

Project Plan for Resolution of the Organic Waste Tank Safety Issues at the Hanford Site

F. R. Reich
J. E. Meacham
J. J. Zach
L. M. Stock

Date Published
September 1996

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management



Westinghouse
Hanford Company

P.O. Box 1970
Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release; distribution is unlimited

RELEASE AUTHORIZATION

Document Number: WHC-EP-0914

Document Title: Project Plan for Resolution of the Organic Waste Tank Safety Issues at the Hanford Site

Release Date: 10/3/96

This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:



Kara M. Broz

October 3, 1996

EXECUTIVE SUMMARY

A multi-year project plan for the Organic Safety Project has been developed with the objective of resolving the organic safety issues associated with the High Level Waste (HLW) in Hanford's single-shell tanks (SSTs) and double-shell tanks (DSTs). The objective of the Organic Safety Project is to ensure safe interim storage until retrieval for pretreatment and disposal operations begins, and to resolve the organic safety issues by September 2001.

Since the initial identification of organics as a tank waste safety issue, progress has been made in understanding the specific aspects of organic waste combustibility, and in developing and implementing activities to resolve the organic safety issues.

Organic Waste History

Various wastes from defense weapons material processing operations, that included some organic constituents, have been accumulated in Hanford Site HLW tanks since 1943. The organic compounds are in intimate contact oxidizers such as sodium nitrite and nitrate. Under specific conditions, these mixtures are potentially combustible, and a condensed phase combustion could result in release of HLW to the environment.

As a result of the continued search of historical data and characterization samples excised from tank wastes, the organic tank waste safety issue has been narrowed and focussed on the organic complexants and organic solvents that were dispersed in Hanford's waste tanks. The original waste organics

consisted principally of organic complexants, such as glycolic acid, citric acid, ethylenediamine tetraacetic acid (EDTA), and N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and organic solvents, such as tributyl phosphate (TBP), normal paraffin hydrocarbons (NPH), and methyl isobutyl ketone (hexone). Studies are showing that decomposition or aging coupled with other physical phenomenon, such as volatility and solubility, are altering these organic wastes.

Organic Waste Hazard

When the organic safety issue was first recognized, it was evident that there was little reliable information about the actual composition of the materials in the waste tanks. Efforts are currently underway to obtain a more comprehensive picture of the organics that are in each individual tank and to use this data to assess the safety status of the tanks.

Three potential hazards were identified for wastes with organic complexants and solvents:

- head space flammability;
- spontaneous chemical runaway (self-heating) reactions occurring throughout the waste mass; and
- ignition of propagating exothermic chemical reactions (combustion) typified by a moving reaction front.

Headspace vapor sampling results have shown low concentrations (below 25% of the lower flammability limit) of organic complexant and solvents. The organic

complexants are essentially non-volatile, and the organic solvents are only semivolatile and exert a low vapor pressure at current tank waste temperatures. Consequently, there is no headspace flammability hazard the organic waste.

No credible mechanism has been identified for tank temperatures to increase and initiate a spontaneous chemical runaway. Waste temperatures, after removal of pumpable liquid, have continued to decline for most of the SSTs. The waste in seven SSTs (C-106, SX-107, -108, -110, -111, -112, and -114) has a high enough decay heat to require active cooling to maintain waste temperatures within acceptable limits. Temperature monitoring and waste cooling controls are currently implemented on these tanks.

If enough complexant-based fuel is present and the waste is sufficiently dry, a propagating combustion event could be initiated by external sources. In the presence of oxidizing materials, such as nitrates or nitrites, it has been shown that organic complexants can be made to react with exothermal behavior by heating to high temperatures (above 220 °C) or by an initiator of sufficient energy. Potential credible ignition sources for complexants have been identified and include hot metal objects, rotary core upsets, burning gasoline spills from a ruptured vehicular fuel tank, and lightning. Solvents can be present as a separate layer that has the potential to combust in air. Therefore, the ignition of complexants and solvents, under these conditions, is being considered in the resolution of the organic safety issues.

Criteria for Safe Storage of Organic Wastes

An initial screening process, based on a total organic carbon (TOC) concentration greater than 3 wt%, identified 20 high hazard tanks which were put on an organic tank Watch List. The safety status of the organic wastes is now known to be affected by a number of chemical and physical properties of the waste matrix containing the organics, the physical and chemical aspects of the organics, and the physical properties of the tank. Safe storage criteria were developed using theory and experiments with waste simulants. Currently the criteria provide three categories: *Safe* (lacks fuel to sustain a propagating combustion), *Conditionally Safe* (contains sufficient fuel, but the waste is too wet to sustain a propagating combustion), and *Unsafe* (does not meet *Safe* or *Conditionally Safe* criteria).

Mitigation and Monitoring

After the hazards in a waste tank have been assessed, actions (or no actions) will be taken to resolve any organic safety issues identified in the safety assessment for that tank. No action is needed for a tank that is categorized as *Safe*. Monitoring and controls are some of the potential actions for organic waste classified as *Conditionally Safe*. Mitigation or remediation is action would be used to bring tanks classified as *Unsafe* into an acceptable safe condition.

Project Activities

A number of activities have been identified to systematically resolve the organic waste safety issues. The major activities include the following:

- Identify organic waste tanks - Historical records, modeling, and characterization data are being used to identify which tanks contain organic waste.
- Assess fuel content and waste energetics - An understanding of the phenomena associated with organic fuel content and the energetics of these fuels within the tank waste matrices including the role of diluents (water), phase relationships, and aging.
- Quantify ignition source requirements - Experiments, theory, and accident analyses are being used to identify credible ignition sources, and their potential impact on safe storage of organic tank wastes.
- Develop and implement methods for monitoring and mitigation - Technologies for monitoring moisture and mitigating *Unsafe* tanks are being investigated.
- Complete safety analyses - Prepare, review, and obtain approvals of safety documentation to close the organic complexant Unreviewed Safety Question and to resolve the organic safety issues.

This page intentionally left blank.

TABLE OF CONTENTS

1.0	INTRODUCTION	1-1
1.0	INTRODUCTION	1-1
1.1	STRATEGY FOR THE WASTE TANK ORGANIC SAFETY PROJECT	1-1
1.2	OBJECTIVES FOR WASTE TANK ORGANIC SAFETY PROJECT	1-2
2.0	BACKGROUND	2-1
2.1	UNDERGROUND WASTE TANK STORAGE	2-1
2.2	WASTE TANK ORGANICS	2-2
2.3	TANK WASTE ORGANIC HAZARD	2-3
2.3.1	Early Tank Waste Organic Hazard Identification	2-4
2.3.2	Organic Waste Tank Watch List	2-5
2.4	TANK WASTE SAFETY ISSUES	2-5
2.4.1	Organic Solubility Relationships	2-7
2.4.2	Organic Waste Species Volatility	2-8
2.4.3	Aging (Decomposition) of Organic Wastes	2-9
2.5	TANK WASTE SAFETY SCREENING CRITERIA	2-13
2.6	TANK ORGANIC WASTE DRIVERS	2-14
2.6.1	Safety Measures Law - The Wyden Amendment	2-15
2.6.2	Atomic Energy Act of 1954	2-15
2.6.3	Code of Federal Regulations	2-15
2.6.4	Washington State Administrative Code	2-16
2.6.5	Defense Nuclear Facilities Safety Board	2-16
2.6.6	Tri-Party Agreement (TPA)	2-16
2.6.7	Safety Initiatives	2-17
2.7	UNREVIEWED SAFETY QUESTION	2-17
2.7.1	Background	2-17
2.7.2	Status	2-18
3.0	TANK WASTE ORGANIC SAFETY HAZARD	3-1
3.1	ORGANIC COMPLEXANT HAZARD	3-1
3.1.1	Headspace Flammability	3-1
3.1.2	Spontaneous Chemical Runaway	3-1
3.1.3	Ignition of Organic Complexants	3-2
3.2	ORGANIC SOLVENT HAZARD	3-2
3.2.1	Headspace Flammability	3-3
3.2.2	Spontaneous Chemical Runaway	3-3
3.2.3	Ignition of Organic Solvents	3-3
4.0	RESOLUTION OF THE ORGANIC WASTE SAFETY ISSUE	4-1
4.1	ORGANIC WASTE SAFETY PROJECT LOGIC	4-1
4.2	CRITERIA FOR SAFE STORAGE OF ORGANIC WASTES	4-1
4.2.1	Organic Complexant Storage Criteria	4-1
4.2.2	Organic Solvent Storage Criteria	4-4
4.3	OPTIONS FOR IMPLEMENTING WASTE TANK SAFETY	4-7
4.4	MANAGEMENT OF THE WATCH LIST	4-8

TABLE OF CONTENTS (Continued)

5.0	ORGANIC SAFETY PROJECT ACTIVITIES	5-1
5.1	IDENTIFICATION OF ORGANIC WASTE TANKS	5-1
5.1.1	Historical Records and Modeling	5-1
5.1.2	Characterization Data	5-2
5.1.3	Data Reconciliation and Model Validation	5-3
5.2	FUEL CONTENT AND WASTE ENERGETICS ASSESSMENTS	5-4
5.2.1	Fuel Diluents	5-4
5.2.2	Aging - Complexants and Solvents	5-5
5.2.3	Energy Content Measurements and Assessments	5-6
5.2.4	Phase Relationships - Solvents and Complexants	5-6
5.3	EXTERNAL IGNITION SOURCE HAZARDS	5-7
5.4	SAFETY ACTIONS	5-8
5.4.1	Monitoring and Mitigation	5-8
5.4.2	Vent Path Assessments	5-9
5.5	SAFETY DOCUMENTATION	5-9
6.0	ORGANIC SAFETY PROJECT SCHEDULES AND MILESTONES	6-1
6.1	ORGANIC SAFETY PROJECT MILESTONES	6-1
6.2	ORGANIC SAFETY PROJECT MILESTONE SCHEDULE	6-5
7.0	REFERENCES	7-1
APPENDIX		
	QUALITY ASSURANCE	A-1

LIST OF FIGURES

4-1	Organic Safety Issues Resolution Logic	4-2
4-2	Safety Criteria for Organic Waste	4-5
4-3	Comparison of Experimental Results to Safety Criteria	4-6
6-1	Organic Safety Project Milestone Schedule	6-6

LIST OF TABLES

2-1	Quantities of the Principal Organic Complexants Used at Hanford . .	2-2
2-2	Quantities of the Principal Organic Solvents Used at Hanford	2-3
2-3	Basis for Organic Watch List Designation and Suspected Waste Sources	2-6

LIST OF TERMS

ANOVA	Analysis of Variance
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DOE-RL	Department of Energy - Richland Operations Office
DQO	data quality objective
DST	double-shell tank
EDTA	ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
FAI	Fauske and Associates, Inc., Burr Ridge, Illinois
HEDTA	N-hydroxyethylethylenediaminetriacetic acid
HDW	Hanford Defined Waste
HLW	high level waste
IDA	iminodiacetate
LFL	lower flammability limit
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PRC	Plant Review Committee
QA	Quality Assurance
REDOX	Reduction-Oxidation
SST	single-shell tank
TBP	tributyl phosphate
TOC	total organic carbon
TPA	Tri-Party Agreement
TWRS	Tank Waste Remediation Systems
USBM	U.S. Bureau of Mines
USQ	unreviewed safety question
WAC	Washington Administrative Codes
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

This document describes the Organic Safety Project plan for the resolution of the organic safety issues associated with the high level waste (HLW) tanks at the Hanford site. Since Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 93-5 was issued in 1994, significant progress has been made in understanding tank organic safety-related phenomena and the resolution of the organic tank waste safety issues (DOE/RL 1996).

The scope of the Organic Safety Project plan is limited to the resolution of the safety issues associated with organics that are currently part of the wastes in Hanford's HLW tanks. The scope includes the interim static storage of the waste but does not include dynamic activities such as retrieval or disposal operations that are being planned. It is important to recognize that the project plan will involve interaction with several other plans that focus on resolving other safety issues, and the characterization of the tank wastes (Flammable Gas Project Plan and the Tank Waste Characterization Plan) (Dukelow and Hanson 1995).

1.1 STRATEGY FOR THE WASTE TANK ORGANIC SAFETY PROJECT

The strategy for the waste tank Organic Safety Project plan is based on the implementation of the strategy outlined in Meacham (1996). The basic strategy consists of identifying the organic safety issues for each tank, identifying a path to ensure the safety of the tank, and then, if deemed necessary, implementing controls and/or mitigation actions that put the waste in an acceptable safety status. For efficient treatment of the issue, similar tanks are treated as a group. Safe, interim storage of tank waste with organics can be ensured in one of the following ways:

- demonstrate through theory, modeling, sampling, and testing, that the waste lacks sufficient organic fuel to combust;
- show through modeling and monitoring that the waste contains sufficient moisture to prevent ignition and combustion;
- demonstrate that ignition sources are controlled; or
- mitigate as required if controls are deemed inadequate.

Presently, no single alternative is believed sufficient to ensure interim safe storage for all tanks containing organic waste. Most of the waste tanks, that do not contain sufficient fuel to combust, can be grouped and treated on a global basis. Other tanks, however, will have to be addressed on a tank-by-tank basis, especially those tanks that may require controls or mitigation. Therefore, activities for all 4 alternatives are included in this project plan.

1.2 OBJECTIVES FOR WASTE TANK ORGANIC SAFETY PROJECT

The primary objective of the Organic Safety Project is to resolve the organic safety issues associated with the HLW in both Hanford's single-shell tanks (SSTs) and double-shell tanks (DSTs) by the September 2001. A systematic approach is used that is consistent with the overall systems engineering strategy being developed for the Tank Waste Remediation Systems (TWRS). Achieving resolution means verifying interim safe storage by developing and demonstrating a thorough understanding of the organic tank waste and the reactive behavior of the waste constituents, and then monitoring and/or mitigation the waste to ensure continued safe storage.

In the process of resolving the organic safety issue, the following tasks will also be addressed:

- Completion of all actions required in the DNFSB 93-5 implementation plan (DOE/RL 1996);
- Completion of actions required by Public Law 101-510, Section 3137 (1990) (the Wyden Amendment);
- Closure of the unreviewed safety question (USQ) on organic complexants (Wicks 1996);
- Fulfillment of Tri-Party Agreement milestones governing the treatment, storage, and disposal of tank wastes containing hazardous organic waste (Ecology et al. 1994);
- Completion of the actions included in the Secretary's Safety Initiatives (O'Leary 1993).

These efforts contain a common work scope, and most tasks are not exclusive to any single effort.

The need for cooperative interactions, assistance, and support between all tank waste safety efforts (including remediation and recovery) is recognized as important aspect for the Organic Safety Project.

2.0 BACKGROUND

This section presents a historical perspective of Hanford's tank wastes, a summary of drivers for conducting Organic Safety Project activities, and the technical basis for identifying Organic Watch List tanks and their safety status.

2.1 UNDERGROUND WASTE TANK STORAGE

Since 1943 various radioactive wastes from defense operations have accumulated in HLW tanks at the Hanford site. The initial waste tanks at Hanford were SSTs with a single containment structures in the bottom and side areas of the tanks. Later tank designs were built using a double-shell design where there are two containment structures in the sides and walls, thus providing an increased assurance of storage integrity. There are 149 SSTs and 28 DSTs, for a total of 177 waste tanks on the Hanford site. One hundred and sixty-one of these tanks are approximately 23 m (75 ft) in diameter and 9 to 16.5 m (30 to 54 ft) high, with nominal capacities of 1,900,000 to 3,790,000 L (500,000 to 1,000,000 gal). The remaining 16 tanks are smaller units of similar design, having a diameter of 6 m (20 ft), a height of 8 m (25.5 ft), and a capacity of 208,000 L (55,000 gal).

The early process wastes were all stored in SSTs while later process wastes, such as Plutonium Uranium Extraction (PUREX) wastes, were put into DSTs. Most of the tanks contain wastes from several processes because of the evolutionary changes made in the processing of weapons materials and as a result of the management of the process wastes in these tanks. The focus of the Organic Safety Project is on the SSTs because the wastes contained in the DSTs are mostly liquid and there are no credible organic safety issues identified for tank wastes which consist of mostly liquid or aqueous dilute solutions (Hanlon 1994). During the waste storage time, the tank environments have included various levels of radiation, temperatures between 20 and 125 °C, and a chemical environment with varying concentrations of hydroxides, nitrates, nitrites, aluminates, oxides, and other materials, including transition metals and radioactive isotopes.

The composition of the wastes varies from tank to tank as well as within a single tank. Typically the waste is stratified into various layers that differ both physically and chemically. Accurate historical records of tank activities were not always kept and changes in waste composition from radiolysis and hydrolysis further complicate the composition issue. Within a single tank there may be one, two, or all three of the waste types described above and they may exist separately, but are most likely intermingled. The SST waste is in three general physical forms: sludge, saltcake, and liquid.

Sludge consists of solid hydrous metal oxides which precipitated during the neutralization of acid wastes before their transfer to the waste tanks. Saltcake consists of the various salts formed from the evaporation of water from the alkaline wastes. Liquids exist as supernatant and interstitial liquid in the tanks.

2.2 WASTE TANK ORGANICS

Although the tank wastes consist mainly of inorganic salts, certain organic chemicals used in the plutonium and uranium separation processes were also disposed to the waste tanks. The known major inorganic constituents in the waste tanks are sodium nitrate, sodium nitrite, silicates, aluminates, hydroxides, phosphates, sulfates, carbonates, ferrocyanides, uranium, and calcium, in addition to fission products created by the processing of irradiated fuel. The principal organic complexants that are believed to have been transferred to the tanks are glycolic acid, citric acid, ethylenediamine tetraacetic acid (EDTA), and N-hydroxyethylethylenediaminetriacetic acid (HEDTA). Allen (1976) provided an estimate of the approximate quantities of these major complexants present in the organic waste tanks as shown in Table 2-1.

Table 2-1. Quantities of the Principal Organic Complexants Used at Hanford

Complexant	Quantity (Metric Tons)
Glycolic Acid	880
Citric Acid	850
HEDTA	830
EDTA	220

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

Significant quantities of process solvents, mainly consisting of tributyl phosphate (TBP), normal paraffin hydrocarbons (NPH), and methyl isobutyl ketone (hexone), have also been dispersed into the HLW tanks. The major sources of the organic process solvents were the PUREX facility and the U-Plant uranium recovery process. The U-Plant process used an organic solvent consisting of TBP in kerosene and the PUREX process used a similar solution of TBP in diluents composed principally of the n-C₁₁H₂₄ to n-C₁₅H₃₂ NPHs. Except for a brief period in early PUREX operations, the process solvents were not ordinarily routed directly to waste tanks, but the process solvents were often entrained in organic solvent wash waste streams.

The historical records suggest that the quantities of organic solvents added to the waste tanks are comparable to the quantities of complexants. From the PUREX Plant process material balances from 1951 to 1991, the following amounts (Table 2-2) of organic process solvents are believed to have been disposed to the tanks (Sederburg and Reddick 1994).

Table 2-2. Quantities of the Principal Organic Solvents Used at Hanford

Solvent	Quantity (Metric Tons)
NPH	1,310
TBP	720
methyl isobutyl ketone	unknown

Other processes also used organic solvents and organic phosphate extractants, but less is known about the quantities that were added to the waste tanks (Gerber et al. 1992). Di(2-ethylhexyl)phosphate diluted with hydrocarbon solvent was used in the waste fractionation and encapsulation process. Hexone and carbon tetrachloride were used in lesser amounts. Quantities of hexone were used in the REDOX process both as an extractant and as a solvent (Gerber et al. 1992); for example, 65 metric tons of hexone were retrieved from a waste tank.

2.3 TANK WASTE ORGANIC HAZARD

The chemical stability of the radioactive wastes in the waste tanks at the Hanford site involves many complex issues, including the specific chemicals present (organic and inorganic) and the physical state of the waste matrix. Potential threats to chemical stability from the organic compounds include organic vapor reactions (combustion with headspace air) and potential condensed-phase organic-nitrate reactions.

Because of the large amounts of inorganic salts in the waste tanks, most of the organic salts (fuel) must be assumed to be in intimate contact with excess quantities of the inorganic salts, such as sodium nitrate and sodium nitrite (oxidizers). The organic safety issue with tank waste specifically concerns the potentially hazardous exothermic reactions that may occur in these waste mixtures. Laboratory studies with tank waste simulants, where sodium acetate was used as a waste fuel, found that these types of mixtures are insensitive to spark, impact, shock, or friction-related ignition sources (Borsheim and Kirch 1991; Fauske et al. 1995; Fauske 1996a). However, waste simulant studies have shown that when mixtures of sodium acetate and sodium nitrate/nitrite are heated above their minimum reaction temperature of about 220 °C (the reaction on-set temperature depends on the type of fuel, and the relative amounts of fuel, oxidizers, and diluents present), an exothermic reaction initiates as the oxidants begin to react with the fuel (acetate) to produce reduced nitrogen compounds and heat. In a large body containing sufficient fuel and where near-adiabatic conditions prevail, the released heat further causes a temperature increase which, in turn, induces more exothermic reactions creating a bulk runaway condition. The combustion "snow balls" until a deflagration occurs (Borsheim and Kirch 1991).

A self-propagating, exothermic reaction creates a potential situation in which high-level waste from a waste tank could be released to the environment from tank temperature and pressure increases. Thus, waste tanks which contain a

relatively high concentration of organic chemicals in addition to their nitrates and nitrites have potential safety issues (Webb et al. 1995).

2.3.1 Early Tank Waste Organic Hazard Identification

The potential danger of organic wastes mixed with oxidizing salts was recognized by Hanford personnel as early as 1967 (Phillips 1967). The stability of organic materials in saltcakes at the Hanford site was investigated in 1976 at which time the saltcakes were found to be stable against exothermic reactions (Beitel 1976). However, this study was directed toward the oxidative power of sodium nitrate rather than toward the reactivity of specific tank waste mixtures. Another study by Beitel (1977) investigated mixtures of HEDTA at 12.5 mol% and 25 mol% with sodium nitrate at temperatures up to 250 °C (482 °F). The mixtures were found to be nonexplosive at the temperatures tested (higher temperatures were not investigated because of equipment limitations).

The tank organic waste safety issue was brought into the foreground in 1989 when information concerning an industrial accident at Kyshtym, U.S.S.R., was released. The accident at Kyshtym was the result of a reaction between sodium acetate and sodium nitrate in a radioactive waste tank where the active cooling system had failed. The heat generated from the high concentration of radioactive isotopes was great enough to boil off the waste's water and raise the temperature to a sufficient level where a self-propagating exothermic reaction was initiated (Fisher 1990). The reacting constituents in the tank at the time of the accident were sodium nitrate and nitrite mixed with about 20 wt% sodium acetate.

The release of information concerning the Kyshtym accident prompted additional investigations at the Hanford site and the need to address both the possible existence of explosive mixtures of organics and oxidizing salts in waste tanks and to examine the reactivity of mixtures containing various proportions of sodium acetate, sodium nitrate/sodium nitrite, and diluents. The possible existence of explosive mixtures was investigated using several sources for estimating the contents of the tanks (Fisher 1990). These sources were limited to TRAC (Jungfleisch 1984), chemical assays from core samples drawn from 15 SSTs as part of early waste tank characterization efforts, and data on waste liquors compositions reported by Schultz (1980).

Reactivity studies exploring mixtures of sodium acetate, sodium nitrate, sodium nitrite, and inert diluents were performed. These studies concluded that mixtures containing a minimum of 10 wt% acetate with at least 20 wt% sodium nitrite plus sodium nitrate would deflagrate when heated to sufficiently high temperatures. This work led to the definition of an upper limit for an acceptable concentration of total organic carbon (TOC) in the waste. The limit was defined as 10 percent organic equivalent weight to sodium acetate, which corresponds to 3 wt% TOC (10 wt% Na Acetate x $\left[\frac{0.2928 \text{ g C}}{\text{g Na Acetate}}\right] = 3 \text{ wt\% TOC dry}$) (Fisher 1990).

This early criterion for waste safety, based on the 3 wt% upper limit of TOC, did not consider the two essential factors of temperature and moisture content in the evaluation of potential reactive mixtures of organic and oxidizing salts. This basis also assumed sodium acetate represents the most energetic

organic waste form. In addition, the 3 wt% TOC criterion was based on limited qualitative laboratory screening studies which would be difficult to validate (Turner 1993).

2.3.2 Organic Waste Tank Watch List

The 3 wt% TOC limit was initially applied to available information on all SSTs at the Hanford Site (Fisher 1990). The 3 wt% TOC safety criterion was not applied to the DSTs because the organic complexants contained in the DSTs are in the liquid phase and there were no credible organic safety issues identified for the waste in this form (Hanlon 1994). The safety concern is with tanks that primarily contain solids because they could potentially dry out, heat up, and reach a temperature sufficient to initiate a spontaneous, bulk runaway exothermic reaction (as happened at Kyshtym).

As a result of the initial screening in 1991, seven waste tanks were found to have TOC levels greater than 3 wt% and subsequently were placed on an Organic Watch List. Thirteen additional tanks were later added to the Organic Watch List. Table 2-3 lists the waste tanks currently on the organic Watch List and the basis for placing each tank on this list.

Further studies indicate that this TOC threshold could be raised to 4.5 wt% (dry basis) (Fauske et al. 1995). However, to ensure a conservative approach in designating Watch List tanks based on historical information, Westinghouse Hanford Company (WHC) has employed the original 3.0 wt% TOC (dry basis) criterion in identifying these additional 10 Watch List tanks (Turner 1994b).

As indicated below, more refined screening criteria, based on historical data, combustion experiments with simulants and actual tank wastes, and total risk analysis are being developed. These new criteria are being applied to all of the waste tanks, including those initially placed on the organic tank Watch List, for a new assessment of their organic safety status (Meacham et al. 1996).

2.4 TANK WASTE SAFETY ISSUES

In the five years since the initial identification of the organic safety issues, significant progress has been made in the refinement and understanding of the problem. The safety status of the organic wastes is now known to be affected by a number of chemical and physical properties of the waste matrix containing the organics, the physical and chemical aspects of the organics themselves, and the physical properties of the tank itself.

When the organic issue was first recognized, it was evident that there was little reliable information about the actual composition of the materials in the waste tanks. The observation that the organic wastes contributed to the evolution of hydrogen and other gases indicated that the organic compounds were undergoing chemical reactions that further complicated the evaluation of the organic safety issues.

Table 2-3. Basis for Organic Watch List Designation and Suspected Waste Sources

Tank	Basis for Watch List Designation	Waste Source (Fowler 1993)
A-101	Review of historical documents	242-A Evaporator bottoms
AX-102	PNNL TOC estimate	Unknown
B-103	Review of historical documents	First and second cycle waste from B-Plant and in-tank solidification (11S-1 & 11S-2) evaporator bottoms.
C-102	Formerly held organic liquid layer	TBP process waste from U-Plant and PUREX organic wash waste.
C-103	Detection of separate floating liquid organic layer	PUREX and insoluble strontium-rich sluicing solids from the operation of 244-CR Vault
S-102	Review of historical documents	REDOX waste
S-111	Review of historical documents	REDOX waste and 242-S evaporator bottoms
SX-103 SX-106	Review of historical documents	Salt waste and first cycle condensate from REDOX and 242-S Evaporator bottoms
TX-105 TX-118	Review of historical documents	TBP process waste
U-106 U-107	Review of historical documents	Evaporator bottoms
T-111	Review of historical documents	Second cycle waste, 224 waste, T-Plant decontamination and decommissioning waste
TY-104	Review of historical documents	Unknown
U-103	Review of historical documents	Unknown
U-105	Review of historical documents	Unknown
U-111	Review of historical documents	Concentrated Hanford B-Plant waste
U-203 U-204	PNNL TOC estimate	Concentrated Hanford B-Plant waste

Recognition of the complexity of the wastes and the equally complex safety issues prompted the initiation of a number of investigations, including work on historical data, targeted experimental studies, and the current characterization program. Technical information is needed on which a credible and technically defensible assessment of tank waste safety status can be based. More specifically, the solubility, volatility, and aging of the tank waste organics are important issues in understanding the organic safety issues.

2.4.1 Organic Solubility Relationships

One of the parameters that impacts the safety issues of organics is the solubility of the organics in the waste matrix. The organic solvents and complexants that were discharged to the waste tanks are mixed in a very alkaline environment with sodium nitrate/nitrite and other inorganic substances to provide a complex mixture of materials distributed among several phases.

As indicated above, the four most abundant complexants in the alkaline wastes are trisodium citrate, HEDTA, sodium glycolate, and EDTA with lesser amounts of other complexants, such as NTA, sodium di(2-ethylhexyl)phosphate, and sodium oxalate. The two organic solvents that were employed in large quantities were TBP and several commercial mixtures of paraffinic hydrocarbons. Hexone and carbon tetrachloride were used in lesser amounts.

Open literature and experimental studies have been used to define the solubility of the organic complexants and solvents and certain aging products in alkaline solutions (Barney 1994, 1996a, 1996b). These measurements were necessary because the solubility data in the literature could not be extrapolated with confidence to predict solubilities of the organics in a tank waste chemical matrix.

Solubilities of Organic Complexants - To date, studies have demonstrated that the solubility of the four most abundant, original complexants are very soluble in aqueous solutions containing high concentrations of sodium hydroxide, sodium nitrate, and sodium nitrite. Preliminary work on the alkylphosphates and their decomposition products suggests that mixtures of these substances have complex phase relationships; sodium di(2-ethylhexyl)phosphate is essentially insoluble in the alkaline aqueous phases of the wastes (Barney 1996b).

It has also been established that several of the decomposition products of the complexants, such as disodium iminodiacetate (IDA) and disodium succinate, are very soluble in the aqueous waste solutions. Many of the one and two carbon atom end products of the complexant aging components, including sodium glycolate, sodium formate, and sodium acetate, are soluble in the aqueous waste phase. Sodium oxalate exhibits only partial solubility in waste simulants and the solubility limit may be exceeded under certain conditions.

Empirical and statistical studies of the TOC content of wastes have provided additional perspectives on the complexant solubility properties. Examination of the available data for the liquid supernatant solutions in 61 waste tanks indicates that only five tanks of this group have TOC content that is greater than 14 g/L (Van Vleet 1993a, 1993b). Statistical evaluation of the data for 143 samples from 78 different SSTs suggests that the mean value is 5.2 g/L of organic carbon (Barney 1996a, Toth et al. 1995). The highest measured value of TOC (approximately 40 g/L) is smaller than the measured solubility limit for the energetic complexants.

Solubilities of Organic Solvents - In contrast to organic complexants, the organic solvents are much less soluble in the tank waste chemical matrix; carbon tetrachloride, hexone, and paraffinic hydrocarbons are essentially

insoluble in aqueous solutions. However, preliminary studies suggest that the products of the aging reactions of the paraffinic hydrocarbons are often acidic substances that are soluble.

TBP is only partially soluble in aqueous solution; but as discussed below, it is converted into several new compounds including disodium butylphosphate, sodium dibutylphosphate, sodium butyrate, and butanol by radiolysis and base-catalyzed hydrolysis reactions. Mixtures of TBP and the two sodium butylphosphates with alkaline aqueous salt solutions apparently exhibit very novel phase relationships (Camaioni et al. 1996). However, the individual sodium butylphosphate salts are soluble in alkaline solution. The calcium, aluminum, and iron dibutylphosphates are insoluble in water, but are soluble in 1 M sodium hydroxide. Thus, there is a high probability that they accumulate in the aqueous supernatant solution.

2.4.2 Organic Waste Species Volatility

Volatility is an important parameter in the understanding of the current organic inventories that are in the organic waste tanks and the safety issues resulting from their presence.

Analyses of the complexants, solvents, and their aging products have indicated that the complexants are generally nonvolatile while the solvents have high vapor pressures and may evaporate to the waste tank headspace atmosphere. In the aging process, the complexants are converted to salts which are also nonvolatile.

Organic Solvent Volatility - Tank waste organic solvents and their decomposition products have demonstrated a high volatility in the tank waste matrix. Analysis of headspace gases and organic layer species have shown selective loss of the more volatile organic constituents.

Ongoing investigations of the composition of the gases in the headspace of the waste tanks provide significant and reliable evidence for the presence of organic solvents and their decomposition products (Huckaby 1995a, 1995b; Huckaby et al. 1995; McVeety et al. 1995; Huckaby and Bratzel 1995, Huckaby 1996). Specifically, compounds such as undecane, dodecane, and tridecane, which are known to be constituents of the paraffinic hydrocarbon mixtures, have been detected in low concentrations in the dome space of several waste tanks. In addition, studies have also shown that the homologous series of ketones and other substances that are plausible products of the radiolytic decomposition reactions of the paraffinic hydrocarbons are also present in the tank head space gases.

Babad and Plys (1996) investigated the rates at which volatile substances can evolve from wastes mixtures. Butanol and typical paraffinic hydrocarbons were selectively evolved from a mixture of butanol, decane, dodecane, tetradecane, and tributyl phosphate at temperatures and ventilation rates that are typical for the Hanford waste tanks.

The potential volatility of solvents has been shown by the investigations of Sederburg and Reddick (1994) where volatile solvents were distilled from the wastes containing enough heat to cause tank wastes to self-boil. These

self-boiling tank waste temperatures ranged from 90 to 125 °C, with a typical self-boiling temperature around 115 °C. These temperatures approach or exceed the normal boiling points of the paraffinic hydrocarbons, hexone, carbon tetrachloride, and butanol (CRC 1981). In addition, process records show that significant volumes of wastes were run through evaporator cycles which also raised the temperatures of tank wastes (Anderson 1990). Agnew (1996a) has discussed the incorporation of alternate organic inventories that recognize the effects of self-heating in the Hanford Defined Waste (HDW) model for estimating the current compositions of the wastes.

The analysis of the supernatant layer in tank SY-101 has shown the presence of paraffinic hydrocarbons in the 40 to 1440 ppm range (Campbell et al. 1994a, 1994b). The quantity of TBP in the vapor is below the detection limit, but the analyses of the vapor space have revealed that butanol, the volatile decomposition product, is present.

Further support of the volatility of organic solvents is shown from the investigations of the solvent layer in tank C-103. Historical processing records imply that the TBP to NPH ratio in the process solvent that was discharged to the waste was approximately 1:2. However, the current analytical results for the solvent layer indicates that the TBP to NPH ratio is now about 2:1 (Pool and Bean 1994, Campbell et al. 1994a). These results support the conclusion that the more volatile hydrocarbons have selectively evolved from tank waste, and in this case, leaving a phosphate-rich organic material.

The analytical information about dome space composition, the rates of evolution of the organic compounds from simulants, and the data for tank C-103 indicate that the more volatile paraffinic hydrocarbons and other organic solvents slowly evolve from the wastes. The chemically neutral products of waste aging, such as butanol and the alkanones, also evolve.

2.4.3 Aging (Decomposition) of Organic Wastes

There is strong evidence that the organic complexants and solvents in the tank wastes are decomposing or aging to less energetic species. Characterization data from organic tank waste samples and literature searches indicate that both organic complexants and solvents are aging in the tank wastes. The organic compounds are continuously being transformed into less energetic compounds, with the thermodynamic end product of this reaction chemistry being sodium carbonate. Eventually all of the organic carbon in the wastes will be converted to this inert substance with the release of hydrogen-rich gaseous molecules.

Aging is a key issue in the assessment of the safety status of a waste tank containing organic wastes. Traditionally, TOC analyses have been used at Hanford to estimate the organic content of the wastes, assigning all of the TOC to sodium acetate for estimating the energy content of the waste. It is now understood that this strategy overestimates the hazards associated with the organic waste because this TOC method does not distinguish between the relatively energy-rich original materials and the energy-poor aging end products.

The aging of organics is a complex process and the reaction rates cannot be accurately predicted from first principles. Both laboratory and theoretical analyses will be needed to estimate the aging reaction patterns of the most important organic components in the tank waste environments. Laboratory investigations of the chemistry of aging in simulants and real wastes and studies of the compositions of the organic molecules currently present in the wastes are being completed. Additional studies will validate the principal conclusions from the initial work which has been performed for the most part since 1990 at the Georgia Institute of Technology (Ashby et al. 1993, 1994; Barefield et al. 1995, 1996), Argonne National Laboratory (Meisel et al. 1991a, 1991b, 1992, 1993), and Pacific Northwest National Laboratory (Bryan and Pederson 1994; Camaioni et al. 1994; Campbell et al. 1994a, 1994b; Campbell et al. 1996). This work has provided a good foundation for understanding the aging process and for identifying avenues that apply these principles to tank wastes.

Organic Complexants - The current investigations show that organic complexants decompose or age under a number of different conditions and by several different processes. The available data suggest that the aging reactions occur with and without radiation exposure, forming hydrogen- and nitrogen-containing gases and an array of oxidized organic molecules. Available data also suggest that the reactions are initiated in essentially the same way in the presence or absence of radiation, but that the radiochemically-induced reactions occur faster at lower temperatures.

The elementary features of the radiation chemistry have been initially examined in Meisel et al. (1993), and results indicate that radiolytic processes initiate the decomposition of the organic molecules and the formation of gaseous products. Their studies also indicate that the radiolysis of water alone could not account for the high yields of hydrogen and that organic degradation reactions are responsible for the formation of the excess hydrogen. The high yields of hydrogen have been related to the carbon-hydrogen bonds in the complexants.

The radiolytic reactions begin with the decay of cesium or strontium to produce hydrogen atoms, hydroxyl radicals, oxygen anion radicals, nitric oxide, nitrogen dioxide, and nitrogen trioxide. The reactive reagents either eject a hydrogen atom or an electron from the organic molecule to initiate reaction sequences in which one of the original hydrogen-rich carbon atoms of an organic molecule experiences oxidation. Some of the products of the decomposition, for example formaldehyde, react in the alkaline tank waste environment to produce hydrogen (Meisel et al. 1993; Ashby et al. 1993). Other products, for example the NTA anion, are relatively stable substances that accumulate in the waste. The radiolytic reactions of the organic compounds are coupled with the reactions of the nitrite ion which is chemically reduced to nitrous oxide, nitrogen, or ammonia.

Studies also indicate that the evolution of hydrogen and the other gases continues even after the radiation is removed. Although the results can be examined in several different ways, it is evident that the organic complexants do decompose even in the absence of radiation to form hydrogen and the nitrogen-containing gases and to produce an array of oxidized organic molecules similar to the array of oxidized organic molecules found in the

radiolytic reactions. The investigations by the Argonne group and the team at Georgia Institute of Technology showed that a significant amount of hydrogen originated from the decomposition products of the original complexants, principally through the formyl groups in the molecules and in molecular fragments. Ashby and coworkers demonstrated that one of these intermediates, formaldehyde, reacts with water in highly alkaline waste simulants to produce hydrogen. Another intermediate, sodium formate, which also rather rapidly disappears from the waste (Lilga et al. 1993, 1994, 1995), presumably also contributes to the formation of hydrogen gas.

The research at Georgia Institute of Technology and related work at Pacific Northwest National Laboratory indicate that the HEDTA ion decomposes rather slowly in alkaline solution to provide the EDTA, IDA, and NTA anions and other intermediates together with sodium formate and sodium oxalate. Although the activation energies are high and the kinetic rate laws are complex, it is reasonably well established that the rates of these non-radioactive based reactions depend on the concentrations of the nitrite, hydroxide, and aluminate anions. In addition, the decomposition reactions of the complexants are inhibited by oxygen.

Several investigators have extrapolated the available decomposition information to estimate the relative reactivities of the organic compounds in the wastes.

For radiolytic decomposition the relative rates are as follows:

HEDTA, EDTA >> Glycolate > Hydrocarbon >> Acetate >> Oxalate

The relative rates between HEDTA and sodium oxalate span about three orders of magnitude.

For non-radiolytic decomposition (relative rates):

Glycolate > HEDTA >> EDTA, IDA, NTA

Further evidence that non-radiolytic pathways contribute to organic decomposition is borne out by the relatively quick disappearance of sodium glycolate in simulated organic wastes. The reactions of many of the other complexants appear to be relatively slow in the absence of radiation. The life times of the organic molecules will depend on the sum of the rates of reactions from both radiolytic and non-radiolytic reactions.

Further evidence of organic decomposition is found from speciation studies of complexants in actual waste tanks (Campbell et al. 1994b). Processing records indicate that HEDTA was a principal component of the SY-101 and SY-103 wastes. However, speciation of samples from these tank wastes shows that it is now a relatively minor constituent and that new, substances (decomposition products) including EDTA, NTA, and IDA anions and sodium formate, acetate, and oxalate have been formed. These initial characterization results clearly establish that sodium oxalate is now the principal organic component in these tank wastes, verifying that the original organic species have decomposed. Results indicate that sodium carbonate formed simultaneously.

Clearly the current inventory of organic species in organic tank wastes is not the same as when the waste was placed in the waste tanks. The technical literature and experiments with simulants and actual tank waste samples show that the original organic content has aged as a result of radiolytic and non-radiolytic decomposition processes. The decomposition sequences eventually lead to sodium carbonate. The rates of aging within a tank waste and its current organic inventory are key issues in the assessment of the safety status of an organic tank waste. Studies are currently underway to confirm the aging process, and this work along with speciation of actual tank waste samples, will provide guidance for assessing the safety status of tank waste containing organic complexants.

Organic Solvents - Aging studies on organic solvents are also underway (Barefield et al. 1995; Camaioni et al. 1994, 1995), and the work has already reaffirmed the dynamic chemical nature of the waste and established that organic solvents undergo decomposition to form less energetic organic molecules and sodium carbonate. The rates at which the organic solvents are transformed into new compounds depend upon the radiation intensity, temperature, hydroxide ion concentration, and the aluminum concentration of the tank wastes.

The effort to understand the potential for aging or decomposition of the organic solvents in tank wastes was initiated by work at WHC (Babad et al. 1993) and work at the Pacific Northwest National Laboratory (Samuels et al. 1993; Camaioni et al. 1994 and 1995; Camaioni et al. 1996). Samuels and coworkers reviewed the literature on the base-catalyzed hydrolysis and radiation chemistry of TBP and related compounds (Samuels et al. 1993). It was found that although TBP is only slightly soluble in water, it undergoes hydrolysis rather rapidly in alkaline solution to form sodium dibutylphosphate. On the other hand, sodium dibutylphosphate hydrolyzes much more slowly than the TBP. A saturated solution of TBP in 1 M sodium hydroxide decomposes at a measurable rate (Burger 1958, Kennedy and Grimley 1953).

Other studies show that the radiolysis of TBP by gamma rays or electrons with energy above 1 MeV produces monobutyl and dibutylphosphate ions and gaseous fragmentation products from the butyl group (Wilkinson and Williams 1961; Burger and McClanahan 1958; Burr 1958). The radiation of the same molecule in hydrocarbons produces the same decomposition products (Barelko et al. 1966). Camaioni has pointed out that the reactions of these phosphates with the hydrogen atoms from the radiolysis of water or other molecules provides a unique pathway for decomposition by the selective cleavage of the P-OR bond rather than the P-OH bond.

Experimental studies with simulants of the radiolysis and base-catalyzed hydrolysis of TBP and its principal decomposition products show that these reactions proceed much more rapidly than suggested by the technical literature, even in the absence of radiation (Camaioni et al. 1996). The reaction rates, derived from these simulant studies, depend on the concentration of the hydroxide ion and are appreciable in solutions containing 1M sodium hydroxide. The decomposition reactions occur much more rapidly in a radioactive environment. From the simulant tests, Linehan and Camaioni estimated that 90% of the dibutylphosphate anion would be destroyed if it experienced an integrated radiation dose of approximately 3×10^7 rad.

Mixtures of TBP, butylphosphate anions, and aqueous simulants exhibit novel phase relationships that appear to slow the decomposition reaction.

The decomposition reactions convert the esters into butanol and sodium butyrate. These compounds decompose to sodium formate and sodium oxalate during radiation (Camaioni et al. 1996). Sodium di(2-ethylhexyl)phosphate and certain of its derivatives have also been found dispersed in the waste. But neither the hydrolytic nor the radiolytic chemistry of these compounds has been investigated.

Radiolysis studies with a wide range of hydrocarbons have been underway for many years, with much of the work being carried out under the sponsorship of the DOE. The reactions of the hydrocarbons have been investigated in dilute homogeneous aqueous solutions (Neta et al. 1988). The rate constants for the abstraction of hydrogen atoms from the organic solvents are comparable to the rate constants for the same reactions of a relatively reactive complexant such as the glycolate anion. Several considerations suggest that the actual rates of decomposition of the solvent waste hydrocarbons will appear to be relatively slow because they have a low solubility in the aqueous solutions containing the radioactive nuclei. However, the decomposition products from the radiolysis of paraffinic hydrocarbons are much more soluble in water and their decomposition reactions should proceed much more rapidly than the reactions of the starting molecules.

In other work with tank waste samples, Campbell has detected paraffinic hydrocarbons ranging from 20 to 1440 ppm in liquid samples from SY-101 (Campbell et al. 1994a). However, no work has been done to determine the rates at which these compounds undergo radiolytic decomposition in the tank environment.

The current work has affirmed the dynamic chemical nature of the waste and established that the organic molecules in the waste undergo decomposition to less energetic molecules, eventually forming sodium carbonate. Studies are currently underway which will help understand both relative and absolute rates of transformation. The goal is to establish the current and future organic solvent contents by acquiring kinetic data for decomposition rates, confirming them with work with simulants, and verifying them by studies of tank wastes. The results will be correlated with tank historical data, characterization data, and other information. The disappearance of the organic fuel components would unambiguously close the tank waste organic solvent safety issue.

2.5 TANK WASTE SAFETY SCREENING CRITERIA

The Organic Safety Project safety criteria (interim criteria) are based not only on presence of fuel (TOC) but also on waste temperature and moisture content (Turner 1993). The rationale behind these criteria was the strategy developed for the Hanford High-Level Waste Tank Safety Issue Resolution (Christensen 1993). That strategy requires an understanding of the conditions necessary for propagating chemical reactions, a knowledge of the condition of a tank's waste, and the instituting of procedures and any necessary changes and controls for operating the tank so that it is within bounds set by the safety criteria.

The evaluation of the storage of waste mixtures containing nitrates and nitrites showed the following necessary tank waste conditions are associated directly with the initiation and propagation of a propagating chemical reaction:

- (1) sufficient fuel (organic content),
- (2) sufficient oxidizers (sodium nitrate/nitrite),
- (3) low moisture values, and
- (4) high temperatures.

Because of the high abundance (relative to the fuel content) of nitrates and nitrites in the tank wastes, the oxidizer concentration is not an issue for tank wastes. Based upon these four conditions, graduated risk safety criteria were developed and three safety levels for classifying the safety status of a tank with organic waste were created: *safe*, *conditionally safe*, and *unsafe*. The safety criteria provides a graduated risk approach in which the individual safety issues of each tank can be addressed. It also provides a mechanism for resolving the organic safety issue by defining the terms necessary for the safe storage of waste for each individual waste tank. If a tank does not meet *safe* or *conditionally safe* storage conditions, then mitigation or remediation of its wastes would be necessary.

The technical bases for the safety criteria were based on the results of a series of organic waste surrogate energetics tests performed by Fauske and Associates, Inc. (FAI) (Kirch 1993) and the U.S. Bureau of Mines (USBM) (Turner 1994a). The studies performed by FAI consisted of calorimetry studies using the reactive systems screening tool (RSST) adiabatic calorimeter and the vent sizing package calorimeter to determine the energetics of several surrogate waste mixtures. The fuel used in these mixtures was sodium acetate which was blended in three concentrations with sodium hydroxide and sodium nitrate/sodium nitrite. FAI also investigated the minimum moisture content necessary to prevent a propagating exothermic reaction.

The USBM conducted a battery of tests to determine the thermal and explosive characteristics of surrogate waste materials. The surrogate waste materials consisted of various ratios of fuel, oxidizer, and diluent. The oxidants were sodium nitrate and sodium nitrite. The fuels tested were sodium salts of oxalate, citrate, and EDTA. Polyethylene powder was also used as a fuel with the oxidants. Sodium aluminate was used as a diluent. The tests performed consisted of three standard explosive tests and one flammability test. The standard explosive tests were friction, impact, and internal ignition tests; the flammability test was the flame spread rate test. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were also performed by the USBM to investigate the exothermic behavior of the waste surrogates.

2.6 TANK ORGANIC WASTE DRIVERS

Several requirements, or drivers, for conducting activities in the Organic Safety Project have been identified and are briefly summarized below. These requirements (laws, codes, regulations, orders, etc.) provide the basis for establishing priorities and the technical criteria for completing activities.

2.6.1 Safety Measures Law - The Wyden Amendment

Waste tank safety is a primary safety concern within the DOE complex. Concern for waste tank safety at the Hanford Site was sufficient to compel the U.S. Congress to pass Public Law 101-510 (1990) (also known as the Safety Measures Law or the Wyden Amendment). This law required the following actions:

- Identify waste tanks that "may have a serious potential for release of high-level waste from uncontrolled increases in temperature or pressure";
- Ensure that "continuous monitoring to detect a release or excessive temperature or pressure" is being carried out;
- Develop "action plans to respond to excessive temperature or pressure or a release from any waste tank identified";
- Restrict additions of high-level nuclear waste to the identified waste tanks unless no safer alternatives exists, or the serious potential for a release of high-level nuclear waste is no longer a threat;
- Report "on actions taken to promote waste tank safety, including actions specifically taken pursuant to this section of the law, and the ... timetable for resolving the outstanding issues on how to handle the waste in such tanks."

The Waste Tank Safety Projects are the key element in responding to this law. (See also Reep 1993).

2.6.2 Atomic Energy Act of 1954

The following DOE orders are major drivers. These orders involve the management of waste containing radioactivity for the DOE under the *Atomic Energy Act of 1954*, as amended by Public Law 83-703:

- DOE Order 5480.1B, *Environmental, Safety, and Health Program for Department of Energy Operations* (DOE 1993);
- DOE Order 5480.5, *Safety of Nuclear Facilities* (DOE 1986);
- DOE Order 5480.21, *Unreviewed Safety Questions* (DOE 1991);
- DOE Order 5480.23, *Nuclear Safety Analysis Reports* (DOE 1992);
- DOE Order 5820.2A, *Radioactive Waste Management* (DOE 1988);
- DOE Order 6430.1A, *General Design Criteria* (DOE 1989).

2.6.3 Code of Federal Regulations

The following Federal regulations are drivers for Waste Tank Safety Projects:

- 10 CFR 962, "Radioactive Waste: Byproduct Material,"
 - 10 CFR 1021, "Department of Energy National Environmental Policy Act (NEPA) Implementing Procedures,"
 - 40 CFR 191, "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes,"
 - 40 CFR 261, "Identification and Listing of Hazardous Waste,"
 - 40 CFR 262, "Standards Applicable to Generators of Hazardous Waste," and
 - 40 CFR 1500-1508, "Regulations for Implementing the Procedural Provisions of the National Environmental Policy Act."
-
-

Mitigation or remediation of the waste in the tanks will comply with:

- 40 CFR 264, "Standards for Hazardous Waste Treatment, Storage, and Disposal Facilities," and
- 40 CFR 265, "Interim Status Standard for Hazardous Waste Treatment, Storage, and Disposal Facilities."

2.6.4 Washington State Administrative Code

Waste Tank Safety Project activities must comply with the state of Washington Administrative Codes (WAC) with respect to managing radioactive and dangerous waste. The specific regulation applicable for tank waste characterization is WAC 173-303, *Dangerous Waste Regulations*, Section 110, "Sampling and Testing Methods." The more general regulations of WAC 246-247, "Radiation Protection Standards," and WAC 296, "OSHA Standards," must also be followed.

2.6.5 Defense Nuclear Facilities Safety Board

The DNFSB was created to provide advice and formal recommendations to the President of the United States and to the Secretary of Energy regarding public health and safety issues at DOE nuclear facilities. The DNFSB reviews operations, practices, and occurrences at DOE nuclear facilities and makes appropriate health and safety recommendations. If any aspect of operations, practices, or occurrences reviewed by the DNFSB is determined to present an imminent or severe threat to the public health or safety, the DNFSB transmits its recommendations directly to the President. The Organic Safety Project periodically holds over-sight reviews with the DNFSB where progress, issues, and plans are reviewed.

The DNFSB issued Recommendation 93-5 with respect to the characterization and safe handling of waste in the tanks including flammable gas, organics, and ferrocyanide (Conway 1993). U.S. Department of Energy - Richland Operations Office (DOE-RL) responded with an implementation plan that included activities and milestones (DOE/RL 1994) which was modified (DOE/RL 1996). The milestones applicable to the Organic Safety Project are identified in Chapter 6.

2.6.6 Tri-Party Agreement (TPA)

The *Hanford Federal Facility Agreement and Consent Order* (TPA) contains provisions governing the treatment, storage, and disposal of hazardous waste, including remedial and corrective action activities (Ecology et al. 1990). During 1993 negotiations were conducted by DOE, Environmental Protection Agency (EPA), and Washington State Department of Ecology (Ecology et al. 1994). New milestones were negotiated and a reduced set of specifications for waste analyses and characterization was adopted. The new milestones do not reflect the addition of 10 waste tanks to the organic tanks Watch List in Turner (1994b). Major milestones important or specific to organic waste tank safety issues are:

- | | |
|---------|---|
| M-20-00 | Submit Part B permit applications or closure plans for all RCRA treatment, storage, or disposal units (February 28, 2000) |
| M-40-00 | Mitigate/Resolve tank safety issues for High Priority Watch List Tanks (September 30, 2001) |

M040-09	Close safety issue USQ (September 20, 1998)
M-41-00	Complete SST interim stabilization (September 30, 2000)
M-41-13	Interim stabilization of three organic watch list tanks in U tank farms (January 31, 1998)
M-41-15	Interim stabilization of two organic watch list tanks in S/SX tank farms (March 31, 1999)
M-41-19	Interim stabilization of one organic watch list tank in C tank farm (March 31, 1999)
M-44-00	Issue Tank Characterization Reports (September 30, 1999)
M-45-00	Complete closure of all 149 SSTs (September 30, 2024)

2.6.7 Safety Initiatives

The Secretary of Energy issued several safety initiatives (O'Leary 1993), including 3 related to organic issues:

- Complete sampling and safety evaluation of liquid organic in Tank C-103;
- Remove organic layer from C-103;
- Continuous temperature monitoring installed in organic tanks.

2.7 UNREVIEWED SAFETY QUESTION

2.7.1 Background

A USQ exists when a condition or activity represents an inadequacy in the authorization basis for a facility. With respect to the organic waste issue at the Hanford site, the Plant Review Committee (PRC) determined that the existing authorization basis does not adequately address the potential effects of an organic-nitrate reaction. Specifically it considered Webb et al. (1995) which stated that the potential exists for an organic-nitrate reaction with the resulting effect of exceeding existing guidelines. DOE (1986 and 1991) state, "A proposed change, test or experiment shall be deemed to involve a USQ if the following apply;

- a. The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased; or
- b. A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

The existing authorization basis is Chapter 6.0 of the Interim Safety Basis (Leach and Stahl 1995). It does not contain a discussion of the potential for an organic-nitrate reaction, i.e., item b above is applicable. It does contain the controls for Watch List tanks of all types (e.g., ferrocyanide, flammable gas, etc). Webb et al. (1995) noted that, without additional information, the possibility of an organic-nitrate reaction in the SSTs must be considered as credible. The PRC finding was forwarded to the DOE-RL by Wicks (1996) and DOE-RL concurred (Wagoner 1996).

Meacham et al. (1996) updated the basis document (Webb et al. 1995) of the USQ including categorizing as *safe*, *conditionally safe*, or *unsafe*, only those waste tanks for which had sufficient sample data. (None of the 67 waste tanks with data was categorized as *unsafe*.)

2.7.2 Status

The existing authorization basis is Leach and Stahl (1995). A Basis for Interim Operation (BIO) is being developed to replace Leach and Stahl (1995). However, it will not contain adequate information to allow the USQ to be closed at this time because sufficient analysis and sample results are not available to address the issue.

The activities described in Chapter 5 of this report will provide the technical basis for closure of the USQ. The organic complexant safety analysis (Meacham et al. 1996) will be updated and the current authorization basis will be amended (either the Basis for Interim Operation or the Final Safety Analysis Report) to close the USQ.

3.0 TANK WASTE ORGANIC SAFETY HAZARD

The current technical bases for the safety criteria are the results of on-going energetics testing, modeling, and analysis work to identify bounding reactivity relationships between fuel, oxidizer and temperature. As a result of continued investigations of historical data and characterization samples excised from tank wastes, the organic tank waste safety issue has been narrowed and focussed on the organic complexants and organic solvents that were dispersed in Hanford's waste tanks. Three potential hazards were identified for wastes with organic complexant and/or solvents (Meacham 1996):

- head space flammability;
- spontaneous chemical runaway (self-heating) reactions occurring throughout the waste mass; and
- ignition of propagating exothermic chemical reactions (combustion) typified by a moving reaction front.

3.1 ORGANIC COMPLEXANT HAZARD

The organic complexants that were discharged to the waste tanks during the defense mission at the Hanford Site include glycolic acid, citric acid, HEDTA, and EDTA that were used during fuel reprocessing, metal recovery operations, and waste management separations. When disposed to the tanks, these materials were mixed with sodium hydroxide, sodium nitrate and nitrite, and other organic diluents already present in the tanks.

In the presence of oxidizing materials, such as nitrates or nitrites, it has been shown that organic complexants can be made to react with exothermal behavior by heating to high temperatures (above 220 °C) or by an initiator of sufficient energy (Fauske 1996a).

3.1.1 Headspace Flammability

Although decomposition of organic complexants can generate flammable gases, organic complexant salts themselves are nonvolatile and exert no vapor pressure. Thus, the original organic complexant salts are not a headspace flammability hazard in the Hanford waste tanks. Aging data has shown that these complexants can break down into smaller organic molecules which may exhibit different chemical and physical properties than the original salts. However, it has also been established from tank vapor space sampling data that these and other organic species (including breakdown products) are being accumulated in the headspace at concentrations that are well below the lower flammability limit (LFL). Thus, organic complexant salts and their breakdown products are not a headspace flammability hazard in Hanford Site waste tanks.

3.1.2 Spontaneous Chemical Runaway

The rate of heating must exceed the rate of cooling for a spontaneous chemical runaway reaction to occur (Gygax 1990). If the temperature is not controlled, then undesirable deflagrations can occur when the large activation energy barriers are exceeded. Preventing spontaneous chemical runaway has been

thoroughly studied in the chemical and petroleum industries (American Institute of Chemical Engineers 1989, 1992, 1995a, 1995b, 1995c, 1995d, and 1995e). Hanford Site tank wastes have been assessed using similar methodology, and the results show that spontaneous conditions leading to a chemical runaway in the passively ventilated tanks are highly unlikely under current storage conditions (Fauske 1996a). However, the waste in seven SSTs (C-106, SX-107, -108, -110, -111, -112, and -114) has high enough decay heat to require active cooling to maintain waste temperatures within acceptable limits. Temperature monitoring and waste cooling controls are currently required for these tanks.

The potential for spontaneous chemical runaway reactions was evaluated by comparing the characteristic time of cooling (i.e., the time required to reach a new equilibrium temperature following an instantaneous change in heating rate) with the waste storage time. Calculations indicate that the characteristic time of cooling ranges from a few hours to 3.1 years for the Hanford Site tanks (Fauske 1996a). Some waste has been stored for more than 40 years, and there have been no transfers of waste into the SSTs for approximately 15 years. Several characteristic times of cooling have passed during the last 15 years of storage; consequently, bulk runaway reactions are not credible.

In addition, no credible mechanisms to increase tank temperatures to chemical runaway reaction levels have been identified for the passively ventilated tanks. Drying the wastes can decrease the thermal conductivity; however, this decrease would not be sufficient to lead to spontaneous chemical runaway (Fauske 1996a). Waste temperatures after removal of the pumpable liquid (interim stabilization) have continued to decline consistent with the principal heat load from radioactive decay rates. Of the 149 SSTs, 114 have been interim stabilized in an on-going program.

3.1.3 Ignition of Organic Complexants

If enough organic-based fuel is present in the waste and the waste is sufficiently dry, an organic-nitrate/nitrite propagating combustion event could be initiated by a variety of external sources. Potential credible ignition sources have been identified and include hot metal objects, rotary core upsets, burning gasoline spills from a ruptured vehicular fuel tank, and lightning (Meacham et al. 1996). An organic complexant, propagating combustion event could lead to consequences that are above acceptable waste tank risk evaluation guidelines; pressurization of a waste tank's dome space with a subsequent release of radioactive materials to the environment. Therefore, ignition of organic complexants from credible ignition sources must be considered in the resolution of the organic safety issue (Meacham et al. 1996).

3.2 ORGANIC SOLVENT HAZARD

Several organic solvents were discharged to the waste tanks during the various separation processes. Subsequent management of the tank waste inventories (such as inter-tank transfers) have further distributed organic solvent within the waste tanks at Hanford (Sederburg and Reddick 1994).

The principal organic solvents are TBP and mixtures of NPH. These solvents are only partially soluble in the aqueous wastes and can therefore exist in several phases dispersed among other liquid and solid phase constituents, or in a separate layer on top of an aqueous phase.

3.2.1 Headspace Flammability

At current tank waste temperatures, the organic solvent vapor contribution to headspace flammability is very low (Claybrook and Wood 1994). Head space, vapor species data from all waste tanks sampled to date supports this conclusion (Huckaby et al. 1995). Tank C-103 is a bounding case tank that has been identified as having a floating organic solvent layer at the top of the waste. However, the organic solvent vapors in this waste tank amount to less than 5% of the lower flammability limit established for organic vapors in waste tank headspace regions (Huckaby and Story 1994, Postma et al. 1994). Most of the organic solvents remaining in the tank waste inventories have relatively low vapor pressures. Consequently, organic solvents are not considered a headspace flammability hazard as presently stored in Hanford's waste tanks.

3.2.2 Spontaneous Chemical Runaway

As discussed in Section 3.1.2 above, the potential for spontaneous chemical runaway has been assessed for the Hanford Site waste tanks (Fauske 1996a). Since several characteristic times of cooling have passed for the stored waste, bulk runaway reactions are not a hazard under current storage conditions. This conclusion is independent of the organic fuel source and is valid for both complexant and solvent-based organic waste constituents. As long as the waste temperatures continue to progressively decrease, thermal runaway is not considered credible in a waste tank containing organic solvents.

3.2.3 Ignition of Organic Solvents

Organic solvents can be entrained or dispersed through a waste or may be present as a separate layer. If a portion of the organic solvent were heated to its flash point by way of a large ignition source, combustion in air would occur. This could produce consequences that exceed acceptable risk guidelines for tank containment and result in a loss of radioactive material to the environment (Postma et al. 1994). Therefore, ignition of organic solvents from credible ignition sources must be considered in the resolution of the organic waste issue.

This page intentionally left blank.

4.0 RESOLUTION OF THE ORGANIC WASTE SAFETY ISSUE

4.1 ORGANIC WASTE SAFETY PROJECT LOGIC

The objective of the Organic Safety Project is to ensure the safe storage of organic waste in Hanford Site waste tanks until it can be retrieved and treated for final disposal. The approach for the resolution of the organic safety issues is based on the strategy that was developed to resolve ferrocyanide safety issues. The strategic logic (presented in Figure 4-1) is comprised of four elements (Meacham 1996).

1. Identify safety issues associated with organic wastes.
2. Identify criteria and conditions under which these wastes can be safely stored.
3. Develop an understanding of the waste phenomenology using theory, modeling, sampling, and testing, that can be used in a risk-based assessment, to determine the safety status of the waste. This will lead to categorizing individual waste tanks as *safe*, *conditionally safe*, or *unsafe*.
4. Resolve safety issues by demonstrating that each organic waste tank fits into one of the following:
 - a. the tank waste lacks sufficient fuel concentration for a propagating combustion;
 - b. the tank waste retains sufficient moisture to prevent a propagating combustion; or
 - c. credible ignition sources of the organic waste are precluded through controls or the ignitable conditions are mitigated.

4.2 CRITERIA FOR SAFE STORAGE OF ORGANIC WASTES

4.2.1 Organic Complexant Storage Criteria

The safety criteria for the Tank Organic Waste Project were developed as the result of studies and experiments with simulant and real tank waste materials. Rapid propagation of postulated reactions in organic salt and nitrate/nitrite mixtures is precluded if the heat of reaction (or the amount of TOC present in the activated substrate) and the moisture content are within specific limits. Evaluations of waste mixture containing nitrates and nitrites identified four necessary conditions associated with the initiation of a propagating chemical reaction (Christensen 1993). These conditions are:

- sufficient fuel (in this case organics),
- sufficient oxidizers (nitrates/nitrites),
- low moisture values,
- high temperatures (initiators).

Because of the relative abundance of nitrates and nitrites in the tank wastes, oxidizer concentration is not considered to be a limiting criterion for determining the safety status of a waste tank. Based on the remaining conditions, safety classifications were defined for application to waste tanks containing organic wastes:

Safe: Tank wastes that lack sufficient fuel to sustain a condensed-phase organic/nitrate propagating combustion.

Conditionally Safe: Tank organic wastes that contain sufficient fuel, but are too wet to sustain a condensed phase propagating combustion.

Unsafe: A waste tank that does not meet the fuel/moisture safe or conditionally safe categories.

The minimum required fuel concentration has been determined using a contact-temperature ignition model (Fauske et al. 1995). Theory indicates that a necessary (but not sufficient) condition for a condensed-phase propagating combustion is that the fuel concentration be greater than 4.5 wt% total organic carbon (TOC), or that fuel concentration exceed 1.2 MJ/kg on an energy equivalent basis. For fuel concentrations between 4.5 and 7.9 wt% TOC, the waste moisture concentration required to prevent a propagating combustion varies linearly from 0 to 20 wt%. Above 20 wt%, the fuel-moisture linear relationship no longer holds because the mixture becomes liquid continuous. A stoichiometric fuel-oxidizer mixture will not propagate when the moisture concentration exceeds 20 wt% (Fauske et al. 1995).

If a waste lacks sufficient fuel to support a propagating combustion (even if the waste were hypothetically dried), the waste is categorized as safe. That is, the waste is safe if the following inequalities are met (Equations 4-1 and 4-3):

$$\text{wt\% TOC} \leq 4.5 \quad (4-1)$$

On a wet TOC basis, the fuel criterion would be the dry TOC multiplied by $(1-x_w)$:

$$\text{TOC}(\text{wet}) < (4.5 - 4.5x_w) \quad (4-2)$$

where x_w is the mass fraction of free water for values less than 0.2 (20 wt%).

In terms of energy (ΔH) the criterion for dry waste is:

$$\Delta H (\text{MJ/kg}) \leq 1.2 \quad (4-3)$$

If waste contains sufficient fuel (i.e., greater than 4.5 wt% TOC or 1.2 MJ/kg), but is too moist to support a propagating combustion, the waste is categorized as *conditionally safe*. In summary, the waste cannot combust if the following inequalities are met (Equations 4-3 and 4-4):

$$\text{wt\% TOC} \leq (4.5 + 17 x_w) \quad (4-4)$$

or in terms of energy (ΔH):

$$\Delta H (\text{MJ/kg}) \leq (1.2 + 4.5 x_w) \quad (4-5)$$

Waste that does not meet the criteria for the *safe* or *conditionally safe* categories is defined as *unsafe*. The criteria are shown graphically in Figure 4-2. Analysis of variance (ANOVA) models have been used to compare TOC and moisture tank waste data to the safety criteria.

Experiments with waste simulants (Fauske et al. 1995; Fauske 1996a, 1996b, 1996c) show that significantly more than 4.5 wt% TOC is required to support a propagating combustion. Mixtures of sodium nitrate/nitrite oxidizer with sodium acetate, sodium citrate dihydrate, and HEDTA dihydrate have been tested. The lower limit concentrations were 6, 8, and 6 wt% TOC, respectively. Two energetic surrogates were found not to have a lower flammability limit, i.e., even stoichiometric concentrations could not sustain a propagating combustion. These were sodium acetate trihydrate and sodium oxalate.

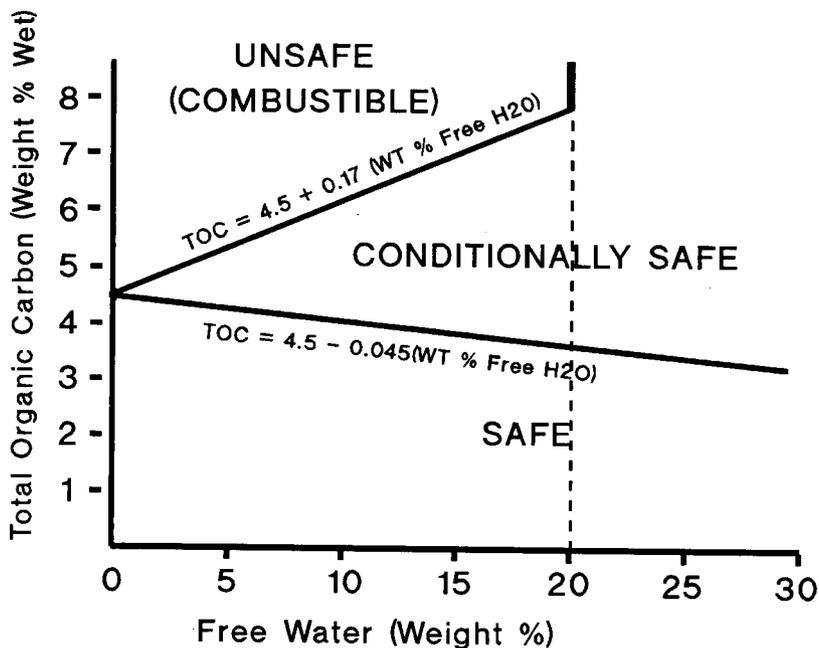
Additional data were taken with varying amounts of water for those simulants that could sustain a propagating combustion. A comparison of the simulant experiments results against the safety criteria is shown in Figure 4-3. All of the empirical data from simulant testing indicate that the criteria are bounding. It was found in all cases that 20 wt% free water was sufficient to prevent even a stoichiometric mixture of these surrogates from sustaining a propagating combustion. The free water equivalent maximum was 15% for sodium HEDTA dihydrate.

4.2.2 Organic Solvent Storage Criteria

The results of experiments and analyses have improved the understanding of the phenomena associated with potential combustion of these organic solvents and have shown that they are difficult to ignite (Fauske 1996a). The credible ignition sources have been narrowed to robust and/or sustained energy sources. The moisture and fuel safety categories established above for complexants provide a bounding case for solvents. However, since these solvents are largely insoluble in tank wastes, there is a potential for condensed liquid-phase pools to accumulate.

An organic pool combustion event would heat waste tank headspace gases and pressurize the tank (Cowley and Postma 1996). The combustion event would continue until the oxygen was depleted with the pressurization increasing with the flame spread rate. If an adequate vent path were available, the waste tank dome would not fail and the radiological consequences are postulated to be within acceptable risks. Therefore, it is desired to identify which waste tanks might contain the equivalent of one-square-meter or larger pool of organic solvent and the adequacy of the tank's vent path for preventing tank pressurization.

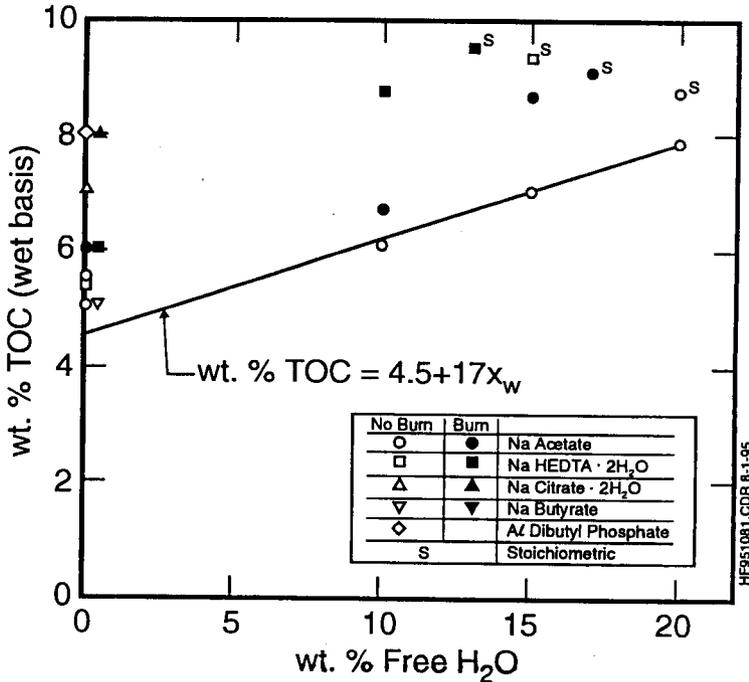
Figure 4-2. Safety Criteria for Organic Waste



AAAACRTE.GAL/000828/ABW

The organic solvent vapors found in a waste tank's headspace are a direct indication of the liquid organic solvents found in the tank waste. The mass transfer of a semivolatile species in an organic liquid (e.g., dodecane, tridecane, or TBP) to the headspace is dependent on several parameters including temperature, the mass transfer coefficient, gas-liquid contact area, ventilation flow rate, and headspace volume. If the organic solvent is present, organic solvent vapors should be detectable in a waste tank headspace, even if a tank is actively ventilated. Most SSTs are only passively ventilated (i.e., the ventilation flow rate is quite small) and thus the organic vapors should be present in near equilibrium concentrations (Huckaby and Story 1994).

Figure 4-3. Comparison of Experimental Results to Safety Criteria



Organic vapor screening criteria are being developed and waste tank vapor space sampling completed for waste tanks. The concentrations of total non-methane hydrocarbons will be measured and compared to the concentrations anticipated from a one-square-meter pool at tank temperatures. If the total non-methane hydrocarbon concentration criterion is exceeded, then the required vent path area will be calculated and the actual vent path area checked against this calculation. If the actual vent path area is inadequate, then controls against potential ignition sources will be required. Mitigation, such as increasing the vent path area, will be required if controls are deemed inadequate.

4.3 OPTIONS FOR IMPLEMENTING WASTE TANK SAFETY

After the hazards in a waste tank have been assessed, then actions (or no actions) will be taken that appropriately solve the safety issues identified in the safety assessment for that tank. Presently, no single action or option is sufficient to ensure interim safe storage for all organic waste tanks; each tank will have to be individually assessed and addressed. The assessment, however, may show that tanks can be grouped and common actions implemented on each tank that will place a tank in an acceptable safety category. These potential actions for a tank are:

Zero Action - This is one of the potential actions for an organic waste tank that is classified as *Safe*. A tank is inherently or passively safe and no controls, monitoring, or mitigation actions are required to maintain the *Safe* status. In this case, adequate data are available to demonstrate that it is not possible for the tank waste to support a propagating combustion from its organic fuel content. The tank waste lacks sufficient fuel to combust regardless of the waste moisture content and cannot be ignited with any credible ignition source. Theory, modeling, sampling, and testing show that the waste lacks sufficient fuel content to support combustion. Zero action is warranted.

Monitoring - This is one of the potential actions for a organic waste tank that is classified as *Conditionally Safe*. Controls and monitoring may be required to obtain sufficient data to demonstrate future combustion is impossible or to ensure that the conditions which might initiate future propagating reactions do not arise. Although a tank waste may be found to have significant fuel content to support and sustain a combustion event, it also may have sufficient moisture that prevents combustion from any credible ignition source. If waste dry out is credible during interim storage, then moisture and/or temperature monitoring may be required to assure that the waste maintains its moisture inventory. A tank waste with changing conditions could eventually become *Unsafe* and the monitoring and controls would assure that a tank remains within the *Conditionally Safe* category.

Mitigation - The waste data show that there is a high, unacceptable probability that a combustion event could be initiated and sustained. Mitigation and/or remediation actions would then be used to bring the waste tank into an acceptable safety status. Mitigation approaches will be identified and evaluated for technical feasibility including safety risks, time for implementation, and effectiveness. Appropriate controls and surveillance would then be used to assure the success of the mitigation. Full remediation may involve retrieval, treatment and final disposal of the waste, including pre-treatment and vitrification of the HLW. To conserve resources and to address any imminent safety concern, mitigation that effectively reduces the fuel concentration or ignition hazard below risk criterion, may also be considered (Meacham 1996). All processes would be evaluated for technical feasibility, including safety risks and time for implementation.

4.4 MANAGEMENT OF THE WATCH LIST

The Wyden Amendment (Public Law 101-510, 1990) was enacted to establish a formal requirement to identify HLW tanks which have a serious potential for material releases from uncontrolled increases of temperature or pressure. As indicated in Section 2.3.2, an initial tank Watch List was established based on a TOC screening criteria. The screening process identified 20 waste tanks with potential organic conditions that exceeded the interim TOC threshold and presented a potentially unacceptable safety condition.

Since the creation of the initial screening criteria and Watch List, the Organic Safety Project has developed a more definitive safety criteria with the three levels of safety, that are discussed in Section 4.2. This revised criteria is being applied to all Hanford waste tanks, resulting in the revision of the status of not only the tanks on the Watch List, but also the status of all HLW tanks. When enough data have been accumulated for each waste tank, a recommendation defining the safety status of a tank will be made. Historical data and modeling will be initially used to establish the potential safety status of a tank, specifically those tanks which may have a high safety risk. Combustion theory, waste modeling and sampling, and experimental testing will then be used to verify the actual safety status. If a waste tank is shown to be in the *Safe* category, a request will be made to remove the tank from the Watch List. If monitoring and/or mitigation is required, the recommendation to remove the waste tank from the Watch List will be made after implementation is completed. The assessment, status, and implementation actions will continue until the organic safety issues for each Hanford waste tank have been satisfactorily resolved.

5.0 ORGANIC SAFETY PROJECT ACTIVITIES

A number of activities are being pursued that will systematically resolve the organic waste safety issues. The objective is to resolve the organic safety issues associated with the HLW in SSTs and DSTs by September 30, 2001 to ensure safe, interim waste storage until retrieval for treatment and/or disposal operations begin. These activities involve obtaining an understanding of organic waste safety phenomena, including energetics and ignition sources, identifying waste tanks with organic safety risks, and implementing measures for continued safe interim storage of the tank wastes. Supporting technical documents that describe the current understanding of the organic complexant and organic solvent safety issues will be issued in December 1996. A description of the milestones and schedules associated with these activities is in Section 6.0.

5.1 IDENTIFICATION OF ORGANIC WASTE TANKS

The objective of this activity is to accurately identify organic waste tanks, based on the use of historical data, waste transfer records, waste processing data, and recent sampling data. The identification of organic waste tanks and the verification of their organic content is one of the most challenging tasks in the resolution of the organic safety issues. In the absence of sampling data for the tanks, and until that information becomes available, no single approach appears to be sufficient and a combination of information sources is being used to identify and group organic waste tanks. The safety project for hydrogen flammability shares aspects of this activity's scope.

5.1.1 Historical Records and Modeling

Objective - Historical sampling data, waste transfer records, and waste processing data have been and are being systematically evaluated and models being developed for predicting tank organic content (Toth et al. 1995, Webb et al. 1995, Agnew 1996a). The adequacy of historical data is being evaluated through the methodology presented in Simpson and McCain (1996). Some of this work provides scoping information based on the quantity and type of material that was purchased and used in the chemical processing at Hanford. The process data records provide information on the disposal of organic compounds to the waste tanks, while tank transfer data shows dispersal operations which resulted in the intermingling of some of the wastes. This activity supports Milestone T22-97-121.

Status - Over the years several studies have been conducted (Allen 1976, Hall 1972, Jungfleisch 1984, Anderson 1990, Klem 1990, Agnew 1994, 1996a, 1996b) to assess the inventory of compounds routed to the waste tanks from various chemical and purification processes. A number of historical record summaries with estimates of radionuclide, chemical compositions and organic contents for Hanford's waste tanks have been developed by Agnew (1994, 1996a, and 1996b). The HDW model attempts to account for the disposition of soluble complexants in the tank farms (Agnew 1996b). Allen (1976) and Sederburg and Reddick (1994) have made estimates of the principal organic complexant and solvent species in the waste tanks, based on these historical records. In addition,

Gerber et al. (1992) have made estimates of hexone quantities which was used as both extractant and solvent in the REDOX process.

Models, such as the ANOVA, are being developed that use this data as a basis for tank grouping schemes and for estimating waste moisture and TOC concentrations (Meacham et al. 1996). These and other models provide the basis for drawing generalized conclusions on waste conditions within a waste type, within a waste tank, or across a family of similar waste tanks. Sampling and characterization data are being used to benchmark these models.

5.1.2 Characterization Data

Objective - Tank waste characterization data are being obtained from tank push-mode and rotary-mode core sampling and from liquid grab and auger sampling. Vapor space sampling is being conducted with sampling canisters and with sample tubes inserted into the head space of waste tanks. The vapor organic content is being used to screen waste tanks for potential organic solvent safety issues. Sampling and characterization is a cross-cutting area which interfaces with other tank safety projects, such as hydrogen flammability. This activity supports Milestone T22-97-123.

Status - Characterization data, generated from a hot cell analysis of the tank waste samples, is providing data on the organic chemical species, TOC, head space organic vapor content, and moisture content of the waste (Turner et al. 1995). The exothermic energy concentration and moisture concentration of the waste are also being measured. The energy and moisture content do not discriminate among the different organic species found in the wastes, but these two parameters are central to the potential for ignition and combustion of the waste. The energy content of the principal waste constituents has been evaluated theoretically and empirically (Burger 1993, Scheele et al. 1995, Fauske 1996a). There are large differences in the energy liberated and the propagating combustion behavior of the different organic molecules. For example EDTA is a relatively energetic species but radiolysis destroys this material under waste storage conditions. By contrast, sodium oxalate (a relatively long-lived product of radiolysis) has a low energy content and cannot support a propagating combustion event, even under stoichiometric conditions (Fauske et al. 1995).

The planned core sampling sequence for the Hanford waste tanks is based on Brown et al. (1996). This is based on Revision 1 of the implementation plan (DOE/RL 1996). The sampling plan identifies the waste tanks that are considered to be high priority tanks, some of which are suspected to have organic safety issues. It has been occasionally necessary to sample the waste in tanks other than high priority tanks as well as others as scheduled because of delays and changes in drivers (delays in deploying the retained gas sampler, imposition of flammability controls on all waste tanks, and need to qualify coring systems for operation in flammable environments). In FY 1995, 39 core samples were obtained and it is anticipated that 57 core samples will be obtained in FY 1996. (Through August 1996, 55 have been obtained from 25 waste tanks with some samples still being analyzed and evaluated.) Forty-eight core samples are scheduled for FY 1997, two from each waste tank sampled. For FY 1998, 29 tanks are scheduled to be sampled with 60 core samples (including the possibility of one tank being repeated). FY 1999 has a

schedule of 72 core samples taken from 36 tanks including the possibility of one tank being repeated. A letter reporting on the speciation results for the organic constituents of core samples for BY-108 and BY-110, and auger samples for C-102 (which were sampled in FY 1995) will be issued October 1996.

Detection of organic compounds in the vapor space samples is being developed as a screening technique to identify waste tanks with significant solvent concentrations, especially those with liquid pools on the waste surface. Vapor samples, obtained from the waste tank head space, are being analyzed for organic content. The organic substances in the vapor samples are potential indicators of significant concentrations of organic materials, such as solvent pools, that may exist in a tank.

As of February 1996, 63 waste tanks have been vapor sampled using the truck-mounted Vapor Sampling System, and the results have been analyzed and evaluated. At that time there were 86 SSTs remaining to be vapor sampled. The base-line planning rate for sampling with the truck-mounted system is to obtain 48 samples per fiscal year (DOE/RL 1996). (Through August 1996, 47 vapor samples have been obtained in FY 1996.) A total of 18 vapor samples are planned to be analyzed from three different tanks (B-103, TY-103, U-112) to confirm the headspace vapor mixing phenomenon. In addition, 20 vapor samples will be analyzed from four additional tanks to improve the understanding of phenomenon associated with headspace vapor content variations from tank breathing (passive ventilation). All SSTs will be vapor sampled for the presence of organic solvent by December 1999, including 28 in FY 1997, 48 in FY 1998, and 60 in FY 1999. Vapor sampling for DSTs will be completed by December 2000. The results from headspace sampling will be used to determine which waste tanks contain a significant amount of organic solvent.

5.1.3 Data Reconciliation and Model Validation

Objective - Reconciliation and validation are needed to assure the accuracy of assessments and predictions from models and to assure the quality of models is maintained as they are developed and used. Sampling and characterization data will be used to benchmark models such as the organic waste distribution models and tank grouping schemes. The assessment of organic content through vapor sampling must be validated with chemical and physical characterization data. Testing and the cross-correlation between simulants and real tank wastes is being done to assure fuel combustion and ignition source characteristics are understood and valid. This activity supports Milestone T22-97-122.

Status - As already mentioned, studies have been conducted (Allen 1976, Hall 1972, Jungfleisch 1984, Anderson 1990, Klem 1990, Agnew 1994, 1996a, 1996b) to assess the inventory of compounds routed to the waste tanks and the consequences of processing operations. Most recently Agnew (1994, 1996a, 1996b) has developed historical record summaries with estimates of radionuclide, chemical compositions, and organic contents for Hanford's waste tanks.

Historical sampling data, waste transfer records, and waste processing data have been and are being systematically evaluated and models being developed for predicting tank waste organic content (Toth et al. 1995, Webb et al. 1995). Some of this work provides scoping information based on the quantity

and type of material that was purchased and used in the chemical processing at Hanford. The process data records provide information on the disposal of organic complexants and solvents to waste tanks while tank transfer data shows dispersal operations which resulted in the intermingling of some of the wastes. These models provide a basis for drawing generalized conclusions on waste conditions within a waste type, within a tank, or across a family of similar tanks. Sampling and characterization data are being used to benchmark these models.

Currently, models such as the ANOVA, are being developed that use this data as a basis for tank grouping schemes and for estimating waste moisture and organic (TOC) concentrations (Meacham et al. 1996). Agnew (1996a) has recently updated the HDW model which attempts to account for the disposition of soluble organics in the tank farms. Supporting technical documents that describe the current understanding of the organic complexant and organic solvent safety issues will be issued in December 1996.

5.2 FUEL CONTENT AND WASTE ENERGETICS ASSESSMENTS

Objective - The objective of this activity is to obtain an understanding of the phenomena associated with organic fuel content and the energetics of these fuels within the tank waste matrices. This activity includes energetics measurements with simulant and real wastes and a correlation of these energetics with models and with waste properties. There are a number of chemical and physical attributes of wastes that affect the energetics and exothermic properties of organic tank wastes, including species and diluents, such as water. The knowledge of fuel content and the energetics associated with fuel species are fundamental needs in a basic understanding of organic waste safety issues. This activity supports Milestone T22-98-110.

Status - A safety assessment covering pool and entrained organic fire scenarios for all Hanford waste tanks will be issued in October 1996. Laboratory testing with simulants and with real wastes to confirm safe storage criteria from fuel content and combustion inhibitors will be issued in November 1998.

5.2.1 Fuel Diluents

Objective - The impact of water and other potential waste materials and properties are being investigated and modeled for their impacts as diluents in waste that contains organic fuels. This activity supports Milestone T22-97-124.

Status - Safe storage criteria have been established through theoretical analysis and tests on waste simulants (Meacham et al. 1996). A necessary (but not sufficient) condition for a propagating reaction is that the fuel concentration be greater than 1,200 J/g (4.5 wt% TOC), on an energy equivalent, dry weight basis (Fauske et al. 1995). For fuel concentrations between 1,200 and 2,100 J/g, the waste moisture (free water) content required to prevent a propagating reaction varies linearly from 0 to 20 wt%. Above 20 wt%, the fuel-moisture linear relationship no longer holds because the mixture

becomes liquid continuous and a stoichiometric fuel-oxidizer mixture reaction will not propagate (Fauske et al. 1995).

Simulant studies with organic complexants indicate that fuel concentrations in the waste tanks have been decreased by saltwell pumping and by waste aging (discussed below). Experiments show that the more reactive organic complexant salts are soluble and are removable by saltwell pumping (Barney 1994, 1996a). Although some decomposition species can be more energetic than their source species, the net effect of decomposition decreases the potential chemical energy of the waste. Data from SY-101 and SY-103 are consistent with organic speciation predictions based on solubility and aging. The sample is aged, forming derivatives of the complexants including IDA and NTA and fragments such as formate and oxalate. The differences between the data for the liquid and solid phases are in accord with the concept that all the complexants and their decomposition products are very soluble except sodium oxalate.

Tube propagating tests have shown that some organic salts will not support propagating reactions (Fauske et al. 1995).

The consequences from an entrained organic solvent fire are less than an organic pool fire. Open literature and preliminary calculations indicate that the spread rate for an entrained solvent fire is an order magnitude lower than that for a pool fire and would not generate enough heat and combustion gases to result in a release hazard. Therefore, the Safety Issue for an organic solvent is bounded by the organic solvent pool fire hazard. A letter reporting the completion of safety assessments covering pool and entrained organic solvent fires will be issued by October 1996.

5.2.2 Aging - Complexants and Solvents

Objective - Aging experiments are being completed to develop an understanding of the aging process with tank waste and to develop a model for predicting the aging organic rate. The impact of aging on the fuel content and energetics of waste organic species is being investigated with both simulants and with real wastes. This activity supports Milestones T22-97-118 and T22-98-105.

Status - Although the processes are not fully understood at this time, there is both literature and experimental data that show that organic compounds present in tank wastes are susceptible to aging. Organic complexants and solvents undergo hydrolytic and radiolytic decomposition (aging) under tank waste conditions. Organic simulant experiments show that the more reactive organic complexant salts decompose to less energetic products (i.e., oxalate) and carbonate.

Analyses of SY-101 and SX-103 wastes indicated that in addition to the original major complexant and solvent species, lower molecular weight substances formed because of aging, were present (Campbell et al. 1994a and 1994b). Studies with surrogate materials in nonradioactive matrices show that organic complexants decompose from thermal mechanisms (Delegard 1987, Ashby et al. 1994, Meisel et al. 1993) and that there may be an acceleration of radiation-induced aging because of thermal interactions and effects. The floating layer in tank C-103 has been sampled and analyzed, with selective loss of the lower molecular weight hydrocarbons. The substances in the dome

space indicate aging from the original solvent species (Pool and Bean 1994, Campbell et al. 1994a).

Chemical and radiological aging studies will be continued to establish models for predicting chemical aging and to corroborate tank waste sampling data with aging data. The Hanford waste tanks contained substantial amounts of organic compounds, so that the substances formed as byproducts may become significant species in assessing waste properties. Surveillance records are being examined to assess the temperatures and radiation dose history of the organic wastes. Once confirmed by organic speciation, the aging model could be used in conjunction with historical data, characterization data, and other information to estimate current and future organic content.

5.2.3 Energy Content Measurements and Assessments

Objective - Because the heats of oxidation of the various organic compounds differ, some information about the identity and functionality of the organic carbon is needed to establish the safety risks of an organic waste. The analyses and experiments in this task will provide an understanding of the issues of energy relationships between organic species, including aging or breakdown products. This activity supports Milestone T22-97-119.

Status - Knowledge of the TOC in a particular waste tank is not sufficient for bounding the safety risk from postulated exothermal organic/nitrite reactions. The aging processes shows that large organic molecules reformat into smaller molecules which affects the expected organics/nitrate reactions. For the larger organic molecules, the heat of combustion are proportional to the number of C-H bonds. For smaller organic molecules, the wider variation in the bond energies of starting species produces a wider variation in this thermal picture.

This diverse picture illustrates the need for a more thorough understanding of the aging process and its impact on combustion parametrics. Fuel content and energy measurements need to be completed with simulants and on real waste samples. Waste samples from six waste tanks (AN-107, BY-104, BY-108, C-201, C-204, and SY-101) have been tested by adiabatic calorimetry (using the Reactive System Screening Tool)¹. None of the wastes tested supported a propagating combustion event. Adiabatic calorimetric measurements need to be obtained from additional waste tanks to complete the understanding of the combustion potential of organic wastes.

5.2.4 Phase Relationships - Solvents and Complexants

Objective - Develop an understanding of the waste organic solvent and complexant phase relationships and identify credible potential impacts on the continued safe storage of tank wastes. This activity supports Milestones T22-97-119 and T22-98-104.

Status - The physical states of complexants, solvents, and their breakdown products affect the safety issues of a tank waste. One of the studies that

¹ Trademark of Fauske and Associates, Inc., Burr Ridge, IL.

investigated the solubilities of the sodium salts of the principal complexants and aging products in nitrate/nitrite/hydroxide solutions, found that five compounds, Na₂EDTA, Na₃NTA, sodium citrate, and formate, have high solubilities. Only sodium oxalate is an exception (Barney 1994, 1996a, 1996b). Supernatant solutions from 61 waste tanks have been analyzed for TOC concentration. Only five of the tank waste supernatants had TOC concentrations greater than 14 g/L with the highest measured value for TOC approximately 40 g/L (Van Vleet 1993a, 1993b). This value is substantially below the measured solubility limit for the energetic complexants which is in the 100 g/L range. Accordingly there is a high probability that the complexants remaining in the waste tanks are present in the supernatant liquids and that sodium oxalate is distributed between the supernatant and the solids.

Although still on-going, tests to date have shown that organic solvents are essentially insoluble (Barney 1994, 1996a). Floating layers of insoluble organic solvents and aging products are of concern in a number of waste tanks, such as in C-103. The combustibility of these insoluble layers is not affected by diluents. The content of the soluble organics is in question, as it is not known how much of the organic solvent has escaped via evaporation, or, in the case of phosphate esters, how much has been saponified in the alkaline tank waste environment (Burger 1955).

There are a number of areas where additional work on organic solubility is needed including the influence of high valent ions, effects of solution densities, impact of having a large diversity of organic species, and effects of organophosphate compounds in the liquid waste.

5.3 EXTERNAL IGNITION SOURCE HAZARDS

Objective - Identify and obtain an understanding of credible external ignition sources and their potential to impact the safe storage of tank organic waste. This activity supports Milestone T22-97-126.

Status - If fuel is present and the waste is sufficiently dry, an organic-nitrate/nitrite propagating combustion event could be initiated by a variety of sources. The potential credible ignition sources include both natural events and tank farm events. The credible sources of ignition include hot metal objects, rotary core upsets, burning gasoline spills from a ruptured vehicular fuel tank, or lightning (Meacham et al. 1996 and Webb et al. 1995). Diluents, organic content, and phase are some of the parameters that have been identified as having significant impacts on a waste's combustion potential. For example, although preliminary experiments demonstrate a 138 joule pyrotechnic "electric match" could ignite dry, stoichiometric simulant waste mixtures, as little as 5 wt% free water would prevent ignition (Fauske 1996).

Organic solvents can be entrained or dispersed throughout a waste, or may be present in a separate layer while complexants are generally soluble and are found more dispersed within the tanks waste matrices. Organic complexants have an ignition threshold and a combustion scenario that is different from organic solvents. Work to date has shown that sparks, impacts, and shocks generally lack sufficient energy to ignite organic complexants or organic

solvents (Fauske et al. 1995, Fauske 1996a). Theoretical analyses and tube propagation experiments with waste simulants have shown that ignition sources greater than three joules are required to initiate an organic complexant propagating event. The waste organic solvents have been shown to be even more difficult to ignite. Hot steel spheres (up to 270 joules) and an electronic match (about 138 joules) failed to ignite an organic solvent simulant (dodecane) (Fauske 1996a). A letter reporting how the external equipment spark sources in flammable gas tanks have been managed by controls or how the equipment has been modified to reduce the hazard will be issued in December 1996.

It may be possible to show that no credible initiators exist for tank wastes with organic solvents or complexants. The potential for water as a diluent to diminish the combustion risk needs to be evaluated further. Therefore, laboratory tests using simulants and hot cell tests with real waste samples are needed to further define the combustion boundaries of stored tank wastes. Work will also continue on examining ignition source requirements for organic solvent pools and entrained organic solvents.

5.4 SAFETY ACTIONS

This activity develops techniques and implements methods for tank waste monitoring and mitigation that will assure continued safe interim storage of tank wastes. Based on the safety status of the wastes, waste tanks will be placed into one of three safety levels (*safe, conditionally safe, and unsafe*). Mechanisms to bring wastes within an acceptable risk criteria will be identified and applied to individual waste tanks. The safety actions to assure interim storage are part of the cross-cutting tank waste safety issues that are part of other tank waste safety projects.

5.4.1 Monitoring and Mitigation

Objective - Identify and implement monitoring and mitigation safety operations that assure the continued safe interim storage of tank wastes. This activity supports Milestones T22-97-127, T22-97-128, and T22-97-130.

Status - For waste tanks that lack sufficient fuel to sustain a propagating combustion event, safe interim storage can be achieved through prudent waste management operations or minimal interim operational safety requirement controls. Monitoring is not required for these waste tanks to assure safe waste storage.

If it is not possible to demonstrate that a waste cannot combust, monitoring may be required to confirm interim safe waste storage. Monitoring, to detect a combustion event, is also required for the 20 organic waste tanks identified in response to the Wyden Amendment (Public Law 101-50 1990). The Wyden Amendment states that "the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive temperature or pressure at each tank so identified." For each waste tank at risk from an event, the strategy is to have either continuous temperature or pressure monitoring. Although the monitoring would not facilitate interdiction of an event, it would detect the occurrence in real time. Temperature and pressure

sensor trees are currently installed and data are being collected for the 20 organic Watch List tanks.

Moisture has been shown that it can prevent a combustion event from being initiated. Routine, in situ measurements of the moisture concentration of the wastes will provide a secure basis for evaluating the safety of a waste tank which, by virtue of the waste moisture content, falls into the *conditionally safe* category. Development work will continue on moisture monitors until monitoring and equipment and procedures are integrated into normal tank farm operations.

If controls alone are not adequate to prevent credible ignition, then mitigation will be required. The simplest mitigation scheme is to maintain sufficient moisture and diluent content in the waste. Methods for assuring moisture content will be identified and applied to waste tanks where there are risks of changes in moisture content. However, for SSTs that are assumed leakers, alternate paths will have to be developed and followed. The approach will be to first evaluate the potential for maintaining the moisture content. If this cannot be safely accomplished and other forms of mitigation are not possible, then retrieval and remediation methods will be recommended for a waste tank. These actions will be integrated with the tank farm remediation efforts being applied to the waste tanks.

5.4.2 Vent Path Assessments

Objective - Complete assessments of the adequacy of vent paths for waste tanks identified with solvent-pool-based safety issues and implement methods to either provide adequate vent paths or other mitigation methods. This activity supports Milestone T22-00-101.

Status - If a waste tank is found to contain significant organic solvent, then the tank configuration will be examined to determine if an adequate vent path area is available to mitigate potential consequences from a combustion event. For those waste tanks with insufficient vent path area, the tank will be reconfigured or mitigated before controls are removed from the tank. A letter reporting the status of vent path in all SSTs suspected of containing organic solvents will be issued in April 2000.

5.5 SAFETY DOCUMENTATION

This activity provides for the preparation, review and approval of documentation associated with the closure of the Tank Organic Waste Safety Issues.

5.5.1 Organic Complexant and Organic Solvent Safety Documentation

Objective - Complete documentation to support the resolution of the Organic Complexant Issue, with a path forward for continued safe storage of HLW wastes with organic complexants. This activity supports Milestones T-22-97-114, T-22-98-107, and T22-99-103.

Complete documentation to support the resolution of the Organic Solvent Issue, with a path forward for continued safe storage of HLW wastes with organic solvents. This activity supports Milestones T22-97-115 and T22-99-104.

Status - The authorization basis was combined into one document, the Interim Safety Basis (ISB) which was approved in November 1993 (Wagoner 1993). Safety documentation concerning the organic nitrate was updated recently (Meacham et al. 1996) and is being incorporated into the basis for Interim Operation (BIO) and the Final Safety Analysis Report (FSAR), which will replace the ISB once each is approved. The authorization basis will be updated as additional information warrants.

5.5.2 Organic Safety Project Plan

Objective - Prepare and issue an Organic Safety Project Plan. This document will be updated on a fiscal year basis and will incorporate significant strategy elements (from the Organic Strategy Document) and technical developments (such as included in SARR-033-Rev. 1, FSAR, VOI, DQO, and supporting documents). The document will also identify activities and milestones for completing work to resolve the tank organic waste issue. This activity supports Milestones T22-97-129 and T22-98-109.

Status - This document (WHC-EP-0914, Rev. 0) is the Organic Safety Project Plan for FY 97. The project plan will be updated annually until the organic safety issues are resolved.

6.0 ORGANIC SAFETY PROJECT SCHEDULES AND MILESTONES

6.1 ORGANIC SAFETY PROJECT MILESTONES

The milestones summarized below specifically address the Organic Safety Project complexant and solvent issues. The milestones are directed at resolving the Hanford tank organic waste safety issue and the close of USQs and resolution of the Organic Tank Watch list. These milestones support the completion of TPA requirements, DNFSB milestones, and directives identified in the Wyden Amendment.

The milestones below cover a four-year fiscal schedule that is shown in Section 6.2. Some of the milestones will be completed in FY 97, while others require a continuation of work or will be begun in future fiscal years. The milestones are identified by their Milestone Control Number. The due date and a brief description is included for each milestone. Additional information can be found on the WHC TWRS Milestone Description Sheets.

- T22-97-121: Complete Temperature and Dose Histories on Organic Tanks
Due Date: September 30, 1997.
Description: Complete temperature and dose histories for organic tanks and release a public document summarizing the results. (This milestone supports confirmation of the aging model on actual waste.)
- T22-96-132: Submit Results of Organic Speciation of Core/Auger Samples for BY-108, BY-110, and C-102 to DOE-RL.
Due Date: September 30, 1996.
Description: Complete organic speciation of core samples for BY-108 and BY-110, and auger samples for C-102. (The interim deliverable supports DNFSB Milestone 93-5.4.3.4.b. DOE-RL will transmit these results to DNFSB one month after the completion of this milestone.)
- T22-97-123: Screen Tanks for Organic Solvents.
Due Date: September 30, 1997.
Description: Compile the results from tank headspace sampling for use by the Organic Safety Project. All new organic sampling data will be reviewed as it is generated against screening criteria specified in SARR-036. Four quarterly progress reports will be issued. This milestone will be complete when the final 4th quarterly report is completed. (This milestone supports DNFSB Milestone 93-5.4.3.4.d.)
- T22-97-122: Update ANOVA With New Data.
Due Date: September 30, 1997.
Description: The ANOVA estimates of tank TOC and moisture will be updated with new data. The ANOVA model will be refined and corroborated as more characterization data becomes available. A report and letter transmitting the results to DOE-RL will be issued. (This milestone supports development of the final safety assessment for the organic complexant tanks.)
-
-

-
-
- T22-97-124: Quantify Organic Ignition Source Requirements.
Due Date: September 30, 1997.
Description: Quantify the ignition source requirements to initiate an organic complexant or organic solvent combustion and submit a letter report to DOE-RL. The report will summarize any mitigating effects of bound and/or free water on ignition. (This milestone supports the development of the final safety assessment for organic complexants and organic solvents.)
- T22-98-110: Submit Report on the Results of Tests Completion (Using Real Waste) to Confirm Safe Storage Criteria and Organic Solubility and Aging Effects on Fuel Content to DOE-RL.
Due Date: September 30, 1998.
Description: Complete testing (using real waste) and issue a report to confirm safe storage criteria and organic solubility and aging effects on organic fuels content. (This deliverable supports DNFSB Milestone 93-5.4.3.3.b. DOE-RL will transmit these results to DNFSB one month after the completion data of this milestone.)
- T22-97-118: Interim Assessment of Organic Aging.
Due Date: September 30, 1997.
Description: Confirm, on actual waste, that the organic complexants decompose over time to less energetic species. Prepare an interim assessment report of the results and conclusions. (This work supports DNFSB Milestone 93-5.4.3.3.b.)
- T22-98-105: Final Assessment of Organic Aging.
Due Date: June 30, 1998.
Description: Confirm aging models, using actual organic wastes. Prepare a final assessment report on the results and conclusions. (This work supports DNFSB Milestone 93-5.4.3.3.b.)
- T22-97-120: Submit Report on Results of PRSST Energetics Test Completion (Using Real Waste Samples) to Confirm Safe Storage Criteria To DOE-RL.
Due Date: September 30, 1997.
Description: Complete a report on the results of Propagating Reactive System Screening Tool (PRSST) energetics testing completion (using real waste samples) to confirm safe storage criteria. (This work supports DNFSB Milestone 93-5.4.3.3.b.)
- T22-97-119: Interim Assessment of Organic Solubility.
Due Date: September 30, 1997.
Description: Confirm, on actual tank waste, that the energetic species are present principally as solutes in the tank liquids. Prepare an interim assessment report of the results and conclusions. (This work supports DNFSB Milestone 93-5.4.3.3.b.)
-
-

-
-
- T22-98-104: Final Assessment of Organic Solubility.
Due Date: June 30, 1998.
Description: Complete the confirmation work, using actual wastes, that shows that the energetic species are present principally as solutes in tank liquids. Prepare a final assessment report of the results and conclusions. (This work supports DNFSB Milestone 93-5.4.3.3.b.)
- T22-97-126: Complete Mitigation of Lightning Threat.
Due Date: May 30, 1997.
Description: Issue a letter report on the completion of tank farm lightning mitigation. Mitigation includes all field activities required to install air terminals and bond and ground risers on at-risk tanks.
- T22-97-127: Install Temperature Monitoring on Organic Tanks.
Due Date: September 30, 1997.
Description: Install continuous temperature monitors on organic tanks, complete the connection of the monitoring equipment to TMACS (A-102, AX-102, B-102, and B-103) and issue a report when installation is completed. (This effort meets the requirements specified in the Wyden Amendment. Note: the milestone is an alternative approach to Safety Initiative SI-2t [MDS T2B-97-117]. Negotiations will take place with DOE Headquarters to modify the SI and it is assumed that DOE Headquarters will accept this alternative.)
- T22-97-128: Organic Nitrate Mitigation Alternatives.
Due Date: April 30, 1997.
Description: Determine alternatives to implement moisture addition for mitigation of organic nitrate tanks. Prepare and release an Engineering Study of the results.
- T22-97-130: Operate Surface Moisture Monitoring System.
Due Date: September 30, 1997.
Description: Report the results of operating the Surface Moisture Monitor System (SMMS) in situ monitor on a minimum of six at-risk tanks. Monitoring will be done off-riser to assist in the determination of safe storage of the organic bearing waste.
- T22-00-101: Submit Letter Reporting Adequate Vent Path in all SSTs Suspected of Containing Organic Solvents to DOE-RL.
Due Date: February 28, 2000.
Description: Confirm/correct vent paths in all SSTs suspected of containing organic solvents and submit an interim report to DOE-RL. (This deliverable supports DNFSB Milestone 93-5.4.3.4.e. DOE-RL will transmit these results to DNFSB two months after the completion date of this milestone.)
-
-

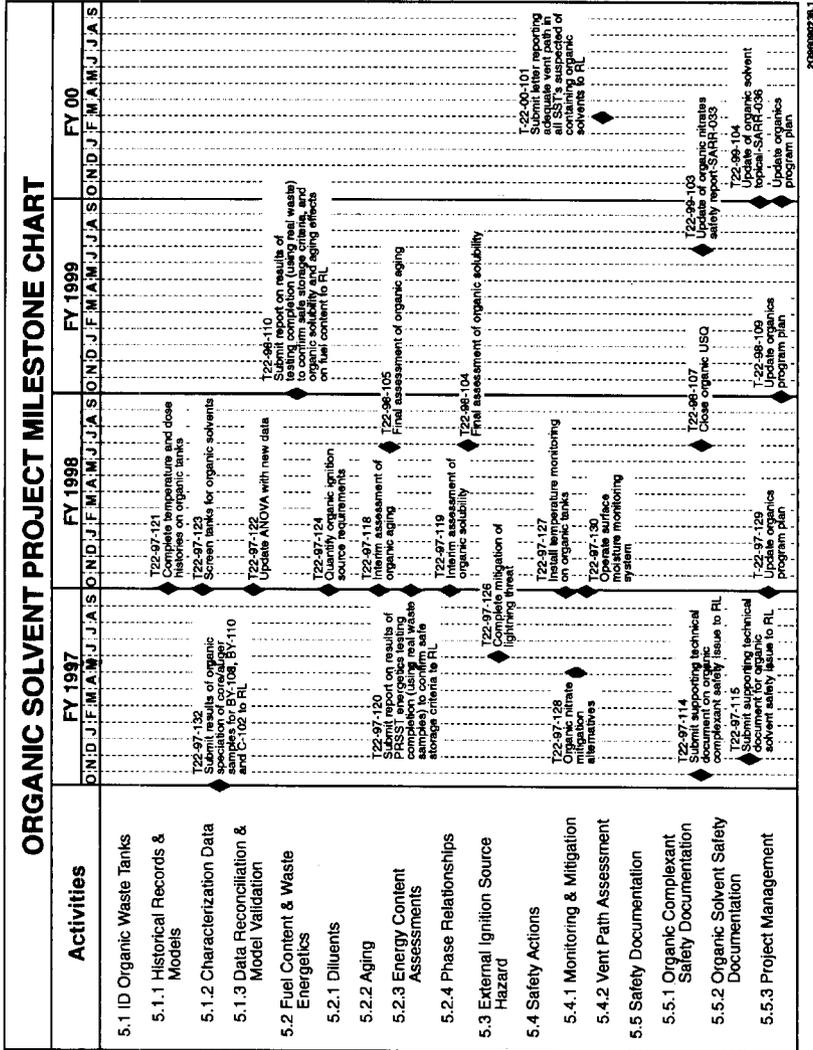
-
- T22-97-114: Submit Supporting Technical Document on Organic Complexant Safety Issues to DOE-RL.
Due Date: October 31, 1996.
Description: Complete a supporting technical document on the Organic Complexant safety Issue. This topical report will describe the current understanding of the issue and future work for resolution of the issues. (This interim deliverable supports DNFSB Milestone 93-5.4.3.3.a. DOE-RL will transmit these results to DNFSB two months after the completion date of this milestone.)
- T22-98-107: Close Organic USQ.
Due Date: June 30, 1998.
Description: Submit Contractor-approved safety documentation to close the Organic Complexant USQ. (This milestone supports TPA Milestone M-40-09.)
- T22-00-103: Update Organic Nitrate Safety Report: SARR-033.
Due Date: June 30, 1999.
Description: Revise WHC-SD-WM-SARR-033, Rev. 1, *Safety Criteria for Organic Watch List Tanks at the Hanford Site*, (Meacham et al. 1996) to incorporate information gained from aging, solubility, tube propagation tests on actual tank waste, and the updated ANOVA analysis. (This milestone supports TPA Milestone M-40-00.)
- T22-97-115: Submit Supporting Technical Document for Organic Solvent Safety Issue to DOE-RL.
Due Date: October 31, 1996.
Description: Complete a supporting technical document for the Organic Solvent Safety Issue. This topical report will describe the current understanding of the issue and future work for resolution. (This interim deliverable supports DNFSB Milestone 93-5.4.3.4.c. DOE-RL will transmit these results to DNFSB two months after the completion of this milestone.)
- T22-99-104: Update Organic Solvent Topical Report, SARR-036.
Due Date: September 30, 1999.
Description: Update the organic solvent topical report, WHC-SD-WM-SARR-036 (Cowley and Postma 1996), to include the latest results from aging, solubility, and volatility investigations.
- T22-97-129: Update the Organics Program Plan.
Due Date: September 30, 1997.
Description: Prepare and issue an Organics Program Plan. This plan will incorporate significant elements of the Organics Strategy Document and significant technical developments from WHC-SD-WM-SARR-033 (Meacham et al. 1996), FSAR, VOI, and the DQO. This plan will be a Contractor-approved document, cleared for public release.
-

T22-98-109: Update the Organic Program Plan.
Due Date: September 30, 1998.
Description: Prepare and issue a Contractor-approved, public cleared update to the Organic Program Plan. The updated document will incorporate significant changes to the organics project strategy and significant technical developments impacting the Organic Safety Project.

6.2 ORGANIC SAFETY PROJECT MILESTONE SCHEDULE

The schedule for the Organic Safety Project milestones is shown below. The descriptions of the milestones, identified by their Milestone Control Number and title, are shown in Section 6.1 above. The schedule shows a four year window of Organic Safety Project activities; the current year with three out-years. The intent is to update this schedule an annual basis so that it represents a current four year activity window. Additional milestone information can be found on the WHC TWRS Milestone Description Sheets.

Figure 6-1. Organic Safety Project Milestone Schedule



7.0 REFERENCES

- Agnew, S. F., 1994, *Hanford Defined Wastes: Chemical and Radionuclide Compositions*, LA-UR-94-2657, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Agnew, S. F., 1996a, *History of Organic Carbon in Hanford HLW Tanks: HDW Model Rev. 3*, LA-UR-96-989, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Agnew, S. F., 1996b, *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 3*, LA-UR-96-858, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Allen, G. K., 1976, *Estimated Inventory of Chemicals Added to the Underground Waste Tanks, 1944 Through 1975*, ARH-CD-6108, Atlantic Richfield Hanford Company, Richland, Washington.
- American Institute of Chemical Engineers, 1989, *Plant Guidelines for Technical Management of Chemical Process Safety*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1992, *Plant Guidelines for Technical Management of Chemical Process Safety*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1995a, *Guidelines for Chemical Reactivity and Applications to Process Design*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1995b, *Tools for Making Acute Risk Decisions: With Chemical Process Applications*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1995c, *Guidelines for Process Safety Management*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1995d, *Guidelines for Process Safety Fundamentals for General Plant Operation*, American Institute of Chemical Engineers, New York, New York.
- American Institute of Chemical Engineers, 1995e, *Guidelines for Safe Process Operations and Maintenance*, American Institute of Chemical Engineers, New York, New York.
- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Ashby, E. C., F. Doctorovich, C. L. Liotta, H. M. Neumann, E. K. Barefield, A. Konda, K. Zhang, and J. Hurley, 1993, "Concerning the Formation of Hydrogen in Nuclear Waste, Quantitative Generation of Hydrogen via a

-
-
- Cannizzaro Intermediate," *Journal of American Chemistry Society*, vol. 115, No. 3, pp. 117-121.
- Ashby, E. C., A. Annis, E. K. Barefield, D. Boatright, F. Doctorovich, C. L. Liotta, H. M. Neumann, 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.
- Babad, H., M. A. Camiaoni, W. D. Lilga, W. D. Samuels, and W. D. Strachan, 1993, *Tank Chemistry - A New Understanding of Waste Aging*, PNL-SA-23183, Pacific Northwest Laboratory, Richland, Washington.
- Babad, H. and M. G. Plys, 1996, *Reduction in Light End Solvents During In-Tank Storage of Solvent Containing Wastes*, (internal memorandum 74E10-96-005 to E. J. Lipke, February 5), Westinghouse Hanford Company, Richland, Washington.
- Barefield, E. K., D. Boatright, A. Deshpande, F. Doctorovich, C. Liotta, H. M. Neumann, and S. Seymore, 1995, *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1994 Progress*, PNL-10822, Pacific Northwest Laboratory, Richland, Washington.
- Barefield, E. K., D. Boatright, A. Deshpande, F. Doctorovich, C. Liotta, H. M. Neumann, and S. Seymore, 1996, *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1995 Progress*, PNL-11247, Pacific Northwest Laboratory, Richland, Washington.
- Barelko, E. P., I. P. Solanina, and Z. I. Tsetkova, 1966, "Radiation-Chemical Stability of TBP in Hydrocarbon Solutions," *Atomic Energy.*, vol. 21, No. 4, pp. 281-285.
- Barney, G. S., 1994, *The Solubilities of Significant Organic Compounds in HLW Tank Supernatant Solutions*, WHC-SA-2565-FP, Westinghouse Hanford Company, Richland, Washington.
- Barney, G. S., 1996a, *The Solubilities of Significant Organic Compounds in HLW Tank Supernatant Solutions--FY 1995 Progress Report*, WHC-EP-0899, Westinghouse Hanford Company, Richland, Washington.
- Barney, G. S., 1996b, *The Solubilities of Significant Organic Compounds in HLW Tank Supernatant Solutions--FY 1996 Progress Report*, WHC-EP-0899-1, Westinghouse Hanford Company, Richland, Washington.
- Beitel, G. A., 1976, *Final Report on Investigation of Stability of Organic Materials in Salt Cake*, ARH-LD-126, Atlantic Richfield Hanford Company, Richland, Washington.
- Beitel, G. A., 1977, *Exothermic Potential of Sodium Nitrate Salt Cake*, ARH-LD-163, Atlantic Richfield Hanford Company, Richland, Washington.
- Borsheim, G. L., and N. W. Kirch, 1991, *Summary of Single-Shell Tank Waste Stability*, WHC-EP-0347, Westinghouse Hanford Company, Richland, Washington.
-
-

-
-
- Brown, T. M., S. J. Eberlein, J. W. Hunt, and T. J. Kunthara, 1996, *Tank Waste Characterization Basis*, WHC-SD-WM-TA-144, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- Bryan, S. A., and L. R. Pederson, 1994, *Composition, Preparation, and Gas Generation from Simulated Wastes of Tank 241-101-SY*, PNL-10075, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., 1955, *The Chemistry of Tributyl Phosphate - A Review*, HW-40910, General Electric Company, Richland, Washington.
- Burger, L. L., 1958, "The Decomposition Reactions of Tributyl Phosphate and its Diluents and Their Effect on Uranium Recovery Process," in *Progress in Nuclear Energy, Series III, Volume 2, Process Chemistry*, Pergamon Press, New York, New York.
- Burger, L. L., 1993, *Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*, PNL-8557, Pacific Northwest Laboratory, Richland, Washington.
- Burger, L. L., and E. D. McClanahan, 1958, "Tributyl Phosphate and Its Diluent Systems," *Ind. Engineering Chem.*, vol. 50, No. 2, pp. 153-156.
- Burr, J. G., 1958, "The Radiolysis of Tributyl Phosphate," *Radiation Res.*, vol. 8, p. 214.
- Camaioni, D. M., W. D. Samuels, B. D. Linehan, S. A. Clauss, K. L. Wahl, and J. A. Campbell, 1994, *Organic Tanks Safety Program Waste Aging Studies*, PNL-10161, Pacific Northwest Laboratory, Richland, Washington.
- Camaioni, D. M., W. D. Samuels, S. A. Clauss, B. D. Lenihan, K. L. Wahl, J. A. Campbell, and W. J. Shaw, 1995, *Organic Tanks Safety Program--FY95 Waste Aging Studies*, PNL-10794, Pacific Northwest Laboratory, Richland, Washington.
- Camaioni, D. M., W. D. Samuels, B. D. Linehan, S. A. Clauss, A. K. Sharma, K. L. Wahl, and J. A. Campbell, 1996, *Organic Tanks Safety Program--FY96 Waste Aging Studies*, PNL-11312, Pacific Northwest Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, K. E. Grant, F. V. Hoopes, B. D. Lerner, R. B. Lucke, G. M. Mong, J. K. Rau, and R. T. Scheele, 1994a, *Flammable Gas Safety Program Analytical Methods Development: FY 1993 Progress Report*, PNL-9062, Pacific Northwest Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, K. E. Grant, F. V. Hoopes, B. D. Lerner, R. B. Lucke, G. M. Mong, J. K. Rau, R. T. Scheele, and K. L. Wahl, 1994b, *Waste Tank Safety Program Analytical Methods Development: FY 1994 Progress Report*, PNL-10128, Pacific Northwest Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, K. E. Grant, V. Hoopes, G. M. Mong, J. Rau, R. Scheele, and K. L. Wahl, 1996, *Flammable Gas Safety Program: Actual Waste Organic Analysis--FY 1996 Progress Report*, PNNL-11307, Pacific Northwest National Laboratory, Richland, Washington.
-
-

-
-
- Christensen, R. F., 1993, *Ferrocyanide Safety Issue Resolution Planning*, (letter 93-CAB-290, 9307347B, to President, Westinghouse Hanford Company, September 16), U.S. Department of Energy, Richland, Washington.
- Claybrook, S. W., and S. A. Wood, 1994, *Organic Evaporation in Waste Tank C-103*, WHC-SD-WM-ER-344, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Conway, J. T. 1993, [transmitting] *Recommendation 93-5 to the Secretary of Energy*, (letter to H. R. O'Leary, DOE, July 19), Defense Nuclear Facilities Safety Board, Washington, DC.
- Cowley, W. L., and A. K. Postma, 1996, *Organic Solvent Topical*, WHC-SD-WM-SARR-036, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- CRC, 1981, *CRC Handbook of Chemistry and Physics, 61st Edition*, CRC Press, Inc., Boca Raton, Florida.
- Delegard, H. C., 1987, *Identities of HEDTA and Glycolate Degradation Products in Simulated Hanford High-Level Waste*, RHO-RE-ST-55P, Rockwell Hanford Operations, Richland, Washington.
- DOE, 1986, *Safety of Nuclear Facilities*, DOE Order 5480.5, U.S. Department of Energy, Washington, DC.
- DOE, 1988, *Radioactive Waste Management*, DOE Order 5480.2A, U.S. Department of Energy, Washington, DC.
- DOE, 1989, *General Design Criteria*, DOE Order 6430.1A, U.S. Department of Energy, Washington, DC.
- DOE, 1991, *Unreviewed Safety Questions*, DOE Order 5480.21, U.S. Department of Energy, Washington, DC.
- DOE, 1992, *Nuclear Safety Analysis Reports*, DOE Order 5480.23, U.S. Department of Energy, Washington, DC.
- DOE, 1993, *Environmental, Safety, and Health Programs for Department of Energy Operations*, DOE Order 5480.1B, U.S. Department of Energy, Washington, DC.
- DOE/RL, 1994, *Recommendation 93-5 Implementation Plan*, DOE/RL 94-0001, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE/RL, 1996, *Recommendation 93-5 Implementation Plan*, DOE/RL 94-0001, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- Dukelow, G. T., and G. A. Hanson, 1996, *Status Report on Resolution of Waste Tank Safety Issues at the Hanford Site*, WHC-EP-600, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
-
-

-
-
- Ecology, EPA, and DOE, 1990, *Hanford Federal Facility Agreement and Consent Order*, 2 vols, as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.
- Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order*, Amendment 4, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.
- Kirch, N. W., 1993, *Adiabatic Calorimetry (RSST and VSP) Tests with Sodium Acetate*, WHC-EP-0683, Westinghouse Hanford Company, Richland, Washington.
- Fauske, H. K., 1996a, *Assessment of Chemical Vulnerabilities in the Hanford High-Level Waste Tanks*, WHC-SD-WM-ER-543, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Fauske, H. K., 1996b, *An Assessment of Requirements for Organic-Nitrate Propagating Reactions Including RSST and Tube Propagation Test Results With Waste Simulants*, FAI/96-48, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Fauske, H. K., 1996c, *Propagation Scale-Up Tests with Organic-Nitrate/Nitrite Mixtures*, FAI/96-45, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Fauske, H. K., D. R. Dickinson, R. J. Cash, and J. E. Meacham, 1995, *The Contact Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Fisher, F. D., 1990, *The Kyshtym Explosion and Explosion Hazards with Nitrate-Nitrite Bearing Wastes with Acetates and Organic Salts*, WHC-SD-CP-LB-033, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Fowler, K. D., 1993, *Action Plan for Responses to Abnormal Considerations in Hanford Site Radioactive Waste Tanks with High Organic Content*, WHC-EP-0461, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Gerber, M. A., 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, AD-940, Pacific Northwest Laboratory, Richland, Washington.
- Gygas, R. W., 1990, "Scaleup Principles for Assessing Thermal Runaway Risks," *Chemical Engineering Progress*, February 1990.
- Hall, J. C., 1972, *Engineering Study of Liquid Organic Waste Collection and Disposal*, ARH-2424, Atlantic Richfield Hanford Company, Richland, Washington.
-
-

-
-
- Hanlon, B. M., 1994, *Tank Farm Surveillance and Waste Tank Summary Report for May 1994*, WHC-EP-0182-74, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995a, *Tank 241-U-107 Vapor Sampling and Analysis Tank Characterization Report*, WHC-SD-WM-ER-451, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995b, *Tank 241-U-106 Vapor Sampling and Analysis Tank Characterization Report*, WHC-SD-WM-ER-460, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and M. S. Story, 1994, *Vapor Characterization of Tank 241-C-103*, WHC-EP-0780, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and D. R. Bratzel, 1995, *Tank 241-U-105 Headspace Gas and Vapor Characterization Results for Samples Collected in February 1995*, WHC-SD-WM-ER-511, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., H. Babad, and D. R. Bratzel, 1995, *Headspace Gas and Vapor Characterization Summary for the 43 Vapor Program Suspect Tanks*, WHC-SD-WM-ER-514, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Jungfleisch, F. M., 1984, *TRAC: A Preliminary Estimation of the Waste Inventories in Hanford Waste Tanks Through 1980*, SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.
- Kennedy, J., and S. S. Grimley, 1953, *Radioactive Studies with Phosphorus-32 Labelled Tri-n-butyl Phosphates*, CE/R-1284, Atomic Energy Research Establishment, Harwell, United Kingdom.
- Klem, M. J., 1990, *Inventory of Chemicals Used at Hanford Site Production Plants and Support Operations (1944-1980)*, WHC-EP-0172, Westinghouse Hanford Company, Richland, Washington.
- Kirch, N. W., 1993, *Adiabatic Calorimetry (RSST and VSP) Tests with Sodium Acetate*, WHC-EP-0683, Westinghouse Hanford Company, Richland, Washington.
- Leach, C. E., and S. M. Stahl, 1995, *Hanford Site Tank Farm Facilities Interim Safety Basis*, WHC-SD-WM-ISB-001, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Lilga, M. A., M. R. Lumetta, and G. F. Schiefelbein, 1993, *Ferrocyanide Safety Project, Task 3: Aging Studies - FY 1993 Annual Report*, PNL-8888, Pacific Northwest Laboratory, Richland, Washington.
- Lilga, M. A., E. V. Alderson, D. J. Kowalski, M. R. Lumetta, and G. F. Schiefelbein, 1994, *Ferrocyanide Safety Project, Task 3: Ferrocyanide Aging Studies - FY 1994 Annual Report*, PNL-10126, Pacific Northwest Laboratory, Richland, Washington.
-
-

-
-
- Lilga, M. A., E. V. Alderson, R. T. Hallen, M. O. Hogan, T. L. Hubler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project: Ferrocyanide Aging Studies - FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.
- McVeety, B. D., T. W. Clauss, M. W. Ligothke, K. H. Pool, R. B. Lucke, G. S. Klinger, J. S. Young, M. McCulloch, and J. S. Fruchter, 1995, *BY-108: Results from Samples Collected on 10/27/94*, PNL-10495, Pacific Northwest Laboratory, Richland, Washington.
- Meacham, J. E., 1996, *Strategy for Resolution of the Organic Complexant and Organic Solvent Safety Issues*, WHC-EP-0908, Westinghouse Hanford Company, Richland, Washington.
- Meacham, J. E., A. B. Webb, M. G. Plys, S. J. Lee, J. M. Grigsby, P. G. Heasler, J. L. Bryant, J. J. Toth, P. M. Daling, 1996, *Safety Criteria for the Organic Watch List Tanks at the Hanford Site*, WHC-SD-WM-SARR-033, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Meisel, D., H. Diamond, E. P. Horwitz, M. S. Matheson, M. C. Sauer, Jr., and J. C. Sullivan, 1991a, *Radiation Chemistry of Synthetic Waste*, ANL-91/40, Argonne National Laboratory, Argonne, Illinois.
- Meisel, D., H. Diamond, E. P. Horwitz, M. S. Matheson, M. C. Sauer, Jr., J. C. Sullivan, F. Barnabas, E. Cerny, and Y. D. Cheng, 1991b, *Radiolytic Generation from Synthetic Waste*, ANL-91/41, Argonne National Laboratory, Argonne, Illinois.
- Meisel, D., C. D. Jonah, M. S. Matheson, M. C. Sauer, Jr., F. Barnabas, E. Cerny, Y. D. Cheng, and T. Wojta, 1992, *Radiation Chemistry of High-Level Wastes ANL/CHM Task Force on Gas Generation in Waste Tanks*, ANL-92/40, Argonne National Laboratory, Argonne, Illinois.
- Meisel, D., C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr., 1993, *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*, ANL-91/43, Argonne National Laboratory, Argonne, Illinois.
- Neta, P., R. E. Huie, and A. B. Ross, 1988, *Rate Constants for Reactions of Inorganic Radicals in Aqueous Solutions*, Journal of Physical Chemistry, vol. 90, p. 4644.
- O'Leary, H. R., 1993, *TWRS Safety Initiatives*, U.S. Department of Energy, Washington, D.C.
- Phillips, J. F., Jr., 1967, *A Survey of B-Plant Waste for Explosion Hazards*, BNWL-CC-1070, Battelle Northwest Laboratory, Richland, Washington.
- Pool, K. H., and R. M. Bean, 1994, *Waste Tank Organic Safety Project - Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403, Pacific Northwest Laboratory, Richland, Washington.
-
-

-
-
- Postma, A. K., D. B. Bechtold, 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.
- Public Law 101-510, Section 3137, 1990, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation*, U.S. Congress, Washington, DC [Also referred to as the Wyden Amendment]
- Reep, I. E., 1993, *Status Report on Resolution of Waste Tank Safety Issues at the Hanford Site*, WHC-EP-0600, Westinghouse Hanford Company, Richland, Washington.
- Samuels, W. D., D. M. Camiaoni, and D. A. Nelson, 1993, *Organic Chemical Aging Mechanisms: An Annotated Bibliography*, PNL-8808-AD-940, Pacific Northwest Laboratory, Richland, Washington.
- Scheele, R. D., J. L. Sobolik, R. L. Sell, and L. L. Burger, 1995, *Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste*, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.
- Schultz, W. W., 1980, *Removal of Radionuclides from Hanford Defense Waste Solutions*, RHO-SA-51, Rockwell Hanford Operations, Richland, Washington.
- Sederburg, J. P., and J. A. Reddick, 1994, *TBP and Diluent Mass Balances in the Purex Plant at Hanford 1955 - 1991*, WHC-MR-0483, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Simpson, B. C., and D. J. McCain, 1996, *Historical Model Evaluation Data Requirements*, WHC-SD-WM-DQO-018, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Toth, J. J., P. G. Heasler, M. E. Lerchen, J. G. Hill, and P. D. Whitney, 1995, *Analysis of Organic Carbon and Moisture in Hanford Single-Shell Tank Waste*, PNL-10360, Pacific Northwest Laboratory, Richland, Washington.
- Turner, D. A., 1993, *Corrective Action Strategy for Single-Shell Tanks Containing Organic Chemicals*, WHC-EP-0671, Westinghouse Hanford Company, Richland, Washington.
- Turner, D. A., 1994a, *Testing of Organic Waste Surrogate Materials in Support of the Hanford Organic Tank Program - Final Report*, WHC-MR-0455, Westinghouse Hanford Company, Richland, Washington.
- Turner, D. A., 1994b, *Revision of the Organic Watch List*, (letter 9453328 to R. E. Gerton, DOE-RL, May 13), Westinghouse Hanford Company, Richland, Washington.
-
-

-
-
- Turner, D. A., H. Babad, L. L. Buckley, and J. E. Meacham, 1995, *Data Quality Objective to Support Resolution of the Organic Complexant Safety Issue*, WHC-SD-WM-DQO-006, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- Van Vleet, R. J., 1993a, *Radionuclide and Chemical Inventories for the Single Shell Tanks*, WHC-SD-WM-TI-565, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Van Vleet, R. J., 1993b, *Radionuclide and Chemical Inventories for the Double Shell Tanks*, WHC-SD-WM-TI-543, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Wagoner, J. D., 1993, *Approval of Hanford Site Tank Farms Interim Safety Basis*, (letter ADT:TOB 93-TOB-209, to T. M. Andersen, Westinghouse Hanford Company, November 18), U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- Wagoner, J. D., 1996, *Recommendation for Declaring an Unreviewed Safety Question (USQ) Regarding Condensed-Phase Organic Nitrate Reactions*, (letter 96-WSD-073 to A. L. Trego, Westinghouse Hanford Company, May 24), U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- Webb, A. B., D. M. Camaioni, J. M. Grigsby, P. G. Heasler, B. Malinovic, M. G. Plys, J. L. Stewart, J. J. Toth, and D. A. Turner, 1995, *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-SD-WM-SARR-033, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Wicks, J. H., 1996, *Recommendation for Declaring an Unreviewed Safety Question Regarding Condensed-Phase Organic Nitrate Reactions*, (letter 9652251, A. B. Sidpara, RL, May 16), Westinghouse Hanford Company, Richland, Washington.
- Wilkinson, R. W., and T. F. Williams, 1961, "The Radiolysis of Tri-n-alkyl Phosphates," J. Chemistry Society (London), p. 4098.
-
-

This page intentionally left blank.

APPENDIX
QUALITY ASSURANCE

Quality Assurance (QA) is an integral part of the Organic Safety Project. It provides independent oversight at planning, implementation, and completion stages to ensure that stated objectives are met. The QA process provides: (1) methodology review; (2) statistical analyses of data collection, analysis, and interpretation; and (3) data validation and records management.

The data quality objective (DQO) process is used to verify and validate the data needed to meet the overall Organic Safety Project goals. Because of differing data sets, separate DQOs were conducted for flammability, toxicity, and health and safety.

The Organic Safety Project will participate in organic liquid, push and rotary-made core drilling DQOs for obtaining and analyzing waste samples. At the Hanford Site, the DOE has the primary responsibility to ensure that performed activities are handled in an efficient and cost-effective manner. To control the quality of activities, DOE issued DOE Order 5700.6C (DOE 1991), which is implemented by the U.S. DOE-RL (1994). This order requires the selective and judicious application of requirements from the national consensus standard (ASME 1989). Projects within the Organic Safety Project that impact the environment will meet quality program requirements imposed by the Tri-Party Agreement (TPA). This agreement (Ecology et al. 1994) specifies that all parties shall use procedures for QA and quality control in accordance with EPA methods. Guidance is provided in EPA (1983 and 1987).

WHC directs compliance with DOE quality program requirements in WHC (1993). This applies the criteria of ASME (1989) to all quality-affecting activities performed by WHC personnel. The EPA quality requirements are specified in the existing quality programs to ensure overall compliance with the TPA.

QA provides independent review and oversight to the Organic Safety Project during all stages of development. This activity provides input regarding requirements and whether they are being met.

QA in the Organic Safety Project follows WHC (1993). A Quality Assurance Project Plan has been written to address characterization of tank C-103, and will be revised to extend coverage to all other sampling events (Osborne et al. 1995). Another Quality Assurance Project Plan has been written for vapor characterization (Keller 1994). Audits, surveillance and assessments will be established according to QA requirements to ensure that activities are completed as defined.

TWRS Program's Quality Assurance organization will be the primary QA point of contact with the Organic Safety Project, and will interface with other quality assurance groups to assure adequate oversight.

DQOs have been developed using guidance provided in EPA (1987). The DQOs used in this program are outlined in Turner et al. (1995). As the project continues, more DQOs may be developed, or the existing DQOs revised in response to the availability of technical information supporting the development of Organic Safety Project. Further development or revision of the organic DQOs will be accomplished using the same guidance as mentioned above.

REFERENCES

- ASME, 1989, *Quality Assurance Requirements for Nuclear Facilities*, ASME NQA-1-1989, American Society of Mechanical Engineers, New York, New York.
- DOE, 1991, *Quality Assurance*, DOE Order 5700.6C, U.S. Department of Energy, Washington, D. C.
- DOE/RL, 1994, *Hanford Analytical Services Quality Assurance Plan*, DOE/RL-94-55, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order*, Amendment 4, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.
- EPA, 1983, *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*, QAMS-005/80, EPA-600/4-83/004, U.S. Environmental Protection Agency, Washington, D.C.
- EPA, 1987, *Data Quality Objectives for Remedial Response Activities: Development Process*, EPA/540/G-87/003, U.S. Environmental Protection Agency, Washington, D.C.
- Keller, K. K., 1994, *Quality Assurance Project Plan for Tank Vapor Characterization*, WHC-SD-WM-QAPP-013, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- Osborne, J. W., J. L. Huckaby, E. R. Hewitt, C. M. Anderson, D. D. Mahlum, B. A. Pulsipher, and J. Y. Young, 1995, *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Turner, D. A., H. Babad, L. L. Buckley, and J. E. Meacham, 1995, *Data Quality Objective to Support Resolution of the Organic Complexant Safety Issue*, WHC-SD-WM-DQO-006, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1993, *Quality Assurance Manual*, WHC-CM-4-2, Westinghouse Hanford Company, Richland, Washington.
-
-

DISTRIBUTION

Number of copies

OFFSITE

3 U.S. Department of Energy
 EM-38, Trevion II
 12800 Middlebrook Road
 Germantown, MD 20874

 Harry Calley
 Maureen Hunemuller
 Ken Lang

U.S. Department of Energy
 Forrestal Building
 1000 Independence Avenue SW
 Washington, DC 20585

 Shirley Campbell, EH-71
 John Kaysak, EM-25

1 Charles S. Abrams
 1987 Virginia
 Idaho Falls, ID 83404

1 David O. Campbell
 102 Windham Road
 Oak Ridge, TN 37830

1 Fred N. Carlson
 6965 North 5th West
 Idaho Falls, ID 83401

1 Billy C. Hudson
 202 Northridge Court
 Lindsborg, KA 67456

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

DISTRIBUTION (Continued)

Number of copies

OFFSITE

1 Thomas E. Larson
2711 Walnut Street
Los Alamos, NM 87544

1 Leon M. Stock
6022 SW Texas Ct.
Portland, OR 97219

1 Brookhaven National Laboratory
Upton, NY 11973

Kamal K. Bandyopadhyay

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

Michael Epstein
Hans K. Fauske

1 G & P Consulting, Inc.
3640 Ballard Road
Dallas, OR 97338

Arlin K. Postma

1 Harvard University
295 Upland Avenue
Newton Highlands, MA 02161

Melvin W. First

1 MIT/Department of Nuclear Engineering
77 Massachusetts Ave.
Room 24-102
Cambridge, MA 02139

Mujid S. Kazimi

DISTRIBUTION (Continued)

Number of copies

OFFSITE

- 1 Nuclear Consulting Services, Inc.
 P.O. Box 29151
 Columbus, OH 43229-0151

 J. Louis Kovach

 Oak Ridge National Laboratory
- 1 Emory D. Collins
 P.O. Box 2008
 7930, MS-6385
 Oak Ridge, TN 37831-6385
- 1 Charles W. Forsberg
 P.O. Box 2008
 MS-6495
 Oak Ridge, TN 37831-6495
- 1 Rice University
 5211 Paisley
 Houston, TX 77096

 Andrew S. Veletsos
- 2 Sandia National Laboratories
 P.O. Box 5800
 Albuquerque, NM 87185

 Dana A. Powers, MS-0744
 Scott E. Slezak, MS-0741

DISTRIBUTION (Continued)

Number of copies

OFFSITE

3 Science Applications International Corporation
20300 Century Blvd, Suite 200-B
Germantown, MD 20874

Paul Hogroian (3)

State of Washington - Department of Ecology

1 Robert C. King
P. O. Box 47600
Olympia, WA 98504-7600

1 Alex B. Stone
1315 W. 4th Avenue
Kennewick, WA 99336

1 Waste Policy Institute
555 Quince Orchard Road, Suite 600
Gaithersburg, MD 20878-1437

Donald T. Oakley

ONSITE

7 U.S. Department of Energy,
Richland Operations Office

D. H. Irby (2)	S7-54
W. F. Hendrickson	S7-54
A. G. Krasopoulos	A4-81
Public Reading Room	H2-53
RL Docket File (2)	B1-17

DISTRIBUTION (Continued)

4	<u>Pacific Northwest Laboratory</u>	
	J. W. Brothers	K5-22
	R. T. Hallen	P8-38
	M. A. Lilga	P8-38
	Hanford Technical Library	P8-55
34	<u>Westinghouse Hanford Company</u>	
	H. Babad	S7-14
	M. V. Berriochoa	B3-30
	J. B. Billetdeaux	S7-15
	J. F. Bores	S1-57
	W. S. Callaway	S3-90
	R. J. Cash (2)	S7-14
	M. D. Crippen	L5-31
	R. D. Crowe	H0-32
	M. L. Dexter	R1-51
	D. R. Dickinson	L5-31
	G. T. Duke low	S7-14
	J. M. Grigsby	A3-37
	M. N. Islam	R3-08
	D. W. Jeppson	L5-31
	N. W. Kirch	R2-11
	C. A. Kuhlman	B3-30
	L. L. Lockrem	S3-90
	J. E. Meacham (5)	S7-14
	N. J. Milliken	A3-376
	S. R. Moreno	B3-06
	F. R. Reich	L5-55
	E. F. Riedel	S3-90
	B. C. Simpson	R2-12
	L. E. Thomas	R3-08
	Central Files	A3-88
	Correspondence Processing	A3-01
	EDMC	H6-08
	DPC	A3-94

This page intentionally left blank.

DISTRIBUTION (Continued)

4	<p><u>Pacific Northwest Laboratory</u></p> <p>J. W. Brothers R. T. Hallen M. A. Lilga Hanford Technical Library</p>	<p>K5-22 P8-38 P8-38 P8-55</p>
34	<p><u>Westinghouse Hanford Company</u></p> <p>H. Babad M. V. Berriochoa J. B. Billedeaux J. F. Bores W. S. Callaway R. J. Cash (2) M. D. Crippen R. D. Crowe M. L. Dexter D. R. Dickinson G. T. Dukelow J. M. Grigsby M. N. Islam D. W. Jeppson N. W. Kirch C. A. Kuhlman L. L. Lockrem J. E. Meacham (5) N. J. Milliken S. R. Moreno F. R. Reich E. F. Riedel B. C. Simpson L. E. Thomas Central Files Correspondence Processing EDMC DPC</p>	<p>S7-14 B3-30 S7-15 S1-57 S3-90 S7-14 L5-31 H0-32 R1-51 L5-31 S7-14 A3-37 R3-08 L5-31 R2-11 B3-30 S3-90 S7-14 A3-376 B3-06 L5-55 S3-90 R2-12 R3-08 A3-88 A3-01 H6-08 A3-94</p>

THIS PAGE INTENTIONALLY
LEFT BLANK