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Flammable Gas Safety Issue Resolution

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U.S. Department of Energy Contract DE-AC27-99RL14047

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Abstract: The document provides the technical bases for removal of 24 high-level waste storage tanks at the Hanford Site from the Flammable Gas Watch List and for resolution of the Flammable Gas Safety Issue. Major items covered in the report are: a review of all data collected and analyzed for the 24 tanks; an overview of the research done on the generation, retention, and release of stored gases, and a summary of controls used for the tanks. This document does not change the AB.

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Flammable Gas Safety Issue Resolution

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

CH2MHILL
Hanford Group, Inc.
Richland, Washington

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

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Flammable Gas Safety Issue Resolution

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EXECUTIVE SUMMARY

This report provides a summary of work completed to evaluate and characterize the behavior of Hanford Site high level waste tanks waste for potential safety issues associated with the presence of flammable gas mixtures. National attention to the potential safety issues with flammable gases started with congressional action in November 1990, when the U.S. Congress enacted Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation." In response to this law a list of tanks, identified as having the potential for ignition of flammable gases, became known as the "Flammable Gas Watch List." Later in 1994, the U.S. Department of Energy (DOE), the Washington State Department of Ecology, and the U.S. Environmental Protection Agency established a specific Tri Party Agreement milestone (M-40-00) for resolving the safety issue associated with flammable gases and other chemical concerns with the waste tanks (Ecology et al. 1996). This milestone has a completion date of September 30, 2001.

The Tri-Party Agreement Milestone (TPA) M-40-00, "Mitigate/Resolve Tank Safety Issues for High Priority Watch List Tanks," addresses four safety issues. Those safety issues are: flammable gas generating tanks, ferrocyanide containing tanks, organic/nitrate containing tanks, and a high heat producing tank. The Ferrocyanide, Organic/Nitrate and High Heat Safety Issues are closed. Flammable Gas is the remaining open safety issue listed in TPA Milestone M-40-00. The basis for meeting the remaining requirements of TPA Milestone M-40-00 is given in this report; approval of this report will resolve the Flammable Gas Safety Issue. The information provided in this report also forms the basis for removing tanks from the Flammable Gas Watch List, and upon approval by the DOE, all remaining actions with respect to Public Law 101-510, Section 3137 will be closed.

The tanks on the FGWL are (note the 241- designation has been deleted from each tank) A-101, AN-103, AN-104, AN-105, AX-101, AX-103, AW-101, S-102, S-111, S-112, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, SX-109, SY-103, T-110, U-103, U-105, U-107, U-108, and U-109. These same 24 tanks are also the subject of TPA Milestone M-40-00. Tank 241-SY-101 was removed from the Watch List and the flammable safety issue was closed for that tank in January 2001 (Huntoon 2001).

Criteria for resolution of the safety issue center around having an approved safety envelope (Authorization Basis) and having an understanding of the behavior of the waste in the tanks and implementing mitigative actions, if required. Over ten years of evaluation of tank contents and behavior of flammable gases has been conducted and, as a result, there is a sufficient understanding of the generation, retention and release of flammable gases in the subject tanks that the "Flammable Gas Safety Issue" can be resolved. The Authorization Basis for the Hanford Site Tank Farms appropriately recognizes the nature of the hazards and effective controls are in place.

Public Law 101-510, Section 3137 required the Secretary of Energy to identify which high level nuclear waste tanks may have a "serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure." Criteria were established for placing tanks on, and removing tanks from, the Flammable Gas Watch List (FGWL). As progress was made

in the understanding of the behavior of these tanks, it was determined that the essence of the criteria for watch list tanks should be interpreted as: "to have significant potential for an unacceptable risk from a spontaneous release of flammable gas." Furthermore this is to be applied to the tanks under what has been termed "safe storage." Safe storage applies to all activities currently authorized in HNF-SD-WM-SAR-067, *Tank Farm Final Safety Analysis Report.*

A major item that pertains to both the Flammable Gas Safety Issue and the Watch List was the Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 93-5. This recommendation noted that insufficient tank waste technical information was available to ensure that Hanford Site wastes could be safely stored, that associated operations could be conducted safely, and that future disposal program data requirements could be met. Recommendation 93-5 was closed in 1999 (Conway 1999).

In the letter that DOE submitted (Richardson 1999) to the DNFSB for closure of Recommendation 93-5 Secretary Richardson noted:

> *"All tanks are sufficiently characterized to support safety of storage and planning for Phase One of waste retrieval and vitrification."*

The same letter also stated:

> *"Flammable gas hazards have been identified and are monitored for specific tanks. Controls are imposed to prevent development or ignition of explosive mixtures."*

Item (a) of Section 3137 of Public Law 101-510 (Appendix A) states: "...single-shelled or double-shelled high level nuclear waste tanks ... may have a serious potential for release of high-level waste due to uncontrolled increase in temperature or pressure." This situation does not exist as noted above by the Secretary of Energy. From this perspective alone, the tanks should be removed from the FGWL and the Safety Issue resolved.

In order to understand the basis for removal of tanks from the watch list a summary of the pertinent data for each tank is provided and evaluated. The main issues that are addressed are: (1) the quantity of gas retained in each tank, (2) the quantity of gas spontaneously released from the waste in each tank, and (3) the likelihood of ignition of released gas, and if ignited, the potential for the resulting pressure transient to compromise tank integrity.

Table ES-1 shows a summary of the data for the 24 tanks. The table lists the estimated retained gas volume and retained hydrogen volume with the uncertainties, the headspace volume calculated from the pre-pumping liquid level (for single-shell tanks [SSTs]), the hydrogen release volume that would bring the well mixed headspace to Lower Flammable Limit (LFL), the maximum observed hydrogen release (both volume and release fraction) since standard hydrogen monitoring system (SHMS) were installed, the maximum hydrogen concentration (release event or steady state) and the fraction of the LFL represented by that concentration.

Table ES-1. Summary of Retained Gas Volume and Release Magnitudes. (2 sheets)

Tank	Retained Gas Volume (Std. m^3)	Retained Hydrogen Volume (Std. m^3)	Headspace Volume (m^3)	Hydrogen Release for LFL (Std. m^3)	Max. Observed Hydrogen Release (Std. m^3)	Release Fraction	Max. Hydrogen Conc (Steady State or GRE) ppm (Date for DST)	Maximum % LFL Value (observed)
AN103	393 ± 64	240 ± 74	1717	62	5.2	0.02	3000 (8/95)	8.3
AN104	259 ± 48	117 ± 42	1352	49	8.2	0.07	6109 (5/96)	17
AN105	202 ± 68	121 ± 23	1074	39	18.2	0.15	17,000 (8/95)	47
AW101	153 ± 38	49 ± 16	1074	39	9.4	0.19	8800 (10/94)	24
SY103	198 ± 86	107	2521	91	12.9	0.12	5110 (12/96)	14
A101	325 ± 80	234 ± 62	1415	51	1.2	<0.01	1540	4.3
AX101	270 ± 100	165 ± 63	2144	77	1.2	<0.01	540	1.5
AX103	43	N.A.	4041	145	None observed	-	380	0.3
S102	215 ± 60	71 ± 21	1933	70	None observed	-	760	2.1
S111	360 ± 85	238 ± 67	1945	70	2.5	0.01	1270	3.5
S112	46 ± 23	N.A.	2007	72	None observed	-	490	0.1
SX101	94 ± 47	N.A.	3218	116	None observed	-	400	0.1
SX102	170 ± 85	N.A.	2947	106	None observed	-	740	0.1
SX103	363	N.A.	2512	90	1.6	-	640	1.8
SX104	250 ± 125	N.A.	2676	96	0.5	-	580	0.6
SX105	180 ± 90	N.A.	2459	89	1.7	-	710	2.0
SX106	400 ± 100	200 ± 54	2890	104	1.0	<0.01	560	0.9
SX109	120	N.A.	3949	142	0.4	-	890	0.3

Table ES-1. Summary of Retained Gas Volume and Release Magnitudes. (2 sheets)

Tank	Retained Gas Volume (Std. m^3)	Retained Hydrogen Volume (Std. m^3)	Headspace Volume (m^3)	Hydrogen Release for LFL (Std. m^3)	Max. Observed Hydrogen Release (Std. m^3)	Release Fraction	Max. Hydrogen Conc (Steady State or GRE) ppm (Date for DST)	Maximum % LFL Value (observed)
T110	50 ± 25	N.A.	1653	60	None observed	-	19	0.1
U103	315 ± 80	72 ± 19	1435	52	2.4	0.03	1670	4.6
U105	270 ± 90	N.A.	1600	58	2.3	-	1490	4.1
U107	180 ± 60	N.A.	1686	61	3.2	-	1900	5.3
U108	390 ± 120	N.A.	1444	52	2.2	-	1530	4.3
U109	320 ± 100	80 ± 27	1464	53	3.2	0.04	2190	6.1

Notes: The retained gas volume for each of the double-shell tanks (DST) is the total taken from Table 5-5 in Section 5 of this report. This includes the gas estimated to be in the crust and convective layers (CL). Since the uncertainty given in Table 5-5 represents one standard deviation it is doubled to approximate a 95% confidence bound. These uncertainties were determined from the void fraction instrument (VFI) and retained gas sampler (RGS) data as described by Hedengren et al. (2000).

The retained gas volumes and uncertainties for the SSTs are taken directly from Table 6-7 in Section 6. The uncertainties for the SSTs are intended to approximate a 95% confidence bound. There are no useable data to determine retained gas volumes for Tanks AX-103, SX-103, and SX-109. Therefore, the gas volumes listed for these tanks represent an assumed in situ gas volume fraction of 0.1 over the entire waste volume.

The release fraction was calculated by dividing column 6 (max observed hydrogen release) by column 3 (retained hydrogen volume).

The hydrogen volumes are computed by multiplying the total gas volume in the first column of the table by the hydrogen fractions determined from RGS data for nonsupernate waste. These data are found in Tables 5-3 and 6-5 for DSTs and SSTs, respectively. No estimate is made for tanks that were not sampled with the RGS except SY-103 whose composition was estimated based on laboratory gas generation experiments. Uncertainties are computed by linear propagation through the product of the uncertainty in the volume and the composition (no uncertainty is given for SY-103 because none was determined for the composition).

The hydrogen release required to bring the well-mixed headspace to the LFL is the product of the hydrogen LFL, 3.6 vol% and the headspace volume. The assumed LFL of 3.6% for a mixture of hydrogen and other flammable gases (versus 4.0% for hydrogen in air) allows for other flammable components such as ammonia and methane.

The maximum observed hydrogen release volume is the product of the maximum observed headspace hydrogen concentration and the headspace volume. The hydrogen concentrations are taken from Table 5-6 for DSTs and Table 6-9 for SST GREs from McCain (2000) for steady state values in SSTs (this does not include effects of salt well pumping).

As noted earlier, the table has the maximum-recorded value for hydrogen in the dome space of each tank (McCain 1999, 2000) and the last column then shows how these values relate to the LFL for hydrogen (3.6 %, Section 5.4). Dates for the DST GREs are from McCain (1999, 2000). The values for the DSTs range from 8 to 47 % LFL and for the SSTs the range is from 0.1 to 6% LFL. Since all are below the LFL, combustion cannot occur and there is no "serious potential for uncontrolled increases in pressure" in these tanks.

Additional discussions are provided for the DSTs and SSTs. More detailed discussions of the data are provided in Sections 5 and 6 of this report.

Double Shell Tanks

Table ES-1 lists data for the five DSTs that are on the FGWL. The waste configurations in these tanks are well understood. The layer dimensions have not changed significantly over the past five years. Estimate of the volumes retained gas range from 153 m^3 to 393 m^3. There have been 85 spontaneous gas releases observed in SHMS data since 1995. The hydrogen concentration exceeded 25% of the LFLs (9,000 ppm) during two of these events. The peak recorded hydrogen concentrations in the dome spaces ranged from 3,000 to 17, 000 ppm (8 to 47% of LFL). Gas generation rates in four DSTs have been decreasing, along with spontaneous gas releases since 1995 as a result of waste cooling. The total gas generation rates for all five DSTs are in the range of 0.20-0.31 m^3/day (standard) and this is much smaller than the ventilation rates, which are on the order of 4,078 m^3/day. Steady state concentrations of hydrogen in the dome spaces are generally in the range of 20 to 55 ppm.

Hydrogen is the most abundant gas retained in the nonconvective layers and crusts. Besides hydrogen, the retained gas contains nitrogen and nitrous oxide with lesser amounts of ammonia, water vapor, methane, and other hydrocarbons.

Flammable conditions have not been created as a result of the GREs and thus the DSTs do not have a serious potential for release of waste due to uncontrolled increases in temperature or pressure.

Single Shell Tanks

Table ES-1 lists data for the 19 single SSTs that are on the FGWL. Estimates of the volumes of retained gas range from 43 m^3 to 400 m^3. The peak recorded hydrogen concentrations in the dome spaces range from 19 to 2190 ppm (0.1 to 6.1 % of the LFL). So even though a number of these tanks contain a significant amount of gas within the waste, the spontaneous GREs are quite small. In addition, the GREs in these SSTs occur over an extended time period, the average duration being six days with an average time to the peak concentration being two days. So these small releases in the SSTs are also slow releases. These release events do not produce flammable conditions. Evaluations of waste behavior have not identified any plausible mechanism for a large spontaneous GRE in these SSTs.

Observations have been made for waste disturbing operations in some SSTs (Section 6.4). In these cases, the gas releases are considered to be "induced." An informal study in 1996 of 77 waste disturbing operations in 47 SSTs showed only minor releases in five cases. Also, a number of the SST have had supernate and/or interstitial liquid removed by pumping. This

process is termed saltwell pumping and for SSTs on the watch list none have exceeded 25% of the LFL during pumping. So, even when the waste is disturbed, flammable conditions are not created. Flammable conditions have not been created as a result of the GREs and thus these tanks do not have a serious potential for release of waste due to uncontrolled increases in temperature or pressure.

Summary

Considering the three issues posed earlier, answers can be stated for each one.

1) The quantity of gas retained in each tank
   - For DSTs the retained gas volumes range from 153 to 393 m^3.
   - For SSTs the retained gas volumes range from 43 to 400 m^3.
   - Thus, the wastes in the FGWL tanks contain a significant amount of gas.
2) The quantity of gas spontaneously released from each tank
   - For DSTs, GREs release from 5.2 to 18.2 m^3 of hydrogen.
   - For SSTS, GREs release from 0.4 to 3.2 m^3 of hydrogen.
   - These volumes are quite small and the release fractions (fraction of stored gas spontaneously released) range from <0.01 to 0.19.
3) The likelihood of ignition of released gas, and if ignited, the potential for the resulting pressure transient to compromise tank integrity
   - For DSTs, the releases range from 8 to 47 % of the LFL
   - For SSTS, the releases range from 0.1 to 6.1 % of the LFL.
   - Thus, in all cases flammable conditions are not created. The gas cannot be ignited.

According to the selection criterion and removal criterion, a tank can be removed from the FGWL when it no longer "can have a flammable gas volume in the dome space that, when ignited, would result in pressure above a containment-related tank design limit." The volumes of gas in the DSTs that are needed to reach the limit for onset of failure of the tank dome are in the range of 71 to 136 m^3. Corresponding volumes of hydrogen needed to reach the LFL (Table ES-1) range from 39 to 91 m^3. Observed gas release volumes have been in the range of 8.3 to 47% of the LFL. Thus it is concluded that tank behavior is such that conditions for reaching the conditions for onset of failure are not plausible in the DSTs. For the SSTs, conditions for onset of failure require gas concentrations that are at least 138% of the LFL. Observed releases have been in the range of 0.1 to 6.1% of the LFL and clearly the associated volumes of hydrogen are well below the requirements for the onset of failure. For both the DSTs

and SSTs the LFL is a conservative measure for evaluating the tanks against the watch list criterion.

So, the observed behavior of the 24 tanks on the FGWL is such that there is **no** serious potential for the release of waste due to an uncontrolled increase in pressure or temperature. Waste temperatures in these tanks have been cooling for several years.

The situation has changed from the time the Flammable Gas Safety Issue was raised in 1990 in that there is no longer an Unreviewed Safety Question with respect to flammable gas in the storage tanks. Activities that are presently authorized take into account the potential for release and/or ignition of flammable gas. During the review process for activities that are not presently authorized, the staff considers many potentially hazardous conditions (including flammable gas) before recommending that the activity be included in the authorization basis. Prior to the addition of any material to a tank, process controls are in place that require review of the material addition and consider potential issues such as criticality, flammable gas, and chemical reactions. Based on contemporary understanding of flammable gas generation and retention/release, controls are in place to preclude a tank from having flammable gas concentrations in excess of the LFL. This applies to existing tank and waste configurations and potential future authorized activities or configurations. We do not expect the hydrogen accumulation in the future to depart from currently observed behavior. While no large sudden gas release is expected, the tanks can cope with a large fractional release of their gas content. For example, 20 to 50% of the retained gas can be released without exceeding LFL. Even higher volumes can be released that might challenge tank integrity but without exceeding the safety limit. The current sudden releases are far below that limit and monitoring will ensure ample time for addressing any alarming departures from expected conditions.

The effects of natural phenomena were evaluated in the Tank Farms Final Safety Analysis Report (FSAR) with respect to flammable gas release. It was determined that the probability of a seismic event at the Hanford Site was too low to merit additional study beyond that which was accomplished in the Tank Farms FSAR. The FSAR noted: "Preliminary investigations of seismically induced gas releases suggest that the design basis earthquake (DBE) could result in a 50% gas release from a DST and a 10% gas release from an SST. These estimates are based on the strength of the waste (i.e., approximately 50 Pa yield for DST waste and 1,000 to 2,000 Pa for SST waste). Gas release fractions of this magnitude may result in small releases or large releases depending on the amount of gas retained within the waste in each tank." The maximum release fraction noted for a DST was 19% while for SSTs the observed releases have been less than 10% (Table ES-1).

No evidence of surface failure exists in the immediate vicinity of the tank farms where the exposed surfaces consist primarily of sands, gravels, and silt deposited through a series of prehistoric cataclysmic floods. The surface also contains outcroppings of the underlying basalt and sedimentary materials. Potential earthquakes at the Hanford Site are dominated by regional crustal faults rather than faults related to the tectonic plate subduction zones located near the Pacific Coast. The Hanford area does not have a history of large earthquakes.

Potential hazards posed by the presence of flammable gases have been evaluated and appropriate controls have been incorporated into the Authorization Basis for the tank farms. These controls address flammable gas monitoring, ventilation, and ignition source controls for tanks and work

activities where potential flammable gas hazards exist. The tank farms also use process control plans for complex processes and perform detailed compatibility analyses prior to any waste transfers. If tank conditions were to change, these controls, plans, and procedures would be reevaluated and modified as necessary. Finally an understanding of gas generation, retention, and release has been obtained. The authors of this report believe that the report provides adequate bases for resolution of the Flammable Gas Safety Issue, removal of the remaining 24 tanks from the FGWL, and completion of the TPA Milestone M-40-00.

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TERMS

BPE	barometric pressure effect
CC	complexant concentrate
CL	convective layer
DC	dilute complexed
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Operations Office
DSS	double-shell slurry
DSSF	double-shell slurry feed
DST	double-shell tank
EDTA	ethylenediaminetetriacetic acid
FGWL	Flammable Gas Watch List
FIC	Food Instrument Corporation
FSAR	Final Safety Analysis Report
GRE	gas release event
HEDTA	hydroxyethylethylenediaminetriacetic acid
HGR	hydrogen gas rate
HMS/TRAC	hydrogen mixing study/transient reactor analysis code
ILL	interstitial liquid level
LANL	Los Alamos National Laboratory
LFL	lower flammability limit
MIE	minimum ignition energy
MIT	multi-function instrument tree
NCL	nonconvective layer
NCPLX	noncomplexed
ORP	Office of River Protection
RGS	retained gas sampler
SC	(primarily) salt cake
SC/SL	salt cake with more than about 10% sludge
SHMS	standard hydrogen monitoring system
SpG	specific gravity
SST	single-shell tank
SWP	saltwell pump
TMACS	Tank Monitor and Control System
TOC	total organic carbon
TPA	Tri-Party Agreement
USQ	unreviewed safety question
VFI	Void Fraction Instrument

1.0 INTRODUCTION

1.1 PURPOSE AND SCOPE

In March 1990, the U.S. Department of Energy, Richland Operations Office (DOE-RL), announced that concerns had been raised about the potential build up of hydrogen in some of the underground nuclear waste storage tanks at the Hanford Site. The main concern was that the hydrogen in one tank (SY-101) might ignite with potential adverse consequences for workers and public health and safety. The contractor, Westinghouse Hanford Company, issued a plan for addressing the potential safety issue in April 1990 (Daugherty 1990). After additional review of the issue, an Unreviewed Safety Question regarding the flammable gases in SY-101 and potentially in similar tanks was declared by DOE-RL in May 1990 (Lawrence 1990). The U.S. Department of Energy (DOE) Office of Nuclear Safety issued an assessment of the safety issues concerning flammable gases and ferrocyanide in July 1990 (DOE/NS 1990).

This attention to the potential safety issues with the waste tanks led to congressional action. On November 5, 1990, the U.S. Congress enacted Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation." In response to this law a listing of tanks was created as having the potential for ignition of flammable gases and actions were completed to meet the immediate requirements of the law. This list became known as the "Flammable Gas Watch List" (FGWL).

It was a DOE and stakeholder priority to understand and reduce the risk associated with FGWL tanks. In 1994, the DOE, the Washington State Department of Ecology, and the U.S. Environmental Protection Agency established a specific milestone for resolving the safety issue associated with flammable gases and other chemical concerns with the waste tanks (Ecology et al. 1996 [also known as the Tri-Party Agreement]). This milestone has a completion date of September 30, 2001.

Considerable work has been done since 1990 in waste sampling, waste gas sampling, waste simulation studies, accident analyses, consultation with industry and subject matter experts, development and approval of an Authorization Basis, and 10 years of closely observed operating experience.

This document summarizes the technical basis for resolving the Flammable Gas Safety Issue and meets the requirements of the Tri-Party Agreement (TPA) Milestone M-40-00, "Mitigate/Resolve Tank Safety Issues for High Priority Watch List Tanks" (Ecology et al. 1996). Also, the information provided in this report forms the basis for removing tanks from the FGWL and to close all actions with respect to Public Law 101-510, Section 3137.

1.2 THE FLAMMABLE GAS SAFETY ISSUE

Radioactive wastes in the underground storage tanks at the Hanford Site slowly generate a gas mixture of hydrogen, nitrous oxide, ammonia, nitrogen, and traces of methane and other organic compounds by radiolysis of water, chemical reactions resulting from the thermal and radiological

decomposition of organic compounds, and corrosion of the steel tank wall. In most tanks, the gas evolves from the liquid and solid wastes into the headspace of a tank at the same rate as it is generated and little gas is retained. This situation is not of concern because the release rate is so low that the existing active and passive ventilation systems are able to keep the mean concentration of flammable gas in the dome space far below the lower flammability limit (LFL) (Hu et al. 2001).

However, some tanks may contain enough retained gas within the waste to cause potential worker injury or damage to equipment if it were suddenly released into the headspace and ignited. Work over the past 10 years has led to the conclusion that gas releases may occur spontaneously or be induced by external forces (e.g., barometric pressure changes, etc.) or by waste intrusion activities (e.g., core sampling, equipment installation, liquid removal operations, etc.). The potential for spontaneous releases and their undesirable consequences constitute the Flammable Gas Safety Issue.

The DOE established a High-Level Waste Tank Working Group to evaluate safety issues at various DOE sites in the United States. Their report (DOE-HQ 1992) provided a definition of a safety issue that provides additional insight. They defined a safety issue as an event or condition that can lead to either:

1) "an uncontrolled release of radionuclides, or exposure to radiation, resulting from operations of the DOE high-level waste storage tank farms that is not (a) within the approved safety envelope (i.e., a USQ), or (b) properly analyzed or mitigated;" or

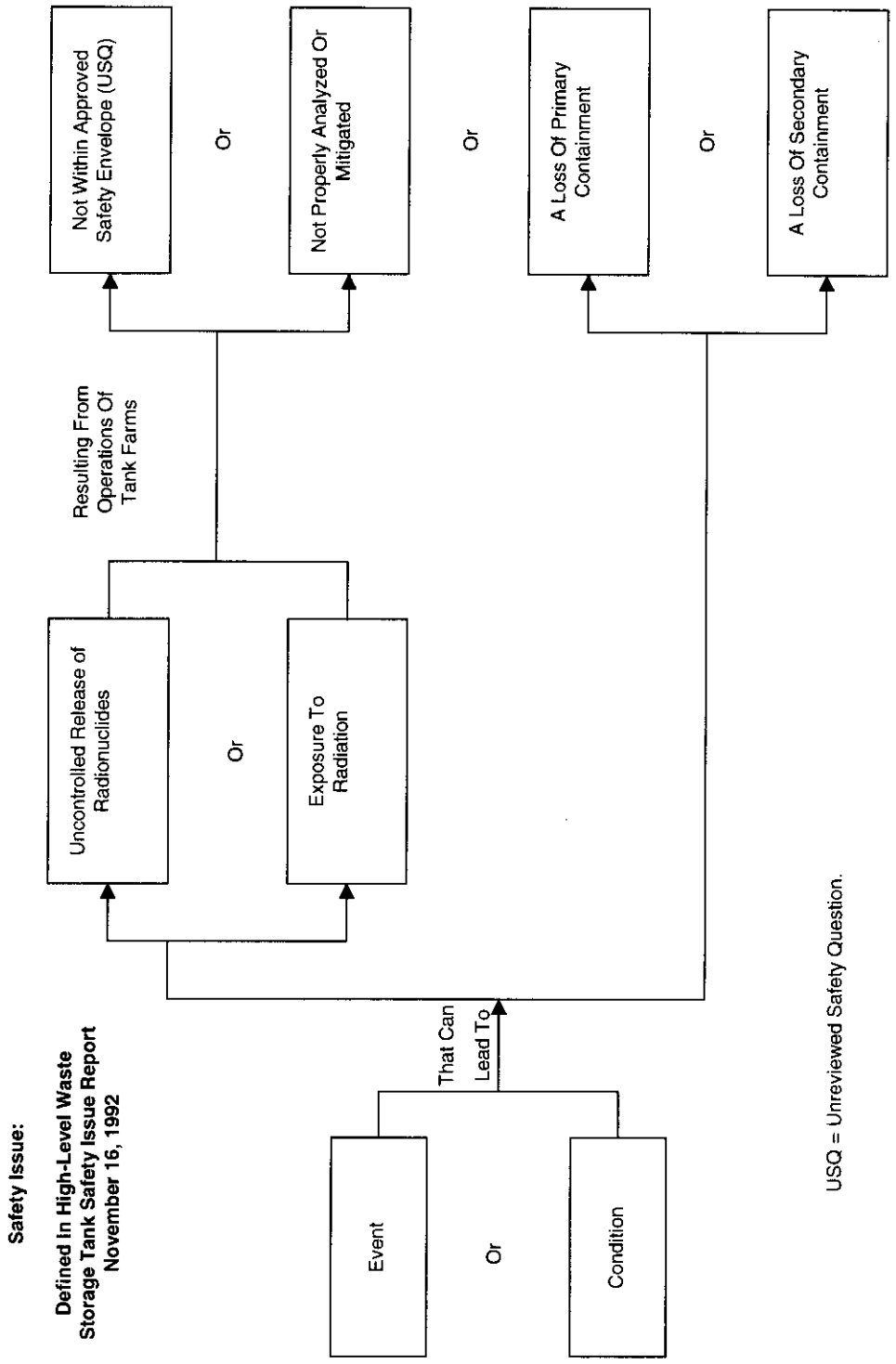
2) "a loss of primary or secondary containment for high-level radioactive waste."

Figure 1-1 provides a logic diagram of this definition of a safety issue. Resolution would occur when it is shown that the conditions listed on the right side of the figure do not exist.

The approach for resolution of the safety issue addresses the right hand side of Figure 1-1 (Johnson 1997) centers on the following:

- Understanding the processes for gas generation, retention, and release
  - Section 2.0
- Collection of data to establish an understanding of the behavior of the waste
  - Means to collect data described in Section 3.0
- Assessment of the potential hazards posed by the presence of flammable gas and potential ignition sources
  - Section 7
- Implementation of appropriate means to monitor tanks
  - Sections 3 and 8

Figure 1-1. Safety Issue Logic Diagram.



- Develop appropriate means to mitigate the accumulation and release of unacceptable quantities of flammable gas
  - Sections 4, 5, and 6
- DOE approval of a Nuclear Safety Authorization Basis commensurate with all of the above and DOE closure of unreviewed safety questions (USQ)
  - Sections 1.4 and 8
- Implementation of effective and appropriate controls in accordance with the Nuclear Safety Authorization Basis
  - Section 8.

Achievement of the above provides the basis for resolution of the Flammable Gas Safety Issue.

The influence of extreme and remotely possible natural phenomena such as high magnitude seismic events does not apply to the Flammable Gas Safety Issue. (For additional discussion concerning seismic issues, see Section 2.3.4.) The principal hazard deterrent for such an event is the aggressive pursuit of waste retrieval and treatment.

1.3 FLAMMABLE GAS WATCH LIST

The tanks covered by the Tri-Party Agreement milestone and the Public Law are known as "watch list" tanks. Watch list tanks arose as the result of a public law. In November 1990 Public Law 101-510 was passed. Section 3137, also known as the Wyden Amendment, was part of this law (Public Law 101-510, 1990). The text of the law is included in Appendix A. This section required the Secretary of Energy to identify which high level nuclear waste tanks may have a "serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure."

The number of tanks identified in 1991 in response to the public law was 23 and in 1993 two tanks were added to the list for a total of 25 tanks on the FGWL. Tank SY-101[1] was removed from the list in 2001 (Huntoon 2001), so the focus of this report is on the remaining 24 tanks. These tanks are: A-101, AN-103, AN-104, AN-105, AX-101, AX-103, AW-101, S-102, S-111, S-112, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, SX-109, SY-103, T-110, U-103, U-105, U-107, U-108, and U-109. These same tanks are also the subject of TPA Milestone M-40-00 (Section 1.5).

[1] Tank 241-XX-nnn will be referred to in this document as XX-nnn, e.g. Tank 241-AN-101 will be referred to as Tank AN-101. Similarly Tank Farm 241-XX will be referred to simply as the XX Tank Farm; e.g., Tank Farm 241-AN will be referred to as the AN Tank Farm.

The process by which the tanks were identified was described in an early 1991 letter (Harmon 1991). A summary of that process is given to show the relationship to waste parameters. It should be noted that these criteria are not the criteria being used today but they are discussed to provide a historical perspective.

An increase in the waste level, without waste additions, was called slurry growth. The original evaluation focused on the slurry growth phenomena; waste level information implied five double-shell tanks (DST) and 15 single-shell tanks (SST) exhibited slurry growth.

Evaluations were conducted for both DSTs and SSTs regarding the slurry growth. Evaluation parameters for DSTs were: (1) level increase without liquid addition, (2) unexplained pressurizations, and (3) unexplained temperature changes. For the SSTs, the parameters were: (1) level increase without liquid addition, (2) presence of a surface crust, (3) total organic carbon content above 3 g/L, and (4) B-Plant waste in the tank (B-Plant waste and its degradation products are believed to be major sources of hydrogen as they breakdown). Use of these parameters resulted in the identification of two more tanks, bringing the total to 22. Tank SX-109 was added because the ventilation system design for the SX Tank Farm results in the vapor space for 6 listed tanks being vented through the vapor space of SX-109. Thus, the original number of FGWL tanks identified in response to Public Law 101-510, Section 3137, was 23.

A more thorough ranking process (Harmon 1991) was also used to evaluate all 177 tanks at that time (late 1990) to rank the tanks regarding (a) the potential for hydrogen or other flammable gases to be produced and (b) for the potential for the gas to be retained and released at concentrations above the lower flammability limit of hydrogen in air. Factors used for item (a) included waste temperature, the presence of organic compounds, the heat load of the tank (total curies), and the presence of flammable gas. Factors for item (b) were volume of waste, observations of surface level changes, observations of dome space pressurization, presence of a crust layer, and waste type (i.e., slurry, salt cake, double-shell slurry feed, sludge, liquid). The more thorough evaluation based on these factors did not result in the addition of any tanks to the FGWL.

Finally, as noted earlier, two other tanks were added to the FGWL in 1993 (AW-101 and U-107); one because of updated data that showed slurry growth (U-107) and the other because of an observed level fluctuation (AW-101). Thus, 25 tanks constituted the watch list due to the Flammable Gas Safety Issue. These two additional tanks were also included in the flammable gas USQ by Payne (1994). As noted earlier, tank SY-101 has been removed from the watch list, so the current number of tanks is 24.

Criteria for selecting FGWL tanks were revised in 1997 (Cash 1997) and they were approved by the Department of Energy (Kinzer 1997). The report listed the following two criteria:

The selection criterion is:

> *Any tank that can have a flammable gas volume in the dome space that, when ignited, would result in pressure above a containment-related tank design limit will be categorized as a Flammable Gas Watch List tank.*

The criterion for removal is:

> *Any tank that no longer satisfies the selection criterion for the Flammable Gas Watch List will be removed from the Watch List.*

In summary, tanks were put on the Watch List on the basis of process history and engineering judgment. At the time the list was created there were no direct measurements of stored gas and there was very little information on the amounts of flammable gas in the dome spaces of the tanks.

In 1997, a document was issued that described the strategy for resolution of the Flammable Gas Safety Issue (Johnson 1997). Facilitated workshops, including representation from the Hanford Site, the National Laboratories, and DOE, were used to develop the strategy, and sessions were devoted to interpretation of the Watch List criteria. A conclusion of the workshop was that the criteria should be interpreted as meaning "to have significant potential for an unacceptable risk from a spontaneous release of flammable gas." Also, as a result of the workshops, the criterion for removing a tank from the Watch List was interpreted to mean (1) a tank that cannot spontaneously release enough flammable gas to the dome space "which, if ignited...tank design limit" has acceptable risk from the perspective of the Watch List, and (2) this acceptable risk will be demonstrated by compliance with DOE orders in implementing an approved Authorization Basis (Johnson 1997). In other words, the removal criteria recognize that adequate controls have to be in place to address potential induced releases. With respect to spontaneous releases, the maximum consequence of an ignition of flammable gas has to be limited such that the tank maintains its structural integrity. Spontaneous releases large enough to cause the tank headspace to exceed the LFL are not credible.

Removal of tanks from the Watch List requires approval from DOE-Headquarters (Lytle 1994).

One of the requirements of the public law was to implement continuous monitoring to detect a gas release or excessive waste temperature or tank pressure. At the time that the law was enacted all DSTs were equipped with: (1) thermocouples to measure the waste and tank structure temperatures, (2) pressure sensors in the tank dome space, and (3) continuous air monitors in the tank annulus to detect any leaks. Thus, the DSTs placed on the FGWL were in compliance with the monitoring requirements.

The SSTs had thermocouples to monitor the tank temperatures but did not have any pressure sensors. Pressure sensors were installed in the ports of the riser than contained the device for measuring waste level. For passively ventilated tanks the daily changes in barometric pressure masked any changes from small gas releases. It was determined that the continuous gas monitors provided a better indication of tank conditions for gas releases; all SSTs on the FGWL were equipped with these monitors (Section 3.1.3).

1.4 THE FLAMMABLE GAS UNREVIEWED SAFETY QUESTION

A USQ exists when DOE determines that the nuclear safety Authorization Basis governing the activities at a facility or site may not adequately protect the health and safety of the public or the workers, the environment, or government assets. DOE compares existing facilities or activities

and proposed activities to radiological and other protection standards. In the case of the Flammable Gas Safety Issue and the observed gas releases in SY-101, DOE declared a USQ in 1990 because the existing controls and analyses did not consider the observed and postulated tank waste phenomena.

The origin of the flammable gas USQ was described in Section 1.1, and the tanks encompassed by that USQ were noted in Section 1.3. In June 1996 DOE-RL (Wagoner 1996a) closed the USQ for SY-101 because the mixer pump had mitigated the spontaneous gas release situation (see Chapter 4.0).

The original USQ was updated in July 1996 bringing a consolidation of earlier determinations into one overall flammable gas USQ determination that was adopted by DOE-RL on November 1, 1996 (Wagoner 1996b). The expanded USQ applied to 149 SSTs and 27 DSTs (excluding SY-101). The expanded USQ for 176 tanks has been closed. The USQ for AX-104 was closed by DOE-RL in April 1998 (Wagoner 1998a) and for other tanks in September 1998 (Wagoner 1998b). The closure of the flammable gas USQ for tank farm SSTs and DSTs was based on flammability, ignition, and monitoring controls implemented as part of the Authorization Basis; the adequacy of controls for safe storage of waste; and the satisfactory implementation of these controls (Wagoner 1998a and 1998b).

Another USQ (TF-97-0975) was declared for tank SY-101 in 1998 because of an unexpected rise in the waste level (Kinzer 1998). This USQ, which was closed in November 2000 (Boston 2000a), is discussed in Section 4.1.

1.5 TRI-PARTY AGREEMENT MILESTONE M-40-00

The Tri-Party Agreement (Ecology et al. 1996) was established between the Washington State Department of Ecology, the U.S. Environmental Protection Agency, and the DOE in 1989. Specific milestones were established for the various programs at the Hanford Site. TPA Milestone M-40-00, "Mitigate/Resolve Tank Safety Issues for High Priority Watch List Tanks," was established in January 1994 and has a due date of September 30, 2001. The specific wording of M-40-00 states:

> "High priority watch list tanks are those single-shell and double-shell tanks identified, in accordance with Section 3137 of Public Law 101-510, which have a serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure. These include flammable gas generating tanks, ferrocyanide containing tanks, organic/nitrate containing tanks, and a high heat-producing tank. Corrective action strategies will be developed for these tanks. This milestone will be complete when mitigation activities, if required, have been implemented in all watch list tanks to ensure safe storage of waste during the interim period until retrieval for treatment and/or disposal operations begin. For those safety issues mitigated pursuant to this milestone, safety resolution will be dependent upon final treatment of the waste. Mitigation will allow, however, the characterization retrieval, etc., of these wastes prior to final treatment. Some safety issues may also be resolved if (1) resolution out-of-tank

> is not required, or (2) resolution out-of-tank with or without treatment takes place within the time period of this milestone."

The safety issues for ferrocyanide, organic/nitrate, and high heat have been resolved. In the case of the ferrocyanide and organic/nitrate issues, closure was based on showing that these compounds did not exist or that the presence of a small amount of these compounds did not result in any type of propagating chemical reactions or that their concentrations were so low that self-sustaining propagating chemical reactions were not plausible. The high heat issue was limited to one SST (C-106) and was resolved by transferring some of the waste from the tank to a DST. The flammable gas issue is quite different in that flammable gases are present in all of the waste tanks. However, evaluations have shown that the hazard can be managed by following the established control process as will be shown in this report.

When the Flammable Gas Safety Issue is closed (see Section 10.0), the TPA milestone will be completed and the DOE will notify the U.S. Environmental Protection Agency and Washington State Department of Ecology. As noted earlier, the Flammable Gas Safety Issue has already been closed for tank SY-101.

1.6 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 93-5

In July 1993 the Defense Nuclear Facilities Safety Board (DNFSB) transmitted Recommendation 93-5 (Conway 1993) on the Hanford Waste Tank Characterization Studies to the DOE. Recommendation 93-5 noted that insufficient tank waste technical information was available to ensure that Hanford Site wastes could be safely stored and that associated operations could be conducted safely. As a result, the DNFSB recommended that the characterization effort be upgraded and expedited.

The DNFSB accepted an Implementation Plan in March 1994 (Conway 1994). Equipment upgrade difficulties and poor rotary-mode sampler reliability prevented completion of the commitments in the original implementation plan. Subsequent revision of the Implementation Plan (DOE/RL 1996) focused characterization efforts on understanding safety-related phenomena to expedite resolution of waste tank safety issues.

The Recommendation 93-5 Implementation Plan (DOE/RL 1996) included twelve deliverables associated with the Flammable Gas Safety Issue. All items, including the ones for flammable gas, were completed and DOE submitted a proposal in October 1999 to the DNFSB for closing Recommendation 93-5 (Richardson 1999). The DNSFB quickly responded and closed 93-5 in November (Conway 1999). One of the significant items of the 93-5 effort centered on characterization of the waste in the tanks (Simpson 1999); this report provided the technical basis that the characterization data were sufficient to ensure safe storage of the waste. The following point was noted in Secretary Richardson's letter to the DNFSB:

> "All tanks are sufficiently characterized to support safety of storage and planning for Phase One of waste retrieval and Vitrification."

The same letter also stated:

> "Flammable gas hazards have been identified and are monitored for specific tanks. Controls are imposed to prevent development or ignition of explosive mixtures."

This is a very important point with regard to meeting the Tri-Party Agreement milestone and for removal of tanks from the FGWL. In conjunction with the observed behavior presented in the documents supporting this report, satisfactory resolution of DNFSB 93-5 is basic to resolution of the Flammable Gas Safety Issue.

1.7 OUTLINE OF THIS REPORT

The approach for resolution of the safety issue was outlined in Section 1.2 and the process was shown in Figure 1-1.

Resolution of the Flammable Gas Safety Issue involves many aspects of understanding the behavior of the waste and the actions needed to revise the Authorization Basis. In dealing with the safety issue, certain "boundaries" needed to be established; actions pertaining to this were:

- The subject tanks for the TPA Milestone M-40-00 were identified.
- The boundary of the safety issue and the Tri-Party Agreement milestone is for "safe storage;" actions pertaining to tank operations for waste mixing, transfers, retrieval or any other "planned operations" are not considered to be part of the safety issue. Approved Authorization Basis controls were in place for the following successful Tank Farm key accomplishments: saltwell pumping of SSTs, sluicing of tank C-106, and operation of mixer pumps in a double-shell waste tank. This experience is directly applicable to future operations for mixing, transfer, and retrieval.

Specific actions completed at the Hanford Site for resolution of the safety issue have included:

- An action plan for response to abnormal conditions was issued (Sherwood 1994)
- A program strategy for resolution of the safety issue was issued (Johnson 1997)
- The only tank "mitigated" was SY-101; this was done with a mixer pump for eliminating the GREs. Transfers coupled with back dilutions remediated the level rise issue.
- Extensive sampling and characterization of the tanks have been accomplished.
- Mitigation is not required for the 24 Watch List tanks; they have been characterized for waste contents, gas compositions, and gas releases.
- A suite of controls (Technical Safety Requirements) has been implemented and has been successfully used since 1997.

- The flammable gas and surface level rise USQs have been closed for the 177 storage tanks and SY-101, respectively.

- Finally, actions regarding DNFSB Recommendation 93-5 have been completed.

The report provides a summary of all of the work completed to evaluate and understand the behavior of the flammable gas tanks. Extensive studies have been conducted to understand gas generation, retention, and release. Chapter 2.0 provides an overview of the conclusion of the studies. Waste characterization, via core sampling, retained gas sampling, in situ measurements of gas content and waste properties, dome space sampling and specialized laboratory tests have been conducted on tank wastes. These efforts are discussed in Chapter 3.0. Since SY-101 was the original reason for the flammable gas USQ, safety issue, and FGWL, it will be discussed in more detail than the other tanks. Chapter 4.0 is devoted to SY-101 and provides an overview of the tank's behavior, results of its characterization studies, and results of operating its mixer pump. Chapter 4.0 also describes the recent work conducted for waste transfers and back dilution of the waste in SY-101.

Data obtained for DSTs and SSTs are reviewed in Chapters 5.0 and 6.0 respectively. Studies were conducted to understand the flammable characteristics of the gas mixtures found in the tanks and that work is described in Chapter 7.0.

Hazards have been assessed and controls are in place with an approved nuclear safety Authorization Basis as noted in Chapter 8.0. Monitoring for flammable gas is required in tanks under specific circumstances as one of the actions required by the Authorization Basis.

Chapter 9.0 summarizes the basis for removing the tanks from the FGWL, and Chapter 10.0 summarizes the bases for resolution of the Flammable Gas Safety Issue.

2.0 THE CHEMISTRY AND PHYSICS OF GAS GENERATION, RETENTION, AND RELEASE

While the observed behavior of the tanks is the key to addressing the Flammable Gas Safety Issue and the FGWL, some discussion concerning the chemistry and physics of flammable gas is warranted. This provides a basis for understanding the observed behavior.

Gas generation is the ultimate source of the hazard, gas retention is a measure of the potential hazard, and gas release coupled with ignition represents the actual hazard. The chemical and physical factors that govern these processes have been investigated during the past decade to define the origins of the gases and their behavior within the waste. The findings of these studies, which are the focus of the following sections, are relevant for the description of the behavior of the waste in other tanks as well as the tanks on the FGWL.

Section 2.1 provides a background on flammable gas generation that is applicable to all tanks in general and Watch List tanks in particular. While gas retention is also applicable to all tanks to some extent, Section 2.2 takes the issue the next step with respect to the Watch List tanks. Section 2.3 becomes the focal area of the Chapter in that the information on gas release is quite specific to FGWL tanks.

2.1 GAS GENERATION

Hydrogen, nitrogen, nitrous oxide, ammonia, methane and other organic compounds are found in the dome spaces of waste tanks and in the liquid and solid wastes (Johnson et al. 1997, Mahoney et al. 1999). Stock (2000) reviewed the work that has been done during the past decade at universities, national laboratories, and the Hanford Site to establish the chemical origins of these gases. This section briefly summarizes the conclusions of those investigations.

Hydrogen is formed in Hanford Site waste in three distinct ways. First, hydrogen is formed by the radiolysis of water. Second, hydrogen is formed during the corrosion of the steel tank walls. Third, hydrogen is formed during the cascade of radiolytic and chemical oxidation reactions of the organic compounds in the waste.

Early investigations established that sodium nitrite and sodium nitrate inhibited hydrogen formation during the radiolysis of water and that the rates of corrosion were too slow to account for the observed rates of hydrogen generation from the prominent FGWL tanks. Consequently, the investigators focused their attention on the pathways that led to the more rapid generation of hydrogen in the presence of organic compounds.

Historical records indicate that organic complexants, organic phosphate esters, and organic hydrocarbons were employed during separations and other operations. Waste characterization work established that the wastes contain portions of the original materials including ethylenediaminetetriacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), glycolic acid, and citric acid in the form of their sodium salts, tributyl phosphate and sodium bis(2-ethylhexyl)phosphate, and an array of paraffinic hydrocarbons with 11 to 14 carbon atoms.

Targeted laboratory work and characterization work showed that the original complexants were converted to other substances including ethylenetriaminetriacetate ion, nitrilotriacetate ion, and iminodiacetate ion. Some degradation reactions of the complexants form two carbon atom compounds including acetate and oxalate ion and others provide formate and carbonate ion.

Other targeted investigations showed that tributyl phosphate decomposes under the conditions that prevail in the waste tanks to produce butanol and dibutylphosphate ion and that dibutylphosphate ion reacts to give butanol and monobutylphosphate ion. The work with the phosphate esters also established that other oxidized and fragmented derivatives were produced.

The characterization work on the dome spaces of the tanks and the other investigations of the volatile and semivolatile organic compounds retained in the liquid and solid wastes are in accord with the idea that a broad array of fragmented and oxidized organic compounds including homologous series of alkanes, alkenes, alcohols, aldehydes and ketones, and nitriles are formed from the original hydrocarbons with 11 to 14 carbon atoms. These fragmented and oxidized compounds are also degraded so that the wastes now contain hundreds of different organic compounds. The analysis of the organic compounds in a sample of retained gas revealed that it contained methane and lesser amounts of other low molecular weight organic compounds with one or two carbon atoms such as methanol and ethanol that are plausible products of the decomposition of the complexants. However, the retained gas also contained many compounds with three or more carbon atoms including propane, cyclopropane, propene, propanol, acetone, and nitropropane that are remnants of the solvents and phosphate esters.

The relative rates of depletion of the principal complexants and phosphate esters have been determined. Among the four original complexants, HEDTA and glycolate ion decompose more rapidly than EDTA or citrate ion. Tributyl phosphate decomposes much more rapidly than bis(2-ethylhexyl)phosphate ion. Formate ion is the most reactive compound among the common highly fragmented end products such as acetate ion or oxalate ion. The hydrocarbons react much more slowly than the complexants or tributyl phosphate. Eventually, the slow aging reactions will convert organic carbon into inorganic carbonate ion.

Targeted investigations have found that the oxidation reactions of the organic compounds occur in several ways. Some of the oxidation reactions are initiated by radiolysis. Similar free radical reactions are initiated by inorganic radicals produced in the waste in the absence of radiation. Lastly, the constitution of the waste, especially the high hydroxide ion concentrations, promotes other ionic reactions that lead not only to the oxidation of the organic molecules but also to the formation of gas.

A chemical model has been used to describe the chemistry that occurs in spurs and the chemistry that is responsible for the oxidation of the organic compounds. The model has been applied to describe the oxidation of formate ion, one of the principal organic compounds remaining in the waste, and glycinate ion, another waste constituent that provides perspective regarding the chemical reactions of the nitrogen-containing complexants. The chemical features of the models are outlined in the following discussion. The radiolytic pathway for the oxidation of the organic compounds and gas formation begins with the decay of radioactive nuclei in the waste. The energetic particles produced in the decay processes ionize the constituents in proportion to their electron density. Consequently, the predominant initial products of the water-rich alkaline solutions of sodium nitrite and sodium nitrate are NO_3^{-2} and the customary products of the

radiolysis of water including H, OH, and the solvated electron. Targeted investigations establish that the solvated electron is consumed in a reaction with nitrate ion and that H, OH and O^-, and NO_3^{-2} are the main products of the very rapid, inhomogeneous initial reactions that occur in spurs. Hydrogen is not produced by the chemical reactions of NO_3^{-2}. Rather, the laboratory work has shown that NO_3^{-2} reacts rapidly with hydroxide ion to produce NO_2. The products of the chemistry in the spur are shown in the equation.

$$\text{Radiolytic processes} \rightarrow \text{H, OH and } O^-, NO_2$$

The free radical reagents that participate in the ensuing homogeneous chemical reactions of the inorganic and organic compounds in the waste are H, OH and O^-, NO, and NO_2. The radiolytic sequence is summarized as follows:

$$\text{Organic compounds} + \text{reactive free radicals} \rightarrow \text{organic free radicals}$$
$$\text{Organic free radicals} + \text{OH and } O^-, NO, NO_2 \rightarrow \text{reactive organic intermediates}$$

The reactive organic intermediates shown in the equation include aldehydes, ketones, nitroso compounds and nitro compounds. Many of the molecules formed from the complexants have more than one functional group bonded to one carbon atom and spontaneously react with water.

Laboratory investigations indicate that reactions between the organic constituents and free radicals can also occur in the absence of radiation. The information on this phase of the reaction chemistry is fragmentary, but the available results imply that NO and NO_2 are the principal reagents. The reaction sequences presumably proceed in the manner outlined in the previous paragraph.

Lastly, other targeted studies have shown that chemical processes that do not involve reactive free radicals occur in parallel with the radical reactions to produce reactive organic intermediates.

$$\text{Organic compounds} + \text{ionic reagents} \rightarrow \text{reactive organic intermediates}$$

The original constituents having hydroxyl groups undergo aluminate ion-catalyzed oxidation reactions. Aldehydes that are formed during the radiolytic and thermal reactions are converted into carboxylate ions in oxidation reactions catalyzed by hydroxide ion. The reactive nitroso and nitro compounds formed during the reactions of the organic radicals with nitric oxide and nitrogen dioxide react with water to give aldehydes and ketones.

These chemical and radiolytic processes have been blended to provide a comprehensive reaction model that is consistent with the characterization results and the laboratory investigations (Stock 2000).

Only a small portion of the hydrogen that is formed in alkaline solutions of the waste is produced through direct radiolysis of the organic compounds because the concentrations (electron density) of the organic compounds are very low compared with water and the inorganic salts. The conditions for hydrogen formation through hydrogen atom abstraction reactions are unfavorable because this reagent reacts so rapidly with other inorganic substances. Rather, hydrogen and the

other gases are formed in the reactions of the reactive organic intermediates in the later stages of the chemistry.

Reactive organic intermediates $\rightarrow$ oxidized organic compounds + gases

Specifically, hydrogen is produced during the hydroxide ion-catalyzed oxidation reactions of the aldehydes that are intermediates in many of the reaction sequences of the organic compounds. The stoichiometry for the oxidation of formaldehyde to formate ion is shown in the next two equations.

$$H_2CO + 2\,HO^- \rightarrow H_2C(O^-)_2 + H_2O$$
$$H_2C(O^-)_2 + H_2O \rightarrow HCO_2^- + H_2 + HO^-$$

The reactions of other aldehydes proceed in a similar fashion. For example, the oxidation of glycolate ion yields glyoxylate ion. The oxidation of this compound to oxalate ion produces hydrogen. Similarly, the base-catalyzed oxidation of formate ion to carbonate ion yields hydrogen. Inasmuch as aldehydes are intermediates in many reactions of the waste molecules, these reactions account for a considerable portion of the hydrogen generated in the waste. Although the initial reagents responsible for the formation of the aldehydes may be formed in radiolytic processes that have no activation energy, hydrogen is formed in a subsequent conventional chemical reaction. Consequently, the measured radiolytic rates of hydrogen formation are temperature dependent.

Ammonia arises in part from the oxidation reactions of the nitrogen-containing complexants. The reaction sequences that degrade EDTA and HEDTA eventually lead to the formation of a molecule with a primary amino group. The radiochemical reactions of glycine, which is a common intermediate in the reaction pathways of these complexants, provide ammonia as one of the reaction products. Ammonia also is formed by the hydrolysis of nitriles and amides that are produced during the oxidation reactions of other organic compounds in the waste.

Targeted laboratory investigations indicate that organic compounds are intimately involved in the formation of nitrogen, nitrous oxide, and additional ammonia. Nitric oxide and nitrogen dioxide are important reagents in reaction cascades that lead to the oxidation of the organic compounds and simultaneously lead to the reduction of nitrate or nitrite ion. The targeted laboratory investigations have led to the identification of the nitrosyl anion and hydroxylamine as important intermediates in the formation of the nitrogen-containing gases. One reaction sequence is displayed to show the conversion of inorganic nitrite ion into hydroxylamine.

$$NO_2^- + H \rightarrow NO + OH^-$$
$$RCH_2 + NO \rightarrow RCH_2NO$$
$$RCH_2NO \rightarrow RCH{=}NOH$$
$$RCH{=}NOH + H_2O \rightarrow RCHO + NH_2OH$$

The first reaction displays the reaction between hydrogen atom and nitrite ion to produce nitric oxide. The second step shows the recombination reaction between a primary radical in the waste and nitric oxide to produce a C-nitroso compound that is converted into an isomeric oxime in the next step. The last step in the sequence shows the reaction of the oxime with water to give an aldehyde and hydroxylamine.

Hydroxylamine is unstable in alkaline solutions and the decomposition is catalyzed by a variety of metal ions. The complex decomposition reactions lead primarily to nitrogen and ammonia, but nitrous oxide is a known byproduct of the chemistry.

Nitrous oxide is also formed by reaction pathways that involve the nitrosyl anion. This anion is produced in several different ways and one general example is shown to illustrate this aspect of the chemistry.

$$NO_3^{-2} + H_2O \rightarrow NO_2 + 2\,OH^-$$
$$RCH_2 + NO_2 \rightarrow RCH_2NO_2$$
$$RCH_2NO_2 + OH^- \rightarrow RCHO + NO^- + H_2O$$
$$H_2O + 2\,NO^- \rightarrow HON{=}NOH + 2\,OH^-$$
$$HON{=}NOH \rightarrow H_2O + N_2O$$

The reaction sequence begins with the formation of nitrogen dioxide. The formation and oxidative decomposition of a nitro compound are illustrated in the next two equations. Nitrosyl anion, which is a product of the third reaction, readily forms an unstable dimer that provides nitrous oxide.

Other studies have demonstrated that the rates of gas generation rates are highly sensitive to temperature and depend on the concentrations of the radioactive isotopes, principally strontium and cesium, organic compounds, and inorganic reagents such as aluminate, nitrite, nitrate, and hydroxide ion.

Hu (2000) developed an empirical rate equation that describes the dependence of the hydrogen generation rates on the properties of the radiolytic constituents and the chemical content of the tank waste and its temperature. In addition to the thermolytic and radiolytic hydrogen generation rates, the total generation rate also includes a factor for tank wall corrosion that conservatively assumes a corrosion rate of 0.003 cm/hr (0.1 mil/yr) for carbon steel and that one mole of hydrogen is generated per mole of iron corroded.

The empirical rate equation for the hydrogen generation rate (HGR) in Hanford Site waste developed by Hu considered the thermal reaction, HGR(thm), the radiolytic rate, HGR(rad), and the corrosion process, GGR(corr). This rate equation considers waste composition (total organic carbon [TOC], Al, NO_3^-, NO_2^-), radiation dose, temperature, liquid fraction, and wetted area. The rates of the thermal and radiolytic reactions are assigned activation energies that are in accord with laboratory observations. This empirical correlation was developed from data for 28 tanks, which included tank 241-SY-101 and 17 tanks that are on the FGWL.

Hu (2000) compared the predictions of the model with the observed hydrogen gas release rates for 28 tanks for which sufficient information was available. Comparison of the calculated generation rates and the observed release rates for the 28 tanks indicated that the calculated generation rates generally were within a factor of 2 to 3 of the field observations. Hu (2000) also found that the calculated rates of gas generation by radiolysis and thermolysis in moles of hydrogen/kg of waste-day spanned a large range for these 28 tanks in accord with the variations in the chemical and physical properties of the wastes. The calculated amounts of hydrogen generated because of corrosion are considerably more uniform and small. When the conditions for the thermolytic and the radiolytic generation of hydrogen are unfavorable, corrosion is the

dominant source of hydrogen. The model indicates this situation prevails in 14 of the 28 tanks and that these tanks generate from 10 to 90 L/d of hydrogen. In contrast, the predicted rates of hydrogen generation for the 14 tanks for which radiolysis and thermolysis are dominant ranged from 100 to 930 L/d.

Applications of the model are discussed in Sections 5, 6, and 7.

2.2 GAS RETENTION MECHANISMS

This section presents an overview of the physics of gas retention in tank waste. As noted in Section 2.1, gas is generated in solution in the liquid waste by radiolysis of water, and by thermal and radiolytic decomposition of organic compounds. However, except for ammonia and, to a lesser extent, nitrous oxide, the generated gases are not very soluble and most of the gas comes out of solution as bubbles. Ammonia is very soluble, and most of it remains in solution. Bubbles are the most important mode of gas retention and release concerning flammability.

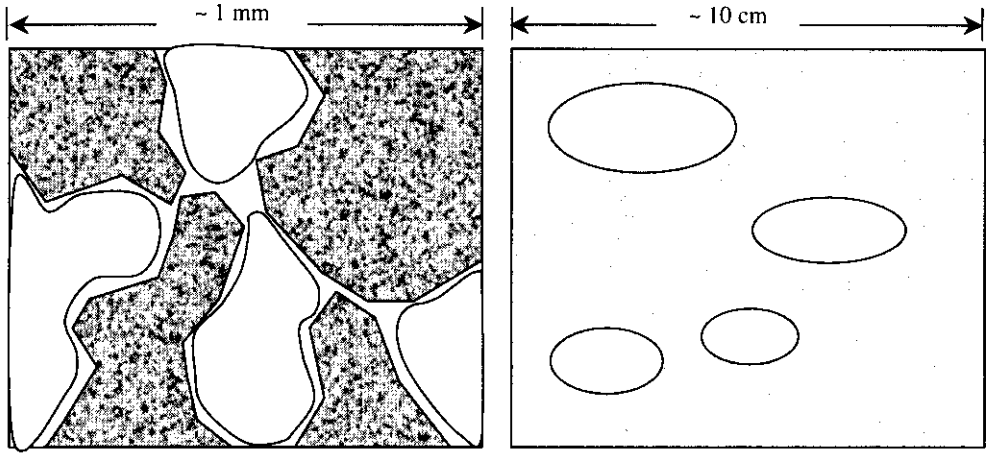
The principal mechanisms of bubble retention can be grouped into three categories: bubbles retained by direct attachment to particles, bubbles retained between particles by capillary forces, and bubbles retained by the strength of the surrounding waste. In layers of liquid-saturated settled solid particles, called sediment, bubble retention is dominated by capillary forces and the waste strength; direct attachment of bubbles to particles plays a minor role. The two dominant bubble retention mechanisms are discussed below.

The experimental and theoretical evidence presented above show that the maximum gas retention occurs in relatively weak waste with minimal lithostatic load. Thus the increased waste strength that might result from future decreases in waste temperatures is not expected to increase gas retention. This is borne out by the absence of any indications of increased gas retention (e.g., waste level rise, increase in nonconvective layer [NCL] thickness) in response to waste temperature decreases over the past 5 years. The dramatic increase in lithostatic load accompanying saltwell pumping further tends to reduce or limit total gas retention as interim stabilization proceeds.

2.2.1 Bubble Retention by Capillary Forces

Lithostatic load at any elevation is given by the weight of the particles above. Bubbles can be held in the interstitial spaces or pores between particles by capillary forces when the lithostatic load is sufficient to hold the particles in contact against the force of the bubble's internal pressure trying to push them apart. This retention mechanism requires either relatively large pores, which reduces the internal bubble pressure, or a deep waste column, which increases the lithostatic load, or both. These bubbles assume an irregular, dendritic shape conforming to the passages between the particles. When the internal pressure of a bubble overcomes the effect of the lithostatic load, it pushes the surrounding particles apart. The bubble is then restrained by the yield strength of the bulk waste as a particle-displacing bubble. The difference between these two types of bubbles is illustrated in Figure 2-1.

Figure 2-1. Bubbles Retained by Capillary Forces and by Waste Strength.



(a) Bubbles held within pores between particles by capillary forces.

(b) Bubbles held by the strength of the waste.

Whether a bubble is held by yield strength or capillary force is indicated by the Bond number criterion developed by Gauglitz et al. (1994, 1995, and 1996). This dimensionless number contains two parameters, a ratio of gravitational force to surface tension force, and a ratio of waste strength force to surface tension force. If the number exceeds unity, a bubble is held by capillary forces between particles in the pore-filling configuration. The Bond number is expressed as:

$$N_{Bo} = \frac{\Delta\rho g H_S D_p}{4\sigma} + \frac{\tau_Y D_p}{4\sigma} A \qquad (2\text{-}1)$$

where

H_S is the height of the lithostatic column above the bubble

D_P is the mean pore diameter through which a bubble must pass to escape retention. Assumed to be represented by the particle diameter.

$\Delta\rho$ is the difference between solid and liquid density

σ is the surface tension

τ_Y is the yield stress

g is the acceleration due to gravity

A is an area ratio related to how the yield stress resists bubble expansion; it was estimated to be 2.8 by Gauglitz et al. (1995) based on laboratory experiments.

The upper limit on the vertical extent of a pore-filling bubble can be derived from the balance of capillary forces and the hydrostatic pressure difference between the top and bottom of the bubble (Stewart et al. 1996a). As the bubble grows, the hydrostatic pressure difference between the top and bottom of the bubble increases. The depth and curvature radii of the liquid-gas interfaces continually readjust themselves so that the uniform and increasing gas pressure inside the bubble balances the external, nonuniform hydrostatic pressure. When the bubble internal pressure overcomes the restraining force of surface tension, gas pushes out of the top of the bubble and liquid flows into the bottom of the bubble causing the bubble to move upward. The gas volume fraction at which this motion occurs is called the percolation threshold. The maximum height, Δh, that a pore-filling bubble can attain before percolating is expressed as

$$\Delta h = 4\sigma/\rho_L g D_p \tag{2-2}$$

where

- σ is the surface tension
- ρ_L is the liquid density
- g is the acceleration of gravity
- D_p the mean pore diameter through which a bubble must pass to escape retention. Assumed to be represented by the particle diameter.

Although they may represent a considerable gas volume, pore-filling bubbles are not a direct flammability concern because there is no mechanism for them to release the gas rapidly. In order for gas in a pore-filling bubble to move, liquid must be displaced from the pores the bubble enters and flow into the pores the bubble vacates. Flow of the liquid through the small pores in the waste is a very slow process.

2.2.2 Bubble Retention by Waste Strength

If a bubble is retained by the strength of the waste, as determined by the Bond number in Equation 2-1, the bubble shape is determined by a balance of surface tension and waste strength. With relatively weak waste or small bubbles, surface tension pulls bubbles into an approximately spherical shape. If the effect of waste strength is greater than surface tension forces, the bubble grows into the weakest area of the waste surrounding it and assumes a dendritic shape. Particle-displacing bubbles that are not dendritic are called "round" bubbles, even though they may be ellipsoidal or similarly distorted from a truly spherical shape. A bubble shape criterion is derived from simple scaling of the relative importance of strength-to-surface tension. The maximum diameter of round bubbles, D_b, before they begin to assume a dendritic shape is given by:

$$D_b < \frac{\sigma}{\tau_y} \tag{2-3}$$

where

τ_y is the yield stress
σ is the surface tension
D_b is the bubble diameter.

A bubble can grow vertically only until its buoyancy exceeds the ability of the waste to hold it in place. The release of small bubbles in this manner is believed to comprise the steady background gas release observed in waste tanks. A criterion for incipient motion of a solid sphere immersed in a Bingham fluid can be derived in terms of the yield stress, bulk density and a critical gravity-yield number, Y_G (Chhabra and Uhler 1986). The resulting limiting diameter is expressed as

$$D_b < \frac{\tau_y}{\rho_w g Y_G} \tag{2-4}$$

where

ρ_w is the bulk waste density

g is the acceleration of gravity

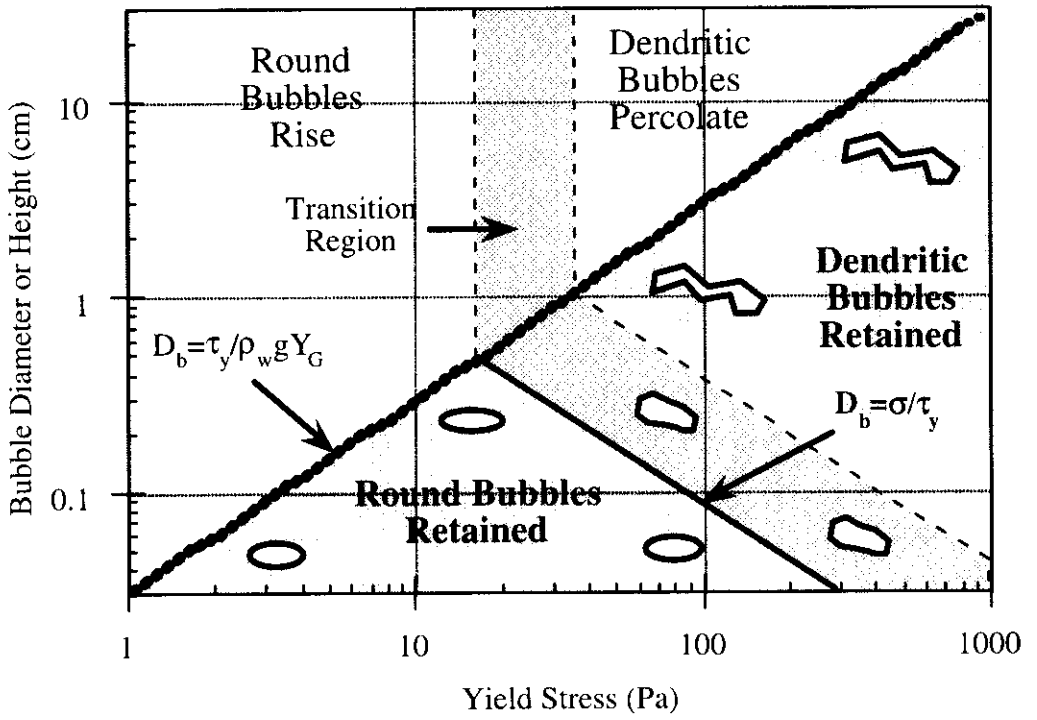
The number Y_G is estimated at 0.2 for use with yield strengths (τ_y) as measured at Hanford (Stewart et al. 1996a).

The combined criteria of Equations 2-3 and 2-4 limit the round bubble diameter to 0.5 to 1 cm. This size is essentially constant over the range of Hanford tank waste properties (bulk nonconvective layer density of 1500 to 1800 kg/m^3, surface tension of 0.08 to 0.1 N/m) as shown in Figure 2-2. The range of yield stresses shown on the abscissa represents the expected range of tank waste strength. This is quite consistent with observations of bubbles in waste samples and simulants.

Equation 2-4, which is quantified on the vertical scale of Figure 2-2, also gives the limiting height of dendritic, particle-displacing bubbles. When they grow to the limiting height, the increased hydrostatic pressure difference pinches off the bottom of the bubble and pushes the top of the bubble upward in a manner similar to the migration of pore-filling bubbles. However, the motion of particle-displacing bubbles is much faster since it does not require liquid to flow through a porous medium. This "percolation" of dendritic, particle-displacing bubbles is believed to be the primary mechanism for the spontaneous releases observed in the headspace gas monitoring data on SSTs.

Figure 2-2 and Equation 2-4 indicate that the limiting height of a dendritic bubble increases with waste strength. Waste with a yield stress of 3500 Pa could theoretically support a dendritic region 1 m in height. However, experiments have shown that if the waste yield stress exceeds a few hundred Pascals, the bubbles do not collapse and a connected network forms that allows the gas to escape and prevents further retention (Gauglitz et al. 1996). The lateral extent of dendritic bubbles also is limited such that voids large enough to collect a significant volume of gas are not plausible (Stewart et al. 1996a).

Figure 2-2. Limiting Bubble Size in Hanford Tank Waste.



2.3 GAS RELEASE

Gas is released from the waste when the gas retention mechanism is interrupted. Gas retention and release mechanisms are determined by the waste layering or configuration as well as the waste composition and physical properties. The effects of the different waste types and configurations on the retention and release of gas are considered in this section. Waste types and configurations are described in Section 2.3.1, buoyant eruptions are discussed in Section 2.3.2, and gas release mechanisms in typical SSTs are summarized in Section 2.3.3. Releases from less common waste configurations are mentioned in Section 2.3.4.

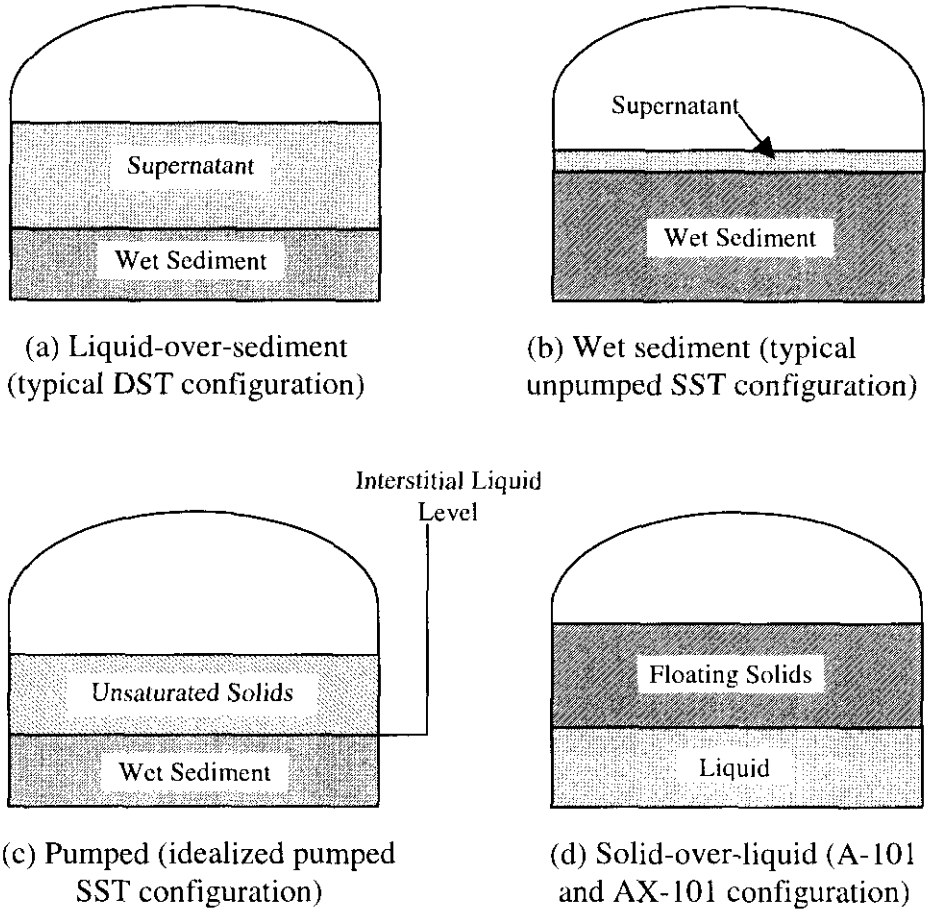
2.3.1 Waste Types and Configurations

The three waste types of interest are liquid, sludge, and salt cake (SC). Liquid is a solution of dissolved inorganic and organic compounds in water that contains at most a small fraction of suspended solid particles. Liquid that lies over a layer of settled solids is called supernatant. The solid particles that have settled to the tank bottom with liquid between them form a sediment layer that consists of sludge or salt cake waste. Sludge consists of fine particles that are mostly metal oxide. Salt cake is the settled precipitate of sodium salts created from cooling saturated solution. Sludge solids are less soluble than salt cake solids. Sludge consists of fine particles (diameters averaging on the order of a micron or less), whereas salt cake particles are generally larger (diameters averaging in the tens of microns). A "salt-slurry" waste type of relatively fine salt cake is typically found in DSTs and some SSTs. Some tanks contain a mixture of sludge and

salt cake that can be considered a "mixed" waste type. However, the mixed waste appears to behave as salt cake in most cases and will not be discussed separately here.

Waste configuration is the arrangement of waste types in layers within a tank. The waste types are distributed within the tanks in only a few different configurations, depending mainly on the amount of liquid. In order of decreasing amount of liquid, the main waste configurations are "liquid," which is almost entirely the liquid waste type; "liquid-over-sediment," where a relatively deep layer of supernatant overlies an equally deep layer of which is a liquid-saturated sediment;[1] "solid-over-liquid," which is the entire mass of undissolved solids in the tank floats on a dense liquid layer; "wet sediment," which is sediment saturated with liquid, and there is little or no supernatant; and "pumped," which has had interstitial liquid reduced by saltwell pumping such that the interstitial liquid level (ILL) is well below the waste surface. The last four of these configurations are illustrated in Figure 2-3.

Figure 2-3. Waste Configurations.



(a) Liquid-over-sediment (typical DST configuration)

(b) Wet sediment (typical unpumped SST configuration)

(c) Pumped (idealized pumped SST configuration)

(d) Solid-over-liquid (A-101 and AX-101 configuration)

[1]Strictly speaking, a porous medium containing even a little gas is not completely saturated. However, if the gas phase is discontinuous (i.e., bubbles), the sediment is considered to be functionally saturated with liquid.

The DSTs contain either the liquid or liquid-over-sediment configurations. The waste configuration in the SSTs is either wet sediment or pumped, except for A-101 and AX-101, which are the only tanks with the solid-over-liquid configuration. In many SSTs, nonuniform cooling, precipitation, and compaction have created a configuration in which the center region is generally wetter and softer, and may have subsided to create a dished upper surface. However, rather than denote this as a separate waste configuration, it is simply noted that there is considerable variation among the tanks with the nominal "wet sediment" and "pumped" waste configurations.

Two other waste configurations are also of interest: "crust," a solid-over-liquid arrangement consisting of a relatively thin floating layer of gas-bearing solids, and "mixed slurry" in which most of the solid particles and small gas bubbles are kept in suspension mechanically. A crust exists only with the more concentrated salt cake wastes in a few DSTs as a modification of the liquid-over-sediment configuration. Mixed slurry existed in SY-101 when the mixer pump was operating and will be created in other DSTs if mixer pumps are installed and operated.

Only the liquid-over-sediment waste configuration has exhibited spontaneous gas releases sufficiently large to make a tank's headspace flammable (this has only occurred in SY-101, see Chapter 4.0). Gas releases in this waste configuration result from the sediment layer becoming buoyant with respect to the supernatant and are called buoyant eruptions or buoyant displacement gas release events (GRE).

2.3.2 Gas Release by Buoyant Displacement

A buoyant displacement gas release can occur in tanks with a deep layer of supernatant when a portion, or "gob," of the settled solids accumulates sufficient gas to become buoyant with respect to the liquid above it, breaks away and rises through the liquid. The stored gas bubbles expand as the gob rises, disrupting the surrounding waste so a portion of the gas can escape into the dome space. After releasing gas until it is no longer buoyant, the gob sinks back to the bottom of the tank. The gas volume fraction, α_{NB}, required for the sediment layer to become neutrally buoyant is defined by:

$$\alpha_{NB} = 1 - \frac{\rho_L}{\rho_W} \tag{2-5}$$

where ρ_L and ρ_W are the liquid density and sediment bulk gas-less density, respectively.

The more nearly equal the densities (i.e., the more concentrated the dissolved solids in the liquid), the smaller the gas volume required for neutral buoyancy.

Whether or not gas can accumulate until the average gas fraction reaches buoyancy depends on the balance between steady-state gas release and gas generation. If generation exceeds release, gas will accumulate. Generally the release rate increases as gas accumulates so that it eventually balances generation, and equilibrium is achieved. A series of physical parameters have been developed to estimate whether the average gas fraction at equilibrium exceeds neutral buoyancy and buoyant eruptions can occur. These range from the average density of the entire waste

volume to a model based on bubble migration and are described in detail by Meyer and Stewart (2001). The parameters used to plan the remediation of SY-101 are described in Chapter 4.0. As of January 2001, only five of the DSTs (AN-103, AN-104, AN-105, AW-101, and SY-103) exhibit buoyancy driven gas releases.

2.3.3 Gas Release Mechanisms in SSTs

Of the 19 SSTs on the FGWL, eight tanks have been saltwell pumped (S-112, SX-104, SX-105, SX-106, T-110, U-103, U-105, U-109), nine have the wet-sediment waste configuration (AX-103, S-102, S-111, SX-101, SX-102, SX-103, SX-109, U-107, U-108) and two tanks have the solid-over-liquid configuration (A-101, AX-101). The wet sediment tanks contain a significant amount (>200 cubic meters) of stored gas. In the salt cake waste type, assuming 30-micron particles, Equation 2-1 states that the upper several meters will retain individual round bubbles while the bottom few meters will contain pore-filling bubbles due to the high lithostatic load. Sludge waste, assuming a 1-micron particle diameter, will retain gas as particle-displacing bubbles at any depth attainable in SSTs. The wet sediment tanks with the salt cake waste type have the highest gas fraction and deepest waste; therefore, they account for most of the total retained gas volume (Hedengren et al. 2001).

The characteristics of spontaneous gas releases from the wet sediment configuration depend to a great degree on how the gas is stored. For example, pore-filling bubbles require liquid to flow through the porous media in order to migrate. This makes gas release a very slow process. Gas release from particle-displacing bubbles should be faster but limited to a small region of a tank's waste. This is consistent with headspace gas monitoring data that show wastes in these tanks typically release on the order of 1 to 2 m^3 (30 to 70 ft^3) of gas over a period of several days (McCain 2000). These tend to occur when the barometric pressure falls rapidly during storm passage in the late fall and early spring (Hedengren et al. 2001).

All of the SSTs on the FGWL that have the wet sediment waste configuration are scheduled to be saltwell pumped as shown in Section 6.4, Table 6-8. Saltwell pumping can induce gas releases by two main mechanisms. The pressure within the waste decreases as liquid is removed, causing trapped gases to expand and percolate to the dome space. As the bulk liquid drains away, dissolved gas evaporates from the newly exposed liquid surface. Gas release by both mechanisms appears to be related to the rate of liquid removal, but the gas release rate can remain elevated for days after pumping stops. However, the maximum observed hydrogen concentration has remained well below 25% of the LFL in these cases (see Chapter 6.0).

In the pumped waste configuration where saltwell pumping has been completed, the ILL is well below the waste level. In the absence of the buoyant force of the liquid, the portion of the waste above the liquid level exerts a high lithostatic load on the waste below. Applying Equation 2-1 with the density difference set equal to the solid density, only one meter of unsaturated salt cake above the liquid level is required to force the entire column into the pore-filling bubble configuration. The small particle size of sludge maintains particle-displacing bubbles regardless of the depth of overburden above the liquid level. The small particles also make it difficult to remove interstitial liquid from sludge effectively by pumping from a single saltwell.

Following saltwell pumping, a large region of the waste should contain pore-filling bubbles. Gas releases from this region should be low. But as gas rises into the upper layers with lower lithostatic loading, the bubbles may again displace particles. The particle-displacing bubbles may then create small spontaneous releases as if from an unpumped tank. The only potential mechanism for a significant gas release from a pumped tank has been postulated to be the waste subsidence that has been assumed to cause the large craters or depressions seen in the waste surface of some tanks months or years after saltwell pumping is completed. Gas still trapped in the subsiding region would hypothetically be subject to release. No subsidence-related gas releases have yet been observed. An evaluation of the post-pumping waste level decreases for 46 SSTs that had been salt well pumped showed that 24 tanks exhibited some form of level decrease. Such decreases in waste level have been attributed to subsidence. These decreases occurred slowly; 19 tanks showed decreases over a period of 1 to 12 years, four tanks showed decreases over a period of 1 to 11 months, and only one tank showed a decrease over a period of 1 week. This indicates that a sudden spontaneous release of gas is not likely to occur during waste subsidence.

2.3.4 Gas Release Caused by Seismic Events

The effects of natural phenomena were evaluated in HNF-SD-WM-SAR-067, *Tank Farms Final Safety Analysis Report* (FSAR), with respect to flammable gas release. It was determined that the probability of a seismic event at the Hanford Site was too low to merit additional study beyond that which was accomplished in the Tank Farms FSAR. The FSAR noted: "Preliminary investigations of seismically induced gas releases suggest that the design basis earthquake (DBE) could result in a 50% gas release from a DST and a 10% gas release from an SST. These estimates are based on the strength of the waste (i.e., approximately 50 Pa yield for DST waste and 1,000 to 2,000 Pa for SST waste). Gas release fractions of this magnitude may result in small releases or large releases depending on the amount of gas retained within the waste in each tank." The maximum release fraction noted for a DST was 19% while for SSTs the observed releases have been less than 10% (Table ES-1).

No evidence of surface failure exists in the immediate vicinity of the tank farms where the exposed surfaces consist primarily of sands, gravels, and silt deposited through a series of prehistoric cataclysmic floods. The surface also contains outcroppings of the underlying basalt and sedimentary materials. Potential earthquakes at the Hanford Site are dominated by regional crustal faults rather than faults related to the tectonic plate subduction zones located near the Pacific Coast. The Hanford area does not have a history of large earthquakes.

Approximately half of the FGWL tanks contain enough flammable gas to generate a concentration above the LFL if it were all released at once because of seismic activity. Approximately half of those tanks have essentially no liquid that could create wave action during a seismic event and resultant gas release. The SSTs that have liquid are planned to complete interim stabilization by fiscal year 2004 (removal of drainable liquid by saltwell pumping). The DSTs that contain LFL quantities of flammable gas are planned to be retrieved and staged for waste treatment by 2016. However, these postulated events are not credible because tank waste has sufficient strength to retain most of the gas during a seismic GRE. The FSAR and a recent seismic event support this conclusion.

On February 28, 2001, there was a magnitude 6.8 earthquake in western Washington; this quake was noticed at the Hanford Site. Acceleration forces in the area of the Tank Farms were 0.005 *g* east-west, 0.0047 *g* north-south, and 0.0031 *g* vertical. Evaluation of gas monitoring data showed that tank AN-104 had a release near the time of the earthquake that elevated the dome space concentration to 350 ppm hydrogen. This value is considered to be very low and is within the historical data for this tank for spontaneous releases. It appears from very limited data that the flammable gas release from tank waste caused by seismic activity of low magnitude would be similar to the tank waste response to rapidly changing barometric pressure.

In summary, while earthquakes may induce gas releases, the risk from them is considered to be acceptable and the situation has been analyzed in the Tank Farms FSAR.

2.3.5 Other Gas Release Mechanisms

The solid-over-liquid configuration of A-101 and AX-101 is similar to the thinner floating crust layer found in several DSTs. While both of these layers can contain a relatively large volume of gas, they are already floating and are thus mechanically stable in terms of gas retention. Unlike the sediment layer in the liquid-over-sediment configuration, there is no mechanism by which the accumulated potential energy of the layer can be released suddenly and accumulation of additional gas increases the potential energy very little.[2] The floating layers appear to behave like a wet sediment layer of similar thickness.

The gas release potential of a thick, gas-bearing, floating layer during waste transfers was revealed by the remediation of the SY-101 crust. The initial 305-cm (120-in.) crust layer in this tank was comparable in both thickness and retained gas volume to the 432-cm (170-in.) floating layer in A-101 and the 356-cm (140-in.) layer in AX-101 (Mahoney et al. 1999, Hedengren et al. 2001). Relatively little gas was released from the SY-101 crust as it descended when the liquid below it was removed. The transfer rate in SY-101 was much faster than saltwell pumping in the SSTs. The largest gas releases occurred while the crust was being dissolved. The maximum observed headspace hydrogen concentration was just over 3,000 ppm, well below 25% of the LFL.

Liquid layers cannot store gas bubbles (except in transit) and are therefore not subject to releases. The mixed slurry waste configuration, when it exists, may retain some gas in the form of very small bubbles attached to particles as measured in SY-101 (Rassat et al. 2000, Mahoney et al. 1999). This gas can only be released at the rate the bubbles can migrate to the surface which is very slow as shown by the mixer pump induced gas releases in SY-101 over the six years of mixer pump operation (see for example Conner and Koreski 1998).

[2]Buoyant eruptions in DSTs that disrupt a crust layer are believed to release some of the gas contained therein. However, this gas release is the result of sudden release of potential energy from the sediment layer, not from the crust.

2.4 CONCLUSION

As a result of numerous evaluations conducted at the Hanford Site, universities, and national laboratories, the following conclusions can be made.

- A functional understanding of the chemical and radiolytic reactions occurring in the high-level radioactive wastes has been developed. Pathways for the production of the major gas species have been described. Gas generation rates depend on the waste temperature and the amounts of radioactive isotopes, organic compounds, and inorganic compounds such as aluminate, nitrate, nitrite, and hydroxide ions.

- Gas can be retained by capillary forces and waste strength; the majority of the gas is retained in the form of bubbles.

- Release of retained gas depends on the form and nature of the waste. For the DSTs of concern, gas is released by a buoyant displacement process. For the SSTs, gas release is a slow process that involves the "percolation" of gas through the waste.

- For the SSTs, the observed gas release has always been slow, thus limiting the maximum concentration in the dome space to much lower than safety limits. The basic nature of the release mechanisms is not expected to change in the foreseeable future.

The following Chapters (4.0, 5.0, and 6.0) discuss the data obtained for the 24 tanks that are on the FGWL and for SY-101. While the resolution of the Flammable Gas Safety Issue must be based on the data and observations of tank behavior, the work done on the chemistry of gas generation and physics of retention and release provide a basis qualitative for understanding the observed behavior. Some of this understanding is qualitative and some is quantitative; nonetheless, it is the basis for the understanding of flammable gas generation and release.

3.0 WASTE TANK DATA COLLECTION METHODS

Development of an understanding of the behavior of flammable gas mixtures in the Hanford Site waste tanks required collection of considerable information about tank waste and the gas generated within it. At the time the tanks were identified for the FGWL, there was little information about the amount of gas being generated, retained, and released. This section gives a brief summary of the methods that were used to obtain data on waste level, waste temperatures, tank dome space gas concentrations, amount and nature of gas stored within the waste, and other chemical and physical properties of the tank wastes. Much of the information obtained by the items discussed in this chapter was used to satisfy the requirements of DNFSB Recommendation 93-5. Monitoring of the tanks was a requirement of Public Law 101-510, Section 3137 (Section 1.3).

3.1 TANK WASTE DATA

The general features of the methods that were used in this work are described in this section. Many of the SSTs and DSTs in the tank farms were investigated in the course of this work. The results for the SSTs and DSTs have been described in previous reports (Hedengren et al. 2000 and 2001), and Chapters 5.0 and 6.0 give summaries of that information.

3.1.1 Waste Surface Level

Waste level data are critical to the evaluation of the behavior of gases being retained and released in the SSTs and DSTs. The tank level monitoring instrument has traditionally been either a manually operated tape with a plummet on the end or a reel type conductivity gauge (made by the Food Instrument Corporation, thus the gauges were termed "FIC"). These units have had a history of maintenance problems requiring them to be flushed periodically with water. Both the manual tapes and the FIC units have been replaced since about 1995 with a buoyancy-tension wire gauge instrument manufactured by Enraf-Nonius (Model 854 ATG) (White 1993 and 1994). The Enraf[1] gauges now provide accurate data for a large number of tanks.

The Enraf buoyancy gauge does not depend on electrical contact and merely sits stationary on the waste surface. Therefore, it is not subject to buildup of waste deposits, nor does it tend to disturb the surface on which it rests. This makes the Enraf the most reliable level indicator of any used.

The absolute accuracy of any of the waste level instruments depends on the degree of surface irregularity and the uncertainty in the reference position. Combined, these could produce a systematic error of 2 to 20 cm (1 to 8 in.), depending on the tank. Sensing level change is far more important than absolute accuracy in level measurement. The Enraf records level in 0.025-cm (0.01-in.) increments and is easily able to resolve level changes to within ± 0.25 cm (0.1 in.). The FIC records level in 0.25-cm (0.1-in.) increments, and its sensitivity is estimated

[1] Enraf is a trademark of Delft, Inc., The Netherlands.

at ± 0.6 cm (0.25 in.) for nearly consecutive readings. However, waste deposit growth and periodic flushing adds an uncertainty of ± 5 cm (2 in.) in long-term measurements.

3.1.2 Waste Temperatures

The tanks have thermocouple trees to measure waste temperatures. The waste temperature is another important parameter in assessing the state of the waste. The gas generation rate increases strongly with temperature, and the temperature distribution reveals regions where the heat load is highest. The amplitude and time delay of the annual temperature cycle provides an indication of the relative heat capacities and degrees of liquid saturation between regions. Changes in temperature trends help monitor the effects of saltwell pumping.

Thermocouple trees are available in each of the SSTs considered in this report. Most of these SSTs have a single thermocouple tree. One exception is SX-109, which has multiple thermocouple trees. The number of thermocouple probes along the various thermocouple trees varies from 6 to 18. The thermocouple probes are spaced vertically with the first reading near the tank bottom. Some of the thermocouple probes are in a tank's dome space. The uncertainty in the temperatures that are obtained from these instruments is estimated to be ±1.7 °C (3 °F) (Brewster et al. 1995).

In order to improve the temperature monitoring of the waste in the DSTs exhibiting buoyant displacement gas releases, new thermocouple systems were installed; these systems are called Multi-function Instrument Trees (MIT). While the uncertainty of individual thermocouple indications is similar to those of the old thermocouple trees, the MITs have an internal well so that a calibration probe can be inserted to provide data at more locations than the fixed location thermocouples. Data from the MITs have been used to assess the releases in the DSTs and to aid in the evaluation of the thickness of waste layers.

3.1.3 Dome Space Gas Measurements

A primary information need for the analysis of the Flammable Gas Safety Issue is the amount and nature of gases being released into the dome space of a tank, both from a steady-state perspective and from GREs. Gas monitoring is primarily directed at detecting hydrogen, since it is the primary fuel component of the gases being produced. On-line gas monitors have been installed in all flammable gas watch tanks (25 including SY-101), 16 other tanks, and on ventilation exhaust stacks of two tank farms. These units are called standard hydrogen monitoring system (SHMS). There are several configurations, but all units have Whittaker electrochemical cells to detect hydrogen; one is set for the range of 0–1% and the other covers the range 0 to 10% hydrogen by volume. Selected SHMS units have a dual column gas chromatograph with thermal conductivity detectors and Buel & Kjaer photo-acoustic infrared analyzers. These additional systems are used to detect hydrogen, nitrous oxide, and ammonia. The SHMS units also have the capability to take "grab samples." The basis for sampling with the SHMS was reported in Estey (1998).

Checks for flammable gases are performed whenever dome intrusive operations are planned. Combustible gas meters are typically used for these measurements. If a high reading (greater

than 25% LFL) is noted, grab samples are taken for further evaluation. This has been done for a number of core sampling operations and the results for some of them have been reported (Siciliano 1998).

The 134 passively ventilated SSTs were vapor-phase sampled for flammable gases and the results have been reported (Johnson et al. 1997). Annual reports on the results from the SHMS have been issued; the most recent one was issued in September 2000 (McCain 2000). The data from all of these sources are used for evaluation of flammable gas behavior in the SSTs and DSTs.

Because adequate data had been collected and the flammable gas risk had been ameliorated in several tanks (e.g., through saltwell pumping), SHMS units were removed from eight tanks in fiscal year 2000. As more data are collected and it is concluded by DOE that additional data will not provide further substantial value, SHMS units will continue to be removed when appropriate.

3.1.4 Tank Data Collection and Reporting

Data recorded for waste level, waste temperatures and dome spaces gas (SHMS) are handled by the Tank Monitor and Control System (TMACS). TMACS also provides information for dome space pressure and ventilation flow for those tanks having the sensors. Features of TMACS include alarm management, data storage, data trending, reporting, event logging, failure status, and graphical presentations. Additional details on TMACS are provided in Scaief (1995).

3.1.5 Evaluation of Stored Gas

As efforts proceeded toward the understanding of the origins of flammable gases it was determined that in situ measurements of the amounts of stored gas were needed to properly assess the flammable gas hazard. Two systems were developed: a void fraction instrument (VFI) and a retained gas sampler (RGS).

The VFI was designed to measure the volume fraction of free (undissolved) gas, or void, at specific locations in a tank. The void is determined by compressing waste, with nitrogen gas, that has been captured in a chamber of known size. Details of the VFI operation are provided by Stewart et al. (1996b). The VFI has been used on tanks AW-101, AN-103, AN-104, AN-105, SY-101, and SY-103.

While the VFI gave data on the void in the waste, it did not provide any information as to the species present in the gas mixture. The RGS is a version of the universal core sampler specifically designed to capture the waste and gas so that they could be analyzed in a hot cell laboratory. Information obtained from the RGS includes void and the chemical composition of the gas. The RGS equipment was deployed in 15 tanks, with 12 of them on the FGWL (A-101, AW-101, AN-103, AN-104, AN-105, AX-101, BY-101, BY-109, S-102, S-106, S-111, SX-106, SY-101, U-103, and U-109). These tanks were chosen to provide data on the tanks suspected of having the highest gas content and to get representative data from FGWL tanks in each farm (Stewart et al. 1996a). The two BY-farm tanks were selected to provide information on

post-saltwell pumping gas retention. The methodology and the results of the investigations are described by Mahoney et al. (1999).

The gas volume stored in a tank can be estimated from the response of the waste surface level to fluctuations in barometric pressure, resulting in compression and expansion of stored gas. This model is referred to as the barometric pressure effect (BPE) model. A detailed derivation of the BPE model is given in Appendix B of Hedengren et al. (2000). Retained gas volume estimates have been completed for the five DSTs and fourteen SSTs that satisfy the criteria for applying the BPE method.

3.1.6 Waste Physical Properties

Early attempts to measure the physical properties of tank waste were frustrated by the fact that the samples cooled so rapidly that precipitation occurred before the rheological properties of the waste could be measured. In addition, handling the samples in the hot cell altered the physical state of the waste and results were ambiguous. Therefore, an instrument was developed to obtain in situ measurements for viscosity, yield strength, and density (Gauglitz and Aikin, 1997). This instrument was called a "ball rheometer."

The device uses a dense metal ball, made of tungsten, which is attached to a cable. In operation, the ball is deployed at a constant speed by rotation of a cable drum. The cable runs from the drum, over a pulley, and down to the ball in the tank. A load cell is attached to the pulley and records the tension in the cable. Part of the total tension is due to the fluid drag force exerted on the ball. The ball position is known from the amount of cable let out from the drum. Analysis of the data coupled with a model for fluid behavior yields the requisite information for viscosity, yield strength, and density. The ball rheometer was used successfully in DSTs (AN-103, AN-104, AN-105, AW-101, SY-101, and SY-103) and additional details on the operation of the ball rheometer are given by Stewart et al. (1996b).

The observed behavior of waste cores during sample extrusion can be used to estimate the sample waste strength, as detailed by Gauglitz and Aikin (1997). This approach was particularly useful for SSTs, since ball rheometry is typically impossible in the relatively strong waste found in those tanks.

The extrusion waste strength estimation method is based on experiments that showed that during the standard horizontal extrusion process waste simulants behaved in a reproducible manner that varied distinctively with strength. Two different waste simulants were used: bentonite clay, mixed with different amounts of water to obtain shear strengths of 31 to 3,670 Pa, and kaolin/Ludox[2], mixed with different amounts of salt and setup times to obtain shear strengths of 625 to 6,500 Pa.

The waste strength can be estimated only within a range of roughly ±50% using the extrusion method, but even this imprecise information is valuable for those tanks in which the waste cannot be subjected to more precise rheometry.

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[2] Ludox HS-30 is a trade name for a colloidal silica dispersion.

3.1.7 Waste Chemical Analyses

Tank waste characterization was conducted to provide information regarding the chemical, radiological, and physical properties of the contents of the waste storage tanks. The data quality objective process was used to develop the information needs for the flammable gas program (Bauer 1998). Analyses were performed for many chemical analytes including an array of elements whose concentrations were determined by conventional plasma methodology. These analyses included measurements of anions, total organic and inorganic carbon, water, radionuclides, and various organic compounds. Tests were performed for solids fraction, settling behavior, density, particle size, viscosity, and yield strength. The data quality objective provides a complete description of all needed parameters.

The results of the laboratory analyses are combined with other available information and are maintained in a tank characterization report for each waste tank. The tank characterization report is a publicly released document that addresses pertinent characterization information about a waste tank. The document is built through an iterative process; available historical records are augmented by results of current activities (e.g., sampling and analyses since 1989) and earlier verified data. The document includes data from the Best-Basis Inventory (a Hanford Site database for waste tank information). The tank characterization report identifies the most current revision of each data quality objective that was used to gather information. In addition the tank characterization report contains a description of the layering of the wastes in the tanks.

The chemical and physical property data contained in the tank characterization reports is also available electronically in the Tank Characterization Database. To allow easy availability of the data, this database may be accessed through the Internet onsite (http://twins.pnl.gov) and through the World Wide Web (http://twins.pnl.gov:8001).

3.1.8 Neutron and Gamma Logging

Many SSTs are equipped with liquid observation wells to permit monitoring of the ILL through the use of neutron and gamma probes. The quality of data initially obtained by these measurements was poor and, thus, the data were of very limited applicability to the evaluation of retained gas (Johnson 1996). However, starting in 1997, the equipment used to monitor the liquid observation wells was upgraded as follows:

- Depth measurement system is 30 times more accurate.
- Encoder has 55 pulses per cm vs. 0.7 pulses per cm in the old system.
- Boom is mechanically stabilized so it does not flex.
- Vertical interface resolution improved from greater than 36 cm to less than 13 cm due to better source-to-detector spacing.
- Data collection digitally automated and rate of scan is programmable allowing increased resolution in the area of interest.

These improvements in the equipment and technique have increased the sensitivity of the system such that evaluations have definitely shown the presence of retained gas (Barker 1998) and have recently been used to estimate the average gas fraction (Hedengren et al. 2001).

A small-bore neutron-gamma probe was designed in 1998 for DSTs with MITs installed. The device is deployed inside the tube used for the calibration probe. During 1999 and 2000 neutron and gamma scans were obtained in all the DSTs on the FGWL plus DST AY-102. The results confirmed the indications of the temperature profiles that the waste layers were not changing. As described in Chapter 4.0, the neutron and gamma scans in SY-101 provided extremely valuable data on the amount and location of gas stored in the crust and helped track the progress of remediation (Mahoney et al. 1999).

3.2 LABORATORY EVALUATIONS

To address the nature of gas generation, retention, and release laboratory investigations were required to assess these processes and how they are related to the various wastes. Investigations were also conducted for the deflagration and detonation behavior of gas mixtures, and techniques were developed to determine the species of organic compounds present in the waste samples.

3.2.1 Gas Generation Tests

In 1990 it was recognized that in order to resolve the Flammable Gas Safety Issue and to ensure that the situation would not be created in future waste processing operations, laboratory studies were needed to understand the mechanisms responsible for the production of gases. Work was initiated at the Argonne National Laboratory, Georgia Institute of Technology, Pacific Northwest Laboratory, and Westinghouse Hanford Company. Initial efforts were directed at evaluations with simulated waste solutions. At that time, core sampling of the waste tanks was proceeding at a slow pace, partly due to equipment difficulties and partly because a USQ for the FGWL tanks precluded in-waste activity. Use of the simulants allowed for a systematic variation in chemical parameters to study the mechanisms for gas generation. These studies looked at effects of dose rate, total dose, temperature, and variations in chemical composition on gas generation rate. Investigations were done to evaluate mechanisms for the formation of hydrogen, nitrous oxide, ammonia, and nitrogen.

The knowledge gained from the simulant work was then applied to tests that were performed with samples obtained from the waste tanks. Special equipment was constructed to perform these tests in hot cells (Person 1993 and Bryan et al. 1996). Tests have been completed on waste samples from tanks SY-101, SY-103, AW-101, AN-103, A-101, S-102, S-106, and U-103.

As noted in Chapter 2.0, the laboratory work formed the basis of the chemical model that was developed for the aging of organic compounds and for the generation of the flammable gases. This work also underpins the empirical model for the estimation of the rates of hydrogen formation in the waste.

3.2.2 Gas Retention and Release Tests

If all of the gas that is generated were to be released to the tank dome space as it was generated, there would be little concern about a Flammable Gas Safety Issue. The generation rates are sufficiently low that the ventilation systems, both passive and active, can accommodate the gases and the concentrations will remain well below the flammability limit. However, the gases are retained in the waste of many tanks and conditions exist whereby sudden releases can occur. Studies were initiated at Pacific Northwest National Laboratory to determine the mechanisms for gas retention.

Work was first done on simulants chosen to simulate the behavior of waste in SSTs. SST wastes have a wide range of physical properties that range from clay-like plastic sludges to hard salt cake. Most of the work was done on fine-particle simulants composed of bentonite clay and water. These tests quantified the ability of the simulants to retain gas and showed how gas is released.

The test method consisted of placing a sample into a transparent vessel and allowing it to settle. It was irradiated with a cesium gamma source to generate a small amount of gas. The sample chamber was then evacuated in a controlled manner to nucleate additional bubbles and to expand existing bubbles. The volume of waste grew as gas was retained and subsided with gas release. The growth and release were monitored with a video camera. The relative contribution of two mechanisms, interstitial liquid displacing or particle displacing bubbles, were deduced from the amount of growth and video results. The test method also determined an upper bound on the retained gas fraction for each test.

After the work was completed on the simulants, the apparatus was used to test samples from waste tanks. Tests were conducted on samples from tanks A-101, S-102, S-106, U-103, AW-101, AN-103, and SY-103. Additional details on the experiments are provided in Pacific Northwest National Laboratory reports (Gauglitz et al. 1996, Rassat et al. 1997 and 1998).

3.2.3 Combustion Tests of Gas Mixtures

Flammability is a fundamental aspect of the Flammable Gas Safety Issue. Virtually all analyses of the flammable gas hazard are aimed at estimating the potential for some volume of gas to become flammable in the tank dome space. A sound knowledge base for the LFL under a variety of conditions is essential for the safety analyses and to resolve the Flammable Gas Safety Issue. Experimental studies were performed to determine the combustion characteristics of a variety of gas mixtures. The focus of the tests was on combustion limits, pressure histories, flame speeds, and detonation properties. Tests were conducted at the Pittsburgh Research Center of the U.S. Bureau of Mines (Cashdollar et al. 1992) and at the California Institute of Technology (Ross and Shepherd 1996; Pfahl and Shepherd 1997; Akbar et al. 1997; Pfahl et al. 1998a and 1998b). Results of these investigations are used in safety analyses and they are discussed in Chapter 7.0.

3.3 CONCLUSIONS

Systems were developed and are being employed for monitoring flammable gases in the dome spaces of the tanks. Characterization of the waste in the FGWL tanks was accomplished through core sampling coupled with laboratory analyses, in situ evaluation of stored gas, in situ evaluation of physical properties, waste temperatures, and waste layers. Completion of these activities meets the following guidelines (Section 1.2) for resolution of the safety issue:

- Collect data to establish an understanding of the behavior of the waste
- Develop and implement appropriate means to monitor the tanks.

4.0 TANK 241-SY-101

SY-101 is a DST in the SY Farm in the 200 West Area of the Hanford Site whose behavior caused the original Flammable Gas USQ to be declared and led to the establishment of the FGWL. It was also the first flammable gas tank for which the USQ was closed and that was removed from the FGWL. Therefore, the history and the mitigation and remediation campaigns on this tank deserve special mention. This section is condensed from the report RPP-6517 (Johnson et al. 2000). The reader should refer to this report for all the details not covered in this summary.

4.1 SUMMARY OF TANK FLAMMABLE GAS HISTORY

4.1.1 Initial Activities

Between 1977 and 1980, tank SY-101 was filled with waste that was the most concentrated material produced by the evaporators. Subsequent waste additions included complex concentrate waste containing significant organic complexant concentrations. The waste in SY-101 was observed to generate a flammable mixture of gases, retain a large volume of the gas mixture within the waste, and spontaneously release large volumes of the gas mixture via buoyant displacement GREs. While periodic in nature, the amount and timing of the gas releases could neither be accurately predicted nor controlled. The periodic retention and release of gas caused the characteristic "saw tooth" fluctuations of the waste level in this tank as shown in Figure 4-1. These level measurements were obtained from a manual tape and an automatic Food Instrument Corporation (FIC) device via Riser 1C. Gas releases were from 85 m^3 to almost 283 m^3 at one atmosphere. A summary of the major gas releases is provided in Table 4-1. The nominal LFL of hydrogen in air is 4% (40,000 ppm). When other gases are included in the evaluation, the LFL is 3.6%. Thus, three of the GREs listed (10/24/90, 12/4/91, and 9/3/92) exceeded the LFL for H_2. Such situations were unacceptable, and efforts were initiated to mitigate the GREs.

In 1990 this behavior was declared a USQ (WHC-UO-90-013-TF-02). In order to control waste gas release behavior and reduce the flammability hazard, a mixer pump was installed in 1993 (Allemann et al. 1994). Routine pump operations prevented the buildup and release of large volumes of flammable gas (Stewart et al. 1994, Brewster et al. 1995). The mixed state of the tank is illustrated by the axial temperature profiles shown in Figure 4-2. The 1993 pre-pump profile shows a bulge at the lower part of the tank indicating a deep, 635 cm (250-in.) nonconvective layer in which gas could accumulate. The profile from 1996 after several years of mixing shows a uniform temperature over almost the whole depth of the waste indicating that mixing prevented formation of a deep nonconvective layer. Measurement of the stored gas distribution was performed in the winter of 1994-95 with the VFI (Stewart et al. 1995). The results of the measurements are shown in Figure 4-3. The calculated volume of stored gas in tank SY-101 (including the crust) based on the data in Figure 4-3 was 195 m^3 at standard conditions. This is compared to as much as 680 m^3 prior to mitigation (LANL 1996). Note that no other Hanford tank required the use of a mixer pump because of waste composition and characteristics.

Figure 4-1. Tank 241-SY-101 Surface Level from 1988 to 1991.

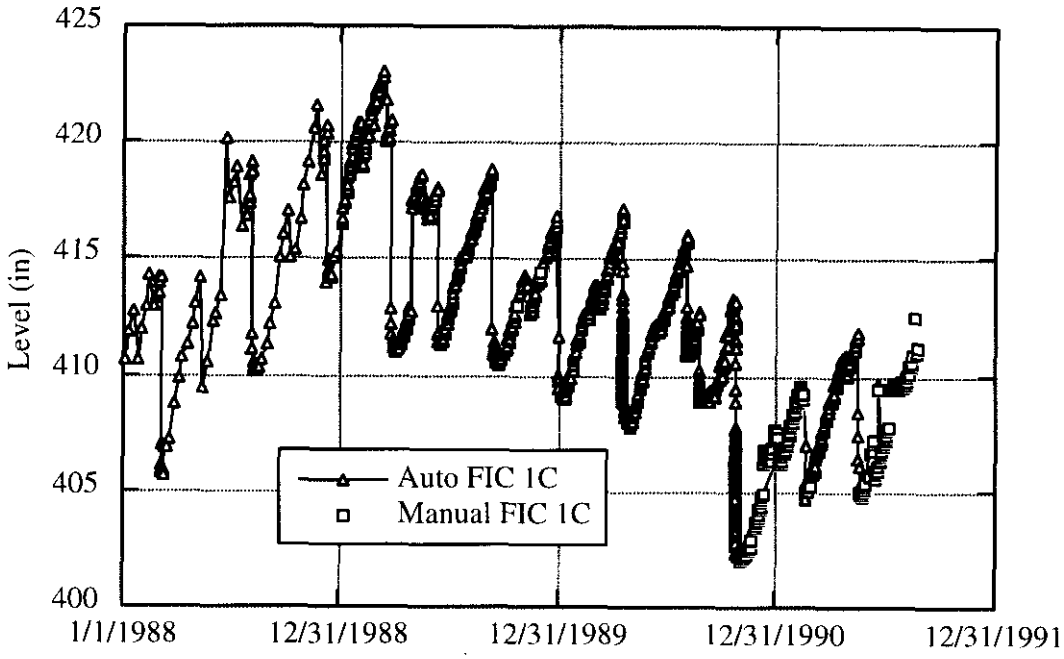


Table 4-1. Gas Release Events in Tank 241-SY-101 Prior to Mitigation.

Date	Maximum H_2 concentration (ppm)	Prompt waste level decrease (cm)	Volume released (m^3 at one atm)
4/19/90	35,000	23	198
8/5/90	12,000	13	113
10/24/90	47,000	25	218
2/16/91	400	10	91
5/16/91	28,000	18	153
8/27/91	3800	15	125
12/4/91	53,000	30	263
4/20/92	14,800	15	130
9/3/92	51,200	25	215
2/2/93	27,400	23	198
6/26/93	34,000	25	215

Figure 4-2. Temperature Profiles Before and After Mixer Pump Operation.

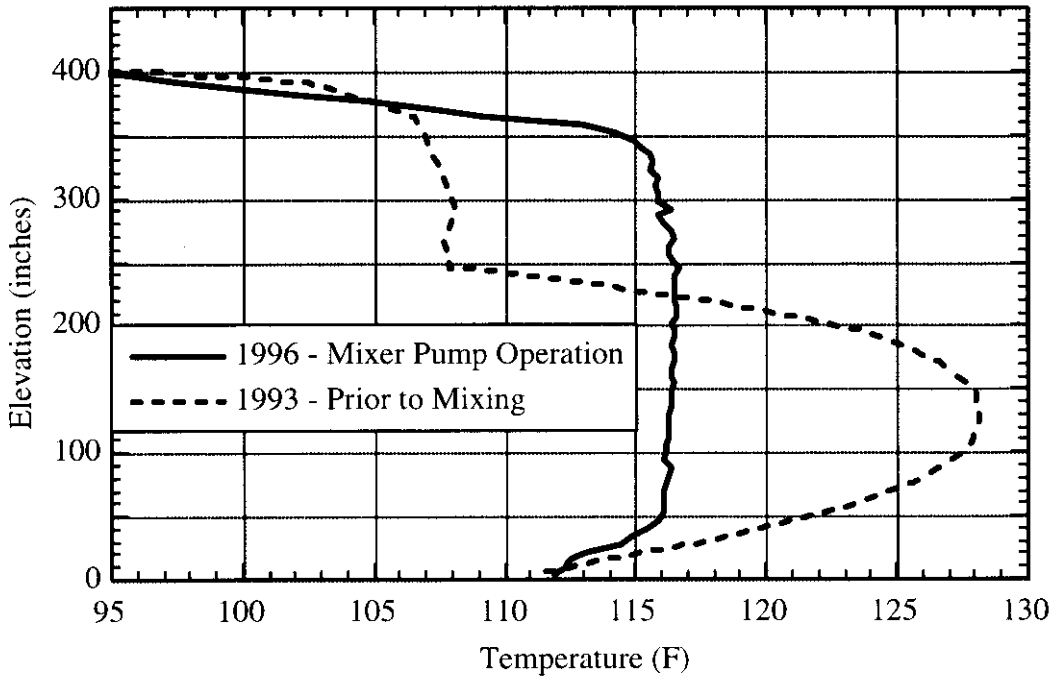
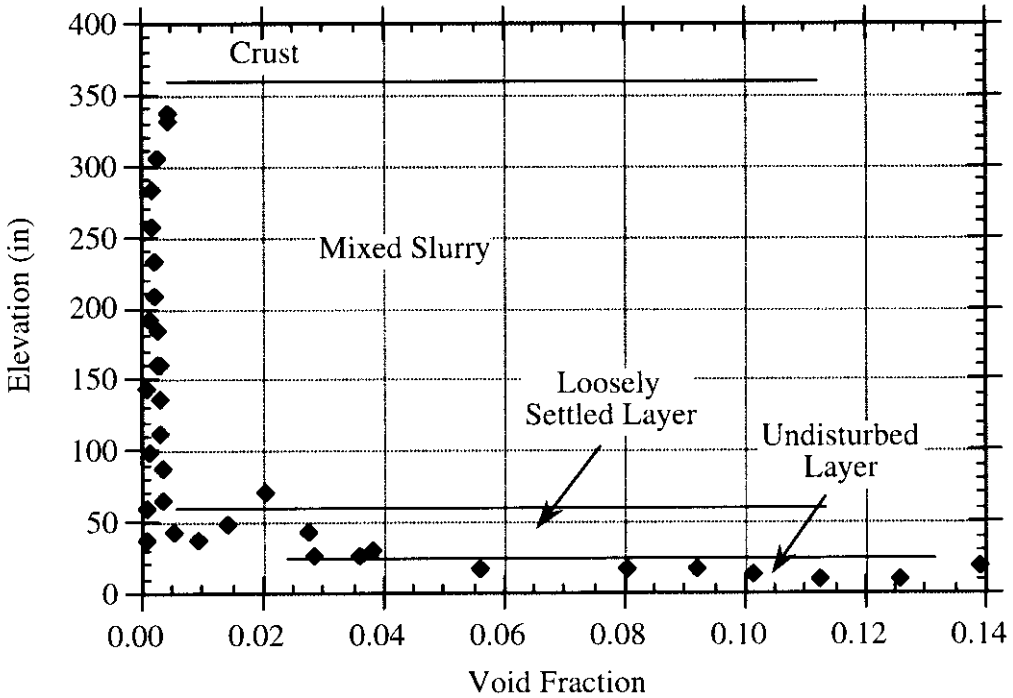


Figure 4-3. Tank 241-SY-101 Void Profile, 1994/1995 Data.



4.1.2 Gas Retaining Crust

The composition and characteristics of the waste in SY-101 created the situation in which significant GREs occurred. That situation was partially remediated by the operation of the mixer pump.

However, an unanticipated consequence of mixer pump operations and mitigation of the large gas releases was an excessive and accelerating growth of a gas-retaining crust on the waste surface. The waste surface level rise caused by accumulation of gas and solids within this crust resulted in declaration of a USQ (TF-97-0975) in 1997. This USQ was revised in 1999 to reflect the results of waste characterization and analysis performed to understand level growth and potential hazards (French 1999).

The waste level rise from January 1995 through November 1999 is shown in Figure 4-4. The waste surface under the level instrument in Riser 1C was flushed regularly with water to remove waste deposits from the level probe. This also dissolved a depression in the crust around the instrument. Because of this, the 1C level was assumed to represent the free liquid level. Since the area under the level instrument in Riser 1A was not flushed, the 1A level was assumed to represent the top of the crust surface. Both level instruments showed a rapidly accelerating level rise from 1996 through the first part of 1999. The crust base was inferred from temperature profiles obtained with the multi-function instrument tree (MIT) validation probe, which allowed the total crust thickness to be estimated.

An evaluation of the crust conditions was performed based on past gas retention studies (Rassat et al. 1999). The analysis showed an increase in both the thickness and the "freeboard" of the crust that is pushed above the liquid layer by the buoyant material below. An increase of the freeboard thickness could only be the result of a higher gas volume fraction in the submerged crust. Figure 4-5 shows the acceleration in the crust thickness and the freeboard increases in 1998. The top of the crust was assumed to be the level measured by the Enraf gauge in Riser 1A.

4.1.3 Final Resolution

Between December 18, 1999, and March 15, 2000, a series of waste transfers and water dilution of the remaining SY-101 waste dissolved most of the soluble sodium salts, changing the state of the waste into one that would not be susceptible to gas retention and buoyant displacement gas eruptions. Three campaigns of transfers followed by back dilutions were accomplished. The first campaign, from December 18 to December 20, 1999, mitigated the immediate level concern by lowering the waste level by almost 38 cm (15 in.) and dissolving a large fraction of the original freeboard. The second transfer and top of waste back dilution, January 25 to 28, 2000, removed the major hazard of level rise by dissolving the crust and releasing most of its stored gas. The subsequent back dilution performed low in the waste from February 21 to February 23, 2000, dissolved most of the soluble solids in the slurry and the remaining crust debris. The third transfer was performed February 27 to March 2, 2000, and the final back dilution was completed on March 15, 2000.

Figure 4-4. Waste Level Rise Since 1995.

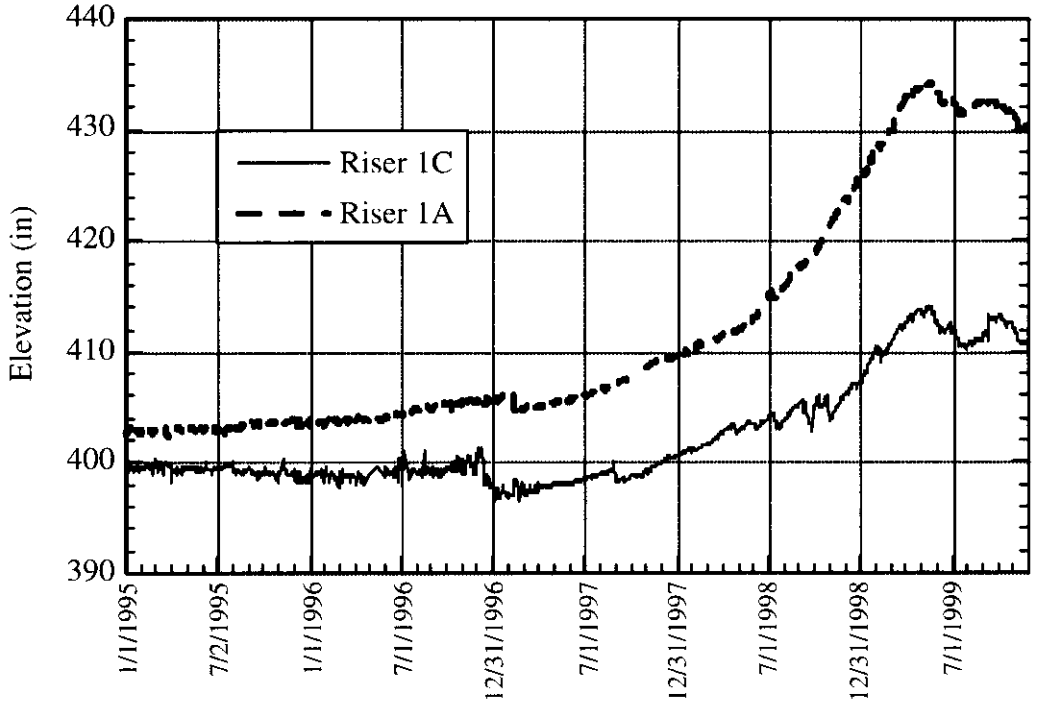
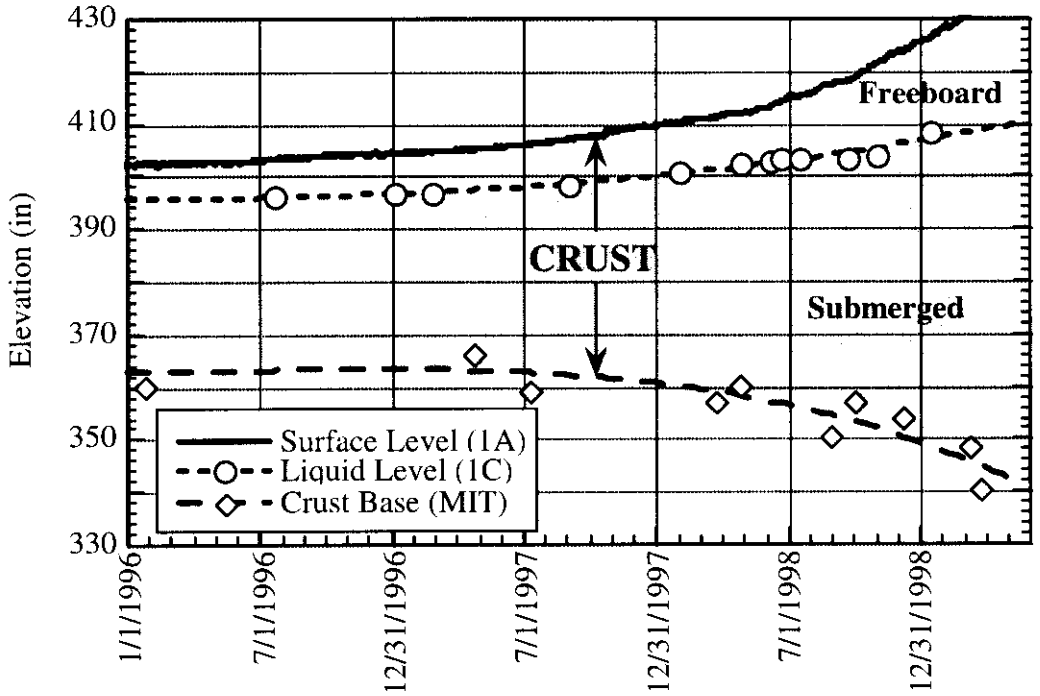


Figure 4-5. Tank 241-SY-101 Crust Growth from 1995 through 1998.



The estimated cumulative gas released during remediation was 415 m^3 (Mahoney et al. 1999). This is very close to the 422 m^3 of gas estimated to be retained in the tank just prior to the first transfer. Table 4-2 provides a summary of the transfer and back dilution volumes. Since the second and third transfers followed dilutions, they also removed some of the dilution water and less of the original, undiluted waste. The actual contents of the tank after each campaign are listed in the last two columns. The net effect was a dilution of the original tank waste by 0.8:1.0 with water.

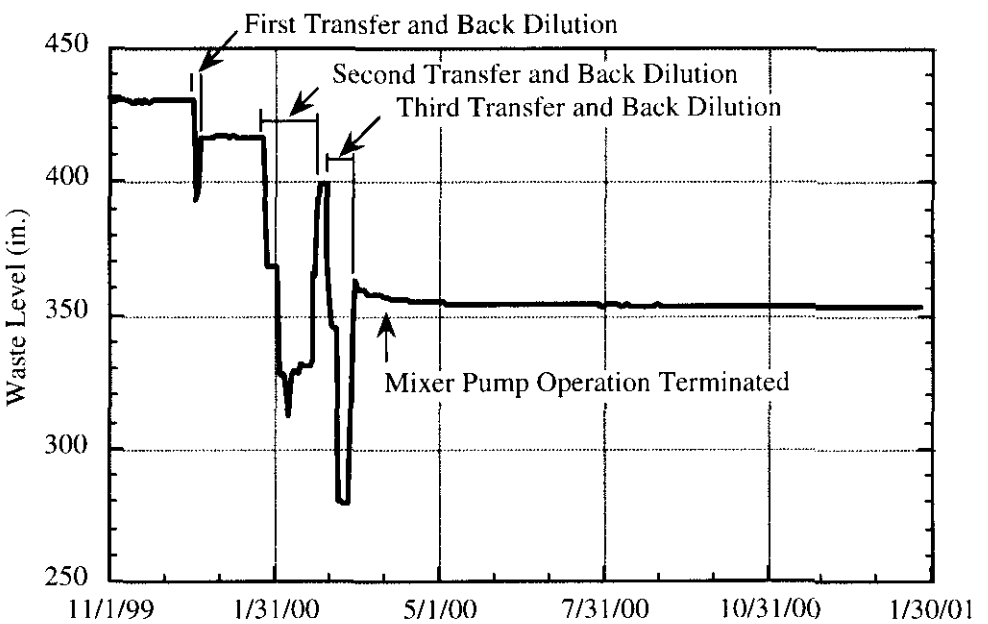
Table 4-2. Tank 241-SY-101 Transfer and Dilution Volumes

	SY-101 Waste Transferred	**Back Dilution**	**Original Waste in Tank**	**Net Water Added to Tank**
Campaign #1	89,500	62,000	974,500	62,000
Campaign #2	240,500	239,500	744,500	291,000
Campaign #3	286,000	223,500	539,000	434,000
Cumulative	616,000	525,000	539,000	434,000

Note: all volumes in gallons (1 gallon = 3.8 liters)

The mixer pump was not operated after March 30, 2000. The gas generation rate was reduced by a factor of seven and the solids volume by 80% from the pre-dilution values. No gas retention has been observed since the mixer pump was shutdown. Gas retention can be detected and the retained gas volume estimated using changes in the waste surface level (Meyer et al. 1997). The waste level from November 1, 1999, to January 25, 2001, is shown in Figure 4-6. No waste level growth, and therefore no gas retention, is visible after remediation. Consideration of evaporation does not change this conclusion (Johnson et al. 2000).

Figure 4-6. Tank 241-SY-101 Waste Surface Level November 1, 1999, to January 25, 2001.



Additionally, dilution eliminated the thick crust and only a thin, foamy layer of floating material that poses no flammable gas hazard remains. Video inspection of the surface indicated a thin scum layer with negligible strength. Sludge weights and grab sample bottles were observed to penetrate this layer easily. Open pools of liquid were observed in May and June 2000 but appeared to have mostly disappeared by mid-July 2000. No large pools were visible as late as September 2000. Video frames of the same location of the edge of the pool captured on June 20 and July 25, 2000, are shown in Figure 4-7. The largest open liquid area was somewhat greater than 10 ft in diameter, and appeared to be under the vent header riser.

Figure 4-7. Video Frames Showing Scum Layer in Tank 241-SY-101.

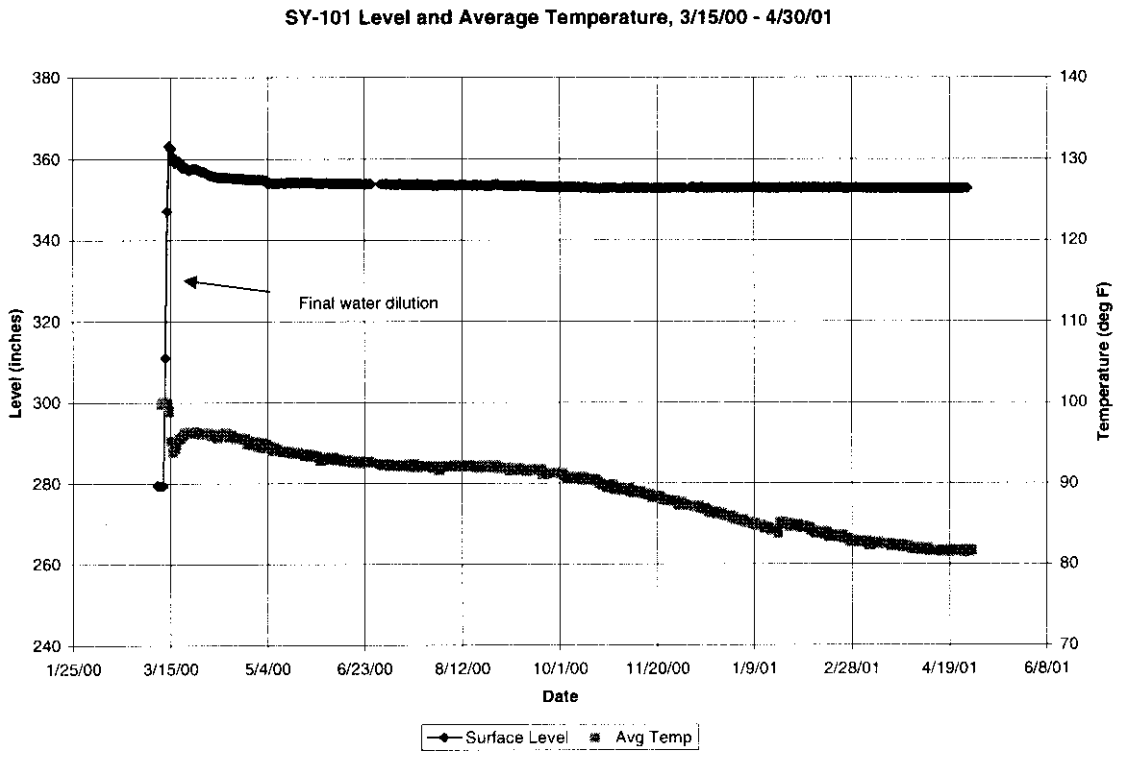
The target waste state resulting from the transfer and back-dilution campaign was one that would not be susceptible to gas retention and buoyant displacement gas releases. This state was selected by comparing values of groups of physical parameters for DSTs that exhibit buoyant eruptions and those that do not (Meyer and Stewart 2001). Remediation transfer and dilution volumes were selected such that the predicted parameter values for tank SY-101 matched those typical of other tanks not exhibiting buoyant eruptions (Bauer 2000). The values of the three physical parameters are given in Table 4-3. SpG_{ave} is the average specific gravity of the waste. $SpG_{CL}*H_{NCL}$ is the product of the convective layer density and nonconvective layer height. It is normalized to the lowest value observed in DSTs exhibiting buoyant displacements. The buoyancy ratio is the predicted average nonconvective layer void fraction at steady state divided by the neutral buoyancy void fraction. The values show the predicted and actual values for all three parameters are below the threshold that indicated potential buoyant eruptions. While the actual ratio is less than the threshold value, the ratio is greater than predicted because of the settling behavior of the solids.

Table 4-3. Tank 241-SY-101 Buoyant Displacement Gas Release Event Predictive Parameter Values.

	SpG_{ave}	**$SpG_{CL}*H_{NCL}$ Normalized**	**Buoyancy Ratio**
As predicted	1.39 ± 0.07	0.54 ± 0.25	0.26 ± 0.19
As of 9/30/00	1.39 ± 0.02	0.85 ± 0.04	0.78 ± 0.19
Threshold value	1.41	1.0	1.0

Available data and evaluations led to the conclusion that since remediation actions have been completed and the mixer pump has been off, there is no indication of significant gas retention. Figure 4-8 provides temperature (the lower line) and level (the upper line) data of the tank since its remediation. Analysis of the physical parameters showed that tank SY-101 met the criteria that exclude buoyant eruptions. Therefore, it can be concluded that hazardous gas retention and release behavior in tank SY-101 has been remediated. Evaluation of the temperature and waste level for SY-101 as of July 18, 2001, showed that the trends in Figure 4-8 continue.

Figure 4-8. SY-101 Temperature and Level Since Remediation.



4.2 REMOVAL OF SY-101 FROM THE FLAMMABLE GAS WATCH LIST

Following mixer pump installation and successful testing in 1993, the contractor prepared an amendment to the Authorization Basis for operation of the mixer pump and closure of the original tank SY-101 USQ. The DOE-RL submitted a request for closure of the USQ for tank SY-101 (Wagoner 1995). The DOE-Headquarters concurred with the request (Guimond 1996), and DOE-RL notified the contractor that the original Flammable Gas USQ for SY-101 was closed (Wagoner 1996a).

While operation of the mixer pump addressed the original flammable gas USQ, it neither addressed the subsequent observation of surface level rise, nor removed the tank from the FGWL, nor returned the tank to normal service. The transfer and back dilutions effectively resolved the surface level and flammable gas safety issues.

The contractor submitted a topical report (Johnson et al. 2000) with Authorization Basis amendments to DOE-Office of River Protection (ORP) to remove tank SY-101 from the FGWL and return it to service (DeLozier 2000). The DOE approved the Authorization Basis amendment and closed the "Waste Surface Change" USQ (Boston 2000a). The ORP submitted a request to DOE-Headquarters to close the safety issue and to remove the tank from the FGWL (Boston 2000b). DOE-Headquarters approved this request in January 2001 (Huntoon 2001).

4.3 APPLICATION OF TANK SY-101 KNOWLEDGE TO FUTURE SITE OPERATIONS

The remediation of tank SY-101 was very successful. The project demonstrated that intensely waste-disturbing operations (transfer, dilution, mixing) that intentionally release a very large volume of flammable gas can be planned and performed safely. There are several valuable lessons and experiences from the project, which will greatly benefit future operations.

Considerable effort was devoted to obtaining data on the waste, including dissolution of solids, solids composition, waste physical properties, and the location and amount of retained gas. This information provided a sound technical basis for evaluation of potential hazards and accurate prediction of the outcome of the operation. Additional instrumentation was provided to monitor the progress of remediation.

The project actively maintained a solid technical basis for all field activities by obtaining the input of scientists, designers, operations staff, and managers on all important issues and questions. A technical review committee evaluated potential hazards, guided the process control plans, and developed an understanding of the monitoring data during the operations. This was invaluable in keeping the project on track and satisfying the needs of reviewers and observers.

Finally, considerable data on the release of flammable gases during waste-disturbing operations were obtained. The data showed that no unacceptable concentrations were reached during these planned global waste-disturbing events. This effort satisfies one of the items needed for resolution of the safety issue; i.e., means to mitigate accumulation and release of unacceptable quantities of gas were developed to be effective. This experience is expected to be applicable to future work of the Waste Feed Delivery and Retrieval programs.

All of the information gained from the SY-101 operations will be valuable for safety analysts who will be doing evaluations for future tank operations. The lessons learned from the removal of waste from tank C-106 were also applied to the SY-101 waste transfer; Industrial Health personnel and equipment were strategically located to monitor for noxious vapors. During the whole operation there were no reportable occurrences or personnel injuries, and there were no major equipment failures.

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5.0 EVALUATION OF FLAMMABLE GAS WATCH LIST DOUBLE-SHELL TANKS

This section summarizes the available information about gas generation, retention, and release in the five DSTs (AN-103, AN-104, AN-105, AW-101, and SY-103) on the FGWL. The discussion presented in this section is based primarily on the comprehensive DST report by Hedengren et al. (2000).

Section 5.1 provides an overview of the efforts to characterize the waste and conditions in the five DSTs. The rates of gas generation and the composition of the stored gas in these tanks are discussed in Section 5.2 and the amounts of gas retained in the tanks are examined in Section 5.3. A discussion on gas release is given in Section 5.4. A summary and the principal conclusions are provided in Section 5.5.

5.1 WASTE CHARACTERIZATION

Five of the 28 DSTs are on the FGWL. These tanks are AN-103, AN-104, AN-105, AW-101, and SY-103. Tank SY-101 was removed from the FGWL and returned to service as described in Chapter 3.0 of this report. General information about the five remaining tanks is presented in Table 5-1.

Table 5-1. Waste Characterization Data for Double-Shell Tanks on the Flammable Gas Watch List.

Parameter[a]	AN-103	AN-104	AN-105	AW-101	SY-103
Waste level (cm)	884±3	978±3	1041±3	1039±3	691±3
Tank headspace (m^3)	1,717	1,352	1,074	1,074	2,521
CL density (kg/m^3)	1,530±50	1,440±30	1,400±60	1,420±20	1,470±30
NCL density (kg/m^3)	1,730±110	1,580±50	1,580±40	1,570±40	1,600±30
CL thickness (cm)	417±8	526±41	546±43	673±38	307±13
NCL thickness (cm)	378±10	411±41	450±41	287±30	335±5
Crust thickness (cm)	89±15	41±8	46±10	79±20	58±13
CL temperature[b] (°C)	38	34	32	33	31
Peak NCL temperature[b] (°C)	40	38	40	36	35
Waste class[c]	DSS	DSSF	DSSF	DSSF	CC

Notes:

[a]Waste layer references (Hedengren et al. 2000) and waste types (Hanlon 2001) are as follows:

CC = complexant concentrate
CL = convective layer
DSS = double-shell slurry
DSSF = double-shell slurry feed
NCL = Nonconvective layer

[b]Temperatures are as of December 31, 2000.

The waste viscosity and yield stress were measured by the ball rheometer in 1995-96 (Hedengren et al. 2000). The convective layers in the five tanks were found to behave as a Newtonian fluid with viscosities of 5 to 20 cP. The yield stress in the nonconvective layer increased approximately linearly from near zero at the upper surface to a maximum of 150 to 300 Pa near the tank bottom.

The concentrations (moles per liter of waste) of the major chemical constituents of the waste in each of the five tanks are given in Table 5-2. The values in the table were computed from the Best Basis Inventory and total waste volumes. The waste composition is very similar in the five tanks, consisting predominantly of sodium, hydroxide, nitrate, nitrite, and aluminum ion. The concentrations of these substances in the three tanks with double-shell slurry feed waste (AN-104, AN-105, and AW-101) are somewhat less than in tank AN-103, which contains double-shell slurry waste. The higher TOC concentration in tank SY-103 reflects the contribution of complexant concentrate waste mixed with double-shell slurry feed.

Table 5-2. Concentrations of Major Waste Constituents in Double-Shell Tanks.

Constituent	AN-103	AN-104	AN-105	AW-101	SY-103
Sodium	13.2	11.6	11.2	10.8	11.1
Hydroxide	12.9	8.31	8.24	9.88	9.35
Nitrate	3.24	2.77	2.66	2.80	2.89
Nitrite	2.98	2.41	2.40	2.45	2.92
Aluminate	2.29	1.30	1.42	1.03	1.91
Carbonate	0.43	0.77	0.77	0.44	0.56
Potassium	0.34	0.16	0.15	0.94	0.12
Total organic carbon	0.24	0.40	0.73	0.38	1.12

Notes:

- Results are moles per liter of waste.
- Hydroxide values are calculated values based on information in the Best Basis Inventory.
- These constituents are listed because of their influence on flammable gas generation. The list is not intended to be inclusive for any other purpose (e.g., dangerous waste from a toxicological viewpoint).

The temperatures in tanks AN-103, AN-104, AN-105, and AW-101 have been decreasing steadily since the ventilation systems were upgraded in 1995-1997. The temperature histories of the waste at 10 cm (4 in.) above the tank bottom in each of the five tanks are shown in Figure 5-1. In mid-1995 the AN farm annulus ventilation rates were increased to approximately 5.7 m^3/min (200 ft^3/min). The tank headspace ventilation flow rates were increased from about 0.6 to 0.9 m^3/min (20 to 30 ft^3/min) to approximately 2.8 m^3/min (100 ft^3/min) in tank AW-101 in mid-1996, and in tanks AN-103, AN-104, and AN-105 in early 1997. As a result, the waste temperatures in these three tanks have decreased. The increased flow rate through the annulus also resulted in a more marked seasonal oscillation in the tank temperatures. The ventilation rate in tank SY-103 has not changed so the average temperature of its waste has remained relatively constant (the abrupt decrease in tank SY-103 temperature in December 1996 was the result of a recalibration of the data acquisition system). The annual cycle in temperature for each tank,

as seen in Figure 5-1, is due to the influence of the seasonal changes on the temperature of the air that is drawn into the tank dome space.

Figure 5-1a. Waste Temperature History in Tanks 241-AN-103, 241-AN-104, and 241-AN-105.

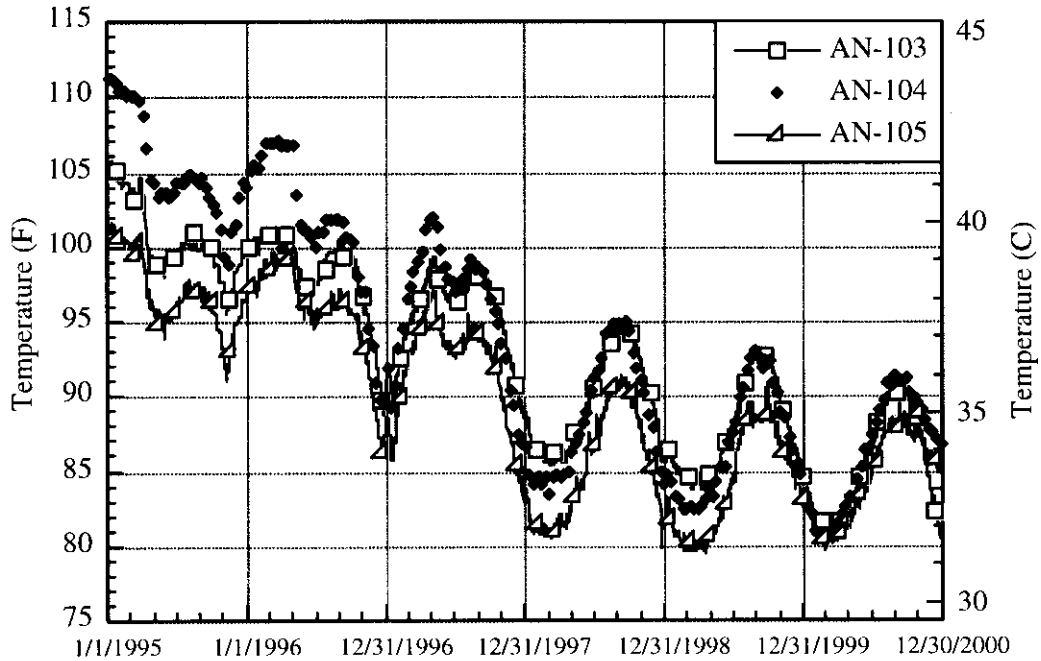
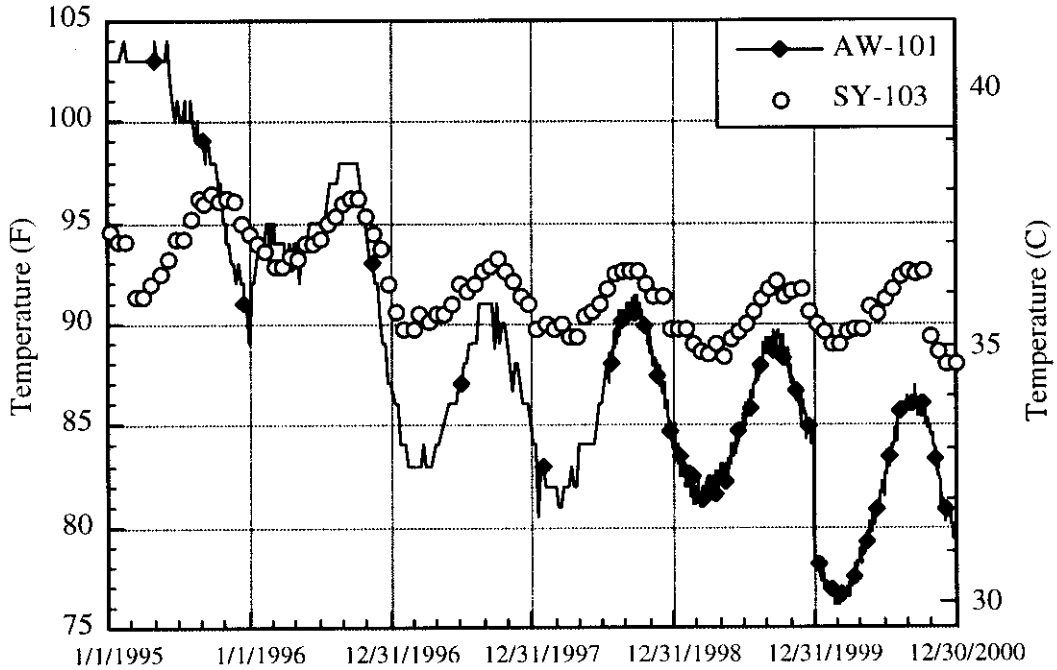


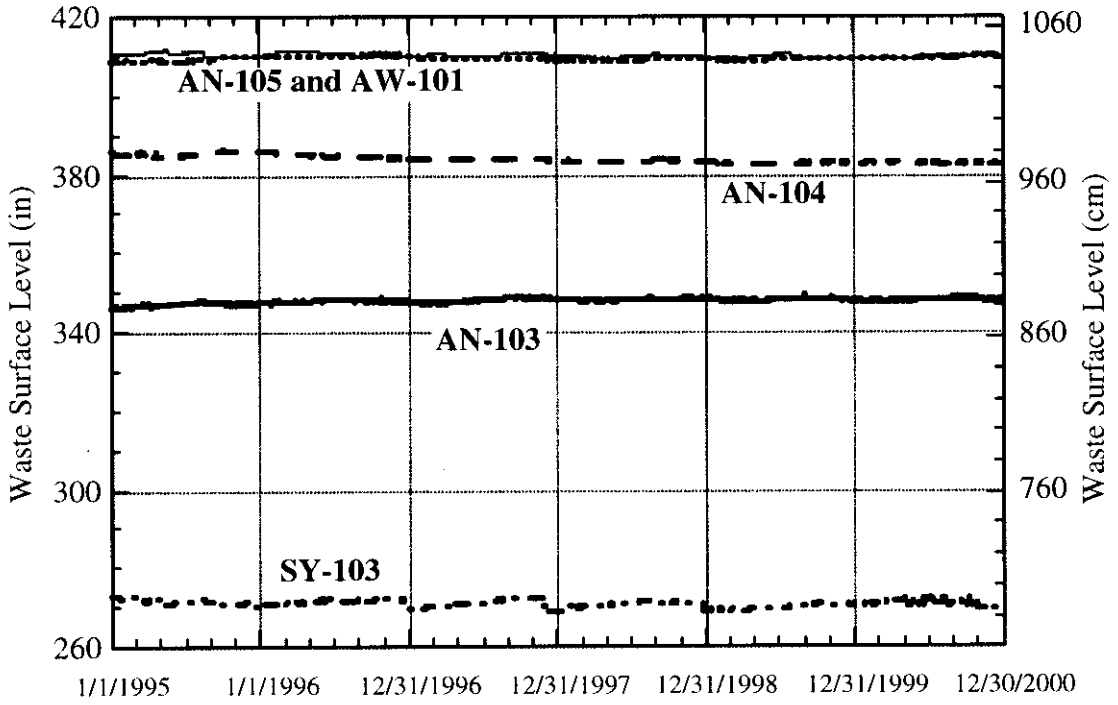
Figure 5-1b. Waste Temperature History in Tanks 241-AW-101 and 241-SY-103.



This cooling trend in the four tanks has strongly influenced the behavior of the gas. Since the thermal component of hydrogen generation is very sensitive to temperature, the gas generation rates have decreased (Figure 5-4). The number and size of spontaneous gas releases has also decreased (Hedengren et al. 2000). The behavior of tank SY-103 has not changed significantly, however, since it has not joined the cooling trend of the other tanks since the ventilation rate in this tank has remained constant.

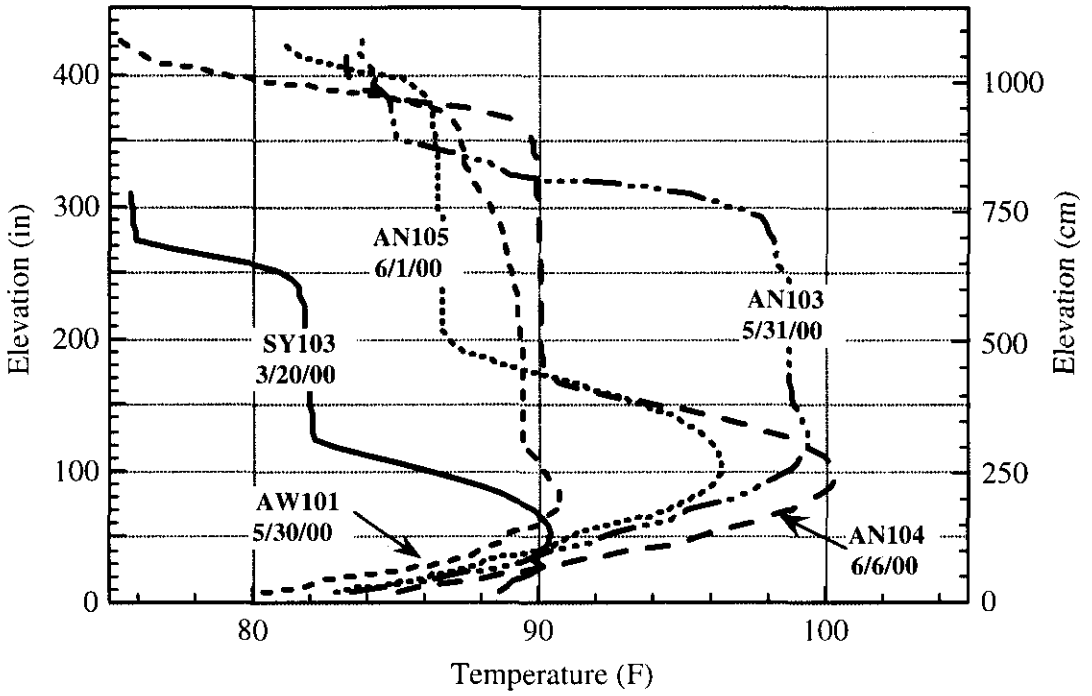
The waste level history of the five DSTs is shown in Figure 5-2. The level has not been increasing in any of these tanks. The coarse scale of the ordinate makes the small fluctuations caused by buoyant displacement GREs detectable only for SY-103.

Figure 5-2. Waste Surface Level Histories in Double-Shell Tanks.



The waste configuration is best shown by the temperature profiles obtained with the MIT validation probe. Profiles obtained in the spring of 2000 are plotted in Figure 5-3. Like the waste level, the crust thickness and nonconvective layer depths in these tanks (shown in Table 5-1) have not changed significantly, though adjustments appear to be occurring in AW-101 and AN-103 as evidenced by their non-uniform convective layer temperatures.

Figure 5-3. Waste Temperature Profiles in Double-Shell Tanks.



5.2 GAS COMPOSITION AND GENERATION

The composition of the gas mixtures being produced in DST tanks has been measured with the RGS (Mahoney et al. 1999). A summary for the major components for the nonconvective layer is given in Table 5-3. Hydrogen fractions range from 0.32 to 0.61. The remaining minor species are methane, ammonia, water vapor, and various organic compounds. No direct measurements were made for tank SY-103. However, composition observed in laboratory gas generation tests was 54 mol% hydrogen, 31 mol% nitrogen, and 14 mol% nitrous oxide (Hedengren et al. 2000).

Table 5-3. Nonconvective Layer Gas Compositions for Double-Shell Tanks.

Tank	Average Mol% Hydrogen	Average Mol% Nitrogen	Average Mol% Nitrous Oxide
AN-103	61 ± 8	33 ± 4	4 ± 0.6
AN-104	45 ± 7	29 ± 4	23 ± 4
AN-105	60 ± 5	24 ± 4	14 ± 2
AW-101	32 ± 3	56 ± 6	7 ± 1
SY-103	54	31	14

As the result of the laboratory work and waste characterization efforts, an empirical equation was developed for estimating hydrogen generation rates in the various tanks (Hu 2000). This empirical correlation was based on data for 12 DSTs and 16 SSTs. The rate equations account for hydrogen production by radiolysis, thermal processes, and corrosion. Recent applications of this model to the five DSTs (Hu et al. 2001) provided the gas generation rate information shown

in Table 5-4. The total gas generation rate is computed from the hydrogen generation rate using the hydrogen fractions from the RGS data in Table 5-3.

Table 5-4. Gas Generation Rates for Double-Shell Tanks.

Tank	Hydrogen generation rate		Total gas generation rate	
	(standard ft^3/day)	(m^3/day)	(standard ft^3/day)	(m^3/day)
AN-103	6.8	0.19	11	0.31
AN-104	3.7	0.10	8	0.23
AN-105	4.4	0.12	7	0.20
AW-101	3.6	0.10	11	0.31
SY-103	5.1	0.14	9	0.25

Accumulation of hydrogen due to steady-state production and release is not an issue since these tanks have active ventilation systems that provide about 4,078 m^3/day of continuous flow of air with a filtered system. Ventilation reduces the steady-state hydrogen concentration in the headspace to 20 to 50 ppm.

The generation rates have been decreasing due to the waste cooling trend. The actual hydrogen generation rates were determined in tanks AN-104, AN-105, and AW-101 for four 12-month periods by integrating the product of the measured hydrogen concentrations and the ventilation rates (Hedengren et al. 2000). Since the waste levels were not changing significantly, the total hydrogen release is an accurate representation of the generation. The decreasing trend in hydrogen generation is shown in Figure 5-4 (Hedengren et al. 2000). The rates have decreased on the order of 50% from 1996 to 1999. Note that the measured rates for 1999 match the predictions of Hu's (2000) model for the three tanks quite well.

Information in Figure 5-4 is from D. C. Hedengren, K. M. Hodgson, W. B. Barton, C. W. Stewart, J. M. Cuta, and B. E. Wells, 2000, *Data Observations on Double-Shell Flammable Gas Watch List Tank Behavior*, RPP-6655, Rev. 0, CH2M HILL Hanford Group, Richland, Washington.

5.3 GAS RETENTION

Direct measurement of the local in situ void fraction in several DSTs with the VFI and RGS and some SSTs using the RGS provides information on the distribution of gas in the waste. The local measurements also yield a good estimate of the total gas volume and average void fraction in the tanks. The results of the retained gas volume calculation from VFI and RGS data for five tanks are summarized in Table 5-5. In the table, "Mean Void" is the average gas volume fraction determined from local measurements. "In situ Vol." is the gas volume at the local temperature and pressure of the layer calculated from the mean void fraction, and "Std. Vol." is the equivalent gas volume at standard temperature and pressure. Uncertainties in the table represent one standard deviation. Gas volumes were calculated from void measurements made in 1995 and 1996. However, available temperature profiles and level trends indicate that the gas content has not changed significantly since then.

Figure 5-4. Hydrogen Generation Trends in Three Double-Shell Tanks.

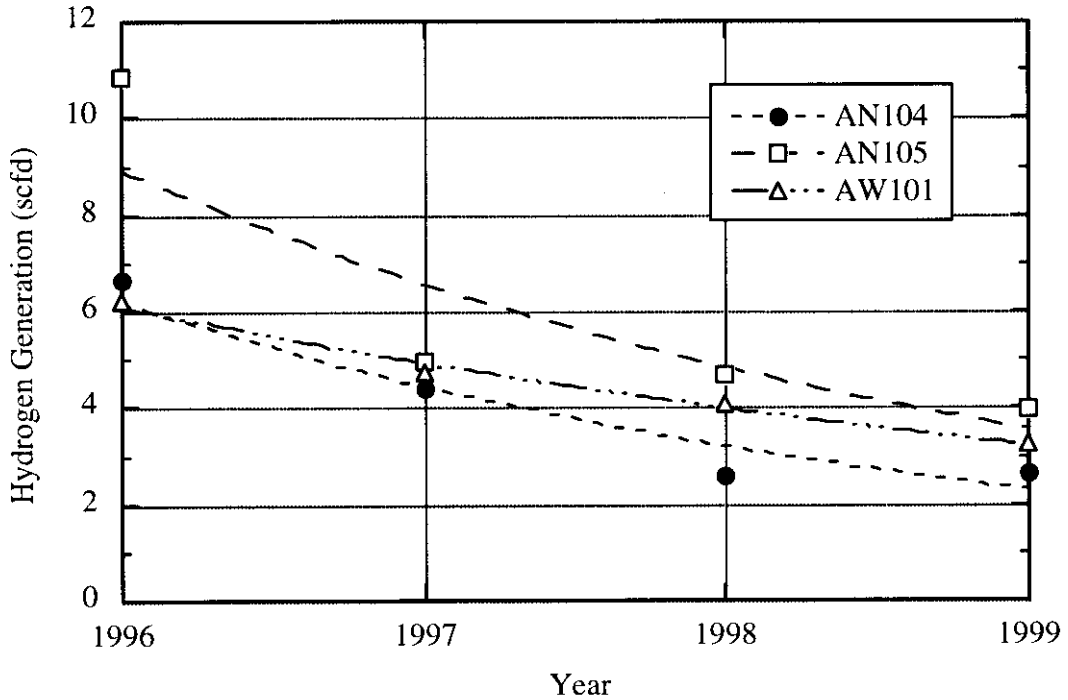


Table 5-5. Retained Gas Volume Summary for Double-Shell Tanks.

	AN-103	AN-104	AN-105	AW-101	SY-103
Crust Layer					
Mean Void (%)	15 ± 6	12 ± 4	14 ± 5	13 ± 4	11 ± 3
In situ Vol.[a] (m^3)	52 ± 22	19 ± 7	25 ± 10	40 ± 15	25 ± 9
Std. Vol.[b] (m^3)	54 ± 23	19 ± 7	25 ± 10	41 ± 15	26 ± 9
Convective Layer					
Mean Void (%)	0.5 ± 0.1	0.4 ± 0.01	0.2 ± 0.1	0.3 ± 0.1	0.7 ± 0.3
In situ Vol.[a] (m^3)	8 ± 2	9 ± 2	4 ± 2	10 ± 2	9 ± 4
Std. Vol.[b] (m^3)	11 ± 3	12 ± 2	6 ± 2	15 ± 3	11 ± 4
Nonconvective Layer					
Mean Void (%)	11.0 ± 0.7	6.6 ± 0.8	4.4 ± 0.9	3.8 ± 0.4	7.0 ± 1.9
In situ Vol.[a] (m^3)	170 ± 10	110 ± 12	80 ± 16	45 ± 5	93 ± 25
Std. Vol.[b] (m^3)	329 ± 22	230 ± 23	170 ± 23	97 ± 11	160 ± 42
Tank Total					
In situ Vol.[a] (m^3)	231 ± 24	138 ± 14	110 ± 19	95 ± 16	127 ± 27
Std. Vol.[b] (m^3)	394 ± 32	261 ± 24	201 ± 34	153 ± 19	197 ± 43

From Hedengren et al. 2000.

[a]In situ Vol. refers to the volume of gas stored in the tank under hydro-static pressure and local waste temperature.

[b]Std. Vol. refers to the volume that the gas would occupy at 1 atm pressure at 298K.

Plots of the local void fractions and uncertainties are shown in Figures 5-5 through 5-9. The legend refers to risers from which the data were obtained. The plot legends show each traverse of the VFI in each riser and each riser of an RGS core sample. Thus "1B-1" indicates the first traverse of the VFI in Riser 1B while "RGS 7B" denotes RGS data from Riser 7B. The data shown in the figures indicate there is essentially no gas in the convective liquid as expected. There are significant variations in the gas content at different locations but the peak gas fractions are less than 0.18. There are also differences in the results obtained with the void fraction instrument (VFI) and the RGS but both measurements follow similar trends.

Figure 5-5. Tank 241-AN-103 Void Profile.

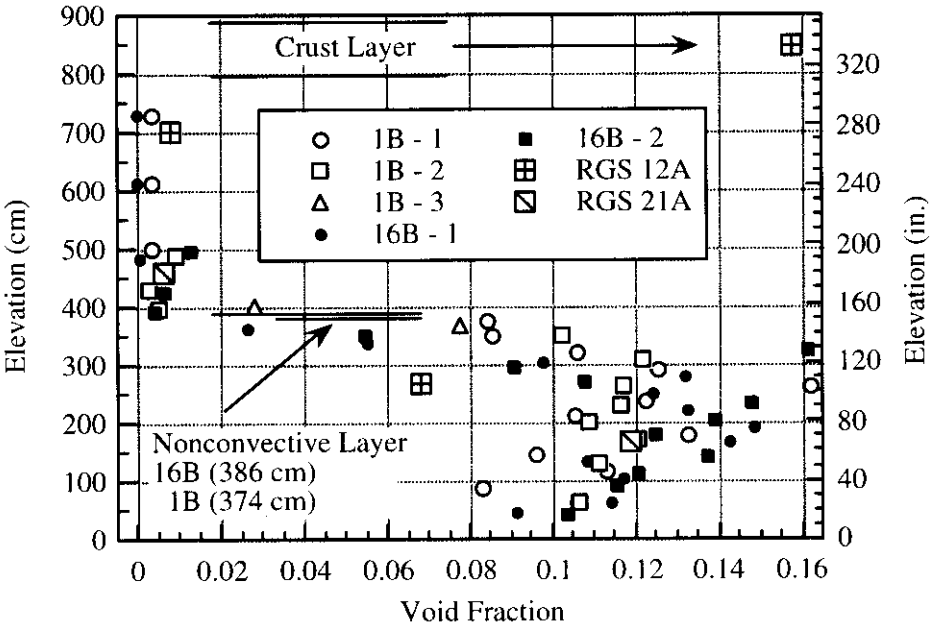


Figure 5-6. Tank 241-AN-104 Void Profile.

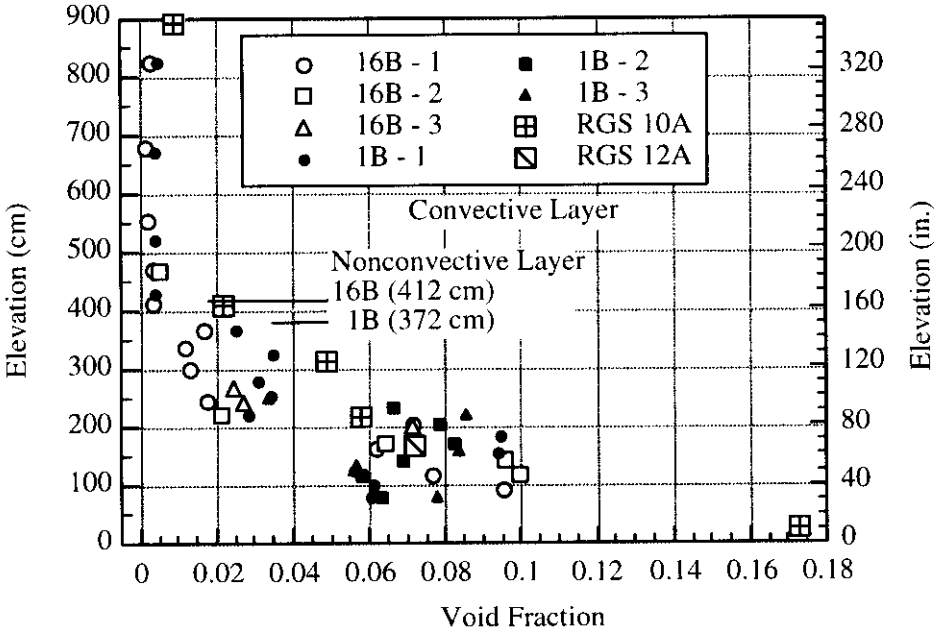


Figure 5-7. Tank 241-AN-105 Void Profile.

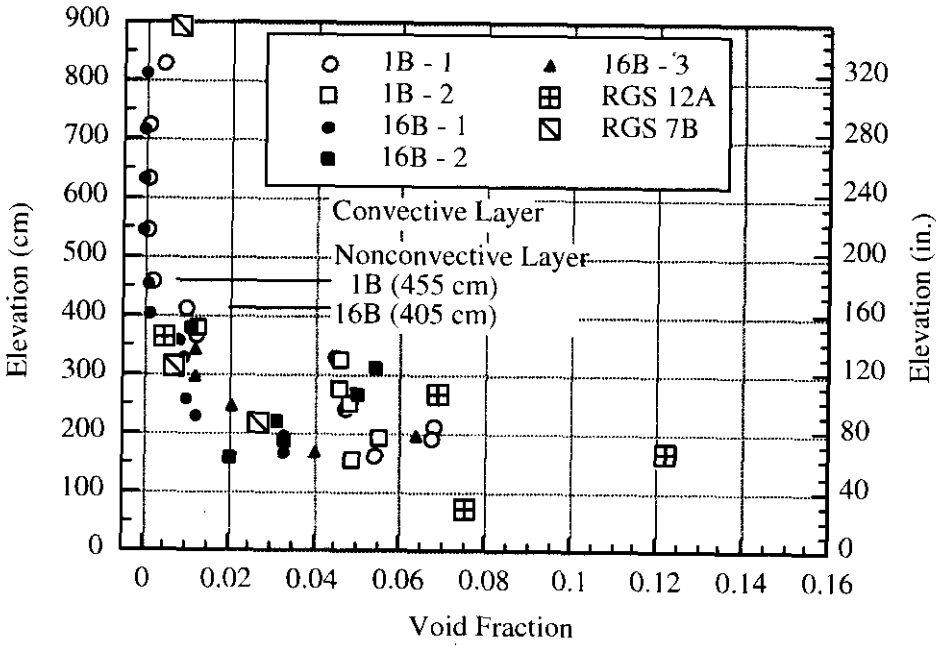


Figure 5-8. Tank 241-AW-101 Void Profile.

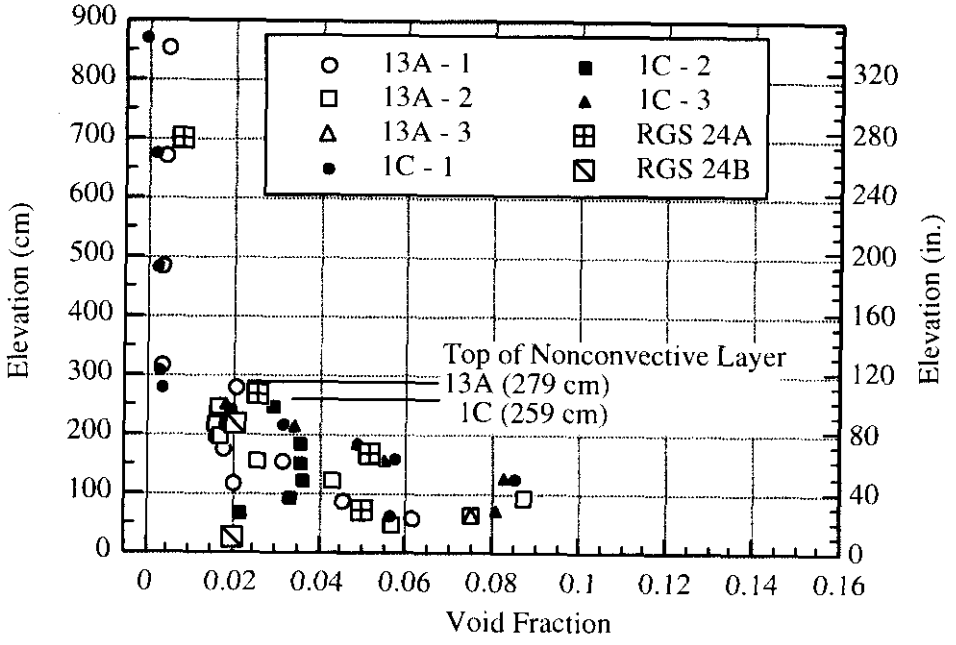
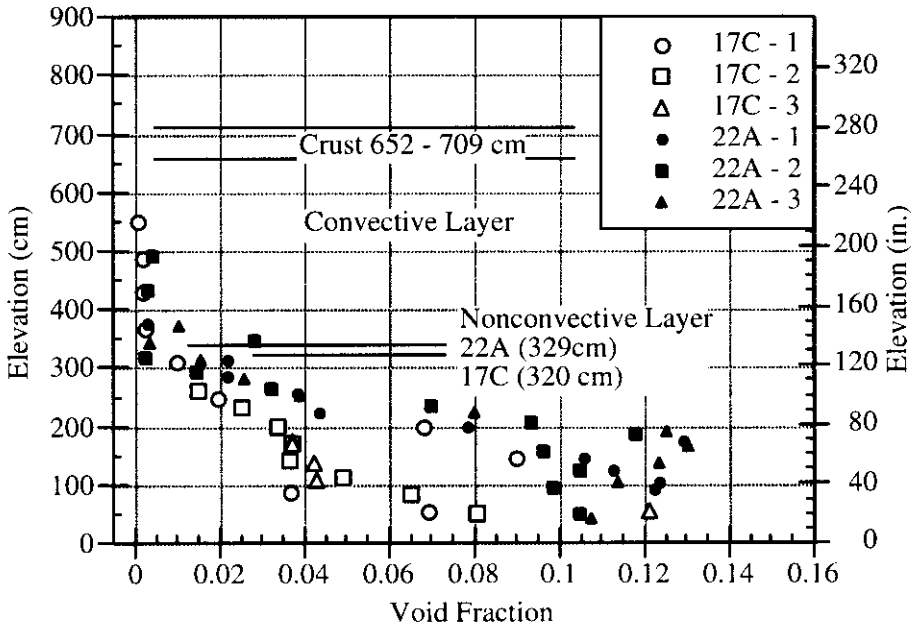


Figure 5-9. Tank 241-SY-103 Void Profile.



5.4 GAS RELEASE

5.4.1 Measured Gas Releases

SHMS monitoring has provided headspace hydrogen concentration data since 1994. The normal steady-state background hydrogen concentration in these tanks is usually less than 100 ppm (McCain 2000). The SHMS data also clearly identify GREs. The information about gas releases for tanks AN-103, AN-104, AN-105, AW-101, and SY-103 is summarized in Table 5-6. The table shows the number of GREs, the number of releases exceeding 1,000 and 9,000 ppm hydrogen concentration and the maximum hydrogen concentration realized in these events. The value of 9,000 ppm was picked because it is 25% of the minimum LFL computed from LeChatelier's Law using RGS data (Mahoney et al. 2000).

Table 5-6. Gas Release Event Summary (1994-2000).

Tank	Number of GREs	Number of Releases with $[H_2]$ > 1000 ppm	Number of Releases with $[H_2]$ > 9000 ppm	Peak $[H_2]$ (ppm)
SY-103	23	16	0	5110
AW-101	26	20	0	8800
AN-103	5	3	0	3000
AN-104	18	7	0	6109
AN-105	13	8	2	17,000

GRE = gas release event.

Gas releases in tanks AN-103, AN-104, AW-101, and SY-103 have not been large enough to cause the headspace concentration to exceed 9,000 ppm in the last five years. Tank AN-105 has had only two releases that have exceeded 25% of the LFL and none exceeded the LFL. The maximum hydrogen concentration was 17,000 ppm, less than 50% of the LFL.

Measurements of the concentration of hydrogen over several years have shown that the steady state values are less than 50 ppm. Data for these grab samples are provided in McCain 1999 and McCain 2000.

Waste level decreases during the GREs in these tanks are generally less than 3 cm. It is important to note that the releases in these five DSTs are significantly less than the releases noted for tank SY-101 prior to mixer pump installation (see Chapter 4.0). Based on the size of the releases seen in these tanks, it appears that the events are localized and do not involve the entire tank contents (Meyer et al. 1997).

5.4.2 Tank Behavior with Respect to Watch List Criterion

The criterion for watch list tanks noted in Section 1.3 is centered on a volume of gas in the dome that if burned would cause the tank to exceed a containment design limit. In the case of tank SY-101 this situation was analyzed for removal of the tank from the watch list (Johnson et al. 2000). The analysis had been done at Los Alamos National Laboratory (LANL) using a hydrogen mixing study/transient reactor analysis code (HMS/TRAC) (LANL 1996). The evaluated failure pressure for the tank structure is approximately 60 psig. Results of the HMS/TRAC evaluations showed that structural acceptance criteria (onset of failure) were met if the burned gas volume was 8,650 scf or less. The hydrogen volume was 30% of the 8,650 scf and this corresponds to 73.5 m^3. A similar analysis by LANL for SY-103 gave a hydrogen volume of 136 m^3. The dome space for SY-101 in the LANL analysis was 1,109 m^3; the other DSTs on the watch list have dome space volumes that range from 1,074 m^3 to 2,521 m^3 (Table ES-1). Thus for a tank with a dome space of 1,074 m^3, the hydrogen volume needed for the onset of failure is about 71 m^3. The values of 71 m^3 to 136 m^3 (SY-101 and SY-103, respectively) are much greater than the volume of hydrogen needed to reach the LFL (as noted in Table ES-1) and since the historical data show that the released volumes of hydrogen ranged only from 5.2 to 18.2% of the LFL, then clearly conditions for reaching the "containment related design limit" are not achievable. Use of the LFL in the discussions relating to removal of tanks from the watch list is a conservative approach.

5.5 SUMMARY OF DOUBLE-SHELL TANK INFORMATION

The information that has been acquired on the five DSTs on the FGWL is presented in this section. The results show that:

- The waste configurations in these tanks are well understood. The layer dimensions have not changed significantly over the past five years (Figures 5-2 and 5-3).
- The chemical composition and physical properties of the wastes are well understood (Table 5-2; Stewart et al. 1996b).

- Waste temperatures in tanks AN-103, AN-104, AN-105, and AW-101 have been decreasing for the past five years due to changes in ventilation rates (Figure 5-1). Tank SY-103 has shown little decrease since its ventilation rate has remained constant.

- The gas generation rates in tanks AN-104, AN-105, and AW-101 have decreased as a result of the waste cooling (Figure 5-4). Since AN-103 is also cooling, it is expected to exhibit a similar trend. Tank SY-103 has had a relatively constant rate since its temperature has shown only small changes. Total gas generation rates for all five tanks (Table 5-4) are in the range of 0.20-0.31 m^3/day and this is much smaller than the ventilation rates, which are on the order of 4,078 m^3/day.

- Hydrogen concentrations retained in the waste range from 32 to 61% of the total inventory (Table 5-3). Besides hydrogen, the retained gas contains nitrogen and nitrous oxide with lesser amounts of ammonia, water vapor, methane, and other hydrocarbons.

- The nonconvective layers in the five tanks contain 97 to 329 m^3 of gas with 19 to 54 m^3 retained in the crust layers (Table 5-5).

- There have been 85 spontaneous gas releases observed in SHMS data since 1994. The hydrogen concentration exceeded 25% of the LFL (9,000 ppm) during two of these events and the maximum concentration was 17,000 ppm (47% of the LFL). The LFL (36,000 ppm) was not exceeded in any of the releases. Typical releases are usually less than 10% of the retained gas volume with the largest release fraction being 19% (Table ES-1).

- Spontaneous gas releases have become smaller in size (as determined by flammable gas concentrations in the headspace) and less frequent since 1995 in four of the tanks (AN-103, AN-104, AN-105, and AW-101) while the waste temperatures and gas generation rates have decreased due to increases in primary and annulus ventilation rates. The ventilation rates in Tank SY-103 have remained constant. Therefore the waste has not cooled significantly and the small releases for SY-103 remain essentially unchanged in size and frequency (McCain 1999).

- Steady state concentrations of hydrogen in the dome spaces are generally in the range of 20 to 55 ppm (McCain 1999).

The summary of DST information indicates that the elements in the strategy for the resolution of the Flammable Gas Safety Issue outlined in Section 1.2 of this report pertaining to the behavior of the waste have been met.

6.0 EVALUATION OF FLAMMABLE GAS WATCH LIST SINGLE-SHELL TANKS

Of the 177 radioactive waste storage tanks at Hanford, 149 are SSTs built in the 1940s, 1950s, and early 1960s. These tanks are beyond their design life and several have leaked and others are suspected to have leaked. To alleviate the concern over leaking tanks, the SSTs were removed from active use in 1980 and their pumpable liquid is being or will be transferred to the DSTs. The ongoing process of interim stabilization (also called saltwell pumping) reduces the volume of waste, the volume of retained gas, and the gas generation rate by removing gas generating material. This section summarizes the information about the interim stabilization, gas generation rates and gas composition, gas retention, and gas release in the 19 SSTs on the FGWL. This discussion is based primarily on the comprehensive report on SSTs by Hedengren et al. (2001).

The work done to determine the physical properties and chemical composition of the wastes is described in Section 6.1. The rates of gas generation and the composition of the stored gas in these tanks are discussed in Section 6.2 and the volumes of gas retained in the waste are examined in Section 6.3. Spontaneous and induced gas releases are considered in Section 6.4 along with passive ventilation rates. A summary and conclusion are provided in Section 6.5.

6.1 WASTE CHARACTERIZATION

Data on the nineteen SSTs on the FGWL, including the type of waste, waste level and ILLs, maximum temperatures, and waste volumes, are listed in Table 6-1 (Hedengren et al. 2001). The numbers listed in parentheses indicate the decreases in the waste level and ILL observed as a consequence of saltwell pumping.

From the standpoint of waste level and temperature trends, the retained gas volume in the SSTs is not increasing and has decreased in a number of them. The changes in waste level in the last 10 years and the changes in the peak waste temperatures in the last 4 years are listed in Table 6-2. Prior to saltwell pumping, the waste levels in 13 of these tanks were decreasing or constant and the waste temperatures were decreasing or constant in all 19. The waste level was rising in six tanks but four of these have been or are being saltwell pumped, including the two with the maximum level rise rate, which was about 1.3 cm per year. The remaining two tanks show a level rise rate of less than 0.6 cm per year. A level rise of 1.3 cm indicates accumulation of about 10 scm of gas assuming an in-situ pressure of 2 atm.

Evaporation, in principle, can mask level growth by gas accumulation. The evaporation rate will depend on the amount of exposed liquid surface, the ventilation rate, temperature, relative humidity, and vapor pressure of the liquid. A very detailed study of evaporation and other factors that could influence the waste level was made by Hodgson et al. (1998). This very conservative study identified 12 tanks as being capable of releasing more than 25% of the LFL based on surface level rise alone. However, evaporation was stated as a major contribution in only one of these tanks. Currently the only FGWL tanks showing significant evaporation are the "hotter" SX-farm tanks where the typical evaporation rate is below 1.3 cm/year. This evaporation rate would not mask significant gas retention. Based on these data, it is not believed that significant gas retention can occur without being readily detectable by level change.

Table 6-1. Single-Shell Tanks on the Flammable Gas Watch List.

Tank	Capacity (kL)	Waste class and type[a]	Waste level (cm)[b]	ILL (cm)[b]	Peak Temp (°C)	Waste volume (kL)	
						Supernatant	Solids
A-101	3,785	DSSF – SC	856 [13]	897 [18]	62	1,832[c]	1,450
AX-101	3,785	DSSF – SC	676 [30]	671 [20]	53	1,431[c]	1,128
AX-103	3,785	CC – SC	97	-	42		424
S-102	2,869	DSSF - SC/SL	429 [91]	429 [91]	37		1,862
S-111	2,869	NCPLX - SC/SL	518	516	31	182	1,715
S-112	2,869	NCPLX – SC	480	312	29		1,980
SX-101	3,785	DC – SC	422	424	54		1,696
SX-102	3,785	DSSF – SC	488	490	59	507	1,438
SX-103	3,785	NCPLX - SC/SL	556 [38]	577 [20]	69		2,354
SX-104	3,785	DSSF - SC/SL	427 [127]	241 [305]	59		1,688
SX-105	3,785	DSSF – SC	394 [213]	343 [8]	72		1,942
SX-106	3,785	NCPLX – SC	264 [239]	183 [312]	37		1,503
SX-109	3,785	NCPLX - SC/SL	244	-	57		942
T-110	2,006	NCPLX – SL	373 [30]	371 [38]	17		1,397
U-103	2,006	NCPLX – SC	414 [43]	152 [300]	31	4	1,578
U-105	2,006	NCPLX – SC	350 [66]	236 [183]	31		1,253
U-107	2,006	DSSF – SC	396	396	26	125	1,419
U-108	2,006	NCPLX – SC	455	452	30	91	1,681
U-109	2,006	NCPLX – SC	404 [46]	201 [249]	29		1,525

Notes:

[a]Waste classes and types are as follows (derived from data in Hanlon 2001):

CC = complexant concentrate.
DC = dilute complexed.
DSSF = double-shell slurry feed.
ILL = interstitial liquid level.
NCPLX = noncomplexed.
SC = primarily salt cake.
SC/SL = salt cake with more than about 10% sludge.
SL = primarily sludge.

[b]The level is as of December 2000. The number in brackets is the level decrease resulting from saltwell pumping.

[c]Liquid is the bottom layer in A-101 and AX-101.

Table 6-2. Waste Level and Temperature Changes in Single-Shell Watch List Tanks.

Tank	Waste level or ILL change 1990 - 2000[a] (cm)	Peak temperature change 1996 - 2000[b] (°C)
A-101	-10	-1
AX-101	0	-3
AX-103	-10	-1
S-102	+13	-1
S-111	+2	-1
S-112	-13	-1
SX-101	-8	-3
SX-102	-23	-3
SX-103	-25	-6
SX-104	-25	-6
SX-105	-23	-5
SX-106	-18	-4
SX-109	0	-7
T-110	0	0
U-103	+5	-1
U-105	+10	-1
U-107	+5	-1
U-108	-3	-1
U-109	+5	0

Notes:

[a]Period ends December 2000 or start of saltwell pumping, whichever is earlier, unless pumping was completed before 1990. ILL is used for pre-Enraf level when recent level and ILL are approximately equal.

[b]Period ends December 2000 or start of saltwell pumping, whichever is earlier, unless pumping was completed prior to 1996 or did not affect temperatures.

ILL = interstitial liquid level.

The liquid and bulk solids densities were obtained from analyses of core samples taken before saltwell pumping. In salt cake tanks, the liquid densities ranged between 1350 and 1550 kg/m^3 and bulk solids densities between 1650 and 1750 kg/m^3. The one sludge tank, T-110, had liquid and solid densities of 1060 and 1260 kg/m^3, respectively.

The concentrations (total moles per liter of waste) of the major chemical constituents of the waste in each of the nineteen tanks are given in Table 6-3. The values in the table were computed from the Best Basis Inventory and total waste volumes. The waste compositions of all nineteen tanks are similar, consisting predominantly of sodium, hydroxide, nitrate, nitrite, and aluminum. The only sludge tank, T-110, is an obvious exception. The TOC concentration found in U-105 is much larger than the other tanks. The same dominant species are found in the DSTs with concentrations similar to the SSTs except that the latter appear to have generally higher nitrate and lower nitrite concentrations. More detailed information on the organic and inorganic constituents is given by Hedengren et al. (2001). Characterization data specific to gas generation, retention, and release are provided in Sections 6.2, 6.3, and 6.4, respectively.

6.2 GAS COMPOSITION AND GENERATION

The radiolytic and thermal rates of generation of hydrogen, nitrous oxide, nitrogen, and methane have been measured at several temperatures for samples of waste from tanks A-101, S-102, S-106, and U-103. This information and the related information about the gas generation rates in the DSTs were used to establish an empirical relationship between the hydrogen generation rate and the chemical and physical properties of the waste (Hu 2000). This relationship was used to estimate the hydrogen generation rates in the SSTs after the completion of saltwell pumping operations. The removal of drainable liquid by saltwell pumping will reduce the rate of hydrogen generation as shown for 17 tanks in Table 6-4 (Hedengren et al. 2001).

The highest initial hydrogen generation rates are 0.5 standard m^3/day in tank A-101 and 0.4 standard m^3/day in tank SX-105. The largest change due to saltwell pumping is expected to occur in tank A-101, which has a relatively high hydrogen generation rate and has a large amount of liquid to be removed. The hydrogen generation rate in A-101 is calculated to decrease from 0.5 to 0.1 standard m^3/day. Very little change in the estimated hydrogen generation rates is predicted for tanks S-112 and T-110 where the initial rate and the decrease in total liquid inventory are relatively small. According to the model (Hu 2000), corrosion, rather than thermal or radiolytic processes, is the dominant hydrogen source in these two tanks.

The waste gas composition has been measured by the RGS in nine SSTs of which seven are on the FGWL. See Section 6.3 for further discussion. The average gas compositions calculated from local RGS measurements in the SSTs are summarized in Table 6-5.

Table 6-3. Concentrations of Major Waste Constituents in Single-Shell Watch List Tanks (Total Moles per Liter).

Tank	Sodium	Hydroxide	Nitrate	Nitrite	Aluminate	Carbonate	Phosphate	TOC
A-101	12.18	10.35	3.38	2.94	1.61	1.08	0.07	0.52
AX-101	12.89	10.47	3.91	3.33	1.72	0.84	0.07	0.42
AX-103	13.03	11.51	2.71	3.03	1.49	1.68	0.08	0.62
S-102	9.16	4.11	5.11	0.96	0.65	0.46	0.53	0.37
S-111	9.47	14.90	4.01	0.96	3.50	0.17	0.15	0.18
S-112	14.56	9.56	7.11	1.76	1.17	0.29	0.45	0.56
SX-101	14.23	18.38	7.05	1.18	3.80	0.19	0.09	0.16
SX-102	14.06	10.94	5.45	2.82	1.78	0.99	0.09	0.47
SX-103	12.69	14.48	5.59	2.65	3.21	0.74	0.07	0.47
SX-104	11.88	14.40	5.63	1.65	3.42	0.78	0.27	0.39
SX-105	11.96	11.54	4.36	2.71	2.24	0.59	0.12	0.34
SX-106	12.17	8.15	5.53	2.27	1.16	0.56	0.20	0.44
SX-109	12.23	19.52	6.87	1.31	5.99	0.20	0.06	0.15
T-110	2.46	2.06	1.12	0.14	0.05	0.11	0.24	0.08
U-103	10.09	8.06	4.24	1.35	0.89	0.69	0.30	0.79
U-105	11.14	12.38	6.15	1.31	1.31	0.95	0.51	1.99
U-107	11.86	6.21	7.25	1.79	1.24	0.42	0.29	0.33
U-108	17.85	9.96	8.00	1.94	1.07	1.12	0.38	0.60
U-109	9.84	5.68	4.69	1.25	1.01	0.65	0.42	0.37

Note:

Hydroxide values are calculated values based on information in the Best Basis Inventory.

TOC = total organic carbon.

Table 6-4. Estimated Hydrogen Generation Rates Before and After Saltwell Pumping.

Tank	Saltwell pumping status	Pre-pumping		Post-pumping	
		Total liquid inventory (kL)	Hydrogen generation rate (m^3/day [ft^3/day])	Total liquid inventory (kL)	Hydrogen generation rate (m^3/day [ft^3/day])
A-101	In Progress	3,009	0.52 (18.5)	787	0.10 (3.6)
AX-101	In Progress	2,278	0.16 (5.6)	598	0.04 (1.5)
S-102	In Progress	670	0.06 (2.2)	130	0.05 (1.6)
S-111	Not Started	1,374	0.04 (1.5)	874	0.04 (1.3)
S-112	Not Started	1,488	0.05 (1.7)	1,222	0.05 (1.6)
SX-101	In Progress	958	0.05 (1.7)	583	0.05 (1.6)
SX-102	Not Started	1,575	0.11 (3.8)	1,136	0.08 (2.9)
SX-103	In Progress	1,703	0.23 (8.0)	1,204	0.17 (5.9)
SX-104	Finished	1,404	0.18 (6.2)	931	0.14 (4.8)
SX-105	In Progress	1,851	0.39 (13.7)	1,317	0.29 (10.2)
SX-106	Finished	1,639	0.06 (2.1)	1,033	0.04 (1.4)
T-110	Finished	1,393	0.04 (1.3)	1,264	0.04 (1.3)
U-103	Finished	1,276	0.06 (2.2)	867	0.05 (1.8)
U-105	Finished	886	0.06 (2.0)	541	0.04 (1.5)
U-107	Not Started	1,177	0.04 (1.3)	742	0.03 (1.2)
U-108	Not Started	1,393	0.05 (1.8)	923	0.05 (1.6)
U-109	In Progress	882	0.04 (1.5)	435	0.04 (1.4)

Table 6-5. Retained Gas Sampler Gas Compositions (mol%). (2 sheets)

Tank layer	Hydrogen	Nitrogen	Nitrous oxide	Ammonia	Methane	Other gases
A-101 NCL	72 ± 7	19 ± 5	6 ± 0.6	2.5 ± 0.9	< 1	< 1
A-101 CL	15 ± 5	64 ± 24	14 ± 5	3.4 ± 1.8	1.6 ± 0.8	2.0 ± 0.9
AX-101 NCL[a]	61 ± 6	17 ± 3	11 ± 1	8.4 ± 1.9	2.4 ± 0.2	< 1
S-102[b]	33 ± 3	32 ± 4	33 ± 3	1.1 ± 0.4	< 1	< 1
S-111	66 ± 10	21 ± 6	11 ± 2	1.1 ± 0.4	< 1	< 1
S-111 liquid	6.3 ± 3.4	90 ± 68	1.7 ± 1.0	< 1	< 1	1.0 ± 0.8
SX-106	50 ± 5	20 ± 4	24 ± 3	5.5 ± 1.2	< 1	< 1
SX-106 liquid	21 ± 5	64 ± 21	12 ± 3	< 1	1.1 ± 0.4	1.4 ± 0.5

Table 6-5. Retained Gas Sampler Gas Compositions (mol%). (2 sheets)

Tank layer	Hydrogen	Nitrogen	Nitrous oxide	Ammonia	Methane	Other gases
U-103[b]	23 ± 1	36 ± 2	39 ± 2	< 1	< 1	< 1
U-109[b]	25 ± 3	46 ± 8	27 ± 4	1.2 ± 0.5	< 1	< 1

Notes:

[a]From only one sample in AX-101.

[b]Tanks S-102, U-103, and U-109 had only one major waste layer.

CC = complexant concentrate.

CL = convective layer.

NCL = nonconvective layer.

The steady state concentrations of hydrogen in single-shell tanks have remained below 1000 ppm. Table 6-6 provides an estimate of the steady state values for each of the 19 SSTs. These values were estimated from SHMS data that are provided in McCain (2000). Spontaneous GREs are discussed in Section 6.4.1 and induced releases are covered in Section 6.4.2.

Table 6-6. Steady State Concentrations of Hydrogen in SSTs.

Tank (241-)	Estimated Current Steady State (ppm)
A-101	200-300
AX-101	200
AX-103	<50
S-102	500
S-111	200
S-112	75
SX-101	50
SX-102	<50
SX-103	<50
SX-104	<50
SX-105	75
SX-106	75
SX-109	<50
T-110	<50
U-103	500
U-105	700
U-107	500
U-108	<100
U-109	600

6.3 GAS RETENTION AND DISTRIBUTION

Gas retention in SSTs on the FGWL has been investigated in several ways. Gas retention tests were performed on waste samples from several tanks, as discussed in Section 3.2.2, and local gas fractions in tanks that were believed to contain the largest volume of retained gas were measured with the RGS. The total stored gas volume has also been estimated for applicable tanks using the BPE method and integration of neutron logs.

RGS samples were obtained from tanks A-101, AX-101, S-102, S-111, SX-106, U-103, and U-109 between 1996 and 1998. The average gas volume fraction and the total retained gas volume for each tank were determined from these data. However, four of these tanks (S-102, U-103, U-109, SX-106) have been saltwell pumped since RGS data were collected. The gas fraction distributions and gas volumes in these tanks have changed as a consequence of pumping.

The local gas volume fractions measured by the RGS in SSTs between 1996 and 1998 are shown in Figures 6-1 through 6-7. The plot legends denote each riser from which an RGS core sample was withdrawn. The vertical line shows the core segment length of 19 in. (48 cm).

Figure 6-1. Local Gas Fractions in Tank 241-A-101 (1996 Data, Pre-Saltwell Pumping).

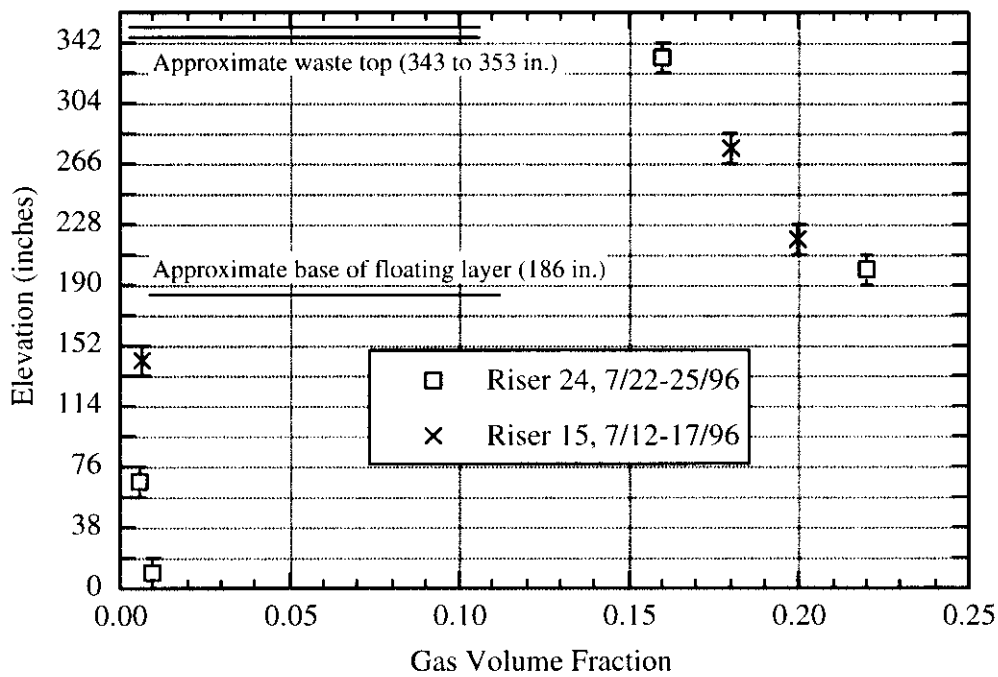


Figure 6-2. Local Gas Fractions in Tank 241-AX-101 (1998 Data, Pre-Saltwell Pumping).

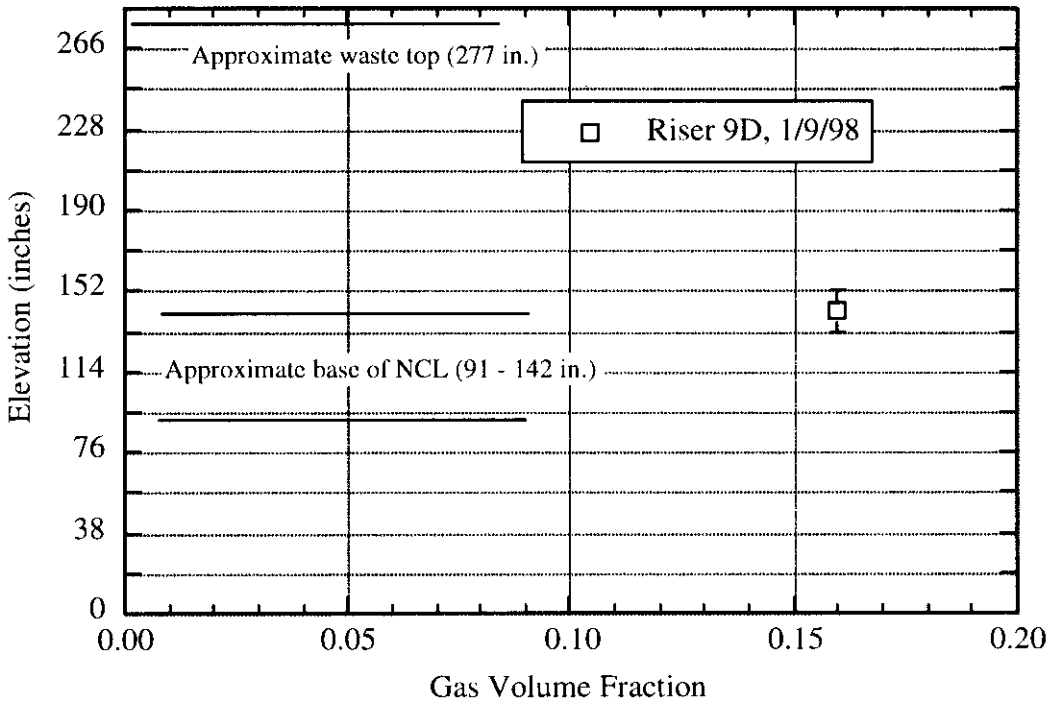


Figure 6-3. Local Gas Fractions in Tank 241-S-102 (1998 Data, Pre-Saltwell Pumping).

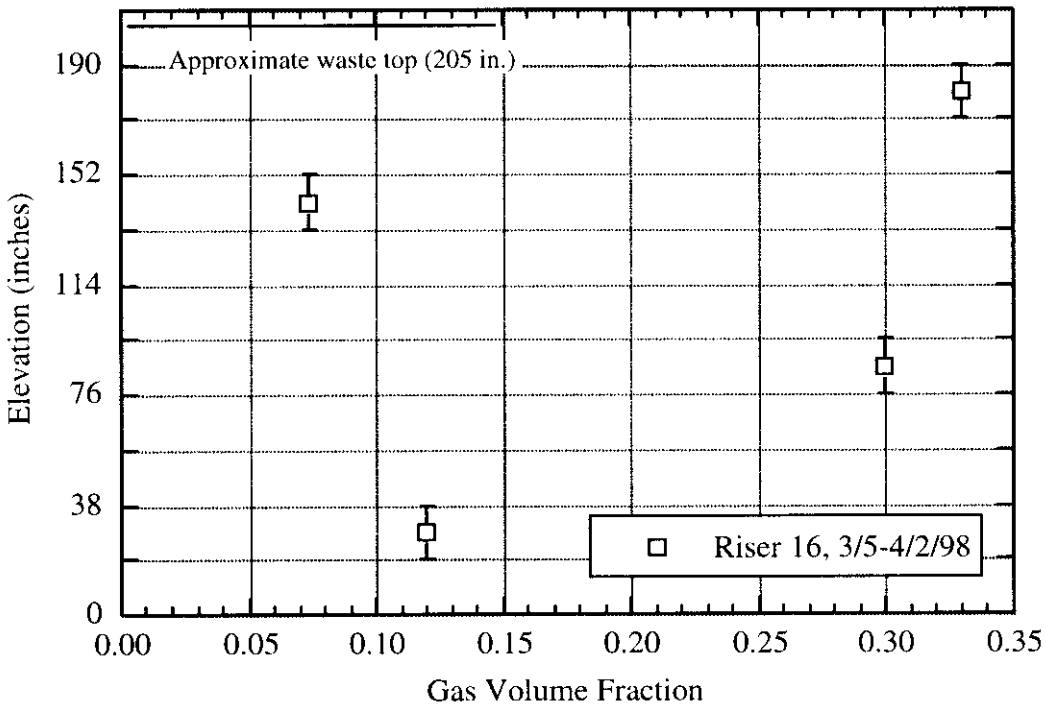


Figure 6-4. Local Gas Fractions in Tank 241-S-111 (1998 Data, Pre-Saltwell Pumping).

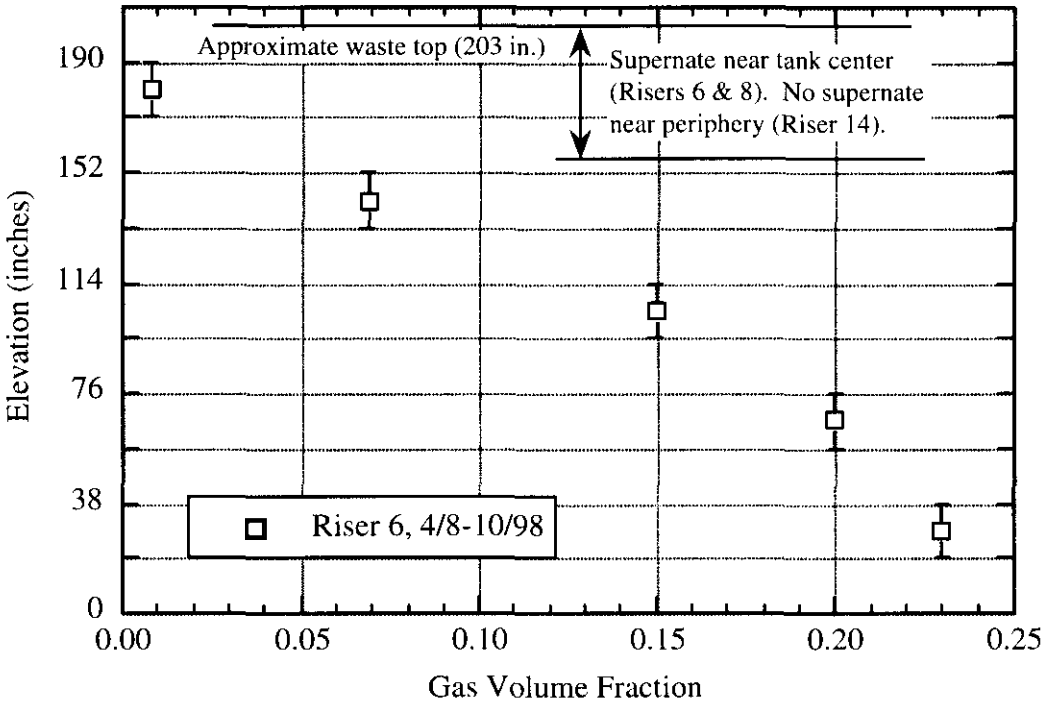


Figure 6-5. Local Gas Fractions in Tank 241-SX-106 (1997 Data, Pre-Saltwell Pumping).

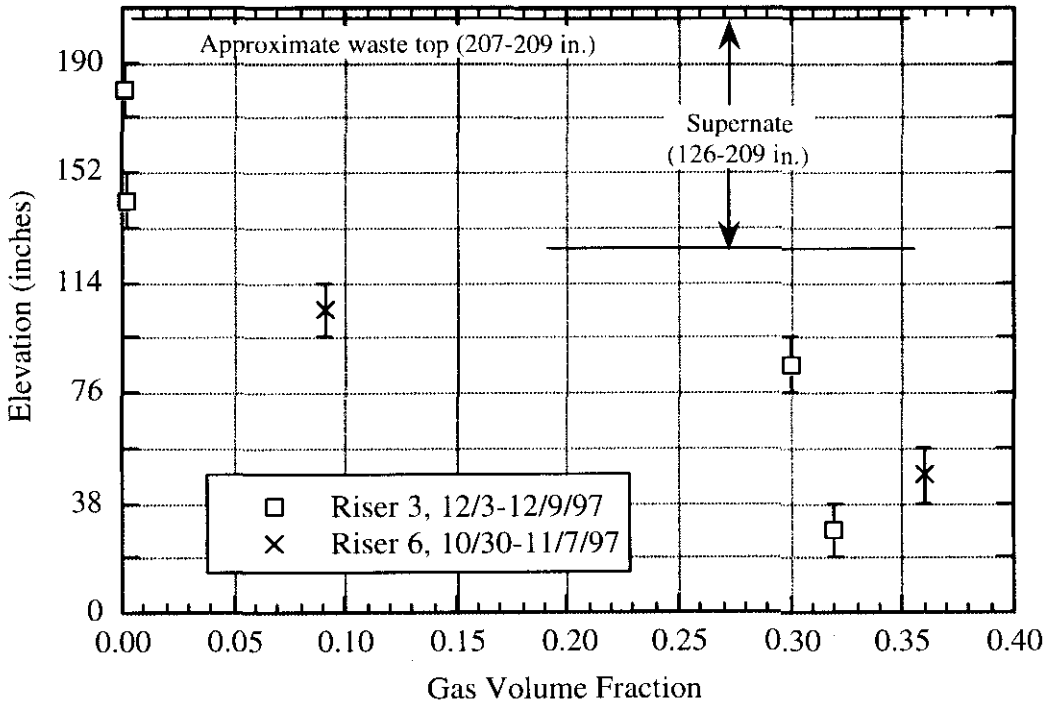


Figure 6-6. Local Gas Fractions in Tank 241-U-103 (1997 Data, Pre-Saltwell Pumping).

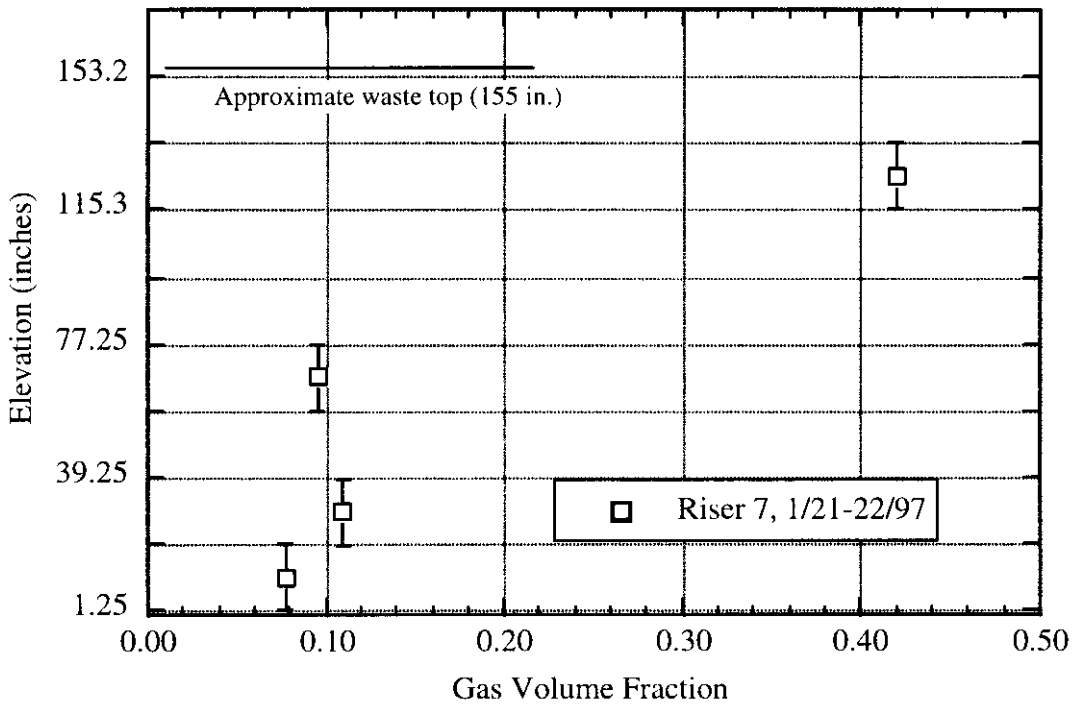
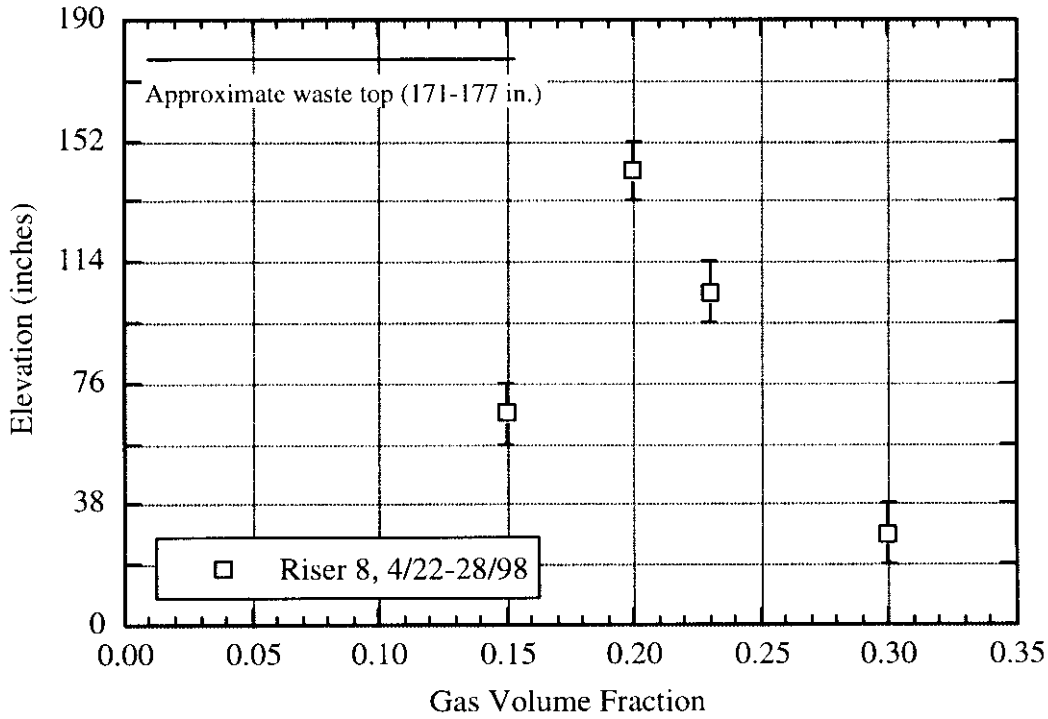


Figure 6-7. Local Gas Fractions in Tank 241-U-109 (1998 Data, Pre-Saltwell Pumping).



The RGS data plotted in Figures 6-1 through 6-7 show that only one to six RGS segments, often from a single riser, are available. Since the uncertainty of gas volume estimates from such a limited data set is very high, other equally uncertain gas volume estimates using the BPE method and integration of neutron logs must also be considered. The retained gas volume estimates from the three methods and the best estimate are given in Table 6-7. The best estimate of the retained gas volume is determined by engineering judgment based on the preponderance of these data plus ancillary evidence such as cumulative waste level rise and gas release history. Generally, the best estimate is the average of all methods applied, even if there are large differences (as in U-109). However, where two results agree and are supported against a third by other evidence, the latter is disregarded (as in S-102). The detailed rationale for the best estimate in each tank is given in Section 6.6 of Hedengren et al. (2001).

Table 6-7. Summary of Pre-Saltwell-Pumping Retained Gas Volume (m^3) Estimates.

Tank	RGS	BPE	Neutron Log	Best Estimate	Pumping Status
A-101	358 ± 180	295 ± 33	323 ± 160	325 ± 80	In progress
AX-101	282 ± 140	(1)	260 ± 130	270 ± 100	In progress
AX-103	No gas volume estimate available; assumed to be 43[(2)]				
S-102	663 ± 332	273 ± 22	155 ± 80	215 ± 60	In progress
S-111	440 ± 220	410 ± 62	230 ± 114	360 ± 85	
S-112		(1)	46 ± 23	46 ± 23	
SX-101		(1)	94 ± 47	94 ± 47	In progress
SX-102		(1)	170 ± 85	170 ± 85	
SX-103	No gas volume estimate available; assumed to be 363[(2)]				In progress
SX-104		(1)	250 ± 125	250 ± 125	Completed
SX-105		(1)	180 ± 90	180 ± 90	In progress
SX-106	487 ± 240	320 ± 56	386 ± 190	400 ± 100	Completed
SX-109	No gas volume estimate available; assumed to be 120[(2)]				
T-110		(1)	50 ± 25	50 ± 25	Completed
U-103	365 ± 180	250 ± 75	330 ± 160	315 ± 80	Completed
U-105		200 ± 82	340 ± 170	270 ± 90	Completed
U-107		140 ± 38	220 ± 110	180 ± 60	
U-108		285 ± 56	490 ± 240	390 ± 120	
U-109	500 ± 250	190 ± 58	284 ± 140	320 ± 100	In progress

[(1)] Waste conditions not applicable for BPE.

[(2)] Note: There are no usable data for tanks AX-103, SX-103 and SX-109. Volumes noted are based on assuming a gas fraction of 0.1 over the entire waste volume.

BPE = barometric pressure effect.

RGS = retained gas sampler.

Insufficient information was available to establish the retained gas volume for tanks AX-103, SX-103, and SX-109, so only an estimate is provided. Tanks AX-103 and SX-109 have been interim stabilized; SX-109 was on the watch list only because it had a common ventilation connection to other tanks in the SX Tank Farm. For the other tanks, the gas volume estimates range from 46 - 400 m^3 with ten tanks in Table 6-7 containing over 200 m^3. Considering the gas composition and tank headspace the ten tanks contain sufficient gas that might make the headspace flammable if all of it were to be released suddenly. However, the gas volumes are not growing, and the plausible gas release mechanisms (Johnson et al. 1997) and gas release data indicate spontaneous releases are small. Saltwell pumping reduces retained gas volumes and the current retained gas volumes are smaller than those shown in the table for pumped tanks.

6.4 SPONTANEOUS AND INDUCED GAS RELEASE BEHAVIOR

Gas monitoring systems show that there is a very slow steady release of hydrogen into the dome space resulting in the low background hydrogen concentration. Gas releases can also be induced by physically disturbing the waste (e.g., by core sampling and saltwell pumping). The time required for the released gas to be swept from the headspace depends on the rates of passive ventilation that exist in the tanks. The spontaneous gas release data for the FGWL SSTs are summarized in Section 6.4.1 and induced gas releases, including those due to saltwell pumping, are covered in Section 6.4.2. Information about headspace ventilation rates is summarized in Section 6.4.3.

Gas retention in the SSTs on the FGWL has been investigated in several ways. Gas retention tests have been performed on waste samples from several tanks as discussed in Section 3.1.2, and the local gas fraction in the tanks that were believed to contain the largest volume of retained gas were investigated during the RGS program as described in Section 3.1.5. The total stored gas volume has also been estimated for applicable tanks by the BPE method and by the evaluation of the neutron flux (see Sections 3.1.5 and 3.1.8).

Retained Gas Sampler samples were obtained from FGWL SSTs (A-101, AX-101, S-102, S-111, SX-106, U-103, and U-109) between 1996 and 1998. The average gas volume fraction and total retained gas volume for each tank was determined from the measured local gas volume fraction data. However, all of these tanks except tank S-111 have undergone saltwell pumping since the RGS samples were collected. The saltwell pumping status of the 19 tanks as of December 2000 is given in Table 6-8. The gas fraction distributions and gas volumes have changed as consequence of these operations.

Table 6-8. Single-Shell Tank Saltwell Pumping Status of Watch List Tanks as of December 2000. (2 sheets)

Tank	Saltwell pumping status		
	Start	End	Status
A-101	5/6/00		In progress[a]
AX-101	7/30/00		In progress[a]
AX-103			Stabilized 8/87
S-102	3/18/99		In progress[a]

Table 6-8. Single-Shell Tank Saltwell Pumping Status of Watch List Tanks as of December 2000. (2 sheets)

Tank	Saltwell pumping status		
	Start	End	Status
S-111	12/30/01		Not started
S-112[b]	11/30/02		Not started
SX-101	11/20/00		In progress
SX-102	12/30/01		Not started
SX-103	10/26/00		In progress
SX-104	7/23/98	7/25/99	Stabilized 4/00[c]
SX-105	8/8/00		In progress
SX-106	10/7/98	12/21/99	Stabilized 5/00
SX-109			Stabilized 5/81
T-110	7/2/98	8/12/99	Stabilized 1/00[c]
U-103	9/26/99	5/11/00	Stabilized 9/00
U-105	12/11/99	7/13/00	Evaluation
U-107	12/30/01		Not started
U-108	12/20/01		Not started
U-109	3/11/00		In progress

Notes:

[a]Pumping in A-101 and AX-101 delayed due to repeated pump motor failure. S-102 pumping delayed due to repeated jet pump or recirculation line plugging.

[b]S-112 was initially saltwell pumped in 1978.

[c]Tanks declared stabilized before minimum draining rate was achieved due to major equipment failure.

6.4.1 Spontaneous Gas Releases

Over 200 spontaneous GREs have been observed since the initiation of SHMS monitoring in SSTs in 1995. Data given in Table 4-7 of McCain (2000) are summarized in Table 6-9 for the SSTs on the FGWL. None of the GREs listed include those induced by saltwell pumping.

The releases that have been observed in the SHMS data are uniformly small and slow. The cumulative distribution of all 204 spontaneous releases listed by McCain (2000) for tanks with a liquid over solid configuration is shown in Figure 6-8. The median hydrogen release volume is about 0.5 m^3, and the 99.9 percentile release is only 3 m^3. The median time to peak hydrogen concentration during these releases is about one day and many releases require several days to reach the peak. The shortest time to peak, recorded in five GREs, was about 4 hours.

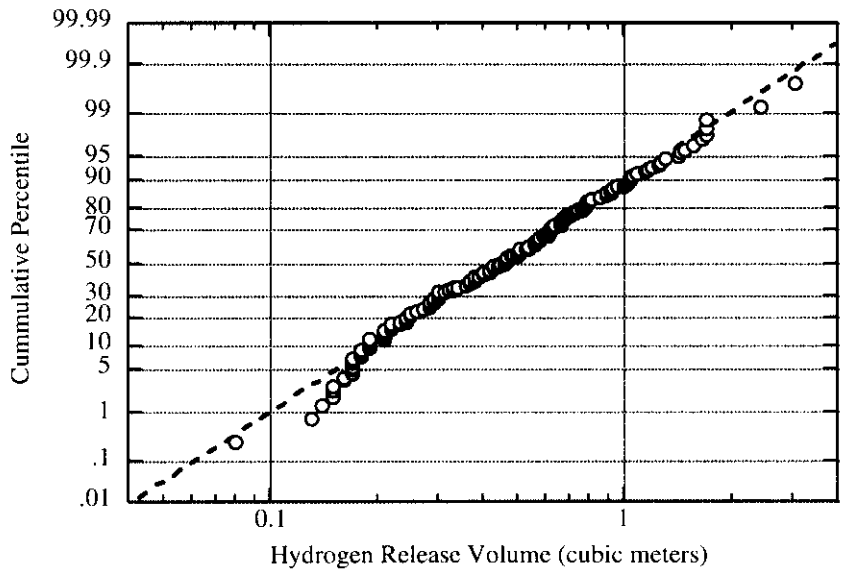
Table 6-9. Spontaneous Gas Release Event Summary for Flammable Gas Watch List Single-Shell Tanks.

Tank	No. of GREs	Date of last GRE	Duration (days)	Time to peak (days)	$[H_2]$ (ppm)	Release volume (m^3)	Max. $[H_2]$ (ppm)	SWP start date	SHMS type, date, removal
A-101	57	6/17/00	3.4 ± 2	1.1 ± 0.7	460 ± 150	0.3 ± 0.2	837	5/6/00	B 3/95, E+ 11/97[a]
AX-101	9	2/26/97	3.2 ± 0.8	1.3 ± 0.7	390 ± 70	0.3 ± 0.1	540	7/30/00	B 3/95
AX-103	0								B 3/95, Removed 8/97
S-102	0							3/18/99	B 3/95
S-111	13	1/9/00	13 ± 8	3 ± 2.4	680 ± 280	0.8 ± 0.4	1270		B 3/95, Standby 2/00
S-112	0							1978	B 3/95, Standby 2/00
SX-101	0								B 3/95
SX-102	0								B 3/95, Standby 2/00
SX-103	10	5/7/98	6 ± 4	3 ± 2	270 ± 160	0.6 ± 0.4	640	10/26/00	B 3/95, E+ 3/98
SX-104	3	11/22/96	7 ± 5	4 ± 3	130 ± 60	0.3 ± 0.2	200	7/23/98	B 3/95, Removed 6/00
SX-105	4	5/15/98	8 ± 6	2.5 ± 2	400 ± 250	0.8 ± 0.4	710	8/8/00	B 3/95
SX-106	6	12/31/97	2.8 ± 1	0.7 ± 0.3	200 ± 70	0.6 ± 0.2	330	10/7/98	B 3/95, Removed 6/00
SX-109	1	12/11/95	7.7	0.8	110	0.4	110		B 3/95, Removed 2/00
T-110	0							1997	B 3/95, Removed 2/00
U-103	17	9/28/99	6 ± 6	2 ± 2	980 ± 250	0.7 ± 0.4	1670	9/26/99	B 3/95
U-105	19	11/25/99	7 ± 5	2 ± 2	660 ± 300	0.6 ± 0.4	1440	12/11/99	B 3/95, E+ 5/98
U-107	14	2/14/00	10 ± 6	2 ± 2	840 ± 400	0.8 ± 0.7	1900		B 3/95
U-108	14	2/14/00	12 ± 7	4 ± 4	960 ± 280	0.7 ± 0.3	1530		B 3/95
U-109	14	2/11/00	6 ± 4	2 ± 1.4	1220 ± 500	0.7 ± 0.3	2190	3/11/00	B 3/95
Average			6 ± 6	2 ± 2	640 ± 400	0.5 ± 0.4			

[a]Only data since 11/97 are included for A-101.

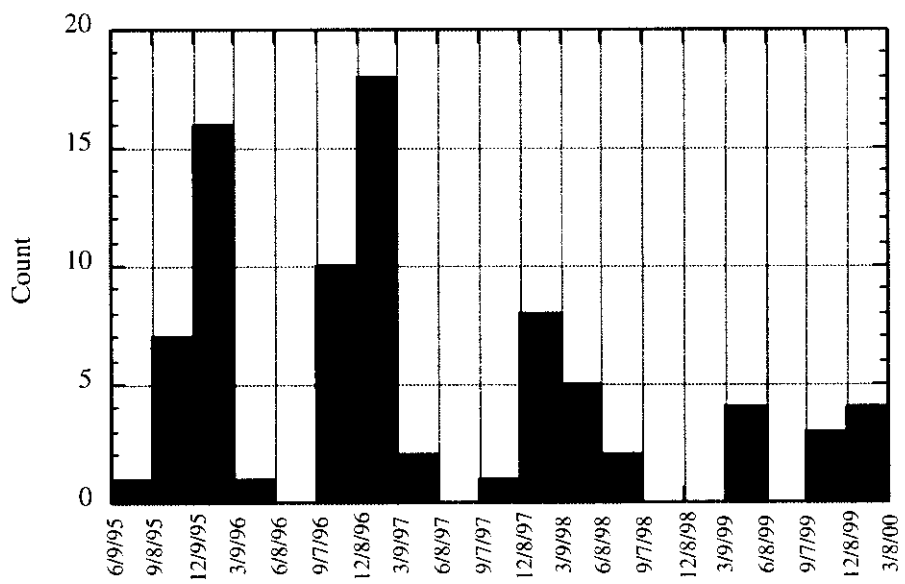
GRE = gas release event.
SHMS = standard hydrogen monitoring system.
SWP = saltwell pump

Figure 6-8. Cumulative Distribution of Spontaneous Hydrogen Release Volumes in Single-Shell Tanks.



Gas releases are becoming less frequent although the hydrogen release volume appears to be steady. The number of GREs in each 3-month period since June 1995 is shown in Figure 6-9. Data from tank A-101 were excluded since they represent only the last two years of the period and the large number of small releases from this tank would dominate the other tanks. It is clear that the GRE frequency for all tanks is decreasing. A definite grouping of the GREs in the winter months can also be seen. The greatest number of GREs occurs in the six months from September through February due to larger atmospheric pressure fluctuations during this period.

Figure 6-9. Single-Shell Tank Gas Release Event Frequency Trend.

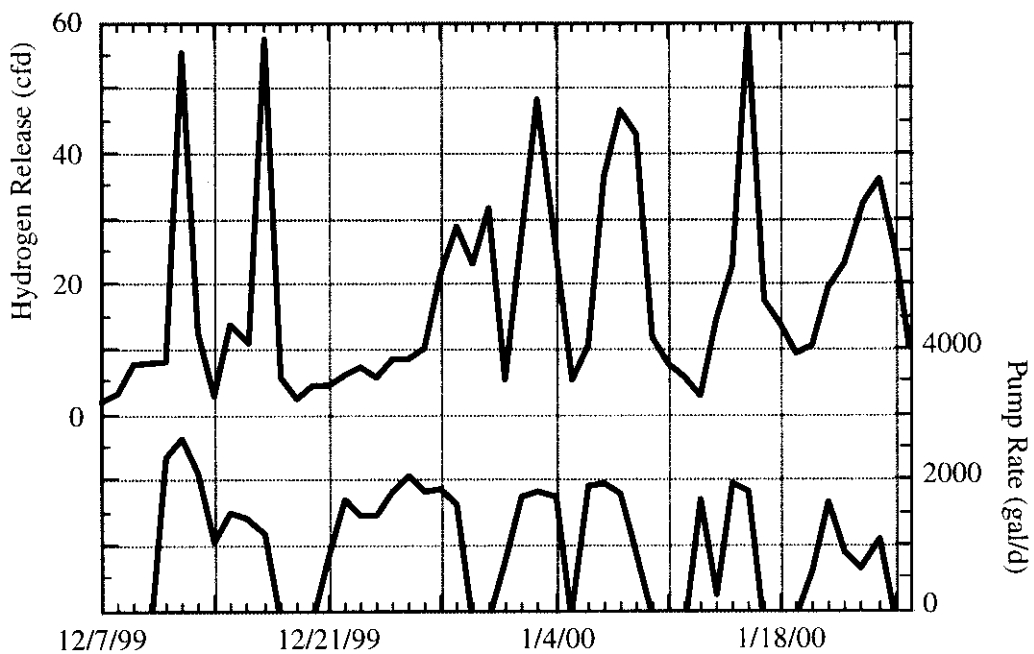


6.4.2 Induced Gas Releases

If a volume of waste containing retained gas is disrupted, some gas will be released from the volume actually disturbed. There is no known or postulated credible mechanism whereby a local disturbance can "trigger" a large, global release for the waste forms in the SSTs. Gas releases observed as a result of local waste disturbances have generally been barely detectable and none have approached 25% of the LFL. Observations of 77 waste intrusive activities in 47 separate SSTs in 1996 showed three probable releases of gas detected with headspace gas monitoring equipment associated with the waste disturbance.

The removal of drainable liquid by saltwell pumping can induce the release of waste gases by various mechanisms. The pressure within the waste decreases as liquid is removed, which causes trapped gases to expand and some of the dissolved gases to evolve to the gas phase. The correlation between saltwell pumping and gas release behavior is illustrated in Figure 6-10, where the hydrogen release rate in tank U-105 has been plotted above the daily volume of liquid pumped for a period including the start of the pumping campaign. There appears to be about a one-day lag between pumping activities and the corresponding gas release, but the lag is greater in several cases, and sometimes pumping activities are not accompanied by increased gas release rates at all. U-105 response is considered prototypical with respect to flammable gas release during saltwell pumping.

Figure 6-10. Tank 241-U-105 Hydrogen Release and Saltwell Pumping Rates.



The fraction of the total stored gas that is released during saltwell pumping can be calculated in tanks where the initial stored gas volume and ventilation rate are known and where the hydrogen concentration is measured accurately. This calculation has been made for three tanks, S-106, U-103, and U-105. The fraction of stored gas released during saltwell pumping ranged from 34% (U-105) to 50% (U-103).

None of the gas releases induced by saltwell pumping have raised the hydrogen concentration above 25% of the LFL for hydrogen. The highest hydrogen gas concentration ever measured by SHMS in any SST was 7,200 ppm, detected in tank BY-106 during saltwell pumping in 1995 (Watrous et al. 2000). The next highest was 4,950 ppm in tank U-103 during saltwell pumping in 1999.

6.4.3 Tank Behavior with Respect to Watch List Criterion

As noted in Section 5.4, the onset of failure for DSTs will occur at an overpressure of approximately 60 psig. In the DSTs this analysis relates to the inner metal shell; this shell does not exist in the SSTs. The dome space of the SSTs is bounded by reinforced concrete. Evaluations for responses to tank pressurization (Han 1996) showed that concrete would start to crack at an overpressure of approximately 11 to 12 psig.

Tests at the U.S. Bureau of Mines (Cashdollar et al. 1992) showed that in order to get this amount of pressure rise, the hydrogen concentration needed to be greater than 5 vol%. As noted in the footnote to Table ES-1, the value used for LFL of hydrogen is 3.6 vol%. Thus, the conditions to reach the containment limit (11 to 12 psig) require hydrogen concentrations at least 138% of the LFL. The LFL values noted by historic data for the SSTs range from 0.1 to 6.1% of the LFL. Since this is so far away from the conditions for failure, it was deemed that using the LFL values adequately describes the basis for removal from the watch list. Evan if the releases were to be 10 times greater, the values would still be less than the LFL.

6.4.4 Ventilation Rates

The passive ventilation rates have been measured using helium tracer gas in twelve SSTs (six on the FGWL) (Huckaby et al. 1997, 1998). The method involved injecting helium into the headspace and periodically sampling the headspace to determine the helium concentration as a function of time. Ventilation rates were observed to fluctuate significantly between the collection of tracer grab samples, with the average ventilation rates over 1- or 2-week periods differing sometimes by a factor of 2. Average ventilation rates measured for selected tanks and the periods for which the measurements apply are listed in Table 6-10.

The passive ventilation rates of the waste tanks depend most heavily on the number and size of pathways available for air exchange. High ventilation rates were measured in the AX-farm, where an underground ventilation system of 20-in. and 24-in. pipes connects the headspaces of the four AX-farm tanks, allowing relatively free exchange of air between these tanks. A similar ventilation system exists in A-farm. Lower ventilation rates measured in S- and U-farms are consistent with the lack of large inter-tank connections (the inter-tank connections are 3-in. cascade pipes), and the field observation that the risers and pit covers of these tanks would not allow significant fugitive air flow.

Table 6-10. Average Ventilation Rates Measured in Flammable Gas Watch List Single-Shell Tanks.

Tank	Tracer gas	Time period	Average ventilation rate	
			ft^3/min	m^3/h
A-101	He	July 9 - July 15, 1997	10	17
AX-103	He	February 28 – March 3, 1997	25	42
S-102	He	Sep. 24, 1996 – Feb. 11, 1997	2.2	3.8
U-103	SF_6 and He	Feb. 27 - October 22, 1997	1.7	3.0
U-103	He	Nov. 18, 1997 – Jan. 8, 1998	2.3	4.0
U-103	He	January 8 - March 24, 1998	0.9 - 6.6	1.5 - 11
U-105	He	July 15 - August 13, 1997	5.0	8.5

In order to establish whether or not changes in meteorological conditions have a significant effect on passive ventilation, a yearlong study was performed of tank U-103. The study indicated only a moderate correlation between measured ventilation rates and seasonal effects (Huckaby et al. 1998). The study suggests that temperature differences between the headspace and atmosphere do play a role in passive ventilation (higher rates are correlated with larger temperature differences), but apparently their effect in this tank is weak. Therefore, the average ventilation rates of individual tanks are assumed not to vary significantly with seasonal changes.

The tanks in the SX farm on the FGWL are actively ventilated. Estimated ventilation rates for these tanks range from 85 to 255 m^3/hour as listed in Table 6-11. Although the ventilation rates of the individual tanks are difficult to estimate because several tanks are connected to each exhauster, the measurements of hydrogen concentrations are comparably small at 10 to 50 ppm for the tanks in the SX Tank Farm.

Measurements of the dome space hydrogen concentration have shown that passively ventilated SSTs are in the range of 100 to 900 ppm and the actively ventilated SSTs are 10 to 50 ppm (McCain 1999).

Table 6-11. Ventilation Rates of Actively Ventilated Tanks.

Tank	Ventilation rate	
	(ft^3/min)	(m^3/hour)
SX-101	50	85
SX-102	100	170
SX-103	150	255
SX-104	50	85
SX-105	100	170
SX-106	150	255
SX-109	150	255

6.5 SUMMARY OF SINGLE-SHELL TANK INFORMATION

There is sufficient information from long-term monitoring of headspace hydrogen concentrations, waste temperatures, levels, and the body of core sampling results, including data from the RGS, to provide a sound basis from which conclusions can be drawn about the 19 SSTs in the FGWL. Key observations and conclusions relevant to the closure of the Flammable Gas Safety Issue and removal of these tanks from the FGWL follow:

- The chemical compositions of the wastes are well understood (Table 6-3).
- The type of waste in the tank has been determined (Table 6-1).
- The steady state concentration of hydrogen in the dome space has been measured (McCain 2000) and GREs have been detected and studied (Section 6.4).
- The composition of the retained gas has been examined for the seven waste tanks that were (originally) thought to have the largest amounts of retained gas (Table 6-5).
- The volumes of retained gas have been estimated for 16 tanks (Table 6-7).
- The waste configurations prior to saltwell pumping have changed by only a few inches during the past 5 years. There is no evidence that the wastes have accumulated gas (Table 6-2).
- The waste temperatures are decreasing slowly or are already near ambient temperature (Tables 6-1 and 6-2).
- Hydrogen is the principal flammable constituent of the gas retained in the wastes. In addition, the retained gas contains nitrogen and nitrous oxide with lesser amounts of ammonia, water vapor, methane, and other hydrocarbons (Table 6-5).
- Ten of these tanks contain a retained gas volume sufficient to raise the headspace hydrogen concentration briefly above the LFL if all of it could be released suddenly (Table 6-7). However, there is no observed or postulated credible mechanism for such a release.
- Steady state concentrations of hydrogen are low for both the actively ventilated tanks (< 50 ppm) and for passively ventilated tanks (< 1,000 ppm) (Table 6-6).
- None of the over 200 spontaneous gas releases observed have exceeded 25% of the LFL. These releases occur over many hours to several days and the maximum hydrogen concentration was 2,200 ppm or about 6% of the LFL (Table 6-9).

Other safety analyses for saltwell pumping operations and the work discussed in this section lead to the following observations.

- Saltwell pumping reduces the rate of gas generation (Table 6-4).
- The maximum headspace hydrogen concentration observed since 1995 that resulted from induced gas releases during saltwell pumping was 7,200 ppm, about 18% of the LFL (Section 6.4.2).
- Saltwell pumping, by releasing 25% to 50% of the retained gas and reducing the volume of wet sediment in the waste that can retain gas, further reduces the already low risk. The removal of less than half of the retained gas during such a global waste disturbance implies that the remaining gas is quite tightly bound and not subject to sudden release. The four pumped SSTs on the FGWL that exhibited spontaneous gas releases prior to pumping (SX-104, SX-106, U-103, and U-105) have had no spontaneous gas releases since being pumped. There has been no change in waste level or ILL in these tanks that indicates gas retention since pumping. In summary, the available data show that the likelihood of hazardous gas releases is reduced in pumped tanks.

Experience with tanks that have been saltwell pumped also implies that the steady state concentrations of hydrogen are far smaller than 25% of the LFL and that GREs that occur sporadically do not increase the hydrogen concentration sufficiently to reach 25% of the LFL. Lastly, there are no known mechanisms by which the gas that is retained within the waste in the saltwell pumped tanks could be suddenly released into the dome space.

Based on these observations and the data on which they are based, the following conclusions can be made regarding the 19 SSTs on the FGWL:

- The waste configurations in all 19 tanks have been stable prior to saltwell pumping. There is no evidence or mechanism for increasing gas retention or increasing potential for a large gas release, and no new hazardous conditions have been identified in studies carried out over the past decade.
- While most of these tanks contain 100 to 400 m^3 of hydrogen-rich retained gas, only small volumes of gas have been released in spontaneous events, during saltwell pumping, or in other waste-intrusive activities. Headspace gas concentrations have remained well below 25% of the LFL during these operations. These observations are consistent with physical models that describe gas retention and gas release.
- Saltwell pumping releases stored gas and reduces the gas generation rate. The resulting waste configurations apparently are stable and do not present any unusual hazards.

The elements in the strategy (Section 1.2) for resolution of the safety issue pertaining to the behavior of the waste have been met.

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7.0 FLAMMABILITY AND IGNITION

This section presents a summary of a report (Mahoney et al. 2000) that examines the flammability of the gases generated and retained in Hanford Site waste tanks. Experimental studies on the flammability of these gas mixtures were performed at the former U.S. Bureau of Mines (Pittsburgh Research Center) and at the California Institute of Technology (Graduate Aeronautical Laboratories). The report by Mahoney et al. (2000) provides a summary of these investigations.

The intrinsic flammability (or nonflammability) of waste gas mixtures is one major determinant of whether a flammable region develops in the tank headspace following release of the gases from the waste. The gases that are of most concern in flammability assessments are hydrogen (H_2), a highly flammable fuel that makes up a large part of the gas in many of the sampled tanks; ammonia (NH_3), a less flammable and less prevalent fuel; and nitrous oxide (N_2O), an oxidant (at sufficiently high temperature).

Methane (CH_4) and other hydrocarbons are highly flammable fuels but are present only in minor concentrations. For example, detailed analyses for RGS samples taken from tank SY-101 showed the presence of more than 100 organic compounds in the vapor phase (Mahoney et al. 1999). The vast majority of these substances was present in very minor concentrations (less than 100 ppm). A few compounds (e.g., ethanol, methanol, propene, methylamine, propane, and 2-butene) were present in the range of 1,000 to 2,000 ppm. These concentrations have a very minor effect on the flammability of the overall gas mixture. These ranges of organic compound concentrations are representative of the tanks on the FGWL.

Nitrogen (N_2) is an inert gas that tends to stifle flammability; water vapor (H_2O) is also an inerting agent but present in smaller concentrations than nitrogen. Oxygen (O_2) is the primary oxidant in the headspace but is not available within the waste. The relative amounts of fuel, oxidant, and inert gas in the waste in a given tank determine the gas flammability.

7.1 FLAMMABILITY OF HYDROGEN, AMMONIA, AND METHANE IN AIR AND NITROUS OXIDE

Flame propagation in fuel-rich mixtures is limited by oxidant availability and in lean mixtures by fuel availability. Thus the conditions of flammability are characterized by the upper (rich) and lower (lean) flammability limits of fuel gas concentration. In considering the flammability hazard associated with tank wastes, the concern is more with the LFL than with the upper flammability limit. The LFL is determined by the gas composition, energy and location of the ignition source, direction of flame propagation relative to gravity, and whether the gas is quiescent or being mixed. The gas composition effects include those associated with different oxidants (O_2 in air versus N_2O) and those associated with inert constituents.

In a quiescent atmosphere, the transition to flammability is abrupt and the LFL is higher (i.e., more fuel is required) for downward flame propagation than for upward propagation because of the buoyancy of the heated gases. In a turbulent, well-mixed atmosphere the transition to flammability is more gradual, with combustion pressures increasing linearly as the

fuel concentration increases from the upward propagation limit. However, the flame propagation speed remains relatively low for concentrations above the upward propagation limit but below the downward propagation limit. A very energetic ignition source (on the order of 10 to 100 Joules) has an effect similar to turbulence.

Mahoney et al. (2000) reviewed the literature and the tests conducted by the former U.S. Bureau of Mines and the California Institute of Technology. Results regarding the flammability limits in air for both upward and downward propagation for H_2, CH_4, and NH_3 are summarized in Table 7-1. The minimum amount of N_2 needed to inert a fuel/air mixture is also given. For example, a mixture consisting of 30 mol% hydrogen/air in any ratio and 70 mol% nitrogen would be inert.

Table 7-1. Flammability Limits of Hydrogen, Ammonia, and Methane in Air.

Fuel	**Lower flammability limit in air (mol%)**		**Upper flammability limit in air (mol%)**	**Minimum nitrogen to inert (mol%)**
	Upward propagation	**Downward propagation**		
Hydrogen	4	8	75	70
Methane	5	5	15	37
Ammonia	15	18	28	17

The corresponding limits for these gases in nitrous oxide are shown in Table 7-2. The table was compiled from experiments using high ignition energies between 5 and 10 J. It is known that N_2O decomposes even in the absence of fuel at very high ignition energies (on the order of 5,000 J). N_2O begins to react with hydrogen only above about 427 °C. Below that temperature it acts as a dilutent. A mole fraction of 0.10 or more is required to fully react N_2O. Therefore, the LFL values for the three fuels in N_2O should be used with caution.

Table 7-2. Flammability Limits of Hydrogen, Ammonia, and Methane in Nitrous Oxide.

Fuel	**Lower flammability limit in N_2O (mol%)**		**Upper flammability limit in N_2O (mol%)**	**Minimum nitrogen to inert (mol%)**
	Upward propagation	**Downward propagation**		
Hydrogen	3	6	84	~60
Methane	2.8	5	50	70
Ammonia	2.6	6.8	71	60

Water vapor raises the LFL of NH_3-air mixtures. If the water vapor mole fraction exceeds 8 to 11 mol%, the mixture is not flammable. For comparison, 17 to 19 mol% N_2 is required to inert a mixture whose other components are NH_3 and air (at any NH_3/air ratio). The amount of water

vapor necessary to prevent combustion increases from about 8 mol% at 25°C to about 9 mol% at 44 °C, and to about 11 mol% at 80 °C. This is important because it is possible for the equilibrium headspace humidity to exceed this value at moderate temperatures.

Although CH_4 and N_2O burn readily, the amount of CH_4 in tank wastes is small. Other hydrocarbons are not a flammability concern, even though their LFLs are even lower than CH_4, because their concentrations are typically much lower even than those of CH_4.

7.2 EVALUATION OF THE FLAMMABILITY OF GAS MIXTURES IN AIR

Experiments (Cashdollar et al. 1992) have shown that the LFL of a mixture of H_2, NH_3, and CH_4 in an air-N_2O atmosphere can be computed from the LFL of each fuel using LeChatelier's linear mixing law:

$$\frac{1}{[MIX]_{LFL}} = \frac{[H_2]_{MIX}}{[H_2]_{LFL}} + \frac{[CH_4]_{MIX}}{[CH_4]_{LFL}} + \frac{[NH_3]_{MIX}}{[NH_3]_{LFL}} \tag{7-1}$$

where

$[MIX]_{LFL}$ = concentration of the gas mixture at the LFL in air,
$[gas]_{MIX}$ = concentration of the gas composing the fuel mixture, and
$[gas]_{LFL}$ = concentration of the pure gas at the LFL in air.

The concentration of H_2 is usually monitored to detect flammable conditions. The H_2 concentration at which a mixture of H_2 with other gases is flammable is given by

$$[H_2]_{MIX,LFL} = X_{H_2}[MIX]_{LFL} \tag{7-2}$$

where X_{H2} = mole fraction of H_2 in the mixture.

In a waste tank 23 m (75 ft) in diameter, the headspace would generally be expected to be turbulent, and the upward propagation flammability limit is appropriate for determining whether ignition is possible.

Gas composition data from tanks sampled with the RGS show that the fraction of H_2 in the mixture at the LFL ranges from 3.6 to 4.0%. Values less than 4% are due to the influence of ammonia and methane.

7.3 SELF-FLAMMABILITY OF HYDROGEN, METHANE, AMMONIA, AND NITROUS OXIDE MIXTURES

The possibility of self-flammability and subsequent flame propagation of the waste gas alone, in the absence of air has been thoroughly considered and determined to be implausible for Hanford Site waste configurations and conditions.

Under airless conditions, N_2O serves as the sole oxidant, and N_2 may in some cases inert the retained gas. This, however, requires an energetic ignition source to raise the temperature sufficiently for N_2O to react. At temperatures below about 427 °C, N_2O acts as a diluent. As the fraction of inert gas (in this case N_2) increases in a mixture, the LFL typically increases slightly and the upper flammability limit decreases steeply. At a fraction of the inert gas that is known as the inerting concentration, the upper flammability limit decreases to the point that it is equal to the LFL. When the inert gas increases above the inerting concentration, combustion cannot occur.

An assessment of the self-flammability of the gases from the gas retaining layer(s) of each of the RGS-sampled tanks showed that in 11 of the 15 cases, the hydrogen mole fraction is equal to or greater than the upper flammability limit for the mixture and thus is not self-flammable. Of the 15 wastes evaluated, 9 retain gas that contains too little oxidant to be self-flammable. Only three were self-flammable and one was considered as "possibly self-flammable."

This self-flammability assessment considers only the intrinsic properties of the gas mixture, as if the gas were contained in a large vessel rather than in the pores, bubbles, or fissures in the waste matrix. It does not consider the amount of ignition energy required to initiate combustion. Many of the data used to support the flammability estimate were obtained with ignition energies of 8 J or more, which would be unusually high energies for accidental sparks (20 mJ energies are typically seen in static sparks on clothing). The self-flammability assessment also does not consider whether interconnected pathways exist in the waste to permit flame propagation or whether heat loss to the walls of a small passage would prevent propagation. All of these limiting factors make flame propagation within the waste implausible.

7.4 PLUME RELEASES

This section summarizes the discussions in Section 8 of Hedengren et al. (2001) concerning the potential for flammable plume releases. A gas release is termed a "plume release," if it represents a localized event and the quantity of flammable gases released is insufficient to exceed the LFL when fully mixed with the air in the tank headspace. In general, a plume release is assumed to be flammable as it exits the waste, but non-flammable after it has been dissipated in the headspace (Johnson et al. 1997). Based on headspace gas monitoring data, there currently are 19 SSTs that have exhibited small local spontaneous gas releases since 1995 that might classify as plume releases (McCain 2000). Five DSTs have exhibited somewhat larger and more rapid releases that also classify as plumes. SY-101 was the only tank known to have released enough gas to exceed the LFL in the entire mixed headspace.

The main issues concerning plume releases are how long a plume remains flammable and what gas volume is flammable at any given time. In waste tanks, plume dispersion occurs due to diffusion and turbulent mixing accelerated by ambient convective turbulence in the headspace. Also, the buoyancy associated with the temperature and composition of the plume causes the plume to entrain surrounding air as it rises, which dilutes the flammable gas concentration.

Epstein and Burelbach (2001) examined the behavior of buoyant plumes using laboratory experiments where fresh water was forced upward through a porous plate into a saltwater solution of higher density. The experiment was carefully scaled for dynamic similitude with a

full-scale tank headspace undergoing release of a buoyant gas mixture to quantify, for the first time, the rate at which a wide-area, inward moving plume entrains overlying fluid. Epstein and Burelbach (2001) observed that the entrainment rate was much higher than in a point-source plume and that most of the mixing occurred within the mixing layer rather than in the plume itself. This is an important result because it implies that the large-area gas releases that occur in the tanks are diluted relatively close to the waste surface. Computational modeling over a period of several years supports the results of the brine-water plume studies and extends the conclusion to a broader range of parameters. (For one of several studies, see Antoniak and Recknagle [1997].)

The experimental and modeling results indicate that all flammable gas plume-type releases that fall within historical SST volume ranges of up to a few cubic meters will create flammable concentrations only during and shortly after the actual release itself as it dissipates in the headspace, and the volume that is flammable will be very small. Considering the relative volume of a plume with concentrations of flammable gas that are potentially above the LFL in relation to the volume of the tank headspace, the likelihood of an ignition source being coincidently present in that volume is quite small.

This also applies to most of the releases in DSTs. Flammable conditions can theoretically persist in a stratified layer an hour or so after a release only when release volume is almost large enough to make the entire mixed headspace flammable. Only one observed release in AN-105 might have been sufficiently large to exhibit this behavior. However, the volume of flammable gas required to exceed the design pressure of the DSTs exceeds that required to reach the LFL. Therefore, the LFL is a conservative limit for evaluating tanks for the FGWL.

7.5 IGNITION

The preceding sections show that some of the gas mixtures created within the waste and released to the headspace of the tank could be flammable. In the presence of an effective ignition source, the undiluted gases could burn. This section evaluates the requirements for initiating a burn of flammable gases.

Mechanisms for ignition of a given mixture of combustible gases are complex and involve formation of a critical concentration of molecular fragments by the energy in electrostatic or mechanical sparks. Several energy sources and configurations have been used to study flame ignition. It has been determined that an ordinary capacitor discharge spark consistently yields the lowest ignition energy for any specific combustible mixture (Strehlow 1984). Therefore, experiments that use capacitive spark discharge may (conservatively) underestimate the ignition energy that would be required for ignition if supplied by less effective energy sources.

Studies of the requirements for ignition of hydrogen have defined the minimum ignition energy (MIE), the energy below which the ignition of a combustible mixture cannot occur and above which ignition occurs. Most of the work on minimum ignition energies was done with capacitive spark discharges. For hydrogen, the MIE is on the order of 0.01 mJ (Pratt 1997). To put this in perspective, the range of energies in sparks from static discharges perceived by humans can range from microjoules to tens of millijoules. A 1-mJ spark is perceptible, a 10-mJ spark is a prick, a 30-mJ spark is a sharp prick, and a 100-mJ spark will result in a slight jerk (Pratt 1997).

Thus, the sparks from static discharge when humans touch metal far exceed the energy required to ignite some hydrogen/air mixtures.

The MIE for a gas varies with the stoichiometry of the mixture. The optimum concentration that gives the lowest MIE is not the stoichiometric fuel/oxidant mixture but a slightly fuel-rich one. The MIE at the LFL is several orders of magnitude greater than that for the optimum mixture. This same situation exists for hydrogen-oxygen systems (Lewis and Von Elbe 1987, p. 347). The MIE is about 0.02 mJ for H_2-O_2-N_2 at 25 to 30% hydrogen. At 5% H_2, the MIE is greater than 1 mJ.

Because the gas mixtures of interest to the Flammable Gas Safety Issue might behave differently than the individual components, an experiment was conducted at the California Institute of Technology to evaluate the effect of various ignition energies on the LFL of three gas mixtures with compositions relevant to Hanford tank waste gases containing H_2, NH_3, N_2O, CH_4, and N_2. The researchers found that none of the three mixtures showed any pronounced dependence of the LFL on ignition energy between 0.04 and 8 J. The flammability limit (in air) of Mixtures 27 (40% H_2, 40% N_2O, 20% CH_4), 28 (35% H_2, 35% N_2O, 10% CH_4, 20% NH_3), and 29 (29% H_2, 24% N_2O, 11% NH_3, 35% N_2, 1% CH_4) occurred at 7%, 9%, and 14% fuel in air, respectively.

Friction sparks that result from the impact of two surfaces can serve as an ignition source for flammable gas mixtures. The temperature of a spark struck from steel can approach 1400 °C. The ignition potential of a spark depends upon its total heat content; thus the size of the particle produced is an important factor. Mechanical sparks cool quickly and can ignite gases only under very favorable and exacting conditions. A study to determine which metal would be best suited for use in tank SY-101 showed that hot-spot temperatures achieved by normal or glancing blows were less than the temperature required to ignite hydrogen-air mixtures; that the presence of rust made ignition more likely; and that stainless steel was one of the most sparking-resistant metals available (Pearce 1992, p. 45-57). The results of this work led to using stainless steel for new components in SY-101 and other tanks. In addition, special tools made of low-sparking alloys are being used at the Hanford Site to minimize the danger of sparks in hazardous locations.

Flammable gas mixtures can be ignited by a hot surface. The minimum temperature at which a mixture will burst into flame spontaneously is known as the auto-ignition temperature. The auto-ignition temperature is typically measured in air. Some typical values are 520 °C for hydrogen, 650 °C for ammonia, and 630 °C for methane (Kuchta 1985). For gas mixtures relevant to the Hanford tanks the estimated auto-ignition temperature is in the range of 457 °C to 507 °C. Technical safety requirement controls restrict activities that might produce such high surface temperatures (i.e., temperatures are restricted to 780 °F or 415 °C).

The headspaces of the Hanford Site tanks are connected to the ambient environment via filtered ventilation systems. Due to the water content of the waste and the humidity of the inlet air, the headspaces have a high relative humidity; that is, the atmosphere in the headspace is not dry. The relative humidity can range from 20 to 60%. The humidity does not have a significant effect on the LFL of gas mixtures in which hydrogen is the main contributor; however, high humidity could be expected to reduce the sparking potential of some materials.

7.6 CONCLUSION ON FLAMMABILITY

The overall conclusion of this review is that most high-level nuclear waste storage tanks at the Hanford Site contain gas with a composition such that it can be readily ignited and burned if present at a sufficiently high concentration. However, as described in Chapters 5.0 and 6.0, release of sufficiently large gas volume to create a flammable gas concentration exceeding the LFL in a tank's headspace is very unlikely. Analyses of the release of gases show that rapid mixing occurs above the waste surface.

While the gas mixture contains several fuel components (e.g., methane, other hydrocarbons, and ammonia) besides hydrogen and a potential oxidizer (nitrous oxide), the mixture basically behaves like a hydrogen-air system with respect to flammability and ignition in the tank headspace. LeChatelier's linear mixing law can be used to determine the LFL.

Thus, sufficient work has been done to satisfy the items in the approach for resolution of the safety issue (Section 1.2) pertaining to the understanding of the flammability limits and potential ignition sources.

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8.0 FLAMMABLE GAS CONTROLS

8.1 EXISTING CONTROLS

The Tank Farms at the Hanford Site are being operated with an approved Authorization Basis. The Final Safety Analysis Report (HNF-SD-WM-SAR-067, *Tank Farms Final Safety Analysis Report*) documents the results of safety analyses that establish and evaluate the adequacy of the safety basis for Tank Farms facilities and establishes the envelope within which these facilities can continue to operate safely. Safety equipment operability and administrative safety controls are specified in the accompanying Technical Safety Requirements (HNF-SD-WM-TSR-006, *Tank Farms Technical Safety Requirements*).

The situation has changed from the time the Flammable Gas Safety Issue was created in 1990 in that there is no longer an Unreviewed Safety Question with respect to flammable gas in the storage tanks. Activities that are presently authorized take into account the potential for release and/or ignition of flammable gas. During the review process for activities that are not presently authorized, the staff considers many potentially hazardous conditions (including flammable gas) before recommending that the activity be included in the authorization basis. Prior to the addition of any material to a tank, process controls are in place that require review of the material addition and consider potential issues such as criticality, flammable gas, and chemical reactions. Based on contemporary understanding of flammable gas generation and retention/release, controls are in place to preclude a tank from having flammable gas concentrations in excess of the LFL. This applies to existing tank and waste configurations and potential future authorized activities or configurations.

During the more than ten years of the existence of the Flammable Gas Safety Issue and the FGWL, the Authorization Basis has evolved from a set of interrelated but separate documents into the Final Safety Analysis Report and Technical Safety Requirements documents. Over the same period, considerable practical experience has been gained about the risks associated with flammable gases. The original controls were established based on limited knowledge of tank contents and flammable gas phenomenology. Knowledge of both aspects has grown over the decade coincident with a maturation of the Authorization Basis and associated USQ process. With the closure of the flammable gas USQ for all DSTs and SSTs (and the level rise USQ for SY-101), the tanks are now within the approved Authorization Basis.

The Final Safety Analysis Report elaborates on the range of potentially hazardous scenarios, which include the following:

- Accumulation of steady-state gas releases in (1) tank dome spaces; (2) pits, risers, and connected air spaces; or (3) waste intrusive equipment
- Retention of gas within the waste matrix followed by (1) natural spontaneous release from, for example, buoyancy instability or (2) release from waste-disturbing action or motion

- Flammable gas burns (1) beneath the waste surface or (2) in vapor spaces following release from stored waste.

The accidents considered by the Final Safety Analysis Report involve the accumulation or spontaneous presence of flammable gas in such a condition that credible ignition sources existing in the Tank Farms can cause the gas to burn. The accident analysis is concerned about any damage to safety systems, structures, and components and any release to the environment once such an accumulation of flammable gas was ignited. The purpose of the Final Safety Analysis Report is to establish the bases of controls determined to be necessary or prudent in light of the hazards of concern.

8.1.1 Steady-State Gas Release

Flammable gas generation does not create a hazardous situation if the gas released from the waste is diluted with air in the dome space and vented to the atmosphere at a comparable rate. Data and analysis show that this situation is realized in most of the tanks in which passive ventilation is sufficient to dilute the flammable gas released from the waste. In some tanks, however, the gas generation rate may be high enough to require small amounts (a few cubic feet per minute) of active mechanical ventilation to prevent flammable gas buildup. Therefore, to prevent the accumulation of flammable gases from steady-state releases, ventilation systems (active or passive) are employed on all SSTs and DSTs. Controls were established to ensure the operability of these systems.

Gases that are released from the waste in a nearly continuous manner are managed quite effectively by ventilation. Less straight forward, however, is the situation where a significant amount of the gas is retained within the waste and released relatively rapidly in a GRE.

8.1.2 Spontaneous or Induced Gas Release

Studies have shown that some tanks store significant volumes of gas in the waste. Free gas can accumulate only in submerged solids lying beneath the free liquid level; gas escapes from unsubmerged solid layers by diffusion. Convective fluid layers cannot retain gas because bubbles rise through a liquid as fast as they are generated. Soluble gases (mainly ammonia, with a small amount of nitrous oxide) are also dissolved in the liquid waste. However, evaporation of dissolved gas is a concern only when a free liquid surface is freshly exposed or agitated by a disturbance such as when liquid waste is transferred to another tank.

Data regarding GREs in these tanks were covered in Chapters 5.0 and 6.0.

- Spontaneous GREs observed in SSTs result in hydrogen concentrations well below 25% of the LFL and occur over many hours or days.

- There is no known mechanism for a large, rapid, spontaneous GRE in the SSTs.

- Induced GREs observed in SSTs (e.g., due to saltwell pumping) result in hydrogen concentrations less than 25% of the LFL.

- Observed spontaneous GREs in the five DSTs have been much less than 25% of the LFL since 1996. Only one of the five DSTs (AN-105) has had GREs > 25% LFL and none approaching the LFL.

- Observed induced GREs in DSTs (e.g., SY-101 dilution or AZ-101 mixing) are very small, remaining well below 25% of the LFL.

Based on observed flammable gas behavior and evaluation of potential waste behavior, safety analyses have concluded that flammable conditions are unlikely to be created as a result of GREs. However, the flammable gas control strategy for GREs, is aimed at preventing ignition to further reduce the risk of a flammable gas deflagration accident. Both ignition source controls and flammable gas monitoring are employed to prevent the introduction of an ignition source into a location where flammable gases may be present.

This control strategy is applied in a graded manner based on a set of conservative postulations regarding the diameter of the waste and its expected behavior, the operational activity, and the specific location in the waste tank in which a given activity is being performed.

More specifically, these three factors are as follows:

1) Type of waste behavior known or postulated to be possible for a given facility

   - Large GRE
   - Small GRE
   - Spontaneous GRE
   - Induced GRE.

   The ignition source and monitoring controls strategy is based on applying controls <u>where</u> and <u>when</u> flammable conditions might be present. Large versus small GRE is used to define <u>where</u> flammable conditions could be present. Spontaneous versus induced is used to define <u>when</u> flammable conditions could be present.

   In this logic structure, the question was under what conditions could flammable conditions be present outside of the tank dome region due to a GRE. A large GRE was thus defined as a GRE that could cause the GRE gases to be discharged into pits and out open risers in flammable concentrations. This is a qualitative definition. Ignition source controls (and monitoring controls during manned activities) would be required in pits and outside open risers if a large GRE were postulated for the particular tank during that activity.

   A small GRE is one where the flammable condition would be limited to the tank dome space region (i.e., would not discharge gas to pits or out open risers in flammable concentrations). This again is a qualitative definition.

   The <u>when</u> question is addressed by postulating whether a GRE can be spontaneous or only induced. If a spontaneous GRE is postulated, controls need to consider that a GRE can occur at any time. If only an induced GRE is postulated, controls can be limited to times when a waste-disturbing operation or activity is being performed.

2) The impact of tank farm operational activities on the waste contained in a facility or structure:

   - Non-waste disturbing activities
   - Locally waste-disturbing activities, including such work as grab sampling, which are not considered to be capable of affecting significant portions of the waste
   - Globally waste-disturbing activities such as saltwell pumping, which more aggressively affect a larger fraction of the waste.

3) The location or region within a waste receptacle where work activities are being performed:

   - Waste intrusive locations are those below the waste surface and within the vapor spaces of waste-intruding equipment where undiluted waste gas may accumulate
   - Dome intrusive locations are those between the top of the risers and the waste surface, including ventilation systems up to the first mixing point
   - Ex-tank intrusive locations are those outside tank openings directly connected to the dome space
   - Non-intrusive locations.

These factors are used to specify the aspects of the monitoring and ignition controls required across the range of facilities and operational activities. Controls differ from facility to facility or from activity to activity in a given facility depending on each factor.

To apply the controls, each tank has been placed in one of four classifications, depending on whether the waste is postulated to present a hazard from large or small GREs. The GREs may be spontaneous or occur only during waste-disturbing (induced) operations. Ignition source controls and monitoring requirements are applied at times <u>when</u>, and in locations <u>where</u>, flammable conditions resulting from GREs can be present, as appropriate to this grouping scheme.

Five DSTs (AN-103, AN-104, AN-105, AW-101, SY-103) that have had GREs are conservatively postulated to have the potential for large, spontaneous and large, induced GREs. These tanks have been assigned to Group 1 and are the FGWL tanks discussed in Chapter 5.0. Tanks that are postulated to have the potential for a small, spontaneous GRE and for a large, induced GRE are assigned to Group 2. The remaining DSTs and all except two of the FGWL SSTs are in this group. The remaining SSTs, which show no propensity for spontaneous GREs but may produce a small, induced GRE, are assigned to Group 3. Facilities with little or no waste solids capable of retaining gases are categorized as non-GRE. It is assumed that the tanks in all facility groups undergo steady-state gas generation, however minor, at all times.

Monitoring for flammable gases during activities being conducted at the tanks is used for the following reasons:

- To prevent the introduction of an uncontrolled or errant spark source into a location when and where flammable gas concentrations are above a level of concern.
- To prevent the continued use of equipment and materials that may present uncontrolled spark sources or errant spark sources if flammable gas concentrations of concern develop during manned work activities.
- To halt waste disturbing operations if concentrations exceed 25% of the LFL.

Two sets of ignition source controls are used depending on the facility and the type of activity performed in the facility. The ignition source controls address electrical equipment requirements, non-electrical equipment and materials requirements, and work practices. Set 1 primarily applies to activities and locations that involve direct contact with undiluted waste gases. Set 2 primarily applies to circumstances where flammable gas conditions may be postulated to occur in the dome space or ex-tank locations. To ensure consistent application and interpretation of industry standards used by these control sets, a Flammable Gas Equipment Advisory Board was formed to oversee implementation of the ignition source controls.

The overall flammable gas control strategy (ventilation, monitoring, and ignition source control) has been judged to be a practical means for preventing the accumulation of flammable gases where ignition sources may be present or to eliminate ignition sources where flammable gases may be present. It has been applied in a graded approach depending upon the nature of the hazard (Facility Group) and the type and location of activity being performed.

8.2 DIRECTION FOR FUTURE CONTROLS

The control strategy for GREs currently employed is based largely on conservative postulations of GRE potential to create flammable conditions, specified in 1995. Observations and evaluations completed since, all point to the conservative nature of these postulations. Some of the assumptions underpinning the controls have been demonstrated to be overly conservative and can be rethought. With the resolution of the safety issue and removal of tanks from the FGWL, there is an opportunity to review the state of knowledge and optimize the controls.

The state of knowledge is highest for current waste conditions and operations that have been performed in the last ten years as part of the safe storage mission. While much of what is known about flammable gas hazards would benefit retrieval and waste feed delivery, controls for those conditions and operations will be based on the knowledge of the waste at that time and the technology that will be used. It is also likely that significant data will be collected in the early efforts (including demonstration efforts) that can be used to further optimize the controls as work moves into the production phase. These operations employ process control plans and the waste transfer operations are not performed until a compatibility evaluation of resulting conditions in the receiver tank has been completed.

8.3 CONCLUSIONS

The flammable gas USQ has been closed and the Authorization Basis has been updated. Controls for monitoring and ignition sources are in place. This completes the items required for resolution of the safety issue as noted in Section 1.2.

9.0 BASIS FOR REMOVAL OF TANKS FROM THE FLAMMABLE GAS WATCH LIST

The creation of the FGWL was a result of a public law that was passed by Congress in 1990. Chapter 1.0 provided a brief history of the events leading to the congressional action and a summary of how the tanks were selected. It is important to note that the behavior of tank SY-101 was the primary driver for the Flammable Gas Safety Issue and the FGWL. SY-101 has been remediated, the safety issue closed, removed from the FGWL, and returned to normal service.

At the time that the FGWL was created there were no direct measurements of the gas concentrations in the dome spaces of the tanks or within the liquid and solid wastes. Many of the tanks were put on the FGWL only because of the process history and the lack of information.

The primary consideration driving the FGWL, the Safety Issue, and DNFSB Recommendation 93-5, was the lack of information and understanding of the behavior of the waste in the tanks. As noted in Section 1.6 of this report, Recommendation 93-5 has been closed by the DNFSB. In his letter to the DNFSB, Secretary Richardson stated: "Flammable gas hazards have been identified and are monitored for specific tanks. Controls are imposed to prevent development or ignition of explosive mixtures." Chapter 8.0 provided an overview of the approach for the controls presently in place with the approved Authorization Basis.

Item (a) of Section 3137 of Public Law 101-510 (Appendix A) states: "...single-shelled or double-shelled high level nuclear waste tanks ... may have a serious potential for release of high-level waste due to uncontrolled increase in temperature or pressure." As is now known (described in the previous sections of this report), and noted in the quote above, the indicated situation does not exist. As such, the remaining tanks should be removed from the FGWL.

According to the selection criterion and removal criterion, a tank can be removed from the FGWL when it no longer "can have a flammable gas volume in the dome space that, when ignited, would result in pressure above a containment-related tank design limit." The volumes of gas in the DSTs that are needed to reach the limit for onset of failure of the tank dome are in the range of 71 m^3 to 136 m^3. Corresponding volumes of hydrogen needed to reach the LFL (Table ES-1) range from 39 m^3 to 91 m^3. Observed gas release volumes have been in the range of 8.3 to 47% of the LFL. Thus it is concluded that tank behavior is such that conditions for reaching the conditions for onset of failure are not plausible in the DSTs. For the SSTs, conditions for onset of failure require gas concentrations that are at least 138% of the LFL. Observed releases have been in the range of 0.1 to 6.1% of the LFL, and clearly the associated volumes of hydrogen are well below the requirements for the onset of failure. For both the DSTs and SSTs the LFL is a conservative measure for evaluating the tanks against the watch list criterion.

Section 1.3 also discussed the specific criteria for removal of tanks from the FGWL. Interpretation of the criterion led to the position that the unacceptable risk was due to a "spontaneous release" of gas and, if a tank could not have a spontaneous release of sufficient magnitude, then the tank could be removed from the FGWL. The determination of the possible magnitude of spontaneous releases is based on tank data and on the theory, analyses, and models

that provide understanding of the data. Chapters 5.0 and 6.0 provide a summary of all of the data and information obtained on the 5 DSTs and 19 SSTs that remain on the FGWL. The theoretical base is embodied in models for the hydrogen generation rate, retained gas bubble size and shape, bubble percolation, and a series of models and criteria for the threshold and size of buoyant displacement gas release. The data coupled with the understanding of the chemical and physical processes provide the technical basis for removal of tanks from the FGWL; the main points are summarized below.

Double-Shell Tanks

- Only one tank, SY-101, has had spontaneous releases that reached and exceeded the LFL; this tank has been remediated and removed from the FGWL (Section 4.2).
- Of the 5 DSTs on the FGWL, only tank AN-105 has had spontaneous releases above 25% of the LFL and none above 50% of the LFL. There have been no releases > 25% LFL since 1996 (Section 5.4; Table 5-6).
- All DSTs have active ventilation systems, and the concentrations of flammable gases are far less than the LFL during steady-state conditions (see Section 5.4).
- Waste layer (convective and non-convective) dimensions are stable as measured by temperature profiles and neutron/gamma scans (Section 5.1).
- Tank contents, including retained gases, have been sampled and analyzed (Section 5.2; Table 5-3).
- The tanks have active monitors for temperature, pressure, waste level, and dome space gases (Chapter 3.0).
- Waste in tanks AN-103, AN-104, AN-105, and AW-101 is cooling; gas release volumes are becoming smaller. Waste in tank SY-103 is cooling only slightly (Section 5.1).
- Experience gained from SY-101 activities can be used for any future activities regarding waste transfers or additions for the subject five DSTs (Section 4.3).
- An understanding of gas release mechanisms has been developed; analysis was successfully applied to describe the release of gas from tank SY-101 (Section 2.3; Section 4.1).
- Controls are in place for all tanks, and the approach for controls was described in Chapter 8.0. Any changes in any tank conditions and all planned activities are evaluated via the USQ process consistent with DOE Order 5480.21, *Unreviewed Safety Questions*, and 10 CFR 830, "Nuclear Safety Management."

Single-Shell Tanks

- There have been no unexplained changes in waste level since the creation of the FGWL (Section 6.1).
- There have been no spontaneous releases of flammable gas exceeding 25% of the LFL (maximum only 5.5% LFL) since the gas monitoring systems were place in operation in 1995 (Table 6-9).
- Measurements with the continuous gas monitors have shown no elevated steady-state concentrations of flammable gas; tank ventilation systems adequately remove the gases (Chapter 6.0).
- Measurements have been made for ventilation rates in 12 SSTs, 6 of which are on the FGWL; rates have been higher than that attributed solely to atmospheric breathing (Section 6.4.3).
- Studies have been conducted to understand gas retention and release mechanisms; none of the SSTs have conditions considered necessary for a large, spontaneous releases (Section 6.4).
- Controls are in place for all tanks, and the approach for controls was described in Chapter 8. Any changes in any tank conditions and all planned activities are evaluated via the USQ process consistent with DOE Order 5480.21 and 10 CFR 830.

Data show that the 24 tanks on the FGWL do not have large spontaneous GREs and as such they should be removed from the FGWL. The bound of activities for the FGWL concern only "safe storage"; this is the situation for the tanks on a daily basis without major activities such as insertion of equipment or removal of waste. The influence of extreme and remotely possible natural phenomena, such as a high magnitude seismic event, does not apply (see Section 2.3.4). The principal hazard deterrent for such an event is the aggressive pursuit of waste retrieval and treatment. SSTs on the FGWL have been, or will be, saltwell pumped to remove liquid. This activity reduces the stored gas inventory; no dome space flammable gas concentrations exceeding 25% of the LFL have been observed during any pumping activity.

Finally, as discussed in Section 1.3, acceptable risk management has been demonstrated by compliance with DOE Orders in implementing an approved Authorization Basis. DOE has approved the Tank Farms Authorization Basis, and controls are in place for flammable gas hazards.

The conditions in the 24 tanks that are on the FGWL do not satisfy the criteria for placement on the FGWL and thus can be removed from the FGWL.

Both routine storage activities and major mission accomplishments (i.e., saltwell pumping, retrieval from tank C-106, remediation of tank SY-101, and demonstration of mixer pumps in an aging waste tank) have been completed safely under the approved Authorization Basis. Attributes of the major mission activities accomplished to date are common to the activities needed for waste retrieval and delivery to the waste treatment facility. These include installation

of mixer pumps, operation of mixer and retrieval pumps, mobilization of settled solids, waste transfers, and dilution of waste. These operations employ process control plans and the waste transfer operations are not performed until a compatibility evaluation of resulting conditions in the receiver tank has been completed. Aspects of retrieval and waste feed delivery activities that may be unique will be identified as part of the USQ process. This process will determine the need for any adjustments to the flammable gas control strategy for future activities.

10.0 BASIS FOR RESOLUTION OF THE FLAMMABLE GAS SAFETY ISSUE

Referring to Figure 1-1, resolution of the Safety Issue can occur when it is shown that the conditions at the right hand side of the figure no longer exist. These conditions are:

- Not within approved safety envelope (USQ), or
- Not properly analyzed or mitigated, or
- A loss of primary containment, or
- A loss of secondary containment.

With respect to the first condition the flammable gas USQ was closed for SY-101 in 1996 (Wagoner 1996a) and for all of the other tanks in 1998 (Wagoner 1998a and 1998b). The level rise USQ for SY-101 was closed in 2000 (Boston 2000b). There are no open USQs with respect to flammable gases for these tanks. Therefore, the tanks are being operated within their approved Authorization Basis safety envelope.

With respect to the second condition, Chapter 4.0 of this report provides a discussion for the characterization and evaluation of SY-101 along with the efforts taken to mitigate the buoyant displacement GREs and the remediation of the tank such that it can return to normal service. Chapters 5.0 and 6.0 cover the evaluations for the rest of the FGWL DSTs and the FGWL SSTs, respectively. In the request for closure of the DNFSB recommendation, as noted in Section 1.6 of this report, DOE stated: "All tanks are sufficiently characterized to support safety of storage..." and "Flammable gas hazards have been identified and are monitored for specific tanks. Controls are imposed to prevent development or ignition of explosive mixtures." Chapter 8.0 provides an overview of the controls.

Thus, the conditions represented by the blocks at the right hand side of Figure 1-1 no longer exist and the Flammable Gas Safety Issue can be resolved.

Satisfactory resolution of the Flammable Gas Safety Issue completes the actions required by TPA Milestone M-40-00. As noted in Section 1.5 the milestone states in part, "This milestone will be complete when mitigation activities, if required, have been implemented in all FGWL tanks to ensure safe storage of waste during the interim period until retrieval for treatment and/or disposal operations begin. For those safety issues mitigated pursuant to this milestone, safety resolution will be dependent upon final treatment of the waste...Some safety issues may also be resolved if (1) resolution out-of-tank is not required..." The Flammable Gas Safety Issue is the last of the safety issues to be resolved.

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APPENDIX A

PUBLIC LAW 101-510 (H.R. 4739), NOVEMBER 1990

NATIONAL DEFENSE AUTHORIZATION ACT FOR FISCAL YEAR 1991

Section 3137: Safety Measures for Waste Tanks at Hanford Nuclear Reservation

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PUBLIC LAW 101-510 (H.R. 4739), NOVEMBER 1990

NATIONAL DEFENSE AUTHORIZATION ACT FOR FISCAL YEAR 1991

Section 3137: Safety Measures for Waste Tanks at Hanford Nuclear Reservation

(a) **Identification and Monitoring of Tanks.** Within 90 days after the date of the enactment of this Act, the Secretary of Energy shall identify which single-shelled or double-shelled high-level nuclear waste tanks at the Hanford Nuclear Reservation, Richland, Washington, may have a serious potential for release of high-level waste due to uncontrolled increase in temperature or pressure. After completing such identification, 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. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring, but only if a type of monitoring that does not itself increase the danger of a release can be installed.

(b) **Action Plans.** Within 90 days after the date of the enactment of this Act, the Secretary of Energy shall develop action plans to respond to excessive temperature or pressure or a release from any tank identified under subsection (a).

(c) **Prohibition.** Beginning 120 days after the date of the enactment of this Act, no additional high-level nuclear waste (except for small amounts removed and returned to a tank for analysis) may be added to tank identified under subsection (a) unless the Secretary determines that no safer alternative than adding such waste to the tank currently exists or that the tank does not pose a serious potential for release of high-level nuclear waste.

(d) **Report.** Within six months after the date of the enactment of this Act, the Secretary shall submit to Congress a report on actions taken to promote tank safety, including actions taken pursuant to this section, and the Secretary's timetable for resolving outstanding issues on how to handle the waste in such tanks.

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