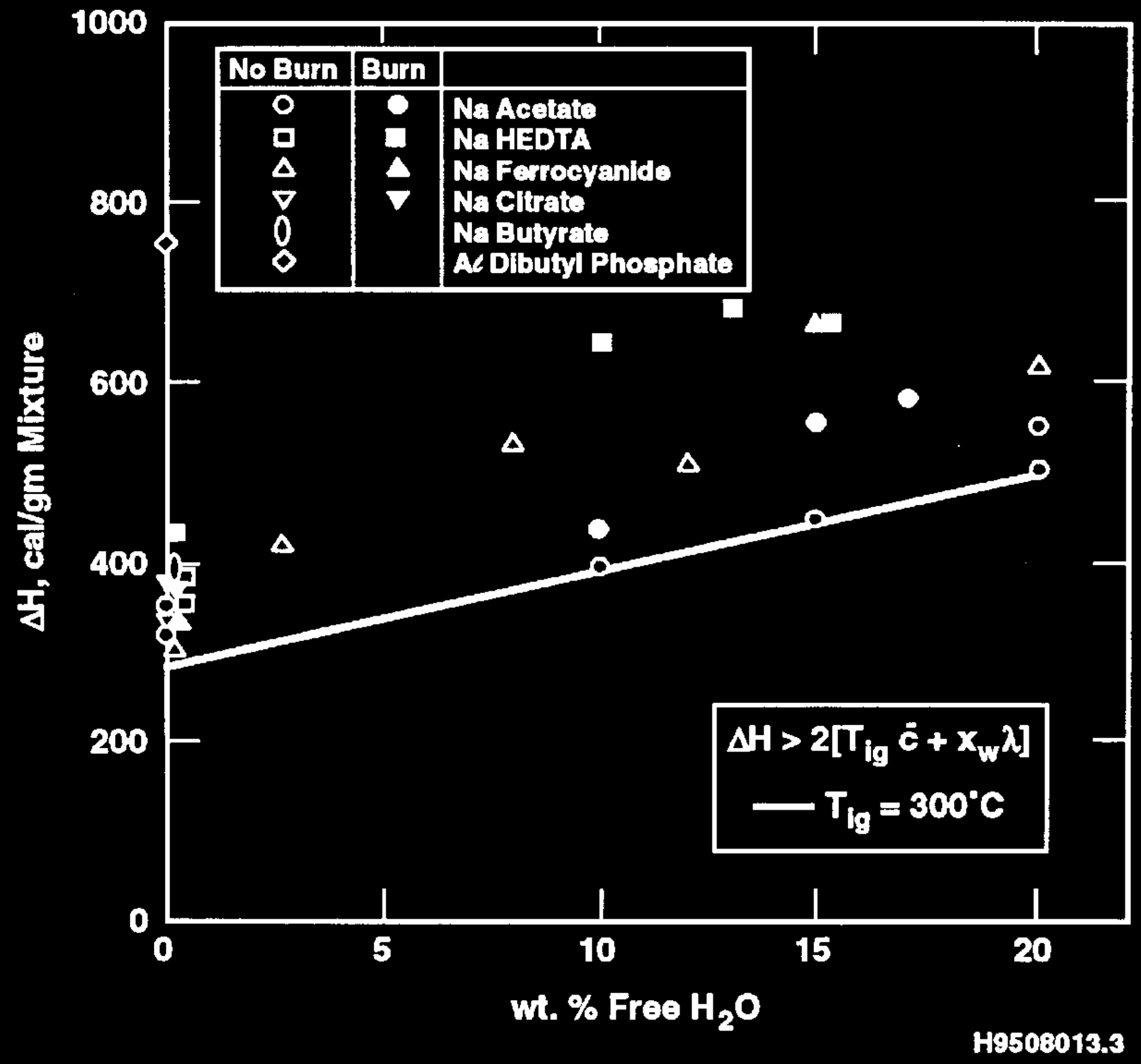
$$\begin{aligned}\text{Energy:}\quad \Delta H_{min}(\text{J/g}) &< 1{,}200 + 45\ (\text{wt\% free } H_2O) \text{ when wt\% free } H_2O < 20\% \\ &\text{or wt\% free } H_2O \geq 20\%.\end{aligned} \tag{5-1}$$

where ΔH_{min} is the heat of reaction in J/g of reactant material and wt% free H_2O is the weight fraction of free water in the material. Converting to a criterion based on TOC and wt% free water and using a ΔH of 2.7×10^4 J/g of TOC in the acetate yields the following form of the criterion.

$$\begin{aligned}\text{TOC:}\quad \text{TOC (wt\%)} &< 4.5 + 0.17\ (\text{wt\% free } H_2O) \text{ when wt\% } H_2O < 20\% \\ &\text{or wt\% free } H_2O \geq 20\%.\end{aligned}$$

where wt% TOC is the wet basis TOC concentration, wt% H_2O is the moisture content of the waste, and no propagating reaction can take place when wt% $H_2O > 20$.

Figure 5-6. Ignition Tube Experimental Results Compared to the Contact Temperature for Ignition Criterion (Based on Sodium Acetate Properties) in Terms of Wet Basis Mixture Energy and Moisture.



The criteria shown in Figures 5-6 and 5-7 conservatively bound the no-go data points. Because 5 wt% TOC is a no-go point for dry sodium acetate surrogate, the criteria contain a margin of safety that exceeds reasonable measurement error in test mixture preparation, estimated at a few percent based on fuel content, which is equivalent to approximately 0.5 wt% TOC.

An inherent safety margin also exists because the criteria line runs through the no-go data points. The inherent safety margin can also be attributed to waste aging because the fuel content required for propagation is directly proportional to the heat of reaction. Thus, for fuel degraded to half the initial energy content per unit mass, the required TOC for propagation would be doubled.

Clearly many fuels, waste thermal properties, and energy contents could be examined both experimentally and theoretically. The criteria line (Equation 5-1) has been chosen simply because it bounds data obtained with the most energetic surrogates, it is independent of actual waste energy, and an additional safety margin is provided by waste aging and organic solubility which prevents fuel concentration in dryer regions.

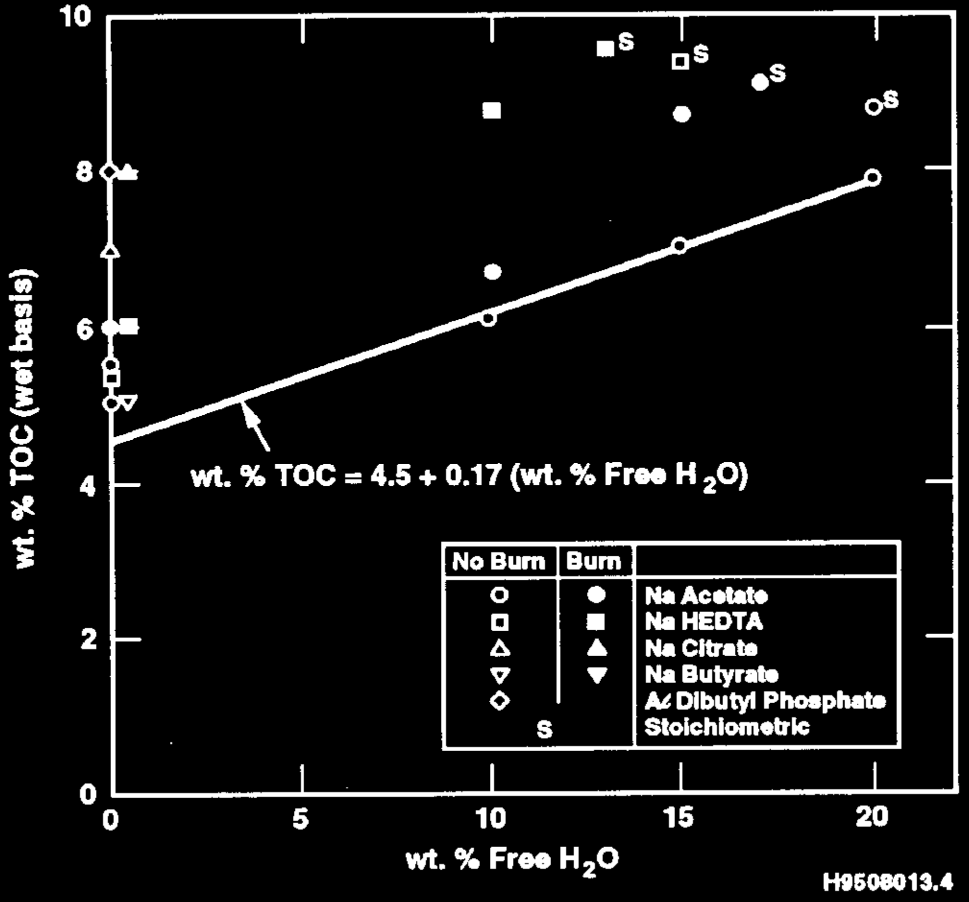
5.5 SAFETY ANALYSIS CONSIDERATIONS

Detailed accident scenario development and consequence assessment are beyond the scope of this report. However, credible accidents involving the chemical reactions described require an initiator. As discussed in Chapter 8, an external energy source (initiator) is required for a propagating reaction to occur. As shown previously, the initiator must heat to the ignition temperature a local waste volume whose concentrations of fuel and moisture (oxidant assumed present) could sustain a propagating reaction. A sufficiently large contiguous region of such waste must exist to pose a threat to tank integrity while the reaction propagates.

Because the reaction propagation velocity is small, on the order of centimeters per minute, significant tank pressurization only occurs when the surface area of the reacting front is large, on the order of 10 m^2 (108 ft^2). However, once the reaction front has attained a large surface area, tank pressurization is sufficient to cause progressively increased damage, including HEPA filter blowout and dome structural failure with consequent radiological releases. Onsite dose limits would be exceeded by propagating reaction events in relatively small waste volume fractions.

Initiating events may be caused by either external natural forces, such as lightning, or human operational errors, as summarized in Chapter 8. However, subsequent conditional probabilities must be considered in order to derive the real accident frequency: for example, the probability that the tank struck by lightning contains potentially reactive waste in sufficient volume to cause tank damage and the probability that the lightning indeed discharges into this region of the waste. Considering human factors leading to an initiating event, preventive controls may be placed upon operation to reduce event frequencies as discussed in Chapter 9.

Figure 5-7. Ignition Tube Experimental Results Compared to the Contact Temperature for Ignition Criterion (Based on Sodium Acetate Properties) in Terms of Wet Basis Total Organic Carbon and Moisture.

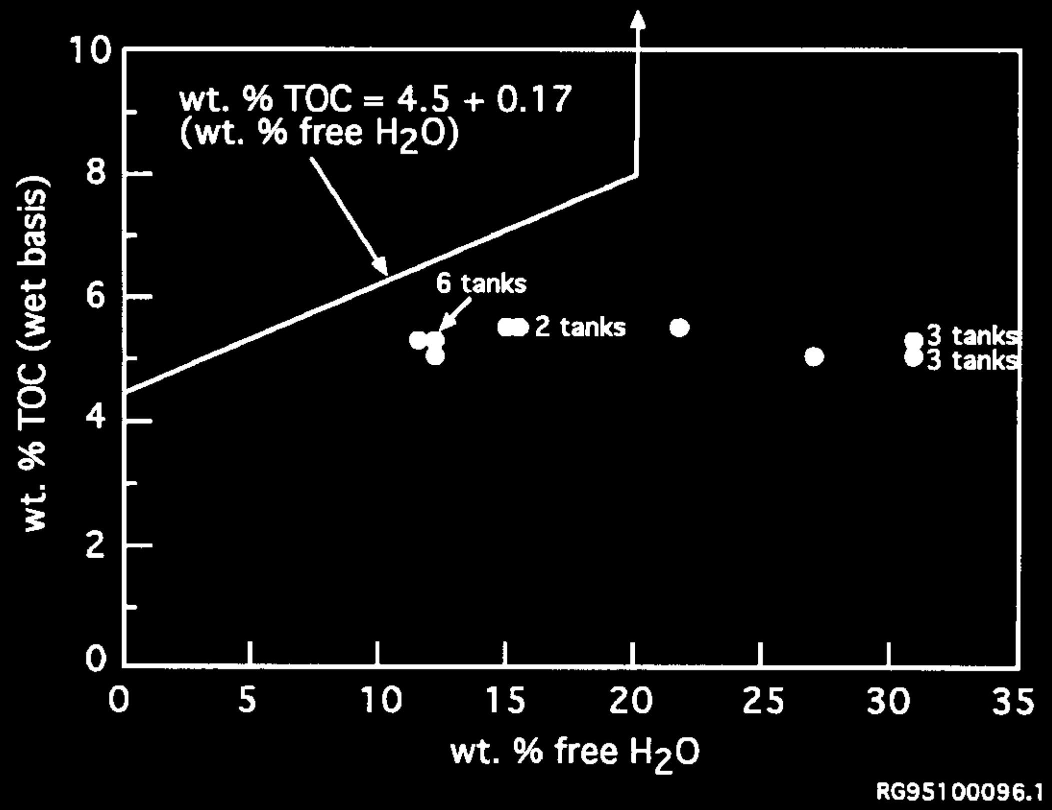


The other type of preventive strategy is an engineered change in the waste composition either by adding moisture or by removing fuel from the vicinity of possible initiators (i.e., the waste surface). Moisture addition is possible but problematic because of the potential for tank leakage in the long run. Simultaneous addition of solution saturated in waste salts (sodium nitrate and sodium hydroxide) and salt well pumping is a potential technique for flushing soluble organic fuels and avoiding the long-term leakage issue.

5.6 CONCLUSIONS

The derived criteria line is compared with the currently estimated state of the 15 most crucial salt cake tanks (presented in Chapter 6) in Figure 5-8. These salt cake tanks were chosen because they have the highest TOC/lowest moisture combination among all tank TOC/moisture estimates (i.e., they have the worst combination in relation to the new criteria line). It is evident that the currently estimated states all fall below the criteria line, and

Figure 5-8. Comparison of 15 Worst 5% Salt Cake Tanks with the Preliminary Safety Criteria.



therefore, by definition, a propagating chemical reaction event is impossible in these tanks as they are today. As discussed in Chapter 6, the data points indicated in Figure 5-8 represent the portions of the waste at the 95th quantile of TOC (95% of the waste in the given tanks has less TOC than indicated) and 95th quantile of moisture (95% of the waste in the tanks has more moisture than indicated), so indeed the median TOC and moisture in these tanks is well below the criteria line.

It can be concluded that the organic tanks are currently safe with respect to potential propagating chemical reactions. In subsequent chapters of this report, mechanisms for moisture loss during long-term waste storage, routine operations, and off-normal situations will be addressed so that a judgement of long-term waste safety may be made. Final conclusions on waste safety are presented in Chapter 9.

6.0 ESTIMATES OF TANK WASTE CONDITIONS

This chapter estimates the TOE and the moisture concentrations in each of the 149 single-shell tanks at the Hanford Site and compares them with the preliminary safety criteria to postulate a probability that the waste in each tank exceeds the safety criteria. When possible, the state of each tank has been determined from actual tank TOE and moisture waste measurements. The state of those tanks containing wastes that have not been measured has been determined by using attributes of tanks with similar characteristics. Attributes of the characteristic groups include the inventory of chemicals added to the tanks and tank waste conditions. An ANOVA-based tank model has been applied to produce estimates of TOC and moisture concentrations in all tanks. The ANOVA model uses average or mean values of the characteristic groups to which a tank belongs to estimate its conditions. This strategy utilizes the characteristic group's mean and between-tank variability to produce a best estimate for unmeasured tank conditions. The descriptive statistical ANOVA methods for estimating the TOC and moisture are presented in PNL-10360, *Analysis of Total Organic Carbon and Moisture in Hanford Single-Shell Tank Waste* (Toth et al. 1995).

Many tanks have not been sampled and consequently the ANOVA-based estimate should be considered an extrapolation. For liquids, salt cakes and sludges, the percentage of tanks without TOC data are 57%, 81%, and 74%. Salt cake tank waste is the least represented phase. Appendix 6A provides a list of the number of sample measurements for each waste phase.

Laboratory measurements of TOC and moisture were compiled from many documented sources, including tank characterization reports, letter reports, and process aids analysis reports. The documents contain information pertaining to the observations and data taken during sample breakdown and preparation as well as results of the analytical determinations. In the case of tank characterization reports, observations taken during actual sampling are available. Each sample was classified as salt cake, sludge, or liquid based on the sample description. Supernatant and liquid samples removed from salt wells were classified as liquids. Samples described as salt cakes, salt/slurries, and salt cake matrixes were classified as salt cakes. All other salt phases were classified as sludges.

6.1 NOMINAL CHARACTERISTICS OF WASTE PHASES

Waste phase, an attribute of the tank and measurement sample, is categorized as liquid, sludge, or salt cake. Initially, all waste admitted to the tanks was liquid, or a liquid slurry, and over time sludge settled. Salt cake was formed by evaporation of waste in a process designed to increase available tank storage capacity. The sludge resulted from settling of alkaline insoluble wastes while salt cake resulted from evaporation and subsequent crystallization of the waste. The measurements taken to date show that there are significant differences in TOC concentrations among these three phases. Consequently, separate TOC (and percent-moisture) estimates have been produced for each waste phase present in a tank. This organization also makes sense from a safety perspective because the different phases can be expected to behave differently during a condensed-phase propagating chemical reaction.

The moisture estimates for each tank have been based on surveillance information in addition to actual tank moisture data. Surveillance information was provided by WHC-EP-0182-72, *Tank Farms Surveillance and Waste Status Summary Report for March 1994* (Hanlon 1994). The Hanlon report (1994) provides information pertaining to the tank phase and tank ventilation status as well as an estimate of liquid volume and solids volume for each tank. The solids volume is partitioned into a sludge and salt cake fraction. The evaluations in this report depend largely upon the waste phase types and amounts reported in the Hanlon report (1994). For example, if Hanlon states that there is 1,760 kL (465 kgal) of salt cake in tank S-106, it is assumed to be accurate even though no laboratory analysis of a salt cake sample was performed for tank S-106. Tank ventilation status also is described in Hanlon (1994).

The data set of tank measurements was compiled from a variety of sources ranging from process aids reports, generated directly by the Hanford Site 222-S and 325 Laboratories, to issued documents, such as waste tank characterization reports. The reports date back to the 1970's. The most recent sample data used in this report are for tank T-107 and BX-107 sludge measurements from August 1994. A number of tanks, such as BY-104 salt cake, have been sampled since this report was published. Because the data set was compiled from such a variety of sources and spanned such a length of time, there are different amounts of detail provided with the sample measurements. The sample data represent the waste conditions that were present during the time of analysis, and waste conditions may have changed since the analysis was reported. Some of the data variability may also be due to the different sampling and analysis techniques that have been used over the years. Sample results for a particular tank should be compared against each other to confirm that each sample is representative or at least bounding for the TOC or moisture.

Table 6-1 summarizes the sample TOC, moisture, and density measurements by phase. It can be clearly seen that salt cake has the highest concentration of TOC relative to the other phases, and sludge has the lowest. The salt cake 95% confidence intervals are large because of the small number of observations available on that waste phase. Salt cake also appears to be the densest phase and contains the least amount of water. Liquids are the lightest phase and contain the greatest amount of water. It is important to note that the mean and confidence intervals for TOC were calculated from the log transformed data and converted back to units of μg/g based on the knowledge that the TOC data are lognormally distributed (Toth et al. 1995). The TOC data were log transformed and were found to be normally distributed. Figure 6-1 also gives a visual overview of all 597 measurements in the database (353 TOC measurements and 231 moisture measurements). This discussion details the methods used in this report. It has been recognized that experiments (Barney 1994b) show that energetic TOC should be nearly all in solution. We plan to update our report with modeling that reflects this solubility data.

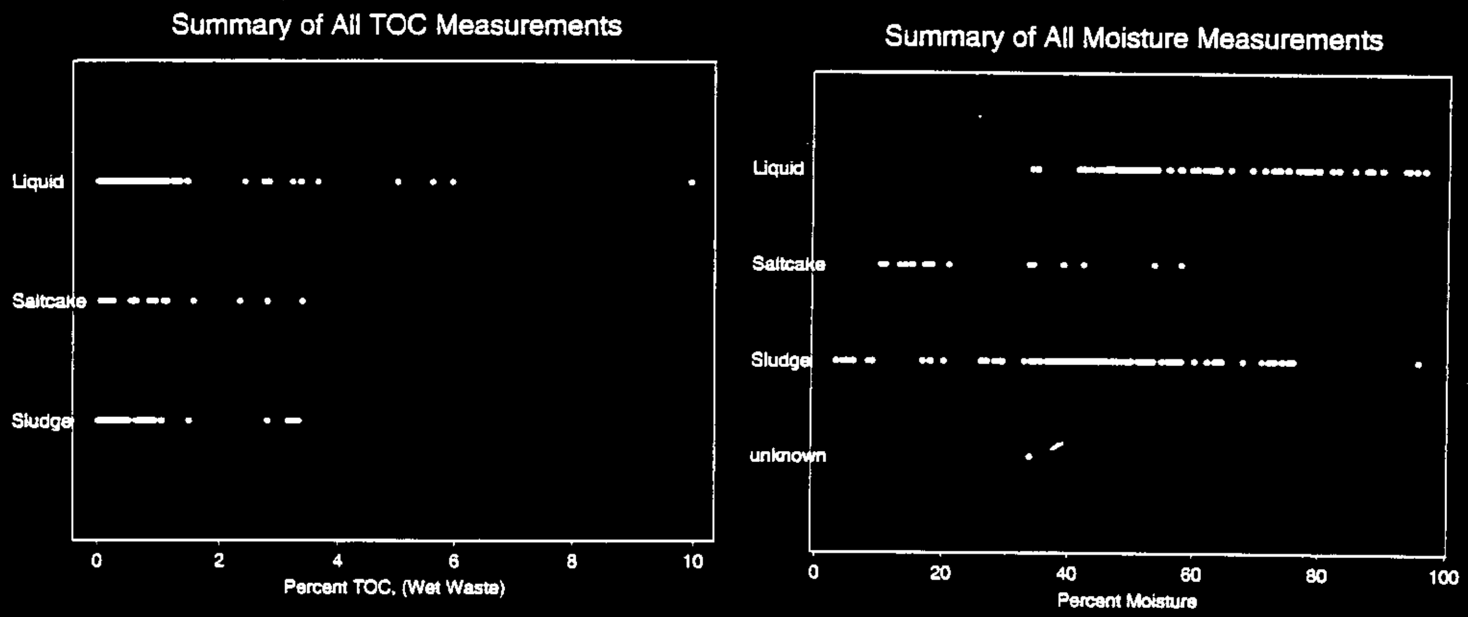
Table 6-2 summarizes the number of TOC observations by phase. From this table, it can be seen that only 21 salt cake measurements are available. This identifies one of the weakest aspects of this analysis: the fewest TOC measurements are on the phase likely to be the most important from a safety perspective. Also, there are very few within-tank measurements for the salt cake phase. Because there are so few salt cake measurements, the salt cake

Table 6-1. Total Organic Carbon, Moisture, and Density Measurements by Phase.

Waste		Number of samples	Lower 95% confidence interval on median	Median value	Upper 95% confidence interval on median
Property	Phase				
TOC (µg/g)*	Liquid	143	3,106	3,775	4,588
	Salt cake	21	3,161	5,296	8,870
	Sludge	202	1,098	1,294	1,527
Water (wt%)	Liquid	78	40.28	66.3	87.30
	Salt cake	18	0.00	25.99	50.98
	Sludge	135	18.65	44.21	69.77
Density (g/ml)	Liquid	43	1.31	1.37	1.43
	Salt cake	8	1.43	1.64	1.84
	Sludge	77	1.40	1.45	1.50

*10,000 µg/g = 1 wt%.
TOC = total organic carbon.

Figure 6-1. Nominal Characteristics for Total Organic Carbon and Moisture Data.


Summary of All TOC Measurements

Summary of All Moisture Measurements

Table 6-2. Summary of Total Organic Carbon Measurements.

Phase	Number of observations	Number of tanks with n observations					
		n=0	n=1	n=2	n=3	n=4	n>4
Liquid	143	90	31	9	7	4	8
Salt cake	21	136	8	3	1	1	0
Sludge	202	114	10	8	2	0	15

estimates can be expected to change significantly as new measurements are taken. Finally, note that most tanks have no measurements (70 out of 129 tanks with liquids have no measurements, 53 out of 65 salt cake tanks have no measurements, and 95 out of 131 sludge tanks have no measurements). Hence, most of the TOC and moisture estimates given in this chapter are extrapolations from the ANOVA model.

Figure 6-1 shows a substantial difference (several orders of magnitude) between the largest TOC measurements and the median values. The waste in the tanks is certainly not homogeneous. An accurate description of the variability in the waste is necessary for evaluating the safety consequences of the waste. Section 6.2 presents an ANOVA model that provides a more complete description of this variability.

It is interesting to note that there is substantial variation within the moisture measurements also. It is particularly surprising that the moisture content of a liquid varies from 40% to nearly 100% and that the typical tank liquid is a little over one-half water. The balance of the liquid is made up primarily of dissolved inorganic salts. The moisture measurements represent waste conditions at the time of analysis, and sampling and analysis variations over the years are included in the variation of the estimates.

6.2 ESTIMATION OF TANK TOTAL ORGANIC CARBON AND MOISTURE

The tank groupings for TOC are based on waste phase and chemical composition. The waste phase groupings are liquid, salt cake, and sludge. Chemical composition groups have been defined by using the SORWT model. The SORWT model categorizes tanks into groups of waste with similar process histories. The SORWT (previously described in Hill et al. [1994]) divides the 149 single-shell tanks into 42 main groups (including 12 ungrouped tanks). Appendix 6B, Table 6B-1, describes the tank wastes in each of the SORWT groups.

For many SORWT groups, no member tanks have been sampled. For these groups, the waste phase average (along with estimates of group-to-group and tank-to-tank variability) is used to construct suitable estimates for the member tanks. Naturally, such an estimate has a great deal of uncertainty associated with it. A very important benefit of the ANOVA-based model is its ability to assign reasonable uncertainties to all produced estimates.

Many of the SORWT groups contain only one tank and therefore are not useful for extrapolation to unmeasured tanks. The SORWT groups containing more than four tanks are listed in Table 6-3. Even if many measurements for an individual tank were available so that the waste within that tank could be empirically described, there would still be a problem associated with TOC estimation.

Table 6-3. Tanks in the Largest Sort on Radioactive Waste Types Groups.

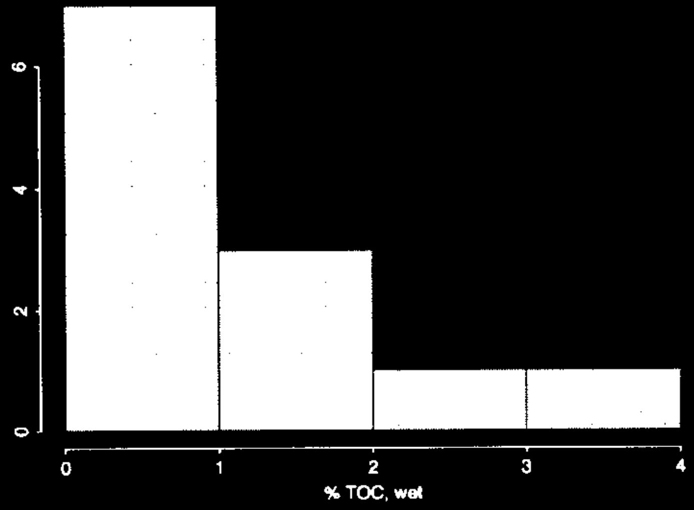
SORWT group	Tanks
I	S-101, S-102, S-103, S-105, S-106, S-107, S-108, S-109, S-110, S-111, S-112, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, TX-102, TX-104, TX-105, TX-106, TX-107
II	B-105, TX-109, TX-110, TX-111, TX-112, TX-113, TX-114, TX-116, TX-117, TY-102
III	BY-101, BY-103, BY-104, BY-105, BY-106, BY-107, BY-108, BY-110, BY-111, BY-112
IV	BX-101, BX-102, BX-103, BX-104, BX-105, BX-106, BX-108, BX-109, C-101
V	B-201, B-202, B-203, B-204, T-201, T-202, T-203, T-204
VI	S-104, SX-107, SX-108, SX-109, SX-112, SX-115, U-101
VII	TX-115, U-102, U-103, U-106, U-111
VIII	C-108, C-109, C-111, C-112, T-107

SORWT = sort on radioactive waste types.

Because the waste in most tanks is not homogeneous, a single value for TOC at one point or from a homogenized core sample will not describe the state of the waste. This problem can be illustrated with tank A-101, a tank in which the measurements vary over one order of magnitude (see Figure 6-2). The minimum TOC value for tank A-101 is 0.38%, the mean is 1.24%, and the maximum observed value is 3.37%. One of these values should be compared to the safety criteria. A central value such as the mean may not adequately describe the portion of the waste of concern relative to the safety criteria. On the other hand, the maximum represents the most extreme portion of the waste, and there may be an insignificant amount of this waste in the tank.

Because there is so much variation in the measurement data, the TOC and moisture concentration has been estimated for the worst 5% of the waste, that is, the 5% of the waste with the highest TOC concentration and the lowest moisture content. (In statistical terminology, these values are called quantile estimates.) For example, given a tank with a mass of 1,000 t, the 50 t of waste containing the highest TOC represents the worst 5% of the waste for TOC, and the driest 50 t represents the worst 5% of the waste for moisture. It is conservatively assumed that the driest 5% of the waste coincides with the 5% with the highest fuel.

Figure 6-2. Histogram of Liquid Measurements Associated with Tank A-101.



Distribution plots of the TOC measurements indicate that they are lognormally distributed (Toth et al. 1995). Consequently, the TOC measurements were fit to an ANOVA model having the following form:

$$\log\ (TOC_{ijk}) = \mu + G_i + T_{ij} + E_{ijk} \tag{6-1}$$

where

μ = log mean of TOC measurements for the phase
G_i = SORWT group effect
T_{ij} = tank effect
E_{ijk} = within-tank variations.

The ANOVA model produced the following information:

- An estimate of the median concentrations for all tanks
- Enough distributional information to predict the 95th quantile (worst 5% of the waste) for sampled tanks (the within-tank variability from the ANOVA model is used for this purpose)
- The uncertainty associated with all median and quantile estimates, expressed in terms of confidence bounds and standard errors.

For tank A-101, liquid phase, the ANOVA results for estimating the median concentration in the tank are as follows:

$\mu = 3.44$
$G_i = -0.37$
$T_{ij} = 0.90$
median log TOC = 3.44 - 0.37 + 0.90 = 3.97
median TOC = 9,332 μg/g or 0.9% wet basis TOC, median value.

The ANOVA model estimates 3.8% TOC (wet basis) for the worst 5% of the liquid waste in tank A-101. The value chosen for comparison to the criteria is 3.8% TOC. The highest sample value measured is 3.37% TOC.

Two ANOVA models were applied to the moisture measurements. For the liquid and sludge phases, the ANOVA model is as follows:

$$M_{ijk} = \mu + G_i + T_{ij} + E_{ijk} \qquad (6\text{-}2)$$

where

M_{ijk} = moisture measurement.
μ = median of moisture measurements for the sludge or liquid phase
G_i = SORWT group effect on moisture for sludge and liquid phase
T_{ij} = tank effect on moisture for sludge and liquid phase
E_{ijk} = within-tank variations on moisture for sludge and liquid phase.

For the salt cake phase, an ANOVA model involving fewer groups was fit because only 13 tanks had salt cake measurements:

$$[\log (M_{ijkl}) = \mu + P_i + V_j + W_k + T_{ijk} + E_{ijkl}] \qquad (6\text{-}3)$$

where

μ = mean of moisture for all salt cake measurements
P_i = pumping effect for salt cake moisture
V_j = ventilation effect for salt cake moisture
W_k = waste type effect for salt cake moisture
T_{ijk} = tank effect for salt cake moisture
E_{ijkl} = within-tank variations for salt cake moisture.

In other words, each salt cake tank is classified as to whether (1) it has been jet pumped or not (i), (2) it is actively or passively ventilated (j), or (3) the salt cake in it originated from the REDOX process or not (k). The eight salt cake moisture groups that comprise the three classifications are shown on Table 6-4. Moisture group numbers 4, 5, 7, and 8 have been used to develop the ANOVA model because these groups have available salt cake moisture sample data. A listing of the salt cake tanks and their corresponding moisture groups is provided in Appendix 6C. REDOX waste

Table 6-4. Salt Cake Moisture Groups.

Moisture group number	Description			Comments
1	Non-REDOX waste	Jet pumped	Active ventilation	There are no actively ventilated tanks that have been jet pumped.
2	REDOX waste	Jet pumped	Active ventilation	There are no actively ventilated tanks that have been jet pumped.
3	Non-REDOX waste	Not jet pumped	Active ventilation	There are no salt cake tanks in this moisture group.
4	REDOX waste	Not jet pumped	Active ventilation	Six total tanks: SX-101 through SX-106
5	Non-REDOX waste	Jet pumped	Passive ventilation	7 BY tanks and 11 TX tanks
6	REDOX waste	Jet pumped	Passive ventilation	Tank S-105 and three TX tanks
7	Non-REDOX waste	Not jet pumped	Passive ventilation	20 tanks
8	REDOX waste	Not jet pumped	Passive ventilation	17 tanks

REDOX = reduction and oxidation.

describes a SORWT group that is characteristic of waste high in nitrate and sodium. Unlike non-REDOX waste, which has higher sodium hydroxide concentrations, the moisture is lower in REDOX-type waste. Higher decay heat loads, active ventilation, and interim stabilization by jet pumping have reduced salt cake moisture.

A summary of the variance components determined by the ANOVA fits is given in Table 6-5. Notice that there are significant differences between the phases. For the TOC ANOVA components, the error of 37.5% is the greatest relative standard deviation (RSD) for liquids, the 52.0% error term is the greatest RSD for salt cake, and the 37.3% error is the greatest RSD for sludge. For half of the cases (three out of six), within-tank variability (error) is the largest source of variability. This means that the waste is not homogeneous even when it is analyzed by phase. For these cases, there will be a large difference between the state of the "average" waste in the tank and the worst 5% of the waste. It is assumed the maximum level of TOC in any tank waste is 25%. This is equivalent to 85 wt% sodium acetate. It is further assumed that maximum TOC and moisture combined will not exceed 100%.

Table 6-5. Summary of Analysis of Variance Components.

Phase	TOC RSD			Moisture RSD		
	Group	Tank	Error	Group	Tank	Error
Liquid	23.5	30.6	37.5	8.4	9.8	9.2
Salt cake	17.1	0.0	52.0	12.5	12.3	3.5
Sludge	45.2	25.7	37.3	10.7	0.0	12.7

NOTE: All values are in percent.
RSD = relative standard deviation; standard deviation divided by median; σ/μ.
TOC = total organic carbon.

6.3 SAFETY CRITERIA EVALUATION

Statistical estimates for the TOC and moisture content in each of the single-shell tanks are based on the available characterization data using the ANOVA technique. This section describes how the best estimates for the 149 single-shell tanks are compared to the preliminary safety criteria to postulate the probability that waste in each tank exceeds the safety criteria. For each tank waste phase, the median tank waste condition has been estimated. In addition, the condition of the worst 5% of each waste phase has been calculated. (The condition of the 5% waste with the highest TOC and lowest moisture content is described as the worst 5% of the waste.) As water evaporates from liquid, it is recognized that the TOC content in the liquid waste may increase. Without a vapor-liquid equilibrium model to estimate this effect, the concentration of TOC increasing as a result of such evaporation was not included in the estimate in this chapter. The estimates in this chapter represent the best estimates of the current conditions of the waste. Predictions about dryout effects are presented in Chapter 7.

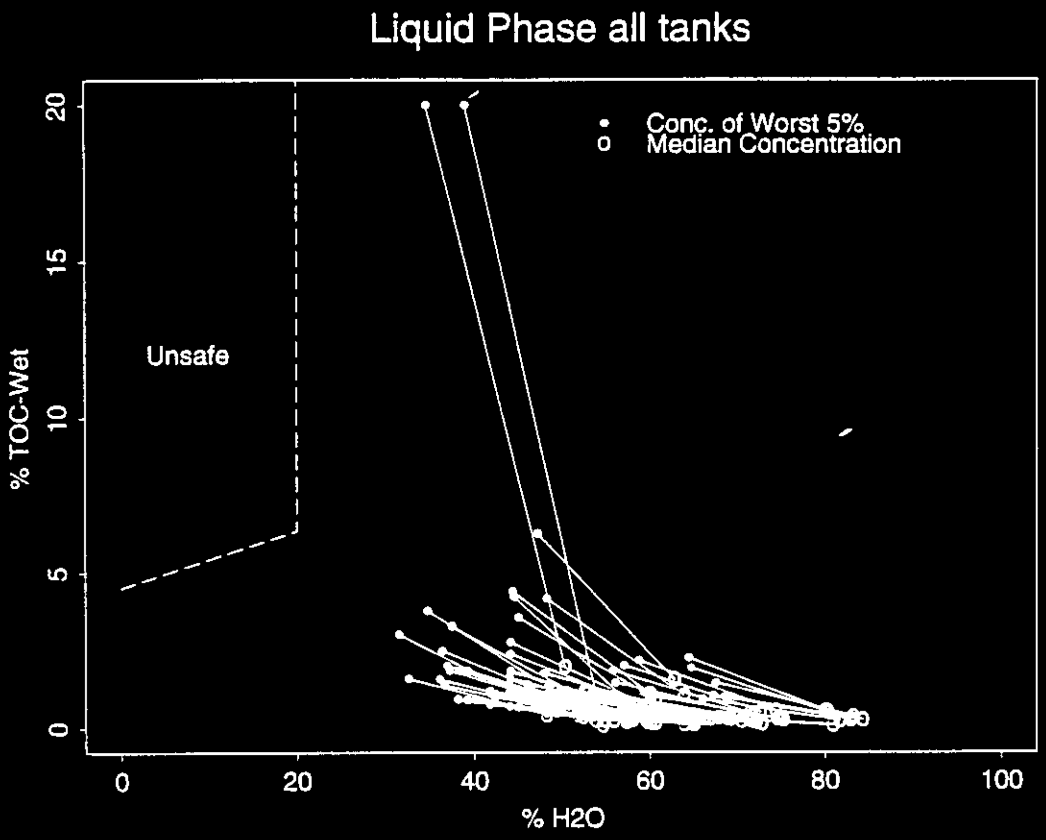
The preliminary safety criteria addressed in Chapter 5 are used as a basis for safety evaluations. The safety criteria are defined by the two points (H_2O = 0%, TOC = 4.5%) and (H_2O = 20%, TOC = 7.9%). The safety criteria are linear between the two points. Waste that exceeds these criteria is unsafe. Additionally, the unsafe region is bounded by moisture being less than 20%.

6.4 STATE OF SUPERNATANT AND/OR INTERSTITIAL LIQUID

Appendix 6D, Table 6D-1, lists TOC and moisture estimates for the median concentration and the worst 5% of the waste in all tanks having a measurable quantity of liquid according to Hanlon (1994); there are 19 tanks that contain no measurable liquids ("drainable liquid" is listed as "0"). Table 6D-1 also provides median TOC and moisture estimates to contrast typical liquid waste with the worst 5% of the waste. If the safety criteria are applied to the worst 5% TOC and moisture values, no liquid exceeds the safety criteria.

Figure 6-3 graphically presents the most important results listed in Table 6D-1. Each tank is represented by line segments connecting two points: (1) the median concentration (moisture, TOC) in the tank and (2) the concentration (moisture, TOC) of the worst 5% of the liquid in the tank. The

Figure 6-3. Total Organic Carbon and Moisture Estimates of Liquid Phase.



distance between the median point and the worst 5% point therefore describes the inhomogeneity of the liquid in the tank.

The safety criteria line is identified on the plot. The region in the upper left hand corner is UNSAFE. All the tanks are to the right of the unsafe region. This means that if the liquid dried out in some of these tanks, they might become UNSAFE. It is noted based on work by Barney (1994b) that draining liquids from a tank is expected to remove substantial amounts of both liquid and TOC. This should improve the safety of the tanks. However, if liquids were allowed to dry out in the tanks, the dissolved energetic organic salts would precipitate, which could lead the tanks to become UNSAFE. This potential is evaluated in Chapter 7.

About 11 tanks have a significant chance (greater than 3%) of exceeding the safety criteria in the liquid phase. Two tanks, A-106 and SX-106, have estimates that are set at maximum physically possible values. In each of these tanks, there are no more than three measurements, and the within-tank variability is much larger than in other tanks. It is quite possible, however, that outlier measurements are the cause of this large variability (and hence the large worst 5% estimates). The large values reported for the rest of the tanks do look reasonable. For example, 11 measurements taken for tank A-101 ranged from 0.4% to 3.4%. So the extreme data value conforms reasonably with the worst 5% estimate of 3.8%.

The 10 tanks with the highest TOC values for the worst 5% of the liquid are listed in Table 6-6. Even though some of these TOC measurements are higher than the TOC safety threshold, none of this waste can be classified as UNSAFE, because all percent moisture estimates are above 20%. The liquid waste in the tanks is currently not a safety concern. However if water is allowed to evaporate from these liquids, they may produce a salt cake that is dangerous. The TOC estimates for liquid will be used in Chapter 7 to assess this problem.

Figure 6-4 displays the 95% confidence bounds on the worst 5% of the waste for the liquid waste phase in: AX-102, B-102, B-201, TX-112, and T-107. The ellipse around the intersection of the vertical and horizontal lines displays the 95% confidence bound region. If the ellipse does not intersect the safety criteria's UNSAFE region, the probability that the tank waste exceeds the safety criteria is no greater than 5%.

6.5 STATE OF SALT CAKE

Appendix 6D, Table 6D-2, lists TOC and moisture estimates for the median concentration and the worst 5% of the salt cake in all tanks having a measurable quantity of salt cake. Only about one-half of the tanks have measurable quantities of salt cake. Salt cake is perhaps the most important phase for this safety analysis. The fact that only 21 salt cake measurements are available greatly increases the uncertainties associated with these measurements.

Table 6-6. Highest "Worst 5%" Total Organic Carbon Estimates in the Liquid Phase.*

		% TOC (wet basis)		% Moisture	
Tank	SORWT group	Median estimate	Worst 5%	Median	Worst 5%
SX-106	1	2.0	19	50.3	34.6
A-106	XXXA	0.1	19	54.6	38.9
U-106	VII	1.6	6.2	62.8	47.2
AX-102	XXVIII	1.1	4.4	60	44.3
TX-118	XXII	0.2	4.2	60.1	44.4
U-111	VII	1.0	4.2	63.9	48.2
A-101	IX	0.9	3.8	50.4	34.7
S-102	I	0.9	3.5	60.7	45.0
AX-103	XXVIII	0.8	3.3	53.1	37.4
AX-101	IX	0.8	3.0	47.1	31.5

*Toth, J. J., M. E. Lerchen, J. G. Hill, P. G. Heasler, and P. D. Whitney, 1995, Analysis of Total Organic Carbon and Moisture in Hanford Single-Shell Tank Waste, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.

SORWT = sort on radioactive waste type.

TOC = total organic carbon.

Figure 6-4. 95% Confidence Bounds on the Worst 5% of the Liquid Waste, Five Typical Liquid Waste Tanks.

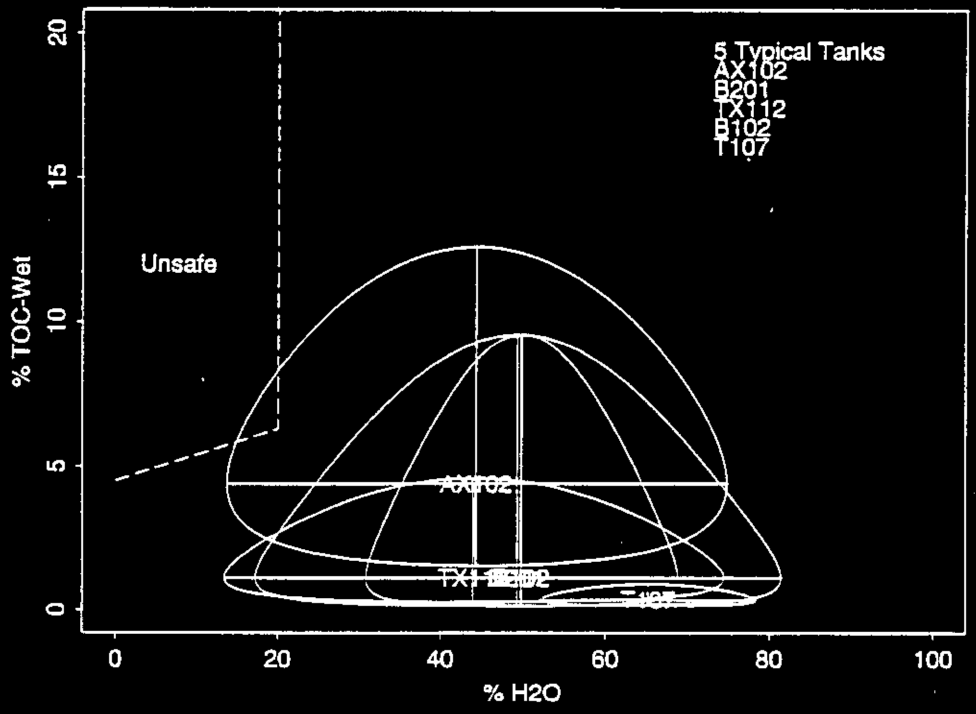
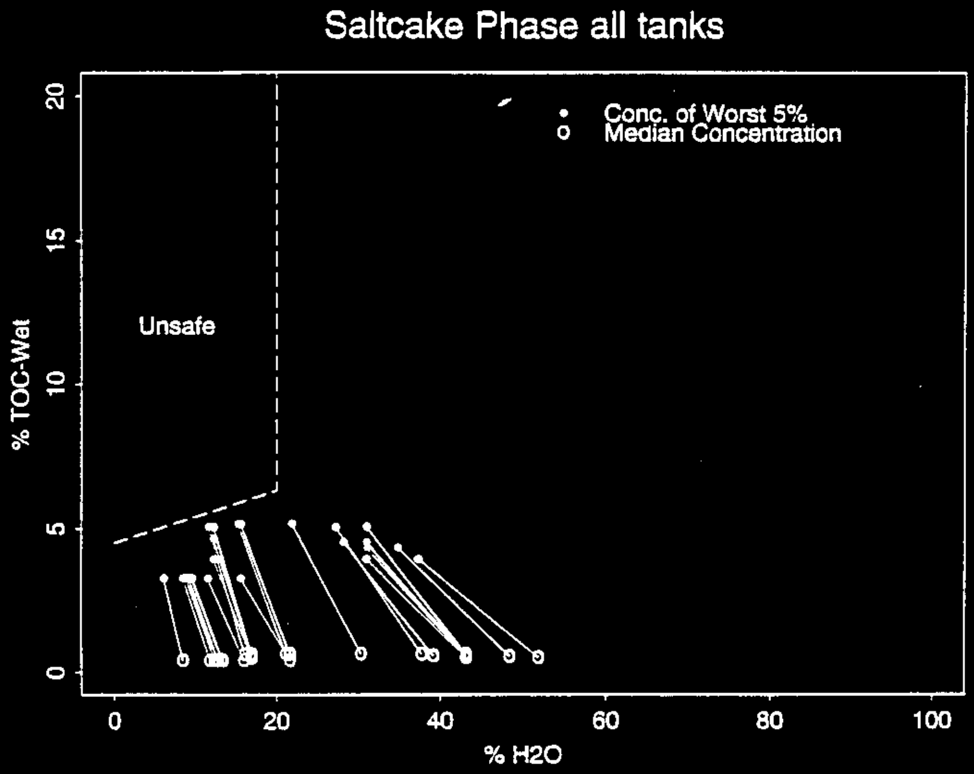


Figure 6-5 graphically presents the salt cake results in a manner similar to Figure 6-3 for liquids. Each tank is represented by line segments connecting two points: (1) the median concentration (moisture, TOC) in the tank and (2) the concentration (moisture, TOC) of the worst 5% of the salt cake in the tank. It should be noted that one line on this plot may represent several tanks because there is so little data; these tanks have not been sampled and are all represented by group estimates. For example, the worst line (the line with a high TOC of 5% and H_2O of 16%) includes the tanks BY-101, BY-104, BY-107, BY-108, BY-111, BY-112, and TX-115.

Figure 6-5. Total Organic Carbon and Moisture Estimates of Salt Cake Phase.



As one can see from the plot, none of the worst 5% estimates lie in the unsafe region. However, several salt cake tanks are close to the unsafe region, and might well move into the unsafe region with the addition of new data to the ANOVA model. Figure 6-6 illustrates the uncertainty associated with these estimates and hence the likelihood that new data might affect the current categorization of the salt cake tanks. Figure 6-6 displays 95% confidence bounds on the worst 5% salt cake estimates for five typical tanks. The confidence bounds are quite large, and more measurements should be taken to reduce this uncertainty.

As one can see from Table 6-7 and Figure 6-6, the salt cake phase is the most important phase from a safety perspective. Even though no tanks are currently in the unsafe region, a small change in their estimates could put them in this region. Such a change could occur because (1) new data causes

Figure 6-6. Total Organic Carbon and Moisture Estimates of Sludge Phase.

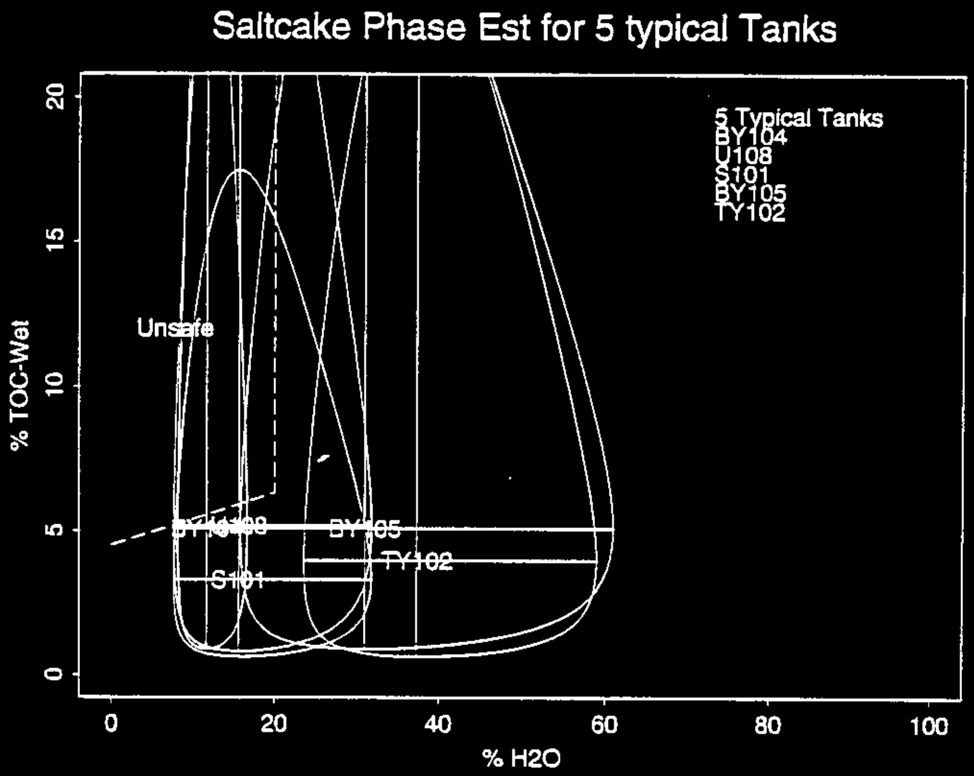


Table 6-7. Highest "Worst 5%" Total Organic Carbon Estimates in the Salt Cake Phase.

		%TOC (wet basis)		% Moisture	
Tank	SORWT group	Median estimate	Worst 5%	Median	Worst 5%
U-105	X	0.7	5.2	21.1	15.2
U-107	X	0.7	5.2	21.6	15.5
U-108	X	0.7	5.2	21.6	15.5
U-109	X	0.7	5.2	30.4	21.8
BY-101	III	0.7	5.1	16.9	12.2
BY-103	III	0.7	5.1	43.1	31.0
BY-104	III	0.7	5.1	16.1	11.6
BY-105	III	0.7	5.1	43.1	31.0
BY-106	III	0.7	5.1	43.1	31.0
BY-107	III	0.7	5.1	16.9	12.2
BY-108	III	0.7	5.1	16.9	12.2
BY-110	III	0.7	5.1	16.9	12.2
BY-111	III	0.7	5.1	16.9	12.2
BY-112	III	0.7	5.1	16.9	12.2
TX-115	VII	0.6	5.0	16.9	12.2
U-102	VII	0.6	5.0	43.1	31.0
U-103	VII	0.6	5.0	43.1	31.0
U-106	VII	0.6	5.0	43.1	31.0
U-111	VII	0.6	5.0	37.7	27.2

SORWT = sort on radioactive waste type.
TOC = total organic carbon.

the estimates to change or (2) modifications to account for waste moisture loss (e.g., jet pumping) put them in the region. The modifications that account for waste moisture loss will be considered by Chapter 7.

Table 6-7 lists the 14 tanks with the highest TOC values (for the worst 5% of the salt cake). This table will allow the reader to identify individual tanks that are the most dangerous. As one can see from Table 6-7, tanks in three SORWT groups (X, II, and VII) comprise the list of most dangerous salt cake tanks. The TOC estimates for each group are the same because only one tank in each group was sampled.

6.6 STATE OF SLUDGE

Appendix 6D, Table 6D-3 lists TOC and moisture estimates for the median concentration and the worst 5% of the waste in all tanks having a measurable quantity of sludge. Figure 6-7 graphically presents the sludge results. This figure shows that the sludge results fall between the liquid and salt cake results. Sludge TOC measurements are lower than the salt cake phase but higher than the liquid phase.

The 10 tanks with the highest TOC estimates (for the worst 5% of the sludge) are listed in Table 6-8. The first tank on the list (B-202) has a TOC estimate of 7.6% and is above the TOC safety threshold. However, its median value (0.2%) is relatively low. The samples from B-202 exhibited substantial within-tank variability, which produced the high TOC estimate for the worst 5% of the waste. These samples may have contained an outlier measurement, so the TOC estimate for this tank may be too high. All other TOC estimates in Table 6-8 are comfortably below the TOC safety threshold. Figure 6-8 shows the 95% confidence bounds for three typical sludge wastes, which are much smaller than the confidence bounds exhibited for salt cake (see Figure 6-6). Although some sludge waste has the potential for being in the unsafe region, all sludge estimates are further away from the unsafe region than the salt cake estimates, indicating that sludge is a much safer phase than salt cake.

6.7 PROTOCOL FOR ESTIMATING WASTE CONDITIONS USING CHARACTERIZATION DATA

Statistical estimates are based on available characterization data. As new data become available from core, auger, or supernatant sampling, the results will be incorporated into the statistical model. This section describes how new characterization data will be treated to estimate moisture and TOC levels in the single-shell tanks.

Figure 6-7. 95% Confidence Bound on of the Worst 5% of the Waste, Five Typical Sludge Phase Waste Tanks.

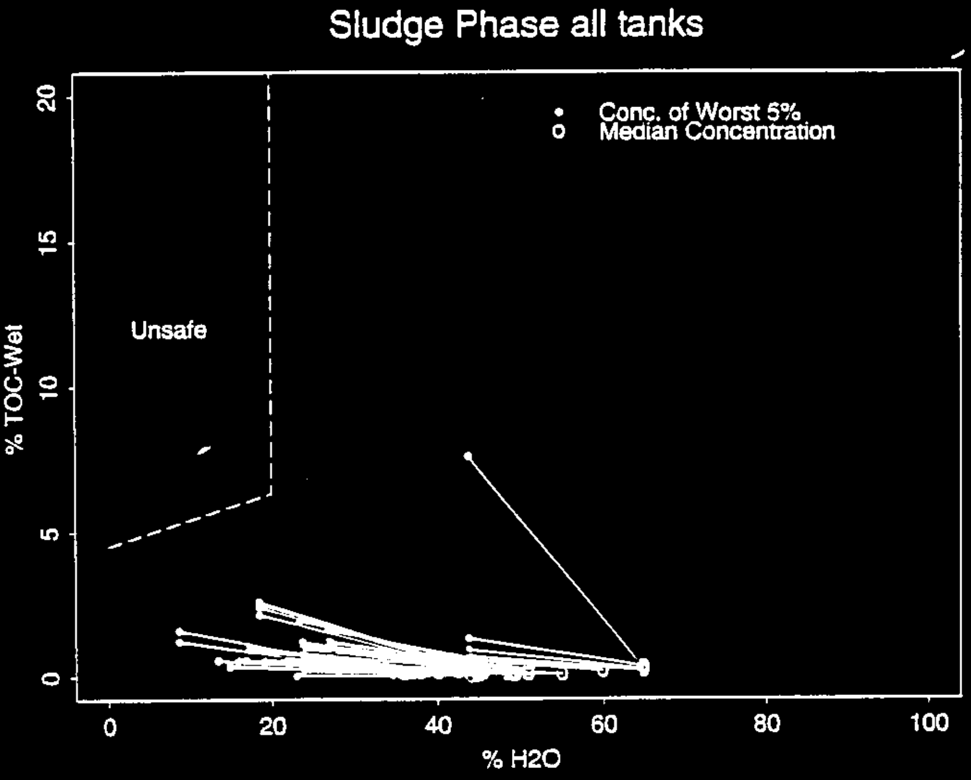
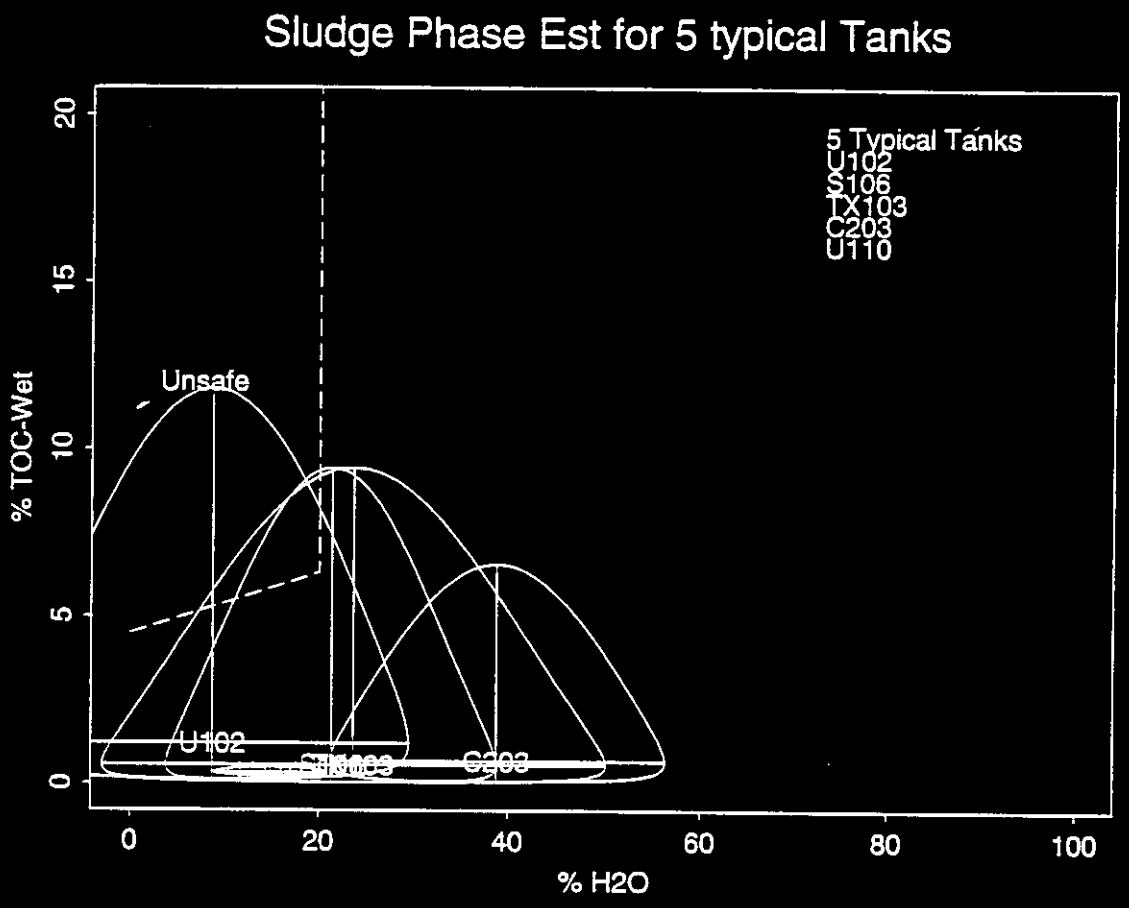


Table 6-8. Highest "Worst 5%" Total Organic Carbon Estimates in the Sludge Phase.

		%TOC (wet basis)		%TOC (wet basis) 95% confidence bound	
Tank	SORWT group	Median estimate	Worst 5%	Median	Worst 5%
B-202	V	0.2	7.6	64.9	43.8
A-103	IX	0.7	2.6	39.5	18.4
A-102	IX	0.6	2.5	39.5	18.4
A-101	IX	0.6	2.4	39.5	18.4
AX-101	IX	0.5	2.1	39.5	18.4
A-106	XXXA	0.5	1.9	44.3	23.2
BX-112	XII	0.4	1.6	47.8	26.7
U-103	VII	0.4	1.6	29.8	8.7
T-204	V	0.3	1.3	64.9	43.8
B-107	XII	0.3	1.2	47.8	26.7

SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Figure 6-8. 95% Confidence Bounds on the Worst 5% of the Waste, Three Typical Sludge Phase Waste Tanks.



6.7.1 Supernatant and/or Interstitial Liquid

The current model for liquids is based on 142 measurements for TOC and 77 measurements for moisture. TOC and moisture estimates for liquids are developed using a grouping technique wherein tanks of the same waste type or SORWT group have similar characteristics.

The protocol for treating new liquid data is to first compare the new liquid data to existing measurements for the tank. If the new data fit the distribution of historical data, the new data are added without any modifications to the earlier liquid data, and the statistical model is rerun. Criteria for new data fitting the current distribution of data are based on a comparison of a histogram of the current and new data plotted together. For TOC measurements, the histogram is plotted according to the log of the measurements. For moisture data the histogram is plotted without log transformation. The determination of whether the new data fit the distribution of the current data will depend on the number of measurements comprising the current tank data.

When the new liquid data do not fit the distribution of previous measurement data for the tank, the pedigrees of the previous data will be examined. Pedigree includes traceability of standards, laboratory sample identification, recording of range of values, recording of holding times, acceptable analytical technique, recording of measurement detection limits, and other similar good laboratory practice identification. If the previous data lack pedigrees and do not fit the distribution of the new liquid data, the previous data will be deleted from the data set and replaced with the new liquid data. If the pedigrees of the previous data are acceptable, and the new data do not fit into the distribution, the reason for the discrepancy will be identified before making any data changes to the model. Resampling of the tank will be considered.

Changes in the model results are summarized in accordance with the model assumptions: lognormal distribution, phase effect, SORWT group effect, and tank variability. For the liquids, it is expected the model assumptions will hold for new data because there is a significant quantity of data on which the current model is based.

6.7.2 Salt Cake

Moisture estimates for salt cakes have been developed using a grouping technique wherein tanks of the same waste type or SORWT group have similar moisture properties. Because there are only 21 TOC and 18 moisture measurements for the 65 salt cake tanks, a significant level of uncertainty is associated with the current model. As new salt cake data become available, the salt cake model can be expected to change.

The protocol for treating new salt cake data is to first compare the new salt cake data to existing measurements for the tank. If the new data fit the distribution of historical data, the new data are added without any modifications to the earlier salt cake data, and the statistical model is rerun. Changes in the model results are summarized in accordance with the model assumptions: lognormal distribution, phase effect, SORWT group effect, and tank variability.

When the new salt cake data do not fit the distribution of previous measurement data for the tank, the pedigrees of the previous data will be examined. If the previous data lack pedigrees and do not fit the distribution of the new data, the previous data will be deleted from the data set and replaced with the new salt cake data for that tank. If the pedigrees of the previous data are acceptable and the new data do not fit into the distribution, the reason for the discrepancy will be identified before making any data changes to the model. Resampling of the tank will be considered. For salt cake data, all TOC measurements, with the exception of those for tank BY-104, were taken prior to 1989, and the pedigrees of the existing TOC and moisture salt cake data are not as good as would be expected for new (post-1980) data.

6.7.3 Sludge

The current model for sludges is based on 199 TOC measurements and 135 moisture measurements. TOC and moisture estimates for sludges have been developed using a grouping technique wherein tanks of the same waste type or SORWT group have similar characteristics.

The protocol for treating new sludge data is to first compare the new sludge data to existing measurements for the tank. If the new data fit the distribution of historical data, the new data are added without any modifications to the earlier sludge data, and the statistical model is rerun. Changes in the model results are summarized in accordance with the model assumptions: lognormal distribution, phase effect, SORWT group effect, and tank variability.

When the new sludge data do not fit the distribution of previous measurement data for the tank, the pedigrees of the previous data will be examined. If the previous data lack pedigrees and do not fit the distribution of the new sludge data, the previous data will be deleted from the data set and replaced with the new sludge data. If the pedigrees of the previous data are acceptable and the new data do not fit into the distribution, the reason for the discrepancy will be identified before making any data changes to the model. Resampling of the tank will be considered. For the sludges, it is expected that the model assumptions will hold for new data because there is a significant quantity of data on which the current model is based.

6.7.4 New Waste Characterization Data

When new data become available, it is assumed that they will have good pedigrees and that several samples will be taken from each tank. If possible, samples from more than one riser location in the tank and samples from the top, middle, and bottom of the waste layers will be taken. This applies to liquid, salt cake, and sludge wastes.

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APPENDIX 6A

QUANTITY OF SAMPLE MEASUREMENTS FOR TANK WASTE TOTAL ORGANIC CARBON AND MOISTURE ANALYTES

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Table 6A-1. Quantity of Sample Measurements for Liquid Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
A-101	8	19	12	34
A-102	3	19	11	34
A-103	3	19	6	34
A-105	0	0	0	0
A-106	2	2	2	2
AX-101	5	19	5	34
AX-102	0	1	3	7
AX-103	1	1	4	7
B-101	0	2	0	0
B-102	1	2	0	0
B-104	0	0	0	0
B-105	0	1	0	8
B-106	1	3	0	2
B-107	0	1	0	1
B-108	0	1	0	1
B-109	1	1	0	1
B-110	0	0	0	0
B-111	0	0	0	0
B-112	0	0	0	0
B-201	0	0	0	0
B-202	0	0	0	0
B-203	0	0	0	0
B-204	0	0	0	0
BX-101	0	5	0	7
BX-102	0	5	0	7
BX-103	1	5	0	7
BX-104	1	5	3	7
BX-105	1	5	2	7
BX-106	1	5	1	7

Table 6A-1. Quantity of Sample Measurements for Liquid Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
BX-107	0	3	1	2
BX-108	0	5	0	7
BX-109	1	5	1	7
BX-110	0	1	1	2
BX-112	0	1	1	1
BY-101	0	3	0	6
BY-102	1	2	2	5
BY-103	1	3	1	6
BY-104	0	3	0	6
BY-105	1	3	2	6
BY-106	1	3	2	6
BY-107	0	3	1	6
BY-108	0	3	0	6
BY-109	1	2	3	5
BY-110	0	3	0	6
BY-112	0	3	0	6
C-101	0	5	0	7
C-102	0	0	1	1
C-103	1	1	6	7
C-104	1	1	1	1
C-105	0	0	1	1
C-106	0	1	1	7
C-107	0	0	1	1
C-109	1	7	0	6
C-110	1	3	1	2
C-112	2	7	2	6
S-101	1	16	0	29
S-102	2	16	2	29
S-103	0	16	0	29

Table 6A-1. Quantity of Sample Measurements for Liquid Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
S-104	0	1	0	1
S-105	1	16	0	29
S-106	1	16	0	29
S-107	3	16	5	29
S-108	0	16	0	29
S-109	0	16	0	29
S-110	0	16	1	29
S-111	1	16	3	29
S-112	0	16	0	29
SX-101	2	16	4	29
SX-102	0	16	0	29
SX-103	0	16	0	29
SX-104	2	16	6	29
SX-105	0	16	0	29
SX-106	2	16	4	29
SX-107	1	1	1	1
SX-108	0	1	0	1
SX-109	0	1	0	1
SX-111	1	1	0	0
SX-112	0	1	0	1
SX-114	0	1	0	0
T-101	0	0	1	1
T-102	0	0	0	1
T-103	0	0	0	1
T-104	0	0	1	1
T-105	0	0	0	0
T-106	0	0	0	0
T-107	3	7	4	6
T-110	1	2	0	1

Table 6A-1. Quantity of Sample Measurements for Liquid Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
T-111	0	2	0	1
T-112	1	2	1	1
T-201	0	0	0	0
T-202	0	0	0	0
T-203	0	0	0	0
T-204	0	0	0	0
TX-101	0	0	0	0
TX-102	0	16	2	29
TX-103	1	2	3	3
TX-104	1	16	0	29
TX-105	0	16	1	29
TX-106	0	16	1	29
TX-107	0	16	0	29
TX-109	0	1	1	8
TX-110	1	1	3	8
TX-111	0	1	1	8
TX-112	0	1	1	8
TX-113	1	1	0	8
TX-114	0	1	1	8
TX-115	0	3	2	4
TX-116	0	1	1	8
TX-117	0	1	0	8
TX-118	0	2	6	7
TY-102	0	1	0	8
TY-103	0	0	1	4
TY-104	0	0	3	4
U-101	0	1	0	1
U-102	1	3	0	4
U-103	1	3	0	4

Table 6A-1. Quantity of Sample Measurements for Liquid Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
U-104	0	0	0	0
U-105	0	1	0	0
U-106	1	3	1	4
U-107	0	1	0	0
U-108	0	1	0	0
U-109	1	1	0	0
U-110	0	0	0	0
U-111	0	3	1	4
U-112	0	0	0	0
U-201	0	1	0	0
U-202	1	1	0	0
U-203	0	1	0	0
U-204	0	0	0	0

*Tanks not listed here are shown as tanks with zero drainable liquid according to Hanlon (1994).

SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Table 6A-2. Quantity of Sample Measurements for Salt Phase Tank Waste Total Organic Carbon and Moisture Analytes. (3 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
A-101	2	2	2	2
A-102	0	2	0	2
AX-101	0	2	0	2
AX-102	0	0	0	0
AX-103	0	0	0	0
B-102	0	0	0	0
B-104	0	0	0	0
B-105	0	1	0	1
BX-105	0	0	0	0
BX-110	0	0	0	0
BX-111	0	0	0	0
BY-101	0	4	0	4
BY-102	0	0	0	0
BY-103	0	4	0	4
BY-104	4	4	4	4
BY-105	0	4	0	4
BY-106	0	4	0	4
BY-107	0	4	0	4
BY-108	0	4	0	4
BY-109	0	0	0	0
BY-110	0	4	0	4
BY-111	0	4	0	4
BY-112	0	4	0	4
S-101	0	6	0	8
S-102	0	6	0	8
S-103	0	6	0	8
S-105	0	6	0	8
S-106	0	6	0	8
S107	0	6	0	8

Table 6A-2. Quantity of Sample Measurements for Salt Phase Tank Waste Total Organic Carbon and Moisture Analytes. (3 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
S-108	0	6	0	8
S-109	0	6	1	8
S-110	0	6	0	8
S-111	3	6	3	8
S-112	0	6	0	8
SX-101	0	6	0	8
SX-102	1	6	2	8
SX-103	0	6	1	8
SX-104	0	6	0	8
SX-105	1	6	0	8
SX-106	1	6	0	8
TX-102	0	6	1	8
TX-104	0	6	0	8
TX-105	0	6	0	8
TX-106	0	6	0	8
TX-107	0	6	0	8
TX-108	0	0	0	1
TX-109	0	1	0	1
TX-110	0	1	0	1
TX-111	0	1	0	1
TX-112	0	1	0	1
TX-113	0	1	0	1
TX-114	0	1	0	1
TX-115	0	2	0	3
TX-116	0	1	0	1
TX-117	0	1	0	1
TX-118	0	0	1	1
TY-102	1	1	1	1
U-102	0	2	0	3

Table 6A-2. Quantity of Sample Measurements for Salt Phase Tank Waste Total Organic Carbon and Moisture Analytes. (3 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
U-103	0	2	1	3
U-105	1	1	1	1
U-106	0	2	0	3
U-107	0	1	0	1
U-108	0	1	0	1
U-109	0	1	0	1
U-111	2	2	2	3

*Tanks not found in this list were shown by Hanlon (1994) to have zero salt cake.

SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Table 6A-3. Quantity of Sample Measurements for Sludge Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
A-101	0	4	1	5
A-102	2	4	2	5
A-103	2	4	2	5
A-104	0	0	0	0
A-105	0	0	0	0
A-106	2	2	2	2
AX-101	0	4	0	5
AX-102	0	0	0	0
AX-103	0	0	0	0
AX-104	0	0	0	0
B-101	1	1	0	0
B-102	0	1	0	0
B-103	0	1	0	0
B-104	0	0	0	0
B-105	1	1	0	1
B-106	0	15	0	14
B-107	1	3	0	3
B-108	0	3	0	3
B-109	0	3	0	3
B-110	0	0	14	22
B-111	0	0	8	22
B-112	0	0	0	22
B-201	1	7	0	17
B-202	2	7	15	17
B-203	1	7	0	17
B-204	2	7	1	17
BX-101	1	1	0	5
BX-102	0	1	0	5
BX-103	0	1	0	5

Table 6A-3. Quantity of Sample Measurements for Sludge Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
BX-104	0	1	3	5
BX-105	0	1	2	5
BX-106	0	1	0	5
BX-107	15	15	9	14
BX-108	0	1	0	5
BX-109	0	1	0	5
BX-110	1	2	2	3
BX-111	1	2	1	3
BX-112	2	3	3	3
BY-101	0	1	0	0
BY-103	0	1	0	0
BY-104	1	1	0	0
BY-105	0	1	0	0
BY-106	0	1	0	0
BY-107	0	1	0	0
BY-108	0	1	0	0
BY-109	0	0	0	0
BY-110	0	1	0	0
BY-111	0	1	0	0
BY-112	0	1	0	0
C-101	0	1	0	5
C-102	0	0	0	0
C-103	0	0	2	4
C-104	0	0	1	1
C-105	0	0	1	1
C-106	0	0	2	4
C-107	0	0	0	0
C-108	0	31	0	38
C-109	0	31	6	38

Table 6A-3. Quantity of Sample Measurements for Sludge Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
C-110	0	15	5	14
C-111	0	31	0	38
C-112	13	31	17	38
C-201	1	2	1	1
C-202	0	2	0	1
C-203	0	2	0	1
C-204	1	2	0	1
S-101	0	2	0	0
S-102	0	2	0	0
S-103	0	2	0	0
S-104	0	0	11	11
S-105	0	2	0	0
S-106	0	2	0	0
S-107	0	2	0	0
S-108	0	2	0	0
S-109	0	2	0	0
S-110	0	2	0	0
S-111	0	2	0	0
S-112	0	2	0	0
SX-101	0	2	0	0
SX-102	0	2	0	0
SX-103	0	2	0	0
SX-104	0	2	0	0
SX-105	0	2	0	0
SX-106	1	2	0	0
SX-107	0	0	0	11
SX-108	0	0	0	11
SX-109	0	0	0	11
SX-110	0	0	0	0

Table 6A-3. Quantity of Sample Measurements for Sludge Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
SX-111	0	0	0	0
SX-112	0	0	0	11
SX-113	0	0	0	0
SX-114	0	0	0	0
SX-115	0	0	0	11
T-101	0	0	0	0
T-102	0	0	0	0
T-103	0	0	0	0
T-104	sludge	2	2	6
T-105	sludge	0	45	0
T-106	sludge	1	45	0
T-107	sludge	18	31	15
T-108	sludge	0	15	0
T-109	sludge	0	0	0
T-110	sludge	0	0	0
T-111	sludge	0	0	8
T-112	sludge	0	0	0
T-201	sludge	0	7	0
T-202	sludge	0	7	0
T-203	sludge	0	7	0
T-204	sludge	1	7	1
TX-101	sludge	0	0	0
TX-103	sludge	0	0	0
TY-101	sludge	2	2	2
TY-103	sludge	2	5	6
TY-104	sludge	3	5	12
TY-105	sludge	1	4	1
TY-106	sludge	3	4	6
U-101	sludge	0	0	0

Table 6A-3. Quantity of Sample Measurements for Sludge Phase Tank Waste Total Organic Carbon and Moisture Analytes. (5 sheets)

Tank*	Number of moisture samples for tank waste	Number of moisture samples in SORWT group belonging to tank	Number of TOC samples for tank waste	Number of TOC samples in SORWT group belonging to tank
U-102	sludge	0	1	0
U-103	sludge	1	1	1
U-104	sludge	0	0	0
U-105	sludge	0	3	0
U-106	sludge	0	1	0
U-107	sludge	1	3	0
U-108	sludge	1	3	0
U-109	sludge	1	3	0
U-110	sludge	44	45	32
U-111	sludge	0	1	0
U-112	sludge	0	0	0
U-201	sludge	0	0	0
U-202	sludge	0	0	0
U-203	sludge	0	0	0
U-204	sludge	1	1	0

*Tanks not found in this list are shown by Hanlon (1994) as having zero sludge.

SORWT = sort on radioactive waste type.
TOC = total organic carbon.

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APPENDIX 6B

DEFINITIONS OF SORT ON RADIOACTIVE WASTE TYPE GROUPS CORRESPONDING TO WASTE TYPES

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Table 6B-1a. Sort on Radioactive Waste Type Groups and Corresponding Waste Types.

SORWT group number	Waste types included in SORWT group
I	R, EB
II	EB, 1C
III	TBP-F, EB-ITS
IV	TBP,CW
V	224
VI	R
VII	EB,R
VIII	TBP-F, 1C
IX	DSSF, NCPLX
X	EB, CW
XI	1C, TBP
XII	1C, EB
XIII	HS
XIV	2C, 224
XV	2C, 5-6
XVI	R, RIX
XVII	1C, CW
XVIII	CW, EB
XIX	CW, MIX
XX	CW
XXI	TBP, EB-ITS
XXII	EB, TBP
XXIII	SRS, SR-WASH
XXIV	1C< EB-ITS
XXV	TBP
XXVI	TBP, EB
XXVII	TBP, 1C
XVIII	CCPLX, DSSF
XXIX	R, DIA
XXX	Solidary tanks (Ungrouped)

SORWT = sort on radioactive waste type.

Table 6B-1b. Brief List of Sort on Radioactive Waste Type Abbreviations.

Waste acronym	Meaning of acronym
R	High-level reduction oxidation (REDOX) waste
EB	Evaporator bottoms
TBP	Tributyl phosphate waste
1C	First-cycle decontamination waste
2C	Second-cycle decontamination waste
224	Lanthanum fluoride decontamination waste
CW	Cladding waste
HS	Hot semiworks waste
SRS	Strontium leached sludge
5-6	High-level B Plant waste
ITS	In-tank solidification
RIX	REDOX ion-exchange waste
DIA	Diatomaceous earth
DSSF	Double-shell slurry feed
CCPLX	Complex concentrate
F	Ferrocyanide-scavenged waste
NCPLX	Non-complexed waste
SR-WASH	Particulates from strontium wash of plutonium-uranium extraction (PUREX) wastes in the AR vault
MIX	Mixture of several miscellaneous wastes
IX	Ion-exchange waste
UK	Unknown waste type
OWW	Organic wash waste

APPENDIX 6C

SALT CAKE MOISTURE GROUP RELATIONSHIPS AND TANK IDENTIFICATION

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Table 6C-1. Salt Cake Moisture Group Relationships to Ventilation, Waste Type, and Jet Pumping.

Moisture group number	Ventilation	Salt cake waste type	Jet pumping status
1	Active	Non-REDOX	Jet pumped
2	Active	REDOX	Jet pumped
3	Active	Non-REDOX	Not jet pumped
4	Active	REDOX	Not jet pumped
5	Passive	Non-REDOX	Jet pumped
6	Passive	REDOX	Jet pumped
7	Passive	Non-REDOX	Not jet pumped
8	Passive	REDOX	Not jet pumped

REDOX = reduction oxidation.

Table 6C-2. Waste Tank Identification of Salt Cake Moisture Groups. (3 sheets)

Tank number	Ventilation	REDOX or non-REDOX waste	Jet pumping status	Volume of salt cake (Kgal)*	Moisture group
A-101	Passive	Non-REDOX	Not jet pumped	950	7
A-102	Passive	Non-REDOX	Not jet pumped	22	7
AX-101	Passive	Non-REDOX	Not jet pumped	745	7
AX-102	Passive	Non-REDOX	Not jet pumped	29	7
AX-103	Passive	Non-REDOX	Not jet pumped	110	7
B-102	Passive	Non-REDOX	Not jet pumped	10	7
B-104	Passive	Non-REDOX	Not jet pumped	69	7
B-105	Passive	Non-REDOX	Not jet pumped	266	7
BX-105	Passive	Non-REDOX	Not jet pumped	3	7
BX-110	Passive	Non-REDOX	Not jet pumped	9	7
BX-111	Passive	Non-REDOX	Not jet pumped	143	7
BY-101	Passive	Non-REDOX	Jet pumped	278	5
BY-102	Passive	Non-REDOX	Not jet pumped	341	7
BY-103	Passive	Non-REDOX	Not jet pumped	395	7
BY-104	Passive	Non-REDOX	Jet pumped	366	5
BY-105	Passive	Non-REDOX	Not jet pumped	459	7
BY-106	Passive	Non-REDOX	Not jet pumped	547	7
BY-107	Passive	Non-REDOX	Jet pumped	206	5
BY-108	Passive	Non-REDOX	Jet pumped	74	5
BY-109	Passive	Non-REDOX	Not jet pumped	340	7
BY-110	Passive	Non-REDOX	Jet pumped	295	5
BY-111	Passive	Non-REDOX	Jet pumped	438	5
BY-112	Passive	Non-REDOX	Jet pumped	286	5
S-101	Passive	REDOX	Not jet pumped	171	8
S-102	Passive	REDOX	Not jet pumped	545	8
S-103	Passive	REDOX	Not jet pumped	221	8
S-105	Passive	REDOX	Jet pumped	454	6
S-106	Passive	REDOX	Not jet pumped	447	8

Table 6C-2. Waste Tank Identification of Salt Cake Moisture Groups. (3 sheets)

Tank number	Ventilation	REDOX or non-REDOX waste	Jet pumping status	Volume of salt cake (Kgal)*	Moisture group
S-107	Passive	REDOX	Not jet pumped	69	8
S-108	Passive	REDOX	Not jet pumped	600	8
S-109	Passive	REDOX	Not jet pumped	555	8
S-110	Passive	REDOX	Not jet pumped	259	8
S-111	Passive	REDOX	Not jet pumped	447	8
S-112	Passive	REDOX	Not jet pumped	518	8
SX-101	Active	REDOX	Not jet pumped	343	4
SX-102	Active	REDOX	Not jet pumped	426	4
SX-103	Active	REDOX	Not jet pumped	536	4
SX-104	Active	REDOX	Not pet pumped	478	4
SX-105	Active	REDOX	Not jet pumped	610	4
SX-106	Active	REDOX	Not jet pumped	465	4
TX-102	Passive	REDOX	Jet pumped	217	6
TX-104	Passive	REDOX	Not jet pumped	64	8
TX-105	Passive	REDOX	Jet pumped	609	6
TX-106	Passive	REDOX	Jet pumped	453	6
TX-107	Passive	REDOX	Not jet pumped	35	8
TX-108	Passive	Non-REDOX	Jet pumped	134	5
TX-109	Passive	Non-REDOX	Jet pumped	384	5
TX-110	Passive	Non-REDOX	Jet pumped	462	5
TX-111	Passive	Non-REDOX	Jet pumped	370	5
TX-112	Passive	Non-REDOX	Jet pumped	649	5
TX-113	Passive	Non-REDOX	Jet pumped	607	5
TX-114	Passive	Non-REDOX	Jet pumped	535	5
TX-115	Passive	Non-REDOX	Jet pumped	640	5
TX-116	Passive	Non-REDOX	Jet pumped	631	5
TX-117	Passive	Non-REDOX	Jet pumped	626	5
TX-118	Passive	Non-REDOX	Jet pumped	347	5

Table 6C-2. Waste Tank Identification of Salt Cake Moisture Groups. (3 sheets)

Tank number	Ventilation	REDOX or non-REDOX waste	Jet pumping status	Volume of salt cake (Kgal)*	Moisture group
TY-102	Passive	Non-REDOX	Not jet pumped	64	7
U-102	Passive	Non-REDOX	Not jet pumped	313	7
U-103	Passive	Non-REDOX	Not jet pumped	423	7
U-105	Passive	REDOX	Not jet pumped	349	8
U-106	Passive	Non-REDOX	Not jet pumped	185	7
U-107	Passive	REDOX	Not jet pumped	360	8
U-108	Passive	REDOX	Not jet pumped	415	8
U-109	Passive	REDOX	Not jet pumped	396	8
U-111	Passive	Non-REDOX	Not jet pumped	303	7

*Hanlon, B. M., 1994, Tank Farms Surveillance and Waste Status Summary Report for March 1994, WHC-EP-0182-72, Westinghouse Hanford Company, Richland, Washington.

REDOX = reduction and oxidation.

APPENDIX 6D

SUMMARY TABLES OF TOTAL ORGANIC CARBON AND MOISTURE FOR LIQUID, SALT CAKE, AND SLUDGE WASTE PHASES FOR THE SINGLE-SHELL TANKS

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Table 6D-1. Summary of the Liquid Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
A-101	IX	0.9	50.4	0	3.8	34.7	0.0
A-102	IX	0.4	48.2	0	1.6	32.5	0.0
A-103	IX	0.6	52.0	0	2.5	36.4	0.0
A-105	XXXJ	0.3	65.0	0	1.1	49.3	0.1
A-106	XXXA	0.1	54.6	0	18.0	38.9	0.1
AX-101	IX	0.8	47.1	0	3.0	31.5	0.0
AX-102	XXVIII	1.1	60.0	0	4.4	44.3	1.1
AX-103	XXVIII	0.8	53.1	0	3.3	37.4	0.2
B-101	XVIII	0.3	68.9	0	1.1	53.2	0.0
B-102	XVIII	0.3	65.6	0	1.1	49.9	0.0
B-104	XXXH	0.3	65.0	0	1.1	49.3	0.1
B-105	II	0.3	59.6	0	1.1	44.0	0.1
B-106	XI	0.2	71.7	0	0.8	56.0	0.0
B-107	XII	0.3	69.1	0	1.1	53.4	0.0
B-108	XII	0.3	69.1	0	1.1	53.4	0.0
B-109	XII	0.3	74.7	0	1.1	59.0	0.0
B-110	XV	0.3	65.0	0	1.1	49.3	0.1
B-111	XV	0.3	65.0	0	1.1	49.3	0.1
B-112	XV	0.3	65.0	0	1.1	49.3	0.1
B-201	V	0.3	65.0	0	1.1	49.3	0.1
B-202	V	0.3	65.0	0	1.1	49.3	0.1
B-203	V	0.3	65.0	0	1.1	49.3	0.1
B-204	V	0.3	65.0	0	1.1	49.3	0.1
BX-101	IV	0.4	71.7	0	1.5	56.0	0.0
BX-102	IV	0.4	71.7	0	1.5	56.0	0.0
BX-103	IV	0.4	83.1	0	1.5	67.4	0.0
BX-104	IV	0.5	80.3	0	1.9	64.6	0.0
BX-105	IV	0.5	74.4	0	2.2	58.8	0.0

Table 6D-1. Summary of the Liquid Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
BX-106	IV	0.4	64.3	0	1.4	48.7	0.0
BX-107	XI	0.2	70.5	0	0.8	54.8	0.0
BX-108	IV	0.4	71.7	0	1.5	56.0	0.0
BX-109	IV	0.3	65.4	0	1.2	49.7	0.0
BX-110	XXIV	0.3	61.7	0	1.4	46.1	0.0
BX-112	XII	0.3	69.1	0	1.2	53.4	0.0
BY-101	III	0.2	58.0	0	1.0	42.3	0.1
BY-102	XXI	0.2	57.3	0	0.7	41.6	0.0
BY-103	III	0.2	54.8	0	0.9	39.1	0.0
BY-104	III	0.2	58.0	0	1.0	42.3	0.1
BY-105	III	0.2	55.9	0	0.9	40.2	0.0
BY-106	III	0.2	53.8	0	0.9	38.1	0.0
BY-107	III	0.3	58.0	0	1.1	42.3	0.0
BY-108	III	0.2	58.0	0	1.0	42.3	0.1
BY-109	XXI	0.3	59.4	0	1.2	43.8	0.0
BY-110	III	0.2	58.0	0	1.0	42.3	0.1
BY-112	III	0.2	58.0	0	1.0	42.3	0.1
C-101	IV	0.4	71.7	0	1.5	56.0	0.0
C-102	XXXB	0.3	65.0	0	1.1	49.3	0.0
C-103	XXIII	0.6	80.1	0	2.3	64.4	0.0
C-104	XXXC	0.5	72.7	0	2.0	57.0	0.0
C-105	XXXD	0.3	65.0	0	1.0	49.3	0.0
C-106	XXIII	0.3	71.4	0	1.1	55.7	0.0
C-107	XXXE	0.2	65.0	0	0.6	49.3	0.0
C-109	VIII	0.2	72.2	0	0.7	56.5	0.0
C-110	XI	0.1	72.9	0	0.5	57.2	0.0
C-112	VIII	0.2	60.7	0	0.7	45.0	0.0
S-101	I	0.5	71.5	0	1.9	55.8	0.0

Table 6D-1. Summary of the Liquid Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
S-102	I	0.9	60.7	0	3.5	45.0	0.0
S-103	I	0.5	59.7	0	1.9	44.0	0.1
S-104	VI	0.3	66.2	0	1.2	50.5	0.0
S-105	I	0.5	54.0	0	1.9	38.3	0.1
S-106	I	0.5	52.8	0	1.9	37.1	0.1
S-107	I	0.5	52.6	0	2.0	36.9	0.0
S-108	I	0.5	59.7	0	1.9	44.0	0.1
S-109	I	0.5	59.7	0	1.9	44.0	0.1
S-110	I	0.7	59.7	0	2.8	44.0	0.2
S-111	I	0.4	51.7	0	1.6	36.0	0.0
S-112	I	0.5	59.7	0	1.9	44.0	0.1
SX-101	I	0.2	84.3	0	1.0	68.6	0.0
SX-102	I	0.5	59.7	0	1.9	44.0	0.1
SX-103	I	0.5	59.7	0	1.9	44.0	0.1
SX-104	I	0.3	57.4	0	1.2	41.7	0.0
SX-105	I	0.5	59.7	0	1.9	44.0	0.1
SX-106	I	2.0	50.3	0	19.0	34.6	0.6
SX-107	VI	0.3	67.9	0	1.3	52.2	0.0
SX-108	VI	0.3	66.2	0	1.2	50.5	0.0
SX-109	VI	0.3	66.2	0	1.2	50.5	0.0
SX-111	XVI	0.3	69.2	0	1.1	53.5	0.0
SX-112	VI	0.3	66.2	0	1.2	50.5	0.0
SX-114	XVI	0.3	66.8	0	1.1	51.1	0.0
T-101	XIX	0.1	65.0	0	0.5	49.3	0.0
T-102	XIX	0.2	65.0	0	0.8	49.3	0.0
T-103	XIX	0.2	65.0	0	0.8	49.3	0.0
T-104	XXXF	0.1	65.0	0	0.5	49.3	0.0
T-105	XVII	0.3	65.0	0	1.1	49.3	0.1

Table 6D-1. Summary of the Liquid Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
T-106	XVII	0.3	65.0	0	1.1	49.3	0.1
T-107	VIII	0.1	80.9	0	0.3	65.2	0.0
T-110	XIV	0.3	82.9	0	1.0	67.2	0.0
T-111	XVII	0.3	75.3	0	1.0	59.6	0.0
T-112	XIV	0.2	81.7	0	0.9	66.0	0.0
T-201	V	0.3	65.0	0	1.1	49.3	0.1
T-202	V	0.3	65.0	0	1.1	49.3	0.1
T-203	V	0.3	65.0	0	1.1	49.3	0.1
T-204	V	0.3	65.0	0	1.1	49.3	0.1
TX-101	XXXM	0.3	65.0	0	1.1	49.3	0.1
TX-102	I	0.3	59.7	0	1.3	44.0	0.0
TX-103	XXVI	0.3	57.5	0	1.1	41.8	0.0
TX-104	I	0.5	54.9	0	1.9	39.2	0.0
TX-105	I	0.6	59.7	0	2.4	44.0	0.1
TX-106	I	0.4	59.7	0	1.8	44.0	0.0
TX-107	I	0.5	59.7	0	1.9	44.0	0.1
TX-109	II	0.4	59.6	0	1.6	44.0	0.1
TX-110	II	0.3	52.3	0	1.4	36.6	0.0
TX-111	II	0.3	59.6	0	1.4	44.0	0.0
TX-112	II	0.3	59.6	0	1.1	44.0	0.0
TX-113	II	0.3	59.6	0	1.1	44.0	0.1
TX-114	II	0.2	59.6	0	1.0	44.0	0.0
TX-115	VII	0.1	63.9	0	0.5	48.2	0.0
TX-116	II	0.2	59.6	0	0.7	44.0	0.0
TX-117	II	0.3	59.6	0	1.1	44.0	0.1
TX-118	XXII	0.2	60.1	0	4.2	44.4	1.0
TY-102	II	0.3	59.6	0	1.1	44.0	0.1
TY-103	XXVII	0.2	65.0	0	0.8	49.3	0.0

Table 6D-1. Summary of the Liquid Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
TY-104	XXVII	0.2	65.0	0	0.8	49.3	0.0
U-101	VI	0.3	66.2	0	1.2	50.5	0.0
U-102	VII	0.4	63.7	0	1.8	48.0	0.0
U-103	VII	0.4	63.5	0	1.8	47.8	0.0
U-104	XXIX	0.3	65.0	0	1.1	49.3	0.1
U-105	X	0.3	64.5	0	1.1	48.9	0.0
U-106	VII	1.6	62.8	0	6.2	47.2	0.0
U-107	X	0.3	64.5	0	1.1	48.9	0.0
U-108	X	0.3	64.5	0	1.1	48.9	0.0
U-109	X	0.3	63.9	0	1.1	48.2	0.0
U-110	XVII	0.3	65.0	0	1.1	49.3	0.1
U-111	VII	1.0	63.9	0	4.2	48.2	0.3
U-112	XXXN	0.3	65.0	0	1.1	49.3	0.1
U-201	XX	0.3	69.2	0	1.1	53.5	0.0
U-202	XX	0.3	74.9	0	1.1	59.2	0.0
U-203	XX	0.3	69.2	0	1.1	53.5	0.0
U-204	XXXL	0.3	65.0	0	1.1	49.3	0.1

*TOC worst 5% values are truncated at 20%.

EP = exceedance probability, probability that true value is in unsafe region.
SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Table 6D-2. Summary of the Salt Cake Phase in Single-Shell Tanks. (3 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5% waste moisture		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
A-101	IX	0.6	39.15	0	4.5	28.16	0.3
A-102	IX	0.6	43.10	0	4.5	31.00	1.0
AX-101	IX	0.6	43.10	0	4.5	31.00	1.0
AX-102	XXVIII	0.6	43.10	0	4.3	31.00	0.9
AX-103	XXVIII	0.6	43.10	0	4.3	31.00	0.9
B-102	XVIII	0.6	43.10	0	4.3	31.00	0.9
B-104	XXXH	0.6	43.10	0	4.3	31.00	0.9
B-105	II	0.5	43.10	0	4.0	31.00	0.8
BX-105	IV	0.6	43.10	0	4.3	31.00	0.9
BX-110	XXIV	0.6	48.39	0	4.3	34.81	0.0
BX-111	XXIV	0.6	43.10	0	4.3	31.00	0.9
BY-101	III	0.7	16.91	0	5.1	12.17	33.1
BY-102	XXI	0.6	43.10	0	4.3	31.00	0.9
BY-103	III	0.7	43.10	0	5.1	31.00	1.2
BY-104	III	0.7	16.08	0	5.1	11.57	36.5
BY-105	III	0.7	43.10	0	5.1	31.00	1.2
BY-106	III	0.7	43.10	0	5.1	31.00	1.2
BY-107	III	0.7	16.91	0	5.1	12.17	33.1
BY-108	III	0.7	16.91	0	5.1	12.17	33.1
BY-109	XXI	0.6	43.10	0	4.3	31.00	0.9
BY-110	III	0.7	16.91	0	5.1	12.17	33.1
BY-111	III	0.7	16.91	0	5.1	12.17	33.1
BY-112	III	0.7	16.91	0	5.1	12.17	33.1
S-101	I	0.4	21.61	0	3.3	15.54	9.6
S-102	I	0.4	21.61	0	3.3	15.54	9.6
S-103	I	0.4	21.61	0	3.3	15.54	9.6
S-105	I	0.4	8.48	0	3.3	6.01	28.1
S-106	I	0.4	21.61	0	3.3	15.54	9.6
S-107	I	0.4	21.61	0	3.3	15.54	9.6
S-108	I	0.4	21.61	0	3.3	15.54	9.6

Table 6D-2. Summary of the Salt Cake Phase in Single-Shell Tanks. (3 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5% waste moisture		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
S-109	I	0.4	21.61	0	3.3	15.54	9.6
S-110	I	0.4	21.61	0	3.3	15.54	9.6
S-111	I	0.4	15.94	0	3.3	11.47	16.4
S-112	I	0.4	21.61	0	3.3	15.54	9.6
SX-101	I	0.4	12.37	0	3.3	8.90	21.5
SX-102	I	0.4	13.30	0	3.3	9.57	20.2
SX-103	I	0.4	12.37	0	3.3	8.90	21.5
SX-104	I	0.4	11.76	0	3.3	8.46	22.7
SX-105	I	0.4	12.76	0	3.3	9.18	21.1
SX-106	I	0.4	12.37	0	3.3	8.90	21.5
TX-102	I	0.4	8.48	0	3.3	3.01	28.1
TX-104	I	0.4	21.61	0	3.3	15.54	9.6
TX-105	I	0.4	8.48	0	3.3	6.01	28.1
TX-106	I	0.4	8.48	0	3.3	6.01	28.1
TX-107	I	0.4	21.61	0	3.3	15.54	9.6
TX-108	XXII	0.6	16.91	0	4.7	12.17	30.1
TX-109	II	0.5	16.91	0	4.0	12.17	23.5
TX-110	II	0.5	16.91	0	4.0	12.17	23.5
TX-111	II	0.5	16.91	0	4.0	12.17	23.5
TX-112	II	0.5	16.91	0	4.0	12.17	23.5
TX-113	II	0.5	16.91	0	4.0	12.17	23.5
TX-114	II	0.5	16.91	0	4.0	12.17	23.5
TX-115	VII	0.6	16.91	0	5.0	12.17	33.2
TX-116	II	0.5	16.91	0	4.0	12.17	23.5
TX-117	II	0.5	16.91	0	4.0	12.17	23.5
TX-118	XXII	0.6	16.91	0	4.7	12.17	30.1
TY-102	II	0.5	51.86	0	4.0	37.31	0.0
U-102	VII	0.6	43.10	0	5.0	31.00	1.2
U-103	VII	0.6	43.10	0	5.0	31.00	1.2
U-105	X	0.7	21.10	0	5.2	15.18	27.8

Table 6D-2. Summary of the Salt Cake Phase in Single-Shell Tanks. (3 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5% waste moisture		
		wt% TOC	wt% H_2O	EP	wt% TOC*	wt% H_2O	EP
U-106	VII	0.6	43.10	0	5.0	31.00	1.2
U-107	X	0.7	21.61	0	5.2	15.54	25.3
U-108	X	0.7	21.61	0	5.2	15.54	25.3
U-109	X	0.7	30.35	0	5.2	21.83	7.5
U-111	VII	0.6	37.74	0	5.0	27.15	0.6

*TOC worst 5% values are truncated at 20%.

EP = exceedance probability, probability that true value is in unsafe region.
SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Table 6D-3. Summary of the Sludge Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC	wt% H_2O	EP
A-101	IX	0.6	39.5	0	2.4	18.4	7.1
A-102	IX	0.6	39.5	0	2.5	18.4	5.8
A-103	IX	0.7	39.5	0	2.6	18.4	6.3
A-104	XXXI	0.1	44.7	0	0.6	23.6	1.4
A-105	XXXJ	0.1	44.7	0	0.6	23.6	1.4
A-106	XXXA	0.5	44.3	0	1.9	23.2	1.4
AX-101	IX	0.5	39.5	0	2.1	18.4	8.6
AX-102	XXVIII	0.1	44.7	0	0.6	23.6	1.4
AX-103	XXVIII	0.1	44.7	0	0.6	23.6	1.4
AX-104	XXXI	0.1	44.7	0	0.6	23.6	1.4
B-101	XVIII	0.1	34.5	0	0.6	13.4	3.3
B-102	XVIII	0.1	34.5	0	0.6	13.4	3.3
B-103	XVIII	0.1	34.5	0	0.6	13.4	3.3
B-104	XXXH	0.1	44.7	0	0.6	23.6	1.4
B-105	II	0.1	45.1	0	0.3	24.0	0.0
B-106	XI	0.1	49.5	0	0.3	28.3	0.0
B-107	XII	0.3	47.8	0	1.2	26.7	0.7
B-108	XII	0.3	47.8	0	1.2	26.7	0.7
B-109	XII	0.3	47.8	0	1.2	26.7	0.7
B-110	XV	0.0	44.7	0	0.2	23.6	0.0
B-111	XV	0.1	44.7	0	0.4	23.6	0.0
B-112	XV	0.1	44.7	0	0.3	23.6	0.0
B-201	V	0.2	64.9	0	0.9	43.8	0.0
B-202	V	0.2	64.9	0	7.6	43.8	0.0
B-203	V	0.2	64.9	0	0.9	43.8	0.0
B-204	V	0.2	64.9	0	0.7	43.8	0.0
BX-101	IV	0.2	38.2	0	0.9	17.1	1.4
BX-102	IV	0.2	38.2	0	0.9	17.1	1.4
BX-103	IV	0.2	38.2	0	0.9	17.1	1.4
BX-104	IV	0.3	38.2	0	1.0	17.1	0.0
BX-105	IV	0.2	38.2	0	1.0	17.1	0.1
BX-106	IV	0.2	38.2	0	0.9	17.1	1.4

Table 6D-3. Summary of the Sludge Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC	wt% H_2O	EP
BX-107	XI	0.1	49.5	0	0.3	28.3	0.0
BX-108	IV	0.2	38.2	0	0.9	17.1	1.4
BX-109	IV	0.2	38.2	0	0.9	17.1	1.4
BX-110	XXIV	0.0	48.9	0	0.2	27.8	0.0
BX-111	XXIV	0.1	48.9	0	0.2	27.8	0.0
BX-112	XII	0.4	47.8	0	1.6	26.7	0.1
BY-101	III	0.1	37.9	0	0.6	16.8	2.5
BY-103	III	0.1	37.9	0	0.6	16.8	2.5
BY-104	III	0.1	37.9	0	0.6	16.8	2.5
BY-105	III	0.1	37.9	0	0.6	16.8	2.5
BY-106	III	0.1	37.9	0	0.6	16.8	2.5
BY-107	III	0.1	37.9	0	0.6	16.8	2.5
BY-108	III	0.1	37.9	0	0.6	16.8	2.5
BY-109	XXI	0.1	44.7	0	0.6	23.6	1.4
BY-110	III	0.1	37.9	0	0.6	16.8	2.5
BY-111	III	0.1	37.9	0	0.6	16.8	2.5
BY-112	III	0.1	37.9	0	0.6	16.8	2.5
C-101	IV	0.2	38.2	0	0.9	17.1	1.4
C-102	XXXB	0.1	44.7	0	0.6	23.6	1.4
C-103	XXIII	0.3	44.7	0	1.0	23.6	0.1
C-104	XXXC	0.3	44.7	0	1.2	23.6	1.1
C-105	XXXD	0.1	44.7	0	0.4	23.6	0.0
C-106	XXIII	0.2	44.7	0	0.8	23.6	0.0
C-107	XXXE	0.1	44.7	0	0.6	23.6	1.4
C-108	VIII	0.2	48.2	0	0.7	27.1	0.0
C-109	VIII	0.2	48.2	0	1.0	27.1	0.0
C-110	XI	0.1	49.5	0	0.3	28.3	0.0
C-111	VIII	0.2	48.2	0	0.7	27.1	0.0
C-112	VIII	0.3	48.2	0	1.2	27.1	0.0
C-201	XIII	0.2	59.8	0	0.7	38.7	0.0
C-202	XIII	0.2	59.8	0	0.7	38.7	0.0
C-203	XIII	0.2	59.8	0	0.7	38.7	0.0

Table 6D-3. Summary of the Sludge Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC	wt% H_2O	EP
C-204	XIII	0.2	59.8	0	0.7	38.7	0.0
S-101	I	0.1	42.4	0	0.6	21.3	1.4
S-102	I	0.1	42.4	0	0.6	21.3	1.4
S-103	I	0.1	42.4	0	0.6	21.3	1.4
S-104	VI	0.2	44.7	0	0.6	23.6	0.0
S-105	I	0.1	42.4	0	0.6	21.3	1.4
S-106	I	0.1	42.4	0	0.6	21.3	1.4
S-107	I	0.1	42.4	0	0.6	21.3	1.4
S-108	I	0.1	42.4	0	0.6	21.3	1.4
S-109	I	0.1	42.4	0	0.6	21.3	1.4
S-110	I	0.1	42.4	0	0.6	21.3	1.4
S-111	I	0.1	42.4	0	0.6	21.3	1.4
S-112	I	0.1	42.4	0	0.6	21.3	1.4
SX-101	I	0.1	42.4	0	0.6	21.3	1.4
SX-102	I	0.1	42.4	0	0.6	21.3	1.4
SX-103	I	0.1	42.4	0	0.6	21.3	1.4
SX-104	I	0.1	42.4	0	0.6	21.3	1.4
SX-105	I	0.1	42.4	0	0.6	21.3	1.4
SX-106	I	0.1	42.4	0	0.6	21.3	1.4
SX-107	VI	0.2	44.7	0	0.6	23.6	0.3
SX-108	VI	0.2	44.7	0	0.6	23.6	0.3
SX-109	VI	0.2	44.7	0	0.6	23.6	0.3
SX-110	XVI	0.1	44.7	0	0.6	23.6	1.4
SX-111	XVI	0.1	44.7	0	0.6	23.6	1.4
SX-112	VI	0.2	44.7	0	0.6	23.6	0.3
SX-113	XXIX	0.1	44.7	0	0.6	23.6	1.4
SX-114	XVI	0.1	44.7	0	0.6	23.6	1.4
SX-115	VI	0.2	44.7	0	0.6	23.6	0.3
T-101	XIX	0.1	44.7	0	0.6	23.6	1.4
T-102	XIX	0.1	44.7	0	0.6	23.6	1.4
T-103	XIX	0.1	44.7	0	0.6	23.6	1.4
T-104	XXXF	0.1	55.0	0	0.2	33.9	0.0

Table 6D-3. Summary of the Sludge Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC	wt% H_2O	EP
T-105	XVII	0.1	35.9	0	0.4	14.8	0.1
T-106	XVII	0.1	35.9	0	0.4	14.8	0.1
T-107	VIII	0.1	48.2	0	0.3	27.1	0.0
T-108	XI	0.1	49.5	0	0.3	28.3	0.0
T-109	XXVI	0.1	44.7	0	0.6	23.6	1.4
T-110	XIV	0.2	44.7	0	0.9	23.6	1.1
T-111	XIV	0.3	44.7	0	1.1	23.6	0.0
T-112	XIV	0.2	44.7	0	0.9	23.6	1.1
T-201	V	0.2	64.9	0	0.9	43.8	0.0
T-202	V	0.2	64.9	0	0.9	43.8	0.0
T-203	V	0.2	64.9	0	0.9	43.8	0.0
T-204	V	0.3	64.9	0	1.3	43.8	0.0
TX-101	XXXM	0.1	44.7	0	0.6	23.6	1.4
TX-103	XXVI	0.1	44.7	0	0.6	23.6	1.4
TY-101	XXXG	0.0	44.0	0	0.0	22.9	0.0
TY-103	XXVII	0.1	51.0	0	0.3	29.9	0.0
TY-104	XXVII	0.2	51.0	0	0.9	29.9	0.0
TY-105	XXV	0.1	40.0	0	0.4	18.9	0.0
TY-106	XXV	0.1	40.0	0	0.6	18.9	0.0
U-101	VI	0.2	44.7	0	0.6	23.6	0.3
U-102	VII	0.3	29.8	0	1.2	8.7	10.2
U-103	VII	0.4	29.8	0	1.6	8.7	9.6
U-104	XXIX	0.1	44.7	0	0.6	23.6	1.4
U-105	X	0.1	45.6	0	0.6	24.5	0.7
U-106	VII	0.3	29.8	0	1.2	8.7	10.2
U-107	X	0.1	45.6	0	0.6	24.5	0.7
U-108	X	0.1	45.6	0	0.6	24.5	0.7
U-109	X	0.1	45.6	0	0.6	24.5	0.7
U-110	XVII	0.1	35.9	0	0.3	14.8	0.0
U-111	VII	0.3	29.8	0	1.2	8.7	10.2
U-112	XXXN	0.1	44.7	0	0.6	23.6	1.4
U-201	XX	0.1	44.7	0	0.6	23.6	1.4

Table 6D-3. Summary of the Sludge Phase in Single-Shell Tanks. (5 sheets)

Tank	SORWT group	Median concentration			Concentration of worst 5%		
		wt% TOC	wt% H_2O	EP	wt% TOC	wt% H_2O	EP
U-202	XX	0.1	44.7	0	0.6	23.6	1.4
U-203	XX	0.1	44.7	0	0.6	23.6	1.4
U-204	XXXL	0.1	37.0	0	0.6	15.9	2.7

EP = exceedance probability, probability that true value is in unsafe region.
SORWT = sort on radioactive waste type.
TOC = total organic carbon.

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7.0 POTENTIAL WASTE MOISTURE AND TOTAL ORGANIC CARBON CONTENT CHANGES

7.1 INTRODUCTION

This chapter evaluates the evolution of moisture and TOC content during interim storage of single-shell tank waste before ultimate disposal. In single-shell tanks, moisture and TOC can change as a result of consolidation, drainage caused by leakage or jet pumping, and evaporation. The methodology presented in this chapter is as follows:

1. Account for moisture losses resulting from drainage and sludge consolidation
2. Calculate the moisture content and TOC of the salt cake tanks, assuming all 65 have been jet pumped
3. Compare post-jet-pumped moisture and TOC values from the salt cake tanks with the preliminary safety criteria
4. Provide evaporative moisture loss estimates for active and passively ventilated tanks
5. Provide 50-year moisture and TOC values for all tanks, assuming all 65 salt cake tanks have been jet pumped
6. Compare 50-year moisture and TOC values for all tanks to preliminary safety criteria
7. Provide sensitivity studies and dryout times for tanks exceeding the preliminary safety criteria during the 50-year mission.

7.2 DRAINAGE AND CONSOLIDATION

Drainage refers to moisture movement from upper to lower portions of the waste because of gravity. The amount drained depends on the waste height and its capillary height, which is a function of particle size, void fraction, and liquid properties. Capillary height is the moisture level maintained by surface tension forces in the liquid. If the capillary height is larger than the waste height, drainage is not significant. If the capillary height is much less than the waste height, drainage is practically complete.

Consolidation is a mechanism by which the waste is compressed under its own weight, reducing the pore volume and forcing out moisture. These mechanisms are discussed for sludge and salt cake.

7.2.1 Sludge Drainage and Consolidation

Sludge heights vary from a few centimeters to several meters. Typical sludge particle sizes are on the order of 10 µm and the associated capillary height is 6.1 m (20 ft) (Atherton 1974). Therefore, drainage of sludges is neglected.

Sludges will consolidate under their own weight, forcing moisture from shrinking pore space into a salt cake or supernatant layer. The extent of consolidation may be estimated by consolidation theory and the application of given sludge properties as described in FAI (1994b). Standard references were used to derive the time constant for consolidation and the equilibrium displacement (Jumukis 1984).

The time constant for consolidation is

$$\tau = \frac{H^2}{C_v} \tag{7-1}$$

where

τ = time constant
H = waste height
C_v = consolidation coefficient.

The consolidation coefficient is

$$C_v = \frac{kE}{\gamma} \tag{7-2}$$

where

k = permeability
E = modulus of elasticity
γ = specific weight.

The equilibrium displacement is

$$S = H + \frac{1}{\beta}\left(1 - \sqrt{1 + 2\beta H}\right) \tag{7-3}$$

where

H = initial waste height
β = for convenience, is defined as

$$B = \frac{n\rho g}{E} \tag{7-4}$$

where

n = number of g's (for centrifugation tests)
ρ = density
g = acceleration of gravity
E = modulus of elasticity.

The terms used to calculate the time constant and equilibrium displacement are based on waste properties. Reasonable values of the parameters were shown to allow agreement with ferrocyanide simulant (Barney 1994a) and T-111 samples (Simmons 1994) at various g loadings and, in particular, to deduce values for E. Even though E varies with moisture content, appropriate values exceed 100,000 Pa for waste below 50% moisture.

The consolidation distance also depends upon the waste height as described previously. Shallow sludge (on the order of 1 m deep) should be consolidated, and deep sludge (3 to 6 m) will be consolidated, to greater than half the long-term value after a 50-year mission.

The loss of moisture in weight percent was shown in FAI (1994b) to be rather small, between 10 wt% (for sludge with high initial moisture) and 3 wt% (for deep sludge with low initial moisture). Consolidation alone is important only for sludge with a low initial moisture content (below 30 wt%) for which the maximum moisture loss is not expected to exceed 3 wt%. This small value is conservatively applied to all sludges for tank safety evaluation.

7.2.2 Salt Cake Consolidation

Salt cakes have low capillary height compared to sludge, on the order of less than a meter (Atherton 1974), so it is prudent to consider all salt cake as having drained to the extent physically possible. In contrast to sludge, in which void space is filled with water, drained salt cake has air and water in the void space. Atherton (1974) cites 7.5% for the expected water fraction in void space of a drained zone. Thus, consolidation will simply reduce the air fraction in salt cake and will have little effect on further moisture reduction.

7.2.3 Salt Cake Drainage

Moisture loss calculations described in this chapter consider all salt cakes as either drained by jet pumping or leakage. The amount of moisture predicted after drainage is assumed to be the same as the companion moisture group, which already has been jet pumped (refer to Table 6-4). Moisture groups would, therefore, change as follows:

- Group 4 would change to group 2

- Group 7 would change to group 5
- Group 8 would change to group 6.

Jet pumping removes the supernatant phase, interstitial liquid TOC, moisture, and dissolved nonfuel salts but does not affect the solid precipitate. Jet pumping does not change interstitial liquid properties (TOC and moisture content), but liquid removal changes the overall salt cake TOC and moisture content; it could increase or decrease the overall salt cake TOC, depending on the liquid TOC content.

Appendix 7A of this document describes the method used to calculate TOC content after jet pumping has occurred it is based on salt cake moisture content after jet pumping (as given by the moisture group changes above), the interstitial liquid TOC, and moisture content. The method uses mean values for initial salt cake TOC, liquid TOC, and liquid moisture content. Mean values are appropriate for mass balances because the probability density functions reflect the spatial distribution in the salt cake. Calculations are conservative, however, because the 95th quantile values were used for salt cake moisture after jet pumping occurred. Input values are shown in Table 7A-1 and results are presented in Table 7A-2.

7.2.4 Salt Cake Equilibrium

Because salt cake equilibrium values vary from tank to tank and may be only a few weight percent in moisture, no credit will be given for equilibrium moisture (as a result of consolidation) in these calculations. Individual tanks could be evaluated for this on the basis of specific monitoring and characterization data.

7.3 CURRENT AND POST-JET-PUMPING COMPARISON WITH CRITERIA

Current moisture content and TOC values for all 149 single-shell tanks were tabulated and compared to the preliminary safety criteria defined in Chapter 5. The concentrations of worst 5% values were used from Tables 6B-1, 6B-2, and 6B-3. When a moisture content and TOC pair fell outside the criteria lines, the tank phase was listed as safe. Results for the current tank conditions are reported in Appendix 7B in the last three columns of Table 7B-1. None of the three phases in any of the 149 single-shell tanks is predicted to be above the safety criteria based on current tank conditions.

This process was repeated for post-jet-pumped tanks. Jet pumping removes supernatant completely but does not alter the sludge. Therefore, these two phases are not considered for post-jet-pumped tanks. Post-jet-pumped salt cake moisture content and TOC values were tabulated and compared to the preliminary safety criteria. Salt cake moisture content was the 95th quantile, after jet pumping, and TOC content was described with a probability density function based on the results in Table 7A-2. Table 7B-2 shows salt cake TOC values for the post-jet-pumped tanks. A probability density function for post-jet-pumping salt cake TOC was created (1) using mean values as input for initial salt cake TOC, liquid TOC, and liquid moisture content, (2) applying the method of Appendix 7A of this document to obtain an expected (or mean) value for salt cake TOC after jet pumping (Table 7A-2), and (3) assuming the salt cake TOC standard deviation is not changed during jet pumping. Several sets of values are listed for salt cake TOC after jet pumping: a mean from Table 7A-2, a median, a 95th quantile, and a 90th quantile.

The results from comparing the mean and 90th quantile against the TOC limit suggest that no salt cake tanks would be above the criteria lines. Comparing the 95th quantile against the TOC limit indicates that 13 salt cake tanks would be on or above the criteria line: tanks A-102, BX-110, BY-102, BY-103[1], BY-105[1], BY-106[1], TY-102, U-102, U-103, U-105, U-107, U-108, and U-109. A common feature among these tanks is a low liquid TOC. Jet pumping therefore removes little TOC, but a great deal of moisture and dissolved nonfuel salts. In the calculation for TOC (wet basis), the numerator (TOC mass) remains about the same while the denominator (salt cake mass) decreases. The net result is an increase in the TOC content; if the post-jet-pumped salt cake TOC value is the 95th quantile, the increase is large enough to push the post-jet-pumped TOC value above the criterion.

Three of the BY tanks have been evaluated further based on recent sampling results. For the ANOVA model, tanks with similar waste types and histories were grouped to estimate TOC and moisture concentrations for tanks that had no data or only limited data. Group III consisted of tanks BY-103, BY-104, BY-105, and BY-106. Table 7-1 reviews the TOC and moisture data available during the initial ANOVA screening. The only salt cake data available for this group of tanks are from tank BY-104; the TOC and moisture estimates for BY-103, BY-105, and BY-106 salt cakes are based on the measurements from BY-104. The waste in tank BY-104 is expected to be similar to that in BY-103, BY-105, and BY-106, the only difference being that BY-104 has been jet pumped while the other tanks have not been jet pumped. It follows that if BY-103, BY-105, and BY-106 are jet pumped, both the TOC and moisture levels following jet pumping should be comparable to BY-104 in its current state.

Limited data were available for use in the ANOVA model, and it was necessary to group tanks and extrapolate the results to other tanks. However, recent data (Table 7-2) from the tanks in this group now allow a more thorough comparison of these tanks.

7.4 EVAPORATION

Evaporative losses normally will be more important than consolidation for both sludges and salt cakes during the 50-year mission. Therefore, long-term sludge moisture content will be evaluated by first accounting for evaporative loss and then deducting an additional 3 wt% for sludge consolidation. Evaporation has been quantified for passively and actively ventilated tanks. Evaporation calculations were based upon average annual values for Hanford relative humidity.

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[1] An alternate evaluation, presented below now shows that these tanks would not exceed the criteria line.

Table 7-1. Data Used in the Analysis of Variance Model for Tanks BY-103, BY-104, BY-105, and BY-106.

Tank	Estimate/ measured	Median TOC (wt%)	Median water (wt%)	Worst 5% TOC (wt%)	Worst 5% water (wt%)
BY-103	Estimated	0.7	43	5.1	31
BY-104*	Measured	0.7	16*	5.1	12*
BY-105	Estimated	0.7	43	5.1	31
BY-106	Estimated	0.7	43	5.1	31

*Tank BY-104 belongs to a different moisture group (non-REDOX waste, jet pumped, passively ventilated) than tanks BY-103, BY-105, and BY-106 (non-REDOX waste, non-jet pumped, passively ventilated. The only difference between the two groups is jet pumping.

Table 7-2. Sampling Results from Tanks BY-103, BY-105, and BY-106.

Tank	Analyses of waste liquid			Analyses of waste solids		
	Median TOC (wt%)	Median water (wt%)	Date	Median TOC (wt%)	Median water (wt%)	Date
BY-103	0.16	N/A	04/95	0.29* 0.02	24 16	04/95 04/95
BY-105	0.11	55	03/95	N/A	N/A	N/A
BY-106	0.17	64	01/95	0.10	19	01/95

*Weight equivalent TOC (as sodium acetate calculated from exothermic energy content).

N/A = not available.
TOC = total organic carbon.

The primary mechanism for moisture loss in the tanks is evaporation of water from the waste surface and natural convection between the tank headspace and the ambient. Large quantities of moisture also can be removed from some tanks during interim stabilization or inadvertently through leakage. Calculations project "dryout" (safety criteria exceeded) from the time the salt cake is actually or potentially drained. Dryout time calculations determine when the safety criteria will be exceeded.

7.4.1 Passively Ventilated Tanks

Moisture estimates in weight percent have been provided for each single-shell tank (i.e., supernatant, salt cake, and sludge phases when present) (Toth et al. 1995). For most tanks, the moisture loss potential is estimated by FAI (1994b); for tanks not included in the FAI (1994b) estimates, moisture loss potential is discussed here. The 16 single-shell tanks not included in FAI (1994b) are the 208-m^3 (55,000-gal) tanks, TX Tank Farm tanks without reliable instrumentation (TX-101, TX-102, TX-114, TX-116, and TX-117), and the actively ventilated tanks. The following evaluations may be used to yield moisture wt% estimates for the tanks after a 50-year mission.

Moisture losses from the 16 208-m^3 (55,000-gal) tanks (those B, C, T, and U Tank Farm tanks numbered 201 to 204) are all negligible because these tanks only breathe barometrically, which is passive. The moisture loss in this case is

$$W = V\left[\frac{\dot{P}}{P}\right](\rho_v - \rho_{v\infty}) \qquad (7\text{-}5)$$

where

V = headspace volume
$\dot{P}/P$ = breathing rate of 1.7/yr
ρ_v = vapor density in the tank
$\rho_{v\infty}$ = ambient vapor density of 5.76 g/m^3 (12 °C [53.6 °F] and 54% relative humidity).

Choosing a headspace volume of 100 m^3 (3 m [10 ft] of open space in a 6-m [20-ft] diameter tank) and using the highest temperature reading of 27 °C (80 °F) for tank U-204, the corresponding vapor density is 25.3 g/m^3 and the moisture loss rate is 3.3 kg/yr. Similarly, in 1,893-m^3 (500,000-gal) tanks with an open volume of 2,000 m^3 at 27 °C (80 °F), the moisture loss is 66 kg/yr, an order of magnitude less than the loss rate for a three-tank cascade configuration.

Reliable vapor space temperatures for tanks TX-101, TX-102, TX-114, TX-116, and TX-117 are not available because of a lack of instrumentation. Instead, average temperature was inferred from the calculated heat load, and the results of FAI (1994b) were applied. A tank vapor space temperature was inferred based on WHC-EP-0709, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures* (Crowe et al. 1993). For this report, Crowe's calculation is inverted and heat load is used to calculate vapor space temperature. The heat load is calculated from the following:

$$Q = C_f\,(T_{vs} - T_{amb}) \qquad (7\text{-}6)$$

where

Q = the heat load
C_f = the conversion factor from Crowe et al. (1993, Figure 6-2)
T_{vs} = the vapor space temperature
T_{amb} = the average outside ambient temperature (T_{amb} is taken to be 13.5 °C [56.3 °F]).

With heat load as the other input, the equation is solved for T_{vs}.

Table 7-3 contains the input data and results for the subject tanks as well as comparisons with the sibling tanks shown below:

Tank	SORWT group	Sibling for
TX-103	XXXVI	TX-101
TX-105	I	TX-102
TX-113	II	TX-114, TX-116, and TX-117.

Table 7-3. Selected TX Farm Tanks Vapor Space Temperature Input Data and Calculations.

Tank	Heat load (Btu/hr)	Total waste amount (kL [kgal])	Factors		Original temperatures* (°C)
			(C_f)	(T_{vs})	
TX-101	7,400	330 (87)	375	76	NC
TX-102	3,400	821 (217)	382	65	NC
TX-103	2,300	594 (157)	377	62	58
TX-105	9,400	2,305 (609)	408	80	73
TX-113	6,800	2,298 (607)	408	73	70
TX-114	7,900	2,025 (535)	405	76	NC
TX-115	5,100	2,423 (640)	411	69	70
TX-117	6,700	2,370 (626)	410	73	NC
TX-118	4,600	1,314 (347)	390	68	NC

*Kummerer, M., 1994, Topical Report on Heat Removal Characteristics of Waste Storage Tanks, WHC-SD-WM-SARR-010, Westinghouse Hanford Company, Richland, Washington (Note: NC indicates that these tanks were not calculated because the vapor space temperature was not available with the final release of Kummerer [1994]).

T_{vs} = vapor space temperature (°C).
C_f = conversion factor (from R. D. Crowe, M. Kummerer, and A. K. Postma, 1993, Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington).

Comparisons with sibling tanks are included for verification. Tank TX-115 was included because it is in the same cascade as tanks TX-113 and TX-114 though it is in SORWT Group VI rather than the SORWT Group II (tanks TX-113 and TX-114). Tank TX-118 also was included because it is on the organic watch list.

In Table 7-3, heat load and waste amount input data are taken from Hanford Tank Content Estimate (Brevick et al. 1995). Conversion factor (C_f) is obtained from Figure 6-2 in Crowe et al. (1993) by entering the figure with the waste quantity; all tanks in question have a 2,840 kL (750,000 gal) capacity. The value for T_{vs} is computed using Equation 7-6. The last column shows the sibling vapor space temperature readings taken from WHC-SD-WM-SARR-010, *Topical Report on Heat Removal Characteristics of Waste Storage Tanks* (Kummerer 1994). Comparisons of calculated vapor space temperatures (using Equation 7-6) with values taken from Kummerer (1994) show fair agreement.

Evaporative losses during the 50-year mission can be estimated for tanks TX-101, TX-102, TX-114, TX-116, and TX-117 using the calculated values for T_{vs}. Applying the results of Figure 2-9 from FAI (1994b) gives the following 50-year moisture losses:

Tank	Moisture loss (t)
TX-101	26.2
TX-102	8.5
TX-114	26.2
TX-116	13.6
TX-117	20.2

7.4.2 Actively Ventilated Tanks

Forced ventilation systems have been retained on single-shell tanks when relatively high decay heat loads are present. Such actively ventilated tanks have the potential to lose moisture at significantly higher rates than passively ventilated tanks. The actively ventilated tanks have much higher ventilation rates, ranging from 9.4×10^{-3} m^3/s to 2.8×10^{-1} m^3/s (20 ft^3/min to 600 ft^3/min), than the passively ventilated tanks, which have ventilation flows in the range of 4.7×10^{-5} m^3/s to 1.4×10^{-3} m^3/s (0.1 ft^3/min to 3 ft^3/min).

The evaporative loss rates for the actively ventilated tanks have been based on psychrometric and flow rate measurements of ventilation system air flows in the SX Tank Farm. These same data, used previously in the estimation of waste decay heat loads in these tanks (Kummerer 1994), are summarized as follows.

7.4.2.1 SX Tank Farm System. Most of the tanks in the SX Tank Farm are connected to the 296-S-15 exhauster (Kummerer 1994). Flow from tanks SX-101 through SX-106 travels through underground duct work into the vapor space of tank SX-109. Flow from tanks SX-107 through SX-112 and tank SX-114 connects to a common aboveground line to the exhauster.

Psychrometric data and flow rates were measured for outlet flows from tanks SX-107 through SX-112, and SX-114. Wet bulb temperature, dry-bulb temperature, and volumetric flow rate data are available. The inlet conditions used were the ambient measurements for that day and time: 23 °C (73 °F) dry-bulb temperature and 17 °C (62 °F) wet-bulb temperature.

Measurements for tanks SX-101 through SX-106 were unavailable. The total flow through this part of the system was taken as the measured flow rate at tank SX-109. The system flow was distributed amongst the tanks in proportion to the calculated distribution of the design flow. The outlet conditions were taken as dry-bulb temperature equal to measured vapor space temperatures and 38% relative humidity. This was the average outlet relative humidity of the tanks for which measurements were available.

The inlet conditions for tank SX-109 were assumed to be the average of the vapor space temperatures from the six tanks feeding it and 38% relative humidity. Inlet conditions for all other tanks were the measured ambient conditions.

Based on these data and ventilation configuration, water loss rates were calculated, and the water removed by ventilation was estimated by the following equation:

$$\dot{m}_w = \dot{m}_a \left(w_o - w_i\right) \tag{7-7}$$

where

$\dot{m}_w$ = net water removed from the waste by ventilation (kg/s [lb_m/h])

$\dot{m}_a$ = mass flow rate of dry air (kg/s [lb_m/h])

w_i = mass fraction of water in the inlet air (kg of water/kg dry air [lb_m of water/lb_m dry air])

w_o = mass fraction of water in the outlet air (kg of water/kg dry air [lb_m of water/lb_m dry air]).

The mass flow rate of dry air, $\dot{m}$, was calculated at the outlet conditions using the outlet-air-specific volumes for dry air. Specific volume and water fractions were taken from psychrometric tables. The temperatures, psychrometric data, and evaporation rates are included in Table 7-4. The evaporation loss rate has been used to calculate the 50-year moisture loss for these tanks.

7.4.2.2 C Tank Farm System. Tank C-106 is actively ventilated because it has a high heat load. Tank C-105 is connected to tank C-106 through a cascade overflow line and thereby receives ventilation from the same system. Water was formerly added to both tanks C-105 and C-106 to provide evaporative cooling. Tank C-106 was placed on a watch list in 1990.

The status of tank C-105 was reevaluated (Bander and Stevens 1993), and the conservative heat load estimated was 7,300 W (25,000 Btu/h). Water additions to the tank were subsequently stopped. Active ventilation is still provided, however, because the ventilation system continues to cool tank C-106. Tank C-104 also receives some cooling by this system through the cascade line between it and tank C-105.

Table 7-4. SX Tank Farm Ventilation Heat Losses and Evaporation Rates.

Inlet conditions									
T dry bulb		T wet bulb		h		w		v	
°C	°F	°C	°F	kJ/kg	Btu/lb$_m$ dry air	kg H_2O/kg air	lb$_m$ H_2O/lb$_m$ air	m^3/kg dry air	ft^3/lb$_m$ dry air
22.8	73	16.7	62	46.77	27.75	0.0094	0.0094	0.85	13.64

Outlet conditions																		
Tank	T dry bulb		RH%	T wet bulb		Flow rate		h		w		v		Heat load		Evap. rate		
	°C	°F		°C	°F	m^3/s	ft^3/min	kJ/kg	Btu/Lbm	kg H_2O/kg dry air	lbm H_2O/lbm dry air	m^3/kg dry air	ft^3/lbm dry air	W	Btu/h	kg/yr	lb/yr	
SX-101	30.2	86.4	38.00	--	--	9.3 E-03	19.7	57.16	31.97	0.0102	0.0102	0.87	14.00	105.5	360	270	595.2	
SX-102	32.9	91.2	38.00	--	--	9.8 E-03	20.8	64.60	35.02	0.0119	0.0119	0.88	14.16	187.5	640	880	1,940.0	
SX-103	46.7	116.1	38.00	--	--	1.1 E-02	22.3	117.4	56.19	0.0255	0.0255	0.95	15.12	738.4	2,520	5,700	12,566.1	
SX-104	29.3	84.8	38.00	--	--	9.7 E-03	20.5	54.83	31.01	0.0097	0.0097	0.87	13.95	85.0	290	110	242.5	
SX-105	29.9	85.9	38.00	--	--	9.5 E-03	20.1	56.37	31.67	0.0101	0.0101	0.87	13.98	99.6	340	220	485.0	
SX-106	27.9	82.3	38.00	--	--	1.0 E-02	21.5	50.80	29.57	0.0894	0.0894	0.87	13.87	46.3	170	<100*	<220*	
SX-107	35.6	96.0	45.26	25.6	78	2.5 E-01	537.0	78.49	41.35	0.0166	0.0166	0.90	14.39	8,921.9	30,450	64,000	141,093.5	
SX-108	35.0	95.0	39.86	23.9	75	2.7 E-01	581.0	71.41	38.37	0.0141	0.0141	0.89	14.31	7,579.9	25,870	45,700	100,749.6	
SX-109	28.9	84.0	56.40	22.2	72	5.9 E-02	125.0	65.05	35.68	0.0141	0.0141	0.88	14.03	1,242.3	4,240	10,100	22,266.3	
SX-110	36.7	98.0	41.42	25.6	78	1.5 E-01	312.0	78.44	41.32	0.0161	0.0161	0.90	14.43	5,156.8	17,600	34,700	76,499.1	
SX-111	43.3	110.0	38.48	30	86	1.7 E-01	367.0	99.14	50.3	0.0215	0.0215	0.93	14.87	9,786.2	33,400	71,500	15,7627.9	
SX-112	40.0	104.0	43.37	26.7	80	1.1 E-01	243.0	83.17	43.37	0.0166	0.0166	0.91	14.60	4,570.8	15,600	28,700	63,271.6	
SX-114	44.4	112.0	31.95	28.9	84	1.6 E-01	330.0	93.44	47.83	0.0189	0.0189	0.93	14.86	7,840.7	26,760	50,200	110,670.2	

*Assumes that the air exiting SX-106 is at 38% relative humidity causes zero moisture loss to be calculated (the actual evaporative losses are expected to be greater than 0 kg/yr but less than 100 kg/yr [220 lb/yr]).

h = specific enthalpy.
RH = relative humidity.
T = temperature.
v = specific volume.
w = absolute humidity.

Psychrometric data for tanks C-104 and C-105 are not available. However, the thermal analysis for tank C-105 indicates that approximately 1,672 kg (440 gal) of water are evaporated each month when the ventilation system is operating (Bander and Stevens 1993). Therefore, the water evaporation rate is approximately 20,000 kg/yr (20 t/yr) or 1,000,000 kg (1,000 t) for a 50-year period.

Because of a lack of psychrometric data and detailed thermal analysis for tank C-104, the evaporation loss rate will be estimated by comparing the estimated heat load and ventilation rate to an SX Tank Farm tank with similar values. The heat load in tank C-104 is estimated to be 3,300 W (11,400 Btu/h) with a headspace temperature of 30 °C (86 °F) (Kummerer 1994). Therefore, the evaporation loss rate for tank SX-101 (3,690 W [12,600 Btu/h] heat load and 30.2 °C [86.4 °F] headspace temperature) will be used as the evaporation rate for tank C-104. Tank C-106 continues to have water added periodically to provide evaporative cooling. The water level is closely monitored, so long-term evaporative losses are not considered in this report.

As previously described, the moisture loss rate appears to be most strongly affected by waste heat load and, as a secondary effect, ventilation flow rate. For several tanks, the evaporative loss rate is sufficiently high such that waste currently projected to have adequate moisture to meet the safety criteria could fall below the criteria following draining of the waste before 50 years have elapsed.

7.5 50-YEAR DRYOUT CALCULATIONS

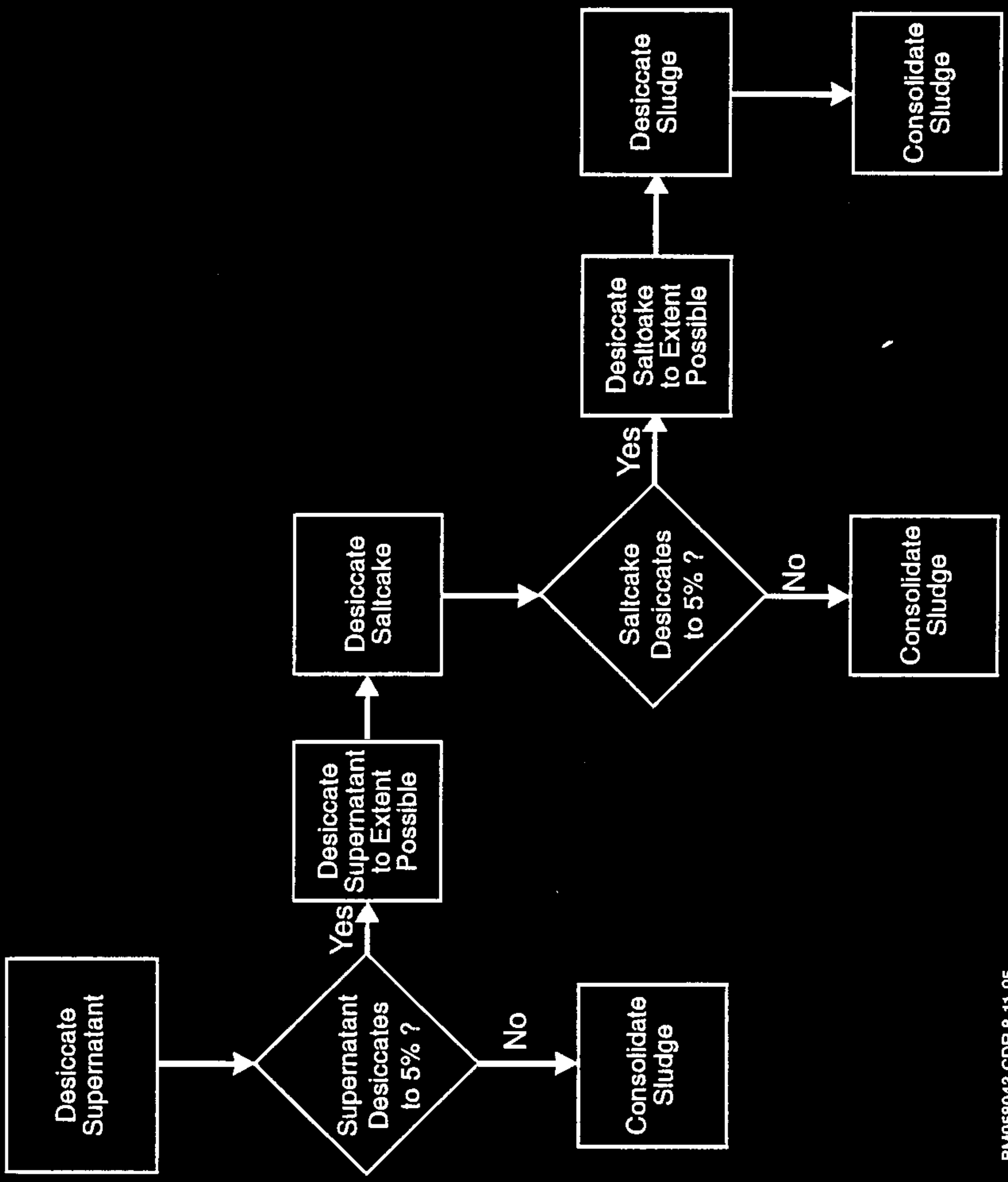
7.5.1 Single-Shell Tank Basic Model for 50-Year Dryout Calculations

After moisture losses from draining were calculated as discussed in Section 7.2 and evaporation losses were calculated as discussed in Section 7.4, further calculations were performed for all single-shell tanks, except tank C-106, to estimate their moisture and TOC content at the end of the 50-year mission.

The moisture loss calculation assumes that the waste phases, if present, are configured as follows: (1) supernatant is the top layer, (2) salt cake is the middle layer, and (3) sludge is the bottom layer. Moisture loss calculation logic is described by Figure 7-1. Calculation details are presented in Appendix 7C.

First, evaporative losses take moisture from the supernatant. If 50-year evaporative losses are not large enough to desiccate the supernatant to 5% moisture, the consolidation loss is applied to the sludge and the calculation is complete. Otherwise, moisture loss continues in the supernatant until the moisture content is 5%, at which time 50-year evaporative losses begin to take moisture from the salt cake. This conservatively forces moisture loss from the salt cake even though 5% moisture remains in the supernatant. If 50-year evaporative losses are large enough, moisture loss in the supernatant continues until it is completely desiccated, even though moisture loss in the salt cake has begun.

Figure 7-1. Moisture Loss Calculation Logic.



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Second, evaporation desiccates the salt cake. Salt cake moisture loss follows the same scheme as supernatant moisture loss. Salt cake moisture losses begin when the supernatant moisture decreases to 5%. If evaporative losses cannot desiccate the salt cake to 5% moisture, the consolidation loss is applied to the sludge and the calculation is complete. Otherwise, moisture loss continues in the salt cake until the moisture content is 5%, at which time evaporative losses begin to take moisture from the sludge. This conservatively forces moisture from the sludge even though 5% moisture remains in the salt cake. If evaporative losses are large enough, moisture loss in the salt cake continues until it is completely desiccated, even though moisture loss in the sludge has begun.

Third, evaporation and consolidation dry the sludge. Sludge moisture loss does not follow the same scheme as the supernatant and salt cake. Since there is no phase below, it makes no difference whether the sludge desiccates to 5%; the 5% values used for the supernatant and salt cake are simply meant to trigger moisture loss from the next phase. Sludge desiccates completely if the evaporative moisture losses are large enough. To account for consolidation, 3% is subtracted from the sludge moisture content after evaporation. Moisture expelled by sludge consolidation is removed from the tank rather than being placed in the salt cake.

To calculate final moisture (metric tons) and moisture content (wt% fraction) values, each phase is desiccated to the extent possible. The 5% residual value is not used for final moisture values.

Input to this procedure is included in Table 7C-1. Table 7C-2 presents the results from 50 years of evaporative and consolidation losses for each tank. The 50-year period begins at the initiation of jet pumping. For single-shell tanks in which jet pumping occurred 20 years ago, the 50-year mission could end in 30 years. For base-case 50-year evaporative loss results, 95th quantile (worst 5%) values were used for phase moisture, and supernatant was removed completely during jet pumping.

7.5.2 Single-Shell Tanks Comparison with Safety Criteria

Following the 50-year dryout calculations, the 133 single-shell tanks (16 200-series tanks were not calculated) were again compared to the preliminary safety criteria. All comparisons with the preliminary safety criteria used 95th quantile values for supernatant and sludge initial TOC. The initial salt cake TOC is the post-jet-pumping, 95th quantile value shown by Table 7B-2. On a wet basis, the TOC content increases with time as water is lost because of evaporation and consolidation. On a dry basis, TOC content stays the same for the supernatant and salt cake, which lose moisture because of evaporation. This is also used as an approximation for the sludge, which loses moisture because of consolidation and evaporation. Therefore, for each phase, a new TOC value is calculated at the end of the 50-year mission, based on the initial phase TOC value and the phase moisture at the end of 50 years. The 50-year TOC and moisture values for each line are then compared to the criteria line. Results for the base case (jet-pumped, 95th quantile moisture values) are presented in Table 7C-3.

7.5.3 Problem Tanks Identified

The following salt cake tanks would exceed the criteria line sometime during the 50-year mission:

- B-102
- BX-105
- BY-108.

These 3 tanks are in addition to the 10 tanks above the criteria line immediately after jet pumping. The number of years to "dryout" for these three tanks can be found from the following:

$$T = \frac{M_{sa}\left(0.045 + 0.17\,X_{w0} - X_{toc0}\right)}{0.215\,W_e} \qquad (7\text{-}8)$$

where

M_{sa} = the salt cake total mass
x_{w0} = the initial moisture content
x_{toc0} = the initial TOC
W_e = the yearly evaporation rate.

This expression shows dryout times vary with the fractional mass loss rate (W_e/M_{sa}). An evaporative loss rate is given by assuming a uniform rate over the 50-year mission. The term in brackets is a "TOC margin" showing the difference between a safe TOC for the salt cake initial moisture according to the criteria line and the initial TOC. Substituting in the appropriate values yields these dryout time results: 15 years for B-102, 7 years for BX-105, and 43 years for tank BY-108.

7.5.4 Sensitivity Cases

Other sensitivity cases considered include: (1) mean phase moisture values, and supernatant removed completely during jet pumping, (2) 95th quantile phase moisture values and no artificial jet pumping, and (3) mean phase moisture values and no artificial jet pumping. Sensitivity cases (2) and (3) consider the scenario in which no more tanks are actually jet pumped.

Sensitivity case 1 (jet pumping, mean phase moisture values for salt cake and sludge) does not produce results that differ from the base case.

Sensitivity cases 2 and 3 consider results of dryout assuming no new jet pumping occurs. In both cases, only tanks BX-110 and A-102 contain salt cake phase mass exceeding the criteria line. For case 2, the dryout time is 22 years for tank A-102 and 24 years for tank BX-110. For case 3, the dryout time is 34 years for tank A-102 and 48 years for tank B-110. The large increase in dryout time for case 3 is explained by the mean salt cake moisture value used; case 2 used the 95th quantile. (All comparisons against the criteria line used 95th quantile salt cake TOC values. Dryout times would increase greatly with mean salt cake TOC values). The primary reason that tanks A-102 and BX-110 are predicted to exceed criteria so soon following draining is that they each contain only a few centimeters of salt cake on top of a much deeper sludge layer. Both tanks A-102 and BX-110 contain a small amount of salt cake, relative to other single-shell tanks, but have a typical evaporation rate. The fractional mass loss rate is relatively high and dryout occurs within 50 years. Conservatively, the phases are treated separately, though the moist sludge layer could keep the salt cake above it moist as well. Further evaluations for tanks A-102 and BX-110 were performed (Appendix 7D) as summarized in Section 7.5.5 below.

7.5.5 Evaluation to Determine Whether Some Tanks May Currently be too Dry

The potential for salt cake in a few tanks to dry out in the relatively short period of a few years raised the questions: 1) could these tanks have already been drained several years ago such that they are already too dry? and 2) does it appear from available data that any of the dryout tanks may have already exceeded the preliminary safety criteria? The first 4 of the 10 CONDITIONALLY SAFE (as a result of draining) tanks (A-102, BX-110, BY-102, TY-102) were evaluated in Appendix 7D to determine whether they may already be too dry based on current data. It is concluded that they do not appear to be too dry at this time but that characterization and measurement should be pursued to verify this conclusion. The remaining six tanks, which are in the U Tank Farm, have not yet been jet-pumped and appear to have ample moisture in them.

The three CONDITIONALLY SAFE (as a result of draining and dryout) tanks (B-102, BX-105, and BY-108) have also been evaluated to determine whether they may already be too dry. B-102 and BX-105 are predicted to exceed safety criteria by evaporation of moisture from salt cake within 15 and 7 years, respectively, if they are first drained. Both of these tanks are reported in Hanlon (1994) and Brevick et al. (1994a) as having supernatant in them at last report. Assuming that this is so, the tank salt cakes cannot be too dry because standing supernatant implies a significant level of dampness in salt cake surfaces. Part of the characterization effort should be to verify the in-tank salt cake moisture (especially surface) conditions. The only other dryout tank is BY-108, which was drained in 1985 and has been calculated to dry out to exceed safety criteria in 43 years. Because BY-108 has apparently been drying out for 10 years, it would have 33 years remaining before it exceeded the preliminary safety criteria.

The results from the evaluation show that though the data from several sources have some conflicts,[1] there is evidence that the tanks are not too dry and do not exceed preliminary safety criteria. It should be recognized that the state of the waste in this report was estimated based upon the best available data in 1994. Recomputations are planned to update the data based

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[1] (The waste phases and types in the Historical Tank Content Estimate documents [Brevick 1994a and 1995] are different than those in the Waste Tank Summary [Hanlon 1995] for three out of the four tanks).

upon the best available late 1995 data. It has also been recommended that priority characterization of the CONDITIONALLY SAFE tanks be pursued to confirm the conclusion that the tanks are not too dry.

7.5.6 Evaluation to Determine Whether There is Alternate Information to Show Tanks Would be Safe After Draining

Six U Tank Farm tanks have been categorized as CONDITIONALLY SAFE because if drained, it is predicted, they would exceed the preliminary safety criteria (Section 7.3). These tanks are U-102, U-103, U-105, U-107, U-108, and U-109. Because these tanks could drain themselves if leaking occurs and because jet pumping is planned to prevent leaks to the environment, an additional evaluation was performed as described in Appendix 7E. This evaluation considered whether there is alternate information, not used in the basic calculations of this report, which may show that these tanks would be safe following draining.

The evaluation in Appendix 7E discussed whether the solubility information being developed using waste surrogates (Barney 1994b) and grab samples of liquids from the tanks could provide a basis for safe jet pumping of these tanks. The evaluation concluded that when solubility of energetic organic compounds is taken into account, jet pumping of these tanks should be safe because energetic organic material will be removed by this process. This will make the tanks safer for both organic salt-nitrate and leak to the environment concerns.

It was concluded that organic solubility appears to be very promising and when more recent information on several more compounds is available, the report will be updated to include this effect. This is expected to provide the basis to remove many tanks from the CONDITIONALLY SAFE category. It is recommended that characterization for CONDITIONALLY SAFE tanks be conducted to help provide actual waste confirmations of the solubility information (Barney 1994b).

7.6 CONCLUSIONS

This chapter has evaluated potential waste moisture and TOC changes using a staged approach. All 149 single-shell tanks were evaluated by simple models. Because tanks containing sludge do not pose a significant hazard for condensed phase reactions, evaluations focused on the remaining 65 tanks containing salt cake. Activities consisted of estimating the probable post-jet-pumping TOC and moisture values for all tanks not yet jet pumped. Estimates for TOC and moisture after jet pumping revealed that 10 salt cake tanks could exceed preliminary safety criteria. This conclusion is based on the 95th quantile salt cake TOC (post-jet-pumping). If the 90th quantile is considered, no tanks exceed the preliminary safety criteria after jet pumping. The tanks identified below are called out nevertheless to establish priorities for characterization and controls.

After calculating post-jet-pumped TOC and moisture content, evaporative loss calculations were performed for all the single-shell tanks except tank

C-106 (C-106 requires periodic moisture addition). These calculations show three tanks could exceed the preliminary criteria line within the 50-year mission: B-102, BX-105, and BY-108. This conclusion is based on calculations using 95th quantile salt cake TOC (post-jet-pumping) and 95th quantile moisture content.

7.6.1 Conditionally Safe Tanks Identified

Tanks A-102, BX-110, BY-102, TY-102, U-102, U-103, U-105, U-107, U-108, and U-109 have been categorized as CONDITIONALLY SAFE single-shell tanks if they are drained. Three additional tanks (B-102, BX-105, and BY-108) are CONDITIONALLY SAFE tanks if they are drained and allowed to dryout.

7.6.2 Characterization Needs and Controls For Conditionally Safe Tanks

Characterization of the 13 tanks discussed above should be given priority to establish liquid and moisture levels as well as energetics and TOC content. Appropriate controls also should be placed upon the 13 CONDITIONALLY SAFE tanks. Characterization information may be used to remove some tanks from the list, but it is appropriate to provide controls, especially for the U tank group. These tanks should not be jet pumped until characterization information and re-evaluation ensure they will remain below the preliminary safety criteria. Because the tanks could inadvertently drain as a result of a leak, characterization of the tanks should be given priority. Controls for the three tanks that dry out after jet pumping should focus on waste characterization, minimizing moisture loses, and ventilation. Details about needed controls are reported in Chapter 9.

APPENDIX 7A

SALT CAKE TOTAL ORGANIC CARBON AFTER JET PUMPING: METHOD AND CALCULATIONS

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APPENDIX 7A

SALT CAKE TOTAL ORGANIC CARBON AFTER JET PUMPING: METHOD AND CALCULATIONS

1.0 METHOD FOR SALT CAKE TOTAL ORGANIC CARBON

A salt cake phase of mass M_T (total) consists of a precipitated solids mass M_p, a liquid mass M_L, water mass M_w, dissolved nonfuel salt mass M_D, and dissolved fuel-carrying salt mass M_F.

$$\gamma = \frac{M_{cF}}{M_F} = \text{mass fraction carbon in a fuel molecule.} \qquad (7A\text{-}1)$$

where

M_{cF} = the carbon content of the fuel-carrying salt.

When all total organic carbon (TOC) is soluble,

$$\chi_{TOC} = \frac{M_{cF}}{M_T} = \frac{\gamma M_F}{M_T}. \qquad (7A\text{-}2)$$

Unprimed M or χ means before pumping, and primed means after pumping.

The moisture content before pumping is

$$\chi_W = \frac{M_W}{M_T}. \qquad (7A\text{-}3)$$

Pumping removes water and all solubles, so

$$\chi_W' = \frac{M_W'}{M_T - (M_W - M_W') - (M_D - M_D') - (M_F - M_F')}. \qquad (7A\text{-}4)$$

The liquid concentration remains the same during pumping:

$$\frac{M_D}{M_W} = \frac{M_D'}{M_W'} \qquad (7A\text{-}5)$$

and

$$\frac{M_F}{M_W} = \frac{M_F'}{M_W'}. \qquad (7A\text{-}6)$$

So, for example,

$$M_D - M_D' = M_D \left[1 - \frac{M_W}{M_W}\right] = \left[\frac{M_D}{M_W}\right] \left(M_W - M_W'\right). \qquad (7A\text{-}7)$$

Let $\Delta M_W = M_W - M_W'$ for simplicity. Note that M_D/M_W = kg salt/kg water conveniently expresses salt fractions in the same units typically used for solubility, so define the ratio

$$r_D = \frac{M_D}{M_W},\ r_F = \frac{M_F}{M_W},\ \text{etc.} \qquad (7A\text{-}8)$$

By combining, new expressions are derived for TOC and moisture content as a result of jet pumping:

$$X_W' = \frac{M_W - \Delta M_W}{M_T - \Delta M_W\left[1 + r_D + r_F\right]} \qquad (7A\text{-}9)$$

and

$$X_{TOC}' = X_W' \left[\frac{\gamma M_F}{M_W - \Delta M_W}\right]. \qquad (7A\text{-}10)$$

Other needed relationships are

$$r_F = \frac{M_F}{M_W} = \frac{M_F}{M_T}\frac{M_T}{M_W} = \frac{\chi_{TOC}}{\gamma\chi_W} \qquad (7A\text{-}11)$$

and

$$M_F' = \frac{M_F}{M_W}M_W' = \frac{\chi_{TOC}}{\gamma\chi_W}\left(M_W - \Delta M_W\right). \qquad (7A\text{-}12)$$

Equation 7A-12 combined with 7A-7 yields

$$\chi_{TOC}' = \chi_{TOC}\left[\frac{\chi_W'}{\chi_W}\right]. \qquad (7A\text{-}13)$$

A further parameter is required to define the amount of TOC to be removed because it is present in the liquid:

$$\chi_{TOCL} = \text{TOC fraction in liquid only} = \frac{\gamma M_{FL}}{M_{WL} + M_{DL} + M_{FL}} \qquad (7A\text{-}14)$$

where the subscript L denotes liquid only.

Now the TOC balance is

$$\chi_{TOC}M_T = \chi_{TOCL}\left(M_T - M_P\right) + \chi_{TOCP}M_P \qquad (7A\text{-}15)$$

so the TOC in precipitate, χ_{TOCP} (i.e., insoluble TOC) is defined and may be found from χ_{TOC} and χ_{TOCL}.

With these definitions, the initial liquid fraction and individual phase masses can be derived:

$$M_D = r_D X_W M_T \tag{7A-16}$$

and

$$M_F = \frac{X_{TOCL}}{Y - X_{TOCL}} \left(M_W + M_D\right). \tag{7A-17}$$

The dissolved nonfuel salt solubility can be written as

$$r_D = \frac{\left(1 - X_{WL} - X_{TOCL}/\ Y\right)}{X_{WL}}. \tag{7A-18}$$

Equation 7A-18 can be re-written using Equation 7A-17 as

$$M_F = \frac{X_{TOCL}\ X_W \left(1 + r_D\right)}{Y - X_{TOCL}} M_T. \tag{7A-19}$$

Define the initial liquid fraction as

$$X_L = \frac{M_W + M_D + M_F}{M_T}. \tag{7A-20}$$

Using Equations 7A-16 and 7A-17,

$$X_L = X_W \left(1 + r_D\right) \left[\frac{Y}{Y - X_{TOCL}}\right]. \tag{7A-21}$$

Finally, the precipitate mass is

$$M_P = M_T\left(1 - X_L\right). \tag{7A-22}$$

Precipitate TOC content is

$$X_{TOCP} = X_{TOC}\left[\frac{M_T}{M_P}\right] + X_{TOCL}\left[1 - \frac{M_T}{M_P}\right] \tag{7A-23}$$

$$X_{TOCP} = \frac{X_{TOC} - X_{TOCL}\,X_L}{1 - X_L}. \tag{7A-24}$$

A total liquid mass ΔM_L and a total water mass are removed by pumping. The two are related by

$$\Delta M_L = \Delta M_W\left(X_L/X_W\right). \tag{7A-25}$$

Pumping removes a TOC concentration X_{TOCL} and the final X_W' and X_{TOC}' are found as follows:

$$X_W' = \frac{M_W - \Delta M_W}{M_T - \Delta M_L} \tag{7A-26}$$

$$X_{TOC}' = \frac{X_{TOC}M_T - X_{TOCL}\Delta M_L}{M_T - \Delta M_L}. \tag{7A-27}$$

If X_W' is known (rather than ΔM_L), then ΔM_L is found by using Equations 7A-21, 7A-25, and 7A-26.

$$\Delta M_L = M_T \frac{X_W' - X_W}{X_W - \frac{X_W}{X_L}}. \qquad (7A\text{-}28)$$

2.0 INPUTS TO THE METHOD AND CALCULATION RESULTS

Table 7A-1 lists the inputs to the calculations for salt cake TOC after jet pumping. Mean values are used for initial salt cake TOC, liquid TOC percent, and liquid moisture content. Mean values are appropriate for mass balances because the probability density functions used reflect spatial variation within the phase. A 95th quantile and median (50th quantile) are given in Chapter 6.0 for both TOC and moisture content in each phase. Using log-normal distributions, the mean is derived from

$$\mu = X_{50}\, e^{\frac{\sigma^2}{2}} \qquad (7A\text{-}29)$$

where

X_{50} = the median value
σ = the logarithmic standard deviation found from

$$\sigma = \frac{\mathrm{Ln}\, X_{95} - \mathrm{Ln}\, X_{50}}{1.645} \qquad (7A\text{-}30)$$

where

X_{95} = the 95th quantile.

TOC calculation results are shown in Table 7A-2. Column definitions, when necessary, are provided below.

- Mass fraction carbon is defined by Equation 7A-1. Sodium acetate, with two carbon atoms and a molecular weight of 82, is used to obtain a value of 0.29.

- Solubility is defined by Equation 7A-18. The maximum value is 1.14, based on sodium acetate solubility data at 50 °C.

Table 7A-1. Input to Post-Jet-Pumping Total Organic Carbon Calculation.* (3 sheets)

Tank	Salt cake initial TOC % (95th)	Salt cake initial TOC % (mean)	Salt cake initial TOC % (median)	Salt cake log TOC % standard deviation	Liquid initial TOC % (95th)	Liquid initial TOC % (mean)	Liquid initial TOC % (median)	Liquid log TOC % standard deviation	Liquid initial % moisture (mean)	Salt cake initial % moisture (95th)
	(X_{TOC})	(X_{TOC})	(X_{TOC})		(X_{TOCL})	(X_{TOCL})	(X_{TOCL})		(X_{WL})	(X_{W})
A-101	4.5	1.27	0.6	1.22	3.80	1.32	0.90	0.88	51.71	28.16
A-102	4.5	1.27	0.6	1.22	1.60	0.57	0.40	0.84	49.60	31.00
AX-101	4.5	1.27	0.6	1.22	3.00	1.10	0.80	0.80	48.53	31.00
AX-102	4.3	1.23	0.6	1.20	4.40	1.57	1.10	0.84	61.03	31.00
AX-103	4.3	1.23	0.6	1.20	3.30	1.16	0.80	0.86	54.32	31.00
B-102	4.3	1.23	0.6	1.20	1.10	0.41	0.30	0.80	66.51	31.00
B-104	4.3	1.23	0.6	1.20	1.10	0.41	0.30	0.80	65.92	31.00
B-105	4	1.11	0.5	1.26	1.10	0.41	0.30	0.79	60.62	31.00
BX-105	4.3	1.23	0.6	1.20	2.20	0.75	0.50	0.90	75.17	31.00
BX-110	4.3	1.23	0.6	1.20	1.40	0.47	0.30	0.94	62.68	34.81
BX-111	4.3	1.23	0.6	1.20	1.40	0.47	0.30	0.94	62.68	31.00
BY-101	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	12.17
BY-102	4.3	1.23	0.6	1.20	0.70	0.27	0.20	0.76	58.40	31.00
BY-103	5.1	1.45	0.7	1.21	0.90	0.30	0.20	0.91	55.97	31.00
BY-104	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	11.57
BY-105	5.1	1.45	0.7	1.21	0.90	0.30	0.20	0.91	57.03	31.00
BY-106	5.1	1.45	0.7	1.21	0.90	0.30	0.20	0.91	55.00	31.00
BY-107	5.1	1.45	0.7	1.21	1.10	0.41	0.30	0.79	59.08	12.17
BY-108	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	12.17
BY-109	4.3	1.23	0.6	1.20	1.20	0.43	0.30	0.84	60.43	31.00
BY-110	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	12.17
BY-111	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	12.17
BY-112	5.1	1.45	0.7	1.21	1.00	0.32	0.20	0.98	59.08	12.17
S-101	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	72.32	15.54

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Table 7A-1. Input to Post-Jet-Pumping Total Organic Carbon Calculation.* (3 sheets)

Tank	Salt cake initial TOC % (95th)	Salt cake initial TOC % (mean)	Salt cake initial TOC % (median)	Salt cake log TOC % standard deviation	Liquid initial TOC % (95th)	Liquid initial TOC % (mean)	Liquid initial TOC % (median)	Liquid log TOC % standard deviation	Liquid initial % moisture (mean)	Salt cake initial % moisture (95th)
	(X_{TOC})	(X_{TOC})	(X_{TOC})		(X_{TOCL})	(X_{TOCL})	(X_{TOCL})		(X_{WL})	(X_{W})
S-102	3.3	0.91	0.4	1.28	3.50	1.27	0.90	0.83	61.71	15.54
S-103	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	15.54
S-105	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	55.19	6.01
S-106	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	54.03	15.54
S-107	3.3	0.91	0.4	1.28	2.00	0.71	0.50	0.84	53.84	15.54
S-108	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	15.54
S-109	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	15.54
S-110	3.3	0.91	0.4	1.28	2.80	0.998	0.70	0.84	60.74	15.54
S-111	3.3	0.91	0.4	1.28	1.60	0.57	0.40	0.84	52.97	11.47
S-112	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	15.54
SX-101	3.3	0.91	0.4	1.28	1.00	0.32	0.20	0.98	84.96	8.90
SX-102	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	9.57
SX-103	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	8.90
SX-104	3.3	0.91	0.4	1.28	1.20	0.43	0.30	0.84	58.49	8.46
SX-105	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	9.18
SX-106	3.3	0.91	0.4	1.28	10.00	3.23	2.00	0.98	51.62	8.90
TX-102	3.3	0.91	0.4	1.28	1.30	0.45	0.30	0.89	60.74	6.01
TX-104	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	56.06	15.54
TX-105	3.3	0.91	0.4	1.28	2.40	0.86	0.60	0.84	60.74	6.01
TX-106	3.3	0.91	0.4	1.28	1.80	0.61	0.40	0.91	60.74	6.01
TX-107	3.3	0.91	0.4	1.28	1.90	0.70	0.50	0.81	60.74	15.54
TX-108	4.7	1.31	0.6	1.25	4.20	1.11	0.20	1.85	61.13	12.17
TX-109	4	1.11	0.5	1.26	1.60	0.57	0.40	0.84	60.62	12.17
TX-110	4	1.11	0.5	1.26	1.40	0.47	0.30	0.94	53.55	12.17

Table 7A-1. Input to Post-Jet-Pumping Total Organic Carbon Calculation.* (3 sheets)

Tank	Salt cake initial TOC % (95th)	Salt cake initial TOC % (mean)	Salt cake initial TOC % (median)	Salt cake log TOC % standard deviation	Liquid initial TOC % (95th)	Liquid initial TOC % (mean)	Liquid initial TOC % (median)	Liquid log TOC % standard deviation	Liquid initial % moisture (mean)	Salt cake initial % moisture (95th)
	(X_{TOC})	(X_{TOC})	(X_{TOC})		(X_{TOCL})	(X_{TOCL})	(X_{TOCL})		(X_{WL})	(X_{W})
TX-111	4	1.11	0.5	1.26	1.40	0.47	0.30	0.94	60.62	12.17
TX-112	4	1.11	0.5	1.26	1.10	0.41	0.30	0.79	60.62	12.17
TX-113	4	1.11	0.5	1.26	1.10	0.41	0.30	0.79	60.62	12.17
TX-114	4	1.11	0.5	1.26	1.00	0.32	0.20	0.98	60.62	12.17
TX-115	5	1.38	0.6	1.29	0.50	0.16	0.10	0.98	64.85	12.17
TX-116	4	1.11	0.5	1.26	0.70	0.27	0.20	0.76	60.62	12.17
TX-117	4	1.11	0.5	1.26	1.10	0.41	0.30	0.79	60.62	12.17
TX-118	4.7	1.31	0.6	1.25	4.20	1.11	0.20	1.85	61.13	12.17
TY-102	4	1.11	0.5	1.26	1.10	0.41	0.30	0.79	60.62	37.31
U-102	5	1.38	0.6	1.29	1.80	0.61	0.40	0.91	64.65	31.00
U-103	5	1.38	0.6	1.29	1.80	0.61	0.40	0.91	64.45	31.00
U-105	5.2	1.47	0.7	1.22	1.10	0.41	0.30	0.79	65.42	15.18
U-106	5	1.38	0.6	1.29	6.20	2.25	1.60	0.82	63.75	31.00
U-107	5.2	1.47	0.7	1.22	1.10	0.41	0.30	0.79	65.42	15.54
U-108	5.2	1.47	0.7	1.22	1.10	0.41	0.30	0.79	65.42	15.54
U-109	5.2	1.47	0.7	1.22	1.10	0.41	0.30	0.79	64.85	21.83
U-111	5	1.38	0.6	1.29	4.20	1.46	1.00	0.87	64.85	27.15

*Only salt cake tanks were calculated as if they had been jet-pumped.

Table 7A-2. Post-Jet-Pumping Total Organic Carbon Calculation Intermediate Values and Results. (3 sheets)

Tank	Salt cake initial mass (t)	Mass fraction carbon	Solubility (kg salt/kg H_2O)	Initial liquid content (mass fraction)	Initial precipitate TOC %	Salt cake % moisture (95th)	Liquid loss* (t)	Salt cake final TOC % (mean)
	(M_T)	(Y)	(r_D)	(X_L)	(X_{TOCP})	(X'_W)	(ΔM_L)	(X'_{TOC})
A-101	5897.03	0.29	0.85	0.54	1.21	12.1	2390.83	1.24
A-102	136.56	0.29	0.98	0.63	2.44	12.1	68.83	1.98
AX-101	462.51	0.29	0.98	0.64	1.56	12.1	2399.21	1.45
AX-102	180.01	0.29	0.55	0.51	0.88	12.1	69.53	1.01
AX-103	682.81	0.29	0.77	0.57	1.32	12.1	305.67	1.28
B-102	62.07	0.29	0.48	0.47	1.94	12.1	21.56	1.66
B-104	428.31	0.29	0.50	0.47	1.96	12.1	150.41	1.67
B-105	1651.16	0.29	0.63	0.51	1.85	12.1	643.18	1.56
BX-105	18.62	0.29	0.30	0.41	1.56	12.1	5.58	1.43
BX-110	55.87	0.29	0.57	0.56	2.18	12.1	25.08	1.85
BX-111	887.66	0.29	0.57	0.49	1.98	12.1	331.69	1.68
BY-101	1725.66	0.29	0.67	0.21	1.74	12.166	0.15	1.45
BY-102	2116.72	0.29	0.70	0.53	2.32	12.1	864.06	1.89
BY-103	2451.92	0.29	0.77	0.55	2.87	12.1	1056.33	2.32
BY-104	2271.91	0.29	0.67	0.20	1.73	11.57	0.00	1.45
BY-105	2849.20	0.29	0.74	0.54	2.82	12.1	1198.53	2.28
BY-106	3395.45	0.29	0.80	0.56	2.93	12.1	1495.90	2.35
BY-107	1278.72	0.29	0.67	0.21	1.72	12.166	0.11	1.45
BY-108	459.35	0.29	0.67	0.21	1.74	12.166	0.04	1.45
BY-109	2110.5	0.29	0.63	0.51	2.07	12.1	825.34	1.74
BY-110	1831.18	0.29	0.67	0.21	1.74	12.166	0.16	1.45
BY-111	2718.84	0.29	0.67	0.21	1.74	12.166	0.23	1.45
BY-112	1775.32	0.29	0.67	0.21	1.74	12.166	0.15	1.45
S-101	1061.47	0.29	0.35	0.21	0.97	6.1	151.37	0.95
S-102	3383.03	0.29	0.55	0.25	0.79	6.1	574.46	0.84
S-103	1371.84	0.29	0.61	0.26	0.98	6.1	237.08	0.96

Table 7A-2. Post-Jet-Pumping Total Organic Carbon Calculation Intermediate Values and Results. (3 sheets)

Tank	Salt cake initial mass (t)	Mass fraction carbon	Solubility (kg salt/kg H_2O)	Initial liquid content (mass fraction)	Initial precipitate TOC %	Salt cake % moisture (95th)	Liquid loss* (t)	Salt cake final TOC % (mean)
	(M_T)	(Y)	(r_D)	(X_L)	(X_{TOCP})	(X'_W)	(ΔM_L)	(X'_{TOC})
S-105	2818.16	0.29	0.77	0.11	0.94	6.009	0.06	0.91
S-106	2774.71	0.29	0.81	0.29	1.00	6.1	546.66	0.96
S-107	428.31	0.29	0.81	0.29	0.99	6.1	84.72	0.96
S-108	3724.44	0.29	0.61	0.26	0.98	6.1	643.67	0.96
S-109	3445.10	0.29	0.61	0.26	0.98	6.1	595.39	0.96
S-110	1607.72	0.29	0.59	0.26	0.88	6.1	277.85	0.89
S-111	2774.71	0.29	0.85	0.22	1.00	6.1	317.73	0.95
S-112	3215.43	0.29	0.61	0.26	0.98	6.1	555.70	0.96
SX-101	2129.13	0.29	0.16	0.10	0.98	3.5	141.11	0.95
SX-102	2644.35	0.29	0.61	0.16	0.95	3.5	280.42	0.94
SX-103	3327.17	0.29	0.61	0.15	0.95	3.5	313.83	0.93
SX-104	2967.14	0.29	0.68	0.14	0.99	3.5	267.41	0.96
SX-105	3786.51	0.29	0.61	0.15	0.95	3.5	375.67	0.93
SX-106	2886.44	0.29	0.72	0.17	0.43	3.5	323.85	0.62
TX-102	1347.01	0.29	0.62	0.10	0.96	3.01	70.00	0.94
TX-104	397.27	0.29	0.74	0.28	0.99	6.1	75.09	0.96
TX-105	3780.30	0.29	0.60	0.10	0.92	6.009	0.07	0.91
TX-106	2812.95	0.29	0.61	0.10	0.94	6.009	0.05	0.91
TX-107	217.26	0.29	0.61	0.26	0.98	6.1	37.55	0.96
TX-108	831.79	0.29	0.57	0.20	1.36	12.166	0.07	1.31
TX-109	2383.64	0.29	0.62	0.20	1.25	12.166	0.20	1.11
TX-110	2867.82	0.29	0.84	0.23	1.30	12.166	0.28	1.11
TX-111	2296.74	0.29	0.62	0.20	1.27	12.166	0.19	1.11
TX-112	4028.60	0.29	0.63	0.20	1.29	12.166	0.33	1.11
TX-113	3767.89	0.29	0.63	0.20	1.29	12.166	0.31	1.11
TX-114	3320.96	0.29	0.63	0.20	1.31	12.166	0.27	1.11

Table 7A-2. Post-Jet-Pumping Total Organic Carbon Calculation Intermediate Values and Results. (3 sheets)

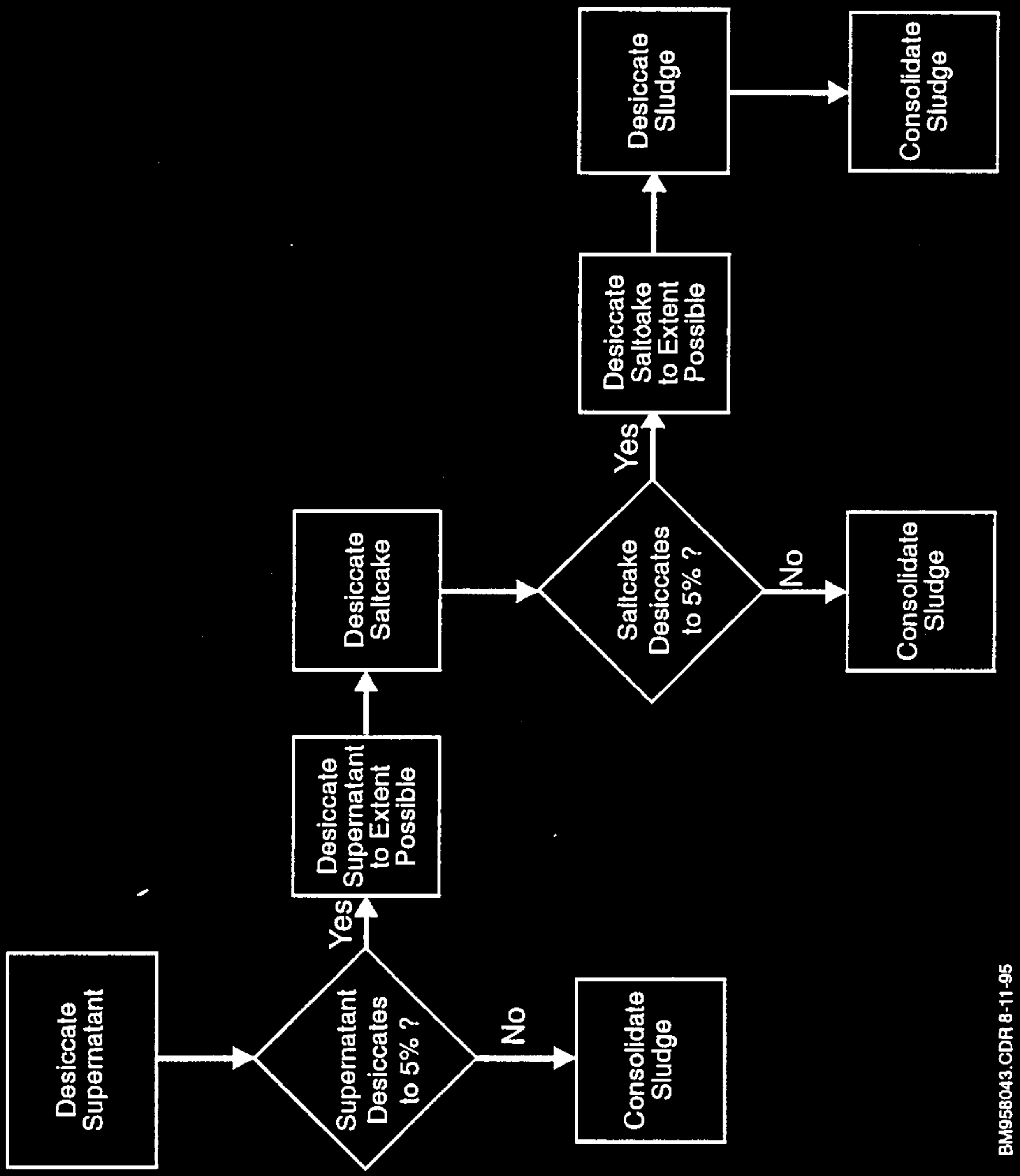
Tank	Salt cake initial mass (t)	Mass fraction carbon	Solubility (kg salt/kg H_2O)	Initial liquid content (mass fraction)	Initial precipitate TOC %	Salt cake % moisture (95th)	Liquid loss* (t)	Salt cake final TOC % (mean)
	(M_T)	(Y)	(r_D)	(X_L)	(X_{TOCP})	(X'_M)	(ΔM_L)	(X'_{TOC})
TX-115	3972.74	0.29	0.53	0.19	1.66	12.166	0.30	1.38
TX-116	3916.87	0.29	0.63	0.20	1.32	12.166	0.32	1.11
TX-117	3885.83	0.29	0.63	0.20	1.29	12.166	0.32	1.11
TX-118	2153.97	0.29	0.57	0.20	1.36	12.166	0.18	1.31
TY-102	397.27	0.29	0.63	0.62	2.23	12.1	206.42	1.87
U-102	1942.92	0.29	0.51	0.48	2.09	12.1	698.90	1.81
U-103	2625.73	0.29	0.52	0.48	2.09	12.1	948.12	1.81
U-105	2166.38	0.29	0.51	0.23	1.79	6.1	331.53	1.66
U-106	1148.37	0.29	0.45	0.49	0.55	12.1	420.28	0.88
U-107	2234.67	0.29	0.51	0.24	1.80	6.1	355.73	1.67
U-108	2576.07	0.29	0.51	0.24	1.80	6.1	410.08	1.67
U-109	2458.13	0.29	0.52	0.34	2.01	6.1	658.15	1.86
U-111	1880.84	0.29	0.46	0.42	1.31	12.1	536.62	1.34

NOTE: t = metric tons.

*Post-jet-pumped total organic carbon calculations show a trivial liquid loss for tanks that have been jet pumped.

- Initial liquid content is initial mass fraction of the liquid (including moisture, dissolved nonfuel salts, and dissolved fuel). See Equation 7A-21.
- Initial precipitate TOC percent is the TOC content of the solids. See Equation 7A-24.
- Liquid loss is the amount of liquid (i.e., moisture, nonfuel dissolved salts, and dissolved fuel) removed by jet pumping. See Equation 7A-28.
- Salt cake final TOC percent is the desired jet-pumped value given by Equation 7A-27. It is the mean of the salt cake post-jet-pumped TOC probability density function.

Figure 7A-1. Moisture Loss Calculation Logic.



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APPENDIX 7B

TANK STATUS TABLES FOR CURRENT AND AFTER-JET-PUMPING CONDITIONS

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APPENDIX 7B

TANK STATUS TABLES FOR CURRENT AND AFTER JET PUMPING CONDITIONS

1.0 CURRENT STATUS TABLE

Table 7B-1 summarizes the status of the single-shell tanks with respect to the preliminary safety criteria. For each phase, the 95th quantile moisture content and total organic carbon are tabulated and compared to the safety criteria line defined in Chapter 5.

If a single-shell tank phase moisture content and TOC lie outside the safety criteria, the phase is listed as "SAFE." If not, it is listed as "CONDSAFE."

2.0 AFTER JET PUMPING STATUS TABLE

Table 7B-2 presents the status of the 65 salt cake tanks with respect to the preliminary safety criteria. Column definitions, when necessary, are provided in the footnotes at the end of the table.

The 95th percentile for salt cake moisture after jet pumping (χ_w') is derived from the current 95th percentile for salt cake moisture by the calculational technique outlined in Section 5.3 of PNL-10360, *Analysis of Total Organic Carbon and Moisture in Hanford Single-Shell Tank Waste* (Toth et al. 1995). The technique is based on the ANOVA salt cake moisture model factors provided in Table 5.6 of PNL-10360 (Toth et al. 1995) and in Table 7B-3 of this Appendix for convenience.

The "Pumped" and "Not Pumped" factors in Table 7B-3 are 63% and 160% respectively. The ratio factor used in PNL-10340 (Toth et al. 1995) for calculating the percent salt cake moisture after jet pumping was determined to be 0.394. The current 95th percentile salt cake moisture, as provided in Table 7B-1 for the tanks that have not been jet pumped, is multiplied by this factor to estimate the jet-pumped salt cake moisture content. These values are provided in Table 7B-2, column 2.

3.0 REFERENCES

Toth, J. J., M. E. Lerchan, J. G. Hill, P. G. Heasler, and P. D. Whitney, 1995, *Analysis of Total Organic Carbon and Moisture in Hanford Single-Shell Tank Waste*, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.

Table 7B-1. Current Total Organic Carbon and Moisture Data. (4 sheets)

Tank	Supernatant initial TOC % (95th)	Salt cake initial TOC % (95th)	Sludge initial TOC % (95th)	Supernatant % moisture (95th)	Salt cake % moisture (95th)	Sludge % moisture (95th)	Supernatant current status	Salt cake current status	Sludge current status
A-101	3.8	4.5	2.4	34.70	28.16	18.40	SAFE	SAFE	SAFE
A-102	1.6	4.5	2.5	32.50	31.00	18.40	SAFE	SAFE	SAFE
A-103	2.5	NA	2.6	36.40	NA	18.40	SAFE	NA	SAFE
A-104	NA	NA	0.6	NA	NA	23.60	NA	NA	SAFE
A-105	1.1	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
A-106	18	NA	1.9	38.90	NA	23.20	SAFE	NA	SAFE
AX-101	3	4.5	2.1	31.50	31.00	18.40	SAFE	SAFE	SAFE
AX-102	4.4	4.3	0.6	44.30	31.00	23.60	SAFE	SAFE	SAFE
AX-103	3.3	4.3	0.6	37.40	31.00	23.60	SAFE	SAFE	SAFE
AX-104	NA	NA	0.6	NA	NA	23.60	NA	NA	SAFE
B-101	1.1	NA	0.6	53.20	NA	13.40	SAFE	NA	SAFE
B-102	1.1	4.3	0.6	49.90	31.00	13.40	SAFE	SAFE	SAFE
B-103	NA	NA	0.6	NA	NA	13.40	NA	NA	SAFE
B-104	1.1	4.3	0.6	49.30	31.00	23.60	SAFE	SAFE	SAFE
B-105	1.1	4	0.3	44.00	31.00	24.00	SAFE	SAFE	SAFE
B-106	0.8	NA	0.3	56.00	NA	28.30	SAFE	NA	SAFE
B-107	1.1	NA	1.2	53.40	NA	26.70	SAFE	NA	SAFE
B-108	1.1	NA	1.2	53.40	NA	26.70	SAFE	NA	SAFE
B-109	1.1	NA	1.2	59.00	NA	26.70	SAFE	NA	SAFE
B-110	1.1	NA	0.2	49.30	NA	23.60	SAFE	NA	SAFE
B-111	1.1	NA	0.4	49.30	NA	23.60	SAFE	NA	SAFE
B-112	1.1	NA	0.3	49.30	NA	23.60	SAFE	NA	SAFE
BX-101	1.5	NA	0.9	56.00	NA	17.10	SAFE	NA	SAFE
BX-102	1.5	NA	0.9	56.00	NA	17.10	SAFE	NA	SAFE
BX-103	1.5	NA	0.9	67.40	NA	17.10	SAFE	NA	SAFE
BX-104	1.9	NA	1	64.60	NA	17.10	SAFE	NA	SAFE
BX-105	2.2	4.3	1	58.80	31.00	17.10	SAFE	SAFE	SAFE
BX-106	1.4	NA	0.9	48.70	NA	17.10	SAFE	NA	SAFE
BX-107	0.8	NA	0.3	54.80	NA	28.30	SAFE	NA	SAFE
BX-108	1.5	NA	0.9	56.00	NA	17.10	SAFE	NA	SAFE
BX-109	1.2	NA	0.9	49.70	NA	17.10	SAFE	NA	SAFE
BX-110	1.4	4.3	0.2	46.10	34.81	27.80	SAFE	SAFE	SAFE
BX-111	NA	4.3	0.2	NA	31.00	27.80	NA	SAFE	SAFE
BX-112	1.2	NA	1.6	53.40	NA	26.70	SAFE	NA	SAFE
BY-101	1	5.1	0.6	42.30	12.17	16.80	SAFE	SAFE	SAFE
BY-102	0.7	4.3	NA	41.60	31.00	NA	SAFE	SAFE	NA

Table 7B-1. Current Total Organic Carbon and Moisture Data. (4 sheets)

Tank	Supernatant initial TOC % (95th)	Salt cake initial TOC % (95th)	Sludge initial TOC % (95th)	Supernatant % moisture (95th)	Salt cake % moisture (95th)	Sludge % moisture (95th)	Supernatant current status	Salt cake current status	Sludge current status
BY-103	0.9	5.1	0.6	39.10	31.00	16.80	SAFE	SAFE	SAFE
BY-104	1	5.1	0.6	42.30	11.57	16.80	SAFE	SAFE	SAFE
BY-105	0.9	5.1	0.6	40.20	31.00	16.80	SAFE	SAFE	SAFE
BY-106	0.9	5.1	0.6	38.10	31.00	16.80	SAFE	SAFE	SAFE
BY-107	1.1	5.1	0.6	42.30	12.17	16.80	SAFE	SAFE	SAFE
BY-108	1	5.1	0.6	42.30	12.17	16.80	SAFE	SAFE	SAFE
BY-109	1.2	4.3	0.6	43.80	31.00	23.60	SAFE	SAFE	SAFE
BY-110	1	5.1	0.6	42.30	12.17	16.80	SAFE	SAFE	SAFE
BY-111	NA	5.1	0.6	NA	12.17	16.80	NA	SAFE	SAFE
BY-112	1	5.1	0.6	42.30	12.17	16.80	SAFE	SAFE	SAFE
C-101	1.5	NA	0.9	56.00	NA	17.10	SAFE	NA	SAFE
C-102	1.1	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
C-103	2.3	NA	1	64.40	NA	23.60	SAFE	NA	SAFE
C-104	2	NA	1.2	57.00	NA	23.60	SAFE	NA	SAFE
C-105	1	NA	0.4	49.30	NA	23.60	SAFE	NA	SAFE
C-106*	1.1	NA	0.8	55.70	NA	23.60*	SAFE	NA	SAFE*
C-107	0.6	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
C-108	NA	NA	0.7	NA	NA	27.10	NA	NA	SAFE
C-109	0.7	NA	1	56.50	NA	27.10	SAFE	NA	SAFE
C-110	0.5	NA	0.3	57.20	NA	28.30	SAFE	NA	SAFE
C-111	NA	NA	0.7	NA	NA	27.10	NA	NA	SAFE
C-112	0.7	NA	1.2	45.00	NA	27.10	SAFE	NA	SAFE
S-101	1.9	3.3	0.6	55.80	15.54	21.30	SAFE	SAFE	SAFE
S-102	3.5	3.3	0.6	45.00	15.54	21.30	SAFE	SAFE	SAFE
S-103	1.9	3.3	0.6	44.00	15.54	21.30	SAFE	SAFE	SAFE
S-104	1.2	NA	0.6	50.50	NA	23.60	SAFE	NA	SAFE
S-105	1.9	3.3	0.6	38.30	6.01	21.30	SAFE	SAFE	SAFE
S-106	1.9	3.3	0.6	37.10	15.54	21.30	SAFE	SAFE	SAFE
S-107	2	3.3	0.6	36.90	15.54	21.30	SAFE	SAFE	SAFE
S-108	1.9	3.3	0.6	44.00	15.54	21.30	SAFE	SAFE	SAFE
S-109	1.9	3.3	0.6	44.00	15.54	21.30	SAFE	SAFE	SAFE
S-110	2.8	3.3	0.6	44.00	15.54	21.30	SAFE	SAFE	SAFE
S-111	1.6	3.3	0.6	36.00	11.47	21.30	SAFE	SAFE	SAFE
S-112	1.9	3.3	0.6	44.00	15.54	21.30	SAFE	SAFE	SAFE
SX-101	1	3.3	0.6	68.60	8.90	21.30	SAFE	SAFE	SAFE
SX-102	1.9	3.3	0.6	44.00	9.57	21.30	SAFE	SAFE	SAFE

Table 7B-1. Current Total Organic Carbon and Moisture Data. (4 sheets)

Tank	Supernatant initial TOC % (95th)	Salt cake initial TOC % (95th)	Sludge initial TOC % (95th)	Supernatant % moisture (95th)	Salt cake % moisture (95th)	Sludge % moisture (95th)	Supernatant current status	Salt cake current status	Sludge current status
SX-103	1.9	3.3	0.6	44.00	8.90	21.30	SAFE	SAFE	SAFE
SX-104	1.2	3.3	0.6	41.70	8.46	21.30	SAFE	SAFE	SAFE
SX-105	1.9	3.3	0.6	44.00	9.18	21.30	SAFE	SAFE	SAFE
SX-106	19	3.3	0.6	34.60	8.90	21.30	SAFE	SAFE	SAFE
SX-107	1.3	NA	0.6	52.20	NA	23.60	SAFE	NA	SAFE
SX-108	1.2	NA	0.6	50.50	NA	23.60	SAFE	NA	SAFE
SX-109	1.2	NA	0.6	50.50	NA	23.60	SAFE	NA	SAFE
SX-110	NA	NA	0.6	NA	NA	23.60	NA	NA	SAFE
SX-111	1.1	NA	0.6	53.50	NA	23.60	SAFE	NA	SAFE
SX-112	1.2	NA	0.6	50.50	NA	23.60	SAFE	NA	SAFE
SX-113	NA	NA	0.6	NA	NA	23.60	NA	NA	SAFE
SX-114	1.1	NA	0.6	51.10	NA	23.60	SAFE	NA	SAFE
SX-115	NA	NA	0.6	NA	NA	23.60	SAFE	NA	SAFE
T-101	0.5	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
T-102	0.8	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
T-103	0.8	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
T-104	0.5	NA	0.2	49.30	NA	33.90	SAFE	NA	SAFE
T-105	1.1	NA	0.4	49.30	NA	14.80	SAFE	NA	SAFE
T-106	1.1	NA	0.4	49.30	NA	14.80	SAFE	NA	SAFE
T-107	0.3	NA	0.3	65.20	NA	27.10	SAFE	NA	SAFE
T-108	NA	NA	0.3	NA	NA	28.30	NA	NA	SAFE
T-109	NA	NA	0.6	NA	NA	23.60	NA	NA	SAFE
T-110	1	NA	0.9	67.20	NA	23.60	SAFE	NA	SAFE
T-111	1	NA	1.1	59.60	NA	23.60	SAFE	NA	SAFE
T-112	0.9	NA	0.9	66.00	NA	23.60	SAFE	NA	SAFE
TX-101	1.1	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
TX-102	1.3	3.3	NA	44.00	3.01	NA	SAFE	SAFE	NA
TX-103	1.1	NA	0.6	41.80	NA	23.60	SAFE	NA	SAFE
TX-104	1.9	3.3	NA	39.20	15.54	NA	SAFE	SAFE	NA
TX-105	2.4	3.3	NA	44.00	6.01	NA	SAFE	SAFE	NA
TX-106	1.8	3.3	NA	44.00	6.01	NA	SAFE	SAFE	NA
TX-107	1.9	3.3	NA	44.00	15.54	NA	SAFE	SAFE	NA
TX-108	NA	4.7	NA	NA	12.17	NA	NA	SAFE	NA
TX-109	1.6	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-110	1.4	4	NA	36.60	12.17	NA	SAFE	SAFE	NA
TX-111	1.4	4	NA	44.00	12.17	NA	SAFE	SAFE	NA

Table 7B-1. Current Total Organic Carbon and Moisture Data. (4 sheets)

Tank	Supernatant initial TOC % (95th)	Salt cake initial TOC % (95th)	Sludge initial TOC % (95th)	Supernatant % moisture (95th)	Salt cake % moisture (95th)	Sludge % moisture (95th)	Supernatant current status	Salt cake current status	Sludge current status
TX-112	1.1	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-113	1.1	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-114	1	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-115	0.5	5	NA	48.20	12.17	NA	SAFE	SAFE	NA
TX-116	0.7	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-117	1.1	4	NA	44.00	12.17	NA	SAFE	SAFE	NA
TX-118	4.2	4.7	NA	44.40	12.17	NA	SAFE	SAFE	NA
TY-101	NA	NA	0	NA	NA	22.90	NA	NA	SAFE
TY-102	1.1	4	NA	44.00	37.31	NA	SAFE	SAFE	NA
TY-103	0.8	NA	0.3	49.30	NA	29.90	SAFE	NA	SAFE
TY-104	0.8	NA	0.9	49.30	NA	29.90	SAFE	NA	SAFE
TY-105	NA	NA	0.4	NA	NA	18.90	NA	NA	SAFE
TY-106	NA	NA	0.6	NA	NA	18.90	NA	NA	SAFE
U-101	1.2	NA	0.6	50.50	NA	23.60	SAFE	NA	SAFE
U-102	1.8	5	1.2	48.00	31.00	8.70	SAFE	SAFE	SAFE
U-103	1.8	5	1.6	47.80	31.00	8.70	SAFE	SAFE	SAFE
U-104	1.1	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE
U-105	1.1	5.2	0.6	48.90	15.18	24.50	SAFE	SAFE	SAFE
U-106	6.2	5	1.2	47.20	31.00	8.70	SAFE	SAFE	SAFE
U-107	1.1	5.2	0.6	48.90	15.54	24.50	SAFE	SAFE	SAFE
U-108	1.1	5.2	0.6	48.90	15.54	24.50	SAFE	SAFE	SAFE
U-109	1.1	5.2	0.6	48.20	21.83	24.50	SAFE	SAFE	SAFE
U-110	1.1	NA	0.3	49.30	NA	14.80	SAFE	NA	SAFE
U-111	4.2	5	1.2	48.20	27.15	8.70	SAFE	SAFE	SAFE
U-112	1.1	NA	0.6	49.30	NA	23.60	SAFE	NA	SAFE

NOTE: Refer to Chapter 7.0, Section 7.3, for discussion related to this table.
*C-106 has periodic additions of water so evaporative losses are not calculated.
NA = not applicable. (Because the phase is not present in the tank, there is no mass present for the phase, no weight percent is applicable, no computations were performed for this phase, and no status is applicable.)

Table 7B-2. Salt Cake Tank Post-Jet-Pumping Status: Comparison of Post-Jet-Pumped Total Organic Carbon Values with Criteria Line. (3 sheets)

Tank	Salt cake % moisture after jet pumping (95th)	Safe TOC criteria line (4.5 + 0.17)	Salt cake final TOC % after jet pumping (95th)	Salt cake final TOC % after jet pumping (90th)	Salt cake final TOC % after jet pumping (mean)	Salt cake TOC status after jet pumping final TOC% (95th)	Salt cake TOC status after jet pumping final TOC% (90th)
	(X'_{w})	(X'_{w})	(X'_{TOC})	(X'_{TOC})	(X'_{TOC})	SAFE	SAFE
A-101	12.10	6.56	4.38	2.81	1.24	SAFE	SAFE
A-102	12.10	6.56	7.02	4.50	1.98	CONDSAFE	SAFE
AX-101	12.10	6.56	5.13	3.29	1.45	SAFE	SAFE
AX-102	12.10	6.56	3.55	2.30	1.01	SAFE	SAFE
AX-103	12.10	6.56	4.50	2.91	1.28	SAFE	SAFE
B-102	12.10	6.56	5.82	3.77	1.66	SAFE	SAFE
B-104	12.10	6.56	5.85	3.79	1.67	SAFE	SAFE
B-105	12.10	6.56	5.61	3.54	1.56	SAFE	SAFE
BX-105	12.10	6.56	5.02	3.25	1.43	SAFE	SAFE
BX-110	12.10	6.56	6.48	4.19	1.85	CONDSAFE[a]	SAFE
BX-111	12.10	6.56	5.89	3.81	1.68	SAFE	SAFE
BY-101	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
BY-102	12.10	6.56	6.62	4.28	1.89	CONDSAFE	SAFE
BY-103	12.10	6.56	8.15[b]	5.26	2.32	SAFE[b]	SAFE
BY-104	11.57	6.47	5.10	3.29	1.45	SAFE	SAFE
BY-105	12.10	6.56	8.03[b]	5.18	2.28	SAFE[b]	SAFE
BY-106	12.10	6.56	8.27[b]	5.34	2.35	SAFE[b]	SAFE
BY-107	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
BY-108	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
BY-109	12.10	6.56	6.10	3.95	1.74	SAFE	SAFE
BY-110	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
BY-111	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
BY-112	12.17	6.57	5.10	3.29	1.45	SAFE	SAFE
S-101	6.10	5.54	3.43	2.15	0.95	SAFE	SAFE

Table 7B-2. Salt Cake Tank Post-Jet-Pumping Status: Comparison of Post-Jet-Pumped Total Organic Carbon Values with Criteria Line. (3 sheets)

Tank	Salt cake % moisture after jet pumping (95th)	Safe TOC criteria line (4.5 + 0.17)	Salt cake final TOC % after jet pumping (95th)	Salt cake final TOC % after jet pumping (90th)	Salt cake final TOC % after jet pumping (mean)	Salt cake TOC status after jet pumping final TOC% (95th)	Salt cake TOC status after jet pumping final TOC% (90th)
	(X'_w)	(X'_w)	(X'_{TOC})	(X'_{TOC})	(X'_{TOC})	SAFE	SAFE
S-102	6.10	5.54	3.04	1.91	0.84	SAFE	SAFE
S-103	6.10	5.54	3.46	2.17	0.96	SAFE	SAFE
S-105	6.01	5.52	3.30	2.07	0.91	SAFE	SAFE
S-106	6.10	5.54	3.49	2.19	0.96	SAFE	SAFE
S-107	6.10	5.54	3.48	2.18	0.96	SAFE	SAFE
S-108	6.10	5.54	3.46	2.17	0.96	SAFE	SAFE
S-109	6.10	5.54	3.46	2.17	0.96	SAFE	SAFE
S-110	6.10	5.54	3.23	2.03	0.89	SAFE	SAFE
S-111	6.10	5.54	3.46	2.17	0.95	SAFE	SAFE
S-112	6.10	5.54	3.46	2.17	0.96	SAFE	SAFE
SX-101	3.50	5.10	3.45	2.17	0.95	SAFE	SAFE
SX-102	3.50	5.10	3.39	2.13	0.94	SAFE	SAFE
SX-103	3.50	5.10	3.38	2.12	0.93	SAFE	SAFE
SX-104	3.50	5.10	3.47	2.18	0.96	SAFE	SAFE
SX-105	3.50	5.10	3.39	2.12	0.93	SAFE	SAFE
SX-106	3.50	5.10	2.24	1.40	0.62	SAFE	SAFE
TX-102	3.01	5.01	3.39	2.13	0.94	SAFE	SAFE
TX-104	6.10	5.54	3.48	2.18	0.96	SAFE	SAFE
TX-105	6.01	5.52	3.30	2.07	0.91	SAFE	SAFE
TX-106	6.01	5.52	3.30	2.07	0.91	SAFE	SAFE
TX-107	6.10	5.54	3.46	2.17	0.96	SAFE	SAFE
TX-108	12.17	6.57	4.70	2.98	1.31	SAFE	SAFE
TX-109	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-110	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE

Table 7B-2. Salt Cake Tank Post-Jet-Pumping Status: Comparison of Post-Jet-Pumped Total Organic Carbon Values with Criteria Line. (3 sheets)

Tank	Salt cake % moisture after jet pumping (95th)	Safe TOC criteria line (4.5 + 0.17)	Salt cake final TOC % after jet pumping (95th)	Salt cake final TOC % after jet pumping (90th)	Salt cake final TOC % after jet pumping (mean)	Salt cake TOC status after jet pumping final TOC% (95th)	Salt cake TOC status after jet pumping final TOC% (90th)
	(X'_W)	(X'_W)	(X'_{TOC})	(X'_{TOC})	(X'_{TOC})	SAFE	SAFE
TX-111	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-112	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-113	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-114	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-115	12.17	6.57	5.00	3.13	1.38	SAFE	SAFE
TX-116	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-117	12.17	6.57	4.00	2.53	1.11	SAFE	SAFE
TX-118	12.17	6.57	4.70	2.98	1.31	SAFE	SAFE
TY-102	12.10	6.56	6.73	4.25	1.87	CONDSAFE	SAFE
U-102	12.10	6.56	6.57	4.11	1.81	CONDSAFE	SAFE
U-103	12.10	6.56	6.58	4.12	1.81	CONDSAFE	SAFE
U-105	6.10	5.54	5.88	3.77	1.66	CONDSAFE	SAFE
U-106	12.10	6.56	3.18	1.99	0.88	SAFE	SAFE
U-107	6.10	5.54	5.91	3.79	1.67	CONDSAFE	SAFE
U-108	6.10	5.54	5.91	3.79	1.67	CONDSAFE	SAFE
U-109	6.10	5.54	6.57	4.22	1.86	CONDSAFE	SAFE
U-111	12.10	6.56	4.87	3.05	1.34	SAFE	SAFE

[a] BX-110 is CONDITIONALLY SAFE for jet pumping because there is virtually no margin available between the criteria value (6.56) and post-jet-pumping value (6-48).

[b] BY-103, BY-105, BY-106 were determined to be SAFE by alternate evaluations - See Section 7-3.

CONDSAFE = the 95th quantile salt cake TOC percent is greater than the safe TOC.
TOC = total organic carbon.

Table 7B-3. Estimated Terms for Moisture Model Fit of the Salt Cake Phase.

Term	Moisture
Mean	14%
R = REDOX	71%
R = Non-REDOX	141%
P = Pumped	63%
P = Not pumped	160%
V = Active	76%
V = Not active	132%
σ_T = Between-tank variability	22%
σ_E = Within-tank variability	17%

REDOX = reduction and oxidation.

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APPENDIX 7C

MOISTURE, TOTAL ORGANIC CARBON CONTENT, AND TANK STATUS AFTER 50 YEARS OF EVAPORATIVE LOSSES

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APPENDIX 7C

MOISTURE, TOTAL ORGANIC CARBON CONTENT, AND TANK STATUS AFTER 50 YEARS OF EVAPORATIVE LOSSES

1.0 SINGLE-SHELL TANK MOISTURE CONTENT AFTER 50 YEARS

Table 7C-1 lists input to the 50-year moisture loss calculations. The table is based on the following assumptions and column definitions:

- For purposes of calculating potential moisture losses, all salt cake tanks not yet actually jet pumped were calculated as if they had been jet pumped. Salt cake tanks are assumed to be jet pumped at the start of the 50 year mission. The initial salt cake moisture content is actually the post-jet-pumping salt cake moisture content. No supernatant remains after jet pumping.

- The initial moisture content of each phase is the 95th quantile. Moisture mass (i.e., metric tons of water) is simply the product of moisture content and phase mass in metric tons.

- Waste loses moisture as a result of evaporation and consolidation. Evaporation removes moisture from the waste in this order: (1) supernatant, (2) salt cake, and (3) sludge. Consolidation removes moisture only from the sludge and decreases the sludge moisture content 3%. The supernatant and salt cake are not consolidating media.

- Fifty-year evaporative losses are taken from FAI/94-114, *Moisture Loss Estimates for Hanford Single-Shell Tanks* (FAI 1994b),[1] or Section 7.4 of this document. Tank C-106 is not considered in these calculations because of moisture addition and level monitoring.

Table 7C-2 lists the moisture content of each single-shell tank phase at the end of 50 years.

- Final supernatant moisture at 5% (metric tons) is defined as the mass of supernatant moisture remaining if the supernatant can desiccate only to 5% moisture content. The 50-year loss is subtracted from the supernatant moisture mass, and this value is entered unless it results in a moisture content less than 5%. If the 50-year loss could reduce the moisture content below 5%, a value which forces the final supernatant moisture content to 5% is entered. This also can be expressed as the maximum of: (1) the (initial) supernatant moisture minus the 50-year evaporative loss and (2) the supernatant moisture that forces a 5% moisture content.

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[1] *Moisture Loss Estimates for Hanford Single-Shell Tanks*, FAI/94-114, Fauske & Associates, Inc., Burr Ridge, Illinois, 1994.

- Final supernatant moisture at 0% (metric tons) is defined as the mass of supernatant moisture remaining if the supernatant can desiccate to 0% moisture content. This is the maximum of: (1) the (initial) supernatant moisture minus the 50-year evaporative loss and (2) zero.

- Final salt cake moisture at 5% (metric tons) is defined as the mass of salt cake moisture remaining if the salt cake can desiccate to 5% moisture content. If desiccating the supernatant to 5% moisture content does not require the entire 50-year evaporative loss, the salt cake is desiccated to 5% moisture content. This column value is then the maximum of two quantities: (1) (initial) salt cake moisture minus (50-year loss minus the final supernatant moisture at 5%) and (2) the salt cake moisture that forces 5% moisture content.

- Final salt cake moisture at 0% (metric tons) is defined as the mass of salt cake moisture remaining if the salt cake can desiccate completely. If desiccating the supernatant to 5% moisture content does not require the entire 50-year evaporative loss, the salt cake is desiccated to the extent possible. This column value is the maximum of two quantities: (1) (initial) salt cake moisture minus 50-year loss minus (supernatant moisture minus final supernatant moisture at 5%) and (2) zero.

- Final sludge moisture (before consolidation) presumes the sludge can dry out completely but does not take into account consolidation. If desiccating both the supernatant and salt cake to 5% moisture content does not require the entire 50-year evaporative loss, the sludge is desiccated to the extent possible. This column value is then the maximum of two quantities: (1) (initial) sludge moisture minus (50-year loss minus [supernatant moisture minus final supernatant moisture at 5%] minus (salt cake moisture minus final salt cake moisture at 5%]) and (2) zero.

- Final sludge percent moisture (before consolidation) computes the sludge moisture content taking into account evaporation but not consolidation. It is defined as

$$\frac{\text{100 x final supernatant moisture}}{\text{supernatant (metric tons) - sludge moisture loss}}.$$

  Sludge moisture loss is simply the initial sludge moisture minus the final sludge moisture (before consolidation).

- Final supernatant moisture percent is defined as

$$\frac{\text{100 x final supernatant moisture}}{\text{supernatant (metric tons) - supernatant moisture loss.}}$$

Table 7C-1. Input to 50-Year Evaporative Losses and Final Moisture Content Calculations. (4 sheets)

Tank	Supernatant % moisture 95th	Sludge % moisture 95th	Salt % moisture 95th (after JP)	Salt cake (t)	Sludge (t)	Supernatant (t) (before JP)	Salt cake moisture (t)	Sludge moisture (t)	Supernatant moisture (t) (after JP)	50 Year Loss (t)
A-101	34.70	18.40	12.10	5,897.03	16.46	0.00	713.54	3.03	0.00	103.00
A-102	32.50	18.40	12.10	136.56	82.32	20.75	16.52	15.15	0.00	69.40
A-103	36.40	18.40	0.00	0.00	2,008.70	25.93	0.00	369.60	9.44	53.00
A-104	0.00	23.60	0.00	0.00	153.67	0.00	0.00	36.27	0.00	98.80
A-105	49.30	23.60	0.00	0.00	104.28	0.00	0.00	24.61	0.00	18.70
A-106	38.90	23.20	0.00	0.00	686.03	0.00	0.00	159.16	0.00	3.60
AX-101	31.50	18.40	12.10	4624.51	16.46	0.00	559.57	3.03	0.00	Isolated
AX-102	44.30	23.60	12.10	180.01	38.42	15.56	21.78	9.07	0.00	Isolated
AX-103	37.40	23.60	12.10	682.81	10.98	0.00	82.62	2.59	0.00	Isolated
AX-104	0.00	23.60	0.00	0.00	38.42	0.00	0.00	9.07	0.00	Isolated
B-101	53.20	13.40	0.00	0.00	620.17	0.00	0.00	83.10	0.00	76.40
B-102	49.90	13.40	12.10	62.07	98.79	20.75	7.51	13.24	0.00	7.20
B-103	0.00	13.40	0.00	0.00	323.81	0.00	0.00	43.39	0.00	5.60
B-104	49.30	23.60	12.10	428.31	1651.96	5.19	51.83	389.86	0.00	6.60
B-105	44.00	24.00	12.10	1651.17	219.53	0.00	199.79	52.69	0.00	6.80
B-106	56.00	28.30	0.00	0.00	636.64	5.19	0.00	180.17	2.90	5.70
B-107	53.40	26.70	0.00	0.00	900.07	5.19	0.00	240.32	2.77	5.80
B-108	53.40	26.70	0.00	0.00	515.90	0.00	0.00	137.74	0.00	5.60
B-109	59.00	26.70	0.00	0.00	697.01	0.00	0.00	186.10	0.00	5.10
B-110	49.30	23.60	0.00	0.00	1344.62	5.19	0.00	317.33	2.56	12.10
B-111	49.30	23.60	0.00	0.00	1295.23	5.19	0.00	305.67	2.56	52.60
B-112	49.30	23.60	0.00	0.00	164.65	15.56	0.00	38.86	7.67	6.80
BX-101	56.00	17.10	0.00	0.00	230.51	5.19	0.00	39.42	2.90	7.50
BX-102	56.00	17.10	0.00	0.00	526.87	0.00	0.00	90.10	0.00	9.00
BX-103	67.40	17.10	0.00	0.00	340.27	20.75	0.00	58.19	13.98	28.50
BX-104	64.60	17.10	0.00	0.00	526.87	15.56	0.00	90.10	10.05	58.10
BX-105	58.80	17.10	12.10	18.62	235.99	25.93	2.25	40.36	0.00	9.90
BX-106	48.70	17.10	0.00	0.00	170.14	77.80	0.00	29.09	37.89	7.60
BX-107	54.80	28.30	0.00	0.00	1887.96	5.19	0.00	534.29	2.84	7.00
BX-108	56.00	17.10	0.00	0.00	142.69	0.00	0.00	24.40	0.00	18.50
BX-109	49.70	17.10	0.00	0.00	1059.23	0.00	0.00	181.13	0.00	9.00
BX-110	46.10	27.80	12.10	55.87	1037.28	0.00	6.76	288.36	0.00	23.40
BX-111	0.00	27.80	12.10	887.66	373.20	0.00	107.41	103.75	0.00	6.30
BX-112	53.40	26.70	0.00	0.00	900.07	5.19	0.00	240.32	2.77	8.30
BY-101	42.30	16.80	12.17	1725.66	598.22	0.00	209.94	100.50	0.00	9.50
BY-102	41.60	0.00	12.10	2116.72	0.00	0.00	256.12	0.00	0.00	26.20
BY-103 (a)	39.10	16.80	12.10	2451.92	27.44	0.00	296.68	4.61	0.00	15.40
BY-104	42.30	16.80	11.57	2271.91	219.53	0.00	262.86	36.88	0.00	32.10
BY-105 (a)	40.20	16.80	12.10	2849.20	241.48	0.00	344.75	40.57	0.00	30.90
BY-106 (a)	38.10	16.80	12.10	3395.45	521.38	0.00	410.85	87.59	0.00	38.50
BY-107	42.30	16.80	12.17	1278.72	329.30	0.00	155.57	55.32	0.00	33.90

Table 7C-1. Input to 50-Year Evaporative Losses and Final Moisture Content Calculations. (4 sheets)

Tank	Supernatant % moisture 95th	Sludge % moisture 95th	Salt % moisture 95th (after JP)	Salt cake (t)	Sludge (t)	Supernatant (t) (before JP)	Salt cake moisture (t)	Sludge moisture (t)	Supernatant moisture (t) (after JP)	50 Year Loss (t)
BY-108	42.30	16.80	12.17	459.35	845.19	0.00	55.88	141.99	0.00	36.50
BY-109	43.80	23.60	12.10	2110.52	455.52	0.00	255.37	107.50	0.00	4.10
BY-110	42.30	16.80	12.17	1831.18	565.29	0.00	222.78	94.97	0.00	23.80
BY-111	0.00	16.80	12.17	2718.84	115.25	0.00	330.77	19.36	0.00	14.90
BY-112	42.30	16.80	12.17	1775.32	27.44	0.00	215.98	4.61	0.00	18.50
C-101	56.00	17.10	0.00	0.00	482.97	0.00	0.00	82.59	0.00	8.40
C-102	49.30	23.60	0.00	0.00	2321.53	0.00	0.00	547.88	0.00	51.10
C-103	64.40	23.60	0.00	0.00	340.27	689.86	0.00	80.30	444.27	68.20
C-104	57.00	23.60	0.00	0.00	1619.03	0.00	0.00	382.09	0.00	13.50
C-105	49.30	23.60	0.00	0.00	823.24	0.00	0.00	194.28	0.00	1000.00 (b)
C-106	55.70	23.60	0.00	0.00	1081.19	165.98	0.00	255.16	92.45	
C-107	49.30	23.60	0.00	0.00	1509.27	0.00	0.00	356.19	0.00	67.50
C-108	0.00	27.10	0.00	0.00	362.22	0.00	0.00	98.16	0.00	143.00
C-109	56.50	27.10	0.00	0.00	340.27	20.75	0.00	92.21	11.72	19.90
C-110	57.20	28.30	0.00	0.00	1026.30	0.00	0.00	290.44	0.00	25.70
C-111	0.00	27.10	0.00	0.00	312.83	0.00	0.00	84.78	0.00	8.40
C-112	45.00	27.10	0.00	0.00	570.78	0.00	0.00	154.68	0.00	22.00
S-101	55.80	21.30	6.10	1061.47	1339.13	62.24	64.75	285.24	0.00	73.70
S-102	45.00	21.30	6.10	3383.03	21.95	0.00	206.37	4.68	0.00	28.30
S-103	44.00	21.30	6.10	1371.84	54.88	88.18	83.68	11.69	0.00	16.40
S-104	50.50	23.60	0.00	0.00	1608.06	5.19	0.00	379.50	2.62	46.20
S-105	38.30	21.30	6.01	2818.16	10.98	0.00	169.34	2.34	0.00	9.40
S-106	37.10	21.30	6.10	2774.71	153.67	20.75	169.26	32.73	0.00	9.70
S-107	36.90	21.30	6.10	428.31	1608.06	72.62	26.13	342.52	0.00	35.90
S-108	44.00	21.30	6.10	3724.44	21.95	0.00	227.19	4.68	0.00	11.20
S-109	44.00	21.30	6.10	3445.11	71.35	0.00	210.15	15.20	0.00	26.20
S-110	44.00	21.30	6.10	1607.72	718.96	0.00	98.07	153.14	0.00	26.60
S-111	36.00	21.30	6.10	2774.71	762.87	51.87	169.26	162.49	0.00	18.50
S-112	44.00	21.30	6.10	3215.43	27.44	0.00	196.14	5.84	0.00	11.30
SX-101	68.60	21.30	3.50	2129.14	614.68	5.19	74.52	130.93	0.00	13.50
SX-102	44.00	21.30	3.50	2644.35	642.13	0.00	92.55	136.77	0.00	44.00
SX-103	44.00	21.30	3.50	3327.17	631.15	5.19	116.45	134.43	0.00	285.00
SX-104	41.70	21.30	3.50	2967.14	746.40	0.00	103.85	158.98	0.00	5.50
SX-105	44.00	21.30	3.50	3786.51	400.64	0.00	132.53	85.34	0.00	11.00
SX-106	34.60	21.30	3.50	2886.44	65.86	316.40	101.03	14.03	0.00	390.00
SX-107	52.20	23.60	0.00	0.00	570.78	0.00	0.00	134.70	0.00	3200.00
SX-108	50.50	23.60	0.00	0.00	477.48	0.00	0.00	112.68	0.00	2285.00
SX-109	50.50	23.60	0.00	0.00	1372.06	0.00	0.00	323.81	0.00	505.00
SX-110	0.00	23.60	0.00	0.00	340.27	0.00	0.00	80.30	0.00	1735.00
SX-111	53.50	23.60	0.00	0.00	686.03	0.00	0.00	161.90	0.00	3575.00
SX-112	50.50	23.60	0.00	0.00	504.92	0.00	0.00	119.16	0.00	1435.00

Table 7C-1. Input to 50-Year Evaporative Losses and Final Moisture Content Calculations. (4 sheets)

Tank	Supernatant % moisture 95th	Sludge % moisture 95th	Salt % moisture 95th (after JP)	Salt cake (t)	Sludge (t)	Supernatant (t) (before JP)	Salt cake moisture (t)	Sludge moisture (t)	Supernatant moisture (t) (after JP)	50 Year Loss (t)
SX-113	0.00	23.60	0.00	0.00	142.69	0.00	0.00	33.68	0.00	16.70
SX-114	51.10	23.60	0.00	0.00	993.37	0.00	0.00	234.44	0.00	2510.00
SX-115	0.00	23.60	0.00	0.00	65.86	0.00	0.00	15.54	0.00	16.70
T-101	49.30	23.60	0.00	0.00	554.31	5.19	0.00	130.82	2.56	12.10
T-102	49.30	23.60	0.00	0.00	104.28	67.43	0.00	24.61	33.24	23.80
T-103	49.30	23.60	0.00	0.00	126.23	20.75	0.00	29.79	10.23	3.50
T-104	49.30	33.90	0.00	0.00	2425.81	15.56	0.00	822.35	7.67	8.10
T-105	49.30	14.80	0.00	0.00	537.85	0.00	0.00	79.60	0.00	21.50
T-106	49.30	14.80	0.00	0.00	104.28	10.37	0.00	15.43	5.11	3.50
T-107	65.20	27.10	0.00	0.00	938.49	46.68	0.00	254.33	30.44	6.60
T-108	0.00	28.30	0.00	0.00	241.48	0.00	0.00	68.34	0.00	6.70
T-109	0.00	23.60	0.00	0.00	318.32	0.00	0.00	75.12	0.00	5.90
T-110	67.20	23.60	0.00	0.00	2063.58	15.56	0.00	487.01	10.46	3.60
T-111	59.60	23.60	0.00	0.00	2502.64	10.37	0.00	590.62	0.00	2.70
T-112	66.00	23.60	0.00	0.00	329.30	36.31	0.00	77.71	23.96	3.00
TX-101 (c)	49.30	23.60	0.00	0.00	461.01	15.56	0.00	108.80	7.67	26.20
TX-102 (c)	44.00	0.00	3.01	1347.01	0.00	0.00	40.54	0.00	0.00	8.50
TX-103	41.80	23.60	0.00	0.00	861.66	0.00	0.00	203.35	0.00	2.30
TX-104	39.20	0.00	6.10	397.27	0.00	5.19	24.23	0.00	0.00	4.10
TX-105	44.00	0.00	6.01	3780.31	0.00	0.00	227.16	0.00	0.00	20.10
TX-106	44.00	0.00	6.01	2811.95	0.00	0.00	168.97	0.00	0.00	3.20
TX-107	44.00	0.00	6.10	217.26	0.00	5.19	13.25	0.00	0.00	3.20
TX-108	0.00	0.00	12.17	831.79	0.00	0.00	101.20	0.00	0.00	4.10
TX-109	44.00	0.00	12.17	2383.64	0.00	0.00	289.99	0.00	0.00	5.90
TX-110	36.60	0.00	12.17	2867.82	0.00	0.00	348.90	0.00	0.00	39.10
TX-111	44.00	0.00	12.17	2296.74	0.00	0.00	279.42	0.00	0.00	18.50
TX-112	44.00	0.00	12.17	4028.60	0.00	0.00	490.12	0.00	0.00	35.60
TX-113	44.00	0.00	12.17	3767.89	0.00	0.00	458.40	0.00	0.00	14.90
TX-114 (c)	44.00	0.00	12.17	3320.96	0.00	0.00	404.03	0.00	0.00	26.20
TX-115	48.20	0.00	12.17	3972.74	0.00	0.00	483.32	0.00	0.00	14.90
TX-116 (c)	44.00	0.00	12.17	3916.87	0.00	0.00	476.53	0.00	0.00	13.60
TX-117 (c)	44.00	0.00	12.17	3885.83	0.00	0.00	472.75	0.00	0.00	20.20
TX-118	44.40	0.00	12.17	2153.97	0.00	0.00	262.05	0.00	0.00	13.20
TY-101	0.00	22.90	0.00	0.00	647.61	0.00	0.00	148.30	0.00	8.20
TY-102	44.00	0.00	12.10	397.27	0.00	0.00	48.07	0.00	0.00	7.30
TY-103	49.30	29.90	0.00	0.00	889.10	0.00	0.00	265.84	0.00	9.50
TY-104	49.30	29.90	0.00	0.00	235.99	15.56	0.00	70.56	7.67	8.10
TY-105	0.00	18.90	0.00	0.00	1267.79	0.00	0.00	239.61	0.00	9.10
TY-106	0.00	18.90	0.00	0.00	93.30	0.00	0.00	17.63	0.00	4.20
U-101	50.50	23.60	0.00	0.00	120.74	5.19	0.00	28.49	7.86	28.50
U-102	48.00	8.70	12.10	1942.92	235.99	93.37	235.09	20.53	0.00	11.10

Table 7C-1. Input to 50-Year Evaporative Losses and Final Moisture Content Calculations. (4 sheets)

Tank	Supernatant % moisture 95th	Sludge % moisture 95th	Salt % moisture 95th (after JP)	Salt cake (t)	Sludge (t)	Supernatant (t) (before JP)	Salt cake moisture (t)	Sludge moisture (t)	Supernatant moisture (t) (after JP)	50 Year Loss (t)
U-103	47.80	8.70	12.10	2625.73	175.62	67.43	317.71	15.28	0.00	16.90
U-104	49.30	23.60	0.00	0.00	669.57	0.00	0.00	158.02	0.00	14.00
U-105	48.90	24.50	6.10	2166.38	175.62	191.92	132.15	43.03	0.00	58.10
U-106	47.20	8.70	12.10	1148.37	142.69	77.80	138.95	12.41	0.00	19.70
U-107	48.90	24.50	6.10	2234.66	82.32	160.80	136.31	20.17	0.00	17.40
U-108	48.90	24.50	6.10	2576.07	159.16	124.49	157.14	38.99	0.00	15.60
U-109	48.20	24.50	6.10	2458.13	263.44	98.55	149.95	64.54	0.00	20.40
U-110	49.30	14.80	0.00	0.00	1020.81	0.00	0.00	151.08	0.00	17.20
U-111	48.20	8.70	12.10	1880.84	142.69	0.00	227.58	12.41	0.00	12.90
U-112	49.30	23.60	0.00	0.00	246.97	20.75	0.00	58.29	10.23	14.30

Note: Average temperature was estimated using the following references.

Kummerer, M., 1994, Topical Report on Heat Removal Characteristics of Waste Storage Tanks, WHC-SD-WM-SARR-010, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

(a)BY-103, BY-105, BY-106 are subject to alternate evaluation of Section 7.3

(b)Tank C-106 is not considered because of active water addition.

(c)Thermocouple trees out of service. Alternate method of computing evaporation based on heat load in C. H. Brevick, L. A. Gaddis, and E. D. Johnson, 1995, Historical Tank Content Estimate for the Northwest Quadrant of the Hanford 200 East Areas, WHC-SD-WM-ER-351, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

JP = jet pumping.

Table 7C-2. Final 50-Year Moisture Contents: Post-Jet-Pumping, 95th Quantile Initial Moisture Values. (4 sheets)

Tank	Final supernatant moisture at 5% (t)	Final supernatant moisture at 0% (t)	Final salt cake moisture at 5% (t)	Final salt cake moisture at 0% (t)	Final sludge moisture (before consolidation) (t)	Final sludge % moisture (before consolidation)	Final supernatant moisture wt%	Final salt moisture wt%	Final sludge moisture wt% (after consolidation)
A-101	0.00	0.00	610.54	610.54	3.03	18.40	0.00	10.54	15.40
A-102	0.00	0.00	6.31	0.00	0.00	0.00	0.00	0.00	0.00
A-103	0.87	0.00	0.00	0.00	325.17	16.55	0.00	0.00	13.55
A-104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A-105	0.00	0.00	0.00	0.00	5.91	6.91	0.00	0.00	3.91
A-106	0.00	0.00	0.00	0.00	155.56	22.79	0.00	0.00	19.79
AX-101	0.00	0.00	559.57	559.57	3.03	18.40	0.00	12.10	15.40
AX-102	0.00	0.00	21.78	21.78	9.07	23.60	0.00	12.10	20.60
AX-103	0.00	0.00	82.62	82.62	2.59	23.60	0.00	12.10	20.60
AX-104	0.00	0.00	0.00	0.00	9.07	23.60	0.00	0.00	20.60
B-101	0.00	0.00	0.00	0.00	6.70	1.23	0.00	0.00	0.00
B-102	0.00	0.00	2.87	0.31	10.68	11.10	0.00	0.57	8.10
B-103	0.00	0.00	0.00	0.00	37.79	11.88	0.00	0.00	8.88
B-104	0.00	0.00	45.23	45.23	389.86	23.60	0.00	10.72	20.60
B-105	0.00	0.00	192.99	192.99	52.69	24.00	0.00	11.74	21.00
B-106	0.12	0.00	0.00	0.00	177.25	27.97	0.00	0.00	24.97
B-107	0.13	0.00	0.00	0.00	237.16	26.44	0.00	0.00	23.44
B-108	0.00	0.00	0.00	0.00	132.14	25.90	0.00	0.00	22.90
B-109	0.00	0.00	0.00	0.00	181.00	26.16	0.00	0.00	23.16
B-110	0.14	0.00	0.00	0.00	307.65	23.05	0.00	0.00	20.05
B-111	0.14	0.00	0.00	0.00	255.49	20.52	0.00	0.00	17.52
B-112	0.87	0.87	0.00	0.00	38.86	23.60	9.95	0.00	20.60
BX-101	0.12	0.00	0.00	0.00	34.70	15.37	0.00	0.00	12.37
BX-102	0.00	0.00	0.00	0.00	81.10	15.66	0.00	0.00	12.66
BX-103	0.36	0.00	0.00	0.00	43.31	13.31	0.00	0.00	10.31
BX-104	0.29	0.00	0.00	0.00	41.76	8.73	0.00	0.00	5.73
BX-105	0.00	0.00	0.86	0.00	31.85	14.00	0.00	0.00	11.00
BX-106	30.29	30.29	0.00	0.00	29.09	17.10	43.15	0.00	14.10
BX-107	0.12	0.00	0.00	0.00	530.01	28.14	0.00	0.00	25.14
BX-108	0.00	0.00	0.00	0.00	5.90	4.75	0.00	0.00	1.75
BX-109	0.00	0.00	0.00	0.00	172.13	16.39	0.00	0.00	13.39
BX-110	0.00	0.00	2.58	0.00	269.14	26.44	0.00	0.00	23.44
BX-111	0.00	0.00	101.11	101.11	103.75	27.80	0.00	11.47	24.80
BX-112	0.13	0.00	0.00	0.00	234.66	26.24	0.00	0.00	23.24
BY-101	0.00	0.00	200.44	200.44	100.50	16.80	0.00	11.68	13.80
BY-102	0.00	0.00	229.92	229.92	0.00	0.00	0.00	11.00	0.00
BY-103[a]	0.00	0.00	281.28	281.28	4.61	16.80	0.00	11.54	13.80
BY-104	0.00	0.00	230.76	230.76	36.88	16.80	0.00	10.30	13.80
BY-105[a]	0.00	0.00	313.85	313.85	40.57	16.80	0.00	11.14	13.80

Table 7C-2. Final 50-Year Moisture Contents: Post-Jet-Pumping, 95th Quantile Initial Moisture Values. (4 sheets)

Tank	Final supernatant moisture at 5% (t)	Final supernatant moisture at 0% (t)	Final salt cake moisture at 5% (t)	Final salt cake moisture at 0% (t)	Final sludge moisture (before consolidation) (t)	Final sludge % moisture (before consolidation)	Final supernatant moisture wt%	Final salt moisture wt%	Final sludge moisture wt% (after consolidation)
BY-106[a]	0.00	0.00	372.35	372.35	87.59	16.80	0.00	11.09	13.80
BY-107	0.00	0.00	121.67	121.67	55.32	16.80	0.00	9.77	13.80
BY-108	0.00	0.00	21.22	19.38	140.15	16.62	0.00	4.58	13.62
BY-109	0.00	0.00	251.27	251.27	107.50	23.60	0.00	11.93	20.60
BY-110	0.00	0.00	198.98	198.98	94.97	16.80	0.00	11.01	13.80
BY-111	0.00	0.00	315.87	315.87	19.36	16.80	0.00	11.68	13.80
BY-112	0.00	0.00	197.48	197.48	4.61	16.80	0.00	11.24	13.80
C-101	0.00	0.00	0.00	0.00	74.19	15.63	0.00	0.00	12.63
C-102	0.00	0.00	0.00	0.00	496.78	21.88	0.00	0.00	18.88
C-103	376.07	376.07	0.00	0.00	80.30	23.60	60.49	0.00	20.60
C-104	0.00	0.00	0.00	0.00	368.59	22.96	0.00	0.00	19.96
C-105	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C-106[b]									
C-107	0.00	0.00	0.00	0.00	288.69	20.02	0.00	0.00	17.02
C-108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C-109	0.47	0.00	0.00	0.00	83.56	25.20	0.00	0.00	22.20
C-110	0.00	0.00	0.00	0.00	264.74	26.46	0.00	0.00	23.46
C-111	0.00	0.00	0.00	0.00	76.38	25.09	0.00	0.00	22.09
C-112	0.00	0.00	0.00	0.00	132.68	24.18	0.00	0.00	21.18
S-101	0.00	0.00	52.43	0.00	223.86	17.52	0.00	0.00	14.52
S-102	0.00	0.00	178.07	178.07	4.68	21.30	0.00	5.31	18.30
S-103	0.00	0.00	67.76	67.28	11.22	20.61	0.00	4.96	17.61
S-104	0.14	0.00	0.00	0.00	335.79	21.46	0.00	0.00	18.46
S-105	0.00	0.00	159.94	159.94	2.34	21.30	0.00	5.69	18.30
S-106	0.00	0.00	159.56	159.56	32.73	21.30	0.00	5.77	18.30
S-107	0.00	0.00	21.15	0.00	311.59	19.76	0.00	0.00	16.76
S-108	0.00	0.00	215.99	215.99	4.68	21.30	0.00	5.82	18.30
S-109	0.00	0.00	183.95	183.95	15.20	21.30	0.00	5.38	18.30
S-110	0.00	0.00	79.41	71.47	145.20	20.42	0.00	4.52	17.42
S-111	0.00	0.00	150.76	150.76	162.49	21.30	0.00	5.47	18.30
S-112	0.00	0.00	184.84	184.84	5.84	21.30	0.00	5.77	18.30
SX-101	0.00	0.00	108.07	61.02	83.87	14.78	0.00	2.88	11.78
SX-102	0.00	0.00	134.22	48.55	51.10	9.18	0.00	1.87	6.18
SX-103	0.00	0.00	168.88	0.00	0.00	0.00	0.00	0.00	0.00
SX-104	0.00	0.00	150.61	98.35	106.72	15.38	0.00	3.32	12.38
SX-105	0.00	0.00	192.20	121.53	14.67	4.44	0.00	3.22	1.44
SX-106	0.00	0.00	146.51	0.00	0.00	0.00	0.00	0.00	0.00
SX-107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 7C-2. Final 50-Year Moisture Contents: Post-Jet-Pumping, 95th Quantile Initial Moisture Values. (4 sheets)

Tank	Final supernatant moisture at 5% (t)	Final supernatant moisture at 0% (t)	Final salt cake moisture at 5% (t)	Final salt cake moisture at 0% (t)	Final sludge moisture (before consolidation) (t)	Final sludge % moisture (before consolidation)	Final supernatant moisture wt%	Final salt moisture wt%	Final sludge moisture wt% (after consolidation)
SX-109	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-113	0.00	0.00	0.00	0.00	16.98	13.47	0.00	0.00	10.47
SX-114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SX-115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
T-101	0.14	0.00	0.00	0.00	121.14	22.24	0.00	0.00	19.24
T-102	9.44	9.44	0.00	0.00	24.61	23.60	21.64	0.00	20.60
T-103	6.73	6.73	0.00	0.00	29.79	23.60	39.01	0.00	20.60
T-104	0.41	0.00	0.00	0.00	821.50	33.88	0.00	0.00	30.88
T-105	0.00	0.00	0.00	0.00	58.10	11.25	0.00	0.00	8.25
T-106	1.61	1.61	0.00	0.00	15.43	14.80	23.48	0.00	11.80
T-107	23.84	23.84	0.00	0.00	254.33	27.10	59.47	0.00	24.10
T-108	0.00	0.00	0.00	0.00	61.64	26.25	0.00	0.00	23.25
T-109	0.00	0.00	0.00	0.00	69.22	22.16	0.00	0.00	19.16
T-110	6.86	6.86	0.00	0.00	487.01	23.60	57.33	0.00	20.60
T-111	0.00	0.00	0.00	0.00	587.92	23.52	0.00	0.00	20.52
T-112	20.96	20.96	0.00	0.00	77.71	23.60	62.94	0.00	20.60
TX-101[c]	0.41	0.00	0.00	0.00	89.86	20.33	0.00	0.00	17.33
TX-102[c]	0.00	0.00	68.72	32.04	0.00	0.00	0.00	2.39	0.00
TX-103	0.00	0.00	0.00	0.00	201.05	23.40	0.00	0.00	20.40
TX-104	0.00	0.00	20.13	20.13	0.00	0.00	0.00	5.12	0.00
TX-105	0.00	0.00	207.06	207.06	0.00	0.00	0.00	5.51	0.00
TX-106	0.00	0.00	165.77	165.77	0.00	0.00	0.00	5.90	0.00
TX-107	0.00	0.00	10.73	10.05	0.00	0.00	0.00	4.70	0.00
TX-108	0.00	0.00	97.10	97.10	0.00	0.00	0.00	11.73	0.00
TX-109	0.00	0.00	284.09	284.09	0.00	0.00	0.00	11.95	0.00
TX-110	0.00	0.00	309.80	309.80	0.00	0.00	0.00	10.95	0.00
TX-111	0.00	0.00	260.92	260.92	0.00	0.00	0.00	11.45	0.00
TX-112	0.00	0.00	454.52	454.52	0.00	0.00	0.00	11.38	0.00
TX-113	0.00	0.00	443.50	443.50	0.00	0.00	0.00	11.82	0.00
TX-114[c]	0.00	0.00	377.83	377.83	0.00	0.00	0.00	11.47	0.00
TX-115	0.00	0.00	468.42	468.42	0.00	0.00	0.00	11.84	0.00
TX-116[c]	0.00	0.00	462.93	462.93	0.00	0.00	0.00	11.86	0.00
TX-117[c]	0.00	0.00	452.55	452.55	0.00	0.00	0.00	11.71	0.00
TX-118	0.00	0.00	248.85	248.85	0.00	0.00	0.00	11.62	0.00
TY-101	0.00	0.00	0.00	0.00	140.10	21.91	0.00	0.00	18.91
TY-102	0.00	0.00	40.77	40.77	0.00	0.00	0.00	10.45	0.00

Table 7C-2. Final 50-Year Moisture Contents: Post-Jet-Pumping, 95th Quantile Initial Moisture Values. (4 sheets)

Tank	Final supernatant moisture at 5% (t)	Final supernatant moisture at 0% (t)	Final salt cake moisture at 5% (t)	Final salt cake moisture at 0% (t)	Final sludge moisture (before consolidation) (t)	Final sludge % moisture (before consolidation)	Final supernatant moisture wt%	Final salt moisture wt%	Final sludge moisture wt% (after consolidation)
TY-103	0.00	0.00	0.00	0.00	256.34	29.14	0.00	0.00	26.14
TY-104	0.41	0.00	0.00	0.00	69.72	29.65	0.00	0.00	26.65
TY-105	0.00	0.00	0.00	0.00	230.51	18.31	0.00	0.00	15.31
TY-106	0.00	0.00	0.00	0.00	13.43	15.08	0.00	0.00	12.08
U-101	0.41	0.00	0.00	0.00	7.45	7.47	0.00	0.00	4.47
U-102	0.00	0.00	223.99	223.99	20.53	8.70	0.00	11.59	5.70
U-103	0.00	0.00	300.81	300.81	15.28	8.70	0.00	11.53	5.70
U-104	0.00	0.00	0.00	0.00	144.02	21.97	0.00	0.00	18.97
U-105	0.00	0.00	107.00	74.05	10.08	7.06	0.00	3.51	4.06
U-106	0.00	0.00	119.25	119.25	12.41	8.70	0.00	10.57	5.70
U-107	0.00	0.00	118.91	118.91	20.17	24.50	0.00	5.36	21.50
U-108	0.00	0.00	141.54	141.54	38.99	24.50	0.00	5.53	21.50
U-109	0.00	0.00	129.55	129.55	64.54	24.50	0.00	5.31	21.50
U-110	0.00	0.00	0.00	0.00	133.88	13.34	0.00	0.00	10.34
U-111	0.00	0.00	214.68	214.68	12.41	8.70	0.00	11.49	5.70
U-112	0.55	0.00	0.00	0.00	53.66	22.14	0.00	0.00	19.14

Note: Average temperature was estimated using the following references.

- Kummerer, M., 1994, Topical Report on Heat Removal Characteristics of Waste Storage Tanks, WHC-SD-WM-SARR-010, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

[a] BY-103, BY-105, BY-106 are subject to alternate evaluation of Section 7.3.

[b] Tank C-106 is not considered because of active water addition.

[c] Thermocouple trees out of service. Alternate method of computing evaporation based on heat load in C. H. Brevick, L. A. Gaddis, and E. D. Johnson, 1995, Historical Tank Content Estimate for the Northwest Quadrant of the Hanford 200 East Areas, WHC-SD-WM-ER-351, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

JP = jet pumping.

Supernatant moisture loss is the initial supernatant moisture minus the final supernatant moisture at 0%.

- Final salt moisture percent is defined as

$$\frac{100 \times \text{Final salt cake moisture at 0\%}}{\text{Salt cake (metric tons)} - \text{Salt cake moisture loss}}.$$

Salt cake moisture loss is the initial salt cake moisture minus the final salt cake moisture at 0%.

- Final sludge moisture percent (after consolidation) simply subtracts 3.0 from the final sludge moisture percent (before consolidation) but limits the final value to zero.

2.0 SINGLE-SHELL TANK STATUS AFTER 50 YEARS

Table 7C-2 shows single-shell tank status at the end of the 50-year mission. As with the current tank status table (Table 7B-1), the TOC and moisture content pair for each phase is compared with the safety criteria line defined in Chapter 5. If the pair meets the criteria, it is listed as "SAFE." If not, it is listed as "CONDSAFE."

Final moisture contents are from Table 7C-1. On a wet basis, TOC values change with time as moisture is lost. Final TOC values on a wet basis are easily computed if it is recognized that TOC values on a dry basis do not change as a result of evaporative moisture loss.[1] Wet basis TOC values and dry basis TOC values are related by

$$X_{TOCW} = X_{TOCD} \left(1 - X_W\right) \qquad (7C\text{-}1)$$

where

X_{TOCW} = the wet basis TOC
X_{TOCD} = the dry basis TOC
X_W = the moisture content.

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[1] This is not necessarily true with regard to consolidation since the liquid expelled contains TOC and dissolved non-fuel salts. Consolidation is not the dominant moisture loss mechanism. However, sludges are far less a concern than salt cakes, which do not undergo consolidation. For practical purposes, the dry basis TOC stays the same in all phases.

Because the dry basis TOC remains the same,

$$\frac{X_{TOCW}}{1-X_W} = \frac{X'_{TOCW}}{1-X'_W} \qquad (7C\text{-}2)$$

where the superscript on the right-hand side denotes the after-50-year values. This equation is used to compute final TOC values on a wet basis given the initial TOC value on a wet basis, the initial moisture content, and the final moisture content.

Table 7C-3 shows the tank status after jet pumping and 50 years of moisture losses.

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
A-101	0.00	10.54	15.40	5.82	4.46	2.49	SAFE	SAFE
A-102	0.00	0.00	0.00	2.37	7.98	3.06	CONDSAFE	SAFE
A-103	0.00	0.00	13.55	3.93	0.00	2.75	N/A	SAFE
A-104	0.00	0.00	0.00	0.00	0.00	0.79	N/A	SAFE
A-105	0.00	0.00	3.91	2.17	0.00	0.75	N/A	SAFE
A-106	0.00	0.00	19.79	29.46	0.00	1.98	N/A	SAFE
AX-101	0.00	12.10	15.40	4.38	5.13	2.18	SAFE	SAFE
AX-102	0.00	12.10	20.60	7.90	3.55	0.62	SAFE	SAFE
AX-103	0.00	12.10	20.60	5.27	4.50	0.62	SAFE	SAFE
AX-104	0.00	0.00	20.60	0.00	0.00	0.62	N/A	SAFE
B-101	0.00	0.00	0.00	2.35	0.00	0.69	N/A	SAFE
B-102	0.00	0.57	8.10	2.20	6.59	0.64	CONDSAFE	SAFE
B-103	0.00	0.00	8.88	0.00	0.00	0.63	N/A	SAFE
B-104	0.00	10.72	20.60	2.17	5.94	0.62	SAFE	SAFE
B-105	0.00	11.74	21.00	1.96	5.63	0.31	SAFE	SAFE
B-106	0.00	0.00	24.97	1.82	0.00	0.31	N/A	SAFE
B-107	0.00	0.00	23.44	2.36	0.00	1.25	N/A	SAFE
B-108	0.00	0.00	22.90	2.36	0.00	1.26	N/A	SAFE
B-109	0.00	0.00	23.16	2.68	0.00	1.26	N/A	SAFE
B-110	0.00	0.00	20.05	2.17	0.00	0.21	N/A	SAFE
B-111	0.00	0.00	17.52	2.17	0.00	0.43	N/A	SAFE
B-112	9.95	0.00	20.60	1.95	0.00	0.31	N/A	SAFE
BX-101	0.00	0.00	12.37	3.41	0.00	0.95	N/A	SAFE
BX-102	0.00	0.00	12.66	3.41	0.00	0.95	N/A	SAFE
BX-103	0.00	0.00	10.31	4.60	0.00	0.97	N/A	SAFE
BX-104	0.00	0.00	5.73	5.37	0.00	1.14	N/A	SAFE

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
BX-105	0.00	0.00	11.00	5.34	5.71	1.07	CONDSAFE	SAFE
BX-106	43.15	0.00	14.10	1.55	0.00	0.93	N/A	SAFE
BX-107	0.00	0.00	25.14	1.77	0.00	0.31	N/A	SAFE
BX-108	0.00	0.00	1.75	3.41	0.00	1.07	N/A	SAFE
BX-109	0.00	0.00	13.39	2.39	0.00	0.94	N/A	SAFE
BX-110	0.00	0.00	23.44	2.60	7.37	0.21	CONDSAFE	SAFE
BX-111	0.00	11.47	24.80	0.00	5.94	0.21	SAFE	SAFE
BX-112	0.00	0.00	23.24	2.58	0.00	1.68	N/A	SAFE
BY-101	0.00	11.68	13.80	1.73	5.13	0.62	SAFE	SAFE
BY-102	0.00	11.00	0.00	1.20	6.70	0.00	CONDSAFE	N/A
BY-103	0.00	11.54	13.80	1.48	8.20	0.62	SAFE[a]	SAFE
BY-104	0.00	10.30	13.80	1.73	5.17	0.62	SAFE	SAFE
BY-105	0.00	11.14	13.80	1.51	8.11	0.62	SAFE[a]	SAFE
BY-106	0.00	11.09	13.80	1.45	8.37	0.62	SAFE[a]	SAFE
BY-107	0.00	9.77	13.80	1.91	5.24	0.62	SAFE	SAFE
BY-108	0.00	4.58	13.62	1.73	5.54	0.62	CONDSAFE	SAFE
BY-109	0.00	11.93	20.60	2.14	6.11	0.62	SAFE	SAFE
BY-110	0.00	11.01	13.80	1.73	5.17	0.62	SAFE	SAFE
BY-111	0.00	11.68	13.80	0.00	5.13	0.62	SAFE	SAFE
BY-112	0.00	11.24	13.80	1.73	5.15	0.62	SAFE	SAFE
C-101	0.00	0.00	12.63	3.41	0.00	0.95	N/A	SAFE
C-102	0.00	0.00	18.88	2.17	0.00	0.64	N/A	SAFE
C-103	60.49	0.00	20.60	2.55	0.00	1.04	N/A	SAFE
C-104	0.00	0.00	19.96	4.65	0.00	1.26	N/A	SAFE
C-105	0.00	0.00	0.00	1.97	0.00	0.52	N/A	SAFE
C-106 [b]								

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
C-107	0.00	0.00	17.02	1.18	0.00	0.65	N/A	SAFE
C-108	0.00	0.00	0.00	0.00	0.00	0.96	N/A	SAFE
C-109	0.00	0.00	22.20	1.61	0.00	1.07	N/A	SAFE
C-110	0.00	0.00	23.46	1.17	0.00	0.32	N/A	SAFE
C-111	0.00	0.00	22.09	0.00	0.00	0.75	N/A	SAFE
C-112	0.00	0.00	21.18	1.27	0.00	1.30	N/A	SAFE
S-101	0.00	0.00	14.52	4.30	3.65	0.65	SAFE	SAFE
S-102	0.00	5.31	18.30	6.36	3.06	0.62	SAFE	SAFE
S-103	0.00	4.96	17.61	3.39	3.50	0.63	SAFE	SAFE
S-104	0.00	0.00	18.46	2.42	0.00	0.64	N/A	SAFE
S-105	0.00	5.69	18.30	3.08	3.31	0.62	SAFE	SAFE
S-106	0.00	5.77	18.30	3.02	3.50	0.62	SAFE	SAFE
S-107	0.00	0.00	16.76	3.17	3.69	0.63	SAFE	SAFE
S-108	0.00	5.82	18.30	3.39	3.47	0.62	SAFE	SAFE
S-109	0.00	5.38	18.30	3.39	3.49	0.62	SAFE	SAFE
S-110	0.00	4.52	17.42	5.00	3.29	0.63	SAFE	SAFE
S-111	0.00	5.47	18.30	2.50	3.48	0.62	SAFE	SAFE
S-112	0.00	5.77	18.30	3.39	3.48	0.62	SAFE	SAFE
SX-101	0.00	2.88	11.78	3.18	3.47	0.67	SAFE	SAFE
SX-102	0.00	1.87	6.18	3.39	3.45	0.72	SAFE	SAFE
SX-103	0.00	0.00	0.00	3.39	3.50	0.76	SAFE	SAFE
SX-104	0.00	3.32	12.38	2.06	3.48	0.67	SAFE	SAFE
SX-105	0.00	3.22	1.44	3.39	3.39	0.75	SAFE	SAFE
SX-106	0.00	0.00	0.00	29.05	2.32	0.76	SAFE	SAFE
SX-107	0.00	0.00	0.00	2.72	0.00	0.79	N/A	SAFE
SX-108	0.00	0.00	0.00	2.42	0.00	0.79	N/A	SAFE

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
SX-109	0.00	0.00	0.00	2.42	0.00	0.79	N/A	SAFE
SX-110	0.00	0.00	0.00	0.00	0.00	0.79	N/A	SAFE
SX-111	0.00	0.00	0.00	2.37	0.00	0.79	N/A	SAFE
SX-112	0.00	0.00	0.00	2.42	0.00	0.79	N/A	SAFE
SX-113	0.00	0.00	10.47	0.00	0.00	0.70	N/A	SAFE
SX-114	0.00	0.00	0.00	2.25	0.00	0.79	N/A	SAFE
SX-115	0.00	0.00	0.00	0.00	0.00	0.79	N/A	SAFE
T-101	0.00	0.00	19.24	0.99	0.00	0.63	N/A	SAFE
T-102	21.64	0.00	20.60	1.24	0.00	0.62	N/A	SAFE
T-103	39.01	0.00	20.60	0.96	0.00	0.62	N/A	SAFE
T-104	0.00	0.00	30.88	0.99	0.00	0.21	N/A	SAFE
T-105	0.00	0.00	8.25	2.17	0.00	0.43	N/A	SAFE
T-106	23.48	0.00	11.80	1.66	0.00	0.41	N/A	SAFE
T-107	59.47	0.00	24.10	0.35	0.00	0.31	N/A	SAFE
T-108	0.00	0.00	23.25	0.00	0.00	0.32	N/A	SAFE
T-109	0.00	0.00	19.16	0.00	0.00	0.63	N/A	SAFE
T-110	57.33	0.00	20.60	1.30	0.00	0.94	N/A	SAFE
T-111	0.00	0.00	20.52	2.48	0.00	1.14	N/A	SAFE
T-112	62.94	0.00	20.60	0.98	0.00	0.94	N/A	SAFE
TX-101	0.00	0.00	17.33	2.17	0.00	0.65	N/A	SAFE
TX-102	0.00	2.39	0.00	2.32	3.41	0.00	SAFE	N/A
TX-103	0.00	0.00	20.40	1.89	0.00	0.63	N/A	SAFE
TX-104	0.00	5.12	0.00	3.13	3.52	0.00	SAFE	N/A
TX-105	0.00	5.51	0.00	4.29	3.32	0.00	SAFE	N/A
TX-106	0.00	5.90	0.00	3.21	3.30	0.00	SAFE	N/A
TX-107	0.00	4.70	0.00	3.39	3.51	0.00	SAFE	N/A

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
TX-108	0.00	11.73	0.00	0.00	4.72	0.00	SAFE	N/A
TX-109	0.00	11.95	0.00	2.86	4.01	0.00	SAFE	N/A
TX-110	0.00	10.95	0.00	2.21	4.06	0.00	SAFE	N/A
TX-111	0.00	11.45	0.00	2.50	4.03	0.00	SAFE	N/A
TX-112	0.00	11.38	0.00	1.96	4.04	0.00	SAFE	N/A
TX-113	0.00	11.82	0.00	1.96	4.02	0.00	SAFE	N/A
TX-114	0.00	11.47	0.00	1.79	4.03	0.00	SAFE	N/A
TX-115	0.00	11.84	0.00	0.97	5.02	0.00	SAFE	N/A
TX-116	0.00	11.86	0.00	1.25	4.01	0.00	SAFE	N/A
TX-117	0.00	11.71	0.00	1.96	4.02	0.00	SAFE	N/A
TX-118	0.00	11.62	0.00	7.55	4.73	0.00	SAFE	N/A
TY-101	0.00	0.00	18.91	0.00	0.00	0.00	N/A	SAFE
TY-102	0.00	10.45	0.00	1.96	6.86	0.00	CONDSAFE	N/A
TY-103	0.00	0.00	26.14	1.58	0.00	0.32	N/A	SAFE
TY-104	0.00	0.00	26.65	1.58	0.00	0.94	N/A	SAFE
TY-105	0.00	0.00	15.31	0.00	0.00	0.42	N/A	SAFE
TY-106	0.00	0.00	12.08	0.00	0.00	0.65	N/A	SAFE
U-101	0.00	0.00	4.47	2.42	0.00	0.75	N/A	SAFE
U-102	0.00	11.59	5.70	3.46	6.61	1.24	CONDSAFE	SAFE
U-103	0.00	11.53	5.70	3.45	6.62	1.65	CONDSAFE	SAFE
U-104	0.00	0.00	18.97	2.17	0.00	0.64	N/A	SAFE
U-105	0.00	3.51	4.06	2.15	6.04	0.76	CONDSAFE	SAFE
U-106	0.00	10.57	5.70	11.74	3.23	1.24	SAFE	SAFE
U-107	0.00	5.36	21.50	2.15	5.96	0.62	CONDSAFE	SAFE
U-108	0.00	5.53	21.50	2.15	5.95	0.62	CONDSAFE	SAFE
U-109	0.00	5.31	21.50	2.12	6.63	0.00	CONDSAFE	SAFE

Table 7C-3. Tank Status After Jet Pumping and 50 Years of Evaporative Losses. (6 sheets)

Tank	Final supernatant moisture wt% at 50 years	Final salt moisture wt% at 50 years	Final sludge moisture wt% at 50 years	Final supernatant TOC % at 50 years	Final salt TOC % at 50 years	Final sludge TOC % at 50 years	Salt cake 50-year status	Sludge 50-year status
U-110	0.00	0.00	10.34	2.17	0.00	0.00	N/A	SAFE
U-111	0.00	11.49	5.70	8.11	4.91	1.24	SAFE	SAFE
U-112	0.00	0.00	19.14	2.17	0.00	0.00	N/A	SAFE

[a] BY-103, BY-105, and BY-106 are re-evaluated in Section 7-3.
[b] C-106 has active moisture addition and therefore evaporation was not calculated.

CONDSAFE = does not meet safety criteria.
SAFE = meets safety criteria.
TOC = total organic carbon.

APPENDIX 7D

POTENTIAL DRYNESS EVALUATION OF TANKS A-102, BX-110, BY-102, AND TY-102

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APPENDIX 7D

POTENTIAL DRYNESS EVALUATION OF TANKS A-102, BX-110, BY-102, AND TY-102

1.0 INTRODUCTION

The computations in this document are based primarily upon laboratory analysis results for tank waste samples and upon WHC-EP-0182-72, *Tank Farm Surveillance and Waste Status Summary Report for March 1994* (Hanlon 1994). The values used from Hanlon (1994) include the wastes identified by phase as "liquids, sludges, and salt cakes" and the volume amounts of each of those phases present in particular tanks. These volume amounts were converted to masses by using phase densities based upon laboratory analyses.

Four CONDITIONALLY SAFE tanks, A-102, BX-110, BY-102, and TY-102 were selected for a dryness evaluation because the results of the analysis described in Chapter 7 indicate that draining the tanks could cause them to lose enough moisture to exceed preliminary safety criteria. The calculations in Chapter 7 were based upon the interim stabilization status presented in Hanlon (1994). Members of the Plant Review Committee thought that these four tanks had already been drained. If that was so, there concern that the tanks were already too dry and therefore should be classified as UNSAFE. This evaluation was conducted to determine from existing data sources whether there was reason to believe that any of these four tanks already may be too dry.

The evaluation showed that there are some conflicts between the March 1994 (Hanlon 1994) data, which forms the primary database for certain parameters, and later information (see references in this appendix). Though there are some conflicting values, the overall assessment is that none of these tanks is expected to be excessively dry based upon the data evaluated. Further tank characterization should be pursued for these selected tanks (and for the remaining CONDITIONALLY SAFE tanks) to verify this conclusion. (Chapter 7's conservative modeling for draining effects did not take full advantage of the solubility of energetic organic compounds. In a future revision of this report, this effect is expected to show that most salt cakes will be very low in fuel as a result of draining. The alternative evaluations performed in this Appendix for the four selected tanks do account for this effect.)

2.0 ALTERNATIVE EVALUATIONS

2.1 TANK A-102

2.1.1 Waste Phase and Amounts Comparisons

Page 41 from WHC-SD-WM-ER-349, *Historical Tank Content Estimate for the Northeast Quadrant of the Hanford 200 East Areas* (Brevick et al. 1994a), indicates that the waste volumes for tank A-102 are as follows:

Supernatant	4 kgal	
A2 Salt slurry	15 kgal	
A1 Salt cake	19 kgal	(34 kgal total salt cake)
B Plant strontium recovery waste (SRR)	3 kgal	
Total	41 kgal.	

Note that WHC-EP-0182-87, *Waste Tank Summary Report for Month Ending June 30, 1995* (Hanlon 1995), reports significantly different values for this tank:

Supernatant	4 kgal	
Salt cake	22 kgal	(22 kgal total salt cake)
Sludge	15 kgal	
(Drainable liquid	6 kgal)	

Total volume agrees with Brevick et al. (1994a).

Because this tank was calculated to exceed safety criteria upon jet-pumping, the difference between the calculation performed for the Hanlon (1995) value of 83 kL (22 kgal) of salt cake and a calculation performed for the Brevick et al. (1994a) value of 129 kL (34 kgal) of salt cake would be negligible. (However, subsequent drying of A-102 salt cake would take longer if the larger amount of salt cake were used for the calculation.)

It is recommended that analysis of material (such as from the recent auger sampling) be conducted to identify major constituents and phases and to resolve the discrepancies between these two major references above.

2.1.2 Sample Dataset

Appendix F of PNL-10360, *Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste* (Toth et al. 1995), provides the laboratory measurement sample dataset. The measurements in Table 7D-1 were taken from that appendix.

If we throw out the suspect total organic carbon (TOC) value in sample T-1243, the average TOC of 11 liquid samples over the years is 0.43 wt%. For the total dataset of liquid samples used in the ANOVA calculations, this falls between the mean of 0.37 wt% and the upper 95% confidence value of 0.46 wt%.

Table 7D-1. Measurements for Tank A-102 Samples.*

Sample ID	Waste phase	Density (g/mL)	H_2O (wt%)	Wet TOC (wt%)	Reference date	Comments
91DX00XX	Liquid	1.5	48.9	0.53	3-6-86	
91XC00XX	Sludge	1.5	40.92	0.72	3-6-86	
92DX00XX	Liquid	1.5	49.60	0.51	3-8-86	
92XC00XX	Sludge	1.7	29.40	0.79	3-8-86	
R-4656	Liquid	NA	NA	0.96	3-14-89	
RAT-A102-1	Liquid	NA	NA	0.12	12-23-80	
RAT-A102-2	Liquid	NA	NA	0.21	10-23-79	
RAT-A102-3	Liquid	NA	NA	0.35	3-14-79	
T-1243	Liquid	NA	NA	0.00	7-17-80	Suspect value
T-1244	Liquid	NA	NA	0.35	7-17-80	
T-1245	Liquid	NA	NA	0.29	7-17-80	
T-2404	Liquid	NA	NA	0.49	8-4-80	
T-2405	Liquid	NA	NA	0.53	8-4-80	
T-6176	Liquid	NA	NA	0.40	12-8-79	
RAT-A102-2	Liquid	NA	41.5	NA	12-23-80	

*Toth, J. J., M. E. Lerchan, J. G. Hill, P. G. Heasler, and P. D. Whitney,, 1995, Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.

It is concluded that the liquid TOC values over this period of years are not unusual and not excessive.

2.1.3 Sampling Results

A recent 45-day auger report for tank A-102, WHC-SD-WM-DP-136, *45-Day Safety Screen Results and Final Report for Tank 241-A-102, Auger Sample 95-AUG-033* (Jo 1995), indicates that because only a single auger sample was obtained from the tank instead of the required two, insufficient information was available to classify the tank as "safe" or "not safe." However, no data were obtained that indicate the tank is "not safe."

The laboratory analysis showed the following for the solid waste in the single sample:

- Water by thermogravimetric analysis: 32.1%

- Exotherm (dry) calculated by differential scanning calorimetry: 312.5 J/g.

If we assume that all of this energy was generated by acetate, then the equivalent TOC in wt% would be

312.5 J/g * 4.5 wt% / 1,200 J/g = 1.17 wt% (dry basis).

This would be a very conservative assumption and yields a TOC value that is well within the 4.5 wt% (dry basis) preliminary safety criteria. The amount of moisture is also very encouraging at 32.1%. This can be used to calculate a wet basis TOC for the salt cake matrix:

1.17 wt% TOC dry * (1 - 0.321) = 0.80 wt% TOC (wet basis).

If it is assumed that the liquid in the solids is 50% water, then this is equivalent to approximately 60% of the matrix being liquids (2 x 32% approximately 60%). If all of the TOC in the solid waste were associated with the liquids, then the equivalent liquids TOC would be

0.80 wt% / (1 - 0.4) = 1.33 wt% TOC (wet basis).

While this is somewhat greater than the analyzed TOC in the liquid, it is still well within the preliminary safety criteria.

2.1.4 Total Organic Carbon Solubility Evaluation

WHC-SA-2565-A, *The Solubilities of Significant Organic Compounds in High-Level Waste Tank Supernate Solutions* (Barney 1994b) established that energetic organic compounds, which could rapidly propagate at sufficient concentrations, are highly soluble. In most cases, all of the compound will be dissolved and there will be no solid precipitates of these salts.

The 1.33 wt% TOC (wet basis) above would correspond to about 18 g/L of TOC on a wet basis. Solubilities of energetic organic salts range from citrate with a low of about 36 g/L to ethylenediaminetetraacetic acid (EDTA) at 96 g/L. If the salts are all energetic, they should all be in solution, with no precipitate. However, if a portion of the salts is oxalate, the oxalate, with a solubility of approximately 0.1 g/L, would nearly all be precipitated. But because oxalate is not energetic and cannot sustain a rapid propagation, it would pose no hazard. It is concluded on this basis that the tank waste should be safe.

2.1.5 Level Information

On August 16, 1995, the surface measurement of waste in tank A-102 was 34.5 cm (13.6 in.) according to the Hanford Site's Surveillance Analysis Computer System (SACS). This compares very well with the visual plot in Brevick et al. (1994a, page 41) that shows something slightly greater than 0.3 m (1 ft). A separate reading for liquid level was not available. The supernatant is about the same level as the surface shown in the Brevick et al. (1994a) plot. This plot is always shown as flat, and the data from the SACS support that it has not changed appreciably. One could conclude that it hasn't dried much in the 6 years since the supernatant was pumped.

2.1.6 Preliminary Dryness Evaluation

On page A-3 of WHC-SD-WM-TI-703, *Hanford Waste Tank Preliminary Dryness Evaluation* (Husa et al. 1995), the level of tank A-102 is listed as 37.8 cm (14.9 in.) somewhat higher than the SACS date. On page B-3 of Husa et al. (1995), tank A-102 was assigned a surface dryness rating of "high" because it satisfied several criteria for a potentially dry surface according to their rating system: pumpable liquids less than 20% of total volume stored, salt cake greater than 20% of waste, surface less than 102 cm (40 in.) total depth. Note, however, that this estimates the potential for a dry surface, it does not prove that the surface is dry. The report states that surfaces that do not at least glisten [are reported] as DRY." This means that waste containing substantial free moisture could be rated as dry by Husa et al. (1995).

2.1.7 Supernatant Status

The Waste Tank Summary Report for June 30 (Hanlon 1995), page E-9, indicates that tank A-102 is sound and has 15 kL (4 kgal) of supernatant over 83 kL (22 kgal) of salt cake. If this is true, it cannot be too dry, as 15 kL (4 kgal) of supernatant would provide approximately 4 cm of liquid over the salt cake of concern. Note also that there are only 155 kL (41 kgal) of total waste in the tank.

2.1.8 Stabilization Evaluation

Tank A-102 stabilization evaluation was performed in July 1989. The surface was described as follows in WHC-SD-RE-TI-178, *Single-Shell Tank Stabilization Record* (Swaney 1994):

> "Mottled light and dark solids cover surface of waste in a broken pattern. Many pieces of crust are tilted, with angular shapes. Fifteen to twenty percent of tank surface is composed of liquid supernatant pools covering solids. Pump and FIC plummet are visible."

By photographing the Food Instrument Corporation (FIC) level gauge contacting solids, it was established that the solids level was 38 cm (15 in.). Drainable liquid remaining was 23,091 L (6,100 gal). (This checks with the value reported in Hanlon [1995]).

2.1.9 Interim Stabilization Declaration

Table I-1, page I-2, of Hanlon (1995) indicates that supernatant pumping of tank A-102 occurred in August 1989 and that the tank is considered interim stabilized.

2.1.10 Pumpable Liquid and Jet Pumping Impracticality

Hanlon (1995), page E-9, also indicates that 0 kgal of pumpable liquid remain in tank A-102. The presence of supernatant, drainable liquid, and "no pumpable liquid" is consistent because it is not practical to try to pump a tank with this little salt cake depth. This would indicate that it is not sensible to try to jet pump this tank. It would be prudent to perform further evaluations to ensure that the post-jet pumped state of the tank would be safe before jet pumping is attempted.

2.1.11 Drainage Impact and Safety Categorization

If tank A-102 drained itself, the basic calculations in this document indicate that it could exceed preliminary safety criteria. Note, however, that Hanlon (1995) reports that there are 83 kL (22 kgal) of salt cake present. This corresponds to roughly 22 cm (9 in.) of waste. We believe that sludge underlying the salt cake could help to keep it moist through capillary action.

2.1.12 Conclusion and Recommendations

There is no clear evidence that tank A-102 may have already dried out too much. There is substantial evidence that it has not and also that the salt cake does not contain excessive TOC. The CONDITIONALLY SAFE categorization is correct and priority for characterization should be pursued to help to verify these conclusions. With sufficient data and evaluation, it is expected that tank A-102 could be recategorized to SAFE.

Because there is substantial conflict between Hanlon (1995) and Brevick et al. (1994a) regarding the contents of the tank, the recent auger sample and planned future auger samples should be evaluated for organic compounds present, types and amounts of phases, energy, TOC, and moisture. Grab samples of liquids should also be obtained and analyzed for the same items. It would be very helpful to cross-correlate these, as it is believed that grab sample results can help to infer salt cake contents, especially regarding the maximum amounts of precipitated energetic organic compounds that may be present.

2.2 TANK BX-110

2.2.1 Waste Phase and Amounts Comparisons

Page 223 of Brevick et al. (1994a) indicates that the waste volumes for tank BX-110 are as follows:

Supernatant	1 kgal
BY salt cake	42 kgal
1st cycle sludge	156 kgal
Total waste	199 kgal.

Table E-6 of the Waste Tank Summary Report for June (Hanlon 1995) indicates that BX-110 contains the following:

Supernatant	3 kgal
Salt cake	9 kgal
Sludge	195 kgal
Total waste	207 kgal.

Note that the Brevick et al. (1994a) and Hanlon (1995) estimates for salt cake are very different. Because the basic calculations in this document assumed effective draining of the salt cake regardless of the amount of it, the salt cake amount would not affect this part of the calculation significantly, and the tank would be categorized as CONDITIONALLY SAFE as a result of the draining effect using either set of data. However, subsequent drying following draining of the salt cake would take more than four times as long if the Brevick et al. (1994a) data were substituted for the Hanlon (1994) data that were used in Chapter 7.

It is recommended that analysis of the material from auger sampling planned for October 1995 be used to help to resolve the discrepancy between the Brevick et al. (1994) and Hanlon (1995) estimates.

2.2.2 Sample Dataset

The analysis of variance (ANOVA) model (Toth et al. 1995) used three measurements in the dataset.

Sample ID	Waste phase	H_2O (wt%)	Wet TOC	Reference date
1010-C	Sludge	NA	0.07%	2/14/79
R-6040	Liquid	NA	0.41%	3/16/90
RAT-BX110-1	Sludge	51.9	0.02%	9/18/80

2.2.3 Sampling Results

There are no recent core, auger, or liquid grab samples available for analysis. Auger sampling of this tank is planned for October 1995.

2.2.4 Total Organic Carbon Solubility Evaluation

Barney (1994b) established the solubilities of energetic organic compounds. In most of our wastes, the energetic organic compounds are highly soluble in typical liquids and therefore will not be precipitated into salt cakes or sludges if their liquid concentrations are found to be lower than their solubility limits. The 0.4 wt% TOC value found in dataset sample R-6040 would correspond to about 5 g/L. Solubilities of energetic organic salts range from a low for citrate of about 36 g/L to a high for EDTA at 96 g/L. Thus, if these salts are present, they would all be in solution. A drained salt cake would retain some liquid in interstitial pores, but both liquid and salt cake would be well below the preliminary safety criteria, and the tank would be safe.

2.2.5 Level Information

The level information over the past few months is the only surface information available as there is no liquid observation well.

On August 14, 1995, the surface measurement of BX-110 was 170 cm (67 in.) according to the SACS. This compares very well with the Brevick et al. (1994a) diagram, page 223, which shows a level approximately half way between 152 and 183 cm (60 and 72 in.). No separate reading for liquid level was provided. If we assume that the 159 kL (42 kgal) of salt cake is correct, then the depth of the salt cake bed is somewhat less than a half a meter.

2.2.6 Preliminary Dryness Evaluation

The Preliminary Dryness Evaluation (Husa et al. 1995) for BX-110 shows a surface level of 180 cm (70.7 in.), which is 8 cm (3 in.) higher than the SACS data. The history of the level should be evaluated to see whether there has indeed been a significant drop in tank level recently.

Page B-4 of the Preliminary Dryness Evaluation (Husa et al. 1995) indicates that tank BX-110 was found to contain more than 20% salt cake and less than 5 kL (1.3 kgal) supernatant, so it was given a dryness rating of "medium." The visual record shows a dry surface according to Husa et al. (1995) criteria.

2.2.7 Supernatant Status

The Waste Tank Summary Report for June 30 (Hanlon 1995), Table E-6, page E-11, indicates that tank BX-110 is an assumed leaker and has 11 kL (3 kgal) of supernatant over 34 kL (9 kgal) of salt cake. If this is true, it cannot be too dry as 11 kL (3 kgal) of supernatant would provide a few centimeters of liquid over the salt cake of concern.

2.2.8 Stabilization Evaluation

Tank BX-110 was jet pumped in October 1994 with poor results. From the basic calculations in this document, it would exceed criteria upon jet pumping and would therefore become UNSAFE when jet pumped. This would seem to indicate that the tank is now UNSAFE. Investigating that possibility is one of the reasons for this evaluation. As noted below, the jet pumping that was performed was not very effective and probably did not remove much moisture, in contrast to the assumptions of the methodology in this document which assumed a large amount of moisture would be removed from the salt cake by draining.

2.2.9 Jet Pumping History

According to the history diagram in Brevick et al. (1994a), page 223, a salt well pump was installed in 1977, and it appears that it may have been used to remove about 3 m of supernatant at that time (i.e., lowered the liquid level of the tank by 3 m). The diagram shows that the current liquid level is approximately the same level as the surface based on the data available <u>before</u> the jet pumping attempted in October 1994. This is discussed below.

2.2.10 Engineer's Report on Interim Stabilization

The October 1994 data input form for the monthly Waste Tank Summary report (see Attachment 7E-1) contained the following for tank BX-110:

Total waste	207 kgal
Supernatant	3 kgal
Drainable liquid	16 kgal
Total pumped	1.5 kgal
Drainable liquid remaining	19 kgal
Sludge	195 kgal
Salt cake	9 kgal.

The narrative is as follows:

> "Video taken 10/13/94. Because of a major equipment failure and the low net pumped volume (1,500 gal of tank waste) and ALARA, it was decided that pumping will not be restarted on this tank. Almost 3,000 gal of waster flushes were needed to produce only 1,500 gal of tank waste."

On October 19, 1994, V. C. Boyles, Interim Stabilization Engineer indicated the following (Attachment 7E-1):

> "[Tank Stabilization and Support Engineering] reviewed the BX-110 video taken on 10/13/94 in riser #6 and compared the video to the 7/14/94 photos taken from the other side of the tank in riser #3. The July photos showed significant quantities of liquid on the surface of the waste but it was difficult to estimate the depth of liquid especially on the back side of the tank. The video, which shows the back side more clearly, demonstrates that there is no more than an average of two inches of liquid covering 50% of the surface. This means that there is only approximately 3,000 gal of supernatant."

2.2.11 Jet Pumping Versus the Analysis of Variance Model

Note that when it came to estimating the jet pumping effect, the ANOVA model results were based upon Hanlon data (1994) that did not show that jet pumping had been conducted, so it was assigned to a different moisture group (not jet pumped) for the calculations that were done subsequently. Note that the Hanlon data (1994) that PNL used for determining phase quantities were pre-jet pumped values. It appears from the above discussion that very little moisture was removed by the jet pumping effort so the tank probably behaves more like a non-jet pumped tank.

The ANOVA calculations were based upon the March 1994 version of the Waste Tank Summary (Hanlon 1994) (for comparison, values from the October jet pumping evaluation are given in parentheses):

Total waste	198 kgal	(207 kgal)
Supernatant	0 kgal	(3 kgal)
Drainable liquid	15 kgal	(16 kgal)
Total pumped	4 kgal	(1.5 kgal)
Drainable liquid remaining	17 kgal	(19 kgal)
Sludge	189 kgal	(195 kgal)
Salt cake	9 kgal	(9 kgal).

Note that the values used in the ANOVA calculation in the first column are more conservative than the recent values in that more drainable liquid and more waste are now thought to be present than was credited in March before the October jet pumping. Rerunning the ANOVA model with more current data is planned for a future update of this document.

2.2.12 Interim Stabilization Declaration

Table I-1, page I-2 of Hanlon (1995) indicates that supernatant pumping of tank BX-110 occurred in August 1985 and that the tank is considered interim stabilized.

2.2.13 Pumpable Liquid and Jet Pumping Impracticality

Hanlon (1995) indicates that there are 49 kL (13 kgal) of pumpable liquid remaining in tank BX-110. However, the cognizant engineer's description indicates that it may be difficult to jet pump more liquid from this tank. Because the tank has been categorized as a CONDITIONALLY SAFE tank, it should be evaluated before further jet pumping is planned. It is also important to obtain more measurements from the tank to verify the current levels of moisture. These measurements may allow the tank to be reclassified as a SAFE tank.

2.2.14 Drainage Impact and Tank Categorization

If tank BX-110 drained itself, basic calculations in this document indicate that it could exceed preliminary safety criteria. It was therefore categorized as CONDITIONALLY SAFE. Hanlon (1995) reports that there are 738 kL (195 kgal) of sludge under 34 kL (9 kgal) of salt cake. The 34 kL (9 kgal) of salt cake would represent about 9 cm (3.5 in.) of depth with the very much deeper layer of sludge underneath it. The sludge is thought to retain its moisture even if the tank drains via leakage. This deep bed of sludge under the salt cake is expected to keep it fairly moist. It is estimated that the capillary height of our typical salt cakes is 20 to 30 cm, so this moistening effect should help. If the 159 kL (42 kgal) of salt cake reported in Brevick et al. (1994a) represents more closely the state of the waste, then this effect is not expected to help keep the upper layers of the salt cake moist.

2.2.15 Conclusion and Recommendations

There is no clear evidence that this tank may have already dried out too much. There is substantial evidence that it has not. However, the considerable conflict between the Brevick et al. (1994a) and Hanlon (1995) estimates, as well as the need for more data on the current state of the tank, indicates that more measurements need to be taken. The CONDITIONALLY SAFE categorization is correct and priority for characterization should be pursued.

It is recommended that BX-110 be auger sampled as scheduled in October 1995 and that liquid grab samples be obtained at the same time, if possible. Samples should be analyzed to establish quantities of the waste phases present, energetics, TOC, and moisture information for both solids and liquids.

2.3 TANK BY-102

2.3.1 Waste Phase and Amounts Comparisons

Page 248 of Brevick et al. (1994b) indicates the following waste volumes for tank BY-102:

Supernatant	0 kgal	(not actually listed)
By salt cake	312 kgal	
Unknown	29 kgal	
Total waste	341 kgal	(not actually listed).

The Waste Tank Summary Report for June 30 (Hanlon 1995) provides the following waste volumes for tank BY-102:

Supernatant	0 kgal
Salt cake	277 kgal
Sludge	0 kgal
Total waste	277 kgal.

The large differences are presumably the result of the 602 kL (159 kgal) of liquid that was pumped from the tank in April 1995.

The March 1994 version of the Waste Tank Summary Report (Hanlon 1994), which served as the basis for the ANOVA calculations, provided the following values:

Supernatant	0 kgal
Salt cake	341 kgal
Sludge	0 kgal
Total waste	341 kgal.

Note that total waste agrees with Brevick et al. (1994a) but that Brevick listed 110 kL (29 kgal) as being of "unknown" composition.

2.3.2 Sample Dataset

Appendix F of Toth et al. (1995) provides the following data for tank BY-102.

Sample ID	Waste phase	H_2O (wt%)	TOC	Reference date
R-8081	Liquid	54	0.1549 wt%	6-3-91
R-8091	Liquid	NA	0.1418 wt%	6-3-91

2.3.3 Sample Results

The following are the supernatant results for samples R8081 and R8091:

Mean value of H_2O is 54 wt%
Mean value of TOC is 2.0 g/L
Mean value of specific gravity is 1.415.

The volumetric TOC would be

2.0 g/L = .002 g/mL.

The wt% TOC would be

0.002 g/L * (1/1.415) * 100% /unit = 0.14 wt% TOC.

2.3.4 Total Organic Carbon Solubility Evaluation

Barney (1994) established the solubilities of energetic organic compounds. In most of our wastes the energetic organic compounds are highly soluble in typical liquids and therefore will not be precipitated into salt cakes or sludges if their liquid concentrations are found to be lower than the solubility limits. The 0.14 wt% TOC value found in sample R-8081 above would correspond to about 2 g/L. Solubilities of energetic organic salts range from a low for citrate of about 36 g/L to a high for EDTA at 96 g/L. Thus, if these salts are present, they would all be in solution. Drained salt cake would retain some liquid in interstitial pores, but both liquid and salt cake would be well below the preliminary safety criteria, and the tank would be safe. It is noted that if oxalate were present, it would nearly all be precipitated because its solubility is only on the order of 0.1 g/L, but because it has low energy and cannot rapidly propagate, it would pose no hazard.

2.3.5 Level Information

A plot of the neutron detector probe counts taken in the BY-102 LOW on January 18, 1993, (before April 1995 jet pumping) and a second plot taken on August 1, 1995 (after jet pumping) is shown in Figure 7D-1. The results show a large response in 1993 when the probe passed the surface (2,900 count peak about a foot below the surface), dropping down to about 2,600 counts at the 3-ft level, whereupon there is a jump to 3,300 counts. This latter spike may be caused by rainwater in the LOW, but Operations has not yet been able to confirm this. However, they do say that the neutron probes retrieved from the LOWs in the BY Tank Farm are usually wet (partly confirming the rainwater hypothesis).

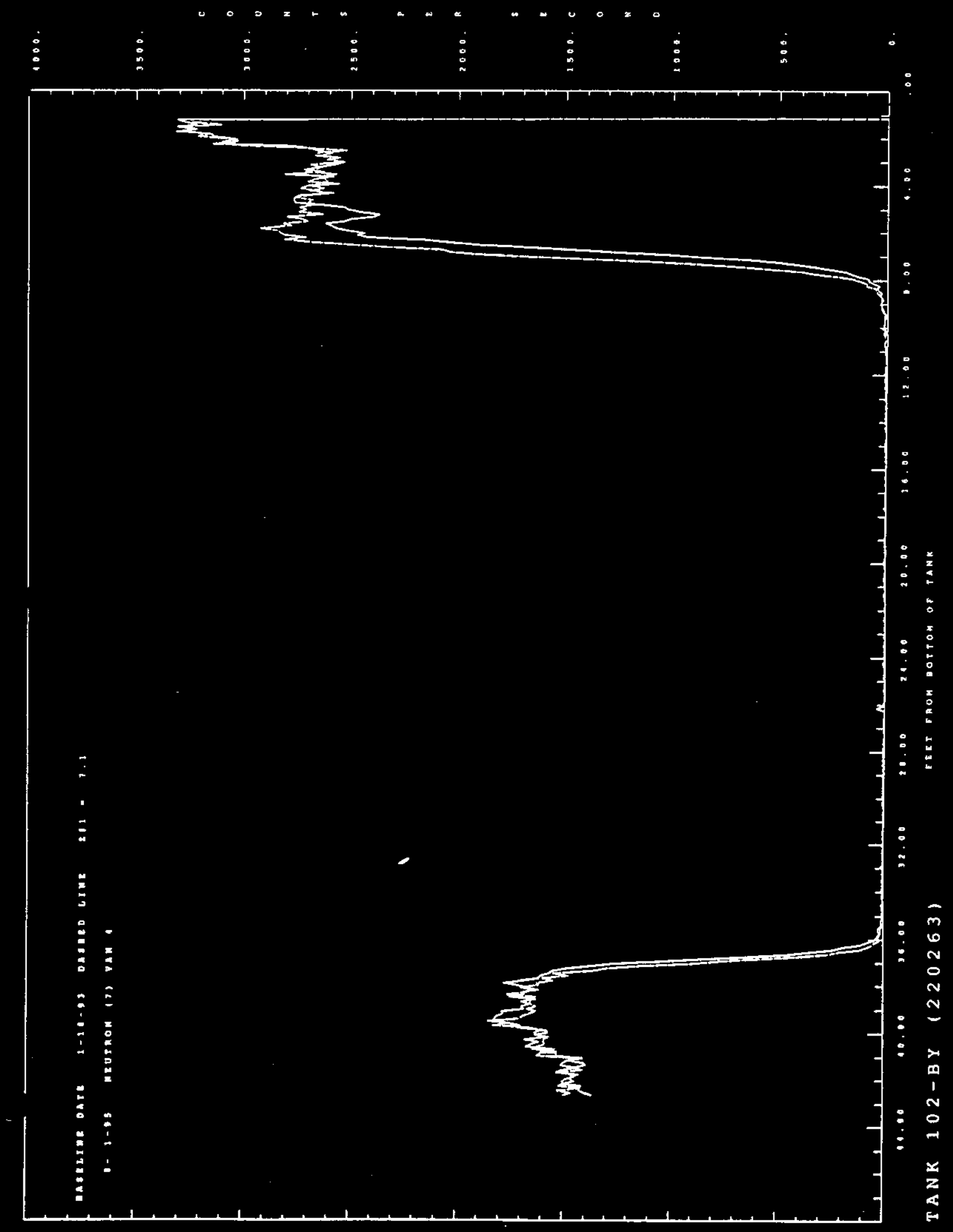
Note that in the stabilization evaluation presented below the liquid level is shown to be 88 cm (34.8 in.) above the bottom. This would be consistent with the lower value for liquid level whether or not the LOW contained rainwater.

The August 1, 1995, neutron probe trace is very similar to the January plot except it is offset about 10 cm (4 in.) (presumably as a result of surface slumping resulting from the jet pumping) and has a lower subsurface spike of 2,600 counts (Figure 7D-1). After a major wiggle, this plot closely follows the January plot starting at 1.5 m (5 ft) of depth, which is the probable interstitial liquid level. The manual tape in July 1995 indicated a surface level of 188 cm (74 in.), which would appear to be too low because the neutron probe indicated 222 cm (87.5 in.) at this same time. This may reflect an actual elevation difference between the LOW regional elevation and that under the manual tape. In January 1995, before jet pumping, the neutron probe gave 223 cm (87.9 in.) versus the 191 cm (75.2 in.) for the manual tape. The difference between level indications is about the same before and after jet pumping.

The relatively strong neutron detector counts received after jet pumping show that the waste is wet at this time. There is no way to determine how much moisture the neutron probe is indicating because it depends somewhat on what species are present and how much void space exists. Calculations indicate that this tank would loose a lot of moisture over a 50-year interval (more than 1,000 t). This would put it in the top 10 salt cake tanks in terms of moisture loss.

It would obviously be very useful to establish the neutron response to waste moisture. It has been recommended that a cross-correlation between neutron responses and various known waste compositions and moisture levels be

Figure 7D-1. Neutron Detector Probe Plot.



developed. There are several approaches that could be taken. Most obvious is to secure more data by means of auger sampling. If interpretations are correct, the waste should still be fairly damp and should probably allow good auger recovery. More sophisticated modeling of evaporation losses, based upon more detailed information regarding tank communication with neighboring tanks, could be used. The tank would have to loose approximately 20 t of water per year over the 50-year cycle to meet our conservative estimates. Presumably, psychrometric data would reveal whether this amount of water was being lost from the tank.

2.3.6 Preliminary Dryness Evaluation

The Preliminary Dryness Evaluation (Husa et al. 1995) for tank BY-102 was performed following the April 1995 jet pumping and uses data consistent with that jet pumping result.

On page B-4, tank BY-110 of the Preliminary Dryness Evaluation (Husa et al. 1995), it is indicated that the tank was found to contain more than 20% salt cake and less than 5 kL (1.3 kgal) supernatant and so was given a dryness rating of medium. The visual record shows a "dry" surface according to the criteria in Husa et al. (1995).

2.3.7 Supernatant Status

Table E-6 of the June 1995 version of the Waste Tank Summary Report (Hanlon 1995) indicates that BY-102 is a sound tank and has 0 kgal supernatant. This permits a dry surface. It may be useful to review the video taken following jet pumping to assess the degree of moisture at the surface.

2.3.8 Stabilization Evaluation

Letter 9552400 *Completion of Interim Stabilization of Single-Shell Tank 241-BY-102 RL Milestone T2A-95-332* (Engelman 1995) provides the following information.

Surface condition and comments:

Dry slumping salt cake with no visible liquid.

Date of most recent photograph: (August 11, 1995) video
Starting liquid level: 166.5 in. by manual tape (June 12, 1991)
Final liquid level: 30.8 in. by dip tube (March 28, 1995)
Total net jet pump production: 158,800 gal
Capillary height used in calculation: 12 in.
Final average flowrate: 0.03 gpm
Calculated porosity: 26%
Drainable interstitial liquid: 11,000 gal
Drainable liquid remaining: 11,000 gal
Pumpable liquid remaining: 0 gal.

Page 2 of Engelman (1995) provides the following waste porosity calculations:

> Dip tube reading adjusted liquid level, September 22, 1994: 59.0 in.
> Dip tube reading adjusted liquid level, March 28, 1995: 30.8 in.
> Volume pumped between given dates: 20,200 gal
> Porosity calculated: 26%.

Page 3 of Engelman provides the following:

> Dip tube is 10 cm (4 in.) above the tank bottom, so the total liquid depth is 88 cm (34.8 in.).

2.3.9 Interim Stabilization Declaration

Table I-1 of the Waste Tank Summary Report for June 30, (Hanlon 1995) indicates that the tank was jet pumped in April 1995, which is consistent with the foregoing discussion.

2.3.10 Pumpable Liquid and Further Jet Pumping Impracticality

Hanlon (1995), in Table E-6, indicates that there is no pumpable liquid remaining in the tank. This is consistent with the stabilization report. This would indicate that no further jet pumping is contemplated.

2.3.11 Drainage Impact and Safety Categorization

The basic calculations in this document indicate that if this tank were drained, its salt cake would exceed the preliminary safety criteria, and it therefore has been categorized as CONDITIONALLY SAFE. These calculations were performed on the data in the Waste Tank Summary Report for March 1994 (Hanlon 1994), which was correct at the time because tank BY-102 had not yet been jet pumped. Because it has now been jet pumped, it is important to establish whether the tank is now UNSAFE. That is one of the main purposes of this evaluation. The tank would not be UNSAFE if it can be shown that the energy or TOC and moisture combinations in the salt cake are not as adverse as the basic calculational results in Chapter 7.

2.3.12 Conclusion and Recommendations

The present evidence suggests that the tank is probably not too dry at this time, and therefore the categorization of CONDITIONALLY SAFE may be correct. However, the data are not conclusive, and it is recommended that auger and liquid grab samples be obtained from the tank to confirm that it is not too dry. Controls should be exercised during these sampling operations in case the actual state of the waste does exceed safety criteria. It would be important to ensure that initiators (ignition sources) are excluded from the waste. It is recommended that the auger samples from the solids and the liquid grab sample be evaluated for waste types, phases, amounts, energy, TOC, and moisture.

2.4 TANK TY-102

2.4.1 Waste Phase and Amounts Comparison

Page 225 of (Brevick et al. 1994b) indicates the following waste volumes for tank TY-102:

Supernatant	0 kgal
T2 salt cake	35 kgal
T1 salt cake	29 kgal
Total waste	64 kgal.

The Waste Tank Summary Report for June 30 (Hanlon 1995) indicates the following waste volumes for this tank:

Supernatant	0 kgal
Salt cake	64 kgal
Total waste	64 kgal.

Note that this is entirely consistent with Brevick et al. (1995b) above. This is also entirely consistent with Hanlon (1994), which was the basis for the ANOVA model calculations in Toth et al. (1995).

2.4.2 Sample Dataset

PNL-10360 (Toth et al. 1995) indicates that tank TY-102 had two measurements that were used in the dataset for the ANOVA model:

Sample ID	Waste phase	H_2O (wt%)	TOC	Reference date
41XC0000	Sludge	No water report	0.0327 wt%	9-9-85
RAT-TY102-1	Salt cake	58	0.236 wt%	2-1-80

Note that this is the only tank in the first four CONDITIONALLY SAFE tanks for which a salt cake measurement is available. If the report of 58 wt% H_2O is correct, this salt cake has more water than most liquids removed from tank waste.

2.4.3 Sampling Results

Letter 65124-80-077, *Physical and Chemical Characteristics of Tanks 105-TY, 103-TY and 102-TY*, (Mitchell 1980) states that the waste was sampled and received in the laboratory during October and November of 1979. Tank TY-102 contained evaporator bottoms salt cake. A portion of the narrative follows:

> "The sample was yellow-gold salt cake containing large chunks of crystaline-appearing material. It is possible that the salt cake is sodium phosphate and X-ray analysis will be requested to determine the actual crystal structure. When blended, the sample became quite liquid. The sample was found to be 58% water. The bulk density was 1.51 gms/cm^3 and the particle density was 3.16 gms/cm^3. The thermal analysis showed no exotherms....
>
> "Major water-soluble salt cake components were sodium, nitrate, phosphate and sulfate with traces of carbonate. The presence of phosphate in large amounts was unanticipated and the concentration of carbonate was less than expected....
>
> "The extremely high phosphate concentration found in Tank 102-TY is also of interest. Reference 1 anticipates no phosphate in salt cake samples. The presence of such a large amount suggests an error in sample preparation or analysis. The sample has been resubmitted for water soluble phosphate analysis and if the results are the same, a second sample will be prepared."

2.4.4 Total Organic Carbon Solubility Evaluation

If the results of the sample analysis above are correct, then a corresponding analysis of liquid could have provided approximately 3 g/L of TOC in the liquid. Barney (1994b) indicates that the solubility of energetic salts ranges from 36 to 96 g/L. It is concluded that this tank should be quite safe based upon very nearly all of the TOC being soluble and no energetic organic compounds having precipitated.

2.4.5 Level Information

The tank data system indicates that the surface level of tank TY-102 is 81 cm (32 in.) as determined by FIC level gauge. The fact that this device is still functioning indicates that the waste surface is still fairly damp, as the FIC level gauge usually stops functioning in automatic mode if the waste surface becomes too dry. The level is reasonably consistent with the level in Brevick et al. (1994b), which is between 0.6 and 0.9 m (2 and 3 ft).

2.4.6 Preliminary Dryness Evaluation

On page A-7 of the Preliminary Dryness Evaluation (Husa et al. 1995), the level of tank TY-102 is listed as 78 cm (30.7 in.), slightly lower than the current tank data system value of 81 cm (32 in.). On page B-4 of the Preliminary Dryness Evaluation (Husa et al. 1995), it is indicated that tank TY-102 contained pumpable liquids less than 20% of total volume stored, supernatant less than 5,110 L (1,350 gal), salt cake greater than 20% of waste, surface less than 102 cm (40 in.) total depth. The tank was rated medium on the basis that visual examination showed a "damp" surface.

2.4.7 Supernatant Status

The Waste Tank Summary Report for June 30 (Hanlon 1995) indicates that this tank contains 0 kgal supernatant, so this suggests that the waste could be somewhat dry, at least on the surface. However, the items above offer other evidence indicating that the tank waste surface is still fairly damp.

2.4.8 Stabilization Evaluation

"Interim Stabilization Evaluation - Non-Jet Pumped Tanks," attached to WHC-SD-RE-TI-178, (Swaney 1994), provides the following information:

Date of most recent photograph: March 26, 1994
Surface description:

Solid surface with small liquid pool in center. Pool is about 16 feet in diameter and about 1 in. deep. FIC is now touching solids.

Solids level: 30.0 in. by "solids weight" method (February 28, 1994)
Liquid level: 30.0 in. by FIC (March 24, 1984)
Solids volume: 62,000 gal
Estimated drainable liquid volume: 13,200 gal
Estimated supernatant volume: 100 gal.

Tank was declared stabilized on August 18, 1979.
6,500 gal of supernatant was removed on March 23, 1984.

The Waste Tank Summary Report for June 30 (Hanlon 1995) indicates the following data for this tank:

Supernatant liquid	0 kgal
Drainable interstitial liquid	14 kgal
Total liquid pumped	6.6 kgal
Drainable liquid remaining	14 kgal
Pumpable liquid remaining	0 kgal
Sludge	0 kgal
Salt cake	64 kgal.

These data are reasonably consistent with the data provided by the Interim Stabiliztion Evaluation (Swaney 1994) above.

2.4.9 Interim Stabilization Declaration

TY-102 was interim stabilized by evaluation on March 26, 1984 and has not been jet-pumped.

2.4.10 Pumpable Liquid and Jet Pumping Impracticality

Hanlon (1995), page E-17, indicates that there is 0 kgal pumpable liquid remaining in tank TY-102. This is consistent with the fact that there is drainable liquid remaining because the waste level is less than 1 m. It is not practical to try to install a jet pump because it could not pump lower than approximately 61 cm (24 in.). If this is contemplated, it is recommended that further evaluation be made to ensure that the post-jet pumped state would be safe.

2.4.11 Drainage Impact and Safety Categorization

If tank TY-102 drained itself, basic calculations in the main body of this document indicate that it could exceed preliminary safety criteria. The present category for tank TY-102 is CONDITIONALLY SAFE because it is predicted to exceed criteria if it were jet pumped.

2.4.12 Conclusion and Recommendations

The available data as discussed above appear to be consistent with the data and assumptions used in the analysis in the main body of this document. The tank has not been jet pumped; it appears to have a normal amount of TOC, which is probably nearly all in solution (if it is energetic); and it appears to have a significant amount of moisture in it. It is concluded that this tank should retain the CONDITIONALLY SAFE category until sufficient data are obtained by auger and liquid grab samples to verify its present condition.

Auger samples should be evaluated for organic compounds present, types and amounts of phases, energy, TOC, and moisture. Grab samples of liquids should also be obtained and analyzed for the same items. It would be very helpful to cross-correlate these as it is believed that grab sample results can help to infer salt cake contents, especially regarding the maximum amounts of precipitated energetic organic compounds that may be present.

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Jo, J., 1995, *45-Day Safety Screen Results and Final Report for Tank 241-A-102, Auger Sample 95-AUG-033*, WHC-SD-WM-DP-136, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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ATTACHMENT 7D-1. WASTE TANK SUMMARY REPORT FOR OCTOBER 1994

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WHC-EP-0182
WASTE TANK SUMMARY REPORT

MONTHLY INPUT FOR OCTOBER 1994

Report Section to be Changed: Inventory and Status by Tank

Tank Farms: SSTs - BX & BY Farms

Name: Vic Boyles R1-49

Position: Sr. Principal Engineer

Group: Tank Stabilization & Support Engineering

Information Change: YES ✓ NO ___ (all East Area SSTs)

Description of Change:

Tank # BX-110 Pumping began: ________

Total waste (Supernatant + Solids) 207 Kgal
Supernatant 3.0 Kgal
Drainable Interstitial 16 Kgal
Pumped this Month ____ Kgal
Total Pumped 1.5 Kgal
Drainable Liquid Remaining 19 Kgal
Pumpable Liquid Remaining 13 Kgal
Sludge 195 Kgal
Saltcake 9 Kgal

Prior Est. of 8/22/85 did not include sludge on outside of tank 2' wide by 3' high (10,000 gal)
Manual tape 67.0"
Use standard equation and 12.5% por.

Other info: (Photograph & stabilization info., etc)

Video taken 10/13/94. Because of a major equipment failure and the low net pumped volume (~1,500 gallons of tank waste) and ALARA, it was decided that pumping will not be restarted on this tank. Almost 3,000 gallons of water flushes were needed to produce only 1,500 gallons of tank waste.

SIGNATURE: V C Boyles DATE: 11/9/94

DUE: November 7, 1994

RETURN TO: B. M. Hanlon, C-117B, R1-80, 3-2053

WHC-EP-0182
TANK FARM SURVEILLANCE AND WASTE STATUS SUMMARY REPORT

DECEMBER MONTHLY INPUT FORM

Report Section to be Changed: Inventory and Status by Tank

Tank Farms: SST

Name: John Huber R1-49 0-129

Position: Engineer, Single-Shell Tanks

Group: Systems Engineering

Information Change: YES X NO ___ (all SSTs)

Description of Change:

Tank # BX-110 Pumping began: 12/4/93

Total waste (Supernatant + Solids) 198 Kgal
Supernatant 0 Kgal
Drainable Interstitial 15.4 Kgal
Pumped this Month 4.0 Kgal
Total Pumped 4.0 Kgal
Drainable Liquid Remaining 16.6 Kgal —??
Pumpable Liquid Remaining 6.0 Kgal
Sludge 189 Kgal
Saltcake 9 Kgal

Other info: (Photograph & stabilization info., etc)

SIGNATURE: JHuber DATE: 1/6/94 1-10-94

FOR MONTH OF: DECEMBER 1993 DUE: JAN 10, 1993
RETURN TO: B. M. Hanlon, C-117B, R1-80, 3-2053

[1] From: Victor C Boyles 10/19/94 2:34PM (4728 bytes: 15 ln, 1 fl)
To: Victor C Boyles
Subject: Video Review of Tank BX-110
------------------------------ Forwarded ------------------------------
From: Victor C Boyles at ~WHC338 10/19/94 2:13PM (4523 bytes: 15 ln, 1 fl)
To: Randolph Ni at ~WHC129
cc: Douglas W Craig at ~WHC129, Donald B Engelman at ~WHC140,
Keith E (Gus) Myers at ~WHC23, David A Bragg, Michael R Koch, Gary J White,
Dirk D Wiggins, Randy L Powers
Subject: Video Review of Tank BX-110
------------------------------ Message Contents ------------------------------

Text item 1:

Guys,
Here is some good news for a change. I have reviewed the video taken last week of tank BX-110. The video shows better clarity of the liquid surface not visible on the July photographs. The video was taken from the opposite side of the tank than the earlier photos. From comparing the video with the photos, I believe we can stop all activities to pump this tank further and turn our efforts to pumping other tanks.
Keep in mind, that declaring this tank "finished" doesn't count in the stabilization numbers because the tank was already declared interim stabilized in 1985.
See attached file for further justification.

Vic Boyles

Guys,

I have good news for a change. TS&ES recommends that no further pumping is required for tank BX-110. This tank meets the interim stabilization requirements as established in the Waste Tank Administration manual, WHC-IP-0842.

TS&ES reviewed the BX-110 video taken on 10/13/94 in riser #6 and compared the video to the 7/14/94 photos taken from the other side of the tank in riser #3. The July photos showed significant quantities of liquid on the surface of the waste but it was difficult to estimate the depth of liquid especially on the back side of the tank. The video, which shows the back side more clearly, demonstrates that there is no more than an average of two inches of liquid covering 50% of the surface. This means that there is only approximately 3000 gallons of supernatant.

The current status of the jet pump system is that it is inoperable and would require significant equipment repair to make operable. Earlier this year an attempt was made to replace the lower piping on the BX-110 jet pump. While attempting to raise the jet pump, it was discovered that the approximately 36 foot long saltwell screen was stuck to the jet pump assembly. TS&ES believes that WHC would have to replace the entire pump assembly and saltwell screen before pumping could resume. This removal and installation of equipment would require a significant amount of flush water to reduce the contamination level on the equipment. In addition, the challenge and cost of disposal for the failed equipment would be significant.

In 1993-1994 WHC pumped 4,400 gallons of liquid waste from this tank. It is estimated that most of the volume pumped was the result of flush water added in installing the original equipment or in the pumping process. Net volume pumped from BX-110 was approximately 1,500 gallons. TS&ES estimates that only a few thousand gallons could be pumped if a new pump and saltwell assembly were installed at BX-110. There would also be a significant amount of flush water needed. Restarting pumping operations at BX-110 does not adhere to ALARA principles of minimizing waste generation, nor is it cost effective considering the end results. Therefore, it is recommended that any preparations to pump tank BX-110 be stopped. The proper paperwork to cease pumping operations will follow shortly. Since this tank is already stabilized from prior pumping in 1985, only the Waste Status Summary, WHC-EP-0182, will be updated showing the current waste volume estimates.

Vic Boyles
Interim Stabilization, Cog. Manager

APPENDIX 7E

U TANK EVALUATION OF LIQUID GRAB SAMPLE RESULTS

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APPENDIX 7E

U TANK EVALUATION OF LIQUID GRAB SAMPLE RESULTS

1.0 REVIEW OF LIQUID GRAB SAMPLE RESULTS

In response to a request from the Interim Stabilization Project, the liquid grab sample results from selected U Tank Farm tanks have been reviewed and the results are reported in this appendix. Of interest were tanks U-102, U-103, U-105, U-107, U-108, and U-109, which were categorized as CONDITIONALLY SAFE tanks by the basic methods of Chapter 7 because they exceed the preliminary safety criteria after jet pumping. These tanks are also identified as being tanks that need to be stabilized by jet pumping. Jet pumping of these tanks is planned for August 1996. (Data from tank U-106 was also included in this evaluation because it was the only tank liquid that was measured and used in the analysis of variance [ANOVA] total organic carbon [TOC] [Toth et al 1995] dataset for the subject group of U tanks [see Chapter 6 of this report].)

The purpose of this evaluation is to determine whether the liquid grab sample results from this group of U Tank Farm tanks provide alternative information that could be used to show that these tanks would be safe to jet pump. The methods of evaluation for jet pumping in Chapter 7 do not depend on a partition of TOC between liquid and solid phases. TOC reported for a laboratory sample of salt cake is simply treated as being distributed throughout the matrix rather than being concentrated in the liquid in the interstices (Barney 1994). Work by Barney (1994) suggests that virtually all energetic organic compounds will be in solution and not in solids in the waste. An update planned for this report will take this into account. The present evaluation shows how this effect can be used to judge the expected safety of jet pumping this group of tanks.

Barney (1994) has performed experiments with surrogate materials that show that most organic salts have high solubility in typical tank waste solutions. Based on results from Barney (1994), all of the energetic organic compounds should be in solution with none of the material precipitated. If oxalate is present (as expected), nearly all of it will be precipitated. Oxalate has low energetics and has been shown in Chapter 5 to be incapable of rapid propagation. Therefore, with all of the energetic organic salts in solution, jet pumping a tank is beneficial. The TOC would be reduced by removing as much as 70% of the liquid from the interstitial pores. The remaining 30% would still be available for reaction, as a portion of the salt cake matrix, but would contribute very little TOC as a percentage of the salt cake matrix, and the salt cake could not support rapid propagation unless the liquid contained excessively large amounts of TOC.

Table 7E-1 was created from grab sample results (Esch 1995a, 1995b, 1995c, 1995d, 1995e; Sutey 1994 [Attachment 7E-1]; and Vogel 1994).

Table 7E-1. Grab Sample Results.

Tank	Specific gravity	% H_2O	TOC (µg C/ML)	OH Liquid (µg/ML)	Nitrate (µg/ML)	Nitrite (µg/ML)	DSC exotherm (J/g)
U-102	1.336	56.52	1.1 E+04	1.5 E+04	9.73 E+04	8.68 E+04	379.1
U-103	1.385	51.53	1.54 E+04	4.6 E+04	2.44 E+05	1.12 E+05	447.9
U-105	1.350	52.72	1.97 E+04	2.23 E+04	1.82 E+05	8.36 E+04	63.5
U-106*	1.335	57.66	3.79 E+04	7.10403	2.09 E+05	8.76 E+04	824.5
U-107	1.395	51.39	4.80 E+03	3.00 E+04	2.00 E+05	8.53 E+04	75.7
U-108	1.39	50.28	7.44 E+03	4.92 E+04	1.74 E+05	1.16 E+05	65.5
U-109	1.365	50.67	8.03 E+03	4.84 E+04	1.48 E+05	9.65 E+04	118.7

*U-106 is not a CONDITIONALLY SAFE tank; it is shown in this table for comparison purposes. It is the only tank liquid that was measured and used in the ANOVA TOC (Toth et al. 1995) dataset for the subject group of U tanks.

DSC = differential scanning calorimetry.
TOC = total organic carbon.
ANOVA = analysis of variance.

For convenience, the values in Table 7E-1 have been converted to wt% by dividing by specific gravity and adjusting the units as reported in Table 7E-2.

Table 7E-2. Total Organic Carbon in Weight Percent.

Tank	TOC laboratory value (µg C/mL)	TOC converted (wt%)
U-102	1.1 E+04	0.80
U-103	1.54 E+04	1.1
U-105	1.97 E+04	1.5
U-106*	3.79 E+04	2.8
U-107	4.80 E+03	0.3
U-108	7.44 E+03	0.5
U-109	8.03 E+03	0.6

*U-106 is not a CONDITIONALLY SAFE tank; it is shown in this table for comparison purposes. It is the only tank liquid that was measured and used in the ANOVA TOC dataset for the subject group of U tanks.

ANOVA = analysis of variance.
TOC = total organic carbon.

Table 7E-3 shows the tanks, the SORWT group they belong to, and the results reported in Chapter 6.

Table 7E-3. Analysis of Variance Model Median and Worst 5% Results.

Tank	SORWT group	TOC ANOVA median value (wt%)	TOC ANOVA worst 5% (wt%)
U-102	VII	0.4	1.8
U-103	VII	0.4	1.8
U-105	X	0.3	1.1
U-106*	VII	1.6	6.2
U-107	X	0.3	1.1
U-108	X	0.3	1.1
U-109	X	0.3	1.1

*U-106 is not a CONDITIONALLY SAFE tank; it is shown in this table for comparison purposes. It is the only tank liquid that was measured and used in the ANOVA TOC dataset for the subject group of U tanks.

ANOVA = analysis of variance.
SORWT = sort on radioactive waste type.
TOC = total organic carbon.

Comparison of Tables 7E-2 and 7E-3 shows that the laboratory values fall between the median and worst 5% values as predicted by the ANOVA model. It is concluded that the grab samples are in reasonable agreement with the values computed with the ANOVA model. It should also be noted that of the group above, only U-106 liquid has a TOC measurement (9.96 wt% measured in January 1980). This earlier U-106 value is used in the dataset in PNL-10360, *Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste*, (Toth et al. 1995). The 1994 value of 2.8 wt% is significantly lower than the 9.96 wt% of the dataset. This may reflect some aging effects but may also be a result of differing sampling and analysis methods.

Barney (1994b) established that energetic organic compounds, which could rapidly propagate at sufficient concentrations, are highly soluble. In most cases, all of the compound will be dissolved and there will be no solid precipitates of these salts. However, oxalate, which is expected to be present is highly insoluble in typical waste solutions and is expected to be nearly all precipitated. Oxalate has low energetics and has been shown to be incapable of supporting rapid propagating reactions.

1.1 TOTAL ORGANIC CARBON SOLUBILITY EVALUATION

The highest TOC value for the CONDITIONALLY SAFE U Tank Farm tanks of interest (all except U-106) is 1.5 wt%. This corresponds to about 20 g/L on a wet basis. Solubilities of energetic organic salts range from citrate with a low of about 36 g/L to ethylenediaminetetraacetic (EDTA) at 96 g/L. If the salts are all energetic, they should all be in solution, with no precipitate. However, if a portion of the salts is oxalate, the oxalate, with a solubility of approximately 0.1 g/L will nearly all be precipitated. But because oxalate is not energetic and cannot sustain a rapid propagation, it poses no hazard. It is concluded on this basis that the tank waste should be safe if U-102, U-103, U-105, U-107, U-108, U-109 are jet pumped. Further evaluations will be made in the update of this document to provide additional confirmations.

2.0 REFERENCES

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Esch, R. A., 1995b, *Waste Compatibility Results for 241-U-105 Grab Samples*, (memorandum 75970-95-052 to M. J. Sutey, August 1), Westinghouse Hanford Company, Richland, Washington.

Esch, R. A., 1995c, *Waste Compatibility Results for 241-U-107 Grab Samples*, (memorandum 8E80-95-027 to M. J. Sutey, May 22), Westinghouse Hanford Company, Richland, Washington.

Esch, R. A., 1995d, *Waste Compatibility Results for 241-U-108 Grab Samples*, (memorandum 75970-95-043 to M. J. Sutey, Rev. 1, July 24), Westinghouse Hanford Company, Richland, Washington.

Esch, R. A., 1995e, *Waste Compatibility Results for 241-U-109 Grab Samples*, (memomorandum 75970-95-050 to M. J. Sutey, July 24), Westinghouse Hanford Company, Richland, Washington.

Sutey, M. J., 1994, *Sample Status Report for R 4090, U102-TOP*.

Toth, J. J., M. E. Lerchan, J. C. Hill, P. G. Heasler, and P. D. Whitney, 1995, *Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste*, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.

Vogel, R. E., 1994, *Results for Tank 241-U-106*, (memorandum 8E80-94-109 to M. J. Sutey, October 18), Westinghouse Hanford Company, Richland, Washington.

ATTACHMENT 7E-1. GRAB SAMPLE RESULT FOR TANK U-102 (SUTEY 1994)

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SAMPLE STATUS REPORT FOR  R 4090.  M.J.SUTEY    U102-TOP  TIME:  6/ 1/94
11:28DISPATCHED:  6/22/93  10:23     SAMPLE HAS NOT BEEN SLURPED
PAGE  1
RECEIVED:    7/29/93   9:19
                                                              OUT OF GOOD CHARGE
EXT.  DETER.    RESULTS OR STATUS                             RANGE? ANS?  CODE
****  ********  **********************************             ***   ***  ******
4520  VISCOSTY  INCOMPLETE                                                N54D2
5706  SPG         CANNOT BE DONE                                          N54D2
5711  DSC       EXOTHERM = 379.1 J/G                                      N54D2
5712  TGA       OUT FOR RERUN                                             N54D2
5712  TGA         9.83800E 01 % H2O                             N     Y   N54D2
5713  pH          6.87000E 00 NONE                              N     Y   N54D2
5714  % H2O       6.52500E 01 % H2O                             N     Y   N54D2
5720  TB        OUT FOR RERUN                                             N54D2
5720  TB          2.48000E 00 uCi/ML                            N     Y   N54D2
5725  AT        OUT FOR RERUN                                             N54D2
5725  AT        < 4.59000E-03 uCi/ML                            N     Y   N54D2
5726  TOC       OUT FOR RERUN                                             N54D2
5726  TOC       OUT FOR RERUN                                             N54D2
5726  TOC         SAMPLE WILL NOT DISSOLVE - FORMS TRANSLUCENT GEL        N54D2
5727  TIC         1.46000E 02 uG C/ML                           N     Y   N54D2
5728  NH4         3.26000E 03 uG/ML                             N     Y   N54D2
5729  OH LIQ      NO OH- PH TOO LOW TO CONTAIN OH-                        N54D2
5730  GEA         2.90000E 00 uCi/ML     Cs-137                 N     Y   N54D2
5750  ICP-LIQ    SAMPLE NEEDED DIGEST                                     N54D2
5771  IC         <1.1  (MATRIX INTERFERENCE)    F-                        N54D2
5771  IC          7.33000E 01 uG/ML        CL-                  N     Y   N54D2
5771  IC          6.90000E 02 uG/ML       NO2-                  N     Y   N54D2
5771  IC          1.14000E 03 uG/ML       NO3-                  N     Y   N54D2
5771  IC        < 1.10000E 01 uG/ML       PO4-                  N     Y   N54D2
5771  IC          2.58000E 01 uG/ML       SO4-                  N     Y   N54D2
5778  CN LIQ    OUT FOR RERUN                                             N54D2
5778  CN LIQ      4.37000E 00 uG/ML                             N     Y   N54D2
5781  Pu239/40  OUT FOR RERUN                                             N54D2
5781  Pu239/40  < 1.35000E-03 uCi/ML                            N     Y   N54D2
5782  Am241     < 1.29000E-03 uCi/ML                            N     Y   N54D2
5783  Np237       5.48000E-05 uCi/ML                            N     Y   N54D2
5786  Sr90        2.94000E-04 uCi/ML                            N     Y   N54D2
8700  ACD DGST  D.F. 100                                                  N54D2
8750  ICP-LIQ     8.26000E-01 uG/ML      Zr                     N     Y   N54D2
8750  ICP-LIQ     1.67000E 00 uG/ML      Sr                     N     Y   N54D2
8750  ICP-LIQ     2.50500E 01 uG/ML      Si                     N     Y   N54D2
8750  ICP-LIQ     5.63000E 00 uG/ML      Al                     N     Y   N54D2
8750  ICP-LIQ     6.95000E 01 uG/ML      Fe                     N     Y   N54D2
8750  ICP-LIQ     6.87000E 01 uG/ML      Ca                     N     Y   N54D2
8750  ICP-LIQ     8.86000E 00 uG/ML      Mg                     N     Y   N54D2
8750  ICP-LIQ     8.50100E 02 uG/ML      Na                     N     Y   N54D2
8750  ICP-LIQ     1.16500E 01 uG/ML      Se                     N     Y   N54D2
8750  ICP-LIQ     5.47000E 00 uG/ML      B                      N     Y   N54D2
8750  ICP-LIQ     3.42900E 01 uG/ML      K                      N     Y   N54D2
8750  ICP-LIQ     6.86000E-01 uG/ML      Mn                     N     Y   N54D2
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PAGE  1
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                                                                OUT OF GOOD CHARGE
EXT.  DETER.    RESULTS OR STATUS                               RANGE? ANS?  CODE
****  ********  **********************************               ***   ***  ******
4520  VISCOSTY  INCOMPLETE                                                  N54D2
5706  SPG        1.33600E 00 NONE                                 N     Y   N54D2
5711  DSC       TOTAL EXOTHERM = 65.5 J/G                                   N54D2
5712  TGA        5.18800E 01 % H2O                                N     Y   N54D2
5713  pH         1.36800E 01 NONE                                 N     Y   N54D2
5714  % H2O      5.65200E 01 % H2O                                N     Y   N54D2
5720  TB         3.86000E 02 uCi/ML                               N     Y   N54D2
5725  AT         2.98000E-01 uCi/ML                               N     Y   N54D2
5726  TOC        1.10000E 04 uG C/ML                              N     Y   N54D2
5727  TIC        5.58000E 03 uG C/ML                              N     Y   N54D2
5728  NH4        1.86000E 02 uG/ML                                N     Y   N54D2
5729  OH LIQ     1.51000E 04 uG/ML                                N     Y   N54D2
5730  GEA        2.50000E 02 uCi/ML     Cs-137                    N     Y   N54D2
5750  ICP-LIQ    SAMPLE NEEDED ACID DIGEST                                  N54D2
5771  IC          MATRIX INTERFERENCE    F-                                 N54D2
5771  IC          6.57000E 03 uG/ML         CL-                   N     Y   N54D2
5771  IC          8.67999E 04 uG/ML        NO2-                   N     Y   N54D2
5771  IC          9.72999E 04 uG/ML        NO3-                   N     Y   N54D2
5771  IC          4.74000E 03 uG/ML        PO4-                   N     Y   N54D2
5771  IC          6.30000E 03 uG/ML        SO4-                   N     Y   N54D2
5778  CN LIQ    OUT FOR RERUN                                               N54D2
5778  CN LIQ      3.88000E 01 uG/ML                               N     Y   N54D2
5781  Pu239/40  OUT FOR RERUN                                               N54D2
5781  Pu239/40  < 8.65000E-04 uCi/ML                              N     Y   N54D2
5782  Am241       1.93000E-02 uCi/ML                              N     Y   N54D2
5783  Np237     < 1.30000E-05 uCi/ML                              N     Y   N54D2
5786  Sr90        6.88000E 00 uCi/ML                              N     Y   N54D2
8700  ACD DGST    D.F. 100                                                  N54D2
8750  ICP-LIQ     6.24000E-01 uG/ML      Sr                       N     Y   N54D2
8750  ICP-LIQ     6.85100E 01 uG/ML      Si                       N     Y   N54D2
8750  ICP-LIQ     1.60830E 04 uG/ML      Al                       N     Y   N54D2
8750  ICP-LIQ     1.58000E 00 uG/ML      Co                       N     Y   N54D2
8750  ICP-LIQ     3.84000E 00 uG/ML      Cu                       N     Y   N54D2
8750  ICP-LIQ     1.03830E 02 uG/ML      Ni                       N     Y   N54D2
8750  ICP-LIQ     1.04600E 01 uG/ML      Fe                       N     Y   N54D2
8750  ICP-LIQ     2.49700E 02 uG/ML      Ca                       N     Y   N54D2
8750  ICP-LIQ     2.55600E 02 uG/ML      Cr                       N     Y   N54D2
8750  ICP-LIQ     1.30790E 03 uG/ML      P                        N     Y   N54D2
8750  ICP-LIQ     2.32000E 00 uG/ML      Mg                       N     Y   N54D2
8750  ICP-LIQ     7.83000E 01 uG/ML      Mo                       N     Y   N54D2
8750  ICP-LIQ     1.45000E 01 uG/ML      Se                       N     Y   N54D2
8750  ICP-LIQ     5.27000E 00 uG/ML      Cd                       N     Y   N54D2
8750  ICP-LIQ     6.31000E 01 uG/ML      B                        N     Y   N54D2
8750  ICP-LIQ     2.88940E 03 uG/ML      K                        N     Y   N54D2
8750  ICP-LIQ     7.11000E-01 uG/ML      Mn                       N     Y   N54D2
8750  ICP-LIQ     1.99000E 05 uG/ML      Na                       N     Y   N54D2
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                                                                OUT OF GOOD CHARGE
EXT.  DETER.    RESULTS OR STATUS                               RANGE? ANS?  CODE
****  ********  *********************************                ***   ***  ******
4520  VISCOSTY  INCOMPLETE                                                  N54D2
5706  SPG         1.37900E 00 NONE                                N     Y   N54D2
5711  DSC       EXOTHERM = 162.3 J/G                                        N54D2
5712  TGA         5.06700E 01 % H2O                               N     Y   N54D2
5713  pH          1.37300E 01 NONE                                N     Y   N54D2
5714  % H2O       5.17600E 01 % H2O                               N     Y   N54D2
5720  TB          4.59000E 02 uCi/ML                              N     Y   N54D2
5725  AT          3.62000E-01 uCi/ML                              N     Y   N54D2
5726  TOC         8.59000E 03 uG C/ML                             N     Y   N54D2
5727  TIC         7.57000E 03 uG C/ML                             N     Y   N54D2
5728  NH4       < 1.60000E 02 uG/ML                               N     Y   N54D2
5729  OH LIQ      1.97000E 04 uG/ML                               N     Y   N54D2
5730  GEA         3.08000E 02 uCi/ML     Cs-137                   N     Y   N54D2
5750  ICP-LIQ    SAMPLE NEEDED ACID DIGEST                                  N54D2
5771  IC          MATRIX INTERFERENCE     F-                                N54D2
5771  IC          6.88000E 03 uG/ML          CL-                  N     Y   N54D2
5771  IC          8.92999E 04 uG/ML         NO2-                  N     Y   N54D2
5771  IC          9.96999E 04 uG/ML         NO3-                  N     Y   N54D2
5771  IC          4.47000E 03 uG/ML         PO4-                  N     Y   N54D2
5771  IC          6.29000E 03 uG/ML         SO4-                  N     Y   N54D2
5778  CN LIQ      3.99000E 01 uG/ML                               N     Y   N54D2
5781  Pu239/40  OUT FOR RERUN                                               N54D2
5781  Pu239/40  < 8.66000E-04 uCi/ML                              N     Y   N54D2
5782  Am241       2.31000E-02 uCi/ML                              N     Y   N54D2
5783  Np237       4.04000E-05 uCi/ML                              N     Y   N54D2
5786  Sr90        8.08000E 00 uCi/ML                              N     Y   N54D2
8700  ACD DGST    D.F. 100                                                  N54D2
8750  ICP-LIQ     5.70000E-01 uG/ML      Sr                       N     Y   N54D2
8750  ICP-LIQ     5.84000E 01 uG/ML      Si                       N     Y   N54D2
8750  ICP-LIQ     1.74413E 04 uG/ML      Al                       N     Y   N54D2
8750  ICP-LIQ     9.77000E-01 uG/ML      Co                       N     Y   N54D2
8750  ICP-LIQ     3.44000E 00 uG/ML      Cu                       N     Y   N54D2
8750  ICP-LIQ     1.08090E 02 uG/ML      Ni                       N     Y   N54D2
8750  ICP-LIQ     1.29000E 01 uG/ML      Fe                       N     Y   N54D2
8750  ICP-LIQ     2.40400E 02 uG/ML      Ca                       N     Y   N54D2
8750  ICP-LIQ     2.70600E 02 uG/ML      Cr                       N     Y   N54D2
8750  ICP-LIQ     1.32320E 03 uG/ML      P                        N     Y   N54D2
8750  ICP-LIQ     2.55040E 03 uG/ML      S                        N     Y   N54D2
8750  ICP-LIQ     7.82000E-01 uG/ML      Mg                       N     Y   N54D2
8750  ICP-LIQ     8.28000E 01 uG/ML      Mo                       N     Y   N54D2
8750  ICP-LIQ     2.33000E 01 uG/ML      Se                       N     Y   N54D2
8750  ICP-LIQ     5.28000E 00 uG/ML      Cd                       N     Y   N54D2
8750  ICP-LIQ     6.41000E 01 uG/ML      B                        N     Y   N54D2
8750  ICP-LIQ     3.22600E 03 uG/ML      K                        N     Y   N54D2
8750  ICP-LIQ     5.87000E-01 uG/ML      Mn                       N     Y   N54D2
8750  ICP-LIQ     2.20000E 05 uG/ML      Na                       N     Y   N54D2
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8.0 EVALUATION OF INITIATING EVENTS AND REQUIRED CONTROLS

Fuel-nitrate safety is ensured if fuel concentrations are sufficiently low or if waste moisture is sufficiently high. The following describes an evaluation of tank farm equipment and operations, including operational upsets and natural phenomena, that could dry SAFE wastes to UNSAFE conditions. In addition, operations and equipment were evaluated for the potential to initiate a reaction in reactive materials. Testing of organic-nitrate surrogates at the U.S. Bureau of Mines, reported in *Testing of Organic Waste Surrogate Materials in Support of the Hanford Organic Tank Program - Final Report* (Turner and Miron 1994), indicated that these materials are not sensitive to initiation by impact or friction but are sensitive only to heating. Therefore, the potential for tank farm equipment and operations to heat a portion of the waste to ignition temperatures also is evaluated.

8.1 LOSS OF WASTE COOLING SCENARIOS

A number of single-shell tanks are provided with forced (active) ventilation, primarily for cooling to remove waste decay heat. The moisture loss rates during normal, active ventilation operations are discussed in Chapter 7, Section 7.4.2. This section addresses the upset condition, where active ventilation is lost or where a change is planned in ventilation configuration from active to passive as exemplified by tanks A-104, A-105 and A-106, which are now passively ventilated. In either case, the waste and tank headspace would heat up over time until a steady, passively ventilated condition was reached. This scenario is similar to normal passively ventilated tank operations, but the decay heat power levels for the normally actively ventilated tanks can be several times higher (tank waste contains significant quantities of strontium and cesium) than for the normally passively ventilated tanks. Moisture loss rates are a strong function of waste decay power. As described in FAI/94-114, *Moisture Loss Estimates for Hanford Single-Shell Tanks* (FAI 1994b), and summarized below, the relatively high-power tanks can lose moisture much faster than the low-power, normally passively ventilated tanks. The moisture loss rates during loss of ventilation scenarios for high-power tanks are roughly comparable to the loss rates during the continued active ventilation condition. In either case, moisture loss can occur at sufficiently high rates that equilibrium moisture levels would be attained within a 50-year mission time. Moisture loss from low-power tanks is slow whether the tank is actively or passively ventilated.

The evaluation was performed by assuming that the tanks currently on active ventilation were placed in a passive ventilation configuration. After ventilation is stopped, and over a period of time, a new steady state heat loss distribution is achieved in which the heat loss is split between being (1) conducted out of the tank sides and bottom and (2) convected from the waste surface to the headspace and then conducted through the soil overburden and convected from the tank with ventilation flow. The power split is given by WHC-SD-WM-SARR-010, *Topical Report on Heat Removal Characteristics of Waste Storage Tanks* (Kummerer 1994), and ranges between 50% and 54% of the heat load being removed through the soil overburden. Given this power split, the effective heat flux through the waste surface has been determined and the expected steady state headspace temperature and evaporation rates determined using the method of FAI/94-114 (FAI 1994b). As indicated in FAI/94-114, Chapter 5, the headspace temperature for moderate-power tanks (less than approximately 7 kW transmitted through the waste surface) remains below approximately 80 °C (176 °F), and only a small portion of the heat flux is lost by natural convection exchange with the environment. Most evaporated water is condensed on the tank dome and refluxes to the waste. For higher power tanks (SX-111 is the highest power tank evaluated at 17.9 kW), temperatures would be expected to approach the boiling temperature of the waste liquids, although convection through risers would probably bring the headspace temperature below the boiling temperature. Regardless of the exact steady-state temperature, the headspace would contain a great deal of water vapor, and moisture losses from the tank would approach (or exceed) 5.0×10^4 kg/yr (50 t/yr).

The moisture loss rates for the tanks currently on active ventilation are indicated in Table 8-1 for both the continued active ventilation case (from Section 7.4.2) and the passive ventilation case. The loss rates for passive ventilation conditions reflect the two-tank cascade configuration, which is considered to represent more realistic loss rates. As can been seen, tanks SX-101, SX-102, SX-103, SX-104, SX-105, and SX-106 would have a relatively low moisture loss rate under either active or passive ventilation conditions. The moisture loss rates under passive ventilation for all other tanks are sufficiently high to be comparable to the substantial loss rates under active ventilation conditions. Thus, generally speaking, the higher powered, actively ventilated tanks could still lose substantial moisture over a 50-year time period even if ventilation were shut down.

8.2 EVALUATION OF OPERATIONS AND OPERATIONAL UPSETS

The following subsections summarize an evaluation of operations for their potential to dry and/or heat the wastes such that the wastes are changed from material that meets CONDITIONALLY SAFE criteria to material that would be categorized as UNSAFE. Operations that could cause this change to waste conditions would need to be modified or eliminated. In addition, operations and equipment were evaluated for the potential to initiate a reaction in reactive materials.

8.2.1 Dryout that Creates a Significant Mass of Reactive Waste

The dryout evaluation methodology consists of reviewing operations and equipment descriptions to identify situations that could result in (1) heating a significant portion of waste until moisture content decreases significantly, or (2) ventilating at high enough rates to remove moisture over a period of time. Normal operating conditions as well as postulated operational upset conditions have been considered.

Table 8-1. Moisture Loss Rates for Actively Ventilated Tanks Under Active and Passive Ventilation Conditions.

Tank	Heat load (W)	Moisture loss rate, actively ventilated		Moisture loss rate, passively ventilated	
		kg/yr	t/yr	kg/yr	t/yr
C-105	7,330	20,000	20	7,500	7.5
SX-101	3,690	300	0.3	1,100	1.1
SX-102	4,410	900	0.9	1,600	1.6
SX-103	8,130	5,700	5.7	8,700	8.7
SX-104	3,570	100	0.1	1,000	1.0
SX-105	3,700	200	0.2	1,100	1.1
SX-106	2,490	<100	0.1	<100	<1.0
SX-107	16,050	64,000	64	>50,000	>50
SX-108	16,400	46,000	46	>50,000	>50
SX-109	9,090	10,000	10	13,400	13.4
SX-110	11,940	35,000	35	43,800	43.8
SX-111	17,880	72,000	72	>50,000	>50
SX-112	12,190	29,000	29	47,300	47.3
SX-114	17,200	50,000	50	>50,000	>50

A significant portion of waste has been defined by reviewing scoping combustion consequences analyses for the amount of reactive material that must burn before significant consequences result. Such scoping analyses are described in Appendix 8A. The conclusion of the analysis is that at least 1 m^3 (264 gal) of reactive material must burn to create unacceptably high consequences (e.g., possible tank dome collapse and release of risk significant amounts of airborne waste material). The energy required to dry 1 m^3 of wet waste to dry reactive conditions depends on how much water is initially present in the waste and on the amount of fuel present, which determines how dry the waste must be to support combustion. High fuel concentration waste is estimated to contain only about 6 wt% TOC (see Chapter 7). Waste with this fuel content must be very dry (<9 wt% water) to support a propagating combustion event. For a waste with a specific gravity of 1.5, the heat required to dry the waste can be estimated as 1 m^3 of waste that is 1 wt% H_2O contains:

$$1 \text{ m}^3 \text{ waste} \times \frac{1.5 \text{ kg waste}}{1 \text{ kg water}} \times \frac{1{,}000 \text{ kg water}}{1 \text{ m}^3} \times \frac{0.01 \text{ kg water}}{\text{kg waste}} = 15 \text{ kg of water}$$

The energy required to evaporate this water is:

$$15 \text{ kg of water} \times \frac{2.3 \text{ MJ}}{\text{kg of water evaporated}} = 34.5 \text{ MJ}$$

Therefore the energy input to evaporate each wt% of water is 34.5 MJs per wt% of water that must be removed from the 1-m^3 volume of waste. Based on the fuel/moisture estimates described in Chapter 7, even relatively dry and fuel-rich wastes such as in tanks BY-104, U-106, and TX-114 would require a water reduction of 5 to 10 wt% to create reactive waste. This would require an energy source of over 170 MJs. Energy sources that may be present in the tanks have been evaluated to determine whether they have such energy potential.

If the waste material is reactive (i.e., has sufficient fuel and low enough moisture to support a propagating reaction), it may be ignited with contact by an energy source of sufficient magnitude or temperature. Energy sources that are of short duration, such as sparks and electrical arcs, generally must contain at least a threshold amount of energy to be considered credible ignition sources. The threshold is often specified by a minimum ignition energy (Kuchta 1985) although this concept is most commonly applied to vapor-oxidant systems. The minimum ignition temperature for a combustible system is generally determined by testing. Some testing has only recently been initiated to better quantify the ignition energy requirements for organic-nitrate surrogates; results to date are presented in Appendix 8B. The testing was performed with a 138-J ignitor and indicated that this energy is sufficient to ignite dry or almost dry stoichiometric mixtures of organic salts and sodium nitrate. A key result, however, is that a small amount of water (5 wt% free water) is adequate to prevent ignition for otherwise reactive mixtures (even the chemical water in the acetate-nitrate material was adequate to prevent ignition). Thus, even though the material could support a propagating reaction given a very robust ignition source, a moderate ignitor (138 J) is not sufficient to cause the event in slightly moist material. Additional testing is planned to better determine the minimum ignition energies for dry (0 wt% free water) materials.

Spark ignition testing has been performed for dry ferrocyanide-nitrate simulants. Testing of ferrocyanide-nitrate waste simulants for sensitivity to initiation by electrostatic sparks indicated that such mixtures are not sensitive to initiation by electrostatic sparks (Cady 1992). At the higher energy settings (2 to 20 J), the spark tester did indicate an apparent reaction. The effect, however, was attributed to thermal decomposition and possible steam formation caused by electric arc heating of the small sample by the large spark energy. Propagation testing indicates very similar behavior between ferrocyanide-nitrate mixtures and organic salt-nitrate mixtures, and therefore, for this evaluation, it is assumed that small electrostatic sparks (microjoule range) would not initiate an organic-nitrate reaction. Larger electrical sources may initiate a reaction in dry material as a result of heating effects.

More sustained energy sources (e.g., contact by hot objects, radiant heating by hot objects or flames) need to heat the material to a threshold temperature to cause ignition. This threshold is often specified by the minimum autoignition temperature. Ignition temperatures have been measured for organic-nitrate surrogates using adiabatic calorimetry as discussed in Chapter 5. The lowest ignition temperature measured for the surrogates tested is 220 °C (428 °F). A long-duration heat source must be able to heat reactive material to at least this temperature to be considered a credible ignition source. Heat sources may heat waste that is not in direct contact by heat conduction through the waste. This heating effect is limited, however, for credible heat sources. Based on the simple heat conduction analysis included in Appendix 8C, waste that is more than 2 cm to 12 cm (0.8 to 4.7 in.) from the heat source will not be heated to ignition temperatures within a period of one hour. It is not credible to ignite even reactive waste if it is more than this distance from the application of the heat source.

Some materials are sensitive to ignition by impact and friction heating. Impact and friction initiation sensitivity testing has been performed at the U.S. Bureau of Mines (Turner and Miron 1994). Stoichiometric mixtures of sodium EDTA with sodium nitrate/nitrite and mixtures of sodium citrate with nitrate/nitrite were subjected to standard impact and friction tests. The results of all tests were negative; that is, no reaction was initiated. The impact tester had an upper limit of 14 J impacted on a 10-mg sample. It should be noted that black powder was used as one of the impact tester calibration materials. Black powder showed a sensitivity at about one-half of the tester's drop height range.

The possibility of the waste containing very sensitive explosive materials (e.g., fulminates, lead azide, and diazo compounds) that might act as fuel-nitrate reaction initiators has been evaluated. Evaluations of the chemistry involved in the waste tanks have been performed to determine whether such sensitive material can be formed or persist in the alkaline wastes. These evaluations are documented in PNL-5453, *Complexant Stability Investigation Task 2 - Organic Complexants* (Martin 1985), and ARH-LD-163, *Exothermic Potential of Sodium Nitrate Salt Cake* (Beitel 1977), and are summarized in WHC-EP-0347, *Summary of Single-Shell Tank Waste Stability* (Borsheim and Kirch 1991). The evaluations concluded that sensitive explosive compounds do not constitute a credible risk. Martin (1985) concluded that it was unlikely that any appreciable amount of mercury fulminate would be generated in the tank farm system because the concentrations of mercury are minimal and the entire waste system is maintained at a pH of 8 to 10. The absence of an acidic environment and the minimal concentrations of mercury virtually preclude the synthesis of this substance. Martin (1985) also concluded that it was possible for lead azide (and other heavy metal azides) to form in some waste tanks because both lead compounds and sodium azide may be present at very low concentrations. However, Borsheim and Kirch (1991) concludes that the formation of azides is extremely unlikely because the heavy metals are expected to be present as very insoluble oxides and hydroxides. Martin (1985) also dismissed the possibility of diazo compounds. This is because use of the aromatic organic compounds necessary for the formation of diazo compounds has not occurred in the B Plant, REDOX, or PUREX facilities. The potential presence of other explosive compounds, such as polynitrated aromatic compounds, nitrate esters, and organohydroperoxides, was also examined. It was concluded that these compounds either could not be formed or could not persist in the alkaline waste (Martin 1985).

The reaction initiation evaluation consisted of reviewing tank farm operations and operational upsets for the potential to heat even a small portion of dry reactive waste to reaction initiation temperatures. The evaluation identified operations that may need to be controlled to eliminate ignition sources if the waste contained in the tank is sufficiently dry and rich in fuel to support a propagating reaction. If the waste is moist or fuel lean, a local initiator is of no consequence as any initiated reaction will quench with no significant reaction occurring.

Operations that were considered in this evaluation are those described in WHC-SD-WM-SARR-009, *Construction, Maintenance, and Operations Accident Analysis* (Bajwa 1994). In addition, the tank farm operations procedures described in the computer network-based, online Tank Farms Procedure Information System were reviewed for additional operations that would involve heating and drying potential.

Operational upsets were considered by using a "what if" approach that focused on upset conditions that would significantly increase the amount of energy deposited in the tank or waste. This includes bringing hot objects in contact with the waste or operational upsets that would significantly increase the electrical or mechanical power output of equipment in or near the waste or reduce the cooling provided to equipment in or near the waste.

The results of the evaluation are summarized in Table 8-2.

8.2.2 In-Tank Instrumentation

Various in-tank instruments are used to monitor tank and waste conditions, including temperature measurement devices and waste level measurement devices. This instrumentation often includes low-power electrical circuits. In-tank instrumentation, including equipment failures, has been evaluated previously for the potential to ignite flammable gases and vapors (Scaief 1991). Equipment that has been evaluated includes the following: Food Instrument Corporation (FIC) waste level measurement devices, manual tape waste level measurement devices, zip cord waste level measurement devices, Enraf waste level measurement devices, thermocouple trees, and other monitoring devices. The instrumentation circuits are low-voltage and or low-current circuits, even under faulted conditions. With the exception of the slack tape circuit on the FIC level gauge, none of the evaluated circuits were capable of igniting hydrogen, even under faulted conditions. The slack tape circuit could develop 179 V and 179 mA under faulted conditions, a current slightly higher than the ignition current for hydrogen but less than the ignition current required for other flammable vapors. The energy required to initiate a reaction in combustible solids is significantly higher than the energy required to ignite flammable vapors. The low likelihood that faulted conditions will exist, coupled with the low power capability of these circuits, is sufficient to conclude that in-tank instrumentation has negligible potential to dry wastes or to initiate propagating reactions.

Table 8-2. Summary of Operations Evaluation.

Operation	Upsets conditions	Potential to initiate an accident in wet waste by drying significant amounts of waste?	Potential to initiate an accident in dry reactive waste by heating a small amount of waste?
Equipment installation or removal near waste	Electrostatic discharge from equipment to the waste	No – Negligible drying is possible	No – Negligible heating is possible
In-tank instrumentation	Electrical overcurrent	No – Negligible drying is possible	No – Negligible heating is possible
Still camera photography	Flash unit dropped onto the waste surface, hot filament contacts waste	No – Negligible drying is possible	Yes - Localized heating to ignition temperatures is possible
Video camera filming	Light unit dropped onto the waste surface, hot filament contacts waste	No – Negligible drying is possible	Yes – Localized heating to ignition temperatures is possible
Installation and removal of in-tank equipment	Equipment dropped to the waste surface, impact heats the waste	No – Negligible drying is possible	No – Heating effects are negligible, waste temperature increase of only a few degrees predicted
Drilling through risers or ventilation ducts to install equipment	Hot metal drilling flakes fall to the waste surface	No – Negligible drying is possible as the heat contained in the flakes is very small	No – Heating effects are negligible as the heat contained in the flakes is very small
Welding and grinding	Sparks and slag reach the waste surface	No – Negligible drying is possible	Yes – Localized heating to initiation temperatures is possible
Interim stabilization using a submersible pump	Loss of cooling to the motor/pump assembly causes overheating	No – Drying of waste not expected	No – High localized waste temperatures are not credible
Core sampling – rotary mode	Loss of bit cooling, failure to shut down drill sampler causes frictional heating of the waste	No – Only very localized drying is possible. Moisture would return following drill shutdown	Yes – Localized heating to ignition temperatures is possible safety interlocks designed to limit waste temperature rise
Vehicle operation above the tank	Rupture of fuel tank on aboveground equipment, fuel leakage into the tank, subsequent fire	No – Less than a few millimeters of waste surface could be dried	Yes – Localized heating to ignition temperatures is possible
Lightning strikes	Lightning strike on or near tank or equipment causes lightning current to reach the waste via equipment inserted in or near the waste	No – Drying is limited to very small waste volumes	Yes – Localized heating to ignition temperatures is possible (lightning can be controlled with bonding and grounding)
Portable exhauster operation	Normal operation increases ventilation rates for short periods of time. No significant upset conditions identified	Yes – But drying effects bounded by normal active ventilation because of short duration of operation	No – No significant heating potential identified

8.2.3 Dropped Objects

During the installation or removal of in-tank equipment, it is possible that the equipment can be dropped and fall to the waste surface. Dropping heavy equipment (e.g., a thermocouple tree) was evaluated in WHC-SD-WM-SAD-014, *Safety Assessment for Thermocouple Tree Installation and Operation in Ferrocyanide Tanks* (Farley 1994). The accident scenario assumed that a thermocouple tree, 7.6 cm (3 in.) in diameter with a sluicing nozzle 1.9 cm (0.75 in.) in diameter and a mass of 252 kg (555 lb), is dropped during installation. The impact of the thermocouple tree will cause impact heating of a cylindrical mass of salt cake, the size of which is dependent upon the surface area impacted and the shear strength of the impacted material. A shear strength of synthetic salt cake, 1.03 MPa (150 lb/in^2), was used. A drop of 6.1 m (20 ft) would produce 15 kJ of energy. If all this energy were used to produce an increase in the temperature, a temperature rise of 1.5 °C (2.7 °F) would occur at the impact site. For a drop of 12.2 m (40 ft), a temperature rise of 3 °C (5.4 °F) would occur at the impact site. Thus, a drop of heavy equipment cannot cause an ignition of the surface material or dry wet waste to dry conditions.

8.2.4 Hot Drilling Flakes

Occasionally drilling operations are performed on ventilation ducts to install equipment such as gas sampling probes. It is possible that drilling through tank risers might also be desired in the future. The possibility of such drilling operations creating hot metal drilling flakes (metal shavings) that could fall to the waste surface and initiate an accident has been analyzed to support operations in flammable gas watch list tanks. A laboratory demonstration was conducted to determine the temperature of the fragments, and an analysis was performed to predict the temperature of the flakes as they reach the waste surface. WHC-SD-WM-SAD-003, *Safety Assessment for Window B Activities in Tank 101-SY* (Marusich 1991), indicates that the highest observed temperature was 260 °C (500 °F). An analysis was conducted to determine the temperature of various size particles (1.5 mm through 0.1 mm [0.06 in. through 0.004 in.]) after a fall of 3 m (9.8 ft). The temperatures varied from 228 °C (442 °F) to 60 °C (140 °F), respectively. Because of the small mass of the particle and the limited specific heat available, no self-propagating exothermic reaction could be initiated.

8.2.5 Torch Burning, Welding, and Grinding

For the purposes of this safety analysis, it is postulated that torch burning, welding, and grinding operations might be desired when modifying tank risers or during intrusion prevention modifications. Sparks and hot slag generated by these activities could fall to the waste surface. If welding is to be performed outside of a designated welding area, a hot work permit is required. Welding and grinding are currently prohibited on organic watch list tanks.

The temperature of steel mechanical sparks is approximately 1,400 °C (2,552 °F) (NFPA 1992), but the available energy for ignition is small as the mass of the hot steel flakes is small. It is incredible for these small objects to dry a significant portion of wet waste. It is unlikely that a few grinding sparks or pieces of welding slag could ignite reactive organic-nitrate mixtures. However, it is conceivable that many sparks or pieces of welding slag could fall to the waste surface. Without further testing or analysis, it must be assumed, however, that the energy transferred from hot sparks and burning or welding slag could be sufficient to initiate a propagating reaction in dry reactive waste. As welding sparks or hot slag are predicted to contain less energy than a 138-J ignitor, ignition does not appear to be possible if the material contains even small amounts of moisture.

8.2.6 Still Camera Photography

The photography system used is a standard 70-mm still camera and flash unit mounted in a metal frame. The system is suspended in the tank by a flexible support hose containing wiring to the camera and flash unit. Power to the flash unit is supplied by a portable generator on the ground surface above the tank. The wiring is sealed but not intrinsically safe. The camera and flash unit are manually lowered into the tank to a level controlled by an adjustable safety stop ("top hat") at the top of the riser. Contamination control to the camera system is implemented by lining the riser with a disposable plastic sleeve.

Upset Conditions

- If the camera is dropped and the safety top hat fails, there will be no electrical power discharged at the waste surface. This is because in order for the camera to fall to the waste surface, the electrical cable would have to break, which would disconnect the camera and flash from the surface-located electrical power supply.

- The failure of a flash unit, allowing the hot filament to fall to the waste surface, allows a small amount of energy to be applied to the waste surface. (Van Vleet [1991] estimates 67 J available from a filament cooling down from 2,000 °C to 180 °C [3,632 °F to 356 °F].) The energy dissipated at the waste surface is too small to dry any significant amount of moist waste. Without further testing and or/analysis, it must be assumed, however, that the energy transferred from the hot filament to the waste can be sufficient to initiate a reaction in dry, reactive waste. However, as the energy contained in the hot filament is less than a 138-J ignitor, ignition does not appear to be possible if the material contains even small amounts of moisture.

- If a top hat is not used, the flash unit could be lowered onto the waste surface. Shorting of connections within or near the waste could conceivably dissipate energy from the 110 VAC supply line and heat the waste locally. The ohmic heating that could occur in moist waste is judged to be small, as moist waste is relatively conductive (1 Ω/m based on Cowley [1994]). Therefore, little waste drying is expected from this scenario. Without further testing and/or analysis, it must be assumed, however, that the energy transferred from the shorting electrical wires to waste can be sufficient to initiate a reaction in dry, reactive waste. This scenario can be eliminated by using the top hat and imposing an operational control that prevents the use of power supply cords long enough to reach the waste surface.

8.2.7 Video Camera Operations

The video equipment consists of a standard video camera with pan and tilt capabilities and illumination lights. The entire unit is connected to a support stem. The camera system is supported by a shield plug that limits the length the system can intrude into the tank.

Upset Conditions

- If the camera support stem fails, there will be no electrical power dissipated at the waste surface. For the camera to fall to the waste surface, the electrical cable would have to break, which would disconnect the camera, pan and tilt, and light from the surface-located electrical power supply.

- The failure of a light unit, allowing the hot filament to fall to the waste surface, allows a small amount of energy to be applied to the waste surface (Van Vleet [1991] estimates 67 J available from a filament cooling down from 2,000 °C to 180 °C [3,632 °F to 356 °F].) The energy dissipated at the waste surface is too small to dry any significant amount of moist waste. Without further testing and or/analysis, it must be assumed, however, that the energy transferred from the hot filament to the waste can be sufficient to initiate a reaction in dry, reactive waste. However, as the energy contained in the hot filament is less than a 138-J ignitor, ignition does not appear to be possible if the material contains even small amounts of moisture.

- If a top hat is not used, the light unit could be lowered to the waste surface. Shorting of connections within or near the waste surface could conceivably dissipate energy from the 110 VAC supply line and heat the waste locally. The ohmic heating that could occur in moist waste is judged to be small as moist waste is relatively conductive (1 Ω/m based on Cowley [1994]). Therefore, little waste drying is expected from this scenario. Without further testing and or/analysis, it must be assumed, however, that the energy transferred from the shorting electrical wires to the waste can be sufficient to initiate a reaction in dry, reactive waste. This scenario can be eliminated by using the top hat and imposing an operational control that prevents the use of power supply cords long enough to reach the waste surface.

8.2.8 Interim Stabilization Using a Submersible Pump

Most interim stabilization operations are performed using a jet-pump system in which the pump and motor are located above the tank. Occasionally, however, a relatively high flow rate submersible pump, along with its motor, may be lowered into the salt well to remove pumpable liquids quickly (e.g., in an emergency pumping situation in which a tank leak is suspected). The salt well system is a 25.4-cm- (10-in.-) diameter casing consisting of a stainless steel screen welded to a schedule 40 carbon steel pipe. The stainless steel screen portion of the salt well extends through the waste to near the bottom of the tank.

The submersible pump is mounted to a 5.1-cm (2-in.) transfer pipe and inserted into the salt well to near the bottom of the tank. The submersible pump is driven by a 5-horsepower, 480-V, 3-phase motor. The motor is located below the pump suction and is submersed in the liquid being pumped. The motor is cooled by the liquid flowing past it during pumping operations. A thermal overload device is installed to shut off the motor in the event that the pump motor temperature increases because of abnormal pumping conditions.

Possible failure modes have been analyzed in previous safety analyses (Milliken 1992) to identify credible overheating scenarios. The results of these evaluations determined that the only reasonable excessive heating scenario would be caused by the pump continuing to run when there is no longer fluid being pumped to cool the motor. Even this condition would open the thermal switch, removing power to the motor. For such a scenario to dry significant portions of waste, flow past the pump would need to stop, the pump would need to overheat, the liquid surrounding the motor (which is below the pump suction) would need to be boiled away, and the heat from the overheating motor would need to be transferred through the salt well and into the surrounding waste at a sufficient rate to cause waste dryout and then to heat a portion of the waste to the ignition temperature.

The potential for an overheated submersible pump to dry waste is evaluated in Appendix 8D. As indicted by that evaluation, evaporation of water within the pump-salt well annulus would require at least 2 hours of high current draw following loss of pump flow cooling. Following the evaporation of the water in the annulus, the pump motor would need to heat up to temperatures above 1,000 °C (1,832 °F) before sufficient heat would be radiated and conducted to the waste outside of the salt well to heat it to 100 °C (212 °F). The motor would not be able to continue to run at such high temperatures. Therefore, pump overheating scenarios are not considered credible mechanisms for waste drying or heating to ignition temperatures. The salt well provides sufficient insulation between the pump motor and the waste to limit waste temperatures below boiling temperature for credible pump motor temperatures.

8.2.9 Core Sampling

The waste characterization effort uses core sampling as an important means for obtaining waste samples. Core sampling trucks provide the means to take a full-depth sample. Two core truck designs are available: one that operates in push mode only and one that can operate in either push mode or rotary mode. In push mode, the core sample is taken using hydraulic pressure to push the samplers through the waste. This works well for soft waste materials. For hard waste materials, rotary-mode sampling is used.

Push-mode core sampling generates very little heat and is not considered to be a credible source for drying or heating wastes. In WHC-SD-WM-TRP-048, *Push Mode Core Sample Test* (Keller 1991), the results of testing the 5.7-cm (2.25-in.) diameter core drill string to determine the effect of frictional heating on both the drill face surface and the waste simulant were reported. The testing was conducted in three simulants: a sludge, a soft salt cake, and a hard salt cake. The results from the test indicated that there was no temperature increase on the drill face surface from push-mode sampling of the sludge material, there was a 6 °C (10.8 °F) increase in the soft salt cake, and there was a 22 °C (40 °F) increase in the hard salt cake. These tests are considered enveloping because they were done at higher insertion rates than can be accomplished in the field (i.e., rather than stopping every 48.3 cm [19 in.] to retrieve a sample, the testing pushed continuously as fast as possible). Based on these results it is concluded that push-mode core sampling has no potential to dry wet waste or to ignite dry waste.

Rotary-mode core sampling, however, can generate significant heat from friction at the drill bit—waste interface. High temperatures have been experienced during testing with waste simulants when drill bit progress through the simulant is slow or stopped, as the heat generated is deposited in nearby waste for an extended period of time. When the bit is progressing through the waste as designed, the bit and waste remain relatively cool, as the bit is continually moving down through and contacting cool waste.

To eliminate the possibility of heating potentially reactive waste to high temperatures, and thus the possibility of initiating a fuel-nitrate deflagration accident, the core drill system was modified to provide bit cooling by nitrogen purge and interlocks to shut down the system if key drilling parameters (bit down force and rotational speed) are exceeded.

A safety envelope was developed through testing and thermal analyses such that operation within the envelope (nitrogen purge on, bit down force below 5.2 kN [1,170 lbf], and rotational speed below 55 revolutions per minute) would maintain cool waste temperatures. Operation outside of the envelope is prevented by shutdown interlocks, which stop drilling operations.

The safety envelope parameters ensure that the drill bit temperature will not increase more than 57 °C (103 °F). This value is based on the drill bit reaching a maximum temperature of 150 °C (302 °F) in the highest measured temperature tank waste. This temperature provides a safety margin below the lowest ignition temperature for fuel-nitrate wastes and provides a safety approach that is applicable to dry, combustible wastes. Additional safety margin is provided, however, by the presence of moisture, which would quench any fuel-nitrate reactions even if they were initiated.

Appendix 8E evaluates the drying effects of drill bit heat dissipation for sludges and salt cakes. The evaluation indicates that sludges are difficult to dry out. Based on methods developed to analyze hot spots (Meacham 1994), the dryout heat flux is about 5.2×10^5 W/m^2, and therefore the heat produced at the end of the drill string (124 W) can drive the moisture out of the sludge only to a radius of approximately 1.2 cm (0.5 in.) from the bit—waste contact area. Thus only a trivial amount of sludge could be dried through this mechanism.

The heat flux required to drive moisture out of a moist, porous salt cake is less than that required to dry sludges. The dryout heat flux for a moist salt cake is estimated to be about 1,500 W/m^2. The heat generated at the bit-waste interface could dry out a small volume, about 0.004 m^3 (0.14 ft^3) of salt cake. Combustion of such a small amount of waste would not be expected to cause either severe pressurization of the headspace or a release of a significant amount of material from the tank.

The conclusion of the evaluation is that rotary drill sampling of sludges has no potential to dry out sludges; therefore, fuel-nitrate combustion accidents caused by core sampling operations are not credible, with or without purge flow, down force, or rotational speed interlocks. Rotary core sampling does have the potential to dry small amounts of salt cake, but the consequences of drying and reacting such small quantities are insignificant. Rotary core drilling has the potential to initiate organic-nitrate reactions if the waste is dry and contains sufficient fuel. Thus, fuel-nitrate combustion accidents in salt cake are avoided if the waste fuel content is low, the salt cakes are moist, or the rotary-core safety interlocks are available to shut down drilling if drill operations exceed the established safety limits.

8.2.10 Vehicle Operation Above the Tank

A number of vehicles are used in the tank farms for construction, surveillance sampling, and maintenance activities.

Two incidents in the last 2 years have raised a concern about motor vehicles that enter the tank farms. There is a possibility that an accident could occur that results in fuel carried by a vehicle entering a waste storage tank and possibly igniting. The frequency of such an event has been analyzed for tank C-103 and is summarized in Appendix 8F. An event tree approach was used to evaluate two scenarios: (1) a vehicle ruptures its gas tank on a riser and the spilling gas is ignited by sparks as it enters the tank and (2) the gasoline enters the tank and is subsequently ignited. The results of the event tree analysis show that the frequency of burning fuel entering a riser and starting an organic pool fire in tank C-103 is 6.71×10^{-5} per year. The frequency of gasoline leaking into a riser and leading to a lower flammability limit condition and eventual ignition is 6.64×10^{-6} per year. The estimated annual frequency of such an event happening at any single-shell tank is greater than estimated for the single tank in the tank C-103 analysis by approximately two orders of magnitude, as there are 149 single-shell tanks in total.

The effects of burning vehicle fuel on waste moisture and temperature are analyzed in Appendix 8F. The analysis indicates that although a small portion of waste may be heated to high temperatures, thus requiring this scenario to be considered as a possible ignition source for combustible wastes, the amount of energy released is too small to dry out a significant portion of moist waste. Therefore, vehicle fuel scenarios are not considered credible dryout mechanisms.

Finally, the waste depth to which a gasoline fire could be an organic-nitrate reaction initiator is analyzed in Appendix 8F. It is concluded that the heating effects of a gasoline fire in raising waste temperature to the organic-nitrate reaction temperature are limited to the top 14 cm (5.5 in.) of the waste.

8.2.11 Lightning Strikes

The likelihood that energy will be delivered to the waste from lightning strikes has been evaluated in WHC-SD-WM-SARR-027, *Evaluation of Hazards to Tank Farm Facilities from Lightning Strikes* (Cowley 1994). The evaluation considered lightning strikes that could damage above ground equipment as well as strikes that could cause lightning current to reach the waste.

The structure of the single-shells, the rebar in the concrete, and the fact that the tank is buried, gives an single-shell tank some of the properties of a faraday cage. Single-shell tanks on the other hand lack a complete steel liner, and this makes a single-shell tank less effective than a double-shell tank as a faraday cage. In addition, construction drawings do not indicate that any effort was made during construction to make electrical connections between risers and the rebar in the concrete. There are, therefore, electrically noncontinuous paths (e.g., risers) through the tank that can result in arching. An single-shell tank typically has 10 to 20 risers penetrating the tank dome that may contain installed equipment such as thermocouple trees, waste level measuring devices, saltwell screens and pumps, air lift circulators, old transfer pumps, liquid observation wells, and other old equipment. Other risers are empty but protrude into the tank headspace varying distances.

A lightning strike that hits the top of an single-shell tank could be expected to create high electrical potentials (voltages) between the risers and the ground. These high voltages could cause lightning current to arc from the risers and installed equipment into the waste and then to ground (through the tank side walls or bottom). As lightning strikes are often composed of multiple strokes (ground leaders, return strokes, dart leaders, return stroke), it is quite possible that lightning current and arcing could occur through multiple paths (e.g., risers). As a conservative safety analysis assumption, the frequency of lightning current arcing to the waste surface in single-shell tanks, is therefore assumed to be equal to the frequency that lightning strikes the top of the tank, or 5 x 10^{-4}/yr per single-shell tank as a reasonable safety analysis assumption.

Lightning current can reach the waste in two different general scenarios. In the first scenario, lightning current reaches the waste by traveling down equipment that extends from the top of the tank downward and is immersed in the waste, such as a thermocouple tree. With this type of configuration, the lightning current is transferred to the ground by arcing to the riser near the top of the tank and by transfer from the thermocouple tree to the waste and then to the tank wall and bottom. If the electrical contact between the object and the waste is good, the energy is dissipated with little waste heating as a result. This is because of the relatively low resistivity of the waste and the relatively large volume of waste into which the energy is deposited. The waste temperature increase was estimated to be no more than 1 °C (1.8 °F). Good electrical contact is expected if the waste contains significant moisture or is saturated with liquid. This scenario has no significant potential to heat or dry waste material.

If, on the other hand, the electrical contact between the object struck and the waste has a high resistance or the waste has relatively high resistivity, the electrical field can break down, and arcing would occur. Poor contact could result because of dry waste or the presence of an annular gap between the object and the waste. Such an annular gap could result from the thermocouple tree installation, which used sluicing or high-pressure jetting to cut a hole in the waste in which to insert the tree. Poor electrical contact between the object and the waste is most likely in relatively dry waste, as might be expected in salt cake wastes following interim stabilization. Electrical arcing can result in very high waste temperatures at the point where the arc contacts the waste. The energy is then dissipated with little ohmic heating. Therefore, such a scenario has little potential to dry a significant amount of waste, but could significantly heat a small portion of waste.

In the second arc-producing scenario, lightning current travels down equipment that is suspended above the waste surface, such as a riser or equipment installed in a riser, and the current arcs from the end of the suspended object to the waste surface. In the arc-gap scenario, the energy deposition is concentrated. The waste temperatures reached are high, but the waste volume that is heated near the point of contact is very small. If the waste resistivity is relatively high, the current will arc through the waste material until the energy density falls, such that the electric field intensity falls below the breakdown field of about 10,000 V/cm. Once below the breakdown field, the current begins to flow in a uniform manner through the waste. Heating during this later condition is by $E=I^2 \times R$ (ohmic) heating. The temperatures reached during arcing through materials can be relatively high, as evidenced by the melting and formation of glass like fulgurites in sands and soils hit by lightning. Ohmic heating depends on the amount and duration of the current, the resistivity of the material and the thermal diffusivity of the material. The evaluation in Cowley (1994) estimated that the lightning current ohmic heating falls below a level that would heat the waste to fuel-nitrate ignition temperatures (assumed to be 150 °C [302 °F]) at a radius of 4 to 5 cm (1.6 to 2 in.) from the arc to uniform current flow transition point. The radius of the waste volume where the ohmic heating would fall below the boiling point of the waste liquids would be less than 10 cm (3.9 in.). Therefore this arc-gap scenario might significantly heat small portions of waste (several kilograms) but does not have the potential to heat or dry a significant quantity of wet waste.

The likelihood and radiological consequences of heating and reacting small quantities of waste as in the arc-gap events have been evaluated in Cowley (1994). If the reacted material is limited to that heated by the ohmic heating (i.e., the reaction does not self-propagate), the risk posed by the event is very low. The reaction would be limited if the waste had low fuel concentration or sufficient moisture to prevent propagation (SAFE or CONDITIONALLY SAFE). Lightning strikes, however, can be an initiator for a propagating reaction if the waste is reactive. The probability of lightning being a fuel-nitrate initiator is the product of the probability that lightning will strike an object, the probability that the current will arc to the waste, the probability that the waste is reactive, and the probability that the lightning current and duration will ignite the waste. Using the described above, as a safety analysis assumption, it is reasonable to assume that the probability that lightning current will arc to the waste is the same as the probability that lightning will strike the ground above the waste tank, or 5×10^{-4}/tank-yr. The probability that the lightning current will reach reactive waste is not known, as the probability of reactive waste or locations for reactive waste is not known or estimated in this analysis. Lightning current, however, can flow through a reasonably large portion of the waste. The probability that lightning current would ignite reactive material is not known, but it is thought that small amounts of free water in the waste would make the waste ignition resistent. This is a result of rapid energy release at or near the lightning arc that would lead to steam explosions resulting in pressurization and formation of a crater where the arc hits. This leaves the boundaries of the crater at temperatures below the ignition temperature because of the rapid cooling provided by the flashing water. The behavior of the waste and or water under conditions of lower energy densities (i.e., some distance from the arc contact point) may differ, but it is expected that the presence of free water significantly reduces the likelihood of ignition.

8.2.12 Portable Exhauster Operation

Some tank farm operations may include the use of a portable exhauster. The effect of using a portable exhauster on waste moisture content has been evaluated, and it is shown that occasional use cannot significantly impact the moisture loss rate of a tank.

The portable exhauster (nominal 0.5 m^3/s [1,000 ft^3/min]) is mounted on a mobile platform and is positioned above the tank. The portable exhauster uses a 30.5-cm (12-in.) flexible duct bolted to a tank riser.

Most portable exhausters have the following equipment, in order of airflow:

- A deentrainer to remove large moisture particles
- A plenum to direct and control airflow
- A preheater to lower relative humidity in the airstream
- A roughing filter to screen large particles ahead of the HEPA filters
- Two banks of HEPA filters in series
- A manual damper to regulate airflow
- A fan/blower to pull air through the system
- A stack to direct exhaust air
- An air sampler to collect record sample of radioactive particles

- A continuous air monitor that detects radioactive particulates in the exhaust
- A seal pot to collect moisture from the system.

Upset Conditions. Failure of the exhauster could cause sparks and hot components (e.g., bearings). However, these would be exterior to the tank and could not heat or dry tank waste. The significant effect portable exhauster operations would have on waste moisture would be possible drying from increased ventilation flow rates.

Dryout Evaluation. The moisture loss rate during portable exhauster operation was evaluated in FAI (1994b). Portable exhauster operation is transient in nature and cannot alter the waste temperature profile significantly, and thereby cannot alter the decay heat power fraction that is transmitted upward through the waste surface and tank headspace. Thus the maximum evaporation rate with exhauster operation is given by the upward power divided by the heat of vaporization.

As indicated in FAI (1994b), Table 2-2, only one tank, A-104, (normally on passive ventilation) has a headspace temperature that exceeds 43 °C (110 °F). From FAI (1994b), Table 5-2, a 43 °C headspace temperature implies a steady heat flux of 7.1 W/m^2 (by interpolation). Therefore, the maximum evaporation loss for tanks other than A-104 is

$$\frac{7.1\ W/m^2 \times 411\ m^2}{2.4 \times 10^6\ J/kg} = 10^{-3}\ kg/s \text{ or } 600\ kg/wk.$$

Thus exhauster operation for several weeks removes only a trivial amount of moisture. For tank A-104, the corresponding evaporation rate is about three times higher, which is still trivial over a short period of time.

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APPENDIX 8A

POTENTIAL REACTION CONSEQUENCES

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APPENDIX 8A

POTENTIAL REACTION CONSEQUENCES

Consequences of a hypothetical reaction of organic nitrate-nitrite waste involve the heating and pressurization of the tank headspace by hot reaction product gases and the entrainment of other vapors or aerosols from waste that may be radiologically active. The degree of tank headspace pressurization is directly related to the amount of waste that is assumed to react.

If the reaction time is on the order of a few minutes, the tank headspace will respond as an essentially closed, adiabatic volume upon introduction of the reaction product gases. This is not expected because measured propagation rates are on the order of 1 cm/min (0.39 in./min). (Therefore, reaction time is expected to be on the order of tens to hundreds of minutes.) However, a conservative estimate may be made of tank headspace response by predicting its final adiabatic pressure and temperature. Such an estimate is conservative in the limits of small reacting volumes or long reaction time when venting and heat losses to tank walls become progressively more important.

Given an assumed quantity and composition (TOC) of reactant and the heat of the reaction, the temperature of the reaction products at equilibrium is calculated. Next, these reaction products are mixed with the tank headspace to yield the final equilibrium temperature and pressure.

The surrogate reaction, based on average energetics, is that between sodium acetate and sodium nitrate. Assumptions in the calculation include the following.

1. The reaction is swift, but shock effects may be neglected. Therefore, venting is unimportant, and the tank headspace maximum pressure is equal to the adiabatic isochoric value. (This is very conservative.)

2. Gas moles and energy yield are given by the surrogate reaction for sodium acetate.

3. The ideal gas law applies.

4. Miscellaneous property and geometry data are chosen.

The adiabatic temperature rise of the products is calculated by

$$\Delta T = \left[\left(1 - \frac{m}{100} \right) \frac{82}{24} \frac{TOC}{100} \Delta H - \frac{m}{100} \lambda \right] \frac{1}{c_{vp}}$$

where

ΔH = effective heat of reaction, J/kg
m = moisture content, (total water) wt%
λ = heat to vaporize water, J/kg
c_{vp} = specific heat of products, J/kg·K.

While the ideal heat of reaction is 7.8 MJ/kg, a value of 4 MJ/kg is used here in accordance with experimental values. The heat to vaporize water accounts for subcooling and is about 2.4 MJ/kg. The specific heat of products is a function of TOC and moisture and is roughly 1,000 J/kg·K. The exact value for specific heat used in the following calculations assumes that solids have a heat capacity of 800 J/kg·K and appropriate values are chosen for each gas.

The number of moles of gas added to the headspace (at a temperature ΔT above the initial temperature) accounts for both product gas and vaporized moisture:

$$\Delta n = \rho v \left[\left(1 - \frac{m}{100} \right) \frac{3}{24} \frac{TOC}{100} + \frac{m}{100} \frac{1}{18} \right]$$

where

ρ = reacting medium density
v = volume reacted.

The yield is 3 moles of product gas per mole of acetate. An energy balance yields the final mixing cup temperature of the headspace:

$$T_2 = \frac{m_1 c_{v1} T_1 + \Delta m \, c_{vm} (T_1 + \Delta T)}{m_1 c_{v1} + \Delta m \, c_{vm}}$$

where

m_1 = initial headspace gas mass
c_{v1} = specific heat
T_1 = temperature.

The added gas mass Δm and heat capacity c_{vm} follow directly from the number of added moles Δn. Finally, the ideal gas law provides the final headspace P_2:

$$\frac{P_2}{P_1} = \frac{n_1 + \Delta n}{n_1} \frac{T_2}{T_1}$$

where

n_1 = initial headspace number of moles
P_1 = pressure.

For the purpose of this calculation, a tank headspace of 2,800 m^3 (approximately 100,000 ft^3), initially at 310 K is chosen, so the initial gas mass is about 3,180 kg on about 110 kg·mol.

The previous equations are only valid when the TOC content is sufficiently high, or the moisture content is sufficiently low, such that all the moisture may be vaporized. The final pressure varies with fuel content (wt% TOC) and moisture content. The effect of increasing mositure increases the number of gas moles added to the headspace, but decreases the final product temperature, so its impact on final pressure is not large. The results for moist waste are similar to those for dry waste, and therefore only the results for dry waste are presented. Table 8A-1 compares the final headspace gas mole and temperature for dry waste.

Table 8A-1. Detailed Reaction Response for 1 m^3 Reacting.

TOC	Final headspace values for 1 m^3 reacting, dry waste	
	Gas moles, n_2	Temperature, T_2 (K)
3	117	339
5	122	387
7	127	454
9	132	535
11	137	629

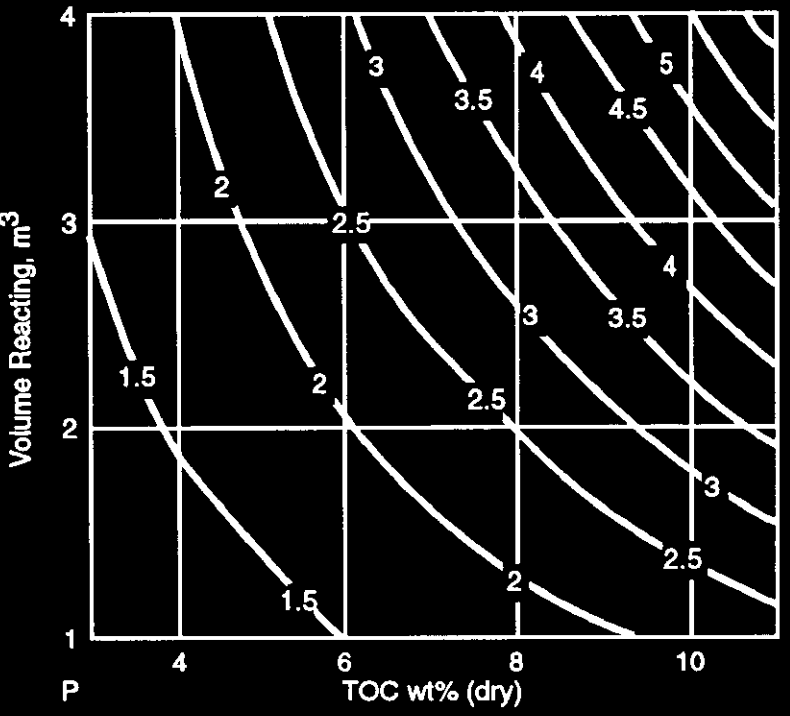
TOC = total organic carbon.

Figure 8A-1 presents a contour plot of final headspace pressure as a function of TOC and the reaction volume; selected values are presented in Table 8A-2.

For a TOC value of 6 wt% (the value at which sodium acetate fuel reactions are observed to propagate), a dry reacting volume of 1 m^3 would pressurize the tank headspace to 151.99 kPa (1.50 atm), or 48.26 kPa (7 lb/in^2 [gauge]) overpressure. This is enough to blow out any filter in the system and release gases and aerosols outside the tank through any tank orifices. A 6 wt% TOC dry reacting volume of 2 m^3 would cause a final pressure of about 212.78 kPa (2.1 atm). Such a pressure would lead to sonic flow through any orifices or failures.

A structural analysis indicates that a pressure of 197 kPa (28.5 lb/in^2 absolute) would cause extensive cracking of the concrete dome of a half-million-gallon tank, and the failure limit for a million-gallon tank is 183 kPa (26.5 lb/in^2 absolute). Upon removal of the internal load (i.e., depressurization of the headspace by venting), the dome could collapse because of soil load overburden. The potential for dispersal of tank contents is, therefore, high for a reaction of 2 m^3 (70.6 ft^3) at 6 wt% TOC.

Figure 8A-1. Headspace Absolute Pressure Response as a Function of Volume Reacting and Total Organic Carbon Concentration Dry Waste.



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P = Pressure, ATM.
Dry Waste

Table 8A-2. Absolute Pressure Response as a Function of Dry Reaction Volume.

Final pressure, kPa				
TOC	Dry reacting volume, m^3			
	1	2	3	4
5	141.25	181.37	221.60	262.03
7	172.15	243.48	315.22	387.26
9	210.96	321.61	432.96	544.62
11	257.26	414.93	573.60	732.78

NOTE: To convert from cubic meters to cubic feet, divide by 2.831685 x 10^{-2}.

TOC = total organic carbon.

APPENDIX 8B

IGNITION ENERGY REQUIREMENTS FOR ORGANIC-NITRATE SURROGATES

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Fauske & Associates, Inc.

DATE: May 9, 1995

TO: Dave Turner

FROM: Hans Fauske

SUBJECT: <u>Minimum Ignition Energies for Organic Waste Surrogate Materials</u>

A test campaign has been initiated to study the minimum ignition energies required for initiating condensed-phase combustion. Previous studies (FAI/94-103) have determined the minimum fuel concentration required for sustained combustion with various organic waste surrogate materials. While the minimum ignition energies for flammable gas mixtures are only a fraction of a millijoule, and therefore difficult to rule out, the required ignition energies for combustible solids appear to be many orders of magnitude larger. As an example, preliminary tests using a very large ignition source of about 138 joules (energy released in about 3 msec)* exhibit the absence of combustion with stoichiometric mixtures of the organic surrogate material and $NaNO_3$ with only 5 wt.% free moisture. A similar behavior is observed when the free water is replaced by a volatile organic liquid like dodecane. We note that such mixtures exhibit sustained combustion given an adequate ignition source (FAI/94-103). In the latter experiments the ignition is provided by an energy source of about 25 w applied to the sample until local combustion occurs. Total energy supplied in this manner usually is in the order of 1 KJ or more.

In the current campaign, test samples are typically about 25 cm^3. The test cell is constructed from a 100 ml glass graduated cylinder, which is cut off at about the 35 ml mark. The ignition source tested to date is a pyrotechnic "electric match". Supplied with 110 VAC this source releases about 138 J over a 3 ms period. The match is placed either on the surface of the sample or immersed in the sample to a depth of about 1 in. (see Figures 1 and 2). Triggering of the match and the subsequent potential for combustion are observed visually as well as videotaped.

Typical results are summarized in Table 1 and Figures 1 and 2.

HKF:lab
cc: J. M. Grigsby
A. B. Webb
J. E. Meacham
R. J. Cash
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*This energy is very large compared to typical spark energies, considering that Eckkoff (1991) estimates that a road tanker (truck) could conceivably produce a static discharge of 0.45 J.

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Table 1
Summary of Ignition Tests

Mixtures (Stoichiometric Fuel/Oxidizer)	Match Immersed	Match on Surface
37% Na Acetate/63% $NaNO_3$	Burn	Burn
50% Na Acetate·$3H_2O$/50% $NaNO_3$	No Burn	No Burn
49% Na Citrate·$2H_2O$/51% $NaNO_3$	Burn	Burn
46.5% Na Citrate·$2H_2O$/48.5% $NaNO_3$/5% Free H_2O	No Burn	No Burn
34% Na HEDTA·$2H_2O$/66% Na NO_3	Burn	Burn
32% Na HEDTA·$2H_2O$/63% $NaNO_3$/5% Free H_2O	No Burn	No Burn
16% Na Acetate·$3H_2O$/15% Na Citrate·$2H_2O$/ 11% Na NEDTA·$2H_2O$/53% Na NO_3/5% Free H_2O	No Burn	No Burn
44% Na Citrate·$2H_2O$/47% $NaNO_3$/9% Dodecane	No Burn	No Burn

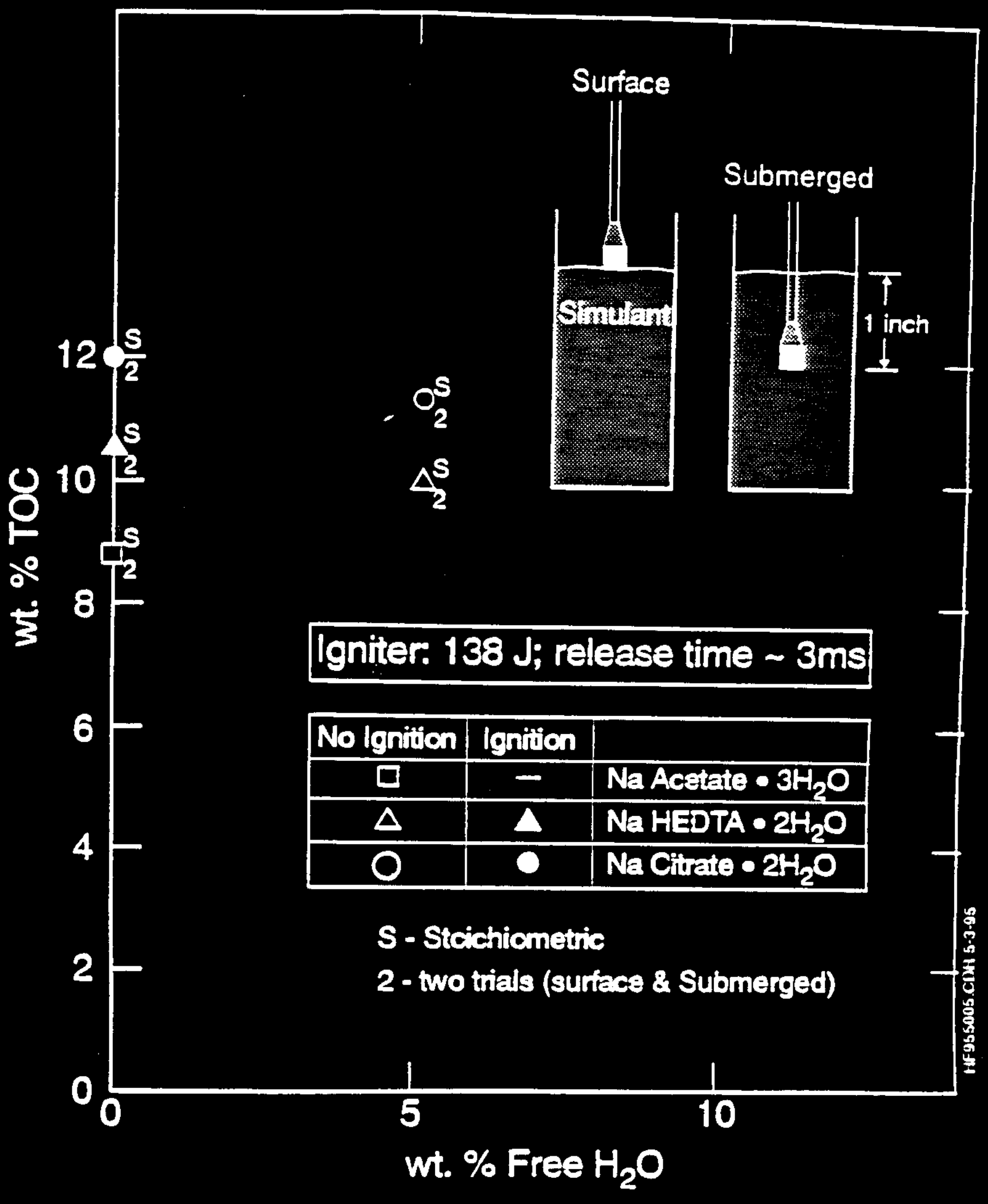

Figure 1 Ignition Potential and the Effect of Free Water

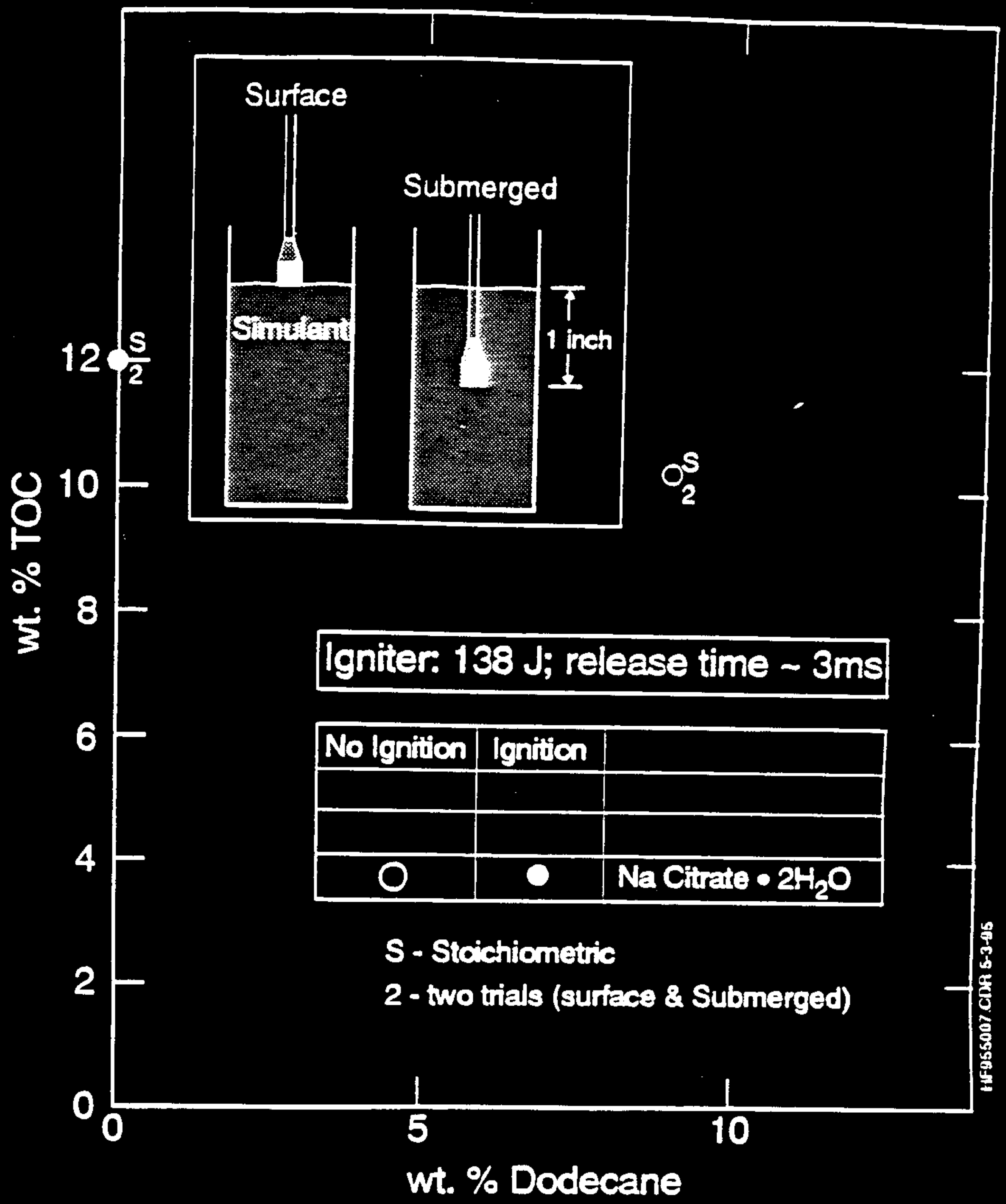

Figure 2 Ignition Potential and Effect of Volatile Organic

APPENDIX 8C

EFFECTIVE MAXIMUM DISTANCE BETWEEN AN ENERGY SOURCE AND REACTIVE MATERIAL FOR IGNITION TO BE CREDIBLE

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APPENDIX 8C

EFFECTIVE MAXIMUM DISTANCE BETWEEN AN ENERGY SOURCE AND REACTIVE MATERIAL FOR IGNITION TO BE CREDIBLE

1.0 INTRODUCTION

Most credible initiators deposit energy on the waste surface (e.g., dropped equipment, shorting electrical wires, falling welding slag), so it is important to determine how far the heating effects can travel and cause ignition. It is not credible to ignite waste that is beyond the region where ignition sources can penetrate. There are two important questions that need to be answered to determine the depth an initiator could penetrate: (1) how far would a hot object penetrate if it fell on the waste and (2) how far would the heat be conducted once an initiator is in contact with the waste?

1.1 PENETRATION BY FALLING OBJECTS

The first question can be answered by examining accident scenarios to determine the size and weight of potential initiators and the likely distance an initiator would fall. Larger objects with the potential to fall into the waste during operations are tethered to reduce the risk of dropping them (e.g., lights, video equipment, still cameras). Other postulated potential initiators, such as hot slag from welding, sparks from grinding, or burning gasoline, do not have a large mass and probably would not penetrate the waste very far. Drier waste is hard (most salt cake waste requires rotary-mode core sampling because the waste cannot be penetrated by the push-mode sampler at the 6,895-kPa [1,000-lb/in^2] pressure limit), and objects would probably not penetrate very far if dropped on the waste. As the moisture content of the waste increases, the waste softens and dropped objects will penetrate farther; but wet waste does not pose a propagation hazard. Sludge waste may have some shallow surface cracks as a result of drying and consolidation; however, sludges retain considerable water, and therefore do not pose a propagation hazard.

1.2 HEAT TRANSFER INTO THE WASTE

For a high temperature instantaneously supplied to the surface of the waste, the temperature at any point can be calculated if some parameters are known. Transient one-dimensional heat conduction in a semi-infinite solid is given by

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha}\frac{\partial T}{\partial t}. \qquad \text{(8B-1)}$$

Some simplifying assumptions are made to solve this equation. The effects of phase changes as a result of waste heating are ignored (the nitrate-nitrite salts would melt around 250 °C [482 °F]), and the boundaries are assumed to be

$T(x,0) = T_0$, $T(\infty,t) = T_0$, and $T(0,t) = T_s$. The solution (Kreith and Black 1980) to Equation 8B-1 is

$$\frac{T(x,t) - T_s}{T_0 - T_s} = \mathrm{erf}\left[\frac{x}{2\sqrt{\alpha t}}\right] \qquad (8B\text{-}2)$$

where

T_0 = ambient temperature
T_s = temperature of hot surface
α = thermal diffusivity
x = distance
t = time
erf = Gauss error function.

The temperature of interest, $T(x,t)$, is 200 °C [392 °F], which is the temperature ignition criterion for condensed-phase propagating reactions (see Chapter 5 of the main report). The ambient waste temperature, T_0, is assumed to be 30 °C (86 °F). A reasonable diffusivity for Hanford Site waste is 10^{-6} m^2/s, which is about the value calculated for waste sludge simulants (Jeppson and Wong 1993). For comparison, the diffusivity of carbon steel, a moist clay (containing 49 wt% water), and wood are about 10^{-5}, 10^{-6}, and 10^{-7} m^2/s, respectively (Kreith and Black 1980). A plot of depth as a function of time for different temperatures is shown in Figure 8C-1.

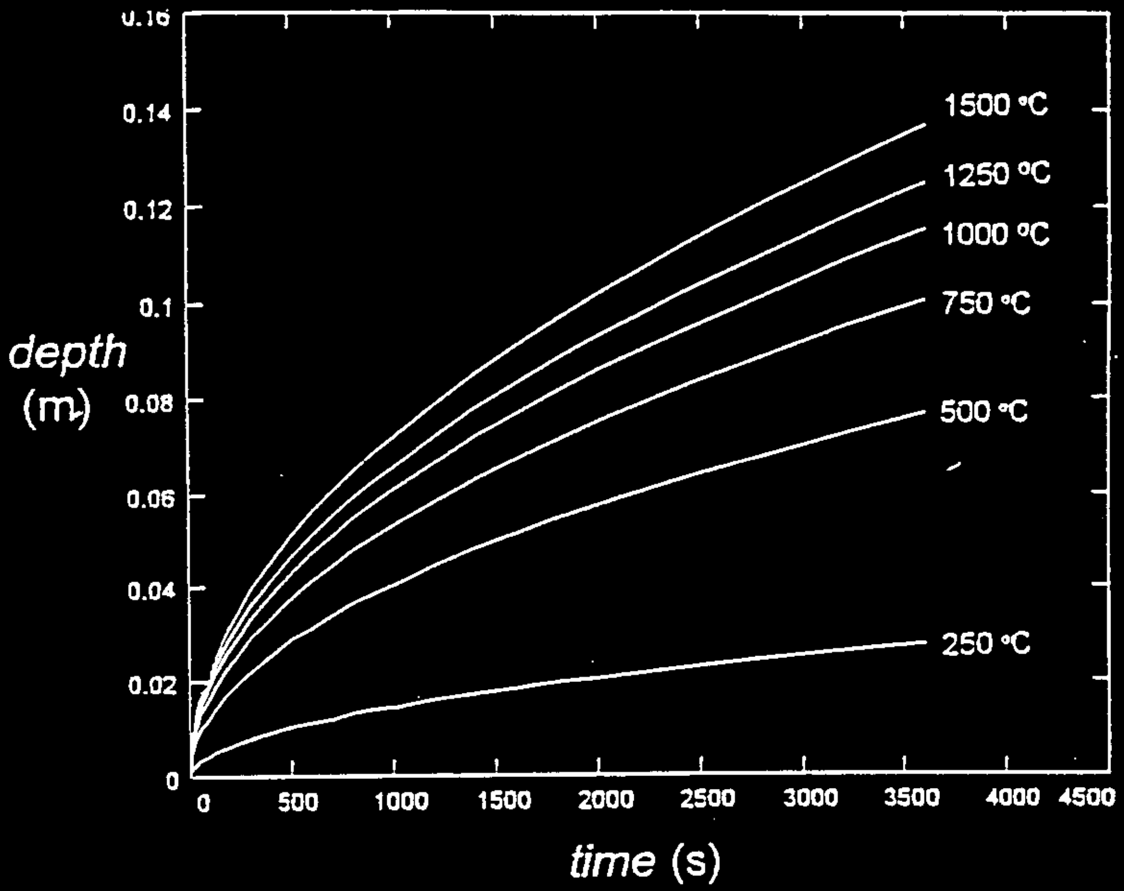
Typical initiators last for only seconds or minutes, and from Figure 8C-1 it can be concluded that the heat would be conducted to a depth of only a few centimeters. However, to adjust for the penetration of a falling initiator and to add conservatism to the calculation, a high initiator temperature (1,500 °C [2,732 °F], about the temperature of molten iron) and a long duration (1 hour) will be used to determine "near surface." For an initiator at 1,500 °C, (2,732 °F) the waste depth of interest is 2 cm to 14 cm (0.8 in. to 5.5 in.).

2.0 REFERENCES

Kreith, F., and W. Z. Black, 1980, *Basic Heat Transfer*, Harper & Row, Publishers, New York, New York.

Jeppson, D. W., and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Figure 8C-1. Depth of Waste Reaching 200 °C as a Function of Time for Various Initiator Temperatures.



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APPENDIX 8D

POTENTIAL WASTE HEATING AND DRYOUT FROM SUBMERSIBLE PUMP OVERHEATING SCENARIO

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APPENDIX 8D

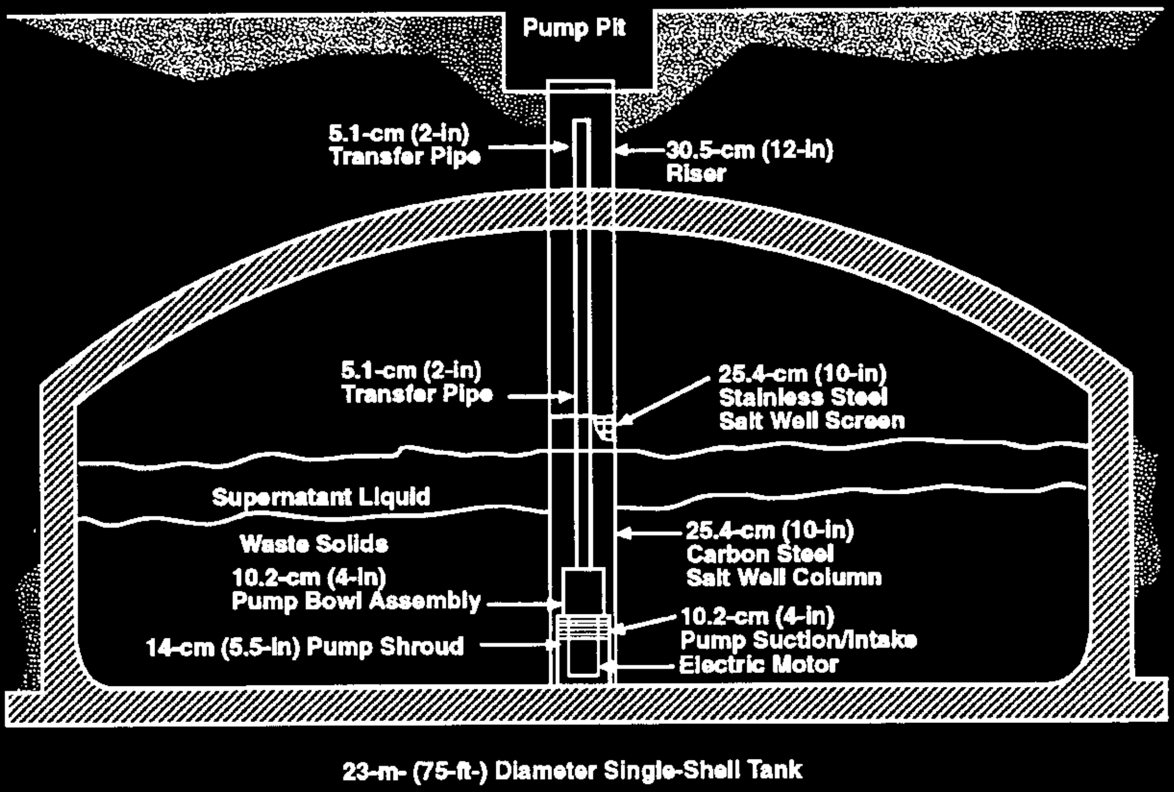
POTENTIAL WASTE HEATING AND DRY OUT DUE TO SUBMERSIBLE PUMP OVERHEATING SCENARIO

1.0 BACKGROUND

The configuration of a submersible pump, motor, and salt well is shown in Figure 8D-1. The submersible pump is mounted to a 5.1-cm (2-in.) transfer pipe extending up through the tank and an adapter flange into the pump pit. The submersible pump is driven by a 5-horsepower, 480-V, 3-phase motor. The motor is located below the pump suction and is submersed in the liquid being pumped. The motor is cooled by the liquid flowing past it during pumping operations. The minimum specified flow velocity past the motor is 1.27×10^{-3} m/s (0.25 ft/min). The pump/motor assembly has a flow director (shroud) installed to aid in maintaining adequate cooling flow. A thermal overload device is installed to shut off the motor in the event that the pump motor temperature increases because of abnormal pumping conditions.

Possible failure modes have been analyzed in previous safety analyses (Milliken 1992) to identify credible overheating scenarios. The results of this evaluation are summarized here.

Figure 8D-1. Submersible Pump and Salt Well Configuration.



1.1 EVALUATION RESULTS

The submersible pump and motor are cooled by the passing flow of the liquid being pumped. If some failure internal to the pump or motor were to cause excessive heating, the thermal switch on the electrical power supply would open if it were working correctly. Most such internal failures would also draw excessive current and blow the 15-amp fuse on the power line. The only reasonable source for excessive heating would be the continued running of the pump when there was no longer fluid to it. Even this condition would open the thermal switch, removing power to the motor. However, there is no flow meter on the output of the pump. Rather, a material balance is calculated and recorded at least once per hour to determine whether the level in the tank is going down and thus whether the pump is still pumping. Therefore, the probability that the pump would continue to run without pumping fluid was estimated based on a combination of human error (e.g., failure to notice that the pump was not pumping or failure to shut off the pump) and failure of the thermal switch to open. The probability was determined to be 3.0×10^{-8} per transfer.

For such a scenario to dry significant portions of waste, flow past the pump would need to stop, the pump would need to overheat, the liquid surrounding the motor (which is below the pump suction) would need to be boiled away, and the heat from the overheating motor would need to be transferred through the salt well and into the surrounding waste at a sufficient rate to cause waste dryout.

1.1.1 Reasonably High Estimate of Faulted Condition Power Generation

It would appear to be unreasonable for the pump motor to continue to draw current above 15 amp for any length of time as this would require the fuse to fail to blow and the thermal protection device to fail to open on high temperature. The maximum power generated might then be estimated as the power produced when the motor is drawing 15 amp at 480 V or 7,200 W. This power is assumed to be produced within the motor enclosure, which is 0.095 m (0.3 ft) in diameter and approximately 0.6 m (2 ft) tall.

1.1.2 Evaluation of Dryout Scenario

Dryout of waste surrounding the salt well because of pump heat can only occur after water in the well is evaporated. Given a 25.4-cm (10-in.) outside diameter salt well, a 12.7-cm- (5-in.-) diameter pump/motor assembly, and a motor that is about 0.6 m (2 ft) tall, the water volume in the annulus between the motor and the salt well is 22.8 L, and the water mass is about 22.3 kg. With a motor producing about 7,200 W, the water would evaporate in about 8,000 seconds, or more than 2 hours.

Even if the water in the annulus were evaporated dry, and no additional water from surrounding waste were to drain into the annulus, drying of the waste outside of the salt well would require the motor to heat up significantly to transfer heat through the annulus to the waste surface. To achieve appreciable drying, the waste would need to be heated to 100 °C 212 °F). To transfer sufficient heat across the 6.4-cm (2.5-in.) gap by radiation and conduction, the motor would need to reach approximately 740 °C (1,364 °F), calculated as follows.

Temperature (T) of motor to yield 7,200 W to salt well at 100 °C (212 °F). Assume parallel plates, salt well area, $\bar{\varepsilon}$

(1) $Q = 7{,}200$ W

(2) $A = \pi\ [2\ \text{ft}/3.28][10\ \text{in.}/(12 \times 3.28)] = 0.487\ \text{m}^2$

(3) $Q/A = 14{,}794\ \text{W/m}^2 = \sigma\varepsilon(T^4 - 373^4)$

(4) $\sigma = 5.67 \times 10^{-8}, \quad \varepsilon = 0.75$

(5) $\therefore T = 778, \quad K = 505\ ^\circ\text{C}$

NOTE: The motor must radiate to the shroud, which radiates to the salt well. Taking 778 K as the shroud T that radiates to the salt well at 373 K, the motor T is given by repeating (3):

(6) $Q/A = \sigma\varepsilon\ (T^4 - 778^4)$

(7) $\therefore T = 919, \quad K = 646\ ^\circ\text{C}$

The motor would actually be hotter because the smaller motor area implies (Q/A) larger by a factor 2, resulting in T = 1,015, K = 742 °C.

It is unrealistic to postulate that the pump/motor would continue to run at such a temperature. Therefore, it is concluded that submersible pump loss of cooling scenarios do not have significant potential to heat or dry waste.

2.0 REFERENCES

Milliken, N. J., 1992, *Basis for Emergency Pumping of Tank 241-T-101 Using a Submersible Pump*, USQ Evaluation Number 8-93-PMP-101-T, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX 8E

WASTE DRYOUT DURING ROTARY CORE DRILLING

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APPENDIX 8E

WASTE DRYOUT DURING ROTARY CORE DRILLING

1.0 INTRODUCTION

Rotary core drilling can produce heat at the drill bit—waste interface, especially if drill progress is impeded. The heat produced may be sufficient to dry waste near the heat generation point. This potential is evaluated for two cases: (1) sludges, which are composed of small particles and have a high capacity to retain moisture, and (2) salt cakes, which are more porous in nature and are less retentive of moisture.

The key parameters that govern bit—waste interface temperatures are drill bit purge flow rate, drill down force, and drill rotational speed. In addition, waste conditions are important as well. Harder wastes, which are more difficult to drill through, generate higher temperatures. Wastes with lower thermal conductivity would also result in higher local waste temperatures.

A safety envelope was developed through testing and thermal analyses such that operation within the envelope would maintain cool waste temperatures. Operation outside of the envelope is prevented by shutdown interlocks, which stop drilling operations.

The operating safety envelope, developed in WHC-SD-WM-TRP-123, *Core Drill Operating Envelope Test Report* (Keller 1993), is as follows:

- Maximum rotational speed of 55 revolutions per minute
- Maximum downward force of 5.2 kN (1,170 lbf)
- Minimum purge gas flow rate of 1.4 x 10^{-2} m^3/s (30 ft^3/min).

These operating parameters ensure that the drill bit temperature will not increase more than 57 °C (103 °F). This value is based on the drill bit reaching a maximum temperature of 150 °C (302 °F) in the highest measured temperature tank waste. This temperature provides a safety margin below the lowest ignition temperature for fuel-nitrate wastes and provides a safety approach that is applicable to dry, combustible wastes. Additional safety margin is provided, however, by the presence of moisture, which would quench any fuel-nitrate reactions even if they were initiated. The effects of rotary core sampling on drying the waste are evaluated below.

The heat generation rate at the drill bit—waste interface has been estimated through thermal analysis and confirmatory testing in waste simulants. The heat generation rate at the bit—waste interface as estimated by the thermal model is indicated in Table 8E-1.

The total heat load increases linearly with axial load and as the square root with rotating speed. This heat load is distributed over about 26 cm^2 (4 in^2) of drill bit—waste contact area.

Table 8E-1. Total Heat Load at Drill Bit—Waste Interface.

Rotating speed (rpm)	Axial load		Total heat load (watts)
	kg	lb	
10	226.8	500	18.7
	453.6	1,000	37.1
	680.4	1,500	55.6
30	226.8	500	32.0
	453.6	1,000	64.1
	680.4	1,500	96.2
50	226.8	500	41.4
	453.6	1,000	82.8
	680.4	1,500	124.2

rpm = revolutions per minute.

Rotary core drilling can produce heat at the drill bit—waste interface, especially if drill progress is impeded. The heat produced may be sufficient to dry waste near the heat generation point. This potential is evaluated for two cases: (1) sludges, which are composed of small particles and have a high capacity to retain moisture, and (2) salt cakes, which are more porous in nature and are less retentive of moisture.

2.0 SLUDGE

Moisture retention and drying of sludges has been evaluated both analytically and through experiments. Experiments were performed with ferrocyanide sludge simulants and kaolin clay. The results of this evaluation are reported in WHC-EP-0816, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout* (Meacham 1994). The evaluation considered both global drying as well as local drying mechanisms. The report concludes that waste sludges, which are composed of fine (micron-sized) precipitate particles, are capable of holding large quantities of water within their pores. The water in sludge is strongly held by the sludge solids as a result of electrostatic forces and is strongly related to the small particle size that comprises the sludge. The tenacity with which the sludge maintains its "grip" on the sludge waste component is illustrated by several experiments, including experiments that included local heat sources.

Based on experiments and analytical modeling, an expression was developed to determine the heat flux required to produce sufficient evaporation from the heated region to exceed the return flow of moisture from consolidation pressure. This expression is described in Meacham (1994), p. 6-23, Equation 6-36, as

$$Q_{cr} = \frac{3\kappa \rho_L h_{fg} \sigma_{cr}}{\mu_L R_{HS}^2}$$

where

Q_{cr} = heat flux needed to drive moisture from the sludge
κ = permeability of the sludge
ρ_L = density of the liquid
h_{fg} = latent heat of evaporation for the liquid.
σ_{cr} = effective stress (particle pressure) when a liquid saturated state can no longer be maintained at the evaporating surface
μ_L = viscosity of the liquid
R_{hs} = radius of the "hot spot."

This equation was rearranged to solve for a heated, dried-out waste radius (R) using the following values:

- $\kappa = 10^{15}$ m^2 (obtained from consolidation [draining] tests performed on sludge simulants [Meacham {1994}, Section 6.3.1])
- σ_{cr} of 10^4 cm water (estimated from the sludge simulant consolidation curve, [Meacham {1994}, p. 6-22])
- $\rho_L = 10^3$ kg/m^3
- $h_{fg} = 2.2 \times 10^6$ J/kg
- $\mu_L = 2.8 \times 10\text{-}3/\mu/s$
- Q_{cr} = 124 W.

The result is that the power (Q) in watts is sufficient to sustain a dried-out region radius (R) of 1.25 cm. Thus, only a trivial amount of waste could be dried.

3.0 SALT CAKE

Salt cakes are composed of salt crystals with significantly greater particle size than sludges. Salt cake is best described as porous in nature.

Porous salt cakes retain moisture with less tenacity. An expression for dryout in a porous medium is given in Meacham (1994), p. 5-17, Equation 5-2, as

$$q_{max} = \frac{h_{fg}\,\kappa\,(\rho_f - \rho_g)\,g}{\nu_g} \qquad (5\text{-}2)$$

where

h_{fg} = latent heat of vaporization of interstitial liquid
κ = permeability of the medium
g = gravitational constant
$\rho_f - \rho_g$ = density difference between the interstitial liquid and its vapor phase
ν_g = kinematic viscosity of the vapor phase.

Using the Kozeny relationship between permeability and particle size d, (Meacham [1994], Equation 5-1), the permeability of salt cake can be estimated:

$$\kappa = \frac{d^2}{180} \cdot \frac{\epsilon^3}{(1-\epsilon)^2}.$$

Substituting estimated salt cake properties (particle diameter $d \approx 50\ \mu m$ and interstitial liquid volume fraction [$\epsilon \approx 0.35$]) into this equation yields

$$\kappa = 1.4 \times 10^{-12}\ m^2$$

for the permeability of porous salt cake. Using this value with the parameters $\rho_f - \rho_g = 10^3\ kg/m^3$, $h_{fg} = 2.2 \times 10^6$ J/kg, and $\nu_g = 2 \times 10^{-5}\ m^2/s$ in Equation 5-2 gives

$$q_{max} = 1{,}500\ W/m^2.$$

Given this critical heat flux, a sphere with radius of approximately R = 0.1 m (0.33 ft) could be dried by the 125 W of heat produced at the drill bit-waste interface. This equals about 0.004 m^3 (0.14 ft^3) of waste material, or about 4 L, of potentially reactive waste. Combustion of such a small amount of waste would not be expected to cause either severe pressurization of the headspace or a release of a significant amount of material from the tank.

4.0 REFERENCES

Keller, C. M., 1993, *Core Drill Operating Envelope Test Report*, WHC-SD-WM-TRP-123, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., 1994, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout*, WHC-EP-0816, Westinghouse Hanford Company, Richland, Washington.

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APPENDIX 8F

SCOPING ANALYSIS OF WASTE DRYOUT CAUSED BY A GASOLINE BURN IN A SINGLE-SHELL TANK

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APPENDIX 8F

SCOPING ANALYSIS OF WASTE DRYOUT CAUSED BY A GASOLINE BURN IN A SINGLE-SHELL TANK

There is a possibility that an accident could occur that results in fuel carried by a vehicle entering a waste storage tank and possibly igniting. An analysis was performed to estimate the likelihood of vehicle accidents causing fuel to enter a tank. The analysis is documented in WHC-SD-WM-SARR-001, *Safety Analysis of Exothermic Reaction Hazards Associated With the Organic Liquid Layer in Tank C-103* (Postma et al. 1994, Appendix E). The analysis was performed to evaluate vehicle fuel related events for tank C-103. The analysis used event tree logic to obtain an estimate of the annual frequency of a pool fire or ignition of gasoline vapors in tank C-103. In the following paragraphs, an event in which vehicle fuel enters a waste tank is considered relative to the potential to heat or dry waste.

1.0 EVENT FREQUENCY

Two possible scenarios are considered in assessing the possibility of heating or drying waste as a result of gasoline spills from vehicles. The first scenario considers a vehicle gasoline leak caused by an accident that results in the puncture of the fuel tank by an object at grade level above a tank. Generally, this accident would be initiated by a vehicle driver backing over an object such as a riser or instruments. The gasoline leaking from the vehicle's fuel tank would then be ignited by a source of sparks from the accident or contact with hot elements of the vehicle's engine or exhaust system. Finally, the burning fuel would enter the tank through cracks in the cover blocks above the pump pit or through a riser damaged in the accident.

The second scenario considers a vehicle gasoline leak similar to the first except that the leaking fuel enters the tank but does not immediately ignite. The gasoline vapor in the waste tank then builds to the lower flammability point and is ignited by an ignition source in the tank. This ignition results in a rapid burn or deflagration.

The results of the tank C-103 analysis show that accidents that could cause fuel to enter a tank have a frequency that is considered credible, that is, greater than 1.0 x 10^{-6} per year. The uncertainty in some of the values used in the event tree analysis necessitated application of conservative values. No compelling evidence was found that indicated less conservative values should be used. The results of the event tree analysis show that the frequency of burning fuel entering a riser and starting an organic pool fire in tank C-103 is 6.71 x 10^{-5} per year. The frequency of gasoline leaking into a riser and leading to a lower flammability limit condition and eventual ignition is 6.64 x 10^{-6} per year. The estimated annual frequency of such an event happening at any single-shell tank is greater than that estimated for the single tank in the C-103 analysis by approximately two orders of magnitude as there are 149 single-shell tanks in total.

2.0 DRYING EFFECTS

The following assessment of waste dryout is based on energy balance considerations in which the combustion energy of an assumed burn is transferred to surfaces inside a partially filled single-shell waste tank. Half of the energy transferred to the waste surface is assumed to cause water evaporation and half is expended in sensible heating of waste solids.

Combustion energy depends on the mass of gasoline burned and on the combustion energy per unit mass. The mass of gasoline burned is based on an estimate of how much could leak into a tank during a vehicle fuel tank/tank riser rupture accident. The quantity could vary from zero to a large fraction of the fuel tank's contents. For purposes of this assessment, the quantity was specified as 0.04 m^3 (10 gal). This quantity is judged to fall at the upper end of possible values. Combustion energy was assigned a value of 45 MJ/kg, a value typical of hydrocarbon fuels (NFPA 1988). Total combustion energy is thus:

$$10 \text{ gal} \times \frac{1 \text{ m}_3}{264 \text{ gal}} \times \frac{800 \text{ kg}}{\text{m}^3} \times \frac{45 \text{ MJ}}{\text{kg}} = 1{,}360 \text{ MJ}.$$

The combustion energy would initially be absorbed as a sensible heat gain in the headspace air in the tank. The hot gas would then cool by heat transfer to exposed surfaces. The exposed area of waste is roughly half of the area of the tank dome and exposed sidewalls. Therefore, an estimated one-third of the total combustion energy would be transferred to the waste:

waste heating energy = 1,360 MJ x 1/3 = 455 MJ.

Part of the energy imparted to the waste would cause it to heat (sensible heat gain) and part would cause the evaporation of water. A rough estimate is that 50% of absorbed energy would be converted to latent heat, so the quantity of water evaporated is

$$455 \text{ MJ} \times 0.5 \times (1 \text{ kg } H_2O/2.3 \text{ MJ}) = 99 \text{ kg } H_2O.$$

This quantity of water is very small compared to the total water in stored waste. For a typical sludge having a water content of 40 wt% and a specific gravity of 2, the volume of waste that contains 99 kg (218 lb) of water is

$$\text{volume} = 99 \text{ kg } H_2O \times \frac{1 \text{ m}^3 \text{ waste}}{2{,}000 \text{ kg waste}} \times \frac{1 \text{ kg waste}}{0.4 \text{ kg } H_2O} = 0.12 \text{ m}^3.$$

For a tank having a diameter of 22.86 m (75 ft), the exposed waste area is 411 m^2 (4,424 ft^2). Thus the depth of waste that contains 99 kg of H_2O is

$$\text{waste depth} = \frac{0.12 \text{ m}^3}{411 \text{ m}^2} = 3.01 \text{ E-04 m} = 0.3 \text{ mm}.$$

A similar calculation for salt cake that contains 10 wt% water initially results in a dryout depth of 1.2 mm (0.05 in.). The dryout depth is thus very small, indicating that one-time gasoline fires could not lead to significant dryout of waste in single-shell tanks.

3.0 REFERENCES

NFPA, 1988, *SFPE Handbook of Fire Protection Engineering*, SFPE-88, National Fire Protection Association, Quincy, Massachusetts

Postma, A. K., G. L. Borsheim, J. M. Grigsby, R. L. Guthrie, M. Kummerer, M. G. Plys, and D. A. Turner, 1994, *Safety Analysis of Exothermic Reaction Hazards Associated With the Organic Liquid Layer in Tank 241-C-103*, WHC-SD-WM-SARR-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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9.0 SUMMARY OF REQUIRED CONTROLS

This chapter provides a summary of the results of the analyses described in this report and a summary of controls required to maintain safety. The results are reported by assigning the waste in each single-shell tank to one of three preliminary fuel-nitrate safety categories. The assignment of waste to a safety category is based on (1) the safety criteria described in Chapter 5, (2) the estimates of waste fuel and moisture concentrations described in Chapter 6, and (3) the analysis of possible moisture loss that can occur during planned interim storage, as described in Chapter 7. Finally, the required safety controls to prevent unacceptable consequences as a result of fuel-nitrate combustion accidents are summarized for each safety category.

9.1 SINGLE-SHELL TANK WASTE SAFETY CATEGORIZATION

The wastes in the single-shell tanks are categorized as either SAFE, CONDITIONALLY SAFE, or UNSAFE when compared to the safety criteria described in Chapter 5 and the estimates of waste conditions and projected moisture loss during planned interim storage described in Chapters 6 and 7. The results of the categorization are indicated in Table 9-1 (all single-shell tank wastes) and Table 9-2 (salt cake tank wastes) at the end of this chapter. Steps leading to determination of the safety category are described in the following paragraphs, and an example is provided. See Chapter 2, Section 2.5, for a detailed categorization process sequence description.

First the waste phases (salt cake, sludge, and liquid) present in the tank are determined. If the tank contains a measurable quantity of salt cake, it is a salt cake tank. If the tank contains a measurable quantity of sludge, but no salt cake, it is a sludge tank. Salt cake tanks and sludge tanks are handled differently. For salt cake tanks, the initial (not yet jet pumped) wt% TOC wet basis and the initial wt% free H_2O values are compared to the TOC/moisture criteria line (Chapter 5, Figure 5-8). Next, the actual or predicted jet-pumped TOC and H_2O values are compared to the criteria line. Finally, the projected 50-year dryout TOC and H_2O values are compared to the criteria line. For sludge tanks, the initial wt% TOC wet basis and the initial wt% H_2O values are compared to the criteria line. Then the initial TOC and 50-year dryout H_2O values are compared to the criteria line. (The conservative modeling for the draining effects did not take full advantage of the solubility of energetic organic compounds. In a future revision of this report, this effect is expected to show that most salt cakes will be very low in fuel as a result of draining. Alternate evaluations were performed in Appendix 7D for four selected tanks that do account for this effect.)

A safety category of SAFE means the tank currently meets and is predicted to meet the safety criteria for all conditions (i.e., initial, drained by jet pumping or leakage, and after 50 years dryout). A safety category of CONDITIONALLY SAFE means the tank is currently in the SAFE region, but jet pumping, leakage, or dryout (or a combination thereof) is predicted to cause the tank to enter the UNSAFE region. A safety category of UNSAFE means the tank does not meet the safety criteria.

Table 9-1. Comparison of All Single-Shell Tank Wastes With Safety Criteria. (5 sheets)

Tank	Total organic carbon,[a] initial-wet basis (wt%)	Moisture,[a] initial (wt%)	Moisture,[a] 50 years (wt%)	Safety category[b]
A-101	Salt cake tank - see Table 9-2			SAFE
A-102	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
A-103 Sludge	2.60	18.40	13.55	SAFE
A-104 Sludge	0.60	23.60	0.00	SAFE
A-105 Sludge	0.60	23.60	3.91	SAFE
A-106 Sludge	1.90	23.20	19.79	SAFE
AX-101[c]	Salt cake tank - see Table 9-2			SAFE
AX-102[c]	Salt cake tank - see Table 9-2			SAFE
AX-103	Salt cake tank - see Table 9-2			SAFE
AX-104 Sludge	0.60	23.60	20.60	SAFE
B-101 Sludge	0.60	13.40	0.00	SAFE
B-102	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
B-103[c] Sludge	0.60	13.40	8.88	SAFE
B-104	Salt cake tank - see Table 9-2			SAFE
B-105	Salt cake tank - see Table 9-2			SAFE
B-106 Sludge	0.30	28.30	24.97	SAFE
B-107 Sludge	1.20	26.70	23.44	SAFE
B-108 Sludge	1.20	26.70	22.90	SAFE
B-109 Sludge	1.20	26.70	23.16	SAFE
B-110 Sludge	0.20	23.60	20.05	SAFE
B-111 Sludge	0.40	23.60	17.52	SAFE
B-112 Sludge	0.30	23.60	20.60	SAFE
B-201 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
B-202 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
B-203 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
B-204 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
BX-101[c] Sludge	0.90	17.10	12.37	SAFE
BX-102[c] Sludge	0.90	17.10	12.66	SAFE
BX-103[c] Sludge	0.90	17.10	10.31	SAFE
BX-104 Sludge	1.00	17.10	5.73	SAFE

Table 9-1. Comparison of All Single-Shell Tank Wastes With Safety Criteria. (5 sheets)

Tank	Total organic carbon,[a] initial-wet basis (wt%)	Moisture,[a] initial (wt%)	Moisture,[a] 50 years (wt%)	Safety category[b]
BX-105	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
BX-106[c] Sludge	0.90	17.10	14.10	SAFE
BX-107 Sludge	0.30	28.30	25.14	SAFE
BX-108 Sludge	0.90	17.10	1.75	SAFE
BX-109 Sludge	0.90	17.10	13.39	SAFE
BX-110	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
BX-111	Salt cake tank - see Table 9-2			SAFE
BX-112 Sludge	1.60	26.70	23.24	SAFE
BY-101	Salt cake tank - see Table 9-2			SAFE
BY-102	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
BY-103[c]	Salt cake tank - see Table 9-2			SAFE
BY-104	Salt cake tank - see Table 9-2			SAFE
BY-105	Salt cake tank - see Table 9-2			SAFE
BY-106	Salt cake tank - see Table 9-2			SAFE
BY-107	Salt cake tank - see Table 9-2			SAFE
BY-108	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
BY-109[c]	Salt cake tank - see Table 9-2			SAFE
BY-110	Salt cake tank - see Table 9-2			SAFE
BY-111[c]	Salt cake tank - see Table 9-2			SAFE
BY-112	Salt cake tank - see Table 9-2			SAFE
C-101 Sludge	0.90	17.10	12.63	SAFE
C-102[c] Sludge	0.60	23.60	18.88	SAFE
C-103[c] Sludge	1.00	23.60	20.60	SAFE
C-104[c,d] Sludge	1.20	23.60	19.96	SAFE
C-105[d] Sludge	0.40	23.60	0.00	SAFE
C-106 Sludge	0.80	23.60	Not calculated	SAFE
C-107 Sludge	0.60	23.60	17.02	SAFE
C-108[c] Sludge	0.70	27.10	0.00	SAFE
C-109 Sludge	1.00	27.10	22.20	SAFE
C-110[c] Sludge	0.30	28.30	23.46	SAFE
C-111[c] Sludge	0.70	27.10	22.09	SAFE
C-112[c] Sludge	1.20	27.10	21.18	SAFE
C-201 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
C-202 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE

Table 9-1. Comparison of All Single-Shell Tank Wastes With Safety Criteria. (5 sheets)

Tank	Total organic carbon,[a] initial-wet basis (wt%)	Moisture,[a] initial (wt%)	Moisture,[a] 50 years (wt%)	Safety category[b]
C-203 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
C-204 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
S-101	Salt cake tank - see Table 9-2			SAFE
S-102	Salt cake tank - see Table 9-2			SAFE
S-103	Salt cake tank - see Table 9-2			SAFE
S-104 Sludge	0.60	23.60	18.46	SAFE
S-105	Salt cake tank - see Table 9-2			SAFE
S-106	Salt cake tank - see Table 9-2			SAFE
S-107	Salt cake tank - see Table 9-2			SAFE
S-108	Salt cake tank - see Table 9-2			SAFE
S-109	Salt cake tank - see Table 9-2			SAFE
S-110[c]	Salt cake tank - see Table 9-2			SAFE
S-111	Salt cake tank - see Table 9-2			SAFE
S-112	Salt cake tank - see Table 9-2			SAFE
SX-101[d]	Salt cake tank - see Table 9-2			SAFE
SX-102[d]	Salt cake tank - see Table 9-2			SAFE
SX-103[c,d]	Salt cake tank - see Table 9-2			SAFE
SX-104[d]	Salt cake tank - see Table 9-2			SAFE
SX-105[d]	Salt cake tank - see Table 9-2			SAFE
SX-106[c,d]	Salt cake tank - see Table 9-2			SAFE
SX-107[d] Sludge	0.60	23.60	0.00	SAFE
SX-108[d] Sludge	0.60	23.60	0.00	SAFE
SX-109[d] Sludge	0.60	23.60	0.00	SAFE
SX-110[d] Sludge	0.60	23.60	0.00	SAFE
SX-111[d] Sludge	0.60	23.60	0.00	SAFE
SX-112[d] Sludge	0.60	23.60	0.00	SAFE
SX-113 Sludge	0.60	23.60	10.47	SAFE
SX-114[d] Sludge	0.60	23.60	0.00	SAFE
SX-115 Sludge	0.60	23.60	0.00	SAFE
T-101 Sludge	0.60	23.60	19.24	SAFE
T-102 Sludge	0.60	23.60	20.60	SAFE
T-103 Sludge	0.60	23.60	20.60	SAFE
T-104 Sludge	0.20	33.90	30.88	SAFE
T-105 Sludge	0.40	14.80	8.25	SAFE

Table 9-1. Comparison of All Single-Shell Tank Wastes With Safety Criteria. (5 sheets)

Tank	Total organic carbon,[a] initial-wet basis (wt%)	Moisture,[a] initial (wt%)	Moisture,[a] 50 years (wt%)	Safety category[b]
T-106 Sludge	0.40	14.80	11.80	SAFE
T-107 Sludge	0.30	27.10	24.10	SAFE
T-108 Sludge	0.30	28.30	23.25	SAFE
T-109 Sludge	0.60	23.60	19.16	SAFE
T-110 Sludge	0.90	23.60	20.60	SAFE
T-111 Sludge	1.10	23.60	20.60	SAFE
T-112 Sludge	0.90	23.60	20.52	SAFE
T-201 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
T-202 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
T-203 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
T-204 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
TX-101[c] Sludge	0.60	23.60	17.33	SAFE
TX-102[c]	Salt cake tank - see Table 9-2			SAFE
TX-103 Sludge	0.60	23.60	20.40	SAFE
TX-104[c]	Salt cake tank - see Table 9-2			SAFE
TX-105[c]	Salt cake tank - see Table 9-2			SAFE
TX-106[c]	Salt cake tank - see Table 9-2			SAFE
TX-107	Salt cake tank - see Table 9-2			SAFE
TX-108	Salt cake tank - see Table 9-2			SAFE
TX-109	Salt cake tank - see Table 9-2			SAFE
TX-110	Salt cake tank - see Table 9-2			SAFE
TX-111	Salt cake tank - see Table 9-2			SAFE
TX-112	Salt cake tank - see Table 9-2			SAFE
TX-113	Salt cake tank - see Table 9-2			SAFE
TX-114	Salt cake tank - see Table 9-2			SAFE
TX-115	Salt cake tank - see Table 9-2			SAFE
TX-116	Salt cake tank - see Table 9-2			SAFE
TX-117	Salt cake tank - see Table 9-2			SAFE
TX-118	Salt cake tank - see Table 9-2			SAFE
TY-101 Sludge	0.00	22.90	18.91	SAFE
TY-102[c]	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
TY-103[c] Sludge	0.30	29.90	26.14	SAFE
TY-104[c] Sludge	0.90	29.90	26.65	SAFE
TY-105 Sludge	0.40	18.90	15.31	SAFE

Table 9-1. Comparison of All Single-Shell Tank Wastes With Safety Criteria. (5 sheets)

Tank	Total organic carbon,[a] initial-wet basis (wt%)	Moisture,[a] initial (wt%)	Moisture,[a] 50 years (wt%)	Safety category[b]
TY-106 Sludge	0.60	18.90	12.08	SAFE
U-101 Sludge	0.60	23.60	4.47	SAFE
U-102	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-103	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-104 Sludge	0.60	23.60	18.97	SAFE
U-105	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-106	Salt cake tank - see Table 9-2			SAFE
U-107	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-108	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-109	Salt cake tank - see Table 9-2			CONDITIONALLY SAFE
U-110 Sludge	0.30	14.80	10.34	SAFE
U-111	Salt cake tank - see Table 9-2			SAFE
U-112 Sludge	0.60	23.60	19.14	SAFE
U-201 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
U-202 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
U-203 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE
U-204 Sludge	See Chapter 7, Section 7.4.1 for discussion			SAFE

[a] Taken from Chapter 7, Table 7C-2.

[b] Safety categories are discussed in Chapter 3, Section 3.2.3 and are determined from Chapter 5, Figure 5-8 (TOC/moisture criteria line). The safety categories mean the following.

SAFE - The tank initially meets and is predicted to meet the safety criteria for all conditions (i.e., initial, drained by jet pumping or leakage, and after 50 years dryout).

CONDITIONALLY SAFE - The tank is initially in the SAFE region, but jet pumping, leakage, dryout (or a combination) is predicted to cause the tank to enter the UNSAFE region.

UNSAFE - Means the tank does not meet the safety criteria.

[c] Solvent tanks (i.e., received organic wash waste).

[d] Actively ventilated tanks; all other tanks are passively ventilated.

Table 9-2. Comparison of Salt Cake Tank Wastes With Safety Criteria. (4 sheets)

Salt cake tank	Jet pumped (yes/no)	Total organic carbon, wet basis			Moisture[a]			Safety category[b]
		Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	
A-101								
Salt cake	No	4.50	4.38	4.46	28.16	12.10	10.54	SAFE
Sludge		2.40			18.40	18.40	15.40	
A-102								
Salt cake	No	4.50	7.02	7.98	31.00	12.10	0.00	CONDITIONALLY SAFE
Sludge		2.50			18.40	18.40	0.00	
AX-101[d]								
Salt cake	No	4.50	5.13	5.13	31.00	12.10	12.10	SAFE
Sludge		2.10			18.40	18.40	15.40	
AX-102[d]								
Salt cake	No	4.30	3.55	3.55	31.00	12.10	12.10	SAFE
Sludge		0.60			23.60	23.60	20.60	
AX-103								
Salt cake	No	4.30	4.50	4.50	31.00	12.10	12.10	SAFE
Sludge		0.60			23.60	23.60	20.60	
B-102								
Salt cake	No	4.30	5.82	6.59	31.00	12.10	0.57	CONDITIONALLY SAFE
Sludge		0.60			13.40	13.40	8.10	
B-104								
Salt cake	No	4.30	5.85	5.94	31.00	12.10	10.72	SAFE
Sludge		0.60			23.60	23.60	20.60	
B-105								
Salt cake	No	4.00	5.61	5.63	31.00	12.10	11.74	SAFE
Sludge		0.30			24.00	24.00	21.00	
BX-105								
Salt cake	No	4.30	5.02	5.71	31.00	12.10	00.00	CONDITIONALLY SAFE
Sludge		1.00			17.10	17.10	11.00	
BX-110								
Salt cake	No	4.30	6.48	7.37	34.81	12.10	0.00	CONDITIONALLY SAFE
Sludge		0.20			27.80	27.80	23.44	
BX-111								
Salt cake	No	4.30	5.89	5.94	31.00	12.17	11.47	SAFE
Sludge		0.20			27.80	27.80	24.80	
BY-101								
Salt cake	Yes	5.10	5.10	5.13	12.17	12.17	11.68	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-102								
Salt cake	No	4.30	6.62	6.70	31.00	12.10	11.00	CONDITIONALLY SAFE
BY-103[d]								
Salt cake	No	5.10	8.15	8.20	31.00	12.10	11.54	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-104								
Salt cake	Yes	5.10	5.10	5.17	11.57	11.57	10.30	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-105								
Salt cake	No	5.10	8.03	8.11	31.00	12.10	11.14	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-106								
Salt cake	No	5.10	8.27	8.37	31.00	12.10	11.09	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-107								
Salt cake	Yes	5.10	5.10	5.24	12.17	12.17	9.77	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-108								
Salt cake	Yes	5.10	5.10	5.54	12.17	12.17	4.58	CONDITIONALLY SAFE
Sludge		0.60			16.80	16.80	13.62	

Table 9-2. Comparison of Salt Cake Tank Wastes With Safety Criteria. (4 sheets)

Salt cake tank	Jet pumped (yes/no)	Total organic carbon, wet basis			Moisture[a]			Safety category[b]
		Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	
BY-109[d]								
Salt cake	No	4.30	6.10	6.11	31.00	12.10	11.93	SAFE
Sludge		0.60			23.60	23.60	20.60	
BY-110								
Salt cake	Yes	5.10	5.10	5.17	12.17	12.17	11.01	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-111[d]								
Salt cake	Yes	5.10	5.10	5.13	12.17	12.17	11.68	SAFE
Sludge		0.60			16.80	16.80	13.80	
BY-112								
Salt cake	Yes	5.10	5.10	5.15	12.17	12.17	11.24	SAFE
Sludge		0.60			16.80	16.80	13.80	
S-101[e]								
Salt cake	No	3.30	3.43	3.65	15.54	6.10	0.00	SAFE
Sludge		0.60			21.30	21.30	14.52	
S-102[e]								
Salt cake	No	3.30	3.04	3.06	15.54	6.10	5.31	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-103[e]								
Salt cake	No	3.30	3.46	3.50	15.54	6.10	4.96	SAFE
Sludge		0.60			21.30	21.30	17.61	
S-105[e]								
Salt cake	Yes	3.30	3.30	3.31	6.01	6.01	5.69	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-106[e]								
Salt cake	No	3.30	3.49	3.50	15.54	6.10	5.77	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-107[e]								
Salt cake	No	3.30	3.47	3.69	15.54	6.10	0.00	SAFE
Sludge		0.60			21.30	21.30	16.76	
S-108[e]								
Salt cake	No	3.30	3.46	3.47	15.54	6.10	5.82	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-109[e]								
Salt cake	No	3.30	3.46	3.49	15.54	6.10	5.38	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-110[d,e]								
Salt cake	No	3.30	3.23	3.29	15.54	6.10	4.52	SAFE
Sludge		0.60			21.30	21.30	17.42	
S-111[e]								
Salt cake	No	3.30	3.46	3.48	11.47	6.10	5.47	SAFE
Sludge		0.60			21.30	21.30	18.30	
S-112[e]								
Salt cake	No	3.30	3.46	3.48	15.54	6.10	5.77	SAFE
Sludge		0.60			21.30	21.30	18.30	
SX-101[e,f]								
Salt cake	No	3.30	3.45	3.47	8.90	3.50	2.88	SAFE
Sludge		0.60			21.30	21.30	11.78	
SX-102[e,f]								
Salt cake	No	3.30	3.39	3.45	9.57	3.50	1.87	SAFE
Sludge		0.60			21.30	21.30	6.18	
SX-103[d,e,f]								
Salt cake	No	3.30	3.38	3.50	8.90	3.50	0.00	SAFE
Sludge		0.60			21.30	21.30	0.00	
SX-104[e,f]								
Salt cake	No	3.30	3.47	3.48	8.46	3.50	3.32	SAFE
Sludge		0.60			21.30	21.30	12.38	

Table 9-2. Comparison of Salt Cake Tank Wastes With Safety Criteria. (4 sheets)

Salt cake tank	Jet pumped (yes/no)	Total organic carbon, wet basis			Moisture[a]			Safety category[b]
		Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	
SX-105[e,f] Salt cake Sludge	No	3.30 0.60	3.39	3.39	9.18 21.30	3.50 21.30	3.22 1.44	SAFE
SX-106[d,e,f] Salt cake Sludge	No	3.30 0.60	2.24	2.32	8.90 21.30	3.50 21.30	0.00 0.00	SAFE
TX-102[d,e] Salt cake	Yes	3.30	3.39	3.41	3.01	3.01	2.39	SAFE
TX-104[d,e] Salt cake	No	3.30	3.48	3.52	15.54	6.10	5.12	SAFE
TX-105[d,e] Salt cake	Yes	3.30	3.30	3.32	6.01	6.01	5.51	SAFE
TX-106[d,e] Salt cake	Yes	3.30	3.30	3.30	6.01	6.01	5.90	SAFE
TX-107[e] Salt cake	No	3.30	3.46	3.51	15.54	6.10	4.70	SAFE
TX-108 Salt cake	Yes	4.70	4.70	4.72	12.17	12.17	11.73	SAFE
TX-109 Salt cake	Yes	4.00	4.00	4.01	12.17	12.17	11.95	SAFE
TX-110 Salt cake	Yes	4.00	4.00	4.06	12.17	12.17	10.95	SAFE
TX-111 Salt cake	Yes	4.00	4.00	4.03	12.17	12.17	11.45	SAFE
TX-112 Salt cake	Yes	4.00	4.00	4.04	12.17	12.17	11.38	SAFE
TX-113 Salt cake	Yes	4.00	4.00	4.02	12.17	12.17	11.82	SAFE
TX-114 Salt cake	Yes	4.00	4.00	4.03	12.17	12.17	11.47	SAFE
TX-115 Salt cake	Yes	5.00	5.00	5.02	12.17	12.17	11.84	SAFE
TX-116 Salt cake	Yes	4.00	4.00	4.01	12.17	12.17	11.86	SAFE
TX-117 Salt cake	Yes	4.00	4.00	4.02	12.17	12.17	11.71	SAFE
TX-118 Salt cake	Yes	4.70	4.70	4.73	12.17	12.17	11.62	SAFE
TY-102[d] Salt cake	No	4.00	6.73	6.86	37.31	12.10	10.45	CONDITIONALLY SAFE
U-102 Salt cake Sludge	No	5.00 1.20	6.57	6.61	31.00 8.70	12.10 8.70	11.59 5.70	CONDITIONALLY SAFE
U-103 Salt cake Sludge	No	5.00 1.60	6.58	6.62	31.00 8.70	12.10 8.70	11.53 5.70	CONDITIONALLY SAFE
U-105[e] Salt cake Sludge	No	5.20 0.60	5.88	6.04	15.18 24.50	6.10 24.50	3.51 4.06	CONDITIONALLY SAFE
U-106 Salt cake Sludge	No	5.00 1.20	3.18	3.23	31.00 8.70	12.10 8.70	10.57 5.70	SAFE
U-107[e] Salt cake Sludge	No	5.20 0.60	5.91	5.96	15.54 24.50	6.10 24.50	5.36 21.50	CONDITIONALLY SAFE

Table 9-2. Comparison of Salt Cake Tank Wastes With Safety Criteria. (4 sheets)

Salt cake tank	Jet pumped (yes/no)	Total organic carbon, wet basis			Moisture[a]			Safety category[b]
		Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	Initial (wt%)	Jet pumped[c] (wt%)	50 years (wt%)	
U-108[e] Salt cake Sludge	No	5.20 0.60	5.91	5.95	15.54 24.50	6.10 24.50	5.53 21.50	CONDITIONALLY SAFE
U-109[e] Salt cake Sludge	No	5.20 0.60	6.57	6.63	21.83 24.50	6.10 24.50	5.31 21.50	CONDITIONALLY SAFE
U-111 Salt cake Sludge	No	5.00 1.20	4.87	4.91	27.15 8.70	12.10 8.70	11.49 5.70	SAFE

[a] Taken from Chapter 7, Table 7C-2, except for initial (before jet pumping) TOC and moisture wt% values, which are taken from Chapter 6, Table 6B-2 (salt cake phase summary).

[b] Safety categories are discussed in Chapter 3, Section 3.2.3 and are determined from Chapter 5, Figure 5-8 (TOC/moisture criteria line). The safety categories are defined as follows:

SAFE - The tank initially meets and is predicted to meet the safety criteria for all conditions (i.e., initial, drained by jet pumping or leakage, and after 50 years dryout)

CONDITIONALLY SAFE - The tank is initially in the SAFE region, but jet pumping, leakage, dryout (or a combination) is predicted to cause the tank to enter the UNSAFE region.

UNSAFE - The tank does not meet the safety criteria.

[c] For tanks that have been jet pumped, the values are based on actual measurements of the interim stabilized tanks. For tanks that have not been jet pumped, the values are based on "artificial jet pumping" of the tanks. There has been some salt well pumping of tanks BX-110 and BY-102 (see Appendix 7-D for further discussion). Tank TY-102 was administratively stabilized and available information indicates that there is no pumpable liquid remaining.

[d] Solvent tanks (i.e., received organic wash waste).

[e] Reduction and oxidation waste.

[f] Actively ventilated tanks; all other tanks are passively ventilated.

For example, the safety category for tank B-102 is currently CONDITIONALLY SAFE. Because salt cake is present in the tank, it is a salt cake tank. First the initial wt% TOC wet basis and the wt% H_2O are compared to the criteria line. The initial wt% TOC for the salt cake phase is 4.30, and the wt% H_2O is 31.00 (see Table 9-2). Comparing these values to the criteria line places the tank in the SAFE region. The predicted jet-pumped wt% TOC is 5.82 and the wt% H_2O is 12.10. Comparing these values to the criteria line again places the tank in the SAFE region. The 50-year wt% TOC is 6.59 and the wt% H_2O is 0.57. Comparing these values to the criteria line places the tank in the UNSAFE region. Therefore, the tank is currently categorized as CONDITIONALLY SAFE.

9.2 CONTROL OF TANK CONFIGURATION

The tanks categorized as SAFE in Table 9-1 will remain sufficiently moist during planned interim storage to remain in the SAFE category with minimal or no control of tank ventilation configuration. This is true for passively and actively ventilated tanks. For passively ventilated tanks, this means the tank configuration should conservatively be controlled to a passive ventilation mode except for allowed short-duration use of portable exhausters (i.e., several weeks duration). Temporary use of a portable exhauster is discussed in Chapter 8. For tanks categorized as CONDITIONALLY SAFE or for tanks that become UNSAFE, control of tank ventilation configuration provides additional safety assurance. For actively ventilated tanks this means no controls are needed. None of the tanks categorized as CONDITIONALLY SAFE are actively ventilated. Even though the evaporative loss rate is high for some actively ventilated tanks, these tanks remain in the SAFE category after 50 years dryout. The moisture loss rates are not predicted to cause these tanks to become CONDITIONALLY SAFE.

In order to control the tank configuration to a passive ventilation mode, passive ventilation (i.e., not actively ventilated) will be specified as a required IOSR Design Feature for all currently passively ventilated tanks. Many of the tanks could be changed to active ventilation and be maintained safe. An appropriate engineering evaluation is needed before this is done.

9.3 CONTROL OF WASTE MOISTURE

The 13 tanks currently categorized as CONDITIONALLY SAFE in Table 9-1 require an IOSR control for waste moisture. That is, the moisture concentrations estimated to currently exist in these tanks meet SAFE criteria, but the moisture concentrations predicted to be reached during planned interim storage fall below SAFE criteria, and controls are required to ensure that waste moisture does not fall below critical levels. IOSR controls must include the safety criteria, periodic verifications against the safety criteria, and controls to ensure the safety criteria are met.

9.4 CONTROL OF IGNITION SOURCES

Currently, there are no tanks categorized as UNSAFE. Therefore, immediate actions to prevent accident initiators are not required. However, if any of the 13 tanks categorized as CONDITIONALLY SAFE in Table 9-1, or any other tanks, eventually become UNSAFE because of insufficient moisture, or high fuel values, then controls on ignition sources must be instituted immediately on the affected tanks. Chapter 8 evaluates tank farm equipment and operations that could potentially initiate an accident in waste by drying significant amounts of waste or by heating small amounts of waste. Based on this evaluation, the following controls on operations are required to preclude ignition sources if a tank becomes UNSAFE.

- Still Camera Photography - Use of an adjustable safety stop ("top hat") is required. A control that prevents the use of power supply cords long enough to reach the waste surface is also required.
- Video Camera Operation - Use of an adjustable safety stop ("top hat") is required. A control that prevents the use of power supply cords long enough to reach the waste surface is also required.
- Torch Cutting, Welding, and Grinding - Controls on welding operations are required (e.g., hot permits) if welding is to be performed outside of a designated welding area. Controls are required to prevent hot slag from entering the tank. Welding and grinding are prohibited on organic watch list tanks.
- Rotary mode core sampling - Drill bit-waste interface temperatures must be maintained within the bounds of the safety envelope for rotary core drilling operations. The controls that govern this requirement are as follows:
  - Operability of shutdown interlocks maintained to keep the drill bit-waste temperatures below the lowest ignition temperature for fuel-nitrate wastes
  - Drill maximum rotational speed of 55 revolutions per minute
  - Drill maximum downward force of 5.2 kN (1,170 lbf)
  - Drill bit minimum purge gas flow rate of 1.4×10^{-2} m^3/s (30 ft^3/min).

  These controls are assumed during drilling in salt cake tanks only. Sludge tanks have too little fuel and also have sufficient moisture to quench a fuel-nitrate reaction if initiated.
- Vehicle Operation Above Tank - Vehicles operating at grade level over tanks must employ fuels (e.g., propane) or fuel tank protection (e.g., skid plate, tank location) that significantly reduces the likelihood of an accident in which ignitible liquid fuel could enter the tank.
- Lightning strikes - Bonding and grounding of equipment and risers, must be adequate to provide protection to the waste.

Controls on ignition sources that are required to prevent other credible accidents are identified in the tank farms hazard and accident analysis, WHC-SD-WM-SAR-065, *Interim Chapter 3.0 Hazard and Accident Analysis* (WHC 1995). Suggested mitigative actions for UNSAFE tanks are discussed in Section 9.5.1.

9.5 SUMMARY OF REQUIRED CONTROLS

In terms of controlling the tank farms fuel-nitrate waste combustion hazard, the safety analysis described in this report concludes that if waste has sufficient fuel to support combustion, maintaining moisture above a specified critical concentration is the key to preventing a condensed-phase propagating chemical reaction. (Even when waste moisture is deficient, heating of waste to ignition temperatures is an additional factor needed to initiate an accident.) Some wastes maintain moisture through inherent chemical and physical properties of the waste. The moisture in other wastes can vary and dry out under analyzed storage conditions.

There are basically two levels of control for fuel-nitrate hazards to prevent a rapid, condensed-phase propagating chemical reaction in the tank farms. Top level controls are included in IOSR documents. IOSRs are used as an enforcement tool to assure safe operation. Lower level controls (non-IOSR), which are included in operational procedures, implement the IOSRs and provide additional safety assurance. Both levels of control are discussed below in Sections 9.5.1 and 9.5.2.

All of the tanks are currently safe with respect to potential propagating chemical reactions. The safety controls required to prevent unacceptable consequences as a result of fuel-nitrate combustion accidents are summarized as follows for each waste safety category or tank.

- SAFE - Currently, all of the single-shell tanks are categorized as SAFE except for 13 tanks, which are CONDITIONALLY SAFE. For passively ventilated SAFE tanks, the only IOSR control required is ventilation configuration. Section 9.2 discusses control of tank configuration. There are no IOSR controls required for actively ventilated tanks.

- CONDITIONALLY SAFE - Currently, there are a total of 13 passively ventilated tanks categorized as CONDITIONALLY SAFE. Ten tanks are categorized CONDITIONALLY SAFE if drained by jet pumping or leakage (see Appendix 7D and 7E for alternate evaluations). For the 10 tanks shown below, part of the waste (worst 5% moisture and worst 5% TOC) is predicted to be UNSAFE immediately after draining by either jet pumping or leakage. It should be noted that tank BX-110 is still SAFE if jet pumped, but it is so close to the safety criteria line that dryout would occur in less than one year. These 10 tanks must be evaluated before jet pumping to ensure that they would retain sufficient moisture following jet pumping:

    - A-102
    - BX-110
    - BY-102

- TY-102
- U-102, U-103, U-105, U-107, U-108, U-109.

Three tanks are categorized CONDITIONALLY SAFE if drained by jet pumping or leakage and then allowed to dry for up to 50 years. For the three tanks shown below, part of the waste (worst 5% moisture and worst 5% TOC) is predicted to become UNSAFE in less than 50 years after draining (see Appendix 7D and 7E for alternate evaluations).

- B-102
- BX-105
- BY-108.

The times to dryout after draining (worst 5% moisture and worst 5% TOC becomes UNSAFE) are 15 years for B-102, 7 years for BX-105, and 43 years for BY-108.

The IOSR controls required for the CONDITIONALLY SAFE tanks are (1) control of tank configuration and (2) control of waste moisture. Sections 9.2 and 9.3 discuss control of tank configuration and waste moisture.

- UNSAFE - Currently, there are no tanks categorized as UNSAFE. Therefore, immediate actions necessary to prevent initiators, increase waste moisture content, or decrease fuel concentration are not required. If a tank becomes UNSAFE, controls on ignition sources must be instituted immediately. Section 9.4 discusses control of ignition sources.

9.5.1 Interim Operational Safety Requirement Controls

IOSRs are those requirements developed from facility safety basis documentation that define the conditions, safe boundaries, and the management or administrative controls necessary to ensure the safe operation of a nuclear facility and to reduce the potential risk to the public and occupational workers from uncontrolled releases of radioactive materials or from radiation exposures resulting from inadvertent criticality. An IOSR document consists of the following as applicable: Safety Limits, Limiting Control Settings, Limiting Conditions for Operation, Surveillance Requirements, Administrative Controls, Design Features, use and application instructions, and the basis thereof.

WHC-CM-4-46, *Safety Analysis Manual*, Chapter 6.0, "Technical Requirements," specifies requirements and criteria for selection of TSRs. IOSRs are identical in intent and content to (DOE Order 5480.22, *Technical Safety Requirements*) but differ in that they are based on an interim safety basis rather than a final safety analysis report that meets the requirements of DOE Order 5480.23, *Nuclear Safety Analysis Reports*. Specific safety requirements pertaining to the tank farm single-shell tanks are included in WHC-SD-WM-OSR-005, *Single Shell Tank Interim Operational Safety Requirements* (Dougherty 1993).

Control of fuel-nitrate hazards at the IOSR level is best satisfied by Administrative Controls and Design Features. Administrative Controls are normally written at the program level and contain program key elements, as applicable. The program key elements are the minimum requirements for the Administrative Controls program. Failure to comply with the program or the intent of the program would constitute an IOSR Violation. Administrative Controls are established (1) when a safety function is best satisfied by a program versus a hardware system, (2) if control of a condition is not measured real-time or near to real-time, (3) if control of a condition is not under the immediate control of the operator, (4) if a condition does not require immediate action and sufficient recovery time exists to permit mitigating action, or (5) if a condition requires evaluation based on prevalent conditions.

Currently, there is no moisture measurement instrumentation installed in the tanks. Therefore, moisture is not measured real-time or near to real-time. Moisture might not always be under the immediate control of tank farm operations (e.g., tank leak). Additionally, if moisture changes only slowly, it is not a time-dependent situation and sufficient time exists for periodic verifications that moisture concentrations still meet the safety criteria. Fuel and nitrate/nitrite oxidizer concentrations in tank wastes are not variables that can be controlled during interim storage of wastes in single-shell tanks. The fuel and oxidizer that are present in the waste are already there and are not under the control of tank farm operations.

Design Features are those features not covered elsewhere in the IOSRs that, if altered or modified, would have a significant effect on safety. One Design Features selection criterion taken from DOE 5480.22, *Technical Safety Requirements*, includes configuration and physical arrangement, where it is a safety concern. The Unreviewed Safety Question process ensures that changes made to Design Features are controlled so that they do not adversely affect safety of the tank farms.

In summary, the required IOSRs include an Administrative Control program and a Design Feature, which are discussed below:

- Administrative Control Program - A program will be established, implemented, and maintained to manage organic tank wastes to prevent a condensed-phase propagating chemical reaction in the tank farms. Program key elements, which are minimum requirements for the program, will include (1) safety criteria based on a combination of waste energy density (or TOC if waste energy density is not known) and moisture, (2) periodic verifications of waste energy density (or TOC) and moisture against the safety criteria as additional tank sample data become available, and (3) controls to maintain waste energy density (or TOC) and moisture to meet the safety criteria. Item (3) specifically means that if a tank is predicted to become UNSAFE from jet pumping, then the tank must be evaluated before pumping to show that the tank will remain safe for a long period of time. This Administrative Control program applicability will be to all tanks that contain potentially hazardous concentrations of organic chemicals mixed with nitrate and/or nitrite salts.

  Failure to comply with the Administrative Control program or the intent of the program (i.e., stay within the safety criteria) will constitute an Administrative Control Violation that is reportable according to DOE occurrence reporting requirements. Actions in response to an Administrative Control Violation will include preparing a recovery plan describing steps leading to compliance with the Administrative Control. For example, if moisture falls too low (e.g., as a result of a tank leak or excessive evaporation), then action to increase moisture or reduce the fuel concentration (i.e., mitigative actions) would be required to meet the program intent. Mitigative actions might include adding water to increase waste moisture content, force ventilating to reduce waste temperature, letting the tank leak (depending on the location of the leak), partially pumping the tank, or leaching fuel from the waste surface to regions below. Remediation actions also might include waste retrieval, out-of-tank waste treatment, or other options. Any recovery action would depend on the tank conditions at the time.

- Design Feature - Tank configuration will be controlled to a passive mode (not actively ventilated) to restrain waste dryout to minimum moisture values. Use of portable exhausters will be limited to short durations (weeks). Use for extended periods of time (months or longer) will be analyzed to determine the effect on waste moisture loss rates. This Design Feature applicability will be to passively ventilated tanks that contain potentially hazardous concentrations of organic chemicals mixed with nitrate and/or nitrite salts.

9.5.2 Non-Interim Operational Safety Requirement Controls

Non-IOSR controls are lower level controls imposed to ensure that the IOSR Administrative Control program requirements are met and to provide additional safety assurance to prevent a condensed-phase propagating chemical reaction. In summary, recommended non-IOSR controls will include the following.

- Periodic surveillances to verify moisture remains above the critical amount. The surveillance frequency should be based on the safety significance of being below the critical amount and on evaluations of moisture loss rates possible for the CONDITIONALLY SAFE tanks during interim storage. If moisture could change only slowly, then the time between surveillances could be long.

- If a tank is predicted to become UNSAFE from jet pumping, then the tank must be evaluated before pumping to show it is "safe" and will remain "safe" for a long period of time. Evaluations might include retrieving and analyzing samples from unmeasured tanks, detailed evaluations of available characterization and other data, comparisons of tanks with sibling tanks from the same cascade or SORWT group, laboratory experiments performed on surrogates or actual waste samples, rerunning the ANOVA models with revised input data, or combinations of these approaches.

- Tank BX-110 must be evaluated before jet pumping. If jet pumped, the waste is estimated to be so close to the safety criteria line that dryout is predicted to occur in less than one year.

- If a tank becomes UNSAFE, controls on ignition sources must be instituted immediately. Initiating events may be caused by either external natural forces (such as lightning) or by internal occurrences (such as human operational errors). Preventive controls should be placed upon operations to reduce event frequencies. The controls on operations required to preclude ignition sources are discussed in Section 9.4. In addition, controls should be emphasized during characterization activities for those tanks that could already be below the minimum safe moisture limit.

- Scheduling of CONDITIONALLY SAFE tanks for waste retrieval, so that the tanks are not likely to experience dryout before retrieval.

- Development of contingency recovery plans for CONDITIONALLY SAFE tanks for immediate implementation if these tanks are discovered to be UNSAFE.

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10.0 SUMMARY OF RECOMMENDED REFINEMENTS

This chapter briefly summarizes recommended "refinements" to the analyses presented in this document. These "refinements" should be considered when the present document is updated.

10.1 REFINEMENTS SUGGESTED BY CHAPTER 1.0

There are no refinements suggested by Chapter 1.0.

10.2 REFINEMENTS SUGGESTED BY CHAPTER 2.0

Refinements suggested by Chapter 2.0 are addressed below.

10.3 REFINEMENTS SUGGESTED BY CHAPTER 3.0

10.3.1 Additional Technical Safety Requirements or Mitigating Actions

Tighter controls would be expected for tanks placed in the UNSAFE category. (As stated in Chapter 9.0, there are no UNSAFE tanks.) This implies that the TSRs would be more stringent and could lead to an expectation that a safety limit should be imposed on something. However, under normal rules for selecting safety limits, it is not clear that a meaningful safety limit be written. It would make more sense to take some kind of mitigating action (e.g., leaching fuel from the waste surface to regions below).

10.4 REFINEMENTS SUGGESTED BY CHAPTER 4.0

Chapter 4.0 describes the origins, amounts, and long-term degradation of the principal chemicals which were disposed to the tanks. It therefore serves as a basis for which types of chemicals should be considered.

10.4.1 Measurements on Actual Wastes for Chemical Compositions

Much of the basis for selecting surrogates for the wastes rests on "inferred fates of constituents." More work on measurements of actual waste to determine actual compositions is needed. Studies of aging tank waste should be used to determine which constituents should be found in the tanks today, and what proportions can be expected. The emphasis from the organic salts-nitrate perspective should be on searching for compounds with higher heat contents or lower contact temperatures for ignition (reference Tables 4-1 and 4-2).

10.4.2 Confirmation of Complexant Solubilities in Actual Wastes

Work on the solubilities of organic chemicals by G. S. Barney (1994b) shows that many of the sodium salts of complexants and aging products are highly soluble in nitrate/nitrite/hydroxide solutions. This indicates that the remaining inventory of complexants is probably in the supernatant and interstitial liquids. This could have a significant effect on the prediction of TOC for salt cakes where most of the liquids could be removed. Actual in-tank confirmation of Barney's work (1994b) could help to reduce uncertainties (reference Section 4.4.1).

10.4.3 Testing to Confirm Thermal Degradation of Solvent Aging Products

NaDBP has been shown by experiment to thermally degrade before it can react energetically. Are there waste factors such as the sheer mass of material in the tanks that could alter this result? For example, must volatile species escape the reaction zone fast enough to ensure this result? Are there scale factors in the actual waste that need to be investigated (reference Section 4.4.2)?

10.4.4 Extension of Aging Tests to Longer Period to Confirm Aging

The aging studies of the waste are only about 2 years old. Tests conducted over a longer period of time will provide more accurate information about the degradation and aging of waste chemicals. Tank samples may provide additional insights when analyzed and compared with these more mature data (reference conversation with D. M. Camaioni, January 24, 1995).

10.4.5 Energetics of More Complicated Mixtures

The energetics of more complicated mixtures that may be in the actual tank wastes are being evaluated. This work may yield information that could affect the safety criteria (reference conversation with D. M. Camaioni, January 24, 1995).

- A testing program should be conducted on simulant PAS 94A. This simulant of B Plant waste currently under testing appeared to exhibit unusually low and unexpected ignition properties. It was speculated that the presence of transition metals may have influenced the ignition temperature.

- Propagation experiments should be conducted on mixtures of two or more surrogate materials (e.g., sodium acetate and sodium HEDTA) to determine whether the resultant ignition temperatures can be predicted by simple superposition or whether some synergistic effect lowers the effective ignition temperature.

10.5 REFINEMENTS SUGGESTED BY CHAPTER 5.0

10.5.1 Tank Characterization to Confirm Choices of Surrogates

The selection of suitable surrogates for the waste can be based, in part, on the degradation and aging effects described in this chapter, but it is more dependent on the FAI experiments. However, the FAI experiments were performed for compounds that are thought to be present in appreciable quantities based on degradation and aging. This appears to be a circular path that needs to be confirmed by more tank characterization work (reference Section 5.2).

10.5.2 Additional Testing to Determine Ignition Temperatures

The experimental data were used to provide conservative fuel-moisture safety criteria. If this conservatism results in excessive costs or operational complexities, it may be beneficial to conduct additional experiments to help reduce the conservatism. These experiments may include testing additional surrogates to ensure that lower ignition temperatures do not exist or that greater energies are not indicated for the new materials.

10.5.3 Sampling of Actual Wastes to Confirm Surrogate Material Selection

Precise knowledge of chemical forms of organic fuels actually in the tanks, or the variety of possible mixtures present, is not available at this time. Surrogate materials thought to bound actual waste properties were tested. Additional sampling of tanks and analysis of tanks may indicate that other surrogates should be tested or may allow preparation of simulants for testing. Additionally, replication testing and other tests may be used to reduce inaccuracies in experimental results and others uncertainties thereby reducing conservatism. However, the uncertainties based on errors and experimental results not yet obtained are small compared to the uncertainties about actual waste character, which should be given priority over additional reaction testing (reference Section 5.3).

10.5.4 Reaction Kinetics Development

The types of fuels, waste thermal properties, energy contents, and reaction kinetics could be examined theoretically and experimentally to improve understanding and to help alleviate conservatism. Measurement error in mixture preparation is estimated to be a few percent so this could potentially be reduced further. However, the present criteria are bounding when using the most energetic proposed mixtures, and they are independent of actual waste energy. As stated above, the uncertainties in establishing the criteria are small compared to the large uncertainties concerning actual waste states, thus improvements in this area should have priority over improvements in establishing criteria (reference Section 5.4).

10.5.5 Perform Safety Analysis

The discussion in Section 5.5 is qualitative and brief. For safety analysis purposes, the accident should be studied to determine accident scenarios and accident progressions. The risks associated with this class of accident should be studied to determine frequencies and consequences. It is noted that the consequences of this class of accident are catastrophic and cannot be practically mitigated. The emphasis here must focus on prevention of the accident. It is suggested that a simplistic analysis should be sufficient to demonstrate the scale of the catastrophe that must be prevented. It will be necessary to upgrade WHC-SD-WM-SAR-065 (WHC 1995) to include treatment of the organic salt-nitrate rapid propagation events (reference Section 5.5).

10.6 REFINEMENTS SUGGESTED BY CHAPTER 6.0

10.6.1 Update to Latest Version of Tank Summary Report

In addition to actual tank moisture data, surveillance information is used as part of the knowledge on which to base the moisture estimates for each tank. Surveillance information was provided by WHC-EP-0182-72, *Tank Farms Surveillance and Waste Status Summary Report for March 1994* (Hanlon 1994). (Implied refinement is to evaluate changes in the Hanlon reference [latest available version] for their impact on the key numbers used in our computations and for any change in status of tank [as it leaked or was jet pumped]. This could lead to the updating of information [reference Section 6.1]).

10.6.2 Obtaining Total Organic Carbon, Energetics, and Moisture Data from Unmeasured Tanks

Obtaining more data from unmeasured tanks should be a priority in the future. The priorities should focus on those tanks projected to have higher TOC values and lower moisture values. There are many SORWT tank groups that have no member tanks measured for these parameters though the priority for obtaining these data should rest on the relative risks posed by these tanks (reference Section 6.1).

10.6.3 Developing Protocol for Database Revision

The protocol for database revision should be developed and implemented to determine what to do with new data and old data as new measurements are obtained. In some cases, new data should displace "suspect data" in their entirety whereas in other cases it should just be added to the existing database (reference Section 6.7).

10.6.4 Refining the Analysis of Variance Model

The data should continue to be evaluated to determine whether a refined grouping or different grouping of TOC or moisture values for tanks (and combinations of TOC and moisture values) would permit better understanding and more accurate estimates for the unmeasured tanks (reference Section 6.2).

10.7 REFINEMENTS SUGGESTED BY CHAPTER 7.0

10.7.1 Salt Cake Top Layer Sampling and Analysis

The top layer of salt cake from representative tanks should be sampled for moisture content, particularly from tanks that are predicted to contain relatively dry salt cakes. This would be especially important for salt cakes that were drained several years ago. This information could be used to calibrate dryout calculations (reference Section 7.2.3).

10.7.2 Salt Cake Moisture Model

Models should be developed to help determine the moisture content of salt cakes. There is some evidence that the salt cakes may be divided into those that readily drain and those that retain large amounts of moisture. Understanding of the moisture retention properties of salt cakes under various conditions appears to be key to determining whether organic salt rapid propagation prevention safety criteria can be met for all tanks when they are jet pumped. Sampling of actual wastes and testing of surrogate and simulant materials should be used to help calibrate this model. Reevaluation using the model could be used to reduce the conservatism in this report (reference Section 7.2.3).

10.7.3 Consolidation of Organic Sludges

Most of the data on water retention of sludges has been performed for sludges that are high in FeCN. Several of the sludges in the salt cake tanks do not contain significant FeCN. Though, in general, sludges tend to have similar water retention properties, depending upon the total amount of initial moisture and the depth of the sludge layer, more water retention information on non-ferrocyanide sludges would help confirm our current suppositions. This could be used to more accurately model water retention and consolidation effects, which could lead to more accurate predictions regarding sludge moisture values following prolonged periods of storage (reference Section 7.2.1).

10.7.4 Logic for Interim Stabilization

The logic for determining whether it is safe to jet pump tanks for interim stabilization should be fully developed and implemented. (WHC-EP-0841, *Logic Supporting Interim Stabilization of Organic Watch List Tanks*, is under development at this time [reference Section 7.3]).

10.7.5 Pre- and Post-Jet-Pumping Characterization

The computations in this report regarding the post-jet-pumped state for salt cake tanks that have not yet been jet pumped rely on ANOVA estimates that rest on a small set of measurements. More measurements of salt cake moistures for tanks about to be jet pumped and siblings that have already been jet pumped would help to confirm and refine the ANOVA estimates. Additionally, it would be helpful to track moisture changes during and following jet pumping to further confirm ANOVA estimates. This would help us to understand better how moisture changes in salt cakes as a result of jet pumping (reference Section 7.3).

10.7.6 Psychrometric and Waste Temperature Data

Where dryout of tank wastes to hazardous levels has been predicted, obtaining psychrometric and waste temperature data should have priority. Evaporation calculations in Chapter 7.0 had to proceed in the absence of several key data elements. Better data could reduce overconservatism in the moisture loss projections (reference Section 7.4).

10.7.7 Evaluations of Current Dryness Conditions

Selected tanks were evaluated in Section 7.5.5 and Appendix 7D to determine whether they could currently be too dry. Four tanks were evaluated by comparing data primarily from Hanlon (1995) and Brevick (1994a and 1995) with references to a Surface Dryness Evaluation report (Husa et al. 1995). Additional tanks should be evaluated by using data from current surveillance, the Tank Characterization Reports, Hanlon (1995) and Brevick (1995). Where significant gaps occur in available data, further characterization and surveillance should be planned (reference Section 7.5.5).

10.7.8 Recommendations for Tank Characterization

It is strongly recommended that priority characterization be pursued to help establish the current and future safety of the CONDITIONALLY SAFE tanks identified. This effort should consider whether tanks will or should be jet pumped for interim stabilization given the overall safety implications (e.g., would tanks drained lose too much moisture thereby becoming an organic salts condensed phase reaction hazard?). It should also be recognized that a tank could drain itself by leakage, and therefore, this information should be obtained as soon as possible. Note that sampling and analysis of tanks that are siblings for the CONDITIONALLY SAFE tanks may provide more useful information than sampling the tank itself (as when estimating a post-jet-pumped state), or such additional tanks could be sampled to complement samples from CONDITIONALLY SAFE tanks (reference Section 7.6 and other sections of the report).

10.7.9 Evaporated Liquid Residue Modeling

The evaporation model used for dryout calculations was initially focused on loss of moisture without provisions for TOC calculations. When refined calculations were developed for problem tanks, simple TOC models were inserted to account for changes in the TOC of the salt cake phase. However, TOC in the liquid phase was only accounted for when draining a salt cake. The liquid residue following evaporation, consisting of various salts (including nitrates and organic carbon compounds), was not accounted for. The liquid phases of certain tanks (especially A-106 and SX-106 at 18 wt% TOC for the worst 5%) may contain high TOC. For tanks that are predicted to lose a lot of moisture, this could result in a TOC-rich residue layer overlying the salt cake or sludge as appropriate. This potential hazard should be investigated (reference not now included in Chapter 7.0).

10.8 REFINEMENTS SUGGESTED BY CHAPTER 8.0

10.8.1 Determining Tanks Not Needing Active Ventilation

It should be determined through further evaluations and measurements which actively ventilated tanks could be taken off active ventilation without jeopardizing their safety. It may be necessary to ensure that adequate temperature monitoring is available to provide long-term confirmation that the tank temperatures will not rise excessively. These tanks could be reduced to passive ventilation now or when and if the ventilation systems failed. Their treatment in this report would be adjusted accordingly (reference Section 8.1).

10.8.2 Electrostatic Spark Ignition Potentials

Perform tests with organic salt-nitrate surrogates to determine their sensitivity to ignition by electrostatic spark discharges. Determining threshold levels could help to reduce overconservatism in spark control measures (reference Section 8.2.1).

10.8.3 Hot Filament and Electric Short Testing for Ignition

Perform tests to determine whether hot filaments, as from photographic flash or other lighting units, could ignite dry reactive wastes. Perform similar tests using shorting wires tested at voltages typical of equipment used in the tanks (such as pumps and exhausters). By obtaining better information on threshold ignition levels, overly conservative controls and restrictions could possibly be relaxed (reference Section 8.2.2).

10.8.4 Lightning Strike Ignition Potential for Dry Wastes

Evaluate whether lightning strikes within dry reactive material, which has poor electrical contact with the lightning conductor, could ignite the waste (reference Section 8.2.11).

10.9 REFINEMENTS SUGGESTED BY CHAPTER 9.0

10.9.1 Perform Safety Analysis

Accident scenarios and consequences should be evaluated and provided as part of a safety analysis dealing with the organic salt-nitrate condensed phase rapid propagation safety issue. This analysis should be provided as an update to the accelerated safety analysis for tank farms and is an important input to the bases for any required safety controls (reference Chapter 9.0).

10.9.2 Characterization Program for CONDITIONALLY SAFE Tanks

The tanks identified as CONDITIONALLY SAFE should have a characterization program designed to sample these or related tank wastes to determine actual levels of moisture, TOC, and energetics. Where it is confirmed that the tanks should remain safe over a long period, even if all moisture were drained from the wastes, the tanks should be recategorized as SAFE. Controls imposed on the tanks and permitted activities could then be reduced (reference Section 9.1).

10.9.3 Characterization Program for Organic Watch List Tanks

Based on the results contained in this report, organic watch list tanks on the current list should have a characterization program designed to sample wastes in these or related tanks to determine that the wastes in these tanks should be categorized as SAFE. Where such a determination exists, WHC should recommend to DOE that these tanks be removed from the watch list (reference Chapter 9.0).

10.9.4 Evaluating Additions to the Organic Watch List

Based on the results from Section 10.9.2, tanks that remain in the CONDITIONALLY SAFE category because their fuel levels are too high and their moisture levels are too low should be placed on the organic watch list (reference Chapter 9.0).

10.9.5 Development of Safety Controls

Safety controls should be developed and implemented to ensure that the CONDITIONALLY SAFE tanks remain safe (reference Section 9.5).

10.10 CHANGES RESULTING FROM SUGGESTIONS BY REVIEWERS

In contrast to other sections of this chapter, the following changes result from suggestions by reviewers.

10.10.1 Consider Additional Waste Categories

The current report uses just 3 waste categories as described in Chapter 3. Consider a refined categorization scheme which incorporates the reasons for categorizing tank waste (e.g. due to draining or due to draining and dryout) and also establishes at least in a qualitative way the margin of safety available (e.g. short term or long term dryout). (These changes are most applicable to Chapters 3, 7 and 9).

10.10.2 Aging is Expected to Significantly Reduce the Proportion of Reactive Organic Compounds in the Waste

The Preliminary Safety Criteria in this report are based upon assuming that the organic compounds present in the waste are in their aggregate as reactive as sodium acetate, which has been found by testing to be the most reactive of the compounds thought to be present in significant quantities. Significant aging of the organic compounds has reduced much of the quantities to less reactive forms. Obtain data from actual tank waste and from simulant testing to estimate the effects of aging, establish the minimum amount that can be expected to have reduced the tank inventory and adjust the models by a similar increment. Confirm the modeling by appropriate experiments. (These changes are most applicable to Chapter 4).

10.10.3 Propagation Tube Experiments with NaDBP

FAI has tested AlDBP but has not yet tested NaDBP. Because our waste likely contains significant quantities of NaDBP, this material should be tested in the RSST and the propagation tube. (This material is most applicable to Chapter 5).

10.10.4 Agnew Waste Models May be Superior to Sort on Radioactive Waste Tank Groups

Investigate models developed by S. Agnew which appear to be superior to SORWT groups for comparing waste properties such as moisture and TOC contents. (This material is most applicable to Chapter 6).

10.10.5 Constrain Analysis of Variance and Dryout Modeling to Realizable Systems

The current report allows parameter values to range independently, without necessarily being constrained to physically realizable quantities. Modeling will be refined based upon calculating total systems to ensure that appropriate proportions of fuel, oxidizers, moisture, and diluents representative of HLW are used. (This material is most applicable to Chapter 6).

10.10.6 Dry Sludge/Wet Salt Cake Lists

DA Reynolds has compiled a listing of some tank wastes based upon phases and relative moisture contents. This listing should be consulted to help refine modeling and determine which methods of grouping tanks for similar waste conditions are valid. (This material is most applicable to Chapter 6).

10.10.7 Solubility of Energetic Organic Compounds in High-Level Waste Tank Supernate Solutions

Energetic organic compounds of interest are highly soluble in typical waste solutions. Where liquid has (or is) communicated with the total volume of waste, it should have dissolved the energetic organic compounds thus assuring that virtually no energetic organic compounds are present as precipitates. Where reliable liquid samples have been obtained (and analyzed) from tanks and these samples show levels of organics well below solubility limits, the solids should be considered to be far below these values and should present no organic salt-nitrate rapid propagation hazard. Obtain data from grab samples, core samples, auger samples, liquid levels, and historical information. Compare this to salt cake models and provide updated tank categorization. (This material is most applicable to Chapters 6 and 7).

10.10.8 Much More Actual Tank Data is Being Generated

At the beginning of the organic salt-nitrate studies data on actual tanks wastes was sparse. As characterization and analysis have expanded more data on tanks is becoming available. Gather appropriate data to help refine understanding of CONDITIONALLY SAFE tanks particularly and for sibling tanks related to these tanks or tanks which could otherwise help to establish current and future tank conditions. Refine models and update the report. (This material is most applicable to Chapters 6 and 7).

10.10.9 Particle Size Influence on Draining

The modeling and evaluation in this report has typically assumed that the wastes could always be grouped by phase as either liquid, salt cake, or sludge. It was also assumed that salt cakes drain well and sludges do not. There is evidence that draining capability is related to particle size in sludges or salt cakes and that small particles in either of these phases will inhibit draining. (This material is most applicable to Chapters 6 and 7).

10.10.10 Actual Tank Experience is that Little Dryout has Occurred

With the exception of high waste heat tanks, passive ventilated tanks do not seem to be drying out appreciably. Thus, our dryout models may be excessively conservative in predicting how much dryout could occur. Seek data from tank measurements on high dryout tanks to improve our models. (This material is most applicable to Chapter 7).

10.10.11 Evaporation is Inhibited by Presence of Solids at the Headspace Interface

The current modeling of evaporation in this report is very simple such that a constant high evaporation rate as from a non-saturated liquid surface is assumed. As a liquid dries and approaches saturation in various salts, the evaporation rate will be reduced. As the liquid surface drops below the surface of the porous salt cake, the evaporation rate will be significantly reduced. Obtain data on changes in evaporation rate for typical substances and systems from the literature and adjust our modeling to account for these effects. Obtain psychrometric data and liquid level information from tanks expected to be high evaporators to develop more realistic evaporation rates for our modeling. (This material is most applicable to Chapter 7).

10.10.12 Lightning Tests on Reactive Organic Wastes

A few small scale tests with waste surrogates have been conducted in the laboratory with an arc-welder which shows that it is not easy to ignite waste surrogates with these comparatively low currents. These tests also suggest that moisture may inhibit ignition by steam bursts which tend to blow material away from the anode. However, it is not clear whether the much larger currents and different waveforms resulting from lightning could ignite actual tank wastes. Larger scale tests with surrogates and simulants using more sophisticated test apparatus and initiated lightning strikes are needed to answer these questions. (This material is most applicable to Chapter 8).

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11.0 REFERENCES

11.1 DOCUMENTS

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11.4 WESTINGHOUSE HANFORD COMPANY CONTROLLED MANUALS

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