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DATA AND OBSERVATIONS OF SINGLE-SHELL FLAMMABLE GAS WATCH LIST TANK BEHAVIOR

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ABSTRACT

This report summarizes the available data, observations, and analyses performed relating to flammable gas generation, retention, and release in the nineteen single-shell nuclear waste storage tanks at the Hanford Site that are on the Flammable Gas Watch List (Public Law 101-510 1990). The tanks and the waste they contain are described in terms of their fill history, chemistry, and waste physical properties and configuration. In-situ measurement and monitoring systems are described and their data are summarized. The gas generation rates, retained gas volumes, and the spontaneous and induced gas release history of each tank are discussed. Saltwell pumping activities are also summarized, and the effects of pumping on gas generation, retention, and release are described.

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SUMMARY

The objective of this report is to describe and document the waste configuration, gas generation, gas retention, and gas release behavior in the single-shell waste tanks at the Hanford Site that are on the Flammable Gas Watch List (Public Law 101-510 1990). Nineteen single-shell nuclear waste storage tanks are on the Flammable Gas Watch List: tanks 241-A-101, 241-AX-101, 241-AX-103, 241-S-102, 241-S-111, 241-S-112, 241-SX-101, 241-SX-102, 241-SX-103, 241-SX-104, 241-SX-105, 241-SX-106, 241-SX-109, 241-T-110, 241-U-103, 241-U-105, 241-U-107, 241-U-108, and 241-U-109. The properties and composition of the waste stored in the single-shell tanks (SSTs) varies widely and tends to be non-uniform. Because of this and the difficulty in obtaining data, the current knowledge of waste properties and behavior in the SSTs has a certain degree of uncertainty. Nevertheless, the trends revealed by long-term monitoring of waste temperatures, levels and/or moisture content, and the body of core sampling results, including data from the Retained Gas Sampler, provide a reasonable basis for understanding the behavior of these SSTs and assessing their potential flammable gas hazard.

The waste configuration in each of these tanks has been stable prior to saltwell pumping. Almost every tank is cooling slowly. The waste levels are nearly constant, some rising very gradually and some falling. The internal condition of the waste as revealed by neutron logs has not changed over the past several years.

Saltwell pumping is completed or in progress in eleven of the nineteen tanks, and five more are scheduled to be pumped by December 2002. Saltwell pumping has lowered the waste level and interstitial liquid level and, in many but not all cases, has accelerated the waste-cooling trend. In some tanks, pumping has caused the central region of the waste to subside to create a pronounced concavity on the surface.

Most of these tanks stored a relatively large volume of gas prior to saltwell pumping. Thirteen contain more than 100 m^3 (3,500 scf), and six of these have more than 300 m^3 (10,600 scf). However, all of the plausible release mechanisms that have been studied can release only a very small fraction of the total stored volume. All spontaneous gas releases observed since monitoring was installed in 1995 have all been less than 3 m^3 (100 scf) of hydrogen and occur over many hours to days. On the order, half of the retained gas is released during saltwell pumping and the maximum hydrogen concentration observed during pumping was 7,200 ppm (less than one-fourth of the lower flammability limit of 40,000 ppm).

Based on the preponderance of data, observations and analysis results available, the nineteen single-shell tanks do not exhibit significant spontaneous gas release events. Saltwell pumping has not induced significant releases, and the steady-state gas release rate is insignificant. The concentration of flammable gases in the tank dome spaces from all causes remains well below 25 percent of the lower flammability limit.

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ANOVA	analysis of variance
atm	atmosphere
BBI	Best-Basis Inventory
BPE	barometric pressure effect
cfm	cubic feet per minute
Ci	curies
cm	centimeters
cm/kPa	centimeter per kilo-Pascal
cm^3	cubic centimeters
CW	cladding waste
dL/dP	correlation of waste level with barometric pressure, cm/kPa or in./in.-Hg
DOE	U.S. Department of Energy
DSSF	double-shell slurry feed
DST	double-shell tank
EB	evaporator bottoms
EDTA	ethylenediaminetetraacetate
eV	electron volt
FGWL	Flammable Gas Watch List
FIC	Food Instrument Corporation
ft	feet
ft^2	square feet
ft^3	cubic feet
ft^3/day	cubic feet per day
ft^3/min.	cubic feet per minute
g/L	grams per liter
g/mL	grams per milliliters
GC-TCD	Gas Chromatograph Thermal Conductivity Detector
gal	gallons
gpm	gallons per minute
GRE	gas release event
HEDTA	hydroxyethylethylenediaminetriacetate
HEPA	high efficiency particulate air
HGR	hydrogen generation rate
HLW	high-level waste
hr	hour
ILL	interstitial liquid level
in.	inch(es)
$in.^2$	square inches
IWW	inorganic wash waste
IR	infra-red/Infra-Red Photo Acoustic Multi-Gas Monitor
K	Kelvin
kg	kilograms
kg/m^3	kilograms per cubic meters

LIST OF TERMS, Continued

kgal	kilogallons
kJ/mol	kiloJoule per mole
kJ/mol-K	kiloJoule per mole per degree Kelvin
kL	kiloliters
L	liters
LFL	lower flammability limit
LLW	low-level waste
LOW	liquid observation well
m	meters
m^2	square meters
m^3	cubic meters
m^3/h	cubic meters per hour
MEV	million electron volts
mL	milliliters
min	minute
mol/day	moles per day
mol/kg/day	moles per kilogram per day
mol%	mole percent
moles/L	moles per liter
OWW	organic wash waste
Pa	Pascal, N/m^2 (unit of pressure)
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
ppmv	parts per million by volume
PUREX	Plutonium Uranium Extraction facility
R/hr	Rems per hour
rad/hr	rads per hour
REDOX	reduction-oxidation
RGS	Retained Gas Sampler
RPP	River Protection Project
SACS	Surveillance Analysis Computer System
scf	standard cubic feet
scfd	standard cubic feet per day
SHMS	standard hydrogen monitoring system
SMM	Supernatant Mixing Model
SMM S1	Supernatant Mixing Model 242-S Evaporator saltcake generated from 1973 until 1976
SMM S2	Supernatant Mixing Model 242-S Evaporator saltcake generated from 1977 until 1980
SORWT	Sort on Radioactive Waste Type (model)
SRR	strontium recovery waste

LIST OF TERMS, Continued

SST	single-shell tank
TMACS	Tank Monitoring and Control System
TOC	total organic carbon
TWINS	Tank Waste Information Network System
USQ	Unreviewed Safety Question
vol%	volume percent
°C	degrees Celsius
°F	degrees Fahrenheit
%	percent
µCi/L	microcuries per liter
µg/g	micrograms per gram
µg/L	micrograms per liter

Units Conversion

Multiply	By	To convert to
centimeters (cm)	0.3937	inches (in)
meters (m)	3.281	feet (ft)
square meters (m^2)	10.764	square feet (ft^2)
cubic meters (m^3)	35.314	cubic feet (ft^3)
kilograms (kg)	2.2	pounds mass (lbm)
Newtons (N)	4.44	pounds force (lbf)
Pascal (Pa)	1.449 E-4	(lbf/in^2 or psi)
Pascal (Pa)	2.9529 E-4	inches of mercury (in-Hg)
degrees Kelvin (K)	1.685	degrees Rankine (R)

1.0 INTRODUCTION

The primary purpose of this report is to document the gas generation, retention, and release behavior in single-shell tanks on the Flammable Gas Watch List (Public Law 101-510 1990) at the Hanford Site. This behavior is described in terms of tank history, waste chemistry, and data from the retained gas sampler, headspace gas monitoring systems, and other tank data. This information is presented in support of closure of the flammable gas safety issue and removal of these tanks from the Watch List.

1.1 BACKGROUND

Radioactive waste is stored in 177 carbon steel tanks with capacities from 190 to 4,500 m^3 (50 to 1,200 kgal). Of these, 149 are single-shell tanks (SSTs) built in the 1940s, 1950s, and early 1960s, and 28 are newer double-shell tanks (DSTs) constructed in the 1960s, 1970s, and 1980s. The SSTs were removed from active use in 1980. Since then, most of their pumpable liquid has been transferred to the DSTs leaving the SSTs generally containing much less waste than their full capacity.

There are four main designs of SSTs as illustrated in Figure 1-1. Three designs are 75 ft in diameter with capacities from 530,000 to 1,000,000 gallons. These are the 100-series tanks that are numbered 241-S-105, for example, where S is the tank farm and 105 is the tank number. The 241- prefix is often omitted. The A, AX, and SX Farms are of 1,000,000 gallon capacity, the tanks in the BY, S, TX, and TY Farms have 758,000 gallon capacities, and the B, BX, C, T, and U-Farm tanks hold up to 530,000 gallons. The A and AX tanks have flat bottoms while the rest are designed with a dished bottom. The smaller 200-series tanks have a diameter of 20 ft and a capacity of 55,000 gallons.

Unlike the DSTs, few of the SSTs are actively ventilated. The SX-Farm has an exhauster serving thirteen of its fifteen tanks, and two tanks in the C-Farm have an exhauster (tanks C-105 and C-106). Exhausters ventilate the tanks at nominally 100 cfm (tank C-106 is ventilated at around 2,000 cfm). The remaining tanks "breathe" passively by thermal convection, barometric pressure changes, and surface wind. These mechanisms generally provide a ventilation rate of several cfm to several tens of cfm.

All Hanford Site wastes generate flammable gases by radiolysis of water, decomposition of organic compounds, and corrosion of the steel tank walls. The main fuel components of the waste gas mixture are hydrogen and ammonia. The gas also contains nitrous oxide (an oxidizer), nitrogen (inert component), and very small amounts of methane and other hydrocarbons.

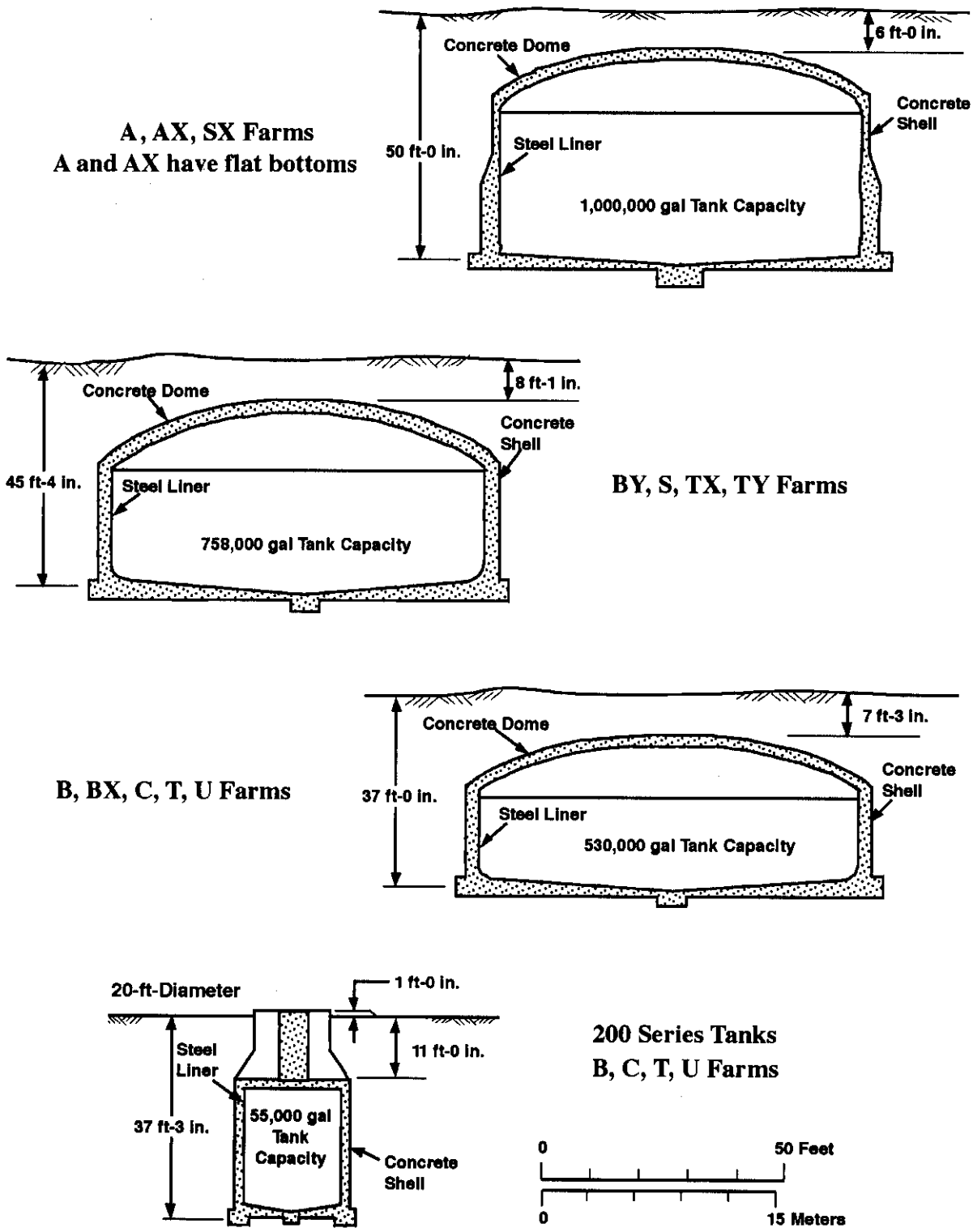

Figure 1-1. Single-Shell Tank Designs

When the gas is released from the waste continuously as fast as it is generated, the rate of release is very slow compared to the headspace ventilation rate and the rapid mixing promptly dilutes the gas. Flammable gas generation by itself is not a hazard. In the DSTs, the highest hydrogen generation rates are less than 32 standard cubic feet per day (the pre-remediation generation rate in tank SY-101). The nominal ventilation rate of at least 100 standard cubic feet per minute keeps the background headspace concentration of flammable gas well below the lower flammability limit (LFL) in all the DSTs. The maximum hydrogen generation rate in the SSTs is estimated to be 21 cubic feet per day (current rate in tank A-101 calculated by Hu [2000]). Although most of the SSTs are passively ventilated, a ventilation rate of less than 1 cfm is required to keep the hydrogen concentration below 25% of the LFL.

Some wastes in both SSTs and DSTs, however, can and do retain relatively large volumes of the gas mixture. In five of the DSTs, which have a relatively deep layer of supernatant liquid, a significant fraction of the stored gas is periodically released rapidly into the tank headspace. This type of release is termed a buoyant displacement gas release event (GRE). Tanks AN-103, AN-104, AN-105, AW-101, and SY-103 currently exhibit buoyant displacement gas releases. Since gas-monitoring instruments were installed in these tanks in 1994 and 1995, none of the gas releases have exceeded the LFL, and only two have exceeded 25% of the LFL by a small amount (Hedengren et al. 2000).

Prior to mixer pump installation, tank SY-101 exhibited buoyant displacement gas releases, an order of magnitude larger than the other DSTs. A few of these were large enough to make the tank headspace flammable. This behavior led to the creation of the Flammable Gas Watch List (Public Law 101-510 1990) for tanks with the "serious potential to release radioactive waste to the environment." Six DSTs and nineteen SSTs were eventually placed on the Watch List. The Flammable Gas Unreviewed Safety Question and Watch List are described in detail in Section 1.1.1.

At least ten SSTs stored over 200 cubic meters (7,000 cubic feet) of gas prior to saltwell pumping (see Table 6-5). However, none of the SSTs have a sufficiently deep layer of supernatant to allow the large buoyant displacement gas releases observed in DSTs.[1] There is no other mechanism for large, spontaneous releases from these tanks. Instead small, relatively slow releases are observed occasionally from the SSTs, particularly during large drops in barometric pressure (McCain 2000). Gas monitoring data show that none of these releases has approached 25% of the LFL.

Most of the SSTs containing a large stored gas volume are being saltwell pumped. Pumping removes supernatant and interstitial liquid so that the interstitial liquid level falls well below the waste surface, releasing on the order of a third to half of the stored gas in the process. The lower interstitial liquid level also reduces the volume of the waste that can retain gas in the future. The history and status of saltwell pumping is described in Section 1.1.3.

[1] Tanks A-101 and AX-101 both have a deep liquid layer, but the tanks are not subject to buoyant displacements since the liquid is already beneath the buoyant solids.

1.1.1 Flammable Gas Watch List and Unreviewed Safety Question

The flammable gas hazard in Hanford Site waste tanks was first recognized in the behavior of tank SY-101. The waste level in this tank began periodically rising and suddenly dropping shortly after it was filled in 1980. The large, sawtooth level drops were taken as an indication of episodic gas releases that might pose a safety hazard. Some of them had sufficient volume to exceed the LFL in the entire headspace and probably would have damaged the tank had the gas ignited.

In 1990, the gas release behavior of tank SY-101 was recognized as a situation requiring special attention and control. In April 1990, administrative controls were implemented to control various tank activities that might increase the risk of a flammable gas burn. In May 1990, the U.S. Department of Energy, Richland Operations Office, determined that hydrogen and nitrous oxide buildup in certain waste tanks and the possibility of their ignition constituted an Unreviewed Safety Question (USQ). The USQ was applied to tank SY-101 and 22 other tanks at that time. The USQ eventually led to the development of a set of administrative flammable gas controls, including controls for ignition sources, ventilation, and monitoring, and of the Facility Group concept as a method to apply the most stringent controls to the most hazardous tanks as discussed in the next section. After an intense period of study and negotiation, a mixer pump was selected to mitigate the large gas releases from tank SY-101 and was installed July 3, 1993. The mixer pump performed as expected, and no gas releases exceeding 25% of the LFL occurred after it was installed.

The Flammable Gas Watch List was a result of Public Law 101-510, which Congress passed in November 1990. Section 3137, also referred to as the Wyden Amendment, was part of this law. This section required the Secretary of Energy to identify within 90 days a "watch list" of the high-level nuclear waste tanks that may have a "serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure." The same tanks defined by the USQ were also used for the initial Flammable Gas Watch List.

The process by which the tanks were identified for the USQ and Watch List was described in early 1991. An increase in the waste level, without waste additions, was called slurry growth. The original evaluation focused on the slurry growth phenomena; five DSTs and 15 SSTs were noted (by waste level data) as exhibiting slurry growth. Next, criteria were developed for both DSTs and SSTs regarding the slurry growth. The criteria for DSTs were: (1) level increase without liquid addition; (2) unexplained dome pressurization; and (3) unexplained temperature changes. For the SSTs, the criteria were: (1) level increase without liquid addition; (2) presence of a surface crust; (3) total organic carbon (TOC) content above 3 grams per liter; and (4) presence of B-Plant waste whose chemistry was thought to contribute to gas retention and release.

Use of these criteria resulted in the identification of two more tanks, bringing the total to 22. Tank SX-109 was added only because the ventilation system design for the SX Tank Farm results in the headspace for five listed tanks being vented through the headspace of tank SX-109. Therefore, the original number of tanks (with respect to flammable gases) identified in response

to Public Law 101-510, Section 3137, was 23. Finally, two other tanks were added to the Flammable Gas Watch List in 1993; one because of an observed level fluctuation and the other because of updated data that showed slurry growth. Therefore, 25 tanks were put on the Watch List due to the Flammable Gas Safety Issue. The SSTs on the Watch List are listed in Table 1-1 along with other pertinent information (Hanlon 2000).

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

Tank	Capacity (kgal)	Waste Type [b]	Waste Volume (kgal)		Pumping Status [c]
			Supernatant	Solids	
A-101	1,000	DSSF - SC	484 [a]	383	In progress
AX-101	1,000	DSSF - SC	378 [a]	298	In progress
AX-103	1,000	CC - SC	0	112	None planned
S-102	758	DSSF - SC/SL	0	492	In progress
S-111	758	NCPLX - SC/SL	48	453	Not started
S-112	758	NCPLX - SC	0	523	Not started
SX-101	1,000	DC - SC	0	448	Not started
SX-102	1,000	DSSF - SC	134	380	Not started
SX-103	1,000	NCPLX - SC/SL	0	622	In progress
SX-104	1,000	DSSF - SC/SL	0	446	Completed
SX-105	1,000	DSSF - SC	0	513	In progress
SX-106	1,000	NCPLX - SC	0	397	Completed
SX-109	1,000	NCPLX - SC/SL	0	249	None planned
T-110	530	NCPLX - SL	0	369	Completed
U-103	530	NCPLX - SC	1	417	Completed
U-105	530	NCPLX - SC	0	331	In progress
U-107	530	DSSF - SC	33	375	Not started
U-108	530	NCPLX - SC	24	444	Not started
U-109	530	NCPLX - SC	0	403	In progress

Notes:

(a) Liquid is the bottom layer in tanks A-101 and AX-101.

(b) Waste types are as follows (Hanlon 2000):

- CC Complexant concentrate
- DSSF Double-shell slurry feed
- DC Dilute complexed
- NCPLX Non-complexed
- SC Primarily saltcake
- SL Primarily sludge
- SC/SL Saltcake with more than about 10% sludge

(c) See Table 1-2 for more detail on saltwell pumping.

Formal criteria for selecting tanks for and removing tanks from the Flammable Gas Watch List were approved by the U.S. Department of Energy (DOE) in 1997. The approved 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."*

The criterion for removing a tank from the Flammable Gas Watch List has been interpreted (Johnson et al. 1997) to mean that: (1) a tank has acceptable risk from the perspective of the Flammable Gas Watch List if it cannot spontaneously release enough flammable gas to the dome space "which, if ignited would result in pressure above a containment-related tank design limit," and (2) this acceptable risk will be demonstrated by compliance with DOE orders in implementing an approved authorization basis.

By early 1995, all 177 tanks had been screened for retained gas using the Barometric Pressure Effect (BPE) method (Whitney 1995). The screening showed 58 tanks with detectable volumes of gas, and flammable gas administrative controls were placed on the 37 tanks not already on the Flammable Gas Watch List. In November 1995, flammability controls for ignition sources, ventilation, and monitoring were placed on all 177 tanks.

The original USQ was updated and consolidated into one overall USQ in July 1996. This expanded and replaced the original 1990 USQ. The USQ for tank SY-101 was closed in June 1996 because of the proven effectiveness of the mixer pump. In 1998 the flammable gas USQ was closed for SSTs and the rest of the DSTs on the basis of improved understanding of the hazard and establishment of effective controls.

1.1.2 The Facility Group Concept

The flammable gas hazard control strategy is twofold. First, adequate passive or active ventilation is required to manage risk associated with a steady background release of flammable gas. Second, controls are required to prevent ignition sources in the tanks to manage risk associated with the potential for sudden spontaneous gas releases.

The controls are graded based on perceived hazards and exempt less hazardous tanks from unnecessarily restrictive or burdensome controls. The grading of controls is based on whether a tank may be subject to large or small GREs. Large GREs may cause the headspace concentration of flammable gas to exceed 25% of the LFL. Small releases may elevate the concentration of

flammable gas beyond 25% of the LFL only in a localized area. Gas release events are further divided into spontaneous and induced releases where the latter are the result of some waste disturbing activity. The use of 25% of the LFL as the maximum allowed gas concentration is intended to provide a significant margin of safety to the concentration where a deflagration is actually possible (100% of the LFL).

To assign graded control sets, each tank has been placed into one of three Facility Groups depending on which types of GREs are associated with the tank. Tanks that have demonstrated a propensity for large spontaneous and induced GREs are in Facility Group 1. Tanks that may be susceptible to large induced GREs, but only small spontaneous GREs are in Facility Group 2. All remaining large underground waste storage tanks are assigned to Facility Group 3, where it is judged that spontaneous releases do not occur, but small induced releases may be possible in some tanks.

The tank grouping is based, in part, on the methodology originally used for the hazard evaluation in 1996. Although this methodology cannot provide precise quantitative results, it does indicate which tanks have large volumes of retained gas. Despite the technical uncertainty, this methodology, coupled with physical observations and sample results, provides a workable basis for the tank grouping.

It should be clear from the foregoing discussion that the Facility Group designation serves an entirely different function from the Flammable Gas Watch List. The latter is a congressionally mandated list of potentially hazardous tanks whose temperature and pressure must be monitored and are prevented from receiving waste. The Facility Groups determine how day-to-day tank farm operations are conducted and controlled. Removing a tank from the Flammable Gas Watch List will not change its Facility Group or control set unless, as in the case of tank SY-101, the waste has also been treated to reduce its ability to retain and release gas.

1.1.3 History and Status of Saltwell Pumping

Of the 149 SSTs at the Hanford Site, 67 are known or suspected to have leaked liquid into the surrounding soil (Hanlon 2000). To minimize the amount of material that could potentially leak from the tanks, drainable liquids are being removed from all SSTs as an aspect of the tank interim stabilization process. Five SSTs on the Flammable Gas Watch List have been stabilized; pumping is in progress in eight; and six are yet to be pumped. Interim stabilization is of interest here because removal of the drainable liquids changes the tank waste configuration, induces the release of some of the trapped gas, and reduces the rates of flammable gas generation and accumulation in the stabilized tank.

Drainable liquids are removed from the SSTs by a method commonly called saltwell pumping. When pumping is complete, the tank is termed to be interim stabilized. In this method, a long cylindrical metal screen (the saltwell screen) is installed as a well casing in the solid waste. In most tanks, the saltwell screen is installed near the center of the tank, and extends virtually to the bottom of the tank. A jet pump located inside and at the bottom of the saltwell screen pumps liquid out as it drains into the saltwell screen. At the onset of pumping, any supernatant liquids

(i.e., free liquid above the solids) drain quickly into the well, and the rate of liquid removal is typically limited by pump capacity. As the liquid inventory is depleted, the pumping rate eventually exceeds the rate that liquids drain into the saltwell screen and the liquid level within the saltwell drops. The pumping rate is then reduced to approximately match the liquid drainage rate to prevent the jet pump from running dry.

Recent pumping campaigns have been as short as three months (tank S-103, from which less than 24,000 gal of liquid were removed) and as long as about one year (tank SX-104, from which about 117,000 gal of liquid were removed). The duration of saltwell pumping in any given tank is a function of the amount of drainable liquid, the drainage rate (which depends on permeability), and the actual times that the system is available for pumping (stoppages for corrective and preventative maintenance are common).

The saltwell pumping status as of December 2000 is summarized in Table 1-2 (Watch List Tanks AX-103 and SX-09 are not scheduled for pumping). Established and projected waste configuration changes associated with the removal of drainable liquid are discussed in Section 4.0. Hydrogen generation rates, which are expected to decrease in proportion to the amount of liquid waste removed from each tank, have been estimated and are discussed in Section 5.0. Gas releases induced by saltwell pumping have been detected by headspace monitoring instrumentation on all Flammable Gas Watch List SSTs that have been pumped recently. Retained gas inventory changes (estimated to have occurred in tanks that have been stabilized and predicted to occur in tanks yet to be stabilized) are given in Section 6.0, and saltwell pumping induced release behavior is described in Section 7.0.

Table 1-2. Saltwell Pumping Status as of December 2000

Tank	Watch List	Pumping Status			Drainable Liquid (kgal)	
		Start [a]	End	Status	Initial Estimate [e]	Volume Pumped [g]
A-101	FGWL	5/6/00		Delayed [c]	587	18
AX-101	FGWL	7/30/00		Delayed [c]	444	9
BY-105		*7/15/01*			111	
BY-106		*7/15/01*			119	
C-103		[b]			83	
S-101		*11/30/02*			80	
S-102	FGWL	3/18/99		Delayed [c]	99	68
S-103		6/4/99	1/4/00	Stabilized	52	28
S-106		4/16/99	1/3/00	Evaluation	76	109
S-107		*11/30/02*			61	
S-109		9/23/00		In progress	83	29
S-111	FGWL	*12/30/01*			132	
S-112 [f]	FGWL	*11/30/02*			70	
SX-101	FGWL	11/20/00		In progress	99	No data
SX-102	FGWL	*12/30/01*			116	
SX-103	FGWL	10/26/00		In progress	132	39
SX-104	FGWL	7/23/98	7/25/99	Stabilized [d]	144	125
SX-105	FGWL	8/8/00		In progress	141	132
SX-106	FGWL	10/7/98	12/21/99	Stabilized	283	160
T-110	FGWL	7/2/98	8/12/99	Stabilized [d]	41	34
U-102		1/20/00		In progress	75	70
U-103	FGWL	9/26/99	5/11/00	Stabilized	99	108
U-105	FGWL	12/11/99	7/13/00	Evaluation	80	91
U-106		8/24/00		In progress	56	39
U-107	FGWL	*12/30/01*			115	
U-108	FGWL	*12/20/01*			124	
U-109	FGWL	3/11/00		In progress	99	72
U-111		*11/30/02*			71	

Notes:

(a) Future dates in italics represent the planned schedule (Hanlon 2000)
(b) Pumping date will be set for tank C-103 in December 2000.
(c) Pumping in tanks A-101 and AX-101 delayed due to repeated pump motor failure. Tank S-102 pumping delayed due to repeated jet pump or recirculation line plugging.
(d) Tanks declared stabilized before minimum draining rate was achieved due to major equipment failure.
(e) Drainable liquid estimates from Fort (2000).
(f) Tank S-112 was initially saltwell pumped in 1978.
(g) Volume given for tanks in which pumping is in progress or recently completed.
FGWL = Flammable Gas Watch List

1.2 OUTLINE OF THE REPORT

This report presents the data and observations that describe and quantify the flammable gas hazard in the single-shell Hanford Site high-level waste tanks on the Flammable Gas Watch List. Section 2.0 describes the characterization events and monitoring instruments that provide useful data on SST waste. Section 3.0 discusses the important aspects of waste chemistry, and the waste configuration and physics properties are presented in Section 4.0. Gas generation and gas composition are covered in Section 5.0, and gas retention is discussed in Section 6.0. Observations of spontaneous and induced gas release behavior are described in Section 7.0, and tank headspace mixing characteristics and passive ventilation rate measurements are summarized in Section 8.0. Section 9.0 gives an overall summary and conclusions, and references are listed in Section 10.0.

The discussion is focused on the SSTs that are on the Flammable Gas Watch List. However, other tanks are mentioned and included in tables and figures, as appropriate to the subjects being treated. Two other tanks, S-103 and S-106, are specifically included in many cases as being similar in configuration and behavior to many Watch List tanks. The background data on these two tanks are given in Appendix A.

2.0 DESCRIPTION OF WASTE CHARACTERIZATION MEASUREMENTS

This section describes the kinds of measurements made, what information the data provide, and the location of the measurements taken in each tank. Waste level is discussed in Section 2.1, waste temperature in Section 2.2, and headspace gas monitoring in Section 2.3. Core sampling is described in Section 2.4. Section 2.5 describes the Retained Gas Sampler (RGS), and Section 2.6 discusses neutron and gamma logs and determining the interstitial liquid level (ILL). Section 2.7 summarizes the location of important instruments and measurements in each of the nineteen SSTs on the Flammable Gas Watch List.

2.1 WASTE LEVEL

The waste depth (elevation of the waste surface above the tank bottom) is a key indicator of tank status and waste behavior. Tanks with a high waste level are potentially more hazardous because gas is stored at a higher pressure and more waste is available to store gas. In the absence of waste addition or removal, a gradual increase in waste level indicates gas accumulation while decrease in waste level is usually associated with evaporation of water. Saltwell pumping generally results in an abrupt and large drop in waste level. The total stored gas volume in a tank can be computed from the correlation of waste level changes with barometric pressure fluctuations, if certain conditions are met (see Section 6.0).

Waste surface level is typically measured with three different devices: the Food Instrument Corporation (FIC) contact probe, a manual tape, and the ENRAF™[2] buoyancy gauge. The FIC and manual tape level readings have been available in each SST from before the early 1980s. ENRAF™ level gauges have been installed only since about 1995. Level measurements may be either manual or automatic. Data obtained prior to 1980 were recorded on a weekly basis. Daily or once-per-shift readings have been available since the early 1980s. The various instruments report different values and trends, mainly because of the irregularity of the crust surface but also because of the peculiarities of the measurement methods.

If the waste surface is moist, the FIC plummet can gradually accumulate waste deposits up to several inches long from repeated contacts. These deposits must be flushed occasionally with water to restore the measurement's accuracy. Repeated flushing can dissolve a cavity or crevice in the waste that can also compromise the accuracy of the measurement. The manual tape is also subject to waste deposits but is seldom flushed and, therefore, disturbs the waste less.

If the waste surface is dry, the FIC probe may not make electrical contact and, therefore, be unable to measure the waste surface level. In most cases, this requires the FIC to be placed in "intrusion mode" where the plummet is held stationary a few inches above the waste surface with the intent of sensing any intrusion of water sufficient to raise the waste level to contact the

[2] ENRAF is a trademark of the ENRAF Corporation, Houston, Texas

plummet. Data recorded in "intrusion mode" is not very useful and has been ignored in this report.

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™ potentially the most reliable level indicator.

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 in. to 8 in.) depending on the tank. Sensing level change is far more important than absolute accuracy. 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 at ± 0.6 cm (0.25 in.) for nearly consecutive readings, but waste deposit growth and periodic flushing adds an uncertainty of ± 5 cm (2 in.) in long-term values.

The manual tape is typically read in 0.64-cm (0.25-in.) increments; therefore, it senses changes only to within ± 2 cm (0.75 in.) at best. Whitney (1995) found that the response of manual tape readings to barometric pressure changes was not a valid indicator of gas retention. Consequently, the manual tape data are not used in this study.

2.2 WASTE TEMPERATURE

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 capacity and 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 tank 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 vapor space. The uncertainty in the temperatures that are obtained from their instruments is estimated to be ±1.8 °C (3 °F) (Brewster et al. 1995).

2.3 HEADSPACE GAS MONITORING

The concentrations of hydrogen and other flammable gases in the tank headspace are monitored to ensure that the headspace is safe and to increase our understanding of the mechanisms for gas release and dilution. Several different systems are used. Depending on the information desired

from a tank, different monitoring instruments are combined into a tank-specific system. These instruments are listed in Table 2-1 with their measurement accuracies and ranges. The following sections describe how the instruments are applied in different monitoring systems.

Table 2-1. Gas Monitoring Instruments

Instrument	Gases Monitored	Range	Accuracy
Whittaker™ Electro-Chemical Cell and Transmitter	Hydrogen-Specific	0 to 1% and 0 to 10% H_2 by Volume	±0.2% by volume absolute (resolution of 50 ppm)
Gas Chromatograph Thermal Conductivity Detector (GC-TCD)	Hydrogen (H_2) Nitrous Oxide (N_2O) Methane (CH_4)	H_2 3 to 3,000 ppm N_2O 10 to 20,000 ppm CH_4 10 to 4,000 ppm	H_2, N_2O, CH_4 ±3 ppm <30 ppm and ±10% of reading >30 ppm
Infra-Red Photo Acoustic Multi-Gas Monitor (IR)	Ammonia (NH_3)	NH_3 10 to 10,000 ppm	NH_3 ±10 ppm <100 ppm and ±10% of reading >100 ppm
Grab Samples - Mass Spectrometer	Hydrogen (H_2) Nitrous Oxide (N_2O) Methane (CH_4) Argon (Ar) Nitrogen (N_2) Oxygen (O_2)	0 to 100% by volume	At least ± 10 ppm

2.3.1 Standard Hydrogen Monitoring Systems

The basic standard hydrogen monitoring system (SHMS) monitors hydrogen continuously. Gas is vacuum-pumped from the tank into a temperature-controlled cabinet that contains the monitoring instrument. For DSTs, the sample is obtained from the tank ventilation exhaust duct; for SSTs, the sample is obtained from a probe that is inserted well into the tank dome space.

The monitoring instrument is a Whittaker[3] electrochemical cell that is hydrogen-specific. The cell generates an electrical signal proportional to the volume percent hydrogen concentration. This signal is processed by a transmitter and sent to a digital data readout and data recorder. The recording channel of the data recorder is programmed to activate an alarm relay, if a preset hydrogen concentration (currently 6,250 ppm) is reached. The alarm relay opens a normally closed contact that serves as the input to a programmable logic controller that controls the annunciation of a high hydrogen alarm and initiates an automatic vapor grab sample. Data are recorded by connection to the Tank Monitoring and Control System (TMACS) and by an on-board chart recorder. The SHMS also has a grab sample station that allows two 75-mL vapor samples to be taken simultaneously from the gas stream, isolated, and transported to a laboratory for analysis. Hydrogen and other gases can be measured in these samples.

[3] Whittaker is a trademark of Whittaker Corporation, Garden Grove, California

These systems are calibrated quarterly. A mixture of 100-ppm hydrogen and air is used to adjust the low end of the hydrogen sensor, and a mixture of 5% hydrogen mixed with nitrogen is used to balance the high end of the sensor. A mid-range standard gas of 1,000-ppm hydrogen is used as an on-line calibration check during system operation (Schneider 1996).

The first SHMS was developed for continuous monitoring of hydrogen concentrations in DST SY-101. Three of the basic units are installed and operating on this tank; one monitors the vent header concentration, and the other two monitor locations within the headspace. Because of the success of these instruments, the system was upgraded by adding the capability to obtain a grab sample automatically on a high hydrogen reading. Also, the Whittaker™ cells were configured so that one covers a high range (0 to 10% by volume) and one a low range (0 to 1% by volume). This modified version is called the SHMS-B.

The SHMS-B is the most widely used of the SHMS instruments. It was originally installed on all SST Flammable Gas Watch List tanks except tanks A-101, SX-103, and U-105. Data are recorded by connection to the TMACS and by the onboard chart recorder. As specific needs arose, the SHMS-B was modified to provide the needed capabilities. This produced the current E and E+ models.

The SHMS-E is an updated version of the SHMS-B and accommodates (although not installed) a dual-column gas chromatograph with a thermal conductivity detector and an infrared (IR) photo-acoustic multi-gas monitor. An onboard digital data logger records data with data retrieval via floppy disk. The upgrade in design from the SHMS-B is in the data recording (the strip-chart is eliminated) and the programmable logic controller. The SHMS-E is intended for use in the same applications as an SHMS-B but has the advantage of easily being upgraded to an E+.

The SHMS-E+ is an SHMS-E with the gas chromatograph and IR monitor installed. The Gas Chromatograph (GC) monitors hydrogen, nitrous oxide, and methane, and the IR monitor detects ammonia. An onboard digital data logger records data with data retrieval via floppy disk or by connection to a host computer via the Hanford Local Area Network (HLAN).

The specific components of each of the monitoring systems described above are summarized in Table 2-2. A complete list of gas monitoring systems installed on the nineteen Flammable Gas Watch List SSTs is given in Table 2-3.

Table 2-2. Components of Gas Monitoring Systems

Systems	Components
SHMS	Whittaker™ cell for H_2, grab-sample station
SHMS-B	High- and low-range Whittaker™ cells for H_2, grab-sample station
SHMS-E	SHMS-B with improved data logging, space for two dual-column GC-TCDs (not installed) and an IR multi-gas monitor (not installed)
SHMS-E+	SHMS-E with GC-TCDs installed for H_2, N_2O, and CH_4, IR multi-gas monitor installed for NH_3

Table 2-3. Gas Monitoring Systems Installed on Single-Shell Flammable Gas Watch List Tanks

Tank	Systems (date installed)
A-101	SHMS-E+ (11/97)
AX-101	SHMS-B (3/95)
AX-103	SHMS-B (3/95)
S-102	SHMS-B (3/95)
S-111	SHMS-B (3/95)
S-112	SHMS-B (3/95)
SX-101	SHMS-B (3/95)
SX-102	SHMS-B (3/95)
SX-103	SHMS-E+ (3/98)
SX-104	SHMS-B (3/95)
SX-105	SHMS-B (3/95)
SX-106	SHMS-B (3/95)
SX-109	SHMS-B (3/95)
T-110	SHMS-B (3/95)
U-103	SHMS-B (3/95)
U-105	SHMS-E+(5/98)
U-107	SHMS-B (3/95)
U-108	SHMS-B (3/95)
U-109	SHMS-B (3/95)

2.4 WASTE CORE SAMPLING

Core sampling is the task of remotely obtaining samples of materials stored in River Protection Project (RPP) Tank Farm waste storage tanks. Push mode and rotary mode are two core-sampling methods used to obtain solid and/or supernatant liquid samples of this waste, possibly including gas samples. Sludge, saltcake, liquid, and gas are the four general waste phases in the various tanks. The samples are obtained from the tanks using specially designed core-sampling trucks and sampling devices. Prior to core sampling, the headspace of the tank is monitored for flammability and organic vapors. A cylindrical cross-section of the tank contents is obtained by pushing or rotating a 2.5 cm x 48 cm (1 in. x 19 in.) stainless steel sampler and bit (Figures 2-1 and 2-2) into the waste through one of the tank risers.

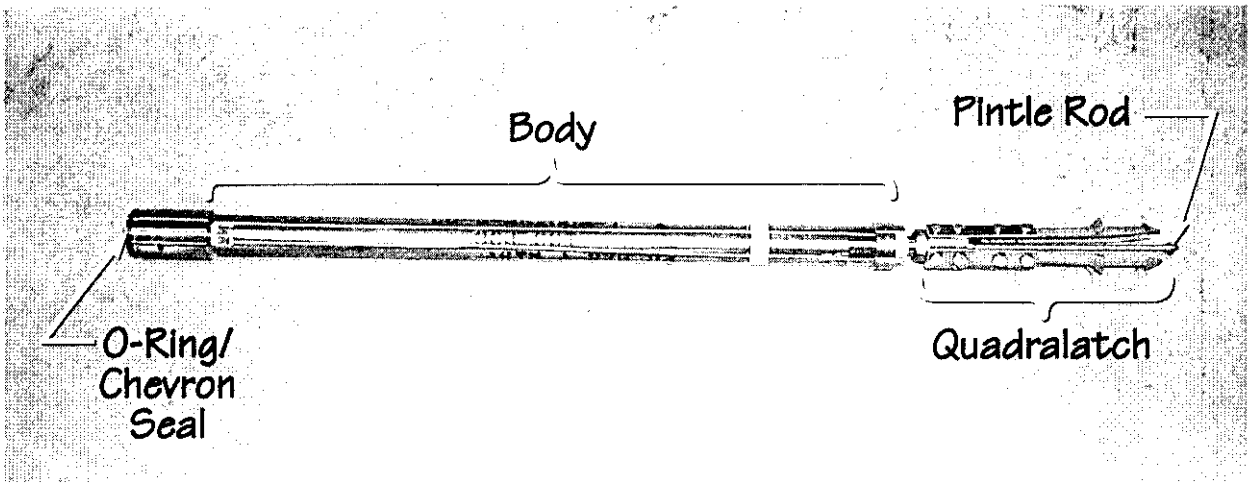

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Figure 2-1. Core Sampler

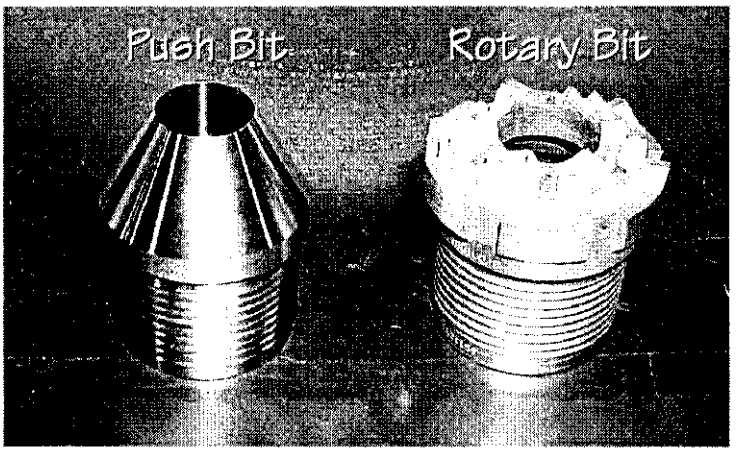

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Figure 2-2. Push and Rotary Mode Bits

Push-mode sampling is performed on tanks containing liquids or soft sludge. This is done by the first generation core sampling truck referred to as the Push Mode Core Sample (PMCS) truck. Rotary-mode sampling is primarily used to sample sludge or hard saltcake, although it may be used to sample other waste types. Because of safety concerns, a second-generation truck, known as the Rotary Mode Core Sample (RMCS) truck was designed. The RMCS truck supplies nitrogen gas to limit drill bit temperature during drilling operations. The RMCS truck can also perform push mode sampling when sample material is soft.

During a sampling event, the stainless steel sampler is lowered down through the drill string; it locks into the core barrel; the drill string is then advanced (typically 19 in. [48 cm]). There is a ball valve at the bottom of the sampler, which is used to contain the collected sample in the tube once the sample has been taken. There are three types of samplers: the O-ring, Chevron, and Retained Gas Samplers. After the sample is taken, it is raised and placed in a cask.

Drill ram hydrostatic pressure is continuously monitored during the sampling operation to measure waste resistance. Core samples are repeatedly taken until the bottom of the tank is reached. The waste approximately 7.6 cm (3 in.) from the tank bottom of SSTs cannot be sampled when using the rotary mode bit because of the design and safety constraints of the sampling method (DeLorenzo et al. 1994). An example of the cross-section or core profile is included as Figure 2-3.

The sampler has a 2.85 to 2.87 cm (1.124 to 1.128 in.) inside diameter which gives a nominal 1.00-in.^{2} cross section and makes the nominal capacity of the sampler for fluid samples 16.4 cm^3 per inch. Before the sample can enter the sampler, it first must pass through a hole in the sampler bit. The diameter of this hole is 1.0 in (2.54 cm). Therefore, when taking a sample of rigid material, the diameter of the sample taken is restricted by the bit diameter, not the sampler diameter. This corresponds to a nominal 12.9 cm^3 per inch. For a full sampler, the volume of material which could theoretically be present in the current universal sampler is:

- 237 cm^3 for a rigid core sample (228 cm^3 for the top segment)
- 237 to 309 cm^3 for nonconvective layers depending on the viscosity of the material (228 to 298 cm^3 for the top segment)
- 309 cm^3 for liquids (298 cm^3 for the top segment) (Schofield 1996).

The most effective method available, at this time, for determining percent recovery with the universal sampler is with the x-ray imaging system, which permits a direct readout of how full a sampler is shortly after it has been removed from the tank, and before it is has been disturbed in the laboratory (Schofield 1996).

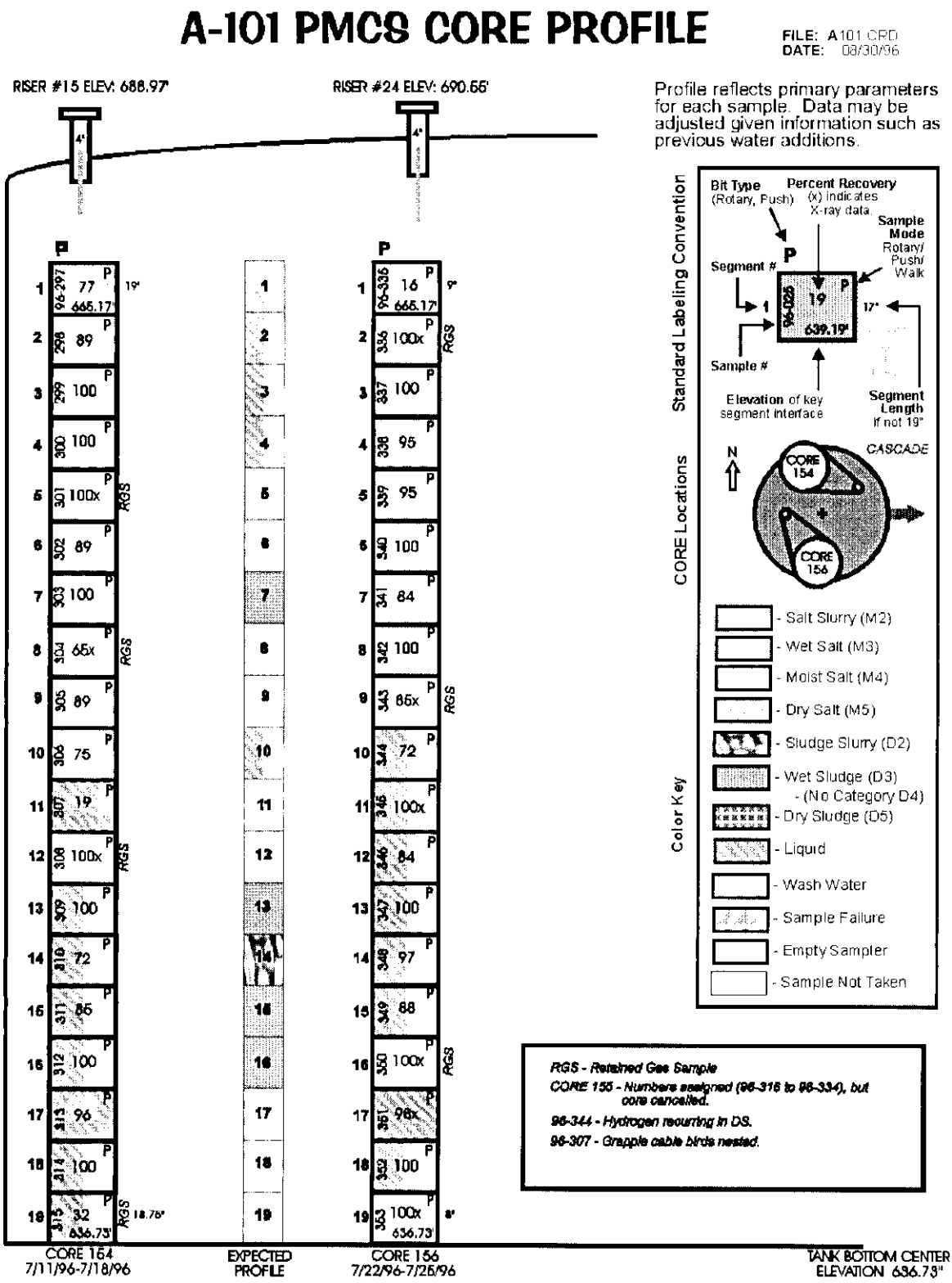


Figure 2-3. Example Core Profile

2.4.1 Core Extrusion Waste Strength Estimation

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 is 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[4] mixed with different amounts of salt and setup times to obtain shear strengths of 625 to 6,500 Pa.

The kaolin/Ludox simulant showed brittle failure with little deformation during extrusion, as can be seen in Figures 4-13 through 4-18 of Gauglitz and Aikin (1997), with the shear strength being related to the length of waste that was rigidly extruded from the sampler before breaking off and falling into the tray. The bentonite simulant failed in the plastic deformation regime, as can be seen in Figures 4-1 through 4-11 of Gauglitz and Aikin (1997). The shear strength of the bentonite was related to the length of the segment before breaking off or, for stronger samples, to the angle at which the simulant dropped from the sampler.

The strengths of waste samples from three DSTs and one SST were estimated by comparing the waste behavior during extrusion, which had been videotaped, to the behavior of the simulants of known strength. The comparison simulant, bentonite or kaolin/Ludox, was chosen according to the lesser or greater rigidity of the waste sample. The results showed that the extrusion method gave estimates that were within a factor of two of those obtained by ball rheometry in the DSTs at the same elevation as the core samples. This is considered reasonably good agreement. Shear vane measurements gave shear strengths a factor of 10 or greater than those measured by core extrusion and ball rheometry. This discrepancy is expected, particularly in materials with a considerable solid structure, because the shear vane measures a somewhat different material property than the other two techniques.

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 whose waste cannot be subjected to more precise rheometry.

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

2.5 RETAINED GAS SAMPLER (RGS)

The RGS system, which obtains waste samples for the measurements of in-situ composition of gases retained in the waste, uses a version of the core sampler (see Figures 2-1 and 2-2) that was designed specifically for sampling waste that contains gas. Other than the modified sampler and sample extraction, the RGS sample is obtained in the same operation as a normal push-mode core sample. Details of the core sampler, modifications made, and operational constraints of the RGS are given in Webb (1994). The complete details of the sample extraction process for the nine SSTs sampled with the RGS (tanks A-101, AX-101, BY-109, S-102, S-106, S-111, SX-106, U-103, and U-109) are described in Shekarriz et al. (1997), Mahoney et al. (1997), and Mahoney et al. (1999). Final results for the SSTs and for several DSTs are given in Mahoney (2000). This section gives a brief description of the RGS system and operation.

To obtain a sample, an RGS is installed in the push-mode core drill string and lowered into the correct vertical position in the tank. The sample is taken by pushing the sampler down into the waste while the sampler piston is held in position. When the piston contacts the top end of the sampler, a spring is triggered that closes the sampler ball valve, hermetically sealing the waste sample solids, liquids, and gases in a chamber approximately 2.8 cm (1.125 in.) in diameter and 48 cm (19 in.) long.

After the valve is closed and the waste sealed in the sampler, the sampler is removed from the tank and transferred to the x-ray cart for imaging. The x-ray images confirm whether a full sample has been recovered and provides information about the gas structure (bubble shape, etc.) and density of the waste. It also allows a semi-quantitative estimate of the amount of gas present. After the x-ray, the sample is placed in a transport cask and delivered to the 222-S hot cell laboratory for extrusion and gas extraction.

To extract the waste, the sampler is connected to a previously evacuated extraction chamber in the hot cell. The sampler ball valve is opened, and a hydraulic ram pushes the sampler piston all the way forward to drive the sampler contents into the extractor. The waste is then stirred at ambient hot cell temperature to free most of the retained gas bubbles, after which the gas that has been released into the extractor is transferred to collector canisters using a mercury displacement pump. During this process, the sampler and canister pressures and temperatures are monitored and recorded for data reduction and analysis. The gases collected in the canisters are analyzed with a mass spectrometer. Isotopic standards of $^{15}NH_3$ vapor or $^{15}NH_4OH$ solution may be added to assist in measuring the sample ammonia concentration.

The data analysis procedure uses the temperature, pressure, and volumes measured during extraction, as well as, the mass spectrometry results to compute the mole fraction and total volume of each gas constituent, the fraction of each component that exists in the gas and is dissolved in the liquid, and the total gas volume fraction at the local hydrostatic pressure from which the sample was taken. The x-ray images are analyzed to provide, in addition to qualitative observations of the phase distribution in the sample, an estimate of the density and gas volume.

Shekarriz (1994) performed a series of flow visualization tests to examine the effectiveness of the RGS drill bit in capturing bubbles in the nonconvective waste during sampling. A transparent simulant with rheological properties similar to DST waste was used. These tests showed that bubble capture error was minimal and that a 60-degree bit was optimal in minimizing the waste disturbance during sampling.

Comprehensive studies were also performed to quantify the uncertainty in measuring retained gases using the RGS (Cannon and Knight 1995; Cannon 1996). It was found that, while the insoluble gas components could be measured with high accuracy, the ammonia measurements were less accurate because unknown amounts of ammonia were retained in the sample and because ammonia was absorbed within the system. It was also established that the gas fraction in each sampler could be determined quite accurately, but the limited number of samples per tank (seldom more than six) create a very high uncertainty in estimates of total gas inventory in the tank.

2.6 NEUTRON AND GAMMA LOGGING

Whenever a tank has had most of the drainable liquids removed, typically by saltwell pumping of an SST, the liquid interface is left below a solid surface. This surface may consist either of drained saltcake or drained sludge, depending on the tank chemistry. This liquid level cannot be monitored by any of the conventional surface level devices previously discussed. The ILL is monitored by installing a liquid observation well (LOW). An LOW consists of a hollow tube, capped on the bottom, inserted into a riser from the surface to the bottom of the tank. It is typically jetted into place with high-pressure water. This leaves the interior of the LOW isolated from the tank contents, but open to the surface, creating an uncontaminated environment from which to monitor the tank contents using neutron and gamma probes. The detection processes are described below.

The LOW Surveillance Van can then drive up to the riser and lower a probe into the LOW opening. A computer program in the Surveillance Van lowers the probe to a pre-determined depth, typically about an inch above bottom, and retrieves the probe at variable speeds. The retrieval and data collection are controlled by a custom software script which is created specifically for the tank being evaluated. The probe can be slowed down to minimum speed across the zone of interest (typically the ILL), and the frequency of data collection increased. In lesser zones of interest (i.e., the vapor space above the waste), the speed can be increased and the data collection frequency decreased to reduce scanning time and file size.

A very basic and inaccurate system for obtaining this form of data was used from 1980 to 1997. The original system had many drawbacks, the most serious being a very inaccurate depth control system. The depth of major waste features, including the ILL, could only be determined within about 3 in. (7.6 cm) on a consistent basis. The primary reasons for this depth discrepancy were a lack of stabilization on the deployment boom, poor resolution of the depth encoder (20 pulses per inch, or about 0.60 in. (1.5 cm) between pulses), and a wide source-detector spacing on the

neutron probe, leading to poor vertical resolution. The survey speed was also constant, and could not be optimized for various zones of interest. The Surveillance Analysis Computer System (SACS) database contains scans obtained since 1980, and the data are available through either the PC-SACS or Tank Waste Information Network System (TWINS) (CHG 2000) computer interface.

In 1997 a new LOW Surveillance System was designed and implemented, which allowed much more accurate measurements. The deployment boom was stabilized with a support leg, eliminating vertical movement. The depth encoder generated 140 pulses per inch (about [0.018 cm] (0.007 in.) per pulse). The source-detector spacing was minimized to help clearly define liquid interfaces. Finally, the scan speed and data collection intervals were programmable on a tank-by-tank basis. The liquid interface data available from the new system are advertised as being accurate within 0.635 cm in 30.5 m (0.25 in. in 100 ft), but in most cases it exceeds 0.25-cm (0.10-in.) resolution. The absolute accuracy and repeatability is variable on a tank-by-tank basis due to data analysis algorithms and the shape of the probe response profile.

The new neutron probe consists of a chemical source (1.5 Curies of americium-beryllium, AmBe) threaded into the bottom of the probe which is immediately adjacent to the thermal neutron detector. The detector consists of a BF_3 gas tube, which only responds to neutrons which are moving slow enough to be captured. The AmBe source emits fast, high-energy neutrons at about 4.5 MEV, which are invisible to the BF_3. The fast neutrons are then moderated by the hydrogen of the surrounding moisture until they lose energy and become "thermal" neutrons. At that point, they are captured and detected by the BF_3. The detector response is a good indicator of the moisture content at the elevation surrounding the LOW. In general, the higher the count rate, the higher the moisture content, although the response is not linear.

Areas of apparent low moisture content can be due to drained waste, reduced waste porosity, increased gas concentration, void space around the LOW above the ILL, and the presence of saltcake/sludge layers. The neutron profile can be very useful in identifying the tank waste layering characteristics, in addition to tracking the movement of the ILL.

The gamma probe is simply a low efficiency Geiger-Mueller tube with no artificial gamma source. It simply detects naturally occurring gamma radiation penetrating the LOW from the waste. Because the survey environment can exhibit very high gamma fields, the tube sensitivity is very low to avoid saturating the detector. The primary waste emitters are cesium-137 and cobalt-60, although secondary gamma from strontium-90 is also picked up. The gamma probe detects "total" gamma, and makes no attempt to identify the source isotope. Spectral gamma tools are available which can identify the parent isotope from their energy spectra, but they are not in common use. The basic assumption in analyzing a gamma profile from a LOW is that cesium is usually the primary emitter, and that it is fairly soluble in water. This means that there should be a sudden change in total gamma concentration at the ILL interface, when the waste goes from liquid saturated to drained. As with the neutron probe, waste layers can often be delineated with the gamma probe. In general, the gamma probe is not run nearly as often as the neutron probe, primarily because the gamma probe is less sensitive to small differences in liquid content.

2.7 SUMMARY OF MEASUREMENT HISTORY IN EACH TANK

This section summarizes thermocouple tree placement, level measurement locations, and risers through which in-situ measurement devices such as the RGS were deployed. Deployment dates are also given. All headspace tanks discussed have a 75-ft inside diameter. Gas monitoring systems are not included because they are discussed in detail in Section 2.3.

2.7.1 Tank 241-A-101 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-4. The waste surface level in Riser 6 is currently measured by an ENRAF™ buoyancy gauge. The ENRAF™ gauge replaced an FIC contact probe in the same riser in April 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 12, with readings monitored and recorded through the TMACS system. Riser 19 accommodates an LOW.

In April 1996, grab samples were taken from Riser 4, which now contains a saltwell screen. Both core samples and RGS measurements were obtained from two risers in August 1996: Risers 15 and 24.

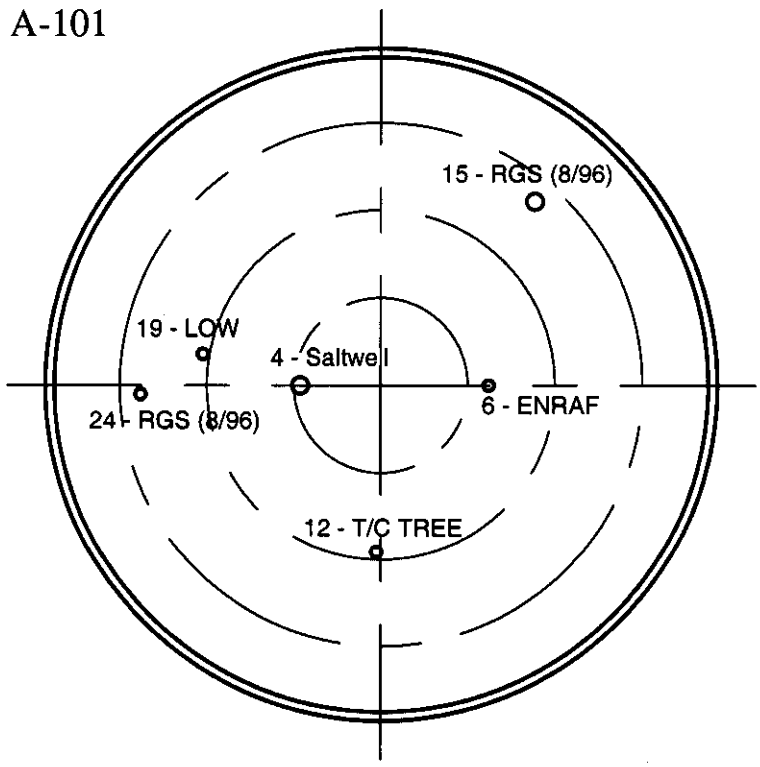


Figure 2-4. Tank 241-A-101 Sample and Monitoring Risers

2.7.2 Tank 241-AX-101 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-5. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 9C. The ENRAF™ gauge replaced a FIC gauge that was used in Riser 8C, in September 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 9B, with readings monitored and recorded through the TMACS system. Riser 9A accommodates an LOW.

In July 1997, grab samples were taken from Riser 5B, which now contains a saltwell screen. Both core samples were obtained from two risers in February 1998: Risers 9D and 9G. The RGS measurements were obtained from Riser 9D.

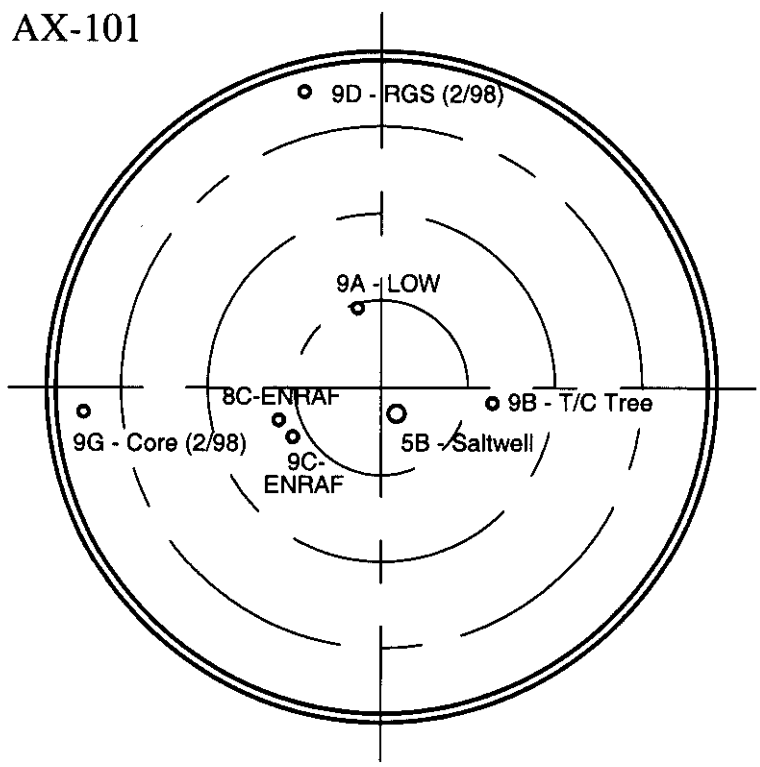


Figure 2-5. Tank 241-AX-101 Sample and Monitoring Risers

2.7.3 Tank 241-AX-103 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-6. The waste surface level in Riser 9C is currently measured by an ENRAF™ buoyancy gauge, which replaced the FIC gauge in September 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 9B, with readings monitored and recorded through the TMACS system. Riser 5A contains a saltwell screen.

Core samples were obtained from two risers in August 1997: Risers 9A and 9F, but the samples were incomplete and inconclusive.

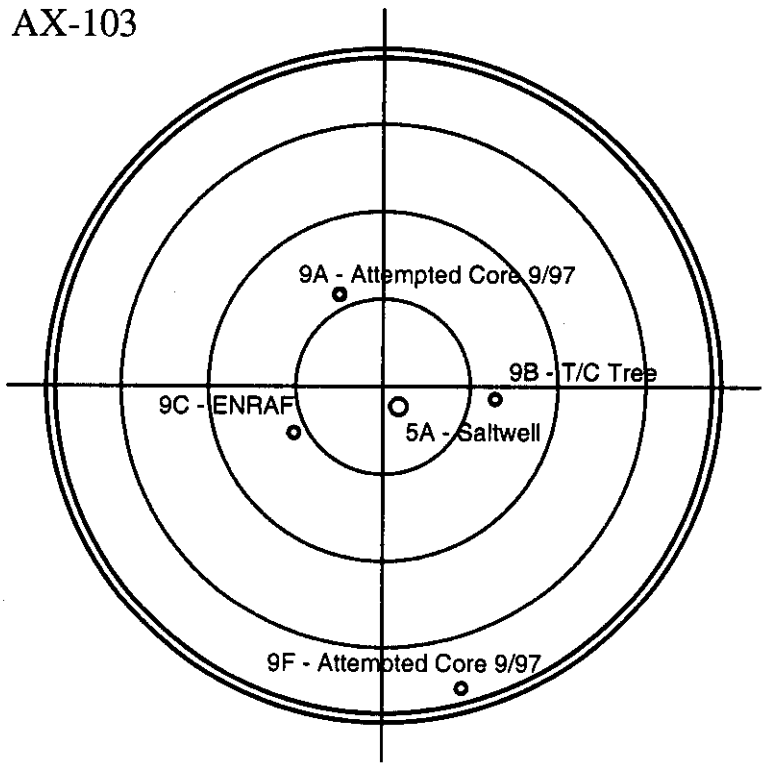


Figure 2-6. Tank 241-AX-103 Sample and Monitoring Risers

2.7.4 Tank 241-S-102 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-7. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 2. The ENRAF™ gauge has been used since May 1995, replacing the FIC and manual tape measurements. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 3, with readings monitored and recorded through the TMACS system. Riser 5 accommodates an LOW.

In June 1995 and October 1998, grab samples were taken from Riser 13, which now contains a saltwell screen and pump. Core samples were obtained from three risers: Riser 11 in January 1996, Riser 14 in March 1996, and Riser 16 in April 1998, when RGS measurements were also made.

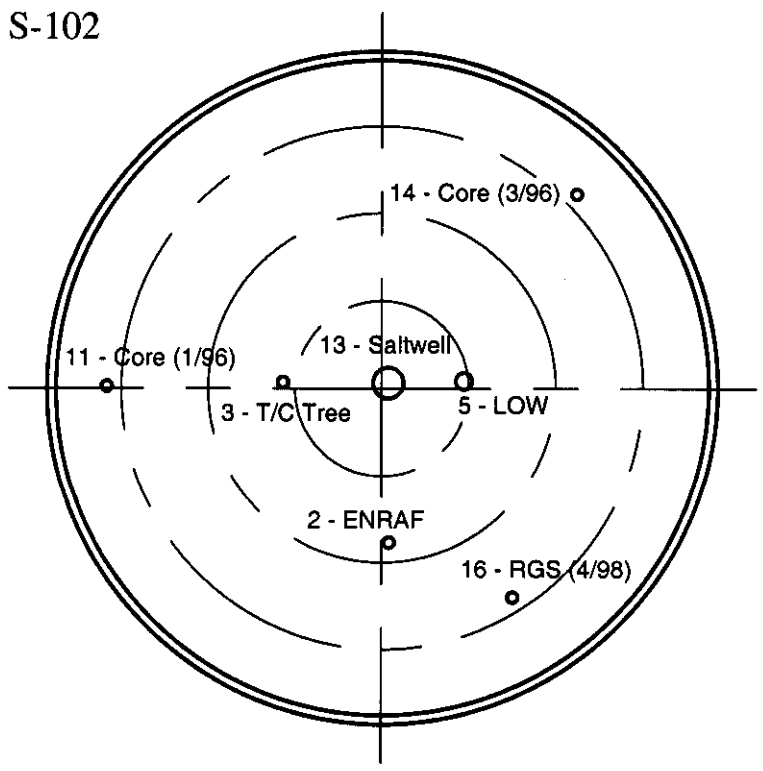


Figure 2-7. Tank 241-S-102 Sample and Monitoring Risers

2.7.5 Tank 241-S-111 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-8. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 3. The ENRAF™ gauge replaced a FIC contact probe in December 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 4, with readings monitored and recorded through the TMACS system. Riser 16 accommodates an LOW.

In August 1999, grab samples were taken from Riser 13, which now contains a slurry distributor. Core samples and RGS measurements were obtained from three risers: Riser 8 in May 1996, Riser 14 in June 1996, and Riser 6 in April 1998, when RGS measurements were also made.

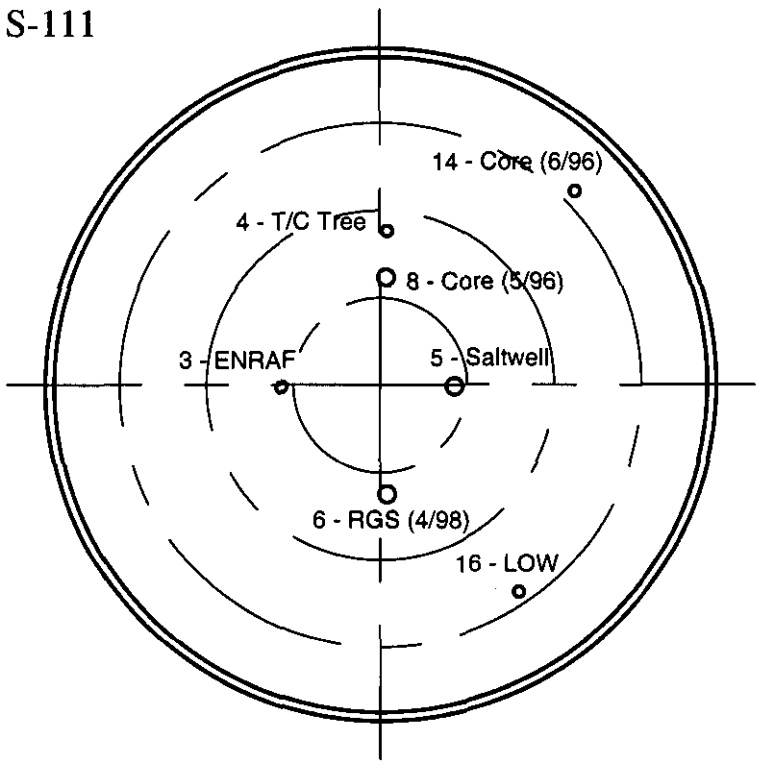


Figure 2-8. Tank 241-S-111 Sample and Monitoring Risers

2.7.6 Tank 241-S-112 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-9. The waste surface level in Riser 3 is currently measured by an ENRAF™ buoyancy gauge installed in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 4, with readings monitored and recorded through the TMACS system. Riser 8 accommodates an LOW, and Riser 5 houses a saltwell screen and pump. No core sampling has been performed in tank S-112.

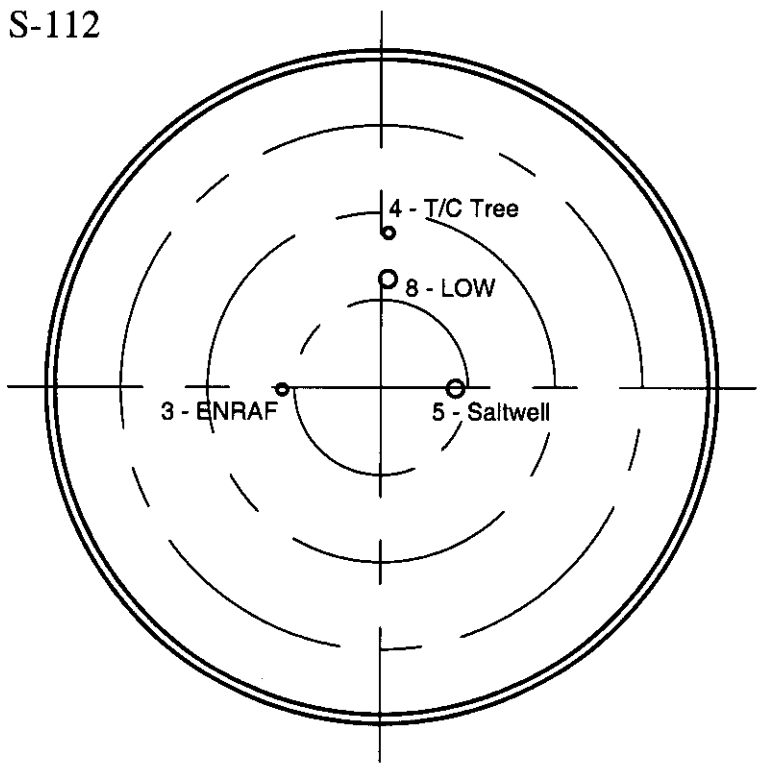


Figure 2-9. Tank 241-S-112 Sample and Monitoring Risers

2.7.7 Tank 241-SX-101 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-10. The waste surface level in Riser 4 is currently measured by an ENRAF™ buoyancy gauge, which replaced an FIC contact probe in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 15, with readings monitored and recorded through the TMACS system. Riser 14 accommodates an LOW, and Riser 9 contains a saltwell pump.

Core samples were obtained from two risers in February 1998: Risers 4 and 19.

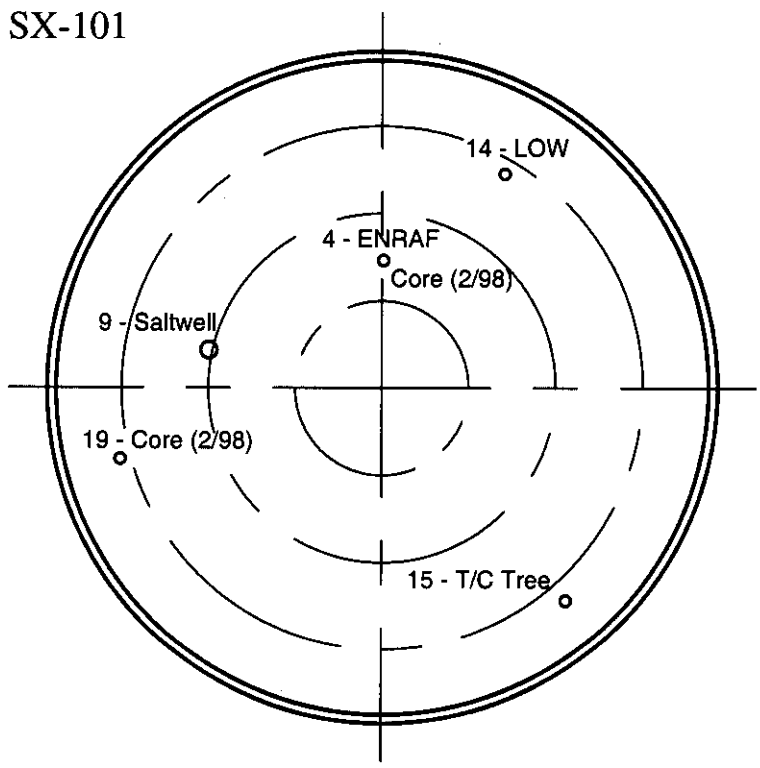


Figure 2-10. Tank 241-SX-101 Sample and Monitoring Risers

2.7.8 Tank 241-SX-102 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-11. The waste surface level in Riser 4 is currently measured by an ENRAF™ buoyancy gauge installed in April 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 16, with readings monitored and recorded through the TMACS system. Riser 14 accommodates an LOW, and Riser 9 contains a saltwell screen and P-10 pump.

Core samples were obtained in July 1998 from two risers: Risers 4 and 8.

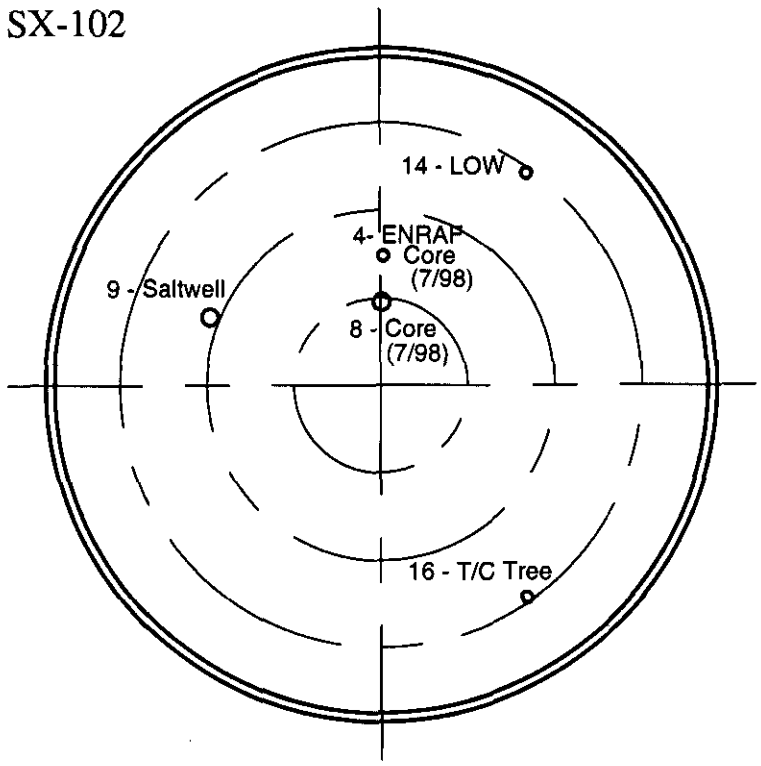


Figure 2-11. Tank 241-SX-102 Sample and Monitoring Risers

2.7.9 Tank 241-SX-103 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-12. The waste surface level in Riser 3 is currently measured by an ENRAF™ buoyancy gauge, which replaced an FIC contact probe in April 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 2, with readings monitored and recorded through the TMACS system. Riser 14 accommodates an LOW.

In June 1997, grab samples were taken from Riser 9, which now contains a saltwell screen and pump. Core samples were obtained from two risers: Riser 11 in April 1998 and Riser 7 in May 1998.

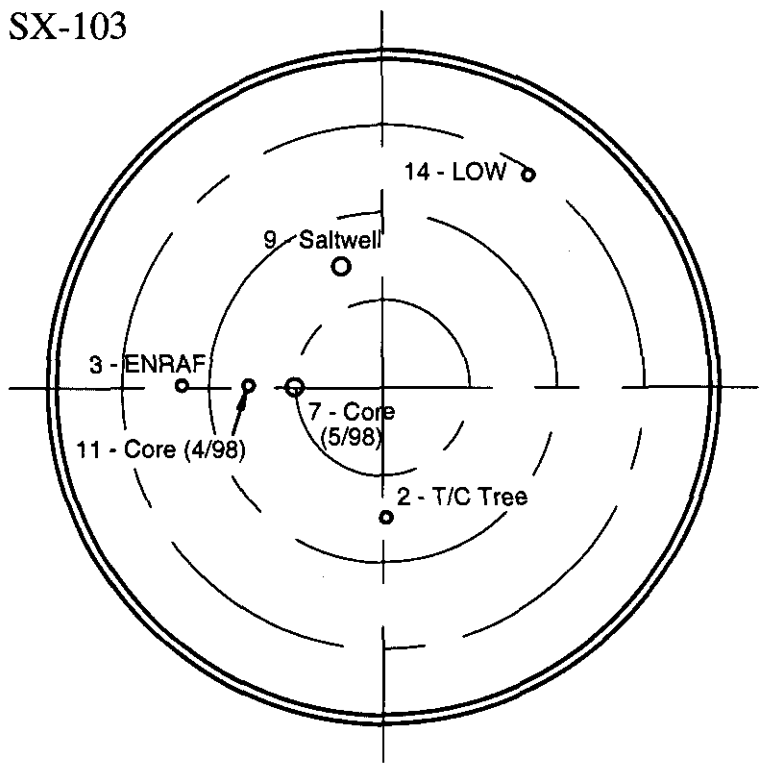


Figure 2-12. Tank 241-SX-103 Sample and Monitoring Risers

2.7.10 Tank 241-SX-104 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-13. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 4 installed in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 2, with readings monitored and recorded through the TMACS system. Riser 16 accommodates an LOW.

In April 1997 and June 1998, grab samples were taken from Riser 13, which now contains a saltwell distributor jet. No core sampling has been performed in tank SX-104.

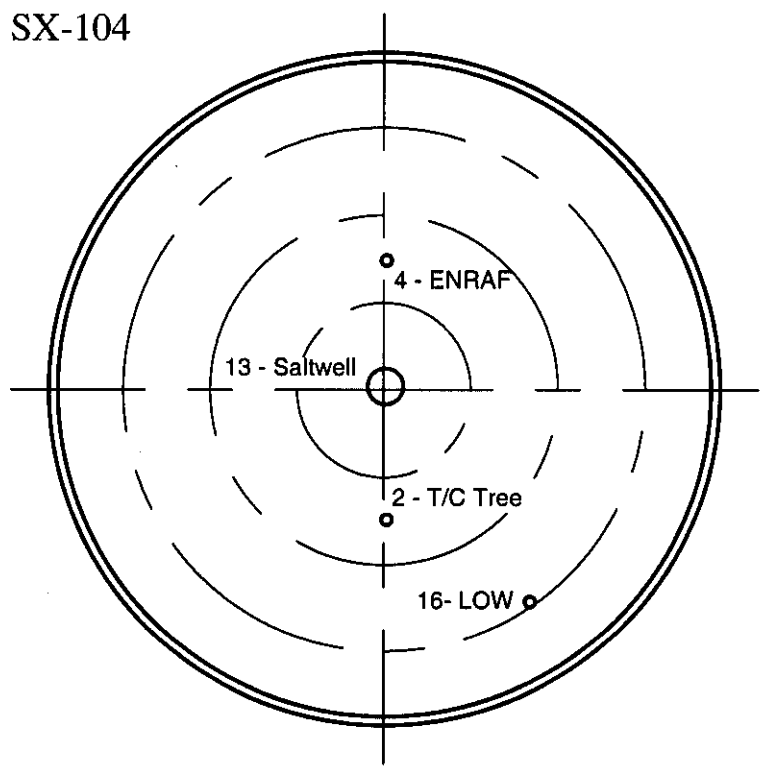


Figure 2-13. Tank 241-SX-104 Sample and Monitoring Risers

2.7.11 Tank 241-SX-105 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-14. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 4 installed in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 2, with readings monitored and recorded through the TMACS system. Riser 16 accommodates an LOW, and Riser 5 contains a saltwell screen and pump.

Core samples were obtained from Risers 6 and 14 in May 1998.

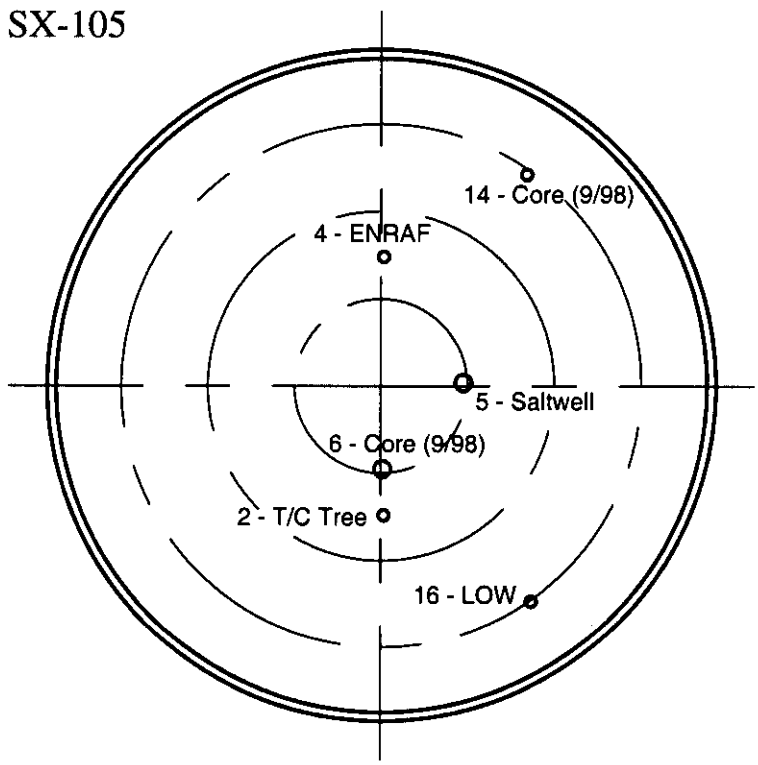


Figure 2-14. Tank 241-SX-105 Sample and Monitoring Risers

2.7.12 Tank 241-SX-106 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-15. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 3, replacing the FIC and manual tape measurements in August 1994. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 16, with readings monitored and recorded through the TMACS system. Riser 14 accommodates an LOW, and Riser 5 contains a saltwell screen and pump.

In August 1998, grab samples were taken from Riser 6, and core samples and RGS measurements were obtained from Risers 3 and 6 in December 1997.

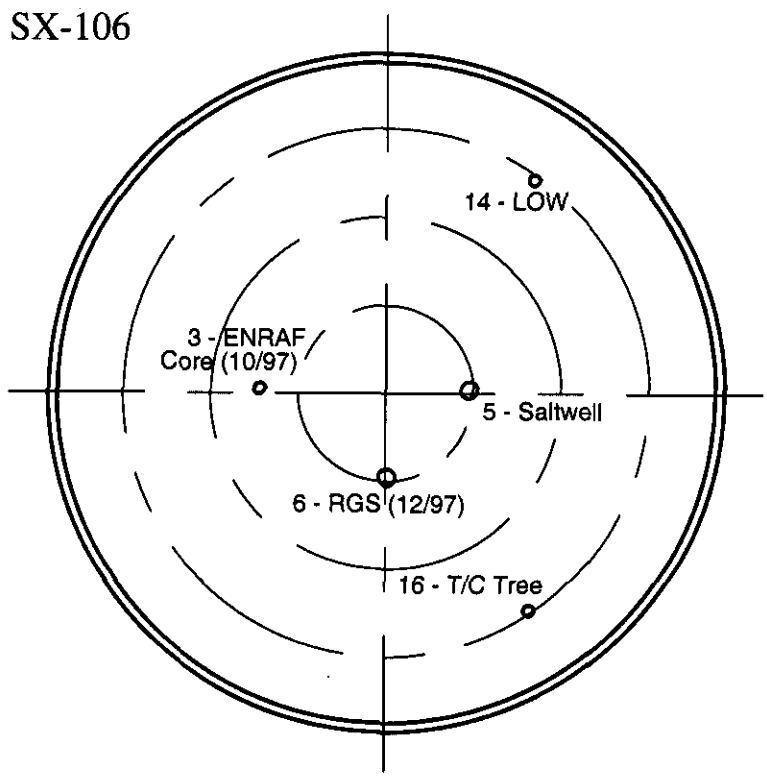


Figure 2-15. Tank 241-SX-106 Sample and Monitoring Risers

2.7.13 Tank 241-SX-109 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-16. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 2 installed in September 1998. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 19, with readings monitored and recorded through the TMACS system. No core sampling has been performed in tank SX-109.

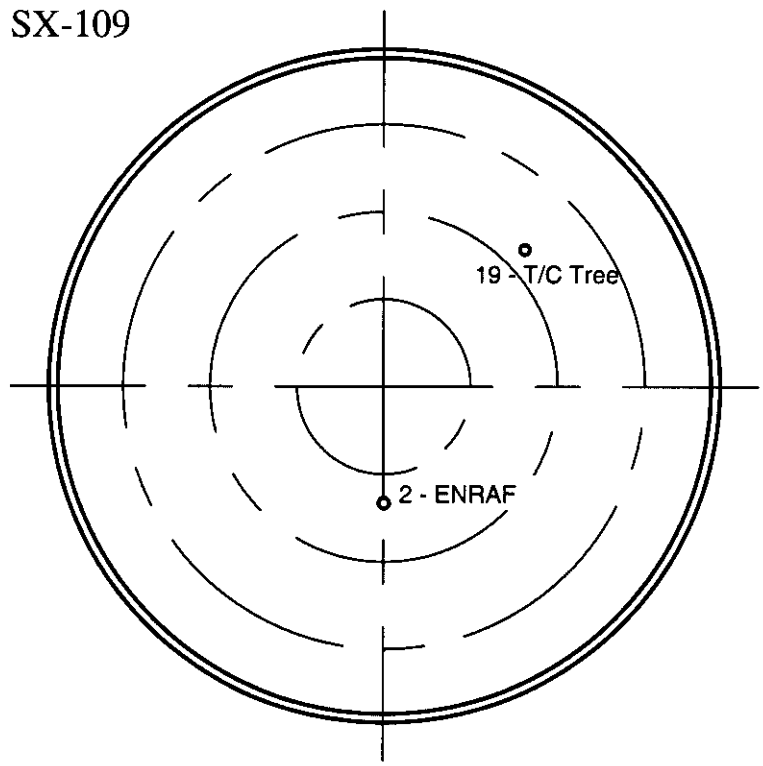


Figure 2-16. Tank 241-SX-109 Sample and Monitoring Risers

2.7.14 Tank 241-T-110 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-17. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 1 installed in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 8, with readings monitored and recorded through the TMACS system. Riser 5 accommodates an LOW.

In January 1997, grab samples were taken from Riser 13, which now contains a saltwell pump. Core samples were obtained from Risers 2 and 6 in February 1996.

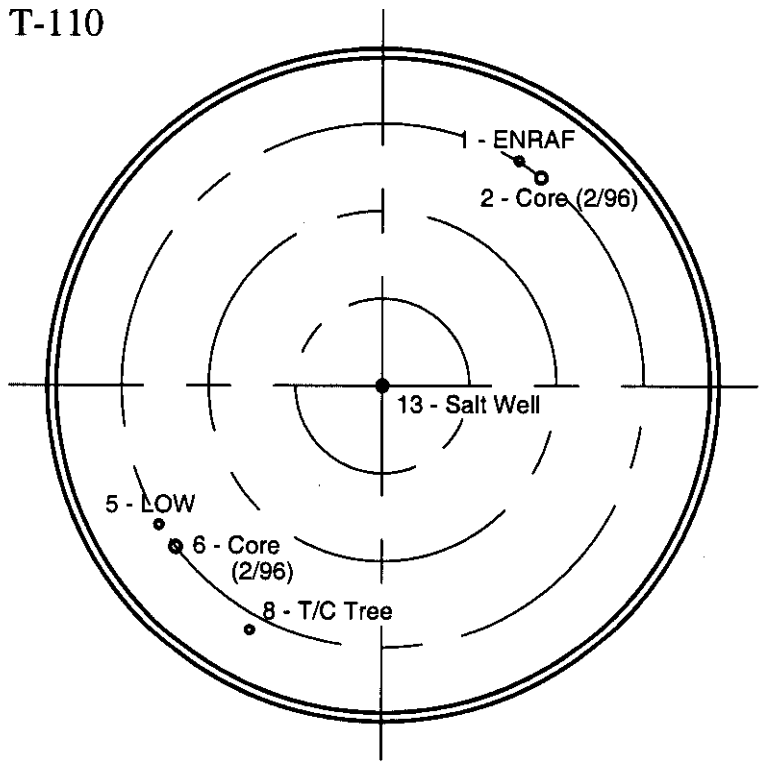


Figure 2-17. Tank 241-T-110 Sample and Monitoring Risers

2.7.15 Tank 241-U-103 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-18. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 8. The ENRAF™ gauge replaced an FIC contact probe in the same riser in July 1994. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 1, with readings monitored and recorded through the TMACS system. Riser 19 accommodates an LOW.

In 1999 grab samples were taken from Riser 13, which now contains a saltwell distribution pit. Core samples were obtained from Risers 2, 7, and 13 in April 1997. Retained gas sampler measurements were taken in Riser 7.

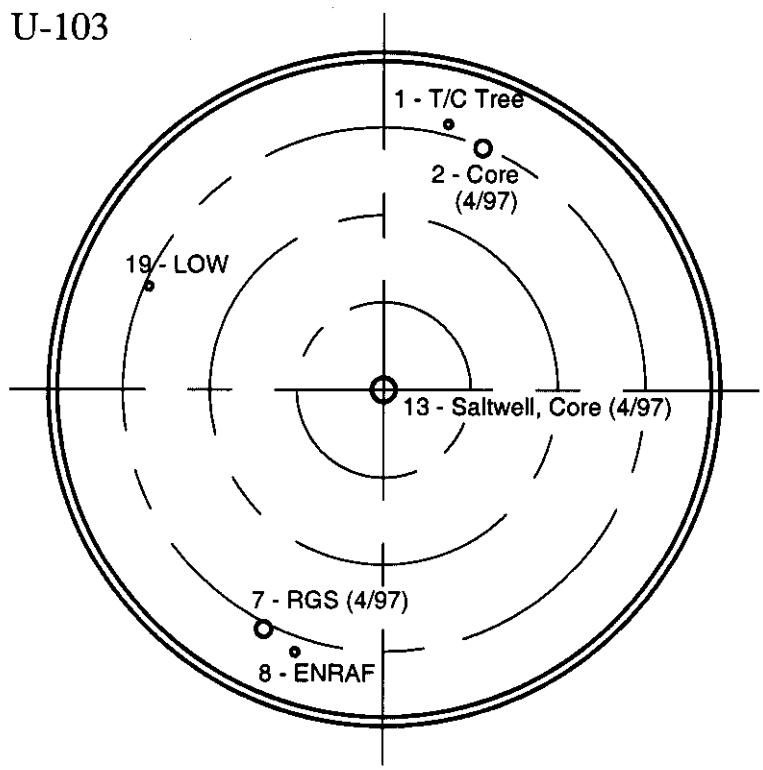


Figure 2-18. Tank 241-U-103 Sample and Monitoring Risers

2.7.16 Tank 241-U-105 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-19. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 8 installed in July 1994. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 1, with readings monitored and recorded through the TMACS system. Riser 19 accommodates an LOW.

In July 1999, grab samples were taken from Riser 13, which now contains a saltwell distributor pit. Core samples were obtained from Risers 2, 7, and 20 in February 1996.

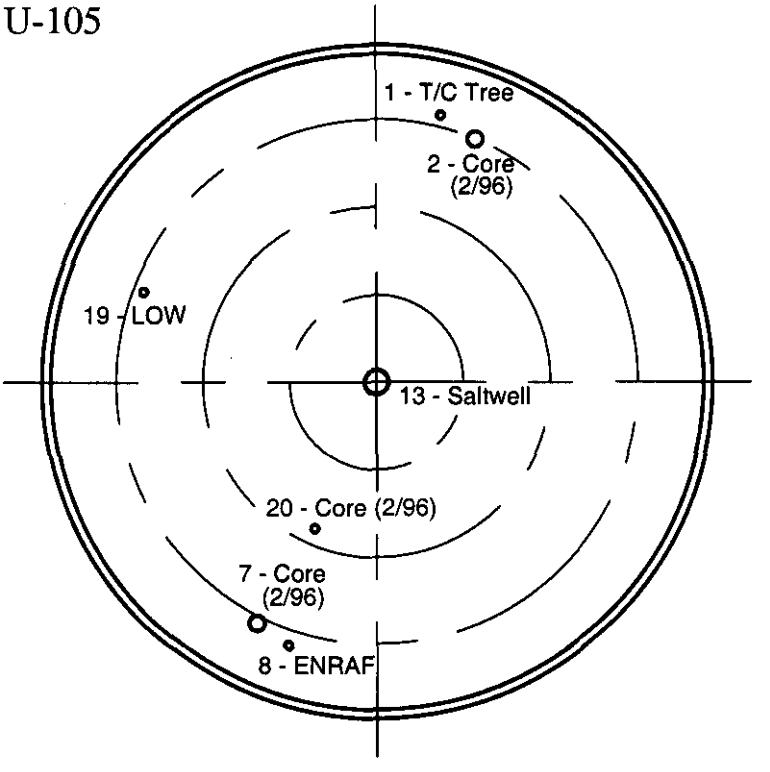


Figure 2-19. Tank 241-U-105 Sample and Monitoring Risers

2.7.17 Tank 241-U-107 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-20. The waste surface level is currently measured by an ENRAF™ buoyancy gauge in Riser 8 installed in August 1994. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 1, with readings monitored and recorded through the TMACS system. Riser 19 accommodates an LOW, and Riser 13 contains a distributor jet for saltwell pumping.

Core samples were obtained in March 1996 from Risers 2 and 7, in April 1996 from Risers 7 and 9, and in July 1998 from Risers 2 and 7.

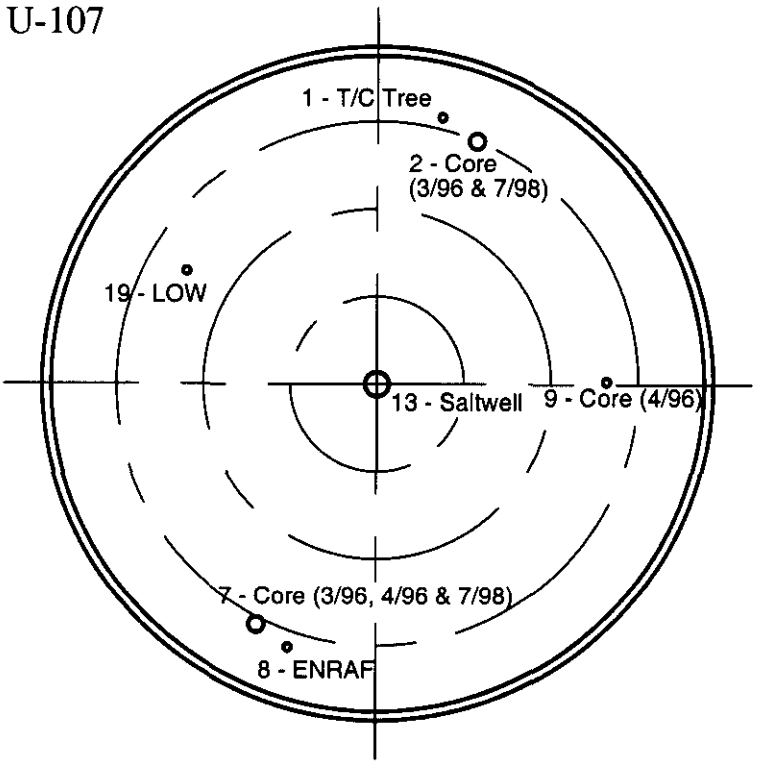


Figure 2-20. Tank 241-U-107 Sample and Monitoring Risers

2.7.18 Tank 241-U-108 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-21. The waste surface level is currently measured in Riser 8 by an ENRAF™ buoyancy gauge, which replaced an FIC contact probe in May 1995. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 1, with readings monitored and recorded through the TMACS system. Riser 19 accommodates an LOW, and Riser 13 contains a distributor jet for saltwell pumping

Grab samples were taken from Riser 7 in May 1996. Core samples were obtained from Risers 2 and 9 in February 1996 and then from Risers 7 and 9 in April 1996.

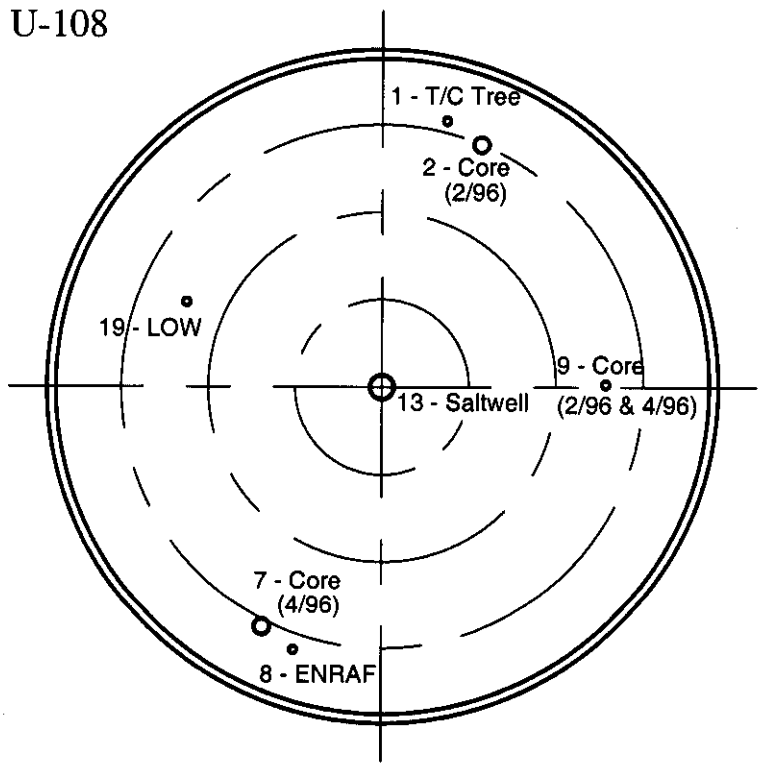


Figure 2-21. Tank 241-U-108 Sample and Monitoring Risers

2.7.19 Tank 241-U-109 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure 2-22. The waste surface level in Riser 8 is currently measured by an ENRAF™ buoyancy gauge installed in July 1994. Vertical temperature measurements are taken from a thermocouple tree mounted in Riser 1, with readings monitored and recorded through the TMACS system. Riser 9 accommodates an LOW.

In June 1995, grab samples were taken from Riser 12, which now contains a saltwell. Core samples were taken in December 1995 from Riser 2, in January 1996 from Risers 7 and 19, and from Riser 8 in April 1998. Retained gas sampler measurements were taken in Riser 8.

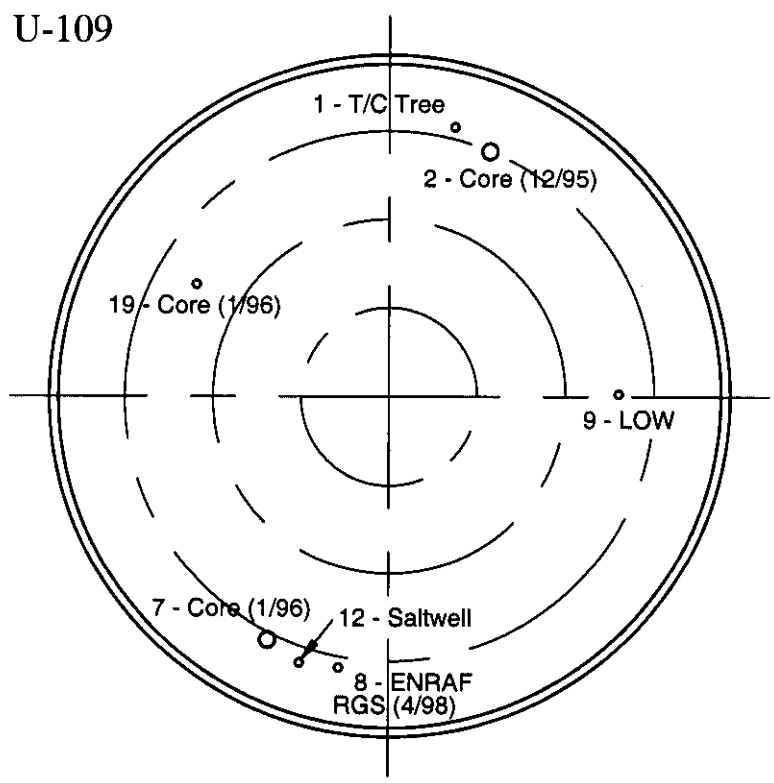


Figure 2-22. Tank 241-U-109 Sample and Monitoring Risers

3.0 WASTE CHEMISTRY

3.1 BEST-BASIS INVENTORY FOR EACH TANK

Single-shell tanks on the Flammable Gas Watch List (tanks A-101, AX-101, AX-103, S-102, S-111, S-112, SX-101, SX-102, SX-103, SX-104, SX-105, SX-106, SX-109, T-110, U-103, U-105, U-107, U-108, and U-109) contain one or more of the waste types of saltcake, sludge, and supernatant. Table 3-1 gives the quantities of each of these waste types in these tanks along with associated tank total volumes and vapor headspace volumes. Table 3-2 presents the total mass of each constituent by tank. The predominant constituents present are sodium, nitrate, nitrite, hydroxide, aluminum, and carbonate. Other noticeable constituents, which are of lesser amounts, are chloride, chromium, phosphate, sulfate, and TOC. Total quantities of each chemical constituent in each tank's liquid (Table 3-3), saltcake (Table 3-4), and sludge (Table 3-5) are also reported. The concentrations of the various chemical constituents in molarity (moles/L) are given for the total waste in each tank (Table 3-6). Molar concentrations of each chemical constituent in each tank's liquid (Table 3-7), saltcake (Table 3-8), and sludge (Table 3-9) are also reported. Concentrations of various organic constituents are reported for each tank's liquid (μg/L) in Table 3-10 and solids (μg/g) in Table 3-11. Activities of cesium-137 and strontium-90 in each tank's total waste and in its liquid, saltcake, and sludge layers are reported in Tables 3-12 and 3-13, respectively.

Waste volumes reported in Table 3-1 and the rest of this section are from Barker and Lechelt (2000). These values were current as of September 1999, but may differ from those in the latest release of Hanlon (2001) because values for SSTs being saltwell pumped may not reflect true waste volumes. Tables 3-2 through 3-9, which list inorganic species, contain data obtained from the Best-Basis Inventory (BBI) subject area in TWINS (CHG 2000, TWINS 2000a - TWINS 2000s) in October 2000. The BBI effort involves developing and maintaining waste tank inventories comprising 25 chemical and 46 radionuclide components in the 177 Hanford Site underground storage tanks. These BBIs provide waste composition data necessary as part of the RPP process flowsheet modeling work, safety analyses, and risk assessments, and system design for waste retrieval, treatment, and disposal operations. Other information presented in this section is from tank characterization data, tank interpretative reports, and tank characterization reports.

Table 3-1. Tank and Waste Volume Specifications for Selected Single-Shell Waste Tanks

Tank I.D.	Waste Class	Supernatant Layer Volume		Saltcake Layer Volume		Sludge Layer Volume		Total Waste Volume		Mean Tank Volume		Headspace Volume	
		(kL)	(kgal)	(kL)	(kgal)	(kL)	(kgal)	(kL)	(kgal)	(kL)	(kgal)	(kL)	(ft^3)
241-A-101	SC/SS-NL	1,923	508	1,673	442	11	3	3,608	953	4,989	1,317	1,382	48,805
241-AX-101	SC/SS-NL	1,461	386	1,359	359	11	3	2,831	747	5,103	1,347	2,271	80,200
241-AX-103	SC/SS-NL	0	0	394	104	30	8	424	112	5,103	1,347	4,679	165,237
241-S-102	SC/SS-NL	0	0	1,548	409	397	105	1,946	514	3,975	1,049	2,029	71,653
241-S-111	SC/SS-LIQ	420	111	1,181	312	443	117	2,044	540	3,975	1,049	1,931	68,193
241-S-112	SC/SS-NL	0	0	1,957	517	23	6	1,980	523	3,975	1,049	1,995	70,453
241-SX-101	SC/SS-NL	0	0	1,696	448	0	0	1,696	448	4,902	1,294	3,206	113,219
241-SX-102	SC/SS-LIQ	507	134	1,438	380	0	0	1,946	514	4,902	1,294	2,956	104,390
241-SX-103	SC/SS-NL	0	0	1,965	519	435	115	2,400	634	4,902	1,294	2,502	88,357
241-SX-104	SC/SS-NL	0	0	1,253	331	515	136	1,768	467	4,902	1,294	3,134	110,676
241-SX-105	SC/SS-NL	0	0	2,165	572	246	65	2,411	637	4,902	1,294	2,491	87,969
241-SX-106	SC/SS-NL	0	0	1,223	323	0	0	1,223	323	4,902	1,294	3,301	116,574
241-SX-109	SC/SS-NL	0	0	662	175	284	75	946	250	4,902	1,294	3,956	139,705
241-T-110	SL-NL	0	0	0	0	1465	387	1,465	387	3,214	848	1,749	61,765
241-U-103	SC/SS-NL	0	0	1,677	443	45	12	1,722	455	3,214	848	1,442	50,924
241-U-105	SC/SS-NL	140	37	1,321	349	121	32	1,582	418	3,214	848	1,632	57,634
241-U-107	SC/SS-NL	125	33	1,363	360	57	15	1,544	408	3,214	848	1,669	58,940
241-U-108	SC/SS-NL	91	24	1,571	415	110	29	1,772	468	3,214	848	1,442	50,924
241-U-109	SC/SS-NL	72	19	1,556	411	132	35	1,760	465	3,214	848	1,454	51,348

Notes: SC/SS-NL: Saltcake/salt slurry - no liquid,
SC/SS-LIQ: Saltcake/salt slurry - liquid,
SL-NL: Sludge: no liquid

Table 3-2. Total Mass of Constituents by Tank (Kilograms) (2 Sheets)

Analyte Name	Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Aluminum	Al	34,300	193,000	62,300	174,000	93,300	208,000	163,000	146,000	49,900	153,000
Calcium	Ca	1,150	356	754	159	608	776	821	896	548	481
Chloride	Cl	8,780	8,430	13,000	22,300	16,800	19,400	10,800	18,500	15,200	7,450
Chromium	Cr	5,820	12,000	16,200	29,700	15,900	13,900	11,400	7,950	9,670	6,430
Fluoride	F	1,670	1,950	8,250	757	858	939	4,850	859	1,290	628
Iron	Fe	1,720	306	4,430	4,120	2,430	4,540	4,770	4,090	2,180	2,280
Mercury	Hg	0.728	12	0.540	28	11	1.810	18	4	0	11
Potassium	K	2,180	2,230	3,190	2,870	5,880	7,360	2,750	6,900	3,350	1,200
Manganese	Mn	776	112	1,580	2,180	1,160	2,540	2,420	2,020	811	2,080
Sodium	Na	410,000	445,000	663,000	555,000	629,000	700,000	483,000	663,000	448,000	266,000
Nickel	Ni	63	63	360	0	244	333	1,320	314	166	663
Nitrite	NO_2^-	86,200	90,000	160,000	92,300	252,000	292,000	134,000	301,000	167,000	56,800
Nitrate	NO_3^-	616,000	508,000	873,000	741,000	657,000	833,000	617,000	652,000	549,000	403,000
Total Hydroxide	OH^-	136,000	518,000	322,000	530,000	362,000	591,000	433,000	473,000	222,000	314,000
Lead	Pb	190	100	387	0	202	279	268	250	185	101
Phosphate	PO_4^{3-}	98,600	28,100	84,700	13,800	16,200	15,000	45,800	28,100	30,100	5,310
Silicon	Si	1,250	551	2,380	705	1,140	1,830	2,490	1,510	2,010	1,930
Sulfate	SO_4^{2-}	18,100	30,300	44,300	5,720	34,700	34,900	23,600	25,800	11,000	2,460
Carbonate	TIC as CO_3^{2-}	53,600	20,300	34,400	18,900	115,000	106,000	82,900	84,700	54,300	11,100
Total Organic Carbon	TOC	8,640	4,450	13,400	3,210	10,900	13,600	8,170	9,900	8,390	1,710
Total Uranium	U	4,460	446	2,430	3,140	1,580	1,560	5,190	1,540	845	4,840
Zirconium	Zr	45	13	103	0	104	46	109	85	40	50

Table 3-2. Total Mass of Constituents by Tank (Kilograms) (2 Sheets)

Analyte Name	Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Aluminum	Al	157,000	131,000	17,000	1,790	42,300	55,800	51,600	51,000	47,900
Calcium	Ca	1,060	690	394	1,180	1,260	169	533	473	380
Chloride	Cl	26,500	22,700	3,300	1,170	8,420	8,840	10,700	10,900	6,620
Chromium	Cr	7,920	3,430	2,570	1,330	5,340	4,930	3,910	12,200	6,600
Fluoride	F	1,600	1,380	689	2,890	2,110	2,600	723	2,870	3,770
Iron	Fe	1,530	3,360	4,710	14,600	3,590	5,810	1,880	530	456
Mercury	Hg	5	18	25	0	0	0	0	0	0
Potassium	K	21,400	19,300	2,060	966	1,780	3,770	3,890	4,790	2,590
Manganese	Mn	240	58	636	722	805	2,110	890	196	121
Sodium	Na	1,010,000	839,000	127,000	82,900	411,000	405,000	421,000	727,000	398,000
Nickel	Ni	429	136	283	76	249	315	86	155	77
Nitrite	NO_2^-	488,000	434,000	59,100	9,270	110,000	95,100	127,000	158,000	101,000
Nitrate	NO_3^-	756,000	687,000	71,300	102,000	466,000	603,000	694,000	879,000	512,000
Total Hydroxide	OH^-	635,000	504,000	83,000	51,300	243,000	333,000	163,000	300,000	170,000
Lead	Pb	681	399	564	823	216	427	379	247	109
Phosphate	PO_4^{3-}	23,300	17,600	3,390	33,400	51,100	76,000	41,900	63,400	70,900
Silicon	Si	2,570	563	1,260	7,170	1,360	1,340	674	857	502
Sulfate	SO_4^{2-}	60,900	35,900	10,700	11,100	25,700	34,700	9,460	44,500	24,200
Carbonate	TIC as CO_3^{2-}	233,000	142,000	42,700	9,600	73,000	90,600	39,000	119,000	68,700
Total Organic Carbon	TOC	22,500	14,300	3,150	1,410	16,800	37,800	6,140	12,800	7,890
Total Uranium	U	2,700	1,290	275	1,320	1,490	15,500	1,060	566	344
Zirconium	Zr	178	62	227	7	59	69	23	25	12

Table 3-3. Total Mass of Constituents in Liquid by Tank (Kilograms) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	N/A	5,300	N/A	47,300	23,100	43,300	N/A	47,700	N/A	N/A
Ca	N/A	7	N/A	38	31	59	N/A	65	N/A	N/A
Cl	N/A	1,160	N/A	10,400	5,170	10,800	N/A	9,750	N/A	N/A
Cr	N/A	738	N/A	7,560	1,410	82	N/A	366	N/A	N/A
F	N/A	19	N/A	N/A	40	99	N/A	113	N/A	N/A
Fe	N/A	4	N/A	N/A	19	N/A	N/A	33	N/A	N/A
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	N/A	298	N/A	1,580	1,800	4,170	N/A	3,660	N/A	N/A
Mn	N/A	0.730	N/A	N/A	6	N/A	N/A	7	N/A	N/A
Na	N/A	39,900	N/A	151,000	119,000	233,000	N/A	256,000	N/A	N/A
Ni	N/A	1.460	N/A	N/A	7	N/A	N/A	13	N/A	N/A
NO_2^-	N/A	12,800	N/A	48,800	76,600	156,000	N/A	155,000	N/A	N/A
NO_3^-	N/A	34,600	N/A	65,600	80,100	156,000	N/A	179,000	N/A	N/A
Pb	N/A	7	N/A	N/A	31	59	N/A	67	N/A	N/A
PO_4^{3-}	N/A	1,850	N/A	3,240	1,770	3,270	N/A	3,540	N/A	N/A
Si	N/A	18	N/A	119	115	143	N/A	153	N/A	N/A
SO_4^{2-}	N/A	787	N/A	1,140	1,690	1,980	N/A	4,550	N/A	N/A
TIC as CO_3^{2-}	N/A	2,340	N/A	5,030	4,460	12,500	N/A	15,300	N/A	N/A
TOC	N/A	258	N/A	209	766	2,610	N/A	3,530	N/A	N/A
U	N/A	0.277	N/A	N/A	152	N/A	N/A	2	N/A	N/A
Zr	N/A	0.730	N/A	N/A	3	N/A	N/A	7	N/A	N/A

Notes:

N/A = Not Available

Table 3-3. Total Mass of Constituents in Liquid by Tank (Kilograms) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	95,600	78,300	N/A	N/A	N/A	N/A	20,600	2,990	N/A
Ca	164	79	N/A	N/A	N/A	N/A	71	N/A	N/A
Cl	16,600	14,000	N/A	N/A	N/A	N/A	7,010	812	N/A
Cr	106	127	N/A	N/A	N/A	N/A	448	116	N/A
F	401	124	N/A	N/A	N/A	N/A	130	72	N/A
Fe	79	39	N/A	N/A	N/A	N/A	29	N/A	N/A
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	13,700	11,700	N/A	N/A	N/A	N/A	2,550	N/A	N/A
Mn	15	8	N/A	N/A	N/A	N/A	10	N/A	N/A
Na	513,000	371,000	N/A	N/A	N/A	N/A	172,000	22,100	N/A
Ni	34	16	N/A	N/A	N/A	N/A	13	N/A	N/A
NO_2^-	305,000	237,000	N/A	N/A	N/A	N/A	86,600	11,800	N/A
NO_3^-	431,000	218,000	N/A	N/A	N/A	N/A	177,000	16,400	N/A
Pb	254	218	N/A	N/A	N/A	N/A	50	N/A	N/A
PO_4^{3-}	10,900	4,470	N/A	N/A	N/A	N/A	2,680	284	N/A
Si	407	183	N/A	N/A	N/A	N/A	140	N/A	N/A
SO_4^{2-}	2,590	3,210	N/A	N/A	N/A	N/A	5,170	384	N/A
TIC as CO_3^{2-}	24,500	16,100	N/A	N/A	N/A	N/A	20,600	2,000	N/A
TOC	6,920	5,080	N/A	N/A	N/A	N/A	3,000	650	N/A
U	762	393	N/A	N/A	N/A	N/A	251	N/A	N/A
Zr	16	8	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Notes:

N/A = Not Available

Table 3-4. Total Mass of Constituents in Saltcake by Tank (Kilograms) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	29,030	31,360	56,500	127,000	70,200	31,400	50,230	39,600	49,880	96,400
Ca	532	245	733	121	577	366	409	243	548	271
Cl	8,270	5,560	12,900	11,900	11,600	6,400	8,240	7,630	15,190	6,470
Cr	5,476	9,358	16,100	22,200	14,500	9,630	8,746	6,360	9,678	5,110
F	1,283	1,886	8,200	757	819	562	3,921	540	1,292	153
Fe	1,536	272	4,290	4,120	2,410	2,290	2,235	405	2,178	979
Hg	N/A	N/A	N/A	28	11	N/A	N/A	N/A	N/A	N/A
K	2,041	1,552	3,160	1,290	4,080	2,480	1,972	2,840	3,349	913
Mn	759	96	1,510	2,180	1,150	1,140	989	385	812	1,340
Na	395,600	348,000	659,000	404,000	510,000	375,000	382,800	353,000	448,600	224,000
Ni	61	53	299	N/A	237	145	155	85	166	62
NO_2^-	80,800	59,500	158,000	43,600	175,000	98,000	95,180	124,000	166,800	41,600
NO_3^-	609,000	438,800	869,000	675,000	577,000	548,000	514,300	415,000	548,400	361,000
Pb	183	69	384	N/A	172	165	202	109	185	69
PO_4^{3-}	95,044	22,500	84,600	10,500	14,400	6,980	41,994	21,100	30,027	3,850
Si	724	267	2,320	586	1,020	566	1,377	430	2,014	1,360
SO_4^{2-}	17,799	28,760	44,200	4,580	33,000	31,700	21,628	20,400	11,010	1,600
TIC as CO_3^{2-}	52,730	16,560	N/A	13,900	110,000	85,400	68,840	61,400	54,310	4,870
TOC	7,687	3,709	13,300	3,000	10,100	7,520	6,701	5,680	8,381	1,040
U	771	340	2,250	3,140	1,430	803	1,729	627	844	3,070
Zr	38	10	100	N/A	101	28	52	14	40	21

Notes:

N/A = Not Available

Table 3-4. Total Mass of Constituents in Saltcake by Tank (Kilograms) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	58,700	52,600	15,400	N/A	33,800	28,480	19,500	48,000	25,550
Ca	760	549	171	N/A	403	92	422	N/A	325
Cl	9,880	8,700	3,280	N/A	8,180	8,410	3,610	10,100	6,280
Cr	7,780	3,300	2,350	N/A	4,960	4,340	3,380	12,000	6,335
F	1,200	1,250	683	N/A	1,810	2,543	449	2,800	3,760
Fe	1,130	2,500	89	N/A	2,500	4,239	1,710	N/A	423
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	7,700	7,670	1,970	N/A	1,740	3,556	1,290	N/A	2,467
Mn	126	50	6	N/A	572	1,871	870	N/A	118
Na	499,000	467,000	125,000	N/A	402,000	383,200	244,000	705,000	383,800
Ni	238	121	28	N/A	164	288	39	N/A	74
NO_2^-	183,000	197,000	59,000	N/A	106,000	89,600	39,700	146,000	95,800
NO_3^-	325,000	469,000	69,000	N/A	460,000	571,600	515,000	863,000	504,200
Pb	271	181	46	N/A	211	362	94	N/A	104
PO_4^{3-}	11,800	13,100	3,250	N/A	49,000	74,933	38,700	63,100	65,177
Si	901	380	301	N/A	1,280	1,066	359	N/A	305
SO_4^{2-}	57,800	32,100	9,110	N/A	24,800	34,160	4,220	44,200	24,040
TIC as CO_3^{2-}	207,000	125,000	42,700	N/A	71,600	86,690	17,700	117,000	30,306
TOC	15,600	8,580	3,020	N/A	16,100	35,800	3,020	12,200	7,460
U	1,910	897	92	N/A	1,240	6,980	367	N/A	279
Zr	96	8	7	N/A	55	62	8	N/A	12

Notes:

N/A = Not Available

Table 3-5. Total Mass of Constituents in Sludge by Tank (Kilograms) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	5,251	155,860	5,760	N/A	N/A	133,000	112,700	58,300	N/A	56,500
Ca	616	103	21	N/A	N/A	351	412	588	N/A	210
Cl	513	1,709	99	N/A	N/A	2,190	2,516	1,150	N/A	973
Cr	339	1,930	135	N/A	N/A	4,180	2,641	1,230	N/A	1,325
F	384	44	48	N/A	N/A	277	936	207	N/A	475
Fe	178	31	133	N/A	N/A	2,250	2,543	3,660	N/A	1,306
Hg	0.728	12	0.540	N/A	N/A	2	18	4	N/A	11
K	140	373	30	N/A	N/A	710	781	400	N/A	290
Mn	16	16	75	N/A	N/A	1,410	1,431	1,630	N/A	735
Na	14,800	56,800	4,270	N/A	N/A	91,200	100,400	54,700	N/A	41,900
Ni	2	8	61	N/A	N/A	188	1,171	216	N/A	602
NO_2^-	5,340	17,610	1,550	N/A	N/A	38,100	38,520	22,500	N/A	15,240
NO_3^-	7,300	34,100	4,230	N/A	N/A	129,000	102,800	58,300	N/A	41,500
Pb	6	23	3	N/A	N/A	55	66	74	N/A	31
PO_4^{3-}	3,554	3,761	149	N/A	N/A	4,700	3,797	3,460	N/A	1,457
Si	522	266	58	N/A	N/A	1,120	1,115	925	N/A	569
SO_4^{2-}	300	714	87	N/A	N/A	1,150	1,966	822	N/A	858
TIC as CO_3^{2-}	817	1,402	N/A	N/A	N/A	8,400	13,980	7,990	N/A	6,250
TOC	958	486	68	N/A	N/A	3,450	1,471	690	N/A	673
U	3,684	105	180	N/A	N/A	761	3,456	908	N/A	1,769
Zr	7	2	3	N/A	N/A	18	57	65	N/A	29

Notes:

N/A = Not Available

Table 3-5. Total Mass of Constituents in Sludge by Tank (Kilograms) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	3,060	N/A	1,590	1,794	8,460	27,266	11,500	N/A	22,421
Ca	131	63	224	1,179	854	77	40	N/A	54
Cl	5	22	18	1,166	235	422	51	N/A	340
Cr	35	N/A	226	1,336	375	587	84	N/A	267
F	2	N/A	6	2,891	297	60	143	N/A	20
Fe	318	814	4,620	14,651	1,090	1,581	141	N/A	34
Hg	5	18	25	N/A	N/A	N/A	N/A	N/A	N/A
K	4	5	97	966	41	212	52	N/A	125
Mn	99	N/A	630	723	233	232	10	N/A	3
Na	2,180	1,690	1,800	82,890	9,100	21,610	4,010	N/A	13,910
Ni	157	N/A	255	76	85	27	34	N/A	3
NO_2^-	38	292	125	9,268	3,170	5,500	1,200	N/A	5,240
NO_3^-	961	2.74E-04	2,330	101,600	6,210	31,540	2,210	N/A	7,770
Pb	156	N/A	517	822	4	64	235	N/A	5
PO_4^{3-}	536	N/A	140	33,274	2,070	1,021	484	N/A	5,737
Si	1,260	N/A	958	7,160	80	273	175	N/A	197
SO_4^{2-}	497	577	1,580	11,146	846	499	62	N/A	154
TIC as CO_3^{2-}	1,180	234	N/A	9,602	1,330	3,829	639	N/A	1,206
TOC	N/A	600	125	1,406	666	2,022	118	N/A	429
U	28	0.940	183	1,315	249	8,550	443	N/A	65
Zr	66	N/A	220	7	4	7	16	N/A	0.305

Notes:

N/A = Not Available

Table 3-6. Total Moles per Liter of Constituents by Tank (Molarity) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	0.653	3.500	1.166	3.802	1.777	3.212	3.417	2.244	1.155	5.994
Ca	0.0147	0.0043	0.0095	0.0023	0.0078	0.0081	0.0116	0.0093	0.0085	0.0127
Cl	0.127	0.116	0.185	0.371	0.244	0.228	0.172	0.216	0.268	0.222
Cr	0.058	0.113	0.157	0.337	0.157	0.111	0.124	0.063	0.116	0.131
F	0.045	0.050	0.219	0.023	0.023	0.021	0.144	0.019	0.042	0.035
Fe	0.016	0.003	0.040	0.043	0.022	0.034	0.048	0.030	0.024	0.043
Hg	1.87E-06	2.90E-05	1.36E-06	8.17E-05	2.74E-05	3.76E-06	5.05E-05	8.95E-06	0.00E+00	5.69E-05
K	0.029	0.028	0.041	0.043	0.077	0.078	0.040	0.073	0.054	0.032
Mn	0.007	9.97E-04	0.015	0.023	0.011	0.019	0.025	0.015	0.009	0.040
Na	9.16	9.47	14.56	14.23	14.06	12.69	11.88	11.96	12.17	12.23
Ni	5.49E-04	5.28E-04	0.0031	0	0.0021	0.0024	0.0127	0.0022	0.0018	0.0119
NO_2^-	0.963	0.957	1.757	1.183	2.815	2.645	1.647	2.714	2.267	1.305
NO_3^-	5.105	4.008	7.111	7.046	5.445	5.598	5.628	4.361	5.530	6.871
OH^-	4.109	14.901	9.562	18.375	10.938	14.479	14.401	11.536	8.153	19.517
Pb	4.71E-04	2.36E-04	9.43E-04	0.00E+00	5.01E-04	5.61E-04	7.32E-04	5.00E-04	5.58E-04	5.15E-04
PO_4^{3-}	0.534	0.145	0.450	0.086	0.088	0.066	0.273	0.123	0.198	0.059
Si	0.023	0.010	0.043	0.015	0.021	0.027	0.050	0.022	0.045	0.073
SO_4^{2-}	0.097	0.154	0.233	0.035	0.186	0.151	0.139	0.111	0.072	0.027
TIC as CO_3^{2-}	0.459	0.166	0.290	0.186	0.985	0.736	0.781	0.585	0.565	0.196
TOC	0.370	0.181	0.563	0.158	0.466	0.472	0.385	0.342	0.436	0.150
U	0.0096	9.17E-04	0.0052	0.0078	0.0034	0.0027	0.0123	0.0027	0.0022	0.0215
Zr	2.52E-04	6.92E-05	5.70E-04	0.00E+00	5.86E-04	2.12E-04	6.76E-04	3.88E-04	2.75E-04	5.75E-04

Table 3-6. Total Moles per Liter of Constituents by Tank (Molarity) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	1.613	1.715	1.486	0.045	0.885	1.307	1.239	1.067	1.009
Ca	0.007	0.006	0.023	0.020	0.018	0.003	0.009	0.007	0.005
Cl	0.207	0.226	0.220	0.023	0.134	0.158	0.195	0.174	0.106
Cr	0.042	0.023	0.117	0.017	0.058	0.060	0.049	0.132	0.072
F	0.023	0.026	0.086	0.104	0.063	0.087	0.025	0.085	0.113
Fe	0.008	0.021	0.199	0.178	0.036	0.066	0.022	0.005	0.005
Hg	7.34E-06	3.10E-05	2.90E-04	0	0	0	0	0	0
K	0.152	0.174	0.124	0.017	0.026	0.061	0.064	0.069	0.038
Mn	0.001	3.74E-04	0.027	0.009	0.008	0.024	0.010	0.002	0.001
Na	12.176	12.891	13.029	2.461	10.089	11.135	11.860	17.846	9.836
Ni	0.0020	8.19E-04	0.0114	8.87E-04	0.0024	0.0034	0.0010	0.0015	7.44E-04
NO_2^-	2.940	3.332	3.030	0.138	1.349	1.307	1.788	1.938	1.247
NO_3^-	3.379	3.914	2.712	1.123	4.241	6.147	7.249	8.000	4.692
OH^-	10.349	10.468	11.510	2.059	8.063	12.377	6.207	9.955	5.680
Pb	0.001	0.001	0.006	0.003	0.001	0.001	0.001	0.001	0.000
PO_4^{3-}	0.068	0.065	0.084	0.240	0.304	0.506	0.286	0.377	0.424
Si	0.025	0.007	0.106	0.174	0.027	0.030	0.016	0.017	0.010
SO_4^{2-}	0.176	0.132	0.263	0.079	0.151	0.228	0.064	0.261	0.143
TIC as CO_3^{2-}	1.076	0.836	1.678	0.109	0.687	0.954	0.421	1.119	0.650
TOC	0.519	0.421	0.619	0.080	0.789	1.989	0.331	0.601	0.373
U	0.0031	0.0019	0.0027	0.0038	0.0035	0.0412	0.0029	0.0013	0.0008
Zr	5.41E-04	2.39E-04	5.87E-03	5.16E-05	3.67E-04	4.78E-04	1.65E-04	1.53E-04	7.41E-05

Table 3-7. Total Moles per Liter of Constituents in Liquid by Tank (Molarity) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	N/A	0.468	N/A	N/A	1.69	N/A	N/A	N/A	N/A	N/A
Ca	N/A	4.34E-04	N/A	N/A	0.00150	N/A	N/A	N/A	N/A	N/A
Cl	N/A	0.0779	N/A	N/A	0.288	N/A	N/A	N/A	N/A	N/A
Cr	N/A	0.0338	N/A	N/A	0.0535	N/A	N/A	N/A	N/A	N/A
F	N/A	0.00239	N/A	N/A	0.00411	N/A	N/A	N/A	N/A	N/A
Fe	N/A	1.56E-04	N/A	N/A	6.53E-04	N/A	N/A	N/A	N/A	N/A
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	N/A	0.0181	N/A	N/A	0.0908	N/A	N/A	N/A	N/A	N/A
Mn	N/A	3.16E-05	N/A	N/A	1.99E-04	N/A	N/A	N/A	N/A	N/A
Na	N/A	4.13	N/A	N/A	10.2	N/A	N/A	N/A	N/A	N/A
Ni	N/A	5.92E-05	N/A	N/A	2.47E-04	N/A	N/A	N/A	N/A	N/A
NO_2^-	N/A	0.662	N/A	N/A	3.28	N/A	N/A	N/A	N/A	N/A
NO_3^-	N/A	1.33	N/A	N/A	2.55	N/A	N/A	N/A	N/A	N/A
Pb	N/A	8.39E-05	N/A	N/A	2.92E-04	N/A	N/A	N/A	N/A	N/A
PO_4^{3-}	N/A	0.0464	N/A	N/A	0.0368	N/A	N/A	N/A	N/A	N/A
Si	N/A	0.00151	N/A	N/A	0.00808	N/A	N/A	N/A	N/A	N/A
SO_4^{2-}	N/A	0.0195	N/A	N/A	0.0347	N/A	N/A	N/A	N/A	N/A
TIC as CO_3^{2-}	N/A	0.0928	N/A	N/A	0.147	N/A	N/A	N/A	N/A	N/A
TOC	N/A	0.0511	N/A	N/A	0.126	N/A	N/A	N/A	N/A	N/A
U	N/A	2.77E-06	N/A	N/A	0.00126	N/A	N/A	N/A	N/A	N/A
Zr	N/A	1.91E-05	N/A	N/A	6.59E-05	N/A	N/A	N/A	N/A	N/A

Notes:

N/A = Not Available

Table 3-7. Total Moles per Liter of Constituents in Liquid by Tank (Molarity) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	1.84	1.99	N/A	N/A	N/A	N/A	6.11	1.22	N/A
Ca	0.00213	0.00134	N/A	N/A	N/A	N/A	0.0143	N/A	N/A
Cl	0.243	0.270	N/A	N/A	N/A	N/A	1.58	0.252	N/A
Cr	0.00106	0.00167	N/A	N/A	N/A	N/A	0.0689	0.0245	N/A
F	0.0110	0.00447	N/A	N/A	N/A	N/A	0.0547	0.0415	N/A
Fe	7.37E-04	4.83E-04	N/A	N/A	N/A	N/A	0.00421	N/A	N/A
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	0.182	0.205	N/A	N/A	N/A	N/A	0.522	N/A	N/A
Mn	1.46E-04	9.81E-05	N/A	N/A	N/A	N/A	0.00147	N/A	N/A
Na	11.6	11.0	N/A	N/A	N/A	N/A	59.9	10.6	N/A
Ni	3.02E-04	1.84E-04	N/A	N/A	N/A	N/A	0.00183	N/A	N/A
NO_2^-	3.45	3.53	N/A	N/A	N/A	N/A	15.1	2.82	N/A
NO_3^-	3.61	2.41	N/A	N/A	N/A	N/A	22.8	2.91	N/A
Pb	6.37E-04	7.20E-04	N/A	N/A	N/A	N/A	0.00193	N/A	N/A
PO_4^{3-}	0.0597	0.0322	N/A	N/A	N/A	N/A	0.226	0.0329	N/A
Si	0.00754	0.00446	N/A	N/A	N/A	N/A	0.0399	N/A	N/A
SO_4^{2-}	0.0140	0.0229	N/A	N/A	N/A	N/A	0.431	0.0439	N/A
TIC as CO_3^{2-}	0.212	0.184	N/A	N/A	N/A	N/A	2.75	0.366	N/A
TOC	0.300	0.289	N/A	N/A	N/A	N/A	2.00	0.595	N/A
U	0.00166	0.00113	N/A	N/A	N/A	N/A	0.00844	N/A	N/A
Zr	9.06E-05	5.90E-05	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Notes:

N/A = Not Available

Table 3-8. Total Moles per Liter of Constituents in Saltcake by Tank (Molarity) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	0.695	0.984	1.07	2.78	1.81	0.592	1.49	0.678	1.51	5.40
Ca	0.00858	0.00517	0.00935	0.00178	0.0100	0.00465	0.00814	0.00416	0.0112	0.0102
Cl	0.151	0.133	0.186	0.198	0.228	0.0919	0.185	0.131	0.350	0.276
Cr	0.0680	0.152	0.158	0.252	0.194	0.0943	0.134	0.109	0.152	0.148
F	0.0436	0.0841	0.221	0.0235	0.0300	0.0151	0.165	0.00924	0.0556	0.0122
Fe	0.0178	0.00412	0.0393	0.0435	0.0300	0.0209	0.0319	0.00693	0.0319	0.0265
Hg	N/A	N/A	N/A	8.17E-05	3.71E-05	N/A	N/A	N/A	N/A	N/A
K	0.0337	0.0336	0.0413	0.0195	0.0726	0.0323	0.0403	0.0486	0.0700	0.0353
Mn	0.00893	0.00148	0.0140	0.0234	0.0146	0.0106	0.0144	0.00659	0.0121	0.0368
Na	11.12	12.82	14.65	10.36	15.43	8.30	13.29	6.04	15.95	14.72
Ni	6.69E-04	7.71E-04	0.00260	N/A	0.00281	0.00126	0.00211	0.00145	0.00232	0.00158
NO_2^-	1.13	1.10	1.75	0.56	2.65	1.08	1.65	2.12	2.96	1.37
NO_3^-	6.34	5.99	7.16	6.42	6.47	4.50	6.62	7.10	7.23	8.79
Pb	5.71E-04	2.83E-04	9.47E-04	N/A	5.77E-04	4.05E-04	7.79E-04	0.001866	7.30E-04	5.04E-04
PO_4^{3-}	0.646	0.201	0.455	0.0652	0.105	0.0374	0.353	0.361	0.259	0.0612
Si	0.0166	0.00805	0.0422	0.0123	0.0253	0.0103	0.0391	0.00736	0.0586	0.0731
SO_4^{2-}	0.120	0.254	0.235	0.0281	0.239	0.168	0.180	0.349	0.0937	0.0252
TIC as CO_3^{2-}	0.568	0.234	N/A	0.137	1.27	0.724	0.916	1.05	0.740	0.123
TOC	0.413	0.261	0.566	0.147	0.585	0.319	0.445	0.0972	0.571	0.131
U	0.00209	0.00121	0.00483	0.00778	0.00418	0.00172	0.00580	0.0107	0.00290	0.0195
Zr	2.66E-04	9.10E-05	5.60E-04	0.00E+00	7.70E-04	1.56E-04	4.58E-04	2.45E-04	3.59E-04	3.41E-04

Notes:

N/A = Not Available

Table 3-8. Total Moles per Liter of Constituents in Saltcake by Tank (Molarity) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	1.30	1.43	1.45	N/A	0.747	0.799	0.530	1.13	0.609
Ca	0.0113	0.0101	0.0108	N/A	0.00600	0.00174	0.00773	N/A	0.00521
Cl	0.167	0.181	0.235	N/A	0.138	0.180	0.074706	0.181	0.114
Cr	0.0894	0.0467	0.115	N/A	0.0569	0.0632	0.0477	0.147	0.0783
F	0.0378	0.0484	0.0912	N/A	0.0568	0.101	0.0173	0.093815	0.127
Fe	0.0121	0.0329	0.00403	N/A	0.0267	0.0575	0.0225	N/A	0.00487
Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
K	0.118	0.144	0.128	N/A	0.0265	0.0689	0.0242	N/A	0.0406
Mn	0.00137	6.74E-04	2.85E-04	N/A	0.006209	0.0258	0.0116	N/A	0.001379
Na	13.0	14.9	13.8	N/A	10.4	12.6	7.79	19.5	10.7
Ni	0.00242	0.00152	0.00122	N/A	0.00167	0.00372	4.88E-04	N/A	8.08E-04
NO_2^-	2.38	3.15	3.25	N/A	1.37	1.47	0.633	2.02	1.34
NO_3^-	3.13	5.57	2.82	N/A	4.42	6.98	6.09	8.86	5.23
Pb	7.82E-04	6.43E-04	5.67E-04	N/A	6.07E-04	0.00132	3.34E-04	N/A	3.22E-04
PO_4^{3-}	0.0743	0.101	0.0869	N/A	0.308	0.597	0.299	0.423	0.441
Si	0.0192	0.00996	0.0272	N/A	0.0272	0.0287	0.00938	N/A	0.00698
SO_4^{2-}	0.360	0.246	0.241	N/A	0.154	0.269	0.0322	0.293	0.161
TIC as CO_3^{2-}	2.06	1.53	1.81	N/A	0.711	1.09	0.216	1.24	0.325
TOC	0.776	0.526	0.638	N/A	0.799	2.26	0.184	0.647	0.399
U	0.00480	0.00277	9.85E-04	N/A	0.00311	0.0222	0.00113	N/A	7.53E-04
Zr	6.28E-04	6.35E-05	1.94E-04	N/A	3.61E-04	5.12E-04	6.27E-05	N/A	8.17E-05

Notes:

N/A = Not Available

Table 3-9. Total Moles per Liter of Constituents in Sludge by Tank (Molarity) (2 Sheets)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Al	0.490	13.0	9.28	N/A	N/A	11.3	8.11	8.78	N/A	7.37
Ca	0.0387	0.00578	0.0231	N/A	N/A	0.0201	0.0200	0.0886	N/A	0.0184
Cl	0.0364	0.109	0.121	N/A	N/A	0.142	0.138	0.173	N/A	0.0966
Cr	0.0164	0.0838	0.113	N/A	N/A	0.185	0.0986	0.185	N/A	0.0897
F	0.0509	0.00528	0.111	N/A	N/A	0.0335	0.0957	0.0312	N/A	0.0880
Fe	0.00805	0.00124	0.104	N/A	N/A	0.0926	0.0884	0.551	N/A	0.0823
Hg	9.14E-06	1.34E-04	1.17E-04	N/A	N/A	2.07E-05	1.73E-04	6.52E-04	N/A	1.90E-04
K	0.00901	0.0215	0.0328	N/A	N/A	0.0417	0.0388	0.0603	N/A	0.0261
Mn	7.56E-04	6.39E-04	0.0593	N/A	N/A	0.0590	0.0506	0.246	N/A	0.0471
Na	1.62	5.58	8.08	N/A	N/A	9.12	8.48	8.24	N/A	6.42
Ni	8.28E-05	3.22E-04	0.0453	N/A	N/A	0.00736	0.0387	0.0325	N/A	0.0361
NO_2^-	0.292	0.864	1.46	N/A	N/A	1.90	1.63	3.39	N/A	1.17
NO_3^-	0.297	1.24	2.97	N/A	N/A	4.78	3.22	8.78	N/A	2.36
Pb	7.60E-05	2.56E-04	6.69E-04	N/A	N/A	6.08E-04	6.19E-04	0.0112	N/A	5.32E-04
PO_4^{3-}	0.0943	0.0894	0.0682	N/A	N/A	0.114	0.0776	0.521	N/A	0.0540
Si	0.0468	0.0214	0.0898	N/A	N/A	0.0917	0.0771	0.139	N/A	0.0713
SO_4^{2-}	0.00786	0.0168	0.0395	N/A	N/A	0.0275	0.0397	0.124	N/A	0.0314
TIC as CO_3^{2-}	0.0343	0.0527	N/A	N/A	N/A	0.322	0.452	1.20	N/A	0.367
TOC	0.201	0.0913	0.248	N/A	N/A	0.660	0.238	0.104	N/A	0.197
U	0.0390	9.97E-04	0.0329	N/A	N/A	0.00735	0.0282	0.137	N/A	0.0262
Zr	1.99E-04	5.86E-05	0.00141	N/A	N/A	4.64E-04	0.00121	0.00972	N/A	0.00112

Notes:

N/A = Not Available

Table 3-9. Total Moles per Liter of Constituents in Sludge by Tank (Molarity) (2 Sheets)

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Al	10.3	N/A	1.96	0.0454	6.97	8.35	7.48	N/A	6.30
Ca	0.297	0.142	0.186	0.0201	0.474	0.0158	0.0173	N/A	0.0102
Cl	0.0135	0.0556	0.0165	0.0224	0.147	0.0984	0.0252	N/A	0.0726
Cr	0.0610	N/A	0.145	0.0175	0.160	0.0933	0.0283	N/A	0.0389
F	0.00813	N/A	0.00990	0.104	0.347	0.0263	0.132	N/A	0.00792
Fe	0.518	1.33	2.76	0.179	0.434	0.234	0.0443	N/A	0.00454
Hg	0.00241	0.00798	0.00410	N/A	N/A	N/A	N/A	N/A	N/A
K	0.00949	0.0121	0.0823	0.0169	0.0232	0.0447	0.0233	N/A	0.0241
Mn	0.164	N/A	0.382	0.00898	0.0942	0.0349	0.00332	N/A	3.74E-04
Na	8.62	6.68	2.61	2.46	8.80	7.77	3.06	N/A	4.58
Ni	0.243	N/A	0.145	8.88E-04	0.0321	0.00382	0.0101	N/A	4.07E-04
NO_2^-	0.0743	0.577	0.0906	0.138	1.53	0.988	0.458	N/A	0.863
NO_3^-	1.41	4.02E-07	1.25	1.12	2.23	4.20	0.625	N/A	0.949
Pb	0.0684	N/A	0.0832	0.00271	4.74E-04	0.00257	0.0199	N/A	1.78E-04
PO_4^{3-}	0.513	N/A	0.0491	0.239	0.484	0.0888	0.0894	N/A	0.458
Si	4.08	N/A	1.14	0.174	0.0635	0.0802	0.109	N/A	0.0530
SO_4^{2-}	0.470	0.546	0.548	0.0792	0.196	0.0429	0.0113	N/A	0.0121
TIC as CO_3^{2-}	1.79	0.354	N/A	0.109	0.493	0.527	0.187	N/A	0.152
TOC	N/A	4.54	0.347	0.0799	1.23	1.39	0.172	N/A	0.270
U	0.0106	3.59E-04	0.0256	0.00377	0.0232	0.297	0.0327	N/A	0.00208
Zr	0.0661	N/A	0.0804	5.15E-05	9.96E-04	6.59E-04	0.00298	N/A	2.53E-05

Notes:

N/A = Not Available

Table 3-10. Concentration of Organics in Liquids by Tank (μg/L)

Constituent	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Acetate	N/A	579,500	N/A	N/A	1,447,844	N/A	N/A	N/A	N/A	N/A
Citrate	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EDTA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Formate	N/A	1,143,500	N/A	N/A	1,970,123	N/A	N/A	N/A	N/A	N/A
Glycolate	N/A	987,600	N/A	N/A	187,179	N/A	N/A	N/A	N/A	N/A
HEDTA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
IDA-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NTA-3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Oxalate	837,358	1,373,331	N/A	1,743,864	922,581	871,840	893,983	1,003,931	749,089	N/A
Total organic carbon	3,905,714	1,422,500	N/A	346,450	1,510,000	3,050,833	2,195,000	3,236,806	3,951,111	N/A

Constituent	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Acetate	3,682,500	N/A	2,369,000	N/A	N/A	N/A	954,815	536,700	1,321,000
Citrate	290,800	N/A	3,165,000	N/A	N/A	N/A	N/A	N/A	N/A
EDTA	117,300	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Formate	4,709,000	N/A	4,570,500	N/A	N/A	N/A	3,216,314	4,690,500	2,832,000
Glycolate	117,050	N/A	3,520,000	N/A	N/A	N/A	2,703,885	3,462,000	3,127,500
HEDTA	163,200	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
IDA-2	1,558,000	N/A	7,628,500	N/A	N/A	N/A	N/A	N/A	N/A
NTA-3	208,000	N/A	1,020,000	N/A	N/A	N/A	N/A	N/A	N/A
Oxalate	748,577	794,238	N/A	N/A	695,261	351,810	776,314	491,922	718,040
Total organic carbon	3,505,325	3,556,250	N/A	45,000	12,781,000	10,360,200	3,312,750	8,950,000	4,432,500

Notes:

N/A = Not Available

Table 3-11. Concentration of Organics in Solids by Tank (µg/g)

Constituent	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Acetate	N/A	278	N/A	N/A	598	N/A	N/A	N/A	N/A	N/A
Citrate	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
EDTA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Formate	N/A	498	N/A	N/A	1,099	N/A	N/A	N/A	N/A	N/A
Glycolate	N/A	430	N/A	N/A	305	N/A	N/A	N/A	N/A	N/A
HEDTA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
IDA-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NTA-3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Oxalate	8,640	6,922	N/A	5,693	9,091	10,031	1,807	6,587	7,333	N/A
Total organic carbon	3,927	2,459	N/A	1,961	3,978	3,825	1,175	2,813	3,744	N/A

Constituent	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Acetate	1,945	N/A	1,039	N/A	N/A	783,311	724	631	647
Citrate	230	N/A	1,127	N/A	N/A	4,556	900	836	N/A
EDTA	259	N/A	N/A	N/A	N/A	3,569,057	N/A	N/A	N/A
Formate	2,419	N/A	2,055	N/A	N/A	8,303,124	839	1,536	1,309
Glycolate	93	N/A	1,690	N/A	N/A	5,181,661	364	1,419	1,190
HEDTA	129	N/A	N/A	N/A	N/A	3,813,277	N/A	N/A	N/A
IDA-2	1,228	N/A	6,029	N/A	N/A	4,849	2,816	4,475	N/A
NTA-3	165	N/A	805	N/A	N/A	649	377	599	N/A
Oxalate	12,749	8,397	7,462	N/A	4,583	21,300	3,152	4,377	5,048
Total organic carbon	5,678	3,862	4,654	N/A	7,932	1,330,425	2,548	4,213	3,899

Notes:

N/A = Not Available

Table 3-12. Total Activity by Layer of Cesium^{137} and Strontium^{90} in Waste (Ci)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Liquid										
Cs^{137}	N/A	54,700	N/A	19,700	247,000	468,000	N/A	459,000	N/A	N/A
Sr^{90}	N/A	42	N/A	N/A	13	123	N/A	192	N/A	N/A
Saltcake										
Cs^{137}	289,900	247,900	433,000	225,000	400,000	264,000	259,400	222,000	405,900	128,000
Sr^{90}	45,350	37,457	52,000	266,000	278,000	149,000	72,910	26,700	11,784	234,000
Sludge										
Cs^{137}	14,780	64,100	3,730	N/A	N/A	94,100	92,600	39,000	N/A	36,620
Sr^{90}	74,004	406,015	25,200	N/A	N/A	736,000	480,007	263,000	N/A	247,600
Total										
Cs^{137}	305,000	367,000	436,000	245,000	647,000	826,000	352,000	721,000	406,000	165,000
Sr^{90}	119,000	443,000	77,100	266,000	278,000	886,000	553,000	290,000	11,800	482,000

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Liquid									
Cs^{137}	811,000	567,000	N/A	N/A	N/A	N/A	296,000	39,100	N/A
Sr^{90}	163	388	N/A	N/A	N/A	N/A	323	N/A	N/A
Saltcake									
Cs^{137}	518,000	455,000	109,000	N/A	238,000	361,800	98,700	437,000	286,700
Sr^{90}	93,200	27,100	25,500	N/A	28,600	22,290	3,320	31,400	14,630
Sludge									
Cs^{137}	2,050	2,010	20,800	49,903	5,160	27,200	3,820	N/A	15,100
Sr^{90}	108,000	109,000	569,000	30,785	34,800	2,534	1,050	N/A	1,602
Total									
Cs^{137}	1,330,000	1,020,000	130,000	49,900	243,000	389,000	398,000	476,000	302,000
Sr^{90}	201,000	137,000	594,000	30,800	63,400	24,800	4,690	31,400	16,200

Notes:

N/A = Not Available

Table 3-13. Total Activity by Layer of Cesium^{137} and Strontium^{90} in Waste (µCi/L)

Analyte	S-102	S-111	S-112	SX-101	SX-102	SX-103	SX-104	SX-105	SX-106	SX-109
Liquid										
Cs^{137}	N/A	130,238	N/A	N/A	487,179	N/A	N/A	N/A	N/A	N/A
Sr^{90}	N/A	101	N/A	N/A	26	N/A	N/A	N/A	N/A	N/A
Saltcake										
Cs^{137}	187,274	209,907	221,257	132,665	278,164	134,351	207,023	102,540	331,889	193,353
Sr^{90}	29,296	31,717	26,571	156,840	193,324	75,827	58,188	12,333	9,635	353,474
Sludge										
Cs^{137}	37,229	144,695	162,174	N/A	N/A	216,322	179,806	158,537	N/A	128,944
Sr^{90}	186,407	916,512	1,095,652	N/A	N/A	1,691,954	932,053	1,069,106	N/A	871,831
Total										
Cs^{137}	156,732	179,550	220,202	144,458	332,477	344,167	199,095	299,046	253,592	174,419
Sr^{90}	61,151	216,732	38,939	156,840	142,857	369,167	312,783	120,282	7,370	509,514

Analyte	A-101	AX-101	AX-103	T-110	U-103	U-105	U-107	U-108	U-109
Liquid									
Cs^{137}	421,737	388,090	N/A	N/A	N/A	N/A	2,368,000	429,670	N/A
Sr^{90}	85	266	N/A	N/A	N/A	N/A	2,584	N/A	N/A
Saltcake									
Cs^{137}	309,623	334,805	276,650	N/A	141,920	273,883	72,414	278,167	184,254
Sr^{90}	55,708	19,941	64,721	N/A	17,054	16,874	2,436	19,987	9,402
Sludge									
Cs^{137}	186,364	182,727	693,333	34,063	114,667	224,793	67,018	N/A	114,394
Sr^{90}	9,818,182	9,909,091	18,966,667	21,014	773,333	20,942	18,421	N/A	12,133
Total									
Cs^{137}	368,625	360,297	306,604	34,061	137,133	245,891	257,772	268,623	171,591
Sr^{90}	55,710	48,393	1,400,943	21,024	35,779	15,676	3,038	17,720	9,205

Notes:

N/A = Not Available

3.1.1 Tank 241-A-101

Waste transaction records show that tank A-101 was initially filled with a combination of high-level waste (HLW) and organic wash waste (OWW) from the Plutonium Uranium Extraction (PUREX) facility. Total volumetric inputs were 18,001 kL (4,756 kgal) of HLW and 7,771 kL (2,053 kgal) of OWW. Condensates from this self-boiling waste tank were routed to cribs. The remaining supernatant was removed from the tank in the first quarter of 1968, after which the tank was sluiced for the first time. Approximately 284 kL (75 kgal) of sludge was retrieved from the tank in 1968 and 1969.

Following this first sluicing, the tank received primarily strontium recovery (SRR) supernatant from B-Plant and supernatants from the sluicing of other HLW tanks in A and AX Tank Farms. The tank was re-sluiced in 1975 and 1976, and an additional 121 kL (32 kgal) of sludge was removed. A sludge map prepared in February 1976 indicates that the sludge was non-uniformly distributed across the bottom of the tank, and confirms the conclusion that the sludge volume was approximately 11 kL (3 kgal).

Tank A-101 was used to stage feed for the 242-A Evaporator and as interim storage for the first-pass evaporator salt slurries started in the third quarter of 1976. Some of these feeds/slurries contained dilute concentrations of complexants. Approximately 1,196 kL (316 kgal) of salt accumulated in the tank as the result of the storage of these solutions. In the fourth quarter of 1980, the tank was filled with evaporator slurry in two campaigns (campaigns 80-10 and 81-1, numbered by fiscal year).

The feeds for evaporator campaigns 80-10 and 81-1 were non-complexed waste, reported in the 242-A Evaporator campaign reports as dilute double-shell slurry feed (DSSF). The TOC concentration for tank A-101 supernatant was 10.7 g/L following evaporator campaign 80-1 and 6.75 g/L following evaporator campaign 81-1. Solid material included with samples taken 0.6 m and 1.2 m (2 and 4 ft) below the surface following evaporator campaign 81-1 was approximately 95 weight percent sodium carbonate. Hydrates of sodium carbonate have relatively low particle densities that may have led to an initial formation of a surface crust in tank A-101. No significant waste transactions involving tank A-101 have taken place since 1980, except that saltwell pumping has begun.

The waste volume is approximately 3,608 kL (953 kgal.) consisting of a supernatant layer 1,923 kL (508 kgal.), a layer of saltcake 1,673 kL (442 kgal.), and 11 kL (3 kgal.) of sludge. The headspace volume in tank A-101 is 1,382 m^3 (48,805 ft^3). This tank is unusual in the fact that the saltcake is situated above the liquid layer.

3.1.2 Tank 241-AX-101

Tank AX-101 received HLW and OWW from the PUREX facility and supernatant from tanks A-102, A-103, AX-102, and B-112 from the first quarter of 1965 until the last quarter of 1967. From the third quarter of 1965 to the fourth quarter of 1967, supernatant was transferred from tank AX-101 to tanks AX-102, AX-103, and A-102. An electric coil was inserted into tank AX-101, and condensate was boiled off between the fourth quarter of 1966 and the fourth quarter of 1967. Cesium/strontium recovery waste from B-Plant was sent to tank AX-101 from the first quarter of 1968 to the first quarter of 1969. The tank received HLW and low-level waste (LLW) from PUREX in the second quarter of 1968 to the second quarter of 1969. Tank AX-101 was then removed from service as a boiling waste receiver tank.

Waste was transferred to tanks A-102, A-103, and AX-103 from the first quarter of 1968 to the second quarter of 1976. From the second quarter of 1973 to the third quarter of 1974, the tank received supernatant from tanks A-104 and AX-102 and received water from dry well installation processes. From the third quarter of 1975 to the second quarter of 1976, the tank received SRR. The tank was also sluiced from the third quarter of 1975 to the second quarter of 1976 to remove the strontium/cesium recovery waste. In the third quarter of 1976, only 11 kL (3 kgal) of sludge remained in the tank.

The tank received DSSF from the 242-A Evaporator through tanks A-102 and A-103 from the fourth quarter of 1976 until the fourth quarter of 1980. In the fourth quarter of 1980, supernatant was transferred to tank AW-103. The tank was pumped, and saltwell liquid was transferred to tank AN-101 in the fourth quarter of 1987. Additional saltwell pumping has begun.

The waste volume is approximately 2,831 kL (747 kgal), consisting of a 1,461 kL (386 kgal) supernatant layer, a saltcake layer of 1,359 kL (359 kgal), and 11 kL (3 kgal) of sludge. The headspace volume in tank AX-101 is 2,271 m^3 (80,200 ft^3). It shares the same solid-over-liquid waste configuration as tank A-101. Tank A-101 integrity is sound (Hanlon 2000).

3.1.3 Tank 241-AX-103

Waste was initially added to tank AX-103 in the first quarter of 1965, consisting of inorganic wash waste (IWW) from PUREX, to the second quarter of 1966. From the first quarter of 1965 to the second quarter of 1968, the tank received OWW from PUREX. In 1965, the tank also received supernatant waste from tank AX-101. In the first quarter of 1965, tank A-102 was used to transfer supernatant waste into tank AX-103. Supernatant waste was transferred into tank A-102 from the third quarter of 1965 to the first quarter of 1969. In 1968 and 1969, the tank received B-Plant SRR, B-Plant LLW, and LLW from PUREX. Supernatant transfers to and from tank A-106 occurred in 1969. The tank again received B-Plant SRR waste in 1972. Before tank AX-103 was sluiced in 1976, many tanks transferred waste into and out of the tank. During that time, the tank also received flush water from various sources and some of the waste evaporated. In 1975, the tank received waste from the AR Vault. Some of the waste sluiced from the tank in 1976 was used for SRR. After the tank was sluiced, transfers of evaporated waste into and out of

the tank occurred, but with a much smaller number of tanks was involved. Supernatant was pumped from the tank in 1980.

The waste volume is roughly 424 kL (112 kgal), with a saltcake layer of 394 kL (104 kgal), no supernatant layer, and 30 kL (8 kgal) of sludge. The headspace volume in tank AX-103 is approximately 4,579 m^3 (165,237 ft^3). Tank AX-103 integrity is sound (Hanlon 2000).

3.1.4 Tank 241-S-102

The S Tank Farm was constructed during 1950 and 1951 and contains twelve, 100 series SSTs. During the third quarter of 1953, tank S-102 received reduction-oxidation (REDOX) HLW from S-Plant. From the fourth quarter of 1953 to the third quarter of 1955, REDOX HLW cascaded from tank S-101 to tank S-102. This was the last waste addition to tank S-102 for the rest of the 1950s and the 1960s. Waste additions to tank S-102 from tank S-101 did not occur again until the fourth quarter of 1973 and continued intermittently until the second quarter of 1979.

Because tank S-102 was the 242-S Evaporator feed tank from 1973 until 1976, frequent transfers were made to tank S-102 from other tanks during this period. The following waste types are an example of what was transferred to tank S-102: REDOX HLW, B-Plant HLW, B-Plant LLW, REDOX LLW, PUREX facility LLW, cladding waste, laboratory waste, Pacific Northwest Laboratory waste, evaporator bottoms (EB), and terminal liquor.

After 1976, tank S-102 received mostly EB and evaporator feed from tanks SY-102, T-101, TX-102, TX-104, and TX-105. In 1979, additions of $HNO_3/KMnO_4$ were received from an unknown source. These receipts were probably associated with evaporator operations, which used $HNO_3/KMnO_4$ in the partial neutralization process. Large, intermittent transfers of water were added to the tank from 1972 through 1976. Approximately 2,078 kL (549 kgal) of waste was left in tank S-102 after the final transfer from it in 1992.

Tank S-102 was removed from service and labeled inactive in 1980. Saltwell liquor waste was transferred from tank S-102 to tank AW-106 during the fourth quarter of 1992 as part of the interim-stabilization process. Tank S-102 was partially interim-isolated in 1982 and is awaiting the completion of interim stabilization.

The waste contained in tank S-102 is classified as DSSF with a waste volume of approximately 1,946 kL (514 kgal). The waste is composed of a saltcake layer of 1,548 kL (409 kgal), no supernatant layer, and 397 kL (105 kgal) of sludge. The headspace volume in tank S-102 is roughly 2,029 m^3 (71,653 ft^3). Tank S-102 integrity is sound (Hanlon 2000).

3.1.5 Tank 241-S-111

Tank S-111 is the second tank in a three-tank cascade series. The tank went into service in 1952 when it received REDOX HLW cascaded from tank S-110. The tank received REDOX HLW and REDOX cladding waste (CW) intermittently until 1957. A small transfer of cladding waste was received from tank S-107 in 1965. From 1974 to 1976, waste from the tank was pumped to tank S-102 for evaporator feed. Evaporator bottoms were returned to the tank intermittently over this time period. The tank was removed from service and declared inactive in 1976. A total of 322 kL (85 kgal) of saltwell liquor was pumped from the tank from 1985 to 1992. The tank was partially interim isolated in 1982. Additional saltwell pumping is scheduled to start in fiscal year 2001 to stabilize the tank.

The waste volume is approximately 2,044 kL (540 kgal), with 420 kL (111 kgal) of supernatant, a saltcake layer of 1,181 kL (312 kgal), and 443 kL (117 kgal) of sludge. The headspace volume in tank S-111 is roughly 1,931 m^3 (68,193 ft^3). The tank is designated as sound. Tank S-111 was removed from the Watch List for Organics when the organic complexants safety issue was closed in December 1998. Tank S-111 integrity is sound (Hanlon 2000).

3.1.6 Tank 241-S-112

Tank S-112 was filled with REDOX HLW from the third quarter of 1952 until the fourth quarter of 1973. The total amount of REDOX HLW, generated between 1952 to 1957, added to the tank was 3,179 kL (840 kgal), all of which was cascaded from tank S-111. The waste in tank S-111 was received in a cascade from tank S-110, which received REDOX HLW and process CW directly from the plant. Large volumes of 242-S EB and recycle supernatants were transferred to tank S-112 beginning in 1974, depositing significant amounts of saltcake. Tank S-112 was removed from service in 1974 and labeled inactive in 1976. A jet pump was installed and initiated in 1978. The tank was primary stabilized in June 1979 and was partially isolated in December 1982. Between 1978 and 1980, 473 kL (125 kgal) of liquid was jet pumped.

The waste volume is about 1,980 kL (523 kgal). The waste consists of 23 kL (6 kgal) of sludge, no supernatant layer, and a saltcake layer of 1,957 kL (517 kgal) predicted from the Supernatant Mixing Model (SMM). The Sort on Radioactive Waste Type (SORWT) model lists REDOX HLW and EB as the primary and secondary waste types respectively. Evaporator Bottom waste is the SORWT definition for saltcake that is equivalent to SMM waste. The headspace volume in tank S-112 is roughly 1,995 m^3 (70,453 ft^3). Tank S-112 integrity is sound (Hanlon 2000).

3.1.7 Tank 241-SX-101

The SX Tank Farm was constructed between 1953 and 1954 in the 200 West area. The SX Tank Farm contains 15 tanks that were constructed to the third-generation design. They were the first tanks designed for self-boiling waste, and the original construction included underground duct headers connected to a common condenser-ventilation system. Waste, consisting of REDOX HLW from 202-S Plant, was initially added to tank SX-101 in the second quarter of 1954. The tank received REDOX HLW from the 202-S Plant and flush water from miscellaneous sources until the third quarter of 1957. During this time and continuing until the third quarter of 1959, condensed waste was sent from the tank to tank SX-106. In the last half of 1954, some of the REDOX HLW cascaded to tank SX-102. In the third quarter of 1958 and the fourth quarter of 1960, condensed waste was sent to a crib.

Tank SX-101 received supernatant waste from tank BX-101 in the fourth quarter of 1971. Flush water from miscellaneous sources was subsequently added to the tank in the second quarter of 1972 and the first quarter of 1974. From the third quarter of 1974 to the fourth quarter of 1975, waste was transferred to and received from tank S-102 in support of 242-S Evaporator operation. Also in support of evaporator operations, from the first quarter of 1979 to the fourth quarter of 1980, supernatant waste was transferred from the tank to tanks SY-102, TX-118, S-103, and BX-105. During this time the tank received waste from tanks SY-102, U-107, U-111, and SX-106. The last addition to tank SX-101 was flush water from miscellaneous sources added in the fourth quarter of 1980. Saltwell pumping began November 21, 2000.

The waste volume is about 1,696 kL (448 kgal), all listed as a saltcake layer. The headspace volume in tank SX-101 is roughly 3,206 m^3 (113,219 ft^3). Tank SX-101 integrity is sound (Hanlon 2000).

3.1.8 Tank 241-SX-102

Tank SX-102 entered service when it initially received HLW from the REDOX plant in 1954. Between 1954 and February 1973, tank SX-102 was actively transferring and receiving waste from other SX tanks and other tank farms. An estimated 223 kL (59 kgal) of solid wastes was retained in tank SX-102 through the third quarter of 1974.

In 1974 and January of 1975, tank SX-102 was receiving EB from 242-S Evaporator through waste transfers from tanks S-106 and SX-106. From February of 1975 to August 1975, tank SX-102 received processed waste (slurry) from the 242-S Evaporator and saltcake solids accumulated. The early campaign 242-S Evaporator concentrate was SMM S1 waste (Supernatant Mixing Model 242-S Evaporator saltcake generated from 1973 until 1976) and late campaign 242-S Evaporator concentrate was SMM S2 waste (Supernatant Mixing Model 242-S Evaporator saltcake generated from 1977 until 1980). During this period, tank SX-102 was pumping supernatant to tank S-102. From 1978 through 1980, tank SX-102 transferred waste to tank SY-102. The tank was removed from service and labeled inactive in 1980. The

total waste volume was adjusted in 1993 to 2,055 kL (543 kgal). The tank was partially isolated in June 1985.

Tank SX-102 has an operating capacity of 3,785 kL (1,000 kgal) and contains 1,946 kL (514 kgal) of DSSF. The waste consists of a supernatant layer of 507 kL (134 kgal), a saltcake layer of 1,438 kL (380 kgal), with no sludge layer. The headspace volume in tank SX-102 is approximately 2,956 m^3 (104,390 ft^3). The waste volume in this tank continues to decrease because of evaporation and waste compaction. Tank SX-102 integrity is sound (Hanlon 2000).

3.1.9 Tank 241-SX-103

Waste was initially added to tank SX-103 in the fourth quarter of 1954 with the cascade of REDOX process HLW from tank SX-102. In the first and third quarters of 1955, waste was received from the 202-S REDOX Plant. In the second quarter of 1958, supernatant was sent to tank U-101. From the fourth quarter of 1958 to the third quarter of 1960, sparge transfers of water were sent to tank SX-106. From the second quarter of 1961 to the second quarter of 1971, supernatant waste was sent to tanks SX-102, TX-101, TX-118, TY-101, and BX-104. From the second quarter of 1961 to the second quarter of 1963, condensate waste was sent to tank SX-106. From the third quarter of 1961 to the third quarter of 1971, the tank received supernatant waste from various SX tanks, tanks TX-118, BX-101, and BX-103.

In support of the 242-S Evaporator campaign, supernatant waste was transferred to and received from tank S-102 from the first quarter of 1975 to the first quarter of 1977. From the second quarter of 1977 to the third quarter of 1980, waste was transferred and received from tank SY-102 in support of the 242-S Evaporator campaign. The tank was labeled as inactive in 1978 and removed from service in 1980. The tank was partially interim isolated in June 1985. Saltwell pumping has begun.

The waste volume is approximately 2,400 kL (634 kgal), consisting of 1,965 kL (519 kgal) of saltcake, no supernatant, and 435 kL (115 kgal) of sludge. The headspace volume in tank SX-103 is roughly 2,502 m^3 (88,357 ft^3). Tank SX-103 integrity is sound (Hanlon 2000).

3.1.10 Tank 241-SX-104

Tank SX-104 was built in 1954 and is the first tank in a cascade series of three tanks including tanks SX-105 and SX-106. The tank entered service in the first quarter of 1955 and received REDOX waste from the first quarter of 1955 until the third quarter of 1971. The tank received EB and REDOX ion exchange waste from the third quarter of 1971 until the second quarter of 1975. From the third quarter of 1975 until the second quarter of 1976, tank SX-104 received EB and recycle wastes from the 242-S Evaporator. The tank received concentrated evaporator feed and residual evaporation liquid during the third quarter of 1976 until the third quarter of 1977. During the fourth quarter of 1977, the tank received partial neutralized feed waste. In the first quarter of 1980, the content of the tank was classified as DSSF. Tank SX-104 is classified as an

assumed leaker with an estimated leak volume of approximately 23 kL (6 kgal) and was designated inactive in 1980. The tank was partially interim isolated in June 1985.

Saltwell pumping began on September 26, 1997; 757 L (200 gal) were pumped in September before the transfer line between tank SX-104 and 244-S became plugged. Pumping was resumed on March 19, 1998, following the installation of a dilution system to dilute the waste in the saltwell in order to make it easier to pump the waste to tank SY-102. Pumping was interrupted and resumed on March 23, 1998, and again interrupted.

Saltwell pumping was restarted on July 23, 1998, and continued until July 27, 1999, when the rear seal of the jet pump ruptured and a major spray leak ensued within the pump pit. A total of 436 kL (115 kgal) of liquid waste was transferred to tank SY-102 before failure occurred. Waste volume calculations show 182 kL (48 kgal) of drainable interstitial liquid remaining in the tank, of which approximately 167 kL (44 kgal) is estimated to be pumpable. On April 26, 2000, tank SX-104 was declared interim stabilized in compliance with the Tank Farm Facility Interim Stabilization Evaluation.

The waste volume is approximately 1,768 kL (467 kgal). The waste consists of a saltcake layer of 1,253 kL (331 kgal), no supernatant layer, and 515 kL (136 kgal) of sludge. The headspace volume in tank SX-104 is around 3,134 m^3 (110,676 ft^3). Tank SX-104 is an assumed leaker (Hanlon 2000).

3.1.11 Tank 241-SX-105

Tank SX-105 entered service in 1955 when it received HLW from the REDOX plant. The tank also received REDOX process waste in a cascade from tank SX-104. Between 1962 and 1965, tank SX-105 received and sent HLW waste to and from six other SX Tank Farm tanks. In 1966 and 1967, waste from the REDOX plant was sent to tank SX-105. During the third and fourth quarters of 1967, the tank received small amounts of Hanford Laboratory Operations waste. Large volumes of recycled supernatant and EB were received and transferred from approximately 1968 through 1980, during which significant amounts of saltcake accumulated. Between 1979 and 1980, the tank sent and received small amounts of waste from tanks S-103, S-107, SY-102, and SX-102, the last transfer being in 1980 from tank S-103. The tank was removed from service in 1980, and was partially isolated in 1985.

The waste volume is approximately 2,411 kL (637 kgal), but the waste volume in this tank continues to decrease due to evaporation, saltwell pumping, and waste compaction. The waste is composed of a saltcake layer of 2,165 kL (572 kgal), a layer of sludge of 246 kL (65 kgal), and no supernatant layer. Tank SX-105 is listed as sound and has a headspace volume of 2,491 m^3 (87,969 ft^3). The tank is estimated to contain 1,083 kL (286 kgal) of drainable liquid and is scheduled to be saltwell pumped in FY 2001. Tank SX-105 integrity is sound (Hanlon 2000).

3.1.12 Tank 241-SX-106

Waste, consisting of flush water from miscellaneous sources, was initially added to tank SX-106 in the third quarter of 1954. From the fourth quarter of 1954 to the fourth quarter of 1963, the tank received condensate waste from various SX-Farm tanks and miscellaneous sources. Waste was transferred from the tank to the S-021 crib from the fourth quarter of 1954 to the third quarter of 1971. From the first quarter of 1956 to the second quarter of 1963, the tank received flush water from miscellaneous sources. From the second to the fourth quarters of 1957, supernatant waste was sent to tank SX-104. From the fourth quarter of 1958 to the third quarter of 1960, the tank received sparse transfers of water from tanks SX-103 and SX-115. From the first quarter of 1959 to the second quarter of 1963, supernatant waste was transferred to various SX-Farm tanks. In the fourth quarter of 1959, flush water was sent from the tank to tank SX-114.

In the second quarter of 1963, waste was transferred from the tank to the 202-S Plant for REDOX processing. From the second quarter of 1964 to the fourth quarter of 1975, flush water from miscellaneous sources was added to the tank. Some of this flush water consisted of Hanford Laboratory Operations and Pacific Northwest Laboratory waste. In the fourth quarter of 1971, waste was sent from the tank to tank SX-111.

In support of the 242-S Evaporator campaign, supernatant waste was transferred to and received from tank S-102 from the third quarter of 1972 to the fourth quarter of 1976. From the first quarter of 1972 to the second quarter of 1976, waste was transferred into and out of the tank into various tanks as feed staging for the 242-S Evaporator. From the second quarter of 1978 to the fourth quarter of 1980, waste was transferred to and received from tank SY-102 in support of the 242-S Evaporator campaign. Waste was transferred into and received from various tanks from the first quarter of 1978 to the fourth quarter of 1979 as feed staging for the 242-S Evaporator. In the third and fourth quarters of 1980, a neutralized solution of $HNO_3/KMnO_4$ was added to the tank to neutralize the waste and increase volume reduction. The tank was removed from service and labeled inactive in 1980. Water from miscellaneous sources (most likely attributed to tank intrusions such as rain water) was added to the tank from 1983 to 1993. The tank was partially interim isolated in 1985. On May 15, 2000, tank SX-106 was declared interim stabilized in compliance with the Tank Farm Facility Interim Stabilization Evaluation.

The waste volume is 1,223 kL (323 kgal), which consists of a saltcake layer and no sludge. The headspace volume in tank SX-106 is about 3,301 m^3 (116,574 ft^3). Tank SX-106 integrity is sound (Hanlon 2000).

3.1.13 Tank 241-SX-109

Tank SX-109 is the last tank in a cascade that includes tanks SX-107 and SX-108. Tank SX-109 was constructed in the early 1950's and was designed to be a self-boiling tank with the condensate directed back to the tank. Tank SX-109 was connected to an exhauster.

HLW REDOX waste was first added to tank SX-109 in 1955. In 1956, 1961, and 1962, tank SX-109 received additional REDOX process HLW. In 1965 tank SX-109 also received a one-time addition of concentrated REDOX process HLW supernatant liquid. All the REDOX process HLW additions are assumed to have contributed to the solid waste now stored in tank SX-109. Beyond such waste additions, there were many liquid transfers into and out of tank SX-109. These included water, condensate from self-boiling tanks including tank SX-109 and supernatant liquid from other SX-Farm tanks.

The waste volume is about 946 kL (250 kgal). The waste consists of a saltcake layer of 662 kL (175 kgal), no supernatant layer, and 284 kL (75 kgal) of sludge. The headspace volume in tank SX-109 is roughly 3,956 m^3 (139,705 ft^3). Tank SX-109 is an assumed leaker (Hanlon 2000).

3.1.14 Tank 241-T-110

Tank T-110 first began receiving second-cycle waste from T-Plant in December 1944. Additional second cycle waste was added from T-Plant in the first quarter of 1948 until the third quarter of 1956. From the second quarter of 1952 to the first quarter of 1953, the tank also received lanthanum fluoride waste from the plutonium concentration facility. Flush water was added in the second and third quarters of 1956 before the tank was placed on standby. The tank was inactive and full until the second quarter of 1974 when waste was sent to tank S-110. Supernatant waste was sent to tank T-101 in the first and second quarters of 1976 and to tank TX-118 in the third quarter of 1978. The last transfer from tank T-110 before the push mode core was taken was saltwell pumping of liquids to tank AN-103 in the fourth quarter of 1983. Saltwell pumping began again in May 1997, and the pump is still situated in the waste. As of August 31, 1997, 63.2 kL of supernatant liquid had been pumped from the tank, including the sluice water and any liquids that may have intruded into the tank from outside, via pump pits. On January 27, 2000, tank T-110 was declared interim stabilized in compliance with the Tank Farm Facility Interim Stabilization Evaluation.

The waste volume is about 1,465 kL (387 kgal) of non-complexed sludge. The headspace volume in tank T-110 is about 1,749 m^3 (61,765 ft^3). Tank T-110 integrity is sound (Hanlon 2000).

3.1.15 Tank 241-U-103

Tank U-103 is the third in a cascade series of three tanks that includes tanks U-101 and U-102. Tank U-103 first received metal waste from T-Plant via the cascade line in February 1947 and was full by July 1947. In January 1952, waste was sent to tank TX-115 to prepare the tank to receive waste from the test sluicing of tank U-101. Flush water from miscellaneous sources was added to the tank in the first quarter of 1952. Metal waste from tank U-101 was sluiced to tank U-103 from April to November 1952. Supernatant from tank U-102 was transferred to tank U-101 through tank U-103 and the 244-CR Vault to mobilize the metal waste sludge. Sluicing of tank U-103 for uranium recovery began in December 1952, and the tank was emptied during August 1953. Supernatant from tanks TX-115, U-104, U-101, and U-102 was used to sluice the solids in tank U-103.

Tank U-103 again began receiving metal waste through the cascade from tank U-102 from the second quarter of 1953 to the second quarter of 1954. Waste from tank U-103 was sluiced to the uranium recovery process during November 1955. The cleanout of the tank was initiated in November 1956 and completed in December 1956.

In the first quarter of 1957, the tank received metal waste and water. Waste was sluiced from the tank to the uranium recovery process in the second quarter of 1957. Tank U-103 was filled with REDOX HLW supernatant from tanks SX-102 and SX-111 during the fourth quarter of 1958. The tank remained inactive until the first quarter of 1974 when waste was sent from tank U-103 to tanks S-101 and S-110. From the first quarter of 1974 to the second quarter of 1976, the tank received flush water from miscellaneous sources. Tank U-103 began receiving EB waste from tank TX-106 in the second quarter of 1975 and from tank TX-118 in the third quarter of 1975. Waste was sent from tank U-103 to tanks U-111 and TX-118 during the first quarter of 1976, nearly emptying the tank. Additional EB waste was received by tank U-103 from tanks TX-108 and T-101 during the second quarter of 1976. Tank U-107 also sent Pacific Northwest Laboratory wastes to tank U-103 during the second quarter of 1976. In addition, tank U-103 exchanged evaporator waste with tank S-102 during the second quarter of 1976.

Tank TX-108 sent EB waste to tank U-103 during the third quarter of 1976, as tank U-103 became the staging tank for the 242-S Evaporator with tank S-102 as the feed tank. Waste was sent to tank S-102 during the fourth quarter of 1976 with EB waste being received into tank U-103 from tank S-102 during the first quarter of 1977. The tank received waste from tank TX-103 and sent waste to tank U-111 during the first quarter of 1977.

In the second quarter of 1977, tank SY-102 became the feed tank for the 242-S Evaporator and continued the exchange of feed and bottoms waste with tank U-103. This ended in the fourth quarter of 1977 with a final exchange of waste with tank SY-102. In the fourth quarter of 1977, $HNO_3/KMnO_4$ was also added to the tank from evaporator operations. The tank was declared inactive in 1978. The tank contains REDOX sludge and SMM S1/SMM S2 saltcake and supernatant. On September 11, 2000, tank U-103 was declared interim stabilized in compliance with the Tank Farm Interim Stabilization Evaluation.

Tank U-103 contains about 1,722 kL (455 kgal) of non-complexed waste and is listed as sound. The waste consists of a saltcake layer of 1,677 kL (443 kgal), and 45 kL (12 kgal) of sludge. The headspace volume in tank U-103 is about 1,442 m^3 (50,924 ft^3). Tank U-103 integrity is sound (Hanlon 2000).

3.1.16 Tank 241-U-105

Tank U-105 is the second in a cascade series of three tanks beginning with tank U-104 and ending with tank U-106. Tank U-105 began receiving waste in the fourth quarter of 1947. It received metal waste that cascaded from tank U-104, until the third quarter of 1948; thereafter, waste was cascaded from tank U-105 to tank U-106. In the first quarter of 1953, the tank received flush water, and waste was sent to tank U-106. In the second quarter of 1953, waste was sent to U-Plant for uranium recovery. In the fourth quarter of 1954, metal waste again cascaded from tank U-104 through tank U-105 to tank U-106.

In the first quarter of 1956, the tank received flush water, and the contents of tank U-104 were pumped to tank U-105 for sluicing in the same period. Waste was periodically sent to U-Plant in 1956 and in the first quarter of 1957. In 1957, the tank was sluiced, and the waste was sent to the U-Plant. After sluicing, the tank was nearly empty. In the third quarter of 1957, flush water was sent to the tank. In the first quarter of 1961, HLW REDOX plant waste was cascaded to tank U-105 from tank U-104; in the fourth quarter of 1961, cladding removal waste was sent from tank U-108.

In the first quarter of 1974, waste was sent to tank S-110. In the second quarter of 1975, tank U-105 received EB waste from tank TX-106. Subsequently, it received evaporator waste from tank TX-118 in the third and fourth quarters of 1975 and the first quarter of 1976. Waste also was sent to tank U-111 during this period. In the remainder of 1976 and in the first quarter of 1977, tank U-105 received waste from tank S-102, and it sent waste to tank U-111.

Tank U-105 was declared inactive in 1979 and underwent partial interim isolation in December 1982. The tank is categorized as sound, but intrusion prevention and saltwell pumping are not yet completed. The current waste level is about 1,582 kL (418 kgal) and is classified as non-complexed. The waste consists of 140 kL (37 kgal) of supernatant, a saltcake layer of 1,321 kL (349 kgal), and 121 kL (32 kgal) of sludge. The headspace volume in tank U-105 is about 1,632 m^3 (57,634 ft^3). Tank U-105 integrity is sound (Hanlon 2000).

3.1.17 Tank 241-U-107

Tank U-107 first received metal waste from T-Plant in September 1948 and was full by December 1948. Tank U-107 is the first in a cascade series of three tanks that include tanks U-108 and U-109. The waste cascaded from tank U-107 until the third quarter of 1949. The waste from tank U-109 was then sent to U-Plant for uranium recovery.

The tank U-107 contents were sluiced and sent to tank U-109 through a direct transfer for uranium recovery in the third quarter of 1953. Metal waste was again transferred from T-Plant to tank U-107 in 1954, a portion of which cascaded to tank U-108. In 1955 waste was sluiced and sent directly to tank U-109 for uranium recovery, and the heel was jet sluiced in 1956.

In the years 1957-1959, tank U-107 received REDOX coating waste supernatant from tank S-107. There were no further transfers until 1968-1969 when supernatant was received from tanks S-107 and SX-105, and waste was sent to tanks U-108, U-109, and TX-101.

No transfer activity for tank U-107 was recorded in 1970 or 1971. Beginning in 1972, activity in the tank resumed. From 1972 to 1976 the tank received N-Reactor and T-Plant decontamination wastes, laboratory waste from Pacific Northwest Laboratory, 204-4S, and 222-S, and supernatant from S-106, S-107, T-103, T-112, and U-110. Waste water was received from various uranium/thorium recovery tanks (tanks TX-002, UR-001, and UR-002), and catch tank TX-302C. Waste cascaded to tank U-108, and supernatant was sent to tanks TX-101, C-104, S-101, S-107, S-110, and U-103. Tank U-107 sent evaporator feed to and from tank S-102 in 1976 and 1977. Waste was sent to and received from tank SY-102 in 1977.

Tank U-107 received slurry from partial neutralization evaporator campaigns at the 242-S Evaporator in 1978 and again in 1980. Between these years, tank U-107 also received supernatant from tank SY-102 and sent waste to tanks U-102, U-111, SX-101, SX-106, and SY-102. Tank U-107 was removed from service in November 1980 and currently contains 1,544 kL (148 in.) of DSSF waste and is listed as sound. The waste consists of 125 kL (33 kgal.) of supernatant, a saltcake layer of 1,363 kL (360 kgal), and 57 kL (15 kgal) of sludge. The headspace volume in tank U-107 is about 1,669 m^3 (58,940 ft^3). Tank U-107 integrity is sound (Hanlon 2000).

3.1.18 Tank 241-U-108

Tank U-108 began receiving metal waste (MW) in the first quarter of 1949 via the cascade line from tank U-107. The tank was full and cascading to tank U-109 by the end of the first quarter, and the cascade continued until the fourth quarter of 1954. The tank received flush water in the third quarter of 1953 and in the third and fourth quarters of 1954. In the fourth quarter of 1955, tank U-108 again received flush water. Some of this waste was sluiced to tank U-109. Most of the waste from the tank U-108 was transferred out for the uranium recovery process by the first quarter of 1956.

From the second quarter of 1959 until the fourth quarter of 1964, tank U-108 received REDOX CW from tank S-107. During the fourth quarter of 1961, tank waste was sent to tank U-105. During the second quarter of 1963, tank waste was sent to tank T-101. From the second through fourth quarters of 1968, tank waste was sent to tank TX-118. In the second quarter of 1964 and the third quarter of 1968, the tank received CW from the REDOX plant. The tank received supernatant waste from tank U-107 from the fourth quarter of 1972 until the first quarter of 1976. During the second quarter of 1972 and the fourth quarter of 1973, the tank waste was sent to

tanks TX-101 and S-101. From the second quarter of 1975 through the first quarter of 1977, the tank received evaporator bottom waste from tank S-102. During the same time period, supernatant waste was sent to tank U-111, and evaporator feed waste was sent to tank S-102.

The waste volume is approximately 1,772 kL (468 kgal), with 91 kL (24 kgal) of supernatant, a saltcake layer of 1,571 kL (415 kgal), and 110 kL (29 kgal) of sludge. The headspace volume in tank U-108 is about 1,442 m^3 (50,924 ft^3). Tank U-108 integrity is sound (Hanlon 2000).

3.1.19 Tank 241-U-109

Tank U-109 is the third in a cascade series of three tanks, beginning with tanks U-107 and U-108. Tank U-109 first received metal waste from tank U-108 in March 1949 and was full by the third quarter of 1949. Removal of the metal waste started in 1953 and was completed in the first quarter of 1954. New metal waste started entering the tank in the third quarter of 1954, and the tank was full by the fourth quarter of the same year. Metal waste was sluiced from tank U-109 in the second quarter of 1956, and the tank was declared empty.

In the third and fourth quarters of 1956, tank U-109 received REDOX CW supernatant. Except for a few additions of water, no tank transfers occurred until 1969 when most of the waste was sent to tank TX-118. In the fourth quarter of 1969, supernatant was received from tank U-107. No further transfers occurred until 1974 when much of the waste was sent to tank S-110. In the fourth quarter of 1975, tank U-109 received EB from the 242-S Evaporator Crystallizer. In the first quarter of 1977, residual liquor was received.

Tank U-109 was declared inactive in the first quarter of 1978 and currently contains 1,760 kL (465 kgal) of waste. The waste consists of 72 kL (19 kgal) of supernatant, a layer of saltcake of 1,556 kL (411 kgal), and 132 kL (35 kgal) of sludge. The headspace volume in tank U-109 is roughly 1,454 m^3 (51,348 ft^3). Tank U-109 integrity is sound (Hanlon 2000).

3.2 DISSOLUTION STUDIES

Waste dissolution studies have been performed on waste from tanks A-101 and S-102.

3.2.1 Tank 241-A-101 Dissolution Studies

Dissolution tests performed on samples of tank A-101 waste illustrated that most of the major salts were dissolved at 100 percent dilution (1g H_2O : 1g undiluted sample), and only slightly more so at 300 percent dilution. Also shown was that under almost all dilution conditions, dissolution was more extensive at 50 °C than at 25 °C. The percentage of sodium in the saltcake that could be retrieved at reasonable dilution levels by pumping liquid from the tank is estimated at greater than 90 percent (Herting 1999).

3.2.2 Tank 241-S-102 Dissolution Studies

Dissolution tests performed on samples of tank S-102 waste illustrated that most of the major salts were dissolved at 100 percent dilution while only slightly more dissolution occurred at 300 percent dilution. Additionally, under almost all dilution conditions, dissolution was more extensive at 50 °C than at 25 °C. The percentage of sodium in the saltcake that could be retrieved at reasonable dilution levels by pumping liquid from the tank is estimated at greater than 95 percent (Herting 1999).

4.0 WASTE CONFIGURATION AND PROPERTIES

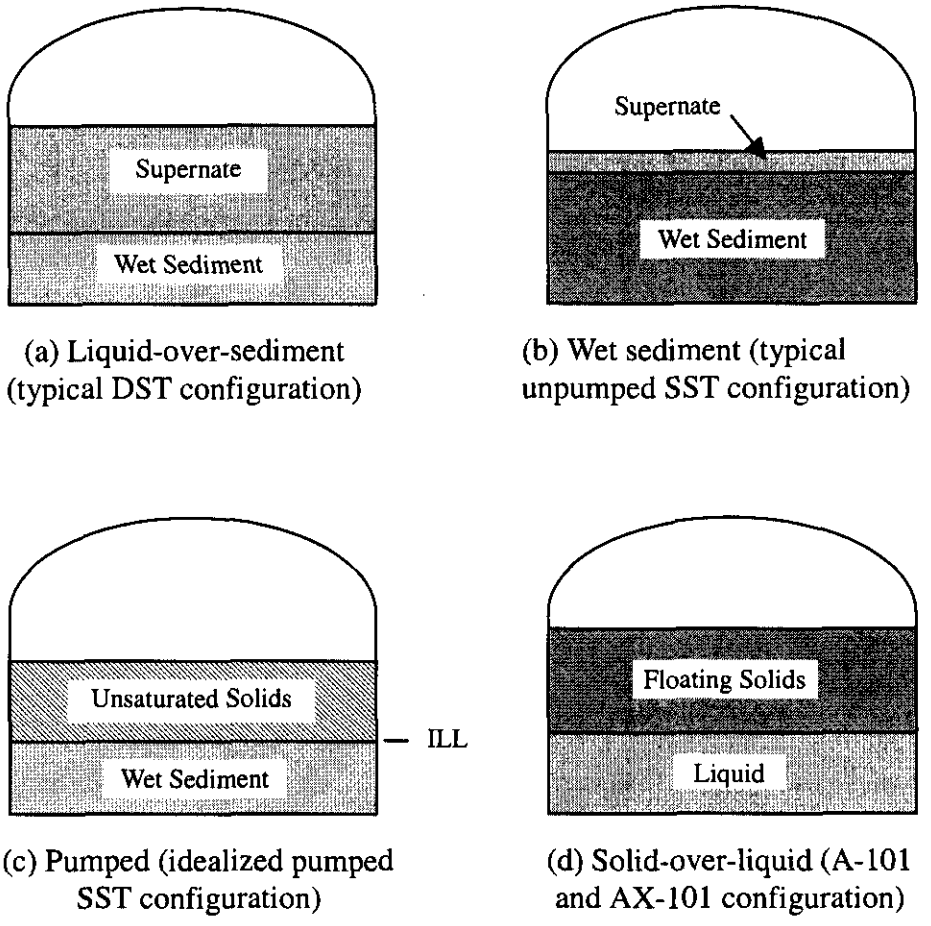
Waste configuration is the physical arrangement of waste types in layers within a tank. The waste configuration has a strong influence on a tank's gas retention and release behavior. The three waste types of interest are liquid, sludge, and saltcake. Liquid is a solution of dissolved inorganic and organic 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 saltcake waste. Sludge consists of fine insoluble particles, which are mostly metal oxides. Saltcake forms by the settling of sodium and aluminum salts precipitated from a saturated solution by cooling and consists of generally larger particles than sludge. A "salt-slurry" waste type of relatively fine particles is typically found in DSTs and some SSTs. Some tanks contain a mixture of sludge and saltcake that can be considered a "mixed" waste type. However, the mixed waste appears to behave as saltcake, in most cases, and will not be discussed separately here.

The waste types are distributed within the tanks in only a few different configurations, depending mainly on the amount of liquid. The DSTs typically contain the "liquid-over-sediment" configuration where a relatively deep layer of supernatant liquid overlies an equally deep layer of liquid-saturated sediment.[5] The main waste configurations in SSTs are "wet sediment," where the sediment is saturated with liquid but there is little or no supernatant; and "pumped," where interstitial liquid has been reduced by saltwell pumping such that the ILL is well below the waste surface. One other waste configuration is of interest in two SSTs: a "solid-over-liquid" configuration where the entire mass of undissolved solids in the tank floats on a very dense liquid layer. The SSTs A-101 and AX-101 are the only tanks in which temperature profiles, neutron logs, and core samples indicate the solid-over-liquid configuration. The important waste configurations are sketched in Figure 4-1.[6]

Nonuniform cooling, precipitation, and compaction have created complex variations on these basic waste configurations in many SSTs. In the "jelly donut" configuration, the outer region is generally dryer and stronger, and the waste may have subsided significantly in the center near the saltwell screen to create a dished upper surface. Layers of different wastes deposited as the tank was last filled can also create vertical nonuniformities in water content, density, strength, and gas retention. 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.

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

[6] A floating solids layer or "crust" and "mixed slurry" where mechanical mixing keeps a large fraction of the solid particles suspended exist in DSTs. See Hedengren et al. (2000) for a discussion of these 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)

Figure 4-1. Waste Configurations

4.1 SINGLE-SHELL TANK WASTE CONFIGURATIONS AND PROPERTIES

The actual waste configuration in a tank can be broadly described in terms of the waste level, the supernatant liquid depth, if any, and the ILL. This allows the waste in each of the Flammable Gas Watch List SSTs to be classified into one of the categories shown in Figure 4-1. Additional data are also given to present a more complete picture of the condition of the waste. Data for each tank are given in separate subsections below. It is important to note that the waste configuration changes rapidly as SSTs are pumped.[7] The core samples from the Flammable Gas Watch List SSTs were, without exception, obtained before pumping. The waste density and strength estimates, as well as the retained gas data from the RGS, may no longer apply after pumping. The waste temperatures, waste level, and neutron logs, however, span the pumping period. The pumping status and schedule of each tank are stated in each section to indicate which data are or may become obsolete.

[7] Besides the disturbance of saltwell pumping, as of this writing, tanks S-102 and S-112, and possibly tank U-107 are scheduled to be retrieved in the next several years.

The saltwell pumping history is described for each pumped tank in terms of the pumping rate, the cumulative volume pumped, in terms of level, and the waste level as functions of cumulative pumping time. The time is the actual time the pump was operating and does not include gaps for downtime. The cumulative volume pumped is converted to level change by dividing the volume by the total tank cross-sectional area. The level change due to pumping is then subtracted from the initial waste level to give the "pumped level." Comparing the pumped level to the waste level can provide some valuable insights into the effects of saltwell pumping. If supernatant is being pumped, the pumped level and waste level decrease together. If interstitial liquid is being extracted, the waste level should remain above the pumped level. If the liquid is non-uniformly distributed and most of it is pumped from the central region of the tank, the liquid level may decrease more rapidly than the pumped level.

The next plot shown for each tank gives the histories of the waste level and ILL from 1990 to December 2000. Periods when the level instrument was left in "intrusion mode" (see Section 2.0) are ignored. A gradual rise in the waste level and ILL over several years is attributed to gas accumulation. Other waste volume growth mechanisms (e.g., intrusion, transfer, condensation) are episodic or seasonal and would not produce steady growth. Determination of the ILL is somewhat subjective. There can be a considerable volume of liquid in unsaturated layers above the ILL, especially in recently pumped tanks. Therefore, the neutron logs are included in a separate plot to show a qualitative vertical distribution of liquid in each tank. The relation of neutron count rate to water content is nonlinear and complicated by the chemistry.[8] Therefore, it is not possible to accurately quantify the liquid fraction from the neutron logs although they can indicate regions where gas fractions exceed 5 to 10% (see Section 6.4.2).

Plots of measured density and estimates of the yield stress (τ_y) for each segment of recent core samples are also shown for several tanks since they have a strong influence on gas retention and release behavior (see Section 6.1). The densities are measured in samples of the drained liquid and the remaining bulk solids from core samples. The volume average of the liquid and solids densities is given for the upper and lower half of each core segment. Since most of the gas retained in the sample is released in the extrusion and sample preparation process, these densities are assumed to be gas-free. The yield stress is estimated by the technique developed by Gauglitz and Aiken (1997) from visual observation of core extrusions compared to the extrusion behavior of materials with known yield stress (see Section 2.4.1). This method has a relatively high uncertainty, but it provides a good indication of whether the waste is relatively weak ($\tau_y \sim 100$ Pa) or strong ($\tau_y \sim 1{,}000$ Pa). The density and yield stress are shown on the same plot along with a neutron profile from prior to saltwell pumping to help identify regions of higher or lower liquid content.

The accuracy of the measured densities and the yield stress estimates depend on the solubility and in-situ temperature of the waste. The measured physical properties represent tank conditions only for relatively cool tanks (temperature < 100 °F). If the waste from a hotter tank cools significantly in the hot cell prior to extrusion, dissolved solids are likely to precipitate. This

[8] The neutron probe does not distinguish between hydrogen atoms in free water molecules and those in water of hydration, organic molecules, ammonia and ammonium ions, hydroxide groups, and other hydrogen-rich species.

causes the density of the liquid to decrease and that of the bulk solids to increase compared to the in-situ value. Solids added by precipitation after the sample has cooled can greatly increase the yield stress. In tank A-101, for example, samples from the liquid layer experienced so much precipitation they actually extruded as a solid.

The temperature history of the waste is also plotted for each tank, both to indicate whether the waste is relatively hot or cold and to illustrate the thermal behavior of the tank. While each tank has at least one thermocouple tree, the thermocouples are spaced relatively far apart, some may be out of service, and there is no means to calibrate them. However, the temperature data are sufficient in both density and quality to show the general cooling trend and the annual thermal cycle of each tank. In the plots below, thermocouple elevations are taken from Tran (1993) where available. Since the document gave no thermocouple elevations for tanks S-112, SX-105, SX-106, SX-109, and T-110, they were assumed to be the same as similar tanks in the same farm.

The following subsections present the waste configuration, properties, temperatures, and saltwell pumping histories for each of the nineteen SSTs on the Flammable Gas Watch List in alphabetical order. Similar data for tanks S-103 and S-106 are provided in Appendix A.

4.1.1 Tank 241-A-101 Waste Configuration

The waste in tank A-101 is highly concentrated saltcake classified as DSSF. Its (and tank AX-101's) configuration is unusual in that the entire 170-inch layer of solids is floating above an equally deep layer of convective liquid by virtue of its retained gas. For a detailed discussion on the history and chemistry of the waste in tank A-101, see Stock (2000b). The average gas volume fraction in the floating layer measured by the RGS was 0.18, which is consistent with both the BPE results and the neutron profile. Saltwell pumping in tank A-101 began May 6, 2000, but only 18 kgal of liquid have been removed as of December 2000 because of mechanical problems. The saltwell pumping history is summarized in Figure 4-2.

The waste level and ILL histories since 1990 are plotted in Figure 4-3. The ILL in tank A-101 corresponds to the top of the floating layer as shown in the neutron log in Figure 4-4. The ENRAF™ and LOW are on opposite sides of the tank (see Figure 2-4) and the 17- to 18-inch difference between the ILL and waste level indicates that the waste surface is uneven or that there is a cavity around the ENRAF™ gauge. This is supported by the agreement of the surface level derived from core samples and the ILL. A cavity or some kind of local depression would help explain the upward spikes in the waste level during initial saltwell pumping. The 6- to 7-inch drop in the ILL and level correspond almost exactly to removal of 18,000 gallons, or 6.5 inches, of liquid. Saltwell pumping to-date has removed liquid only from the lower layer as shown by the neutron log in Figure 4-4. The shape of the neutron profile for the upper layer descended but did not change significantly. The lower neutron count in the upper layer is believed to be mostly to retained gas.

The density and yield stress profiles derived from core samples obtained prior to saltwell pumping are shown in Figure 4-5. The density of the floating layer averages about 1.7 g/mL while the liquid density is approximately 1.54 g/mL. The strength assessment for the waste in this tank is almost certainly compromised by the relatively high waste temperature of around 140 °F. After the core samples reach hot cell temperature of 90 to 100 °F, solids precipitation would significantly increase the apparent waste strength observed during extrusion. This is evidenced by the apparent 100 Pa yield stress in samples from below the base of the floating layer. The yield stress in the floating layer is relatively uniform, possibly decreasing near the upper surface.

The waste temperature history shown in Figure 4-6 indicates a gradual cooling trend of about 1 °F per year. Only the portion of the waste above the 292-inch thermocouple shows a discernable seasonal trend. The 340-inch thermocouple shows an annual variation of about 6 °F. The 412-inch thermocouple is in the tank headspace and registers a 10 °F seasonal swing. The liquid layer temperature is essentially uniform at about 142 °F. The floating layer temperature decreases from 140 °F to 110 °F with an average of approximately 130 °F. The slight temperature decrease of the thermocouple readings in the lower part of floating layer during saltwell pumping is consistent with a uniform descent of the layer as liquid was removed.

4.1.2 Tank 241-AX-101 Waste Configuration

Like tank A-101, tank AX-101 waste is DSSF with the same solid-over-liquid configuration. A 138-inch liquid layer lies under a 128-inch floating solids layer. Based on a single RGS sample and the neutron log, the floating layer has a gas volume fraction of 0.14 to 0.16. Saltwell pumping began July 30, 2000, and about 9 kgal of liquid has been pumped as of December 2000. Pumping has been delayed by repeated failures of a newly designed pump. The saltwell pumping history for tank AX-101 is shown in Figure 4-7.

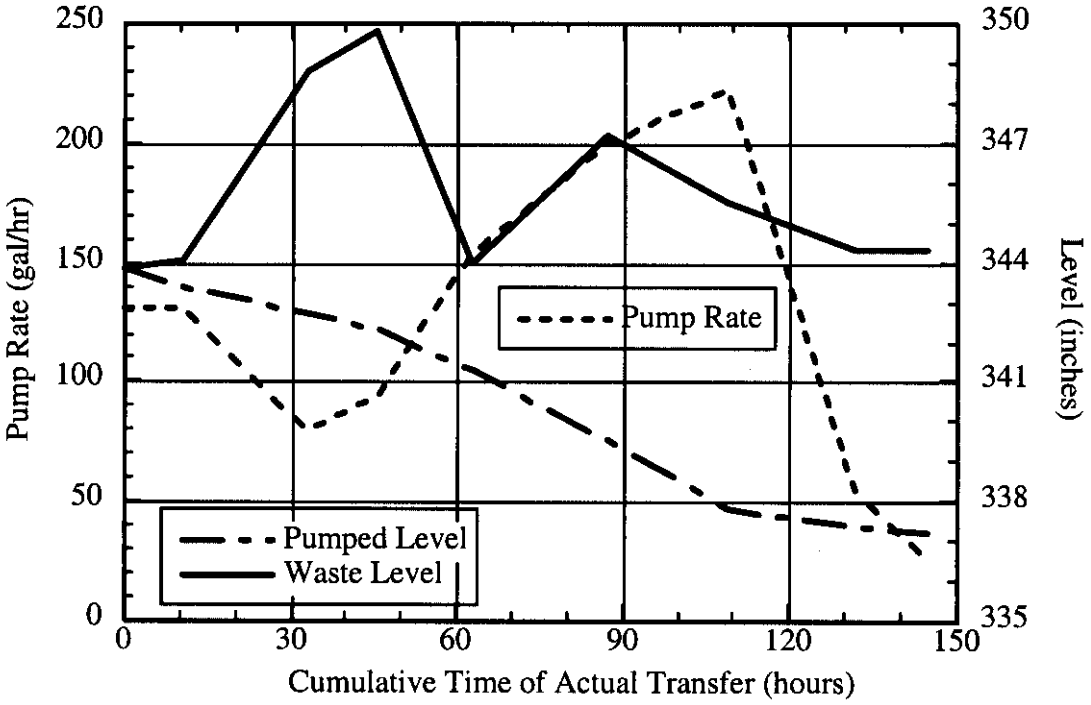


Figure 4-2. Tank 241-A-101 Saltwell Pumping History

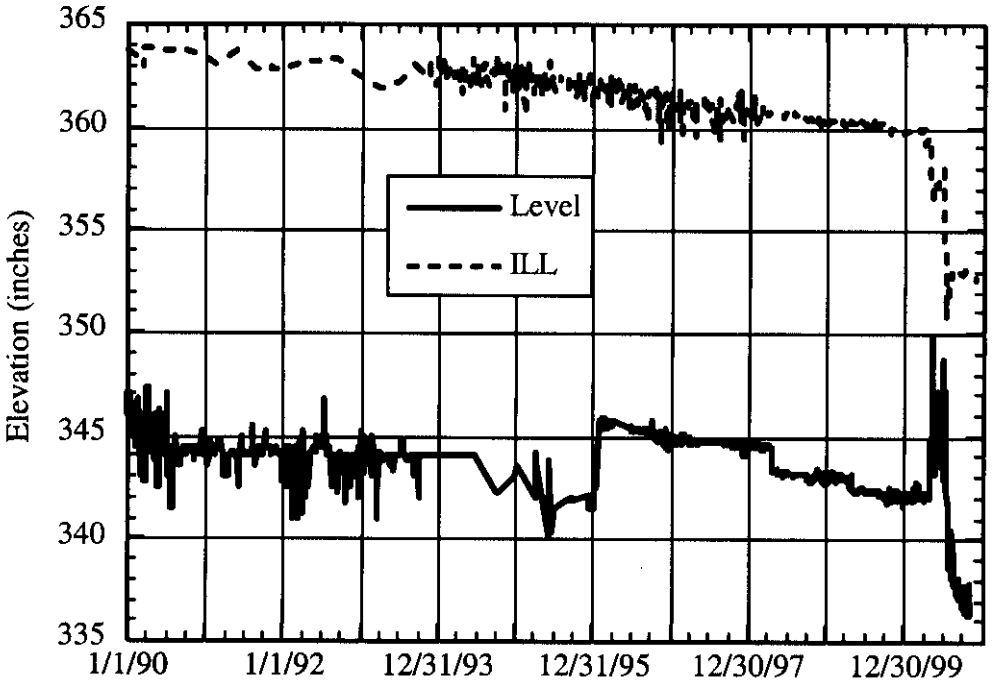


Figure 4-3. Tank 241-A-101 Waste Level and Interstitial Liquid Level History

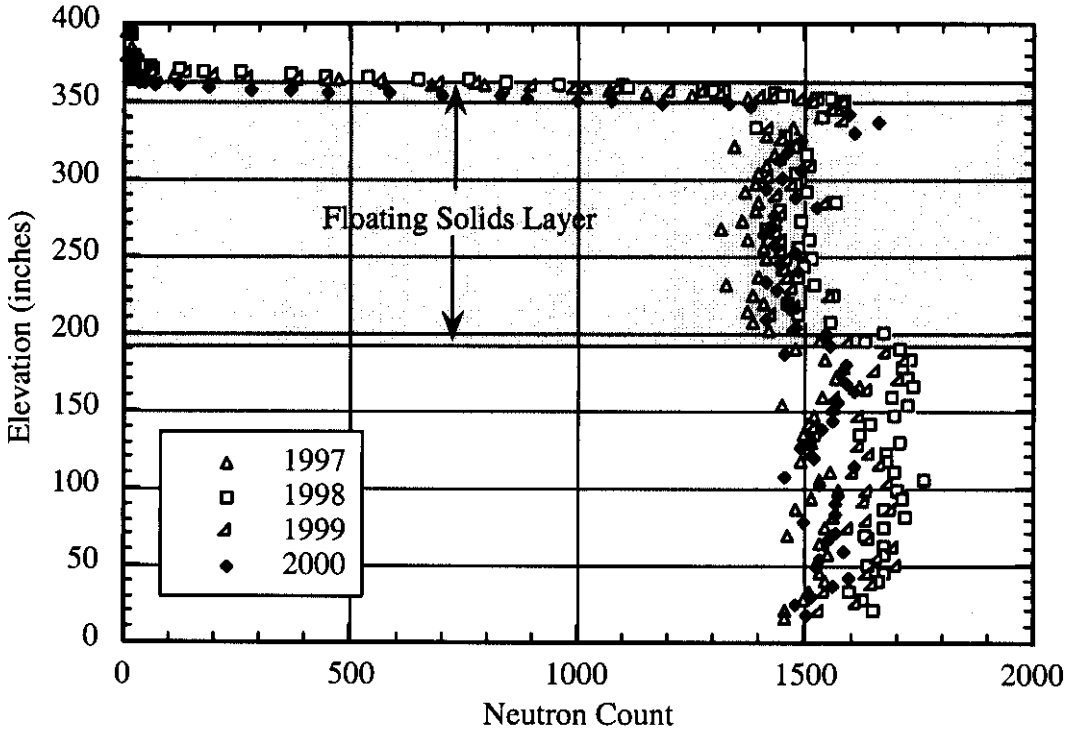


Figure 4-4. Tank 241-A-101 Neutron Logs

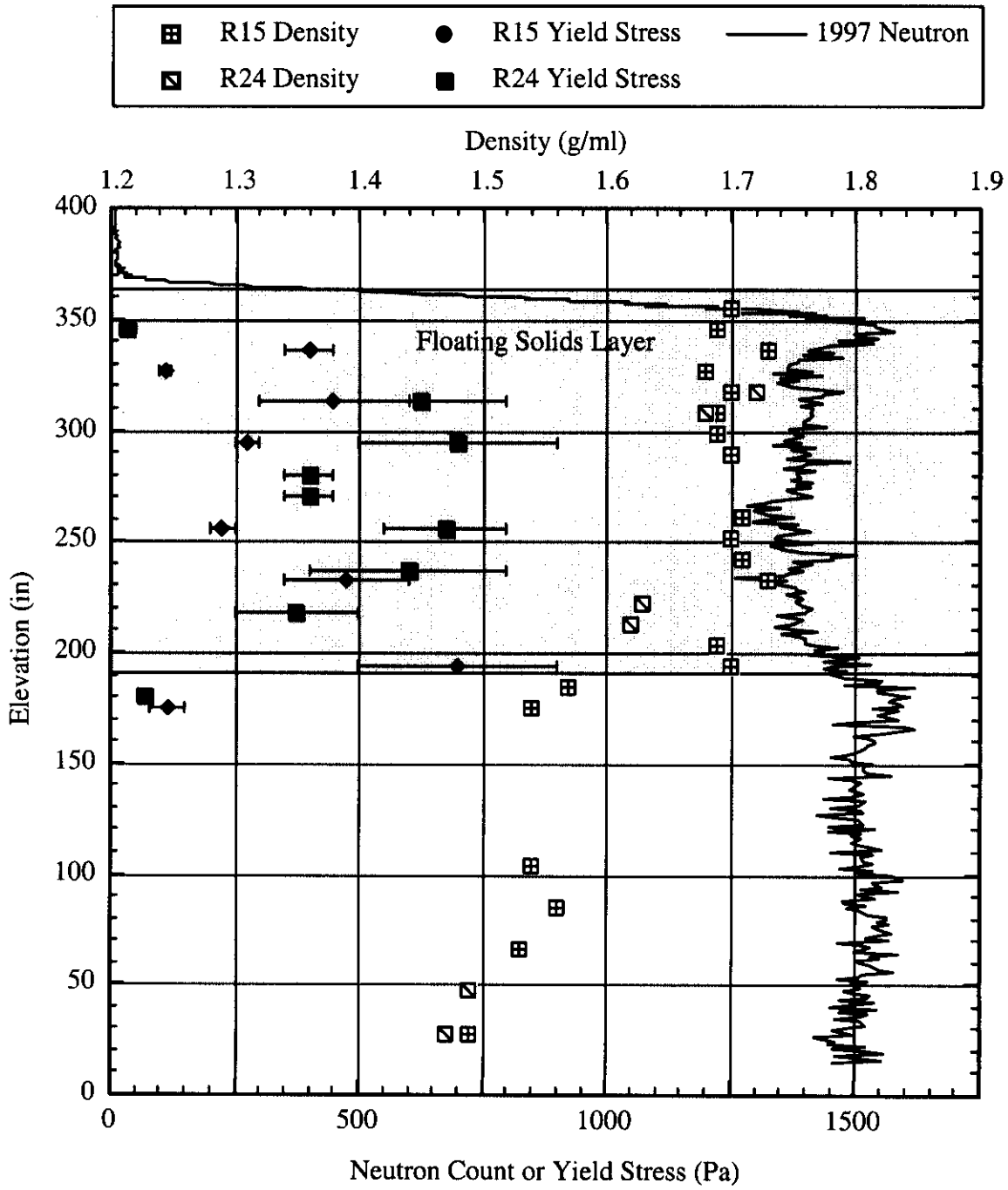


Figure 4-5. Tank 241-A-101 Strength and Density Profile

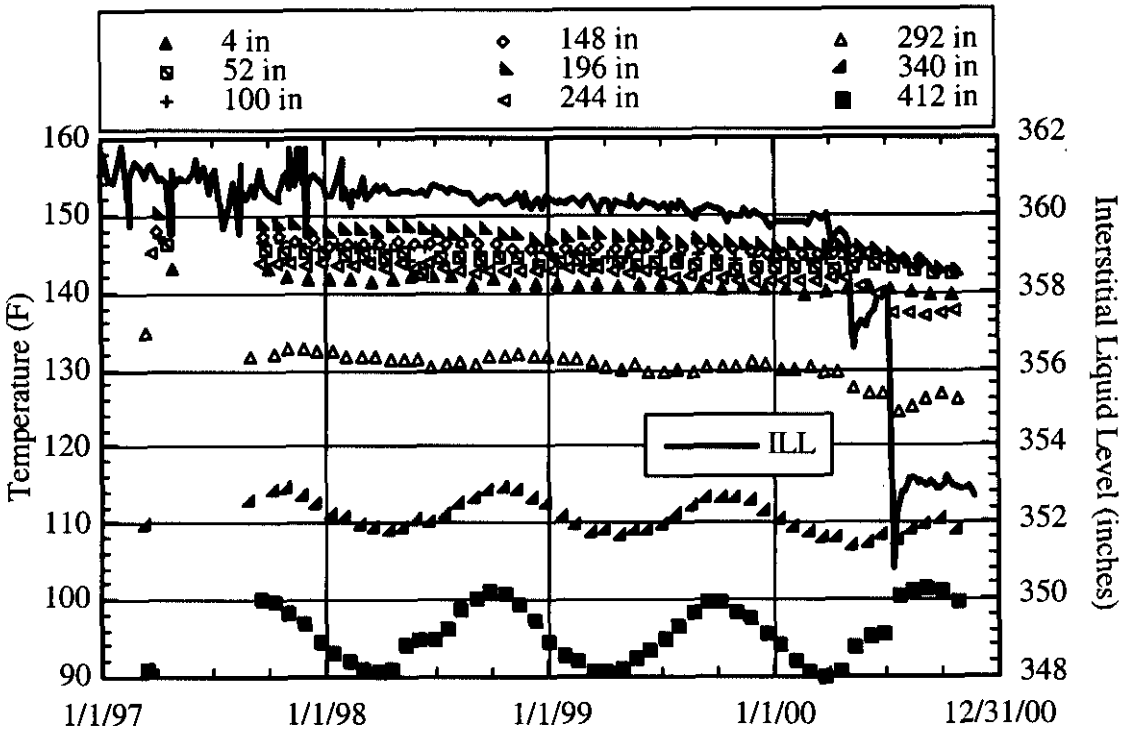


Figure 4-6. Tank 241-A-101 Waste Temperature History

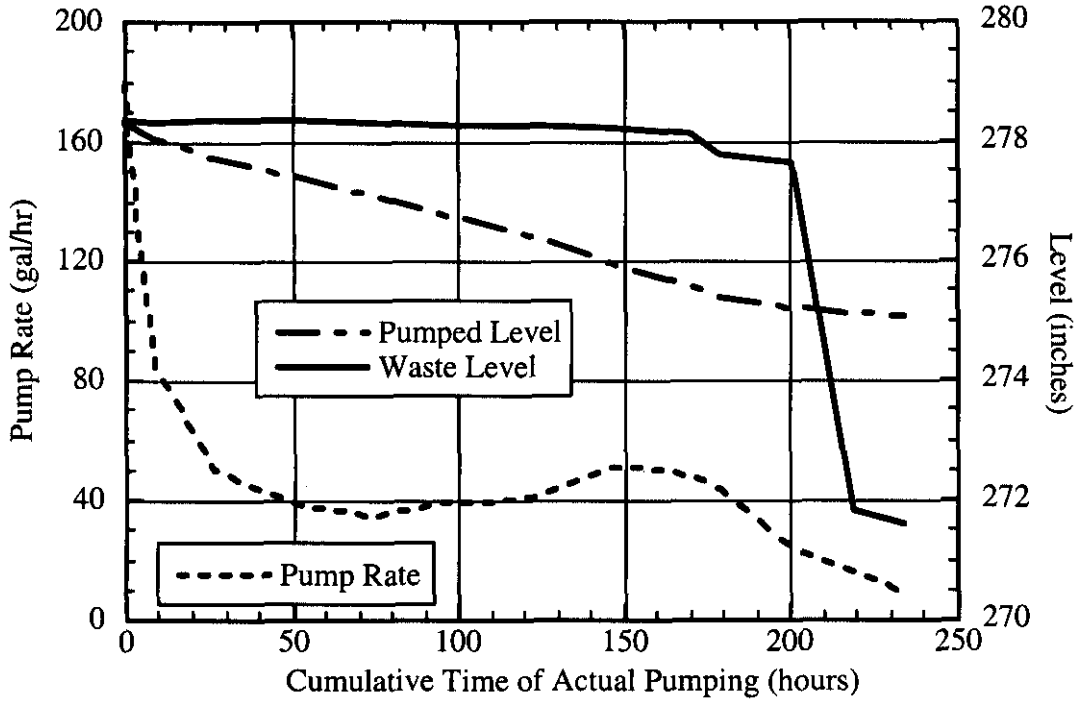


Figure 4-7. Tank 241-AX-101 Saltwell Pumping History

The liquid level and ILL measurements for tank AX-101 are shown in Figure 4-8 and the neutron logs in Figure 4-9. In tank AX-101, the recorded ILL is based on the gamma log rather than the neutron log and corresponds to the base of the floating layer. The neutron ILL represents the top of the floating layer as in tank A-101. However, only one neutron log has been recorded since July 1998, so the gamma ILL are the only data available to track recent events. Both the waste surface level and ILL have been lowered by saltwell pumping, but the 8- to 12-inch drop recorded is more than three times the calculated 3 inches of liquid removed. Since this tank has two arrays of seven and fourteen airlift circulators at 1/3 and 2/3 of the tank radius, respectively, it is likely that waste adhering to these structures reduces the effective area of the waste and amplifies the response to pumping. The sudden drop in level after 200 hours of pumping in Figure 4-8 may be the result of a sudden failure of waste attachment to a nearby airlift circulator.

The density measured from core samples obtained prior to saltwell pumping is shown in Figure 4-10 along with the pre-pumping neutron profile. Most of the data are compromised by contamination with hydrostatic head fluid. Also, the two cores (Risers 9D and 9G, see Figure 2-5) were taken from very near the tank wall, and the waste there may not represent the bulk of the tank. Nevertheless, ignoring the densities above 1.8 g/mL in the liquid from Riser 9D, the floating layer and liquid layer average densities are roughly the same as measured in tank A-101 where central risers were sampled.

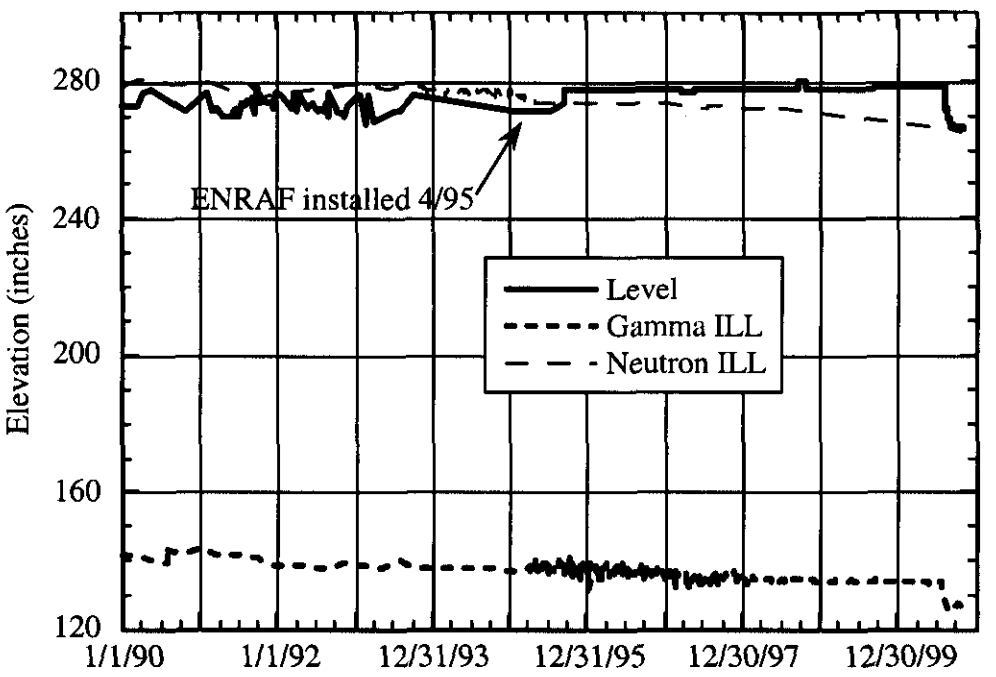


Figure 4-8. Tank 241-AX-101 Waste Level and Interstitial Liquid Level History

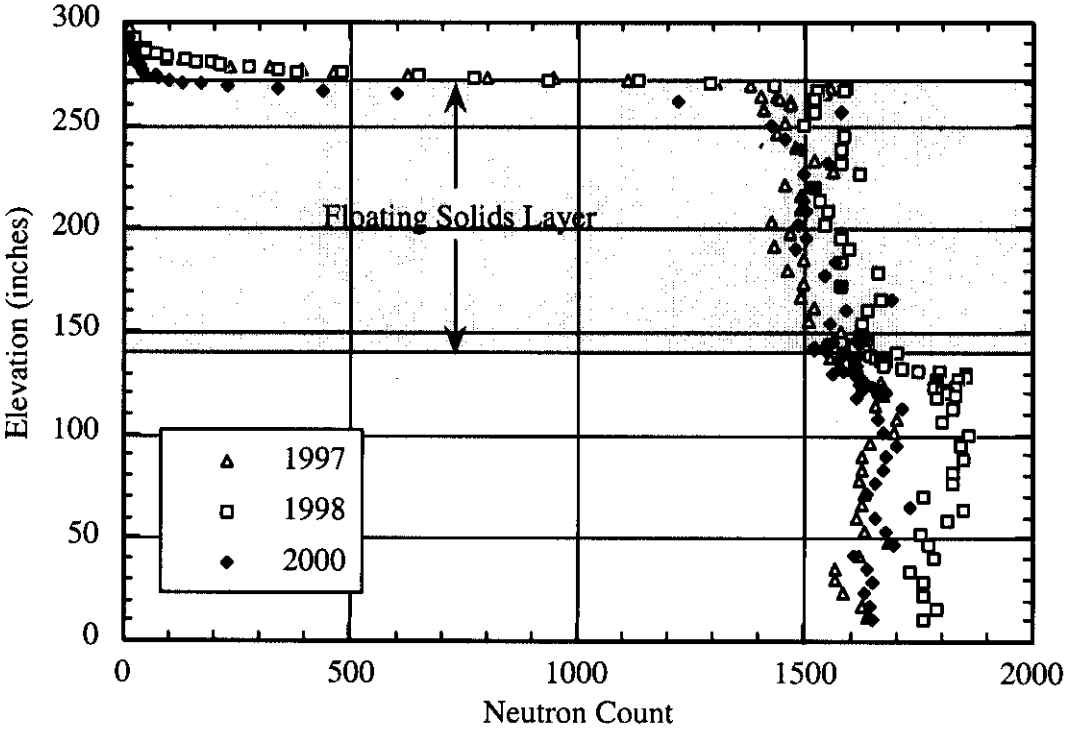


Figure 4-9. Tank 241-AX-101 Neutron Logs

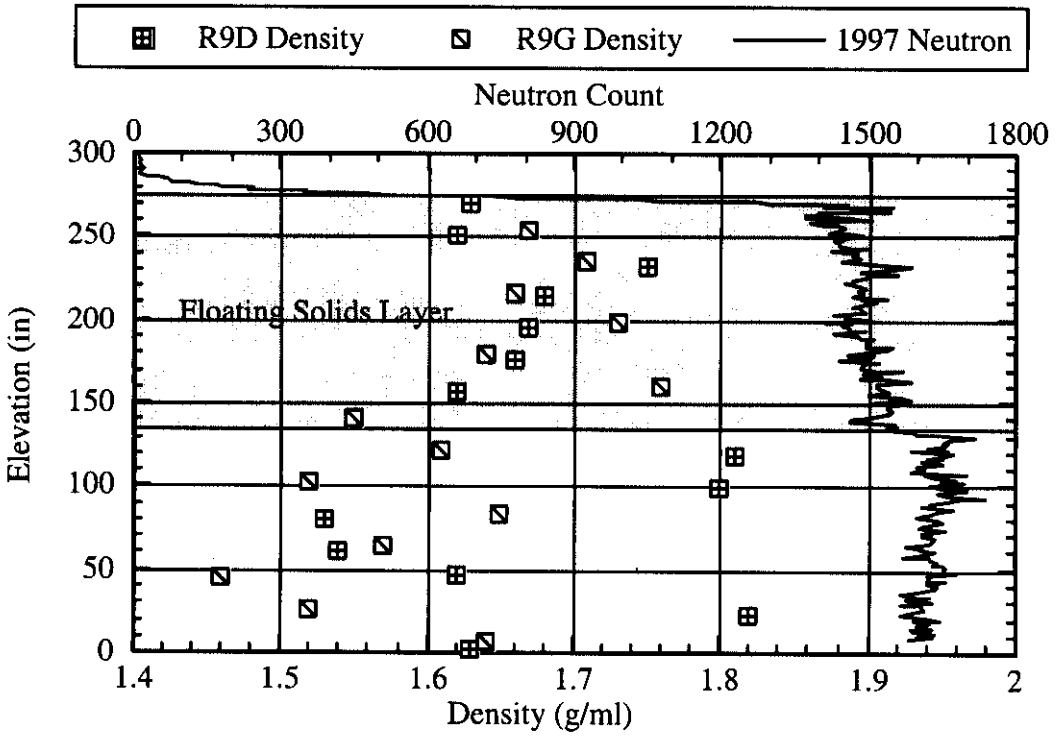


Figure 4-10. Tank 241-AX-101 Density Profile

The tank AX-101 temperature history, shown in Figure 4-11, is also similar to that of tank A-101. The smoother curves after mid-1998 are the result of connecting thermocouples to the TMACS system. Thermocouples above 270 inches also ceased being read at that time, however. The peak waste temperature was decreasing at about 2 °F per year prior to pumping, about twice as fast as in tank A-101. The liquid temperature was a uniform 126 °F, and the floating layer temperature ranges from 125 to 95 °F with an average of about 113 °F. The temperatures exhibit an annual cycle of about 10 °F amplitude near the upper surface and a barely noticeable one at 198 inches, 70 inches below the surface.

It is probable that the sudden temperature spike during saltwell pumping at the 246-inch thermocouple was a "splash" of hot liquid resulting from a sudden release of waste locally attached to the airlift circulators. Saltwell pumping began July 30, 2000, and ended August 11, 2000. The temperature spike occurred between August 4 and August 15, 2000. The ENRAF™ level did not change until August 9 when it suddenly fell 6 inches. The gamma ILL fell 3 inches between July 30 and August 3 and another 3 inches between August 9 through18.

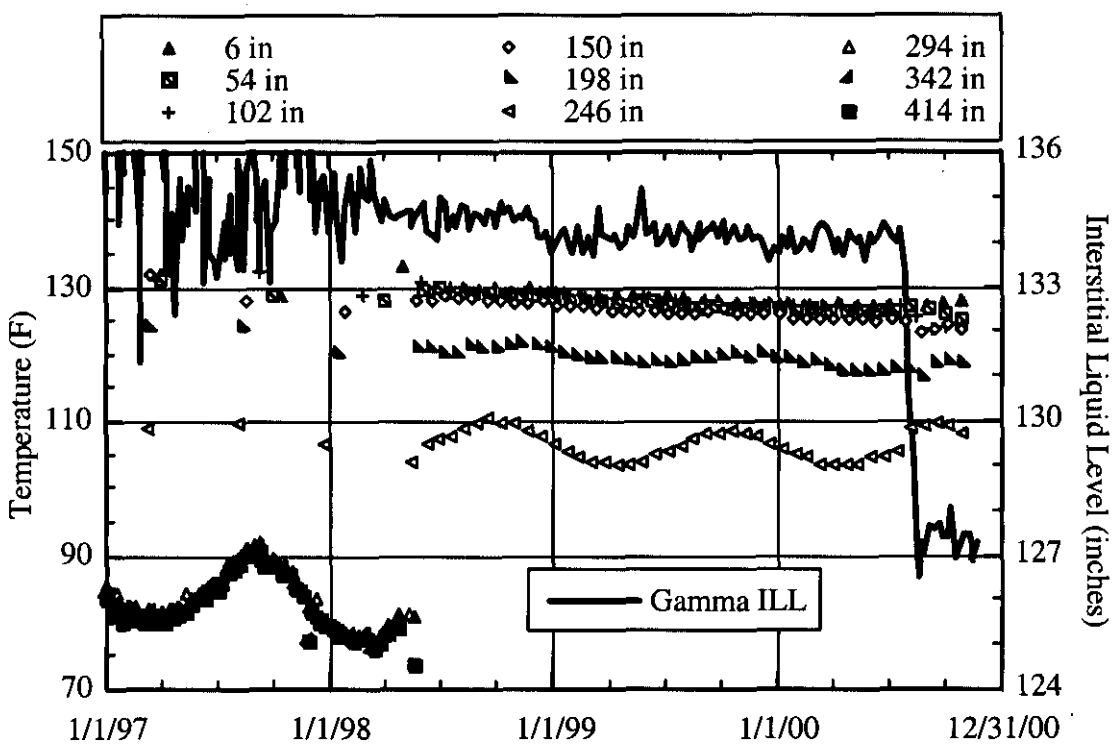


Figure 4-11. Tank 241-AX-101 Waste Temperature History

4.1.3 Tank 241-AX-103 Waste Configuration

Tank AX-103 contains only 38 inches of saltcake waste classified as complex concentrate. Although this waste contains a relatively high concentration of organics, the small waste volume would preclude it from being added to the Watch List, if evaluated today. The waste level and temperature history are given in Figures 4-12 and 4-13, respectively. Aside from a very gradual level decrease (4 inches in nine years) that could be attributed to evaporation, the waste condition has been quite stable. Neutron logs are available for this tank.

4.1.4 Tank 241-S-102 Waste Configuration

The 169 inches of waste in tank S-102 is classed as DSSF, like tanks A-101 and AX-101. However, unlike these tanks, it also contains a significant amount of sludge in the lower 75 inches. This is evidenced by a higher concentration of metal oxides and aluminum and lower concentration of sodium salts. Saltwell pumping began in tank S-102 March 18, 1999, and was halted June 4, 2000, removing a cumulative volume of 68 kgal of liquid out of an estimated drainable volume of 99 kgal. Pumping has been delayed by mechanical problems. The saltwell pumping history is illustrated in Figure 4-14. Prior to saltwell pumping, tank S-102 contained a very large volume of retained gas. The average gas volume fraction measured by the RGS was 0.26, but the BPE method and neutron log indicate less than half that value at 0.11 and 0.06, respectively.

The waste level and neutron ILL and the neutron logs for tank S-102 are provided in Figure 4-15 and Figure 4-16, respectively. The waste level and ILL correspond quite closely, including the saltwell-pumping period. Both were rising at a rate of about 0.5 inches per year prior to pumping, which indicates gradual gas accumulation. The waste level and ILL have dropped 36 inches since saltwell pumping began, a somewhat greater drop than the equivalent of 25 inches of liquid removed, indicating a non-uniform distribution of liquid. The equal drops of the ILL and ENRAF™ level indicate that the liquid being removed is behaving more like supernatant than interstitial liquid, although tank S-102 had no identifiable supernatant layer.

The lack of change in the neutron logs below 150 inches also indicates that only non-interstitial liquid has been removed so far. In fact, it appears that free liquid is accumulating near the current waste surface. Both show there is a significant volume of liquid left to be pumped. The decrease in neutron count below 50 inches can be attributed to retained gas, although the RGS recorded much larger gas fractions in tank S-102 at higher elevations. However, the LOW is much nearer the tank center than the RGS, therefore, significant differences could be expected. The presence of sludge would not be expected to cause the observed large drop in neutron count below 40 inches.

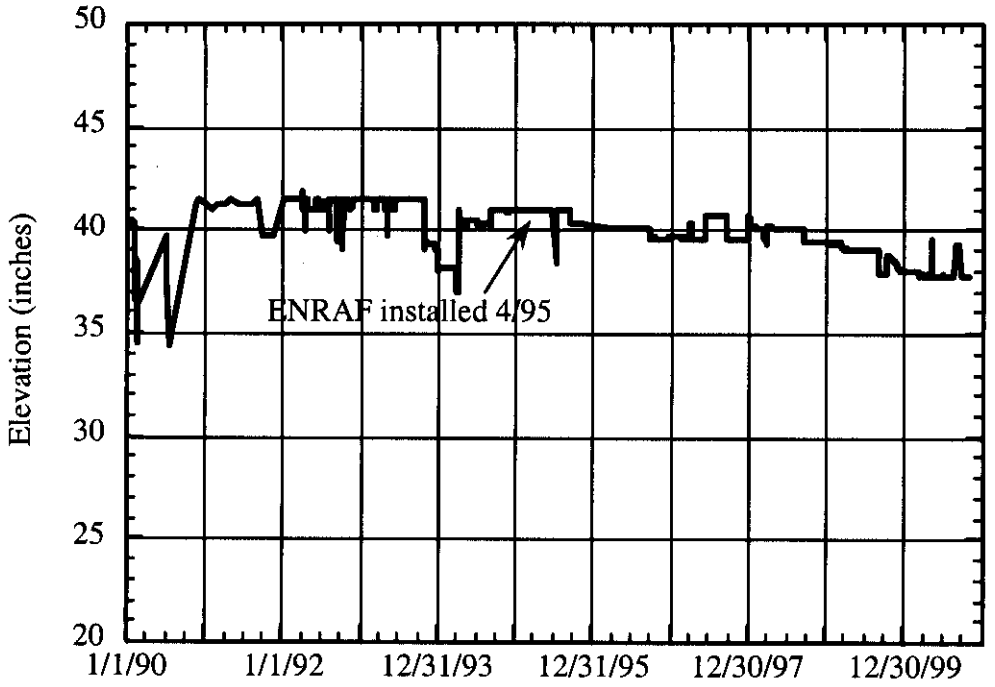


Figure 4-12. Tank 241-AX-103 Waste Level and Interstitial Liquid Level History

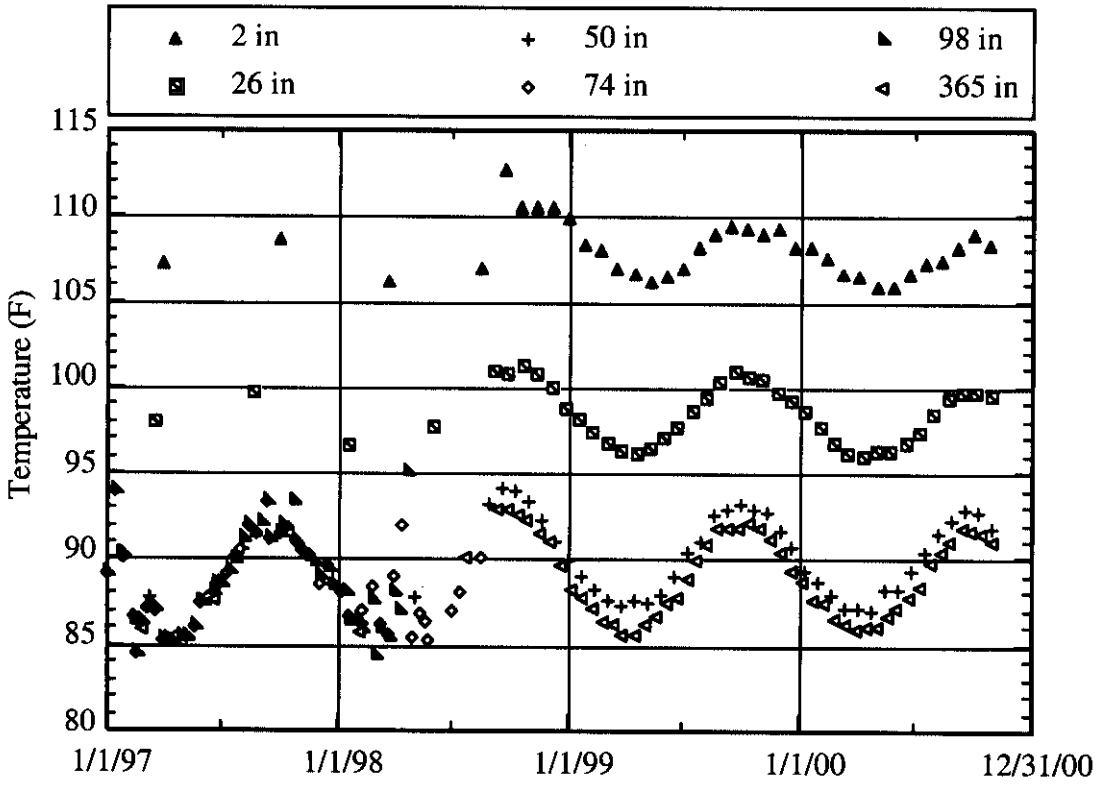


Figure 4-13. Tank 241-AX-103 Waste Temperature History

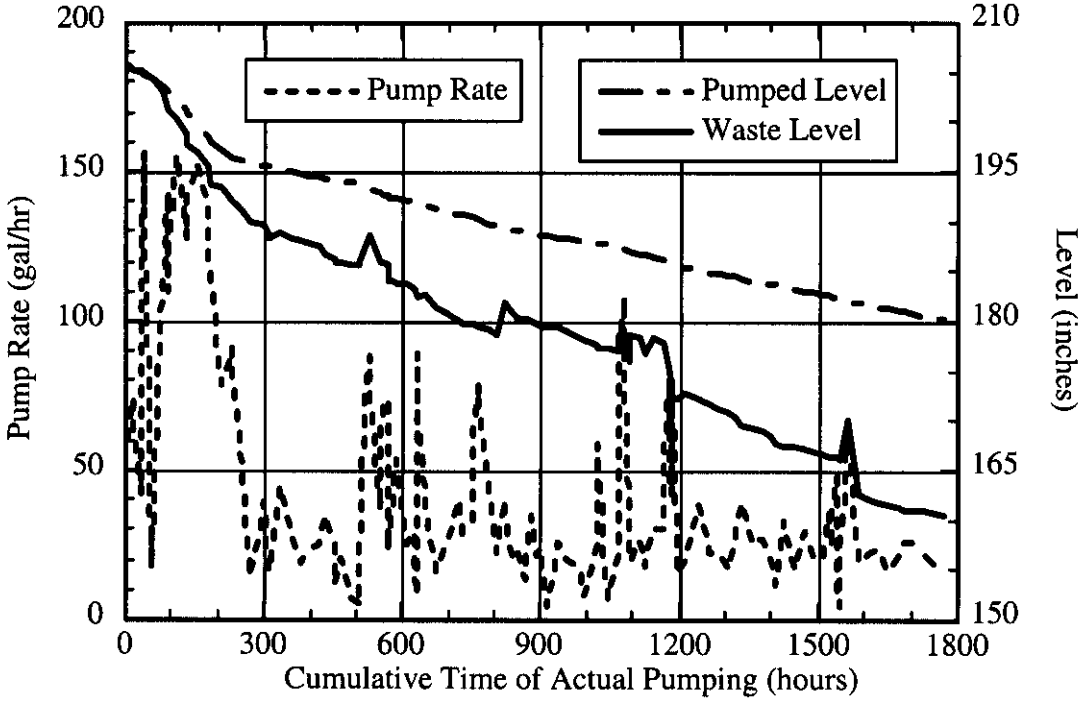


Figure 4-14. Tank 241-S-102 Saltwell Pumping History

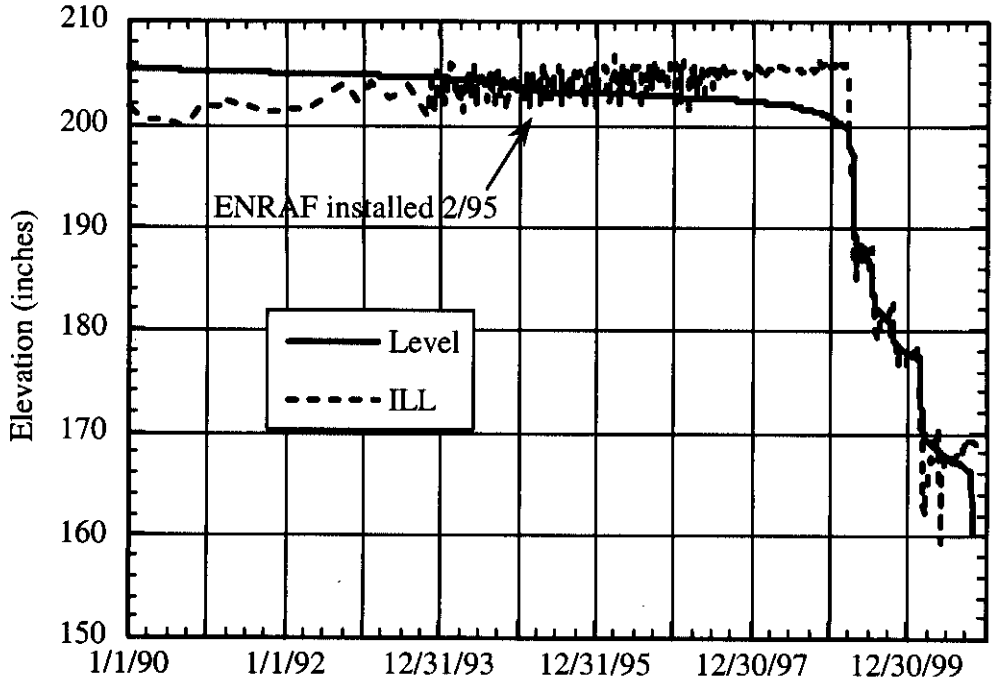


Figure 4-15. Tank 241-S-102 Waste Level and Interstitial Liquid Level History

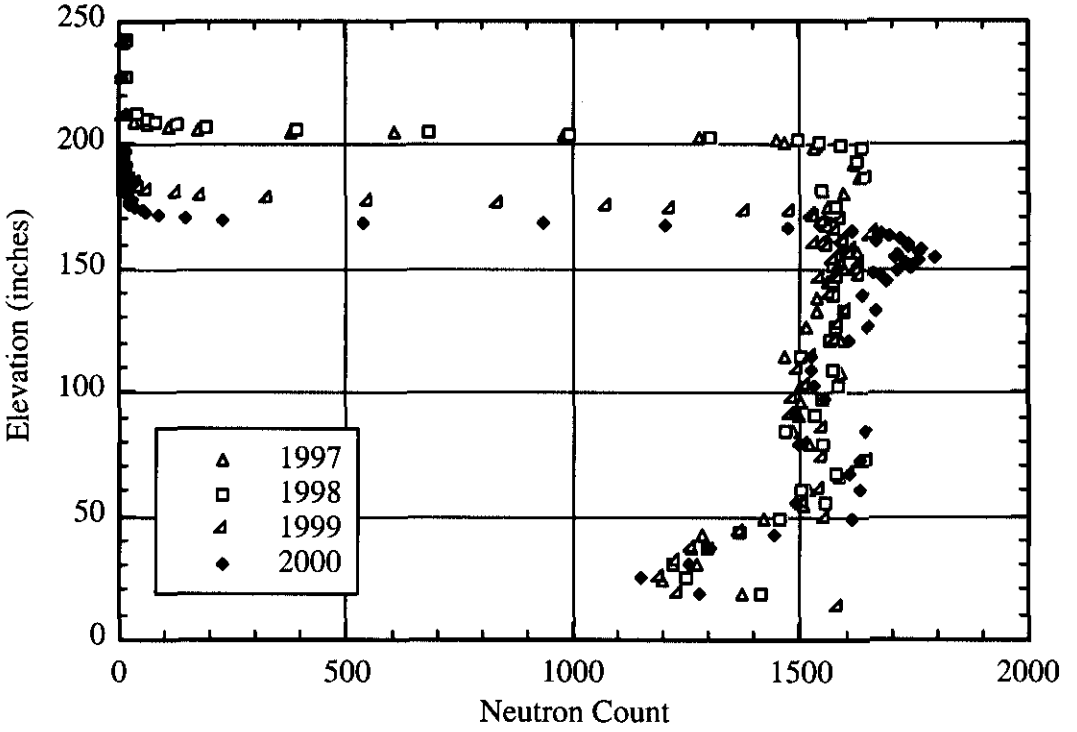


Figure 4-16. Tank 241-S-102 Neutron Logs

The waste densities, estimated yield stress from waste samples prior to pumping, and the 1997 neutron profile are plotted in Figure 4-17. The plots show a general trend of increasing density and strength with depth with relatively uniform values below about 150 inches. This is consistent with a higher liquid fraction near the top of the waste column. The average waste temperature near 100 °F is a good match for the hot cell temperature and solids precipitation, prior to extrusion would not be significant.

The waste temperature history is shown in Figure 4-18. The thermocouple at 294 inches is in the headspace. Unfortunately, there are no thermocouples between 102 and 294 inches. The ILL is plotted with the temperatures to indicate the progress of saltwell pumping. Prior to pumping, the waste temperatures were decreasing at about 1 °F per year. Saltwell pumping has accelerated the rate of decrease to approximately 3 °F per year with no significant changes in the temperature distribution. No significant seasonal temperature variation is visible on the available thermocouples in the waste.

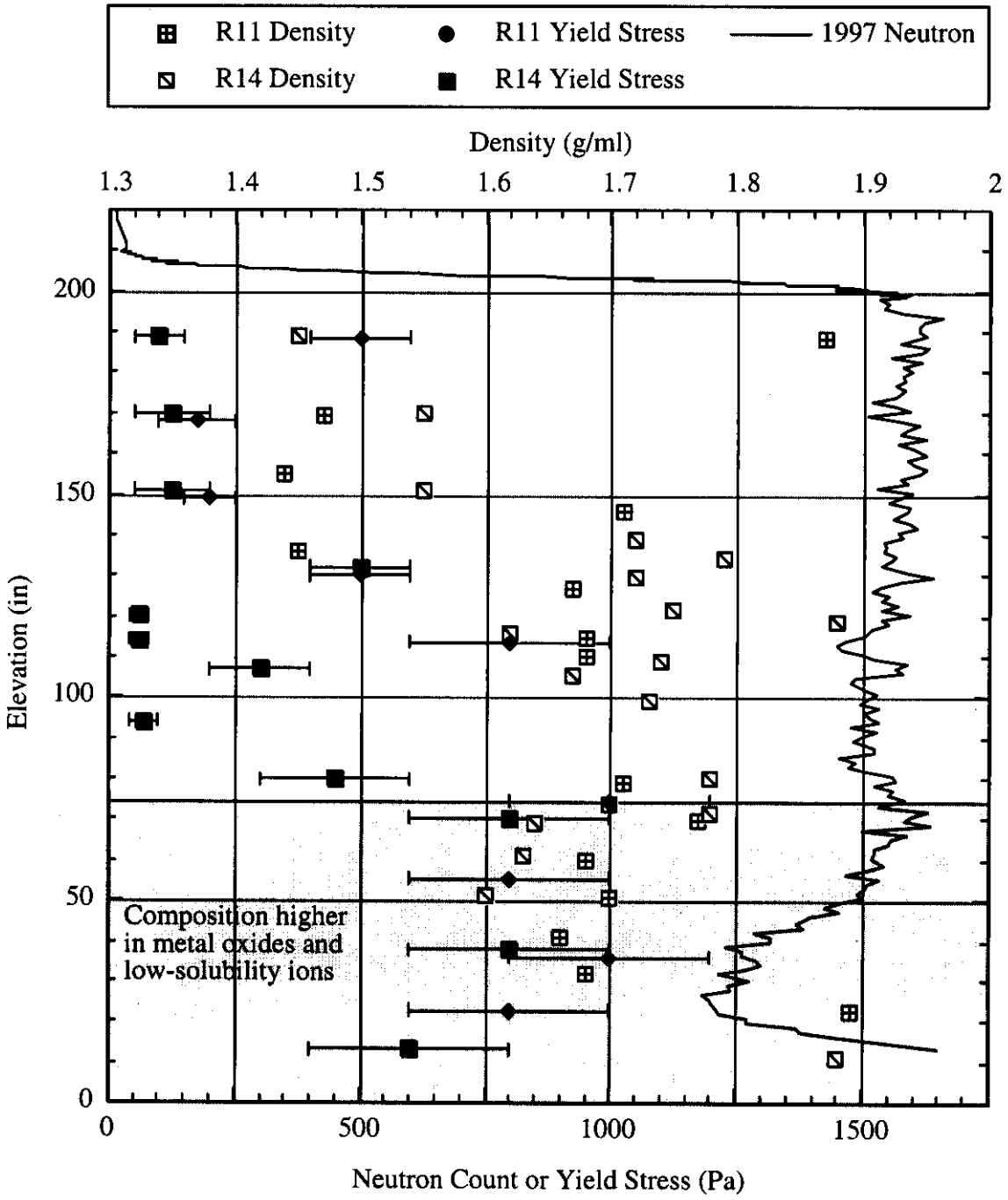


Figure 4-17. Tank 241-S-102 Strength and Density Profile

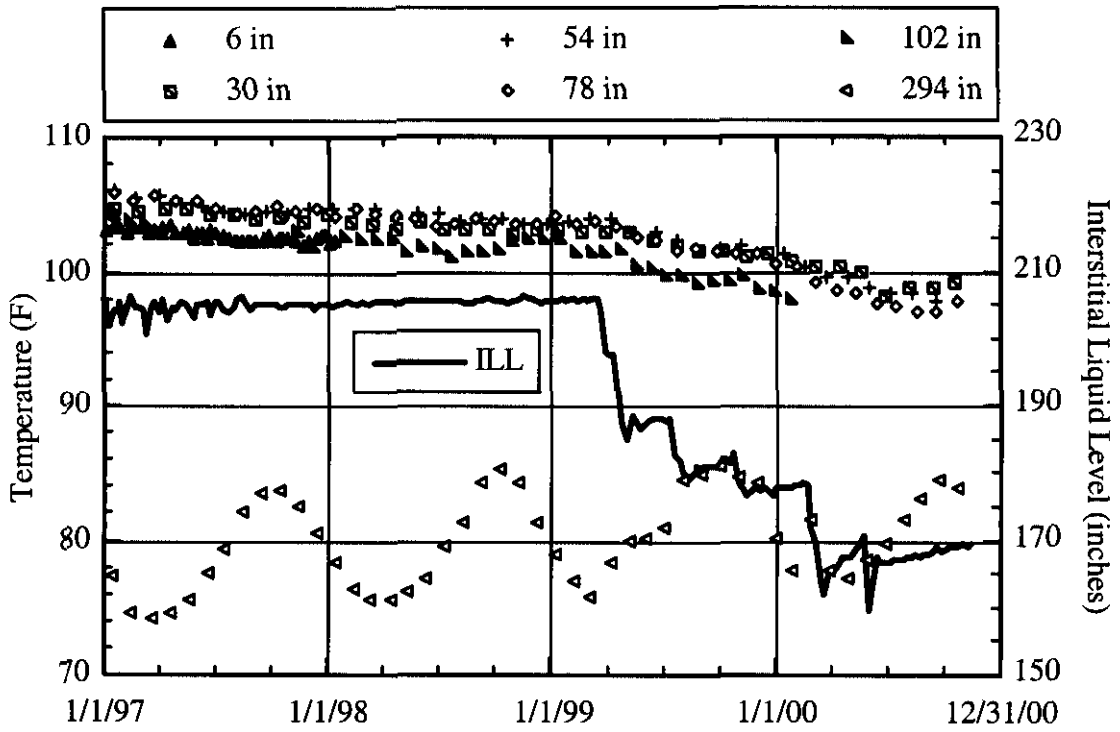


Figure 4-18. Tank 241-S-102 Waste Temperature History

4.1.5 Tank 241-S-111 Waste Configuration

The waste in tank S-111 is a mixture of saltcake and sludge classified as noncomplexed. The waste level is currently 204 inches of which 12 to 60 inches is supernatant as deduced from core samples and the neutron log. The sludge fraction occupies the lower 30 inches of waste. The average gas volume fractions from the RGS, BPE method, and neutron log range from 0.15 to 0.08. The RGS data show the gas fraction increasing almost linearly from zero in the supernatant at the top to almost 0.25 at the tank bottom. Saltwell pumping has not yet begun in tank S-111.

Figure 4-19 shows that both the waste level and ILL have remained essentially constant over the last ten years, rising at most about one inch during that period. The neutron log shown in Figure 4-20 has more variation than that of tank S-102 and may indicate sludge-saltcake layering, retained gas, or both. The generally high neutron counts indicate a high liquid fraction throughout.

The density profile and temperature histories are given in Figures 4-21 and 4-22, respectively. The density increases with depth in the same trend as the gas fraction. The density of the supernatant is typical of that associated with concentrated saltcake. The temperature history shows a discernable annual cycle all the way to the bottom. The lower half of the waste has an average temperature of about 87 °F while the top half averages about 80 °F. The average temperature in the bottom 54 inches is decreasing at slightly less than 1 °F per year while the temperature of the rest of waste is constant.

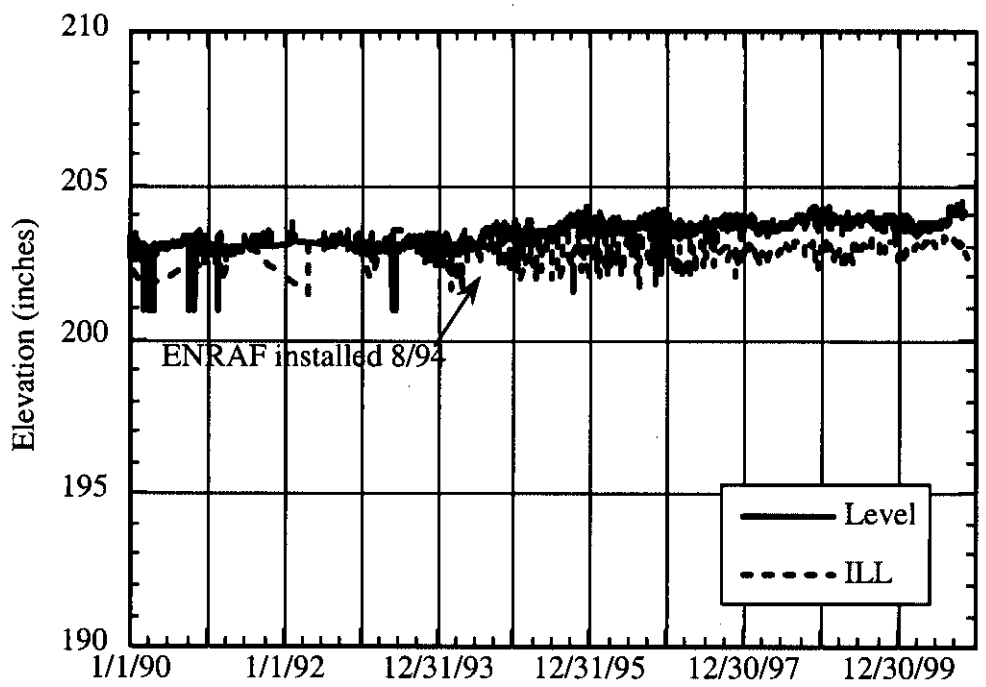


Figure 4-19. Tank 241-S-111 Waste Level and Interstitial Liquid Level History

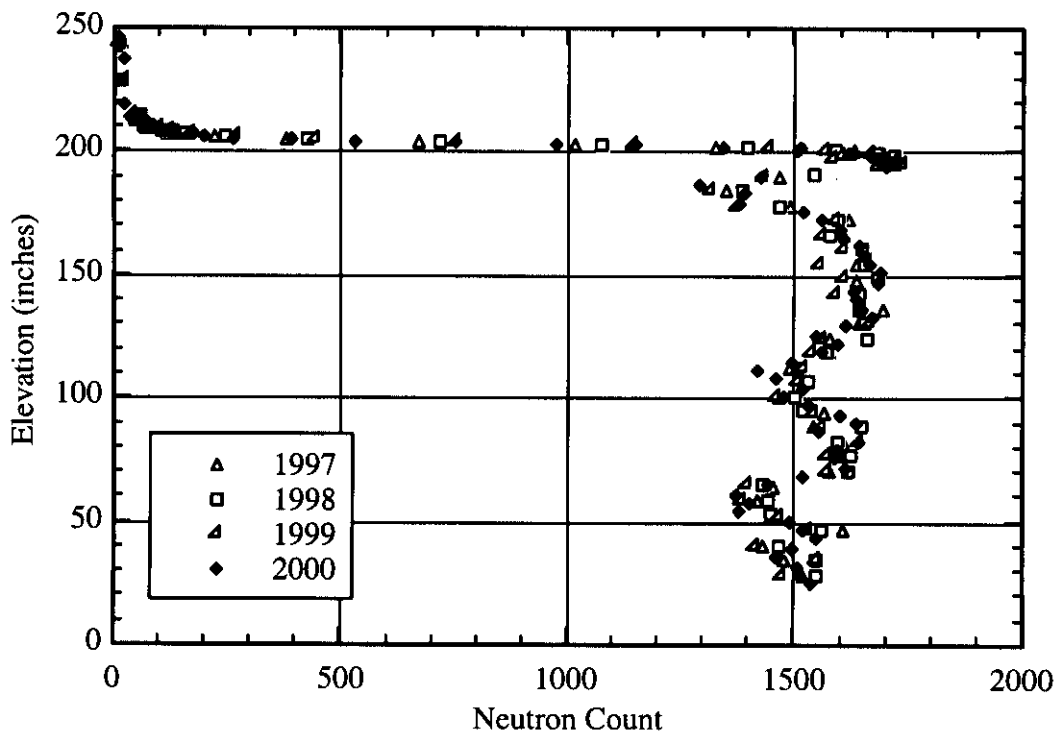


Figure 4-20. Tank 241-S-111 Neutron Logs

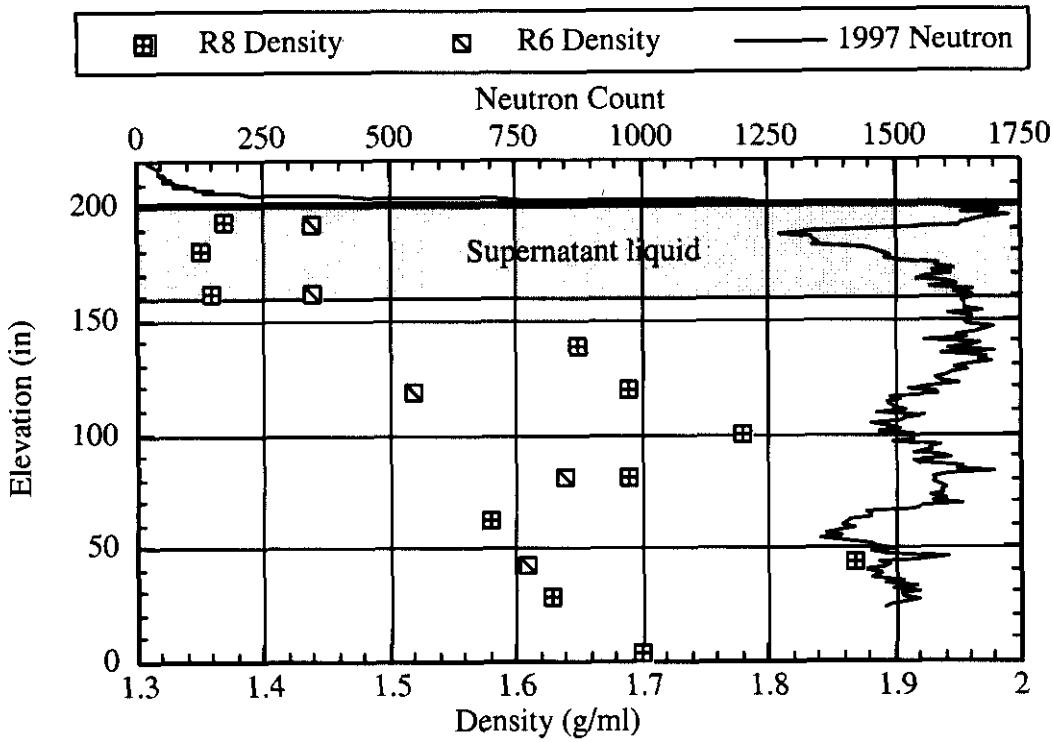


Figure 4-21. Tank 241-S-111 Density Profile

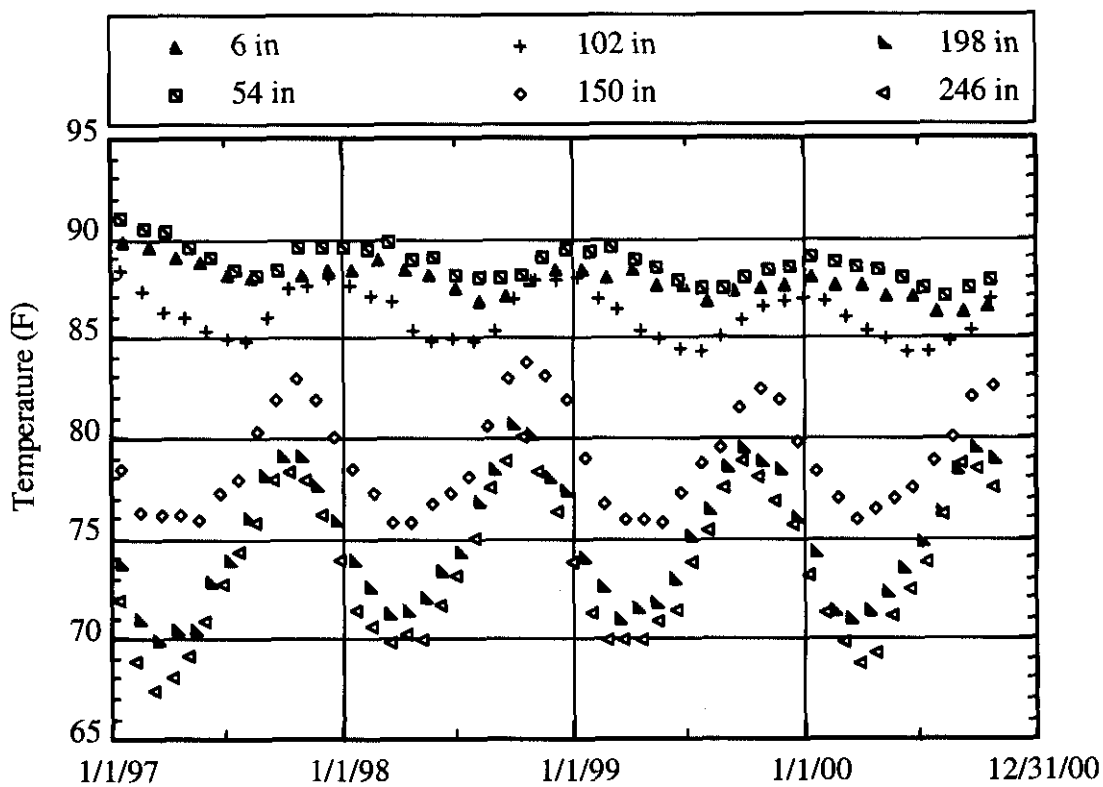


Figure 4-22. Tank 241-S-111 Waste Temperature History

4.1.6 Tank 241-S-112 Waste Configuration

Tank S-112 contains 189 inches of saltcake that is classified as noncomplexed, like tank S-111. However, tank S-112 has considerably less liquid. The tank was saltwell pumped in 1978, which removed 150 kgal of liquid. A mosaic of still photographs constructed in 1988 shows a large, steep-sided irregular cavity in the central region of the tank. The current data are consistent with this 12-year old photograph.

The ILL is about 123 inches, 66 inches below the ENRAF™ waste level, as shown in Figure 4-23. The waste level has remained constant except for ± 10-inch fluctuations in 1996 and early 1997, apparently involved with installation and initial operation of the ENRAF™ level gauge, that brought the level to its current steady value after a last abrupt drop. The ILL has been rising linearly at a rate of slightly less than one inch per year. This indicates a gradual gas accumulation in pore-filling bubbles.

The neutron log shown in Figure 4-24 clearly shows a very "dry" region from the waste level down to the ILL where the liquid content increases abruptly to approximately full saturation. The evolution of the neutron logs also shows a definite liquid accumulation at 110 to 130 inches. The decrease in neutron count between 90 and 110 inches suggests gas accumulation in this region. A rough estimate of the average gas fraction based on the neutron log is 0.10 to 0.15 in the lower 120 inches.

The tank S-112 waste temperature history, given in Figure 4-25, is similar to that of tank S-111 with a discernable annual cycle, except at the very bottom. The average temperature of the lower, "wet" portion of the waste is about 83 °F while that of the "dry" portion is approximately 78 °F.

4.1.7 Tank 241-SX-101 Waste Configuration

Tank SX-101 contains about 450 kgal of saltcake classified as dilute complexed waste. The ILL, measured by the neutron probe in Riser 14 at about the 28-ft radius, is about one inch higher than the waste level measured at Riser 4 at the 15-ft radius. A rough estimate from the neutron log places the average retained gas volume fraction in tank SX-101 at 0.05. Saltwell pumping began November 20, 2000, and is not reflected in the data presented in this section.

The level history and neutron logs are provided in Figures 4-26 and 4-27, respectively. The ILL is a good indication of the waste surface near the 30-foot radius and has been declining steadily since 1990, probably by evaporation due to the relatively high waste temperature. The abrupt, 5-inch rise in August 2000 was the result of water added during installation of the saltwell screen. Pumping, which began November 20, 2000, is not shown on the plot.

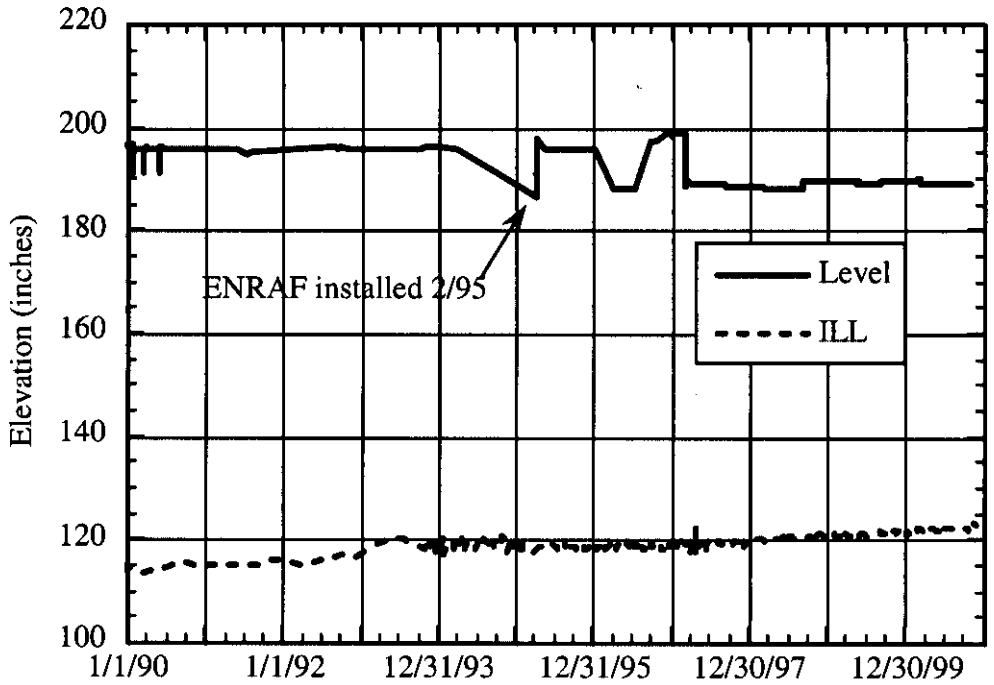


Figure 4-23. Tank 241-S-112 Waste Level and Interstitial Liquid Level History

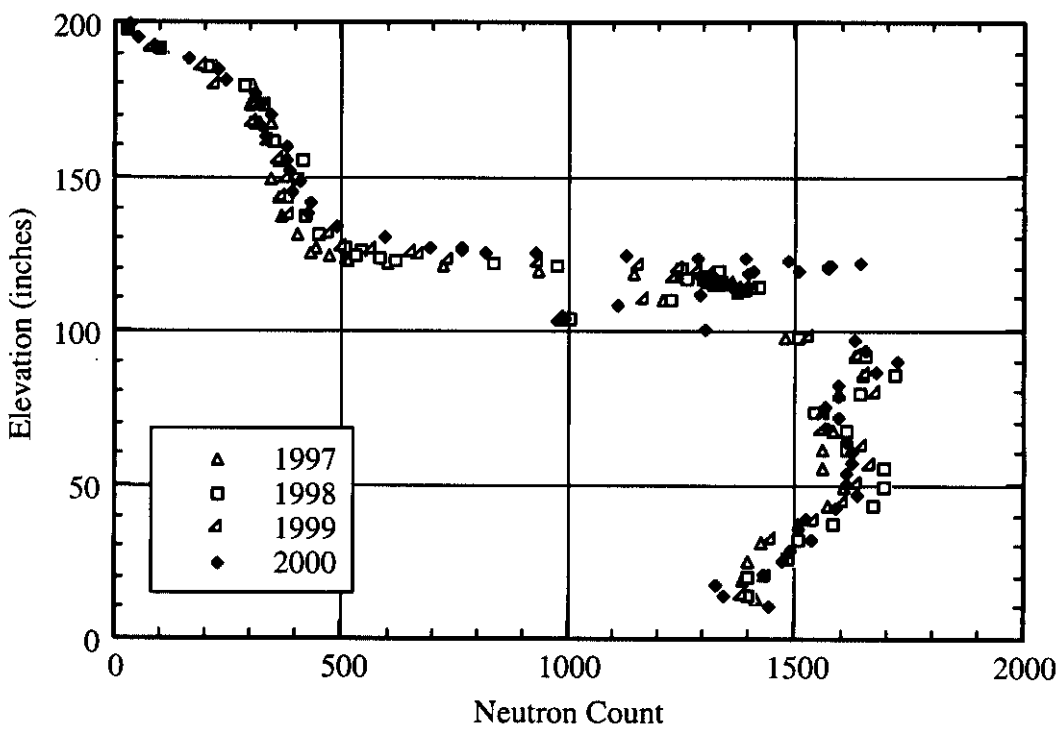


Figure 4-24. Tank 241-S-112 Neutron Logs

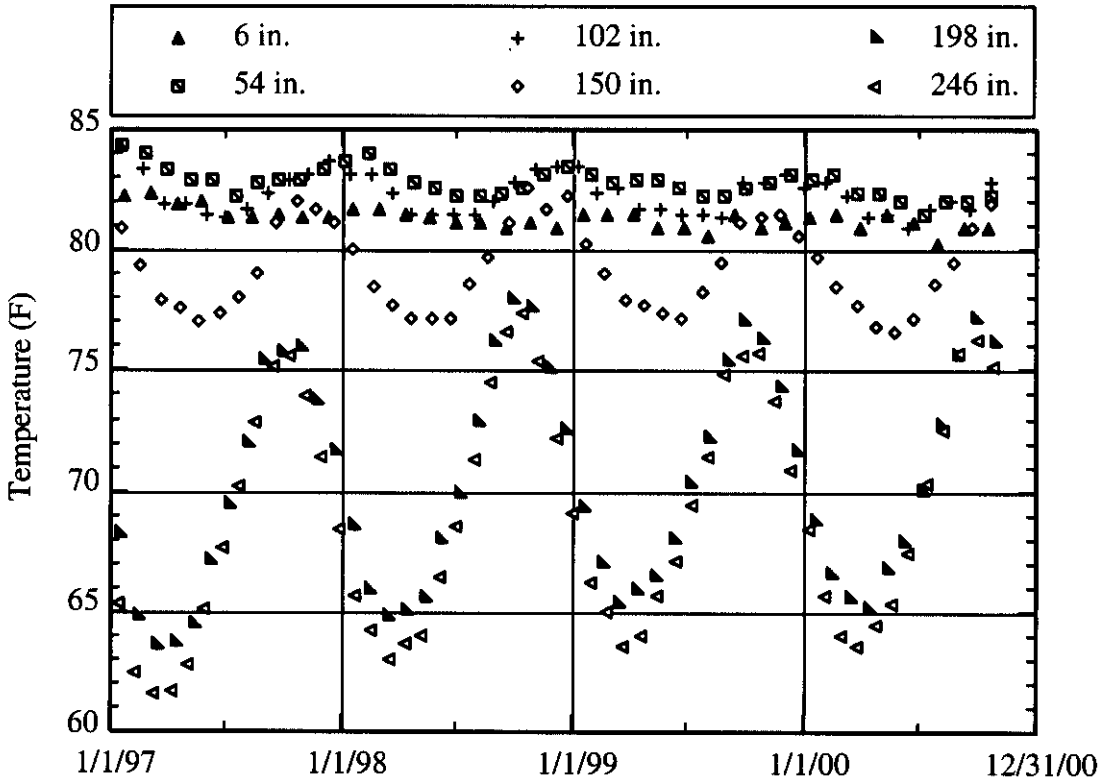


Figure 4-25. Tank 241-S-112 Waste Temperature History

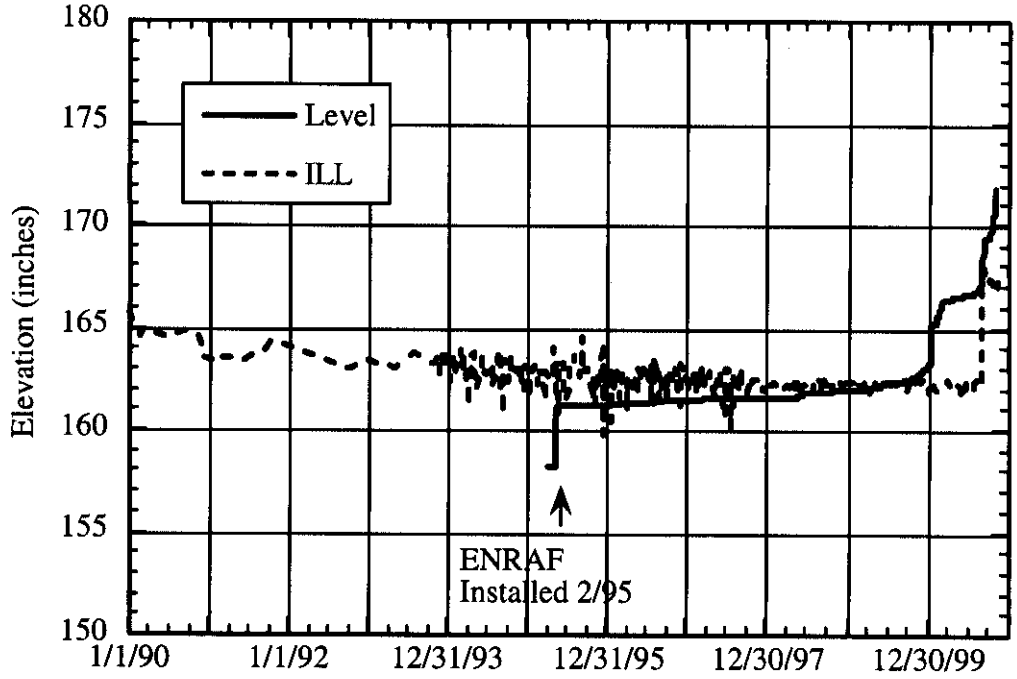


Figure 4-26. Tank 241-SX-101 Waste Level and Interstitial Liquid Level History

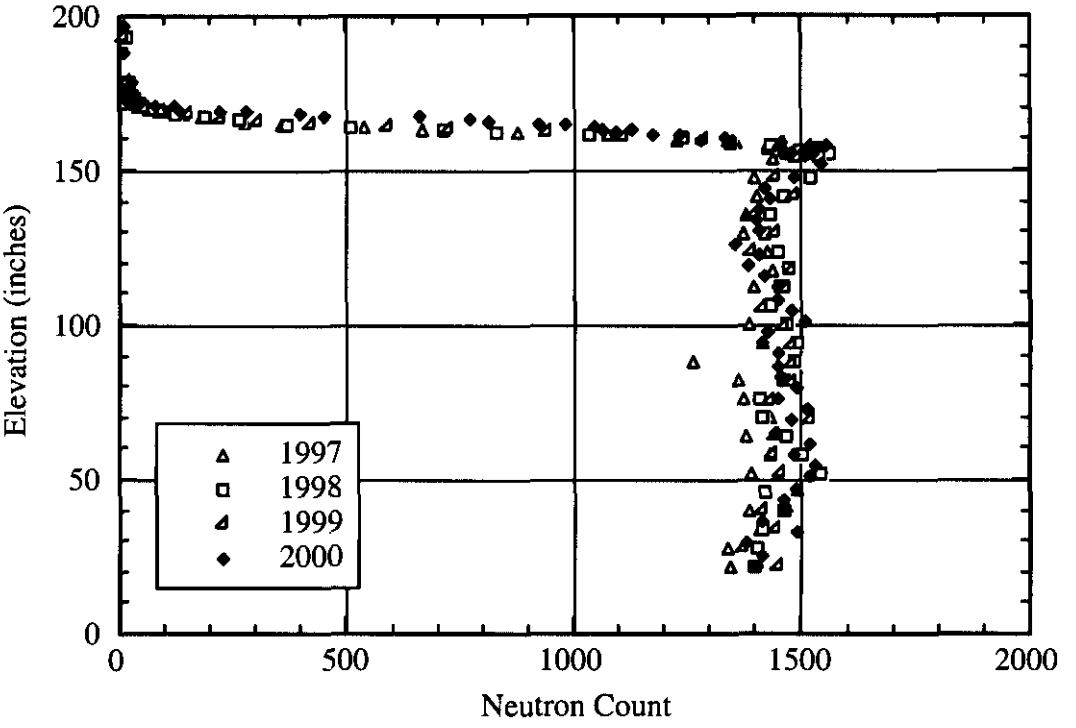


Figure 4-27. Tank 241-SX-101 Neutron Logs

The density profile and 1997 neutron log are plotted in Figure 4-28. The relatively low densities from the core in Riser 19 indicate a high liquid content that is inconsistent with the relatively low and uniform neutron count, especially since Riser 19 is near the tank wall at about the 31-ft radius. The density of samples from Riser 4, in the central region of the tank at about the 15-ft radius matches the expected value. The temperature history in Figure 4-29 shows almost constant temperatures with a barely perceptible annual cycle of 1 to 2 °F with waste temperatures ranging from 130 °F down to 115 °F at 116 inches. There are no thermocouples in the upper 50 inches of waste.

4.1.8 Tank 241-SX-102 Waste Configuration

Tank SX-102 contains saltcake concentrated sufficiently to classify as DSSF. The waste level, measured in Riser 4 at the 15-ft radius, is currently 192 inches while the ILL, measured in Riser 14, near the 30-ft radius, is one inch higher. The tank has not yet been pumped. The gas volume fraction estimated from the neutron log is approximately 0.07, somewhat higher than tank SX-101.

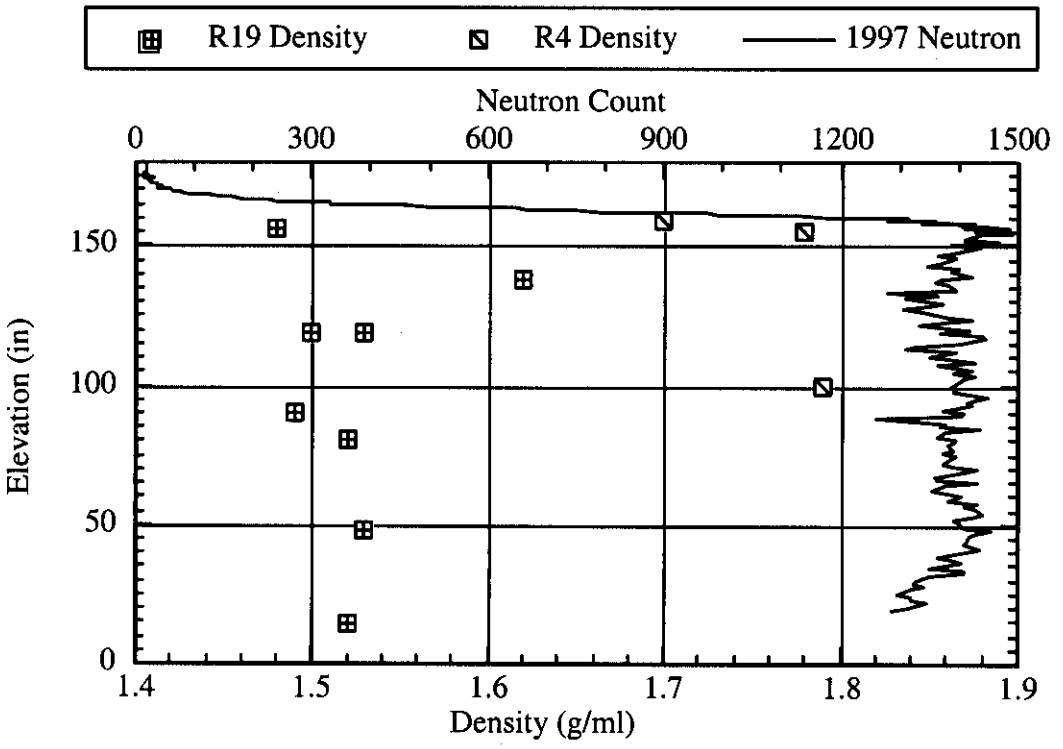


Figure 4-28. Tank 241-SX-101 Density Profile

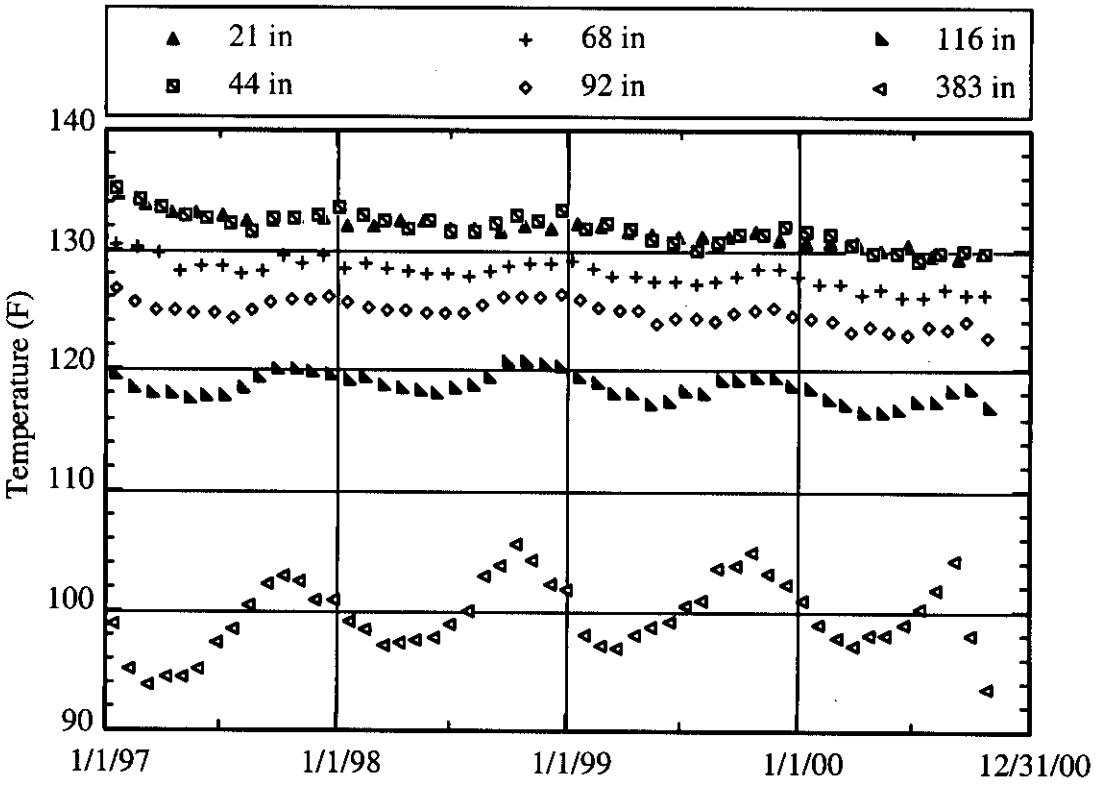


Figure 4-29. Tank 241-SX-101 Waste Temperature History

The level history in Figure 4-30 shows that the ILL has decreased steadily since 1990 at the rate of 1/2 inch per year, probably from evaporation due to the relatively high waste temperature. The rate appears to have flattened almost entirely since 1998. The level measurement began following the ILL in 1995, and has remained 1 to 3 inches below the ILL since then. Since the LOW and ENRAF™ are at different radii, this may be more of an indication of a dished surface than of supernatant.

The neutron logs given in Figure 4-31 show a relatively high moisture content but probably not a supernatant layer. Surface photos from 1988 show an apparently dry surface around the LOW at that time. The density profile and the 1997 neutron log are plotted in Figure 4-32. The density increases with depth from 1.5 to 1.6 g/mL near the top to about 1.8 g/mL near the bottom.

The temperature history shown in Figure 4-33 is uninteresting. The waste temperatures in the lower 89 inches are decreasing at about 1 °F per year. The 89- and 113-inch thermocouples indicate a barely discernible annual cycle. There are no thermocouples in the upper 80 inches of the waste.

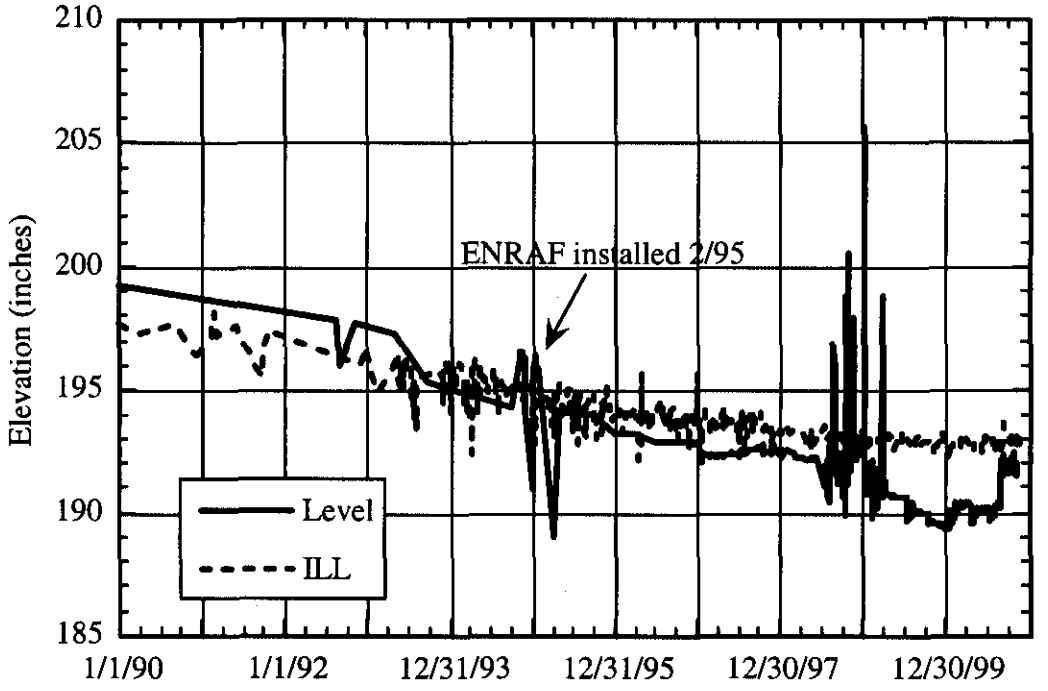


Figure 4-30. Tank 241-SX-102 Waste Level and Interstitial Liquid Level History

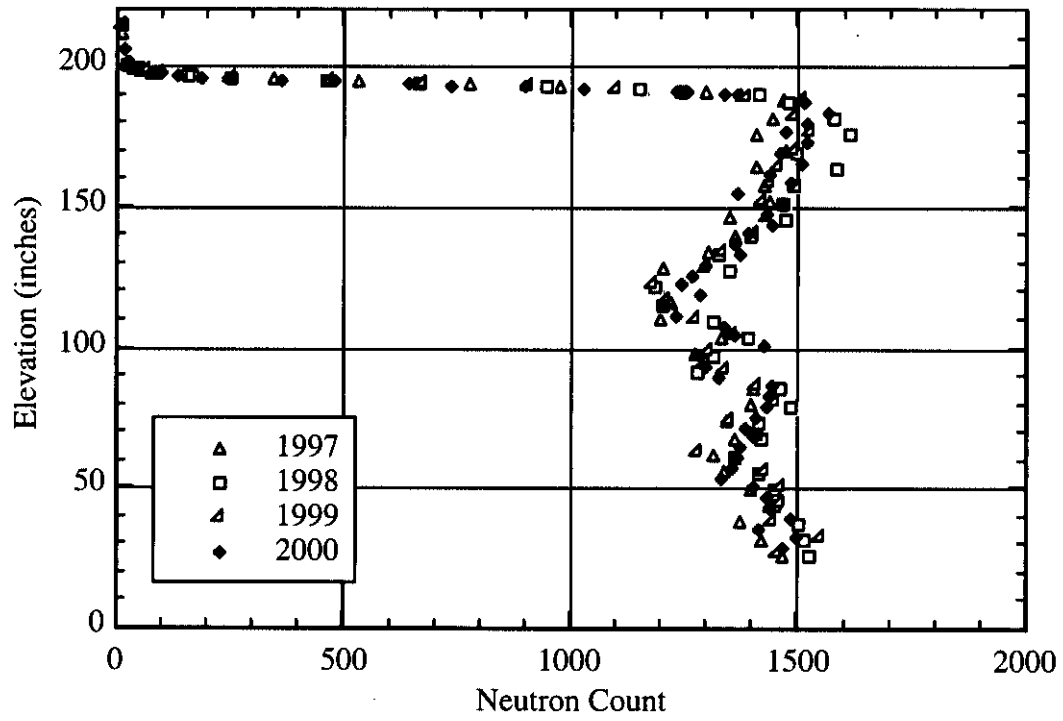


Figure 4-31. Tank 241-SX-102 Neutron Logs

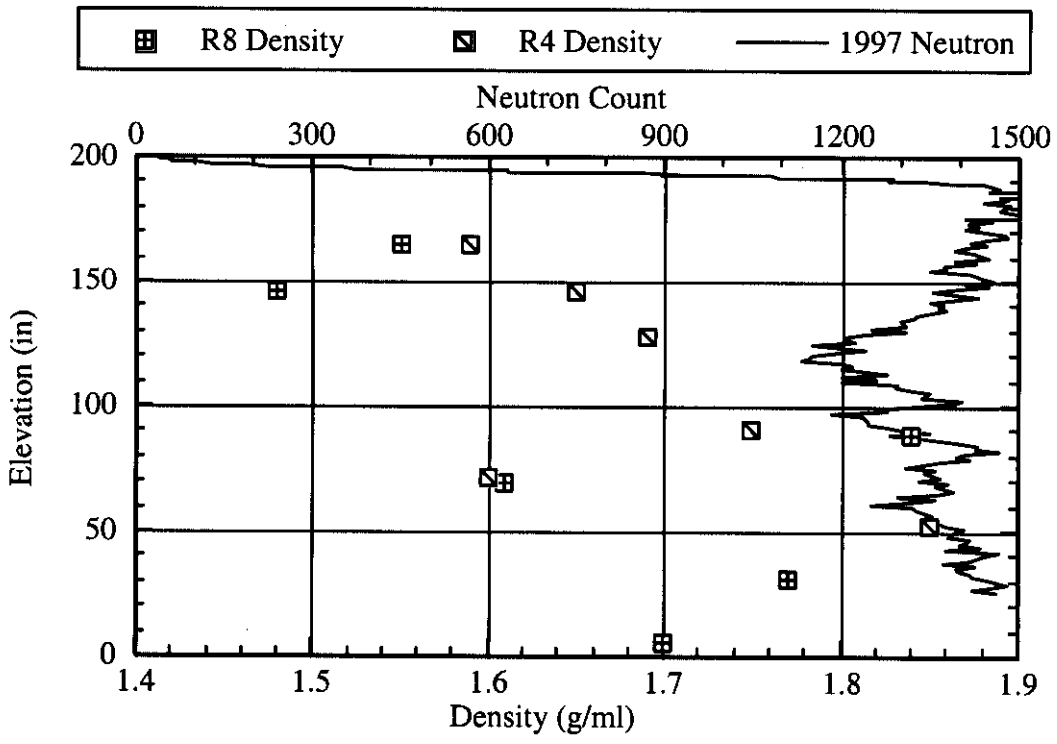


Figure 4-32. Tank 241-SX-102 Density Profile

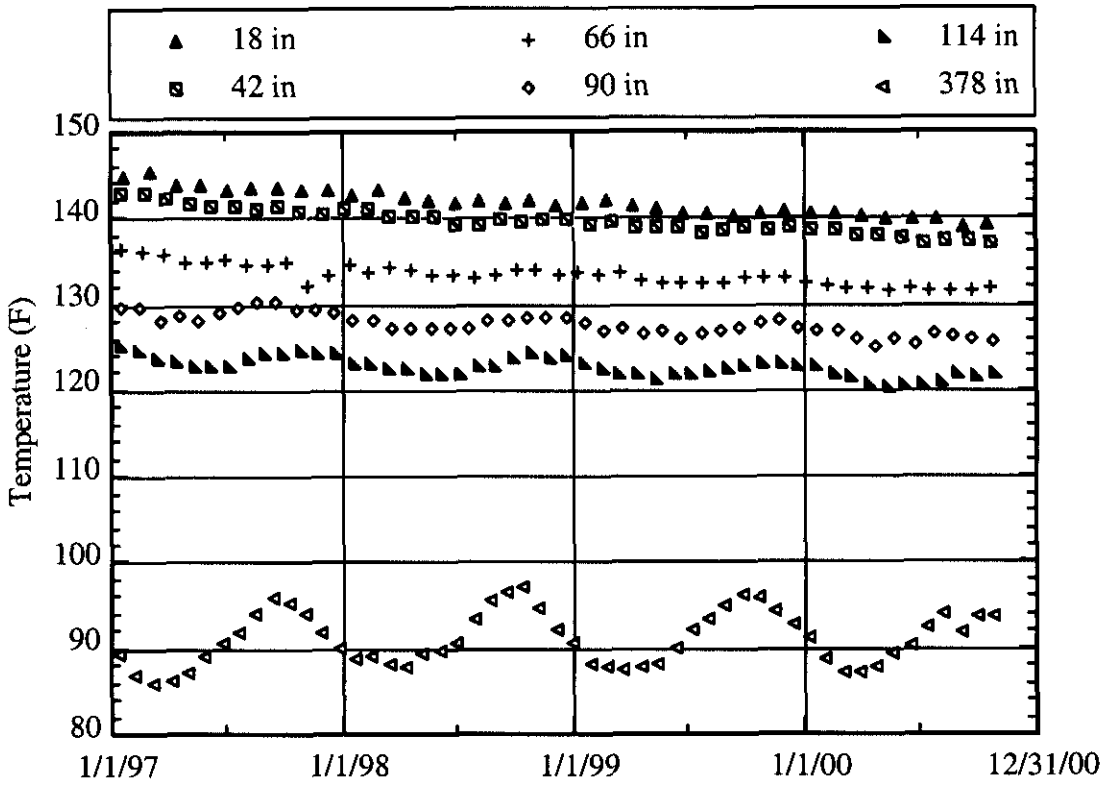


Figure 4-33. Tank 241-SX-102 Waste Temperature History

4.1.9 Tank 241-SX-103 Waste Configuration

The waste in tank SX-103 contains both saltcake and sludge. It is classified as noncomplexed, which implies a relatively low concentration of organic components. Saltwell pumping was initiated October 26, 2000, and 39 kgal out of an estimated total of 132 kgal of liquid have been removed to date. The first month's saltwell pumping history in tank SX-103 is shown in Figure 4-34.

The level history is shown in Figure 4-35. Since 1990, the ILL has declined at about 1/2 inch per year and the surface level at close to 1 inch per year. The differing rates may be the result of the LOW being much closer to tank wall than the ENRAF™ (see Figure 2-12). The waste level is currently at 219 inches and dropping with continued pumping. At this early stage of pumping, the waste level has dropped 15 inches, which is a good match for the 14-inch equivalent depth of liquid removed. The ILL has only dropped 8 inches due to pumping, apparently because it is further from the saltwell screen and drainage from this area has been slow.

The tank SX-103 neutron log is shown in Figure 4-36. Prior to pumping, the high neutron count near the waste surface indicates a layer of supernatant on the order of 12 inches thick. Core samples indicated a much thicker liquid layer nearer the tank center. Riser 11 core samples from between 50 and 125 inches indicate a very low water content at about the same radius as the

LOW. Riser 8 samples show a more normal liquid fraction. There is probably an intermediate layer of liquid between 125 and 140 inches above the dry layer.

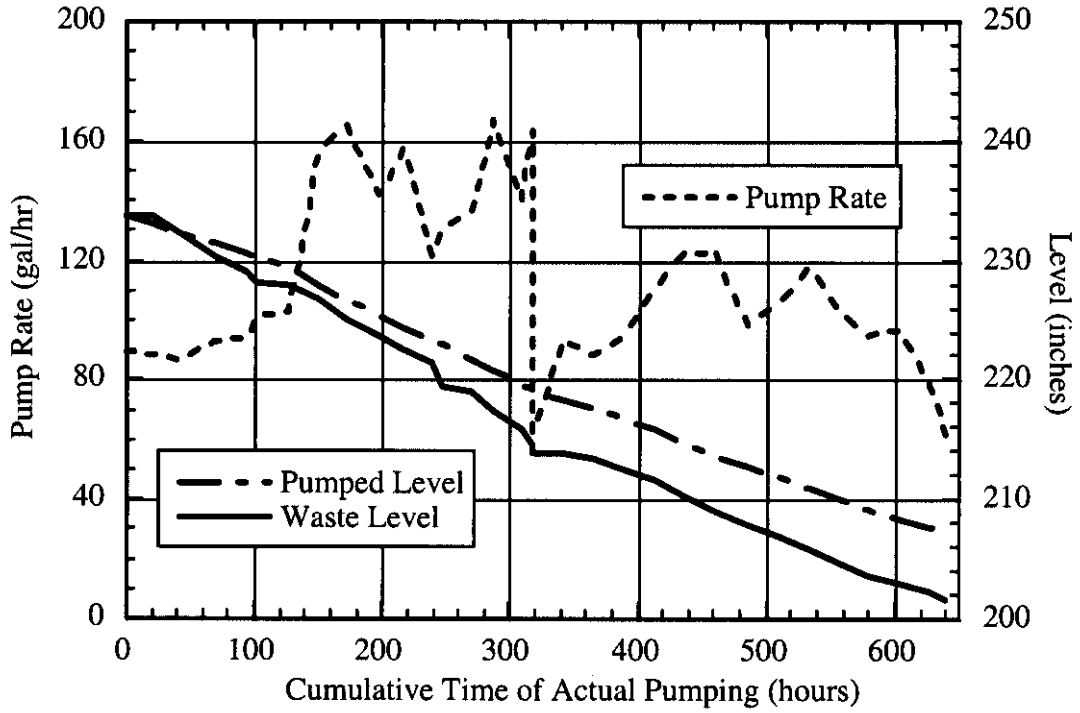


Figure 4-34. Tank 241-SX-103 Saltwell Pumping History

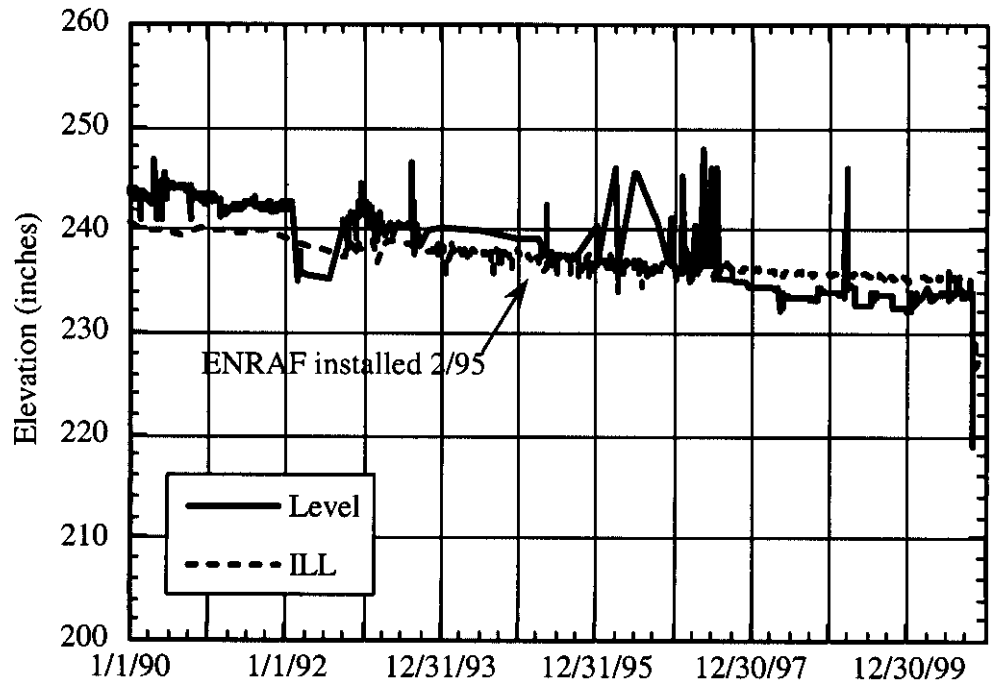


Figure 4-35. Tank 241-SX-103 Waste Level and Interstitial Liquid Level History

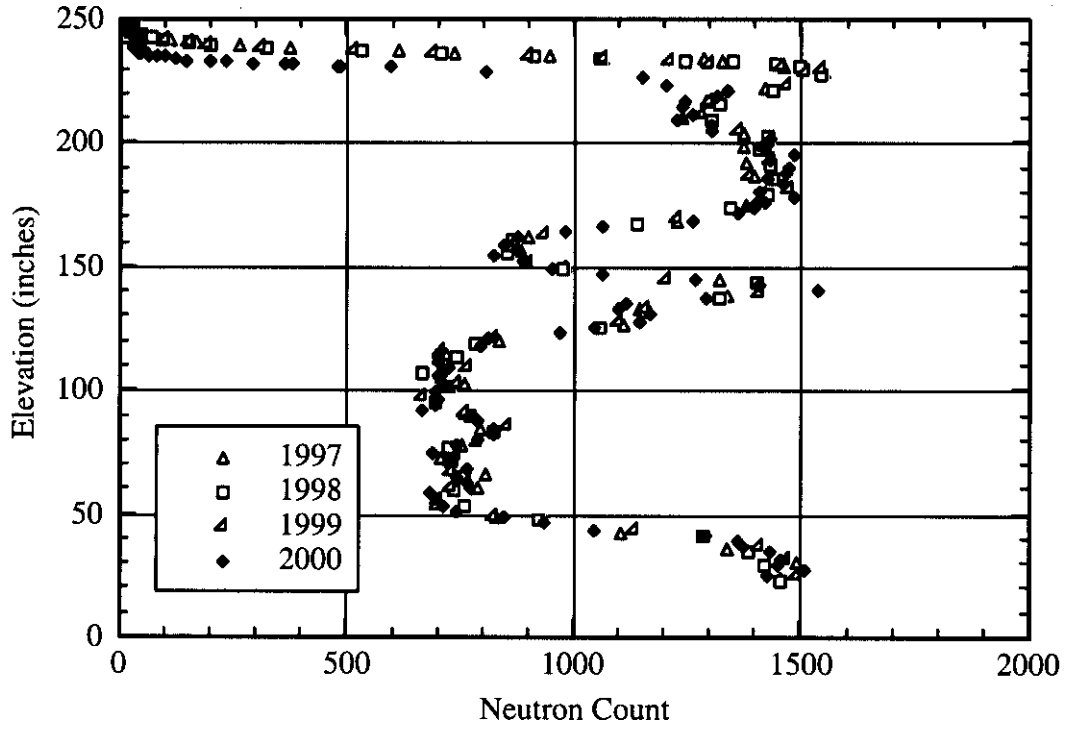


Figure 4-36. Tank 241-SX-103 Neutron Logs

The density profiles for the two risers core sampled in 1998 are given in Figure 4-37 along with the 1997 neutron log. The core from Riser 7 shows a probable layer of supernatant that is at least 70 inches and up to 120 inches deep. A 70-inch layer of supernatant is implied at Riser 11, which is farther from the tank center. The very high densities between 100 and 150 inches in Riser 11 may be indicative of the conditions responsible for the very low neutron counts near the tank wall at the LOW.

Tank SX-103 temperature history is shown in Figure 4-38. Tank SX-103 is one of the warmer tanks with waste temperatures at a relatively uniform at 155 to 157 °F up to 52 inches decreasing to about 142 °F at 100 inches. The 367-inch thermocouple is in the tank headspace. The temperatures are decreasing at about 2 °F per year. No annual cycle is visible in the waste at 100 inches and below.

4.1.10 Tank 241-SX-104 Waste Configuration

Tank SX-104 contains concentrated saltcake with some sludge that is classified as DSSF. Saltwell pumping began July 23, 1998, and was terminated one-year later on July 25, 1999, because of equipment failure. The saltwell pumping history in tank SX-104 is summarized in Figure 4-39. When pumping ceased, 125 kgal, or 86%, of liquid out of an estimated total drainable volume of 144 kgal had been removed. The retained gas volume fraction based on the neutron logs is only 0.08. The BPE result prior to pumping indicated an immeasurably small retained gas volume.

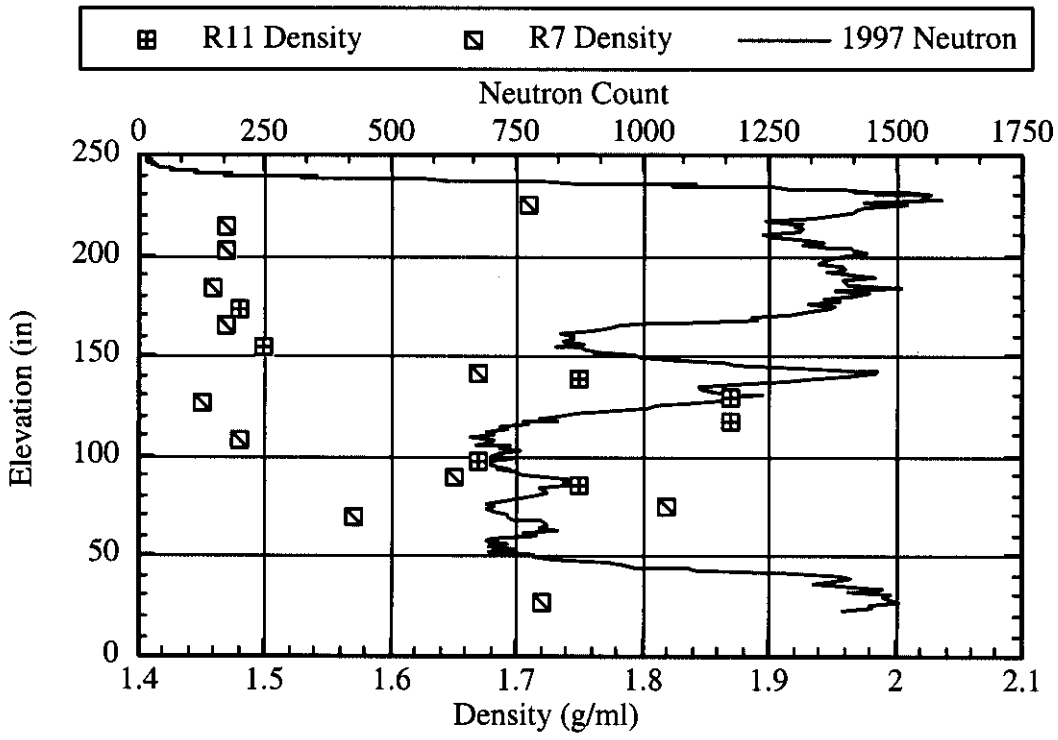


Figure 4-37. Tank 241-SX-103 Density Profile

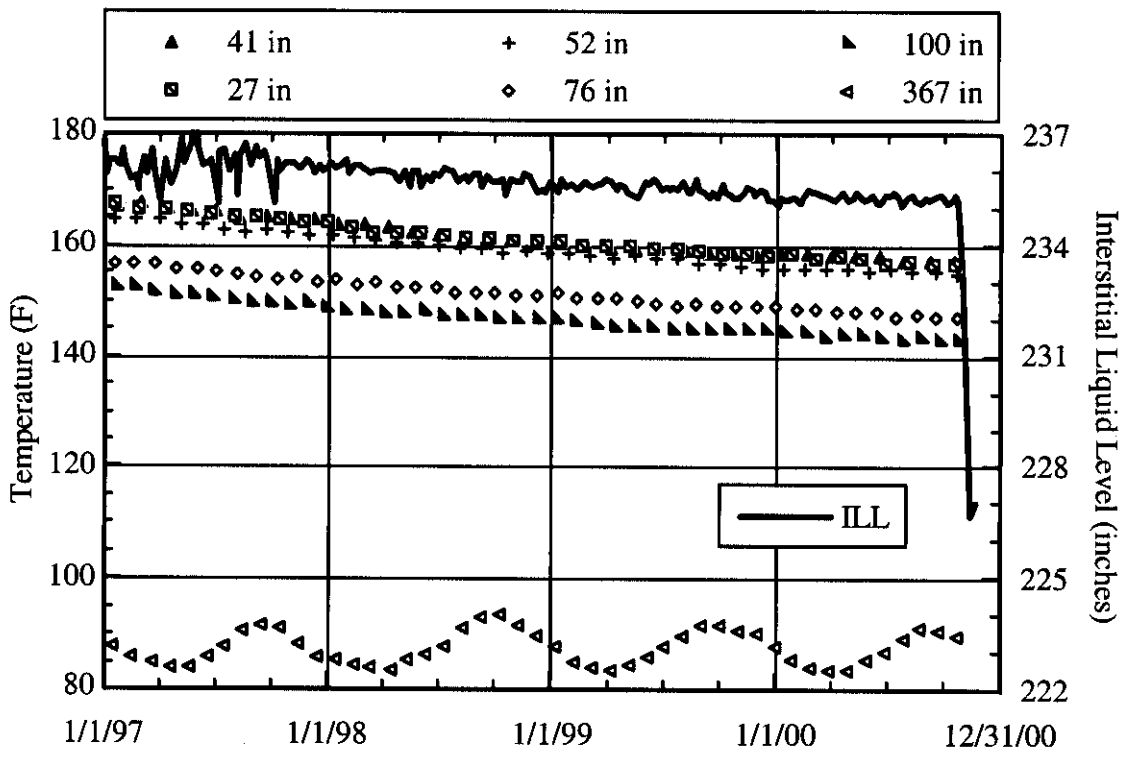


Figure 4-38. Tank 241-SX-103 Waste Temperature History

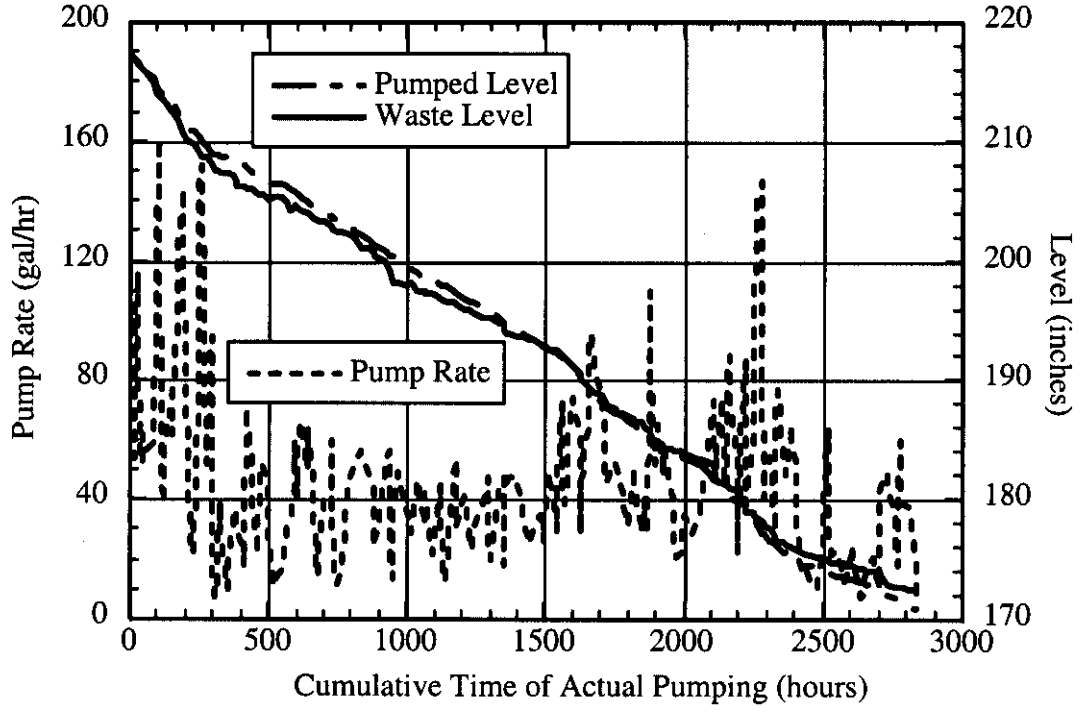


Figure 4-39. Tank 241-SX-104 Saltwell Pumping History

The waste levels and neutron logs for tank SX-104 are shown in Figures 4-40 and 4-41, respectively. Prior to pumping, both remained essentially constant. During pumping the surface level closely followed the pumped level (see Figure 4-39) indicating the liquid was behaving as supernatant throughout the campaign. The ILL dropped to 73 inches during pumping but recovered 22 inches to its current level after about six months as some of the liquid in the unsaturated layer above slowly drained. During the same period, the surface level gradually subsided an additional 3 inches. The neutron logs show that most of the liquid was removed from the upper 130 inches or 60% of the waste column. However, the region below about 80 inches has not changed significantly.

The waste temperature history given in Figure 4-42 shows a 15 °F drop in temperature below 100 inches during pumping, but the difference between temperatures in this layer did not change. The ILL indicates all four of the bottom thermocouples are still in waste that is saturated. However, the difference between the 76-inch and 100-inch thermocouple temperatures, the latter being above the ILL, increased from 7 °F to 16 °F in the last months of pumping. The waste temperatures in the saturated layer range from 120 to 140 °F.

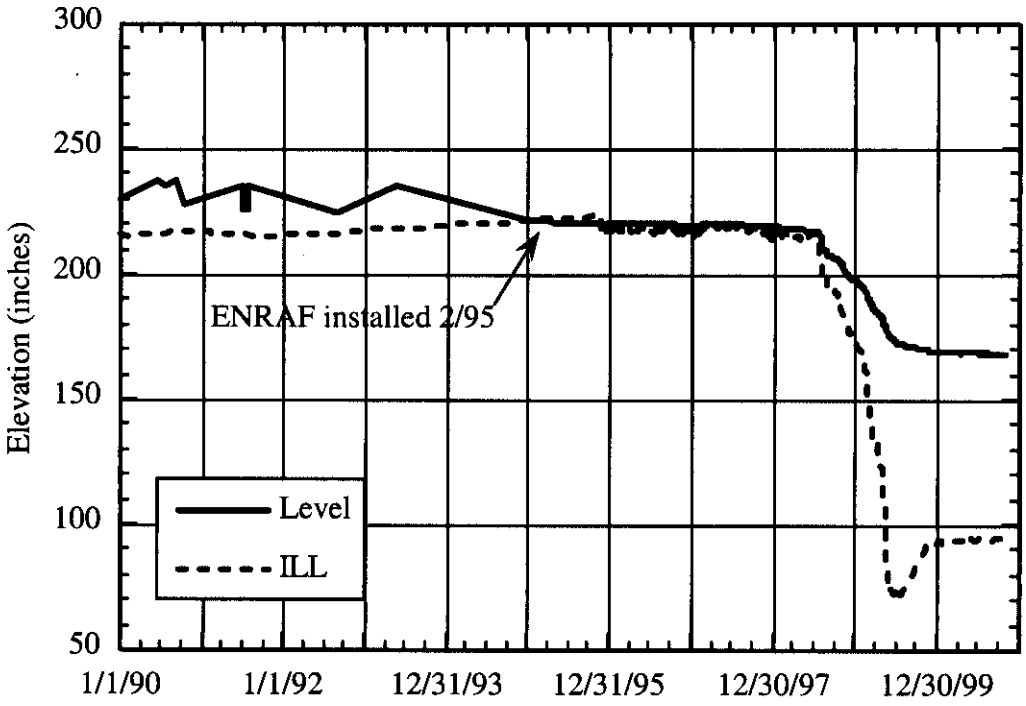


Figure 4-40. Tank 241-SX-104 Waste Level and Interstitial Liquid Level History

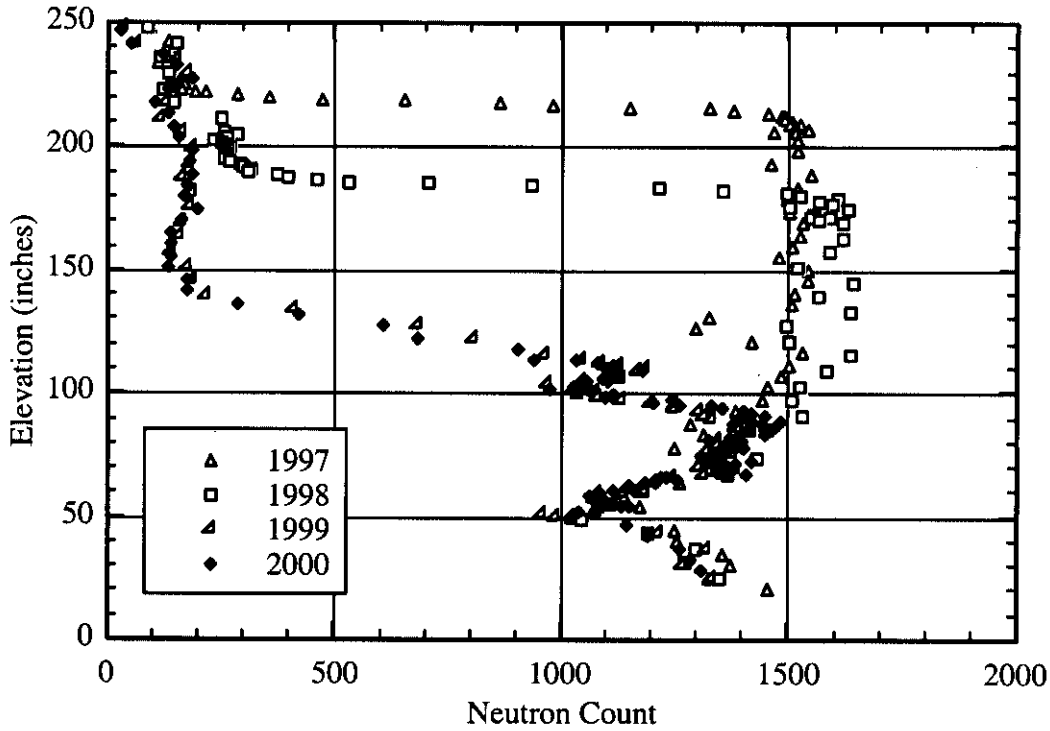


Figure 4-41. Tank 241-SX-104 Neutron Logs

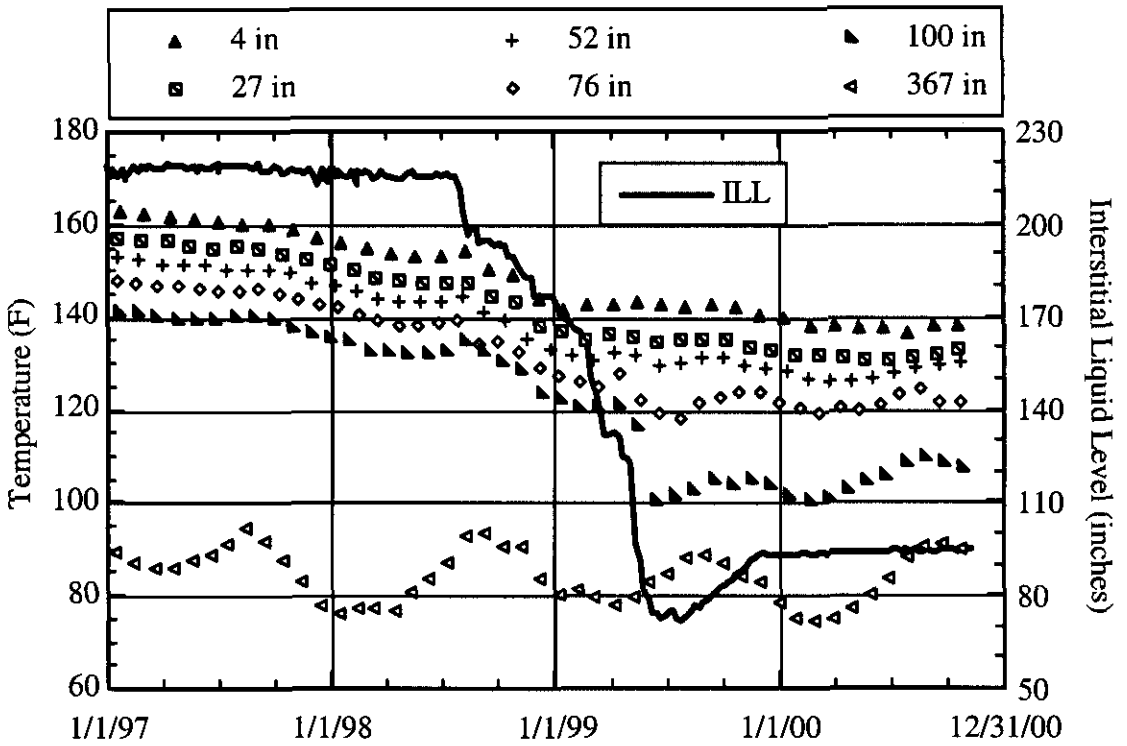


Figure 4-42. Tank 241-SX-104 Waste Temperature History

4.1.11 Tank 241-SX-105 Waste Configuration

Tank SX-105 contains saltcake concentrated to DSSF. Saltwell pumping began August 8, 2000, and 132 kgal of the estimated 141 kgal of pumpable liquid have been removed. Saltwell pumping progress is summarized in Figure 4-43. The pumping rate remained between 1 and 2 gpm for the first 54 days of pumping time as the free liquid was removed. The pumping rate in the last 500 hours has been on the order of 1/2 gpm, more typical of draining interstitial liquid. The relatively high current drainage rate suggests there may be more drainable liquid than originally estimated. The average retained gas volume fraction prior to pumping was estimated at roughly 0.06 based on the neutron log.

The waste level history in Figure 4-44 shows a large and abrupt drop at the beginning of saltwell pumping. The level drop as of November 2000 was 84 inches, which is almost twice the 48-inch equivalent depth of liquid removed from the full tank area (see Figure 4-43). This indicates that the liquid removal is not uniform across the tank. The ILL provides little additional information on pumping since the last available log was August 15, only a week after pumping started. Both level and ILL had been declining gradually prior to pumping at a rate of approximately one-inch per year, probably from evaporation. The neutron logs shown in Figure 4-45 indicate a very wet and relatively uniform waste column.

The density profile from September 1998 core samples in tank SX-105 is given in Figure 4-46. Riser 6 is at the 10-ft radius and Riser 14 at 30 ft, less than 10 ft from the tank wall. The densities between about 140 inches and the waste surface average 1.5 g/mL, which is consistent with supernatant liquid. The densities between about 60 and 130 inches are also relatively uniform with lower values nearer the tank center in Riser 6. However, the densities from both risers indicate a relatively high liquid content consistent with the generally high neutron counts in Figure 4-45.

Figure 4-47 presents the tank SX-105 temperature history. Tank SX-105 is the warmest of the Watch List SSTs with a peak temperature currently at 162 °F. Only three thermocouples have been operable in the waste since late 1998 covering the region between 27 and 76 inches. The 367-inch thermocouple is in the tank headspace. The three waste temperatures show a steady, gradual decrease at almost 3 °F per year with no seasonal variation until late June 2000. The 52- and 76-inch thermocouples began dropping at an accelerated rate on June 22, and the 27-inch thermocouple suddenly increased about 4 °F on June 30.

The waste temperature changes that pre-date saltwell pumping by over a month are attributed to the disturbance of installing the saltwell screen. In tank SX-105 this process was reported to use 1,300 gal of water. Saltwell pumping had the additional effect of further accelerating the waste temperature decrease. The headspace temperature (367-inch thermocouple) rose 6 °F during the first week of saltwell pumping. This might be the result of some hotter waste appearing at the surface or around the periphery; a tank wall area is exposed by the descending waste level.

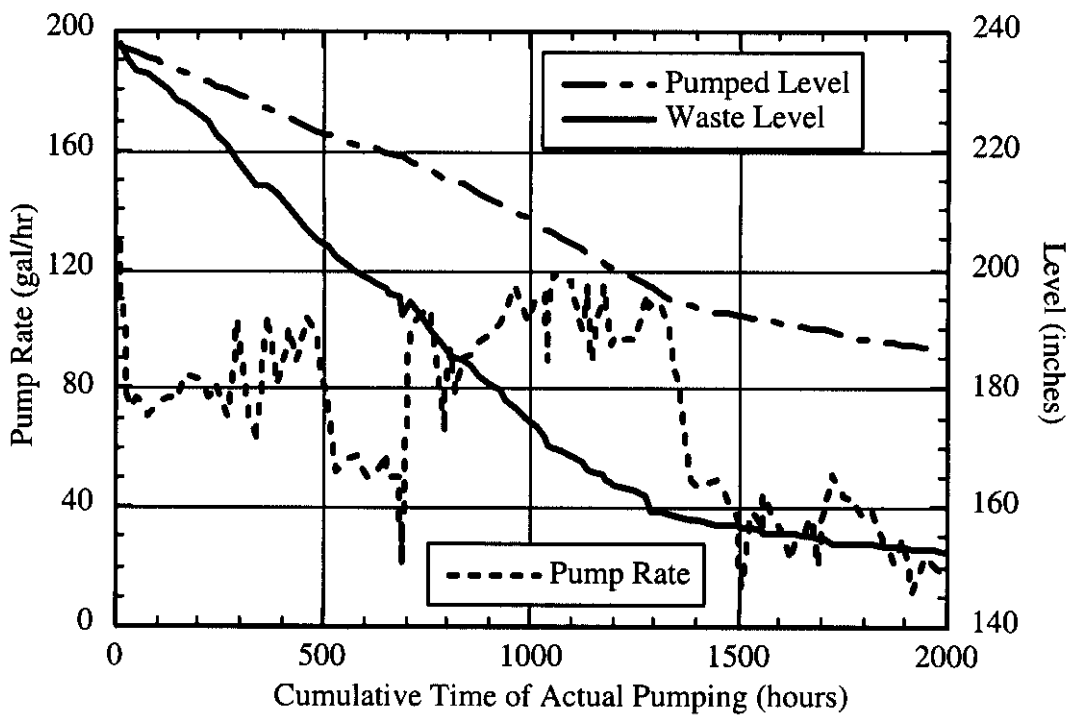


Figure 4-43. Tank 241-SX-105 Saltwell Pumping History

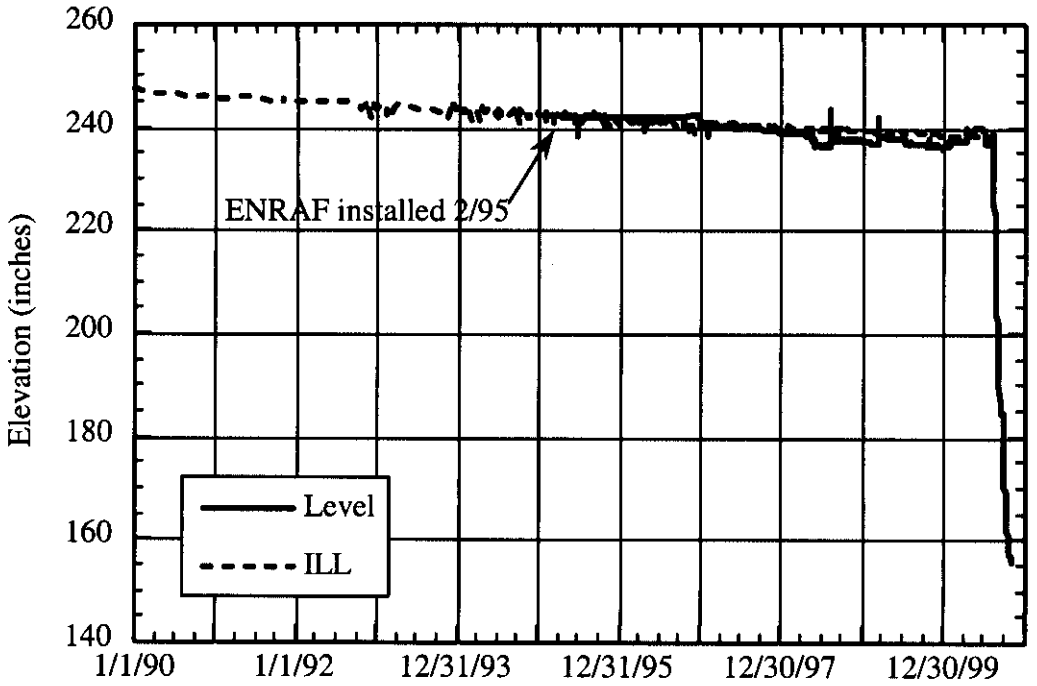


Figure 4-44. Tank 241-SX-105 Waste Level and Interstitial Liquid Level History

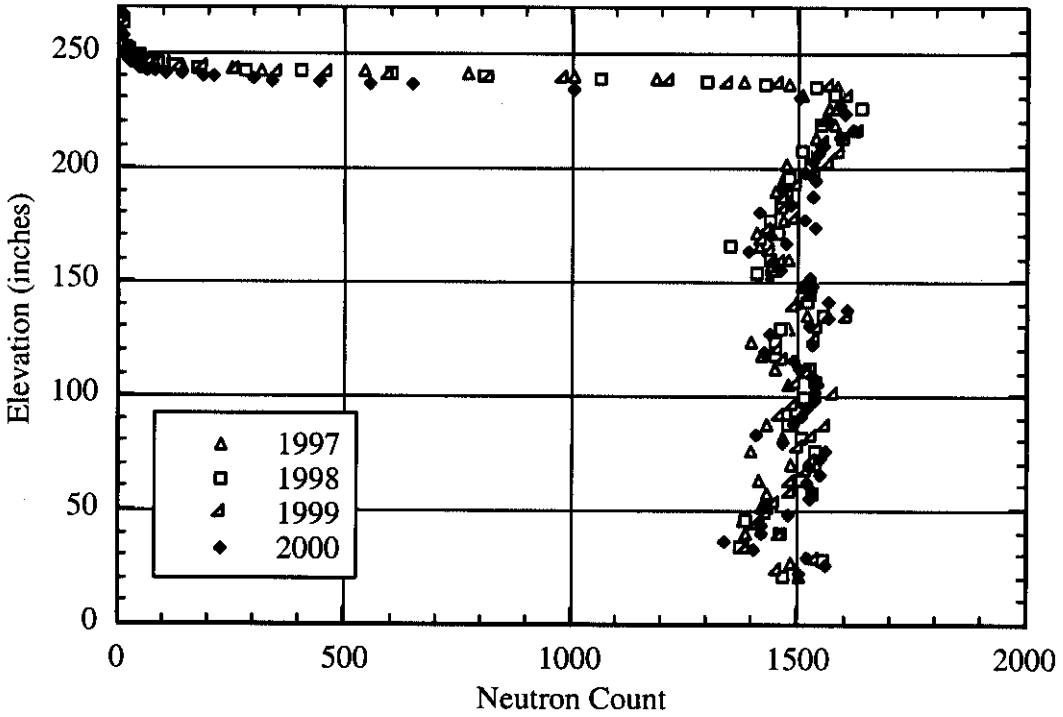


Figure 4-45. Tank 241-SX-105 Neutron Logs

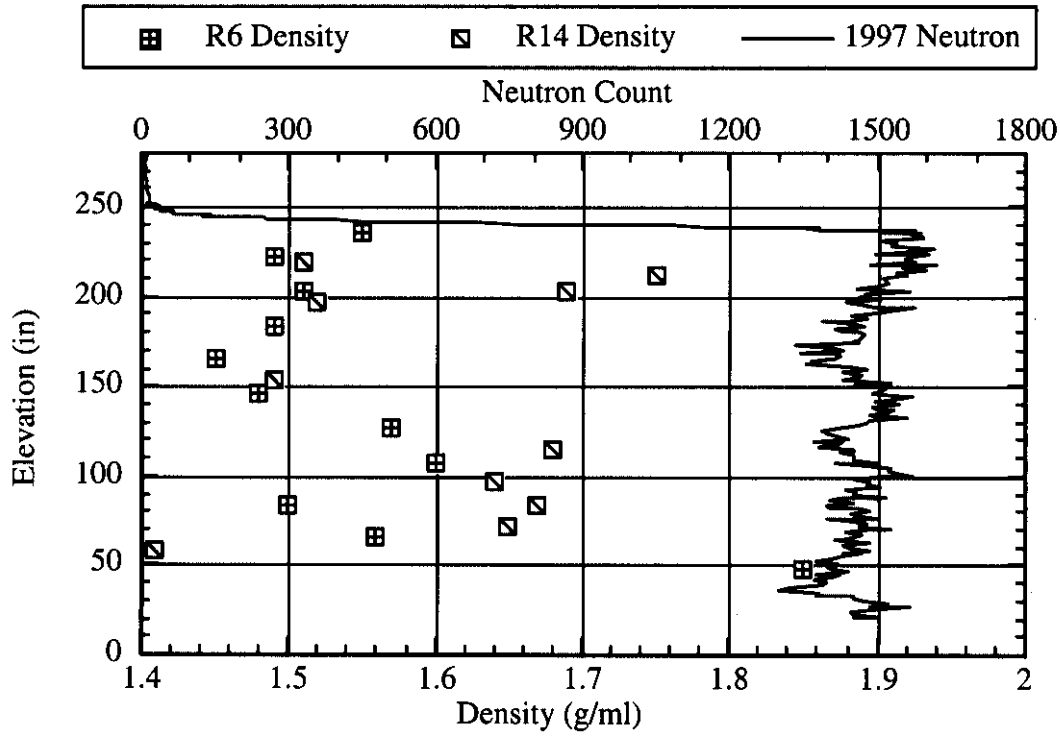


Figure 4-46. Tank 241-SX-105 Density Profile

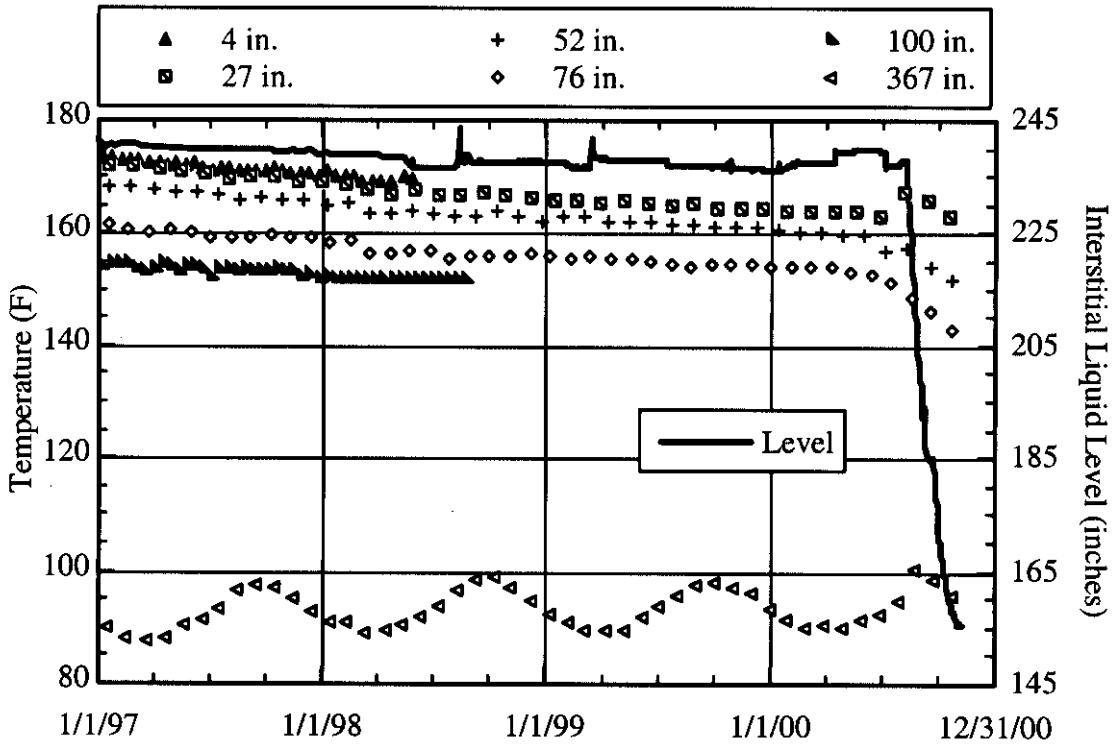


Figure 4-47. Tank 241-SX-105 Waste Temperature History

4.1.12 Tank 241-SX-106 Waste Configuration

Tank SX-106 contains about 400 kgal of saltcake classified as noncomplexed. Saltwell pumping was performed on this tank between October 7, 1998, and December 21, 1999. The saltwell pumping history shown in Figure 4-48 exhibits the "classic" pattern of a relatively high and constant rate during supernatant removal followed by an exponential decline in rate as interstitial liquid drains from a decreasing head. Pumping removed 160 kgal or about 60% of the estimated drainable liquid inventory. The gas volume fraction measured with the RGS in December 1997 averaged 0.18. The gas fraction estimated from the BPE method and neutron logs was 0.11 and 0.13, respectively.

An interesting picture of the waste configuration and location of the retained gas in tank SX-106 is revealed by comparing the waste level history in Figure 4-49 to the neutron logs in Figure 4-50. First, comparing the post-pumping waste level of about 102 inches to the 160-inch waste surface level indicated by the 2000 neutron log gives evidence of a very pronounced dish on the waste surface. The LOW is about 30 ft from the tank center and the ENRAF™ is at about 15 ft (see Figure 2-15). This dished configuration is consistent with the much larger 94-inch drop in waste level compared to the equivalent depth of liquid pumped of 58 inches (see Figure 4-48). Most of the pre-pumping retained gas at the 30-ft radius of the LOW is likely associated with the low neutron count from about 75 to 125 inches. The RGS measured gas volume fractions exceeding 0.3 from 28 to 85 inches from two cores at the 10-ft radius. The 1999 and 2000 neutron logs show that some of this gas may still exist from about 120 to 140 inches at the 30-ft radius of the LOW.

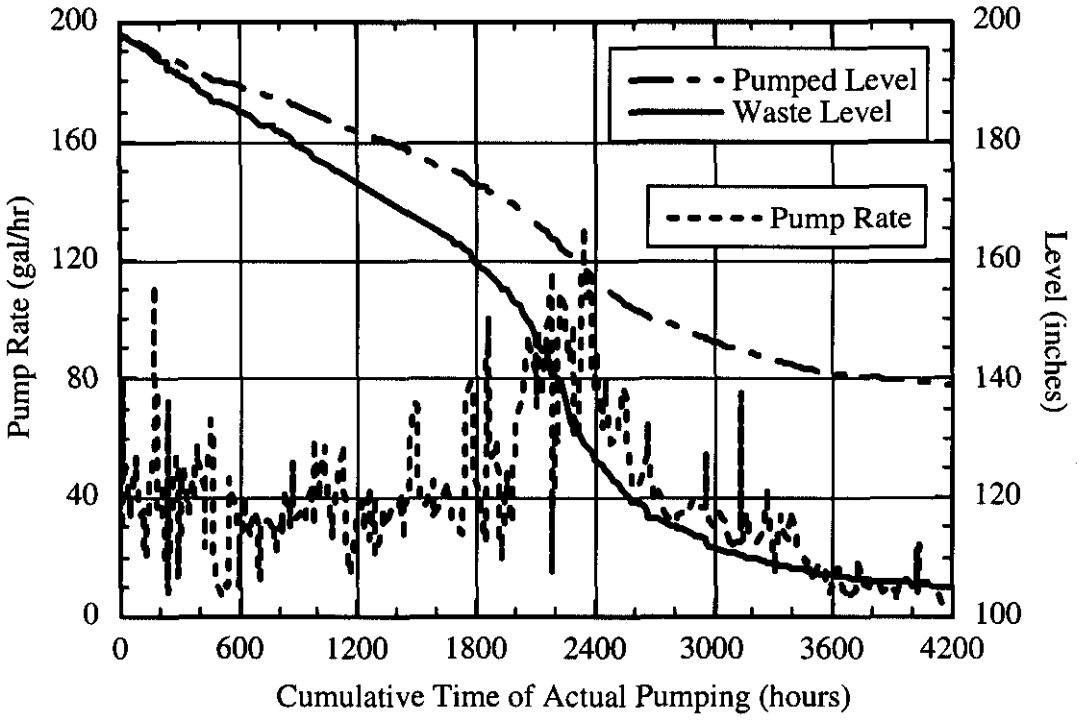


Figure 4-48. Tank 241-SX-106 Saltwell Pumping History

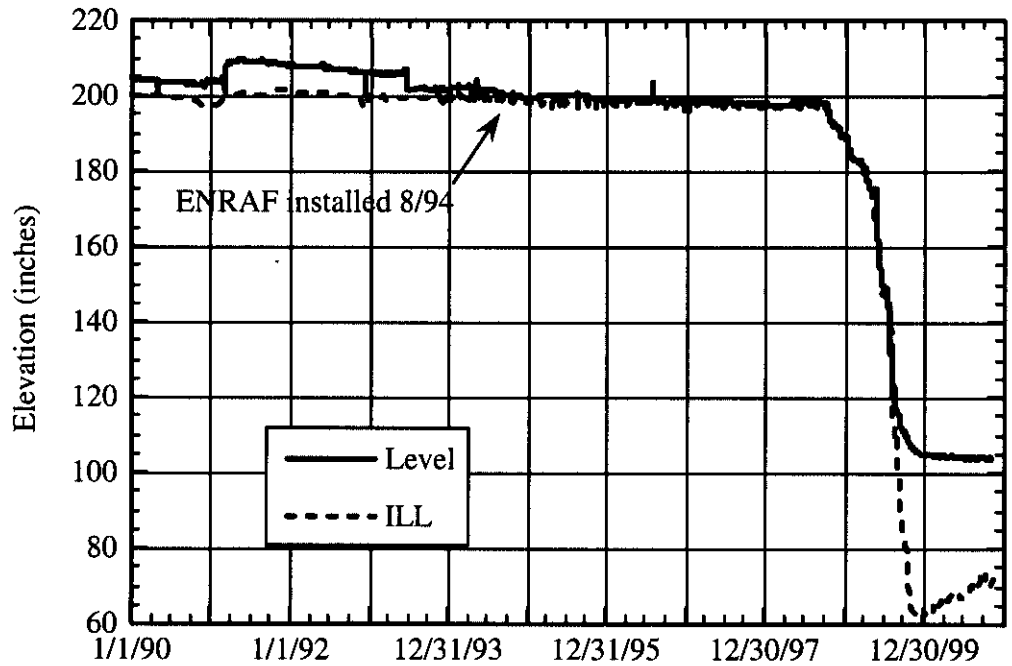


Figure 4-49. Tank 241-SX-106 Waste Level and Interstitial Liquid Level History

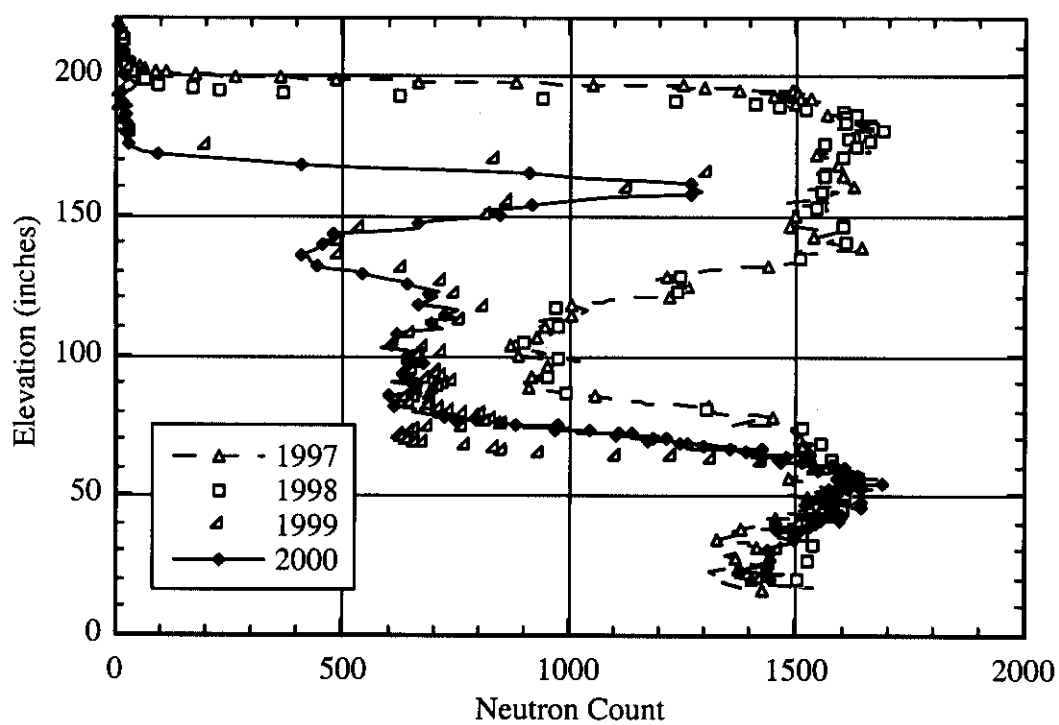


Figure 4-50. Tank 241-SX-106 Neutron Logs

The density profile measured from December 1997 core samples taken from the 10-ft radius in tank SX-106 is shown in Figure 4-51. The segments from 110 inches up the waste surface contained supernatant liquid with a density averaging about 1.45 g/mL. The pre-pumping neutron logs show a high count consistent with supernatant above about 130 inches at the 30-ft radius.

The temperature history in tank SX-106 is given in Figure 4-52. This is by far the coolest Watch List tank in the SX-Farm with a current peak waste temperature of only 98 °F. Prior to pumping, the waste was cooling steadily at about 1.5 °F per year with no annual cycling in the lower 100 inches of waste. There are no thermocouples in the waste above 100 inches. Saltwell pumping in this tank had a gradual but definite effect on the temperatures. All thermocouples down to the 4-inch level show an annual cycle and the temperature differences between thermocouples are relatively even, spanning about 10 °F. The amplitude of the annual cycle in the headspace temperature (367-inch thermocouple) increased markedly after pumping from about 6 °F to almost 20 °F after a large fraction of the waste's thermal inertia was removed.

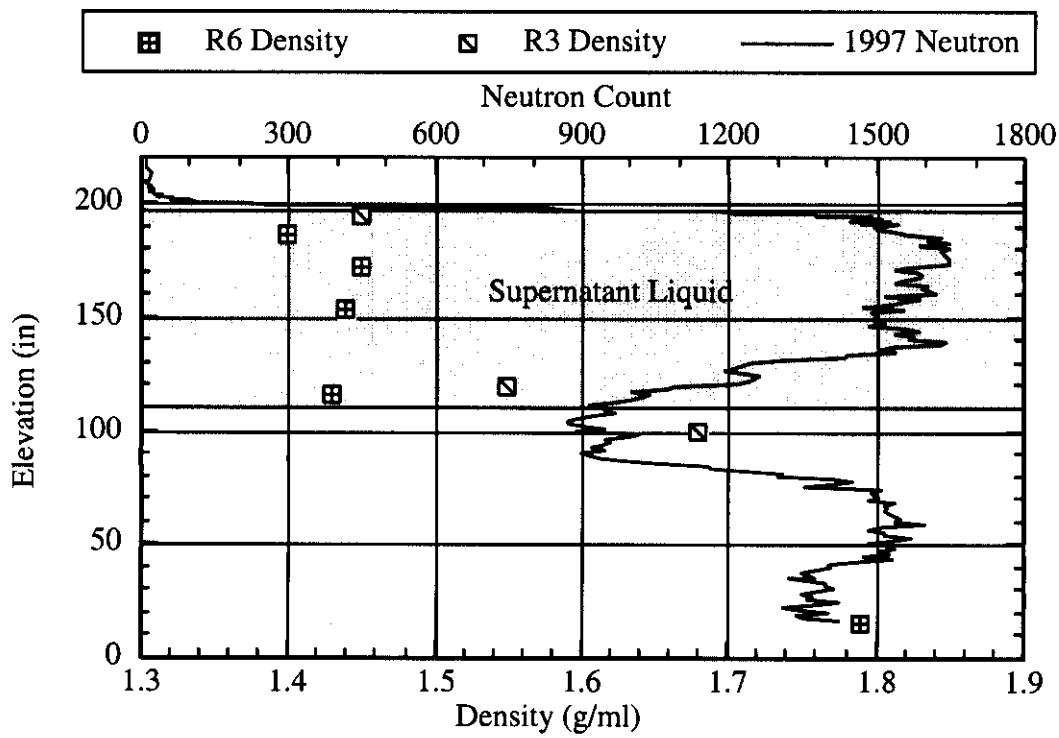


Figure 4-51. Tank 241-SX-106 Density Profile

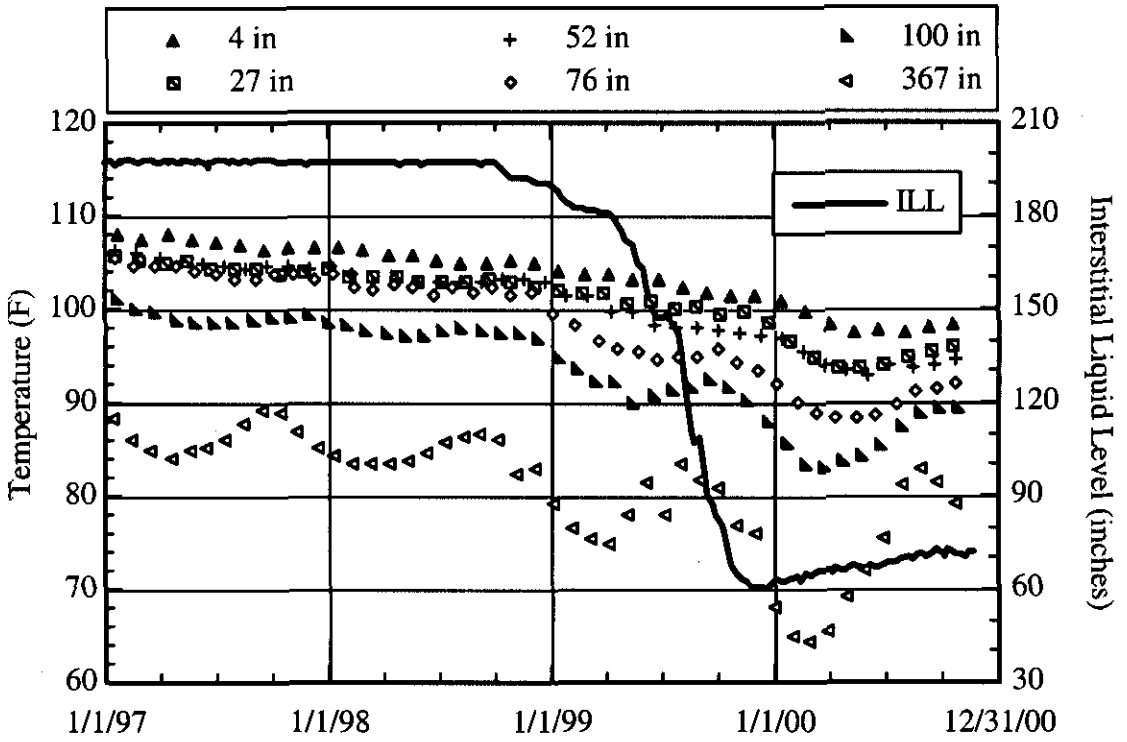


Figure 4-52. Tank 241-SX-106 Waste Temperature History

4.1.13 Tank 241-SX-109 Waste Configuration

Tank SX-109 contains both saltcake and sludge classified as noncomplexed waste, like tank SX-106. The tank has not been saltwell pumped, and no estimate of retained gas fraction has been made. In view of the shallow waste depth, this tank would not be on the Flammable Gas Watch List except that six other SX-Farm tanks on the Watch List vent through it.

Only waste level and temperature histories are available for tank SX-109. The level history is shown in Figure 4-53 and the temperatures in Figure 4-54. The waste level has remained essentially constant at about 95 inches since 1992. The waste temperature everywhere in the waste has been decreasing at about 3 °F per year with a nearly uniform annual cycle throughout of about 3 °F amplitude. The common annual cycle at all depths indicates that the waste has a relatively low thermal inertia and may, therefore, have a relatively low liquid content. The waste temperature currently ranges from 132 to 114 °F near the peak of the annual cycle.

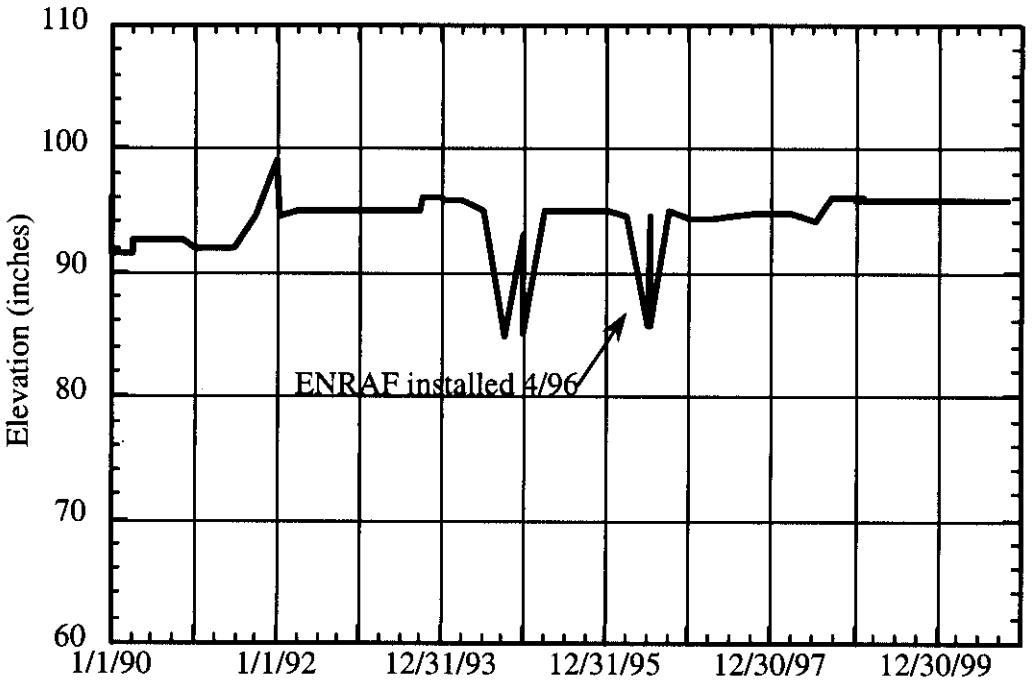


Figure 4-53. Tank 241-SX-109 Waste Level History

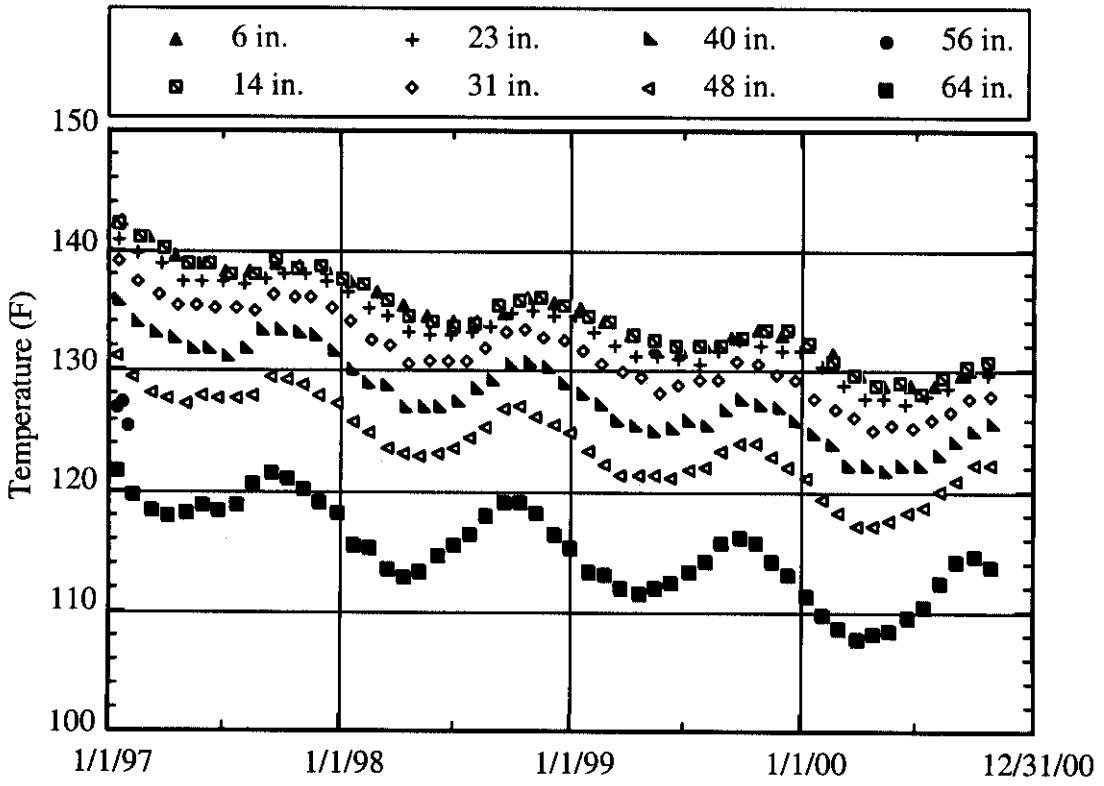


Figure 4-54. Tank 241-SX-109 Waste Temperature History

4.1.14 Tank 241-T-110 Waste Configuration

Tank T-110 is the only tank on the Flammable Gas Watch List that contains mostly sludge rather than saltcake. The waste is classed as noncomplexed implying that it contains a relatively low concentration of organics. Saltwell pumping began in tank T-110 in March 1997 but was suspended between August 31, 1997, and July 2, 1998. When pumping ceased August 12, 1999, 34 kgal, or about 80%, of the estimated 41 kgal of remaining drainable liquid had been removed. Pumping proceeded at an essentially constant low rate typical of sludge as shown in Figure 4-55. Pumping was terminated early because of equipment failure. Both the BPE and the neutron log indicate essentially zero gas retention.

The level history and neutron logs for tank T-110 are shown in Figures 4-56 and 4-57, respectively. Unfortunately, all the available risers in this tank are near the tank wall. The LOW and level gauges are on opposite sides of the tank at the 30-ft radius. An ENRAF™ level gauge was installed in June 1995, and the sudden 12-inch jump in early 1996 is attributed to correcting the gauge reference to the tank bottom center from the sidewall bottom. After this correction, the surface level was about two inches below the ILL. Since surface photos from 1984 show a "muddy" surface with cracks, this 2-inch difference indicates the surface profile, not supernatant.

Both the surface level and ILL began descending in May 1997 with the initial saltwell pumping campaign. The surface level eventually dropped 5 inches and the ILL dropped 8 inches during this period. Beginning in July 1998, resumption of saltwell pumping reduced both levels an additional 5 inches. The waste subsided an additional 2 inches after pumping ended. The neutron logs[9] show no discernable effect of saltwell pumping below the surface as is typical of a sludge tank. The change in neutron profile from 1996 to 2000 is apparently subsidence resulting from liquid removal.

The density profile and temperature history are given in Figures 4-58 and 4-59, respectively. Neither shows any apparent effect of saltwell pumping below the waste level. Tank T-110 waste has a very low density and is the coldest of the SSTs on the Flammable Gas Watch List.

4.1.15 Tank 241-U-103 Waste Configuration

The waste in tank U-103, like all but one of the U-Farm Watch List tanks, is saltcake classified as noncomplexed. Saltwell pumping was performed in tank U-103 from September 26, 1999, to May 11, 2000. Pumping removed 108 kgal, 9 kgal more than the initially estimated 99 kgal of drainable liquid. The saltwell pumping history for tank U-103 is given in Figure 4-60. The pumping behavior shows the classic exponential decline in pumping rate after a short period of high-rate supernatant drainage. The average retained gas volume fraction measured with the

[9] The 1996 neutron count was normalized to overlay the 1997-2000 profiles below 100 inches.

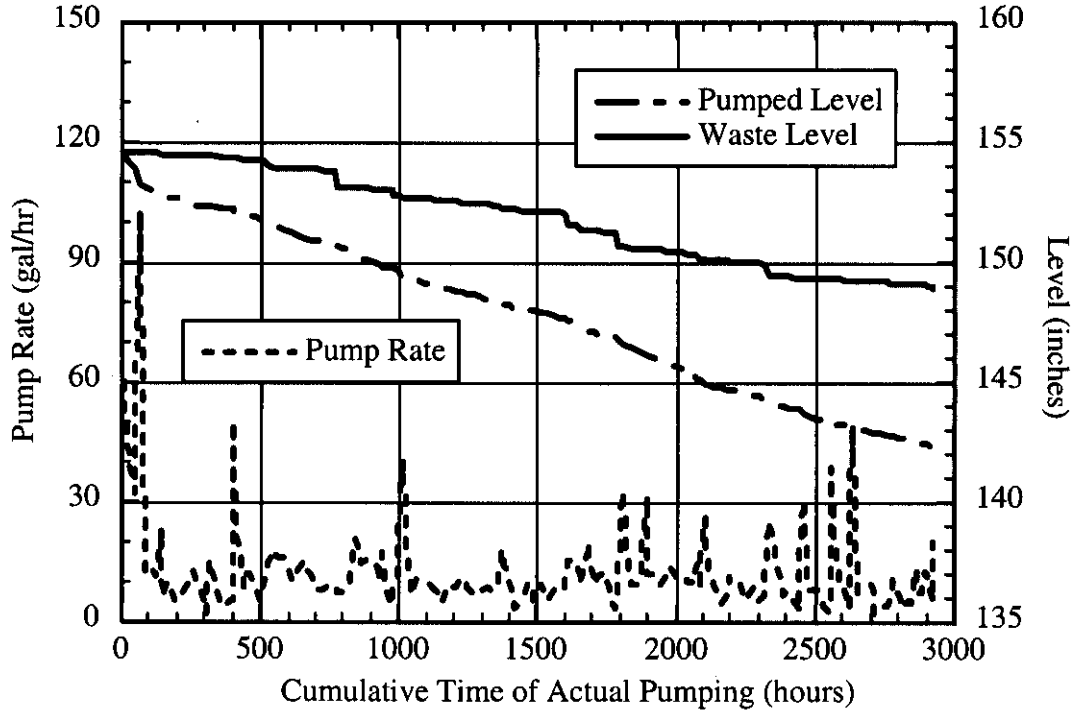


Figure 4-55. Tank 241-T-110 Saltwell Pumping History

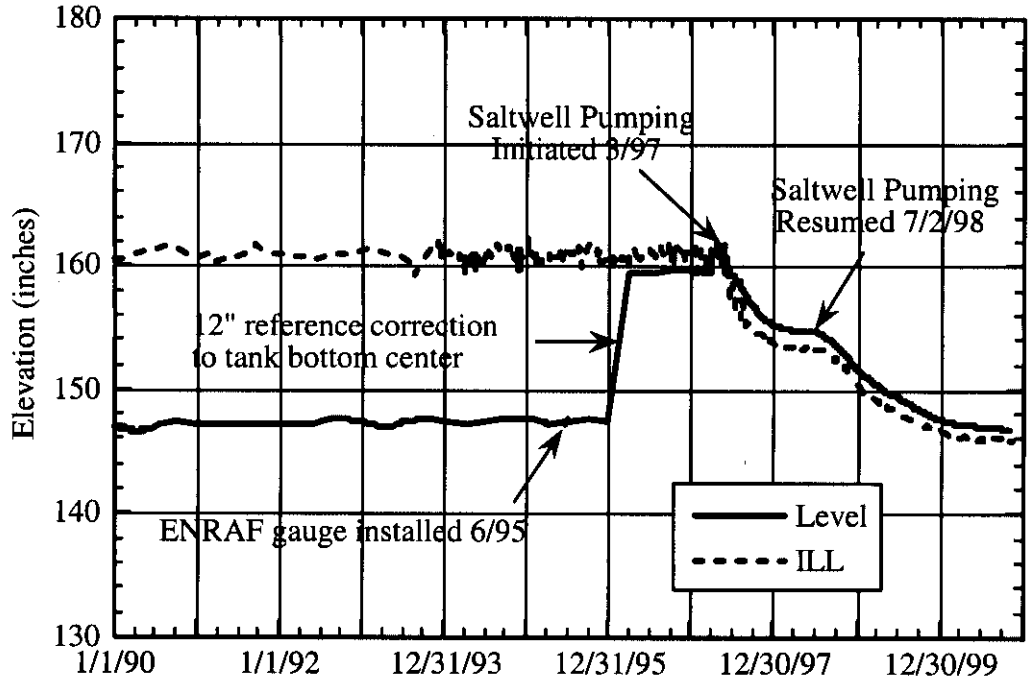


Figure 4-56. Tank 241-T-110 Waste Level and Interstitial Liquid Level History

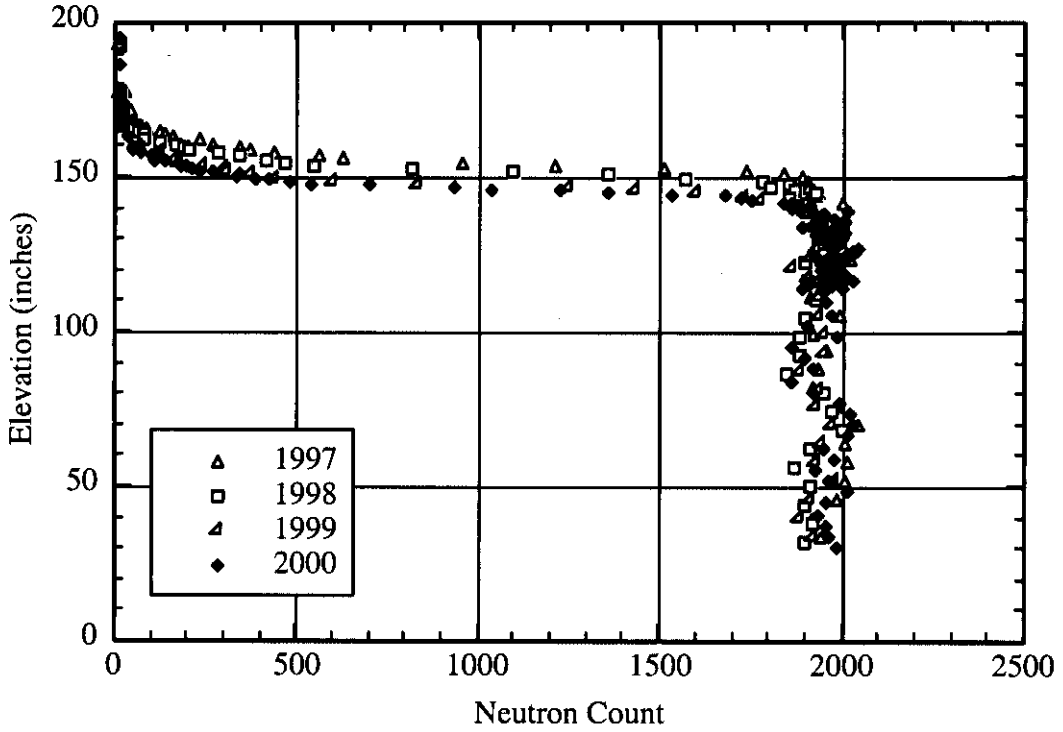


Figure 4-57. Tank 241-T-110 Neutron Logs

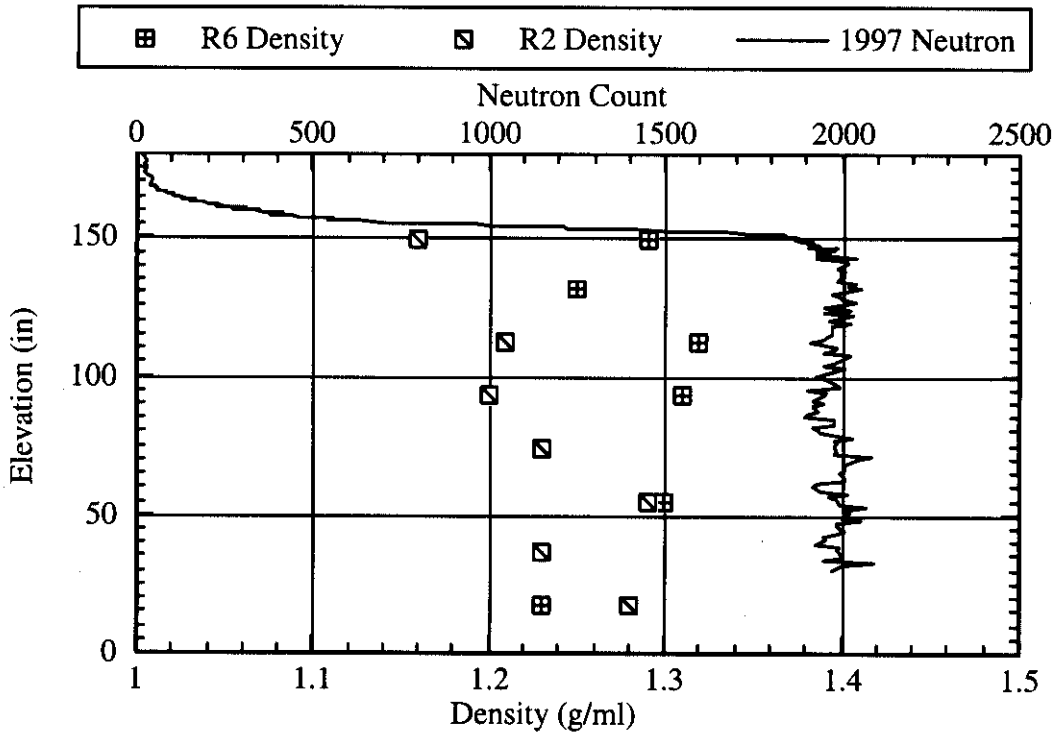


Figure 4-58. Tank-241-T-110 Density Profile

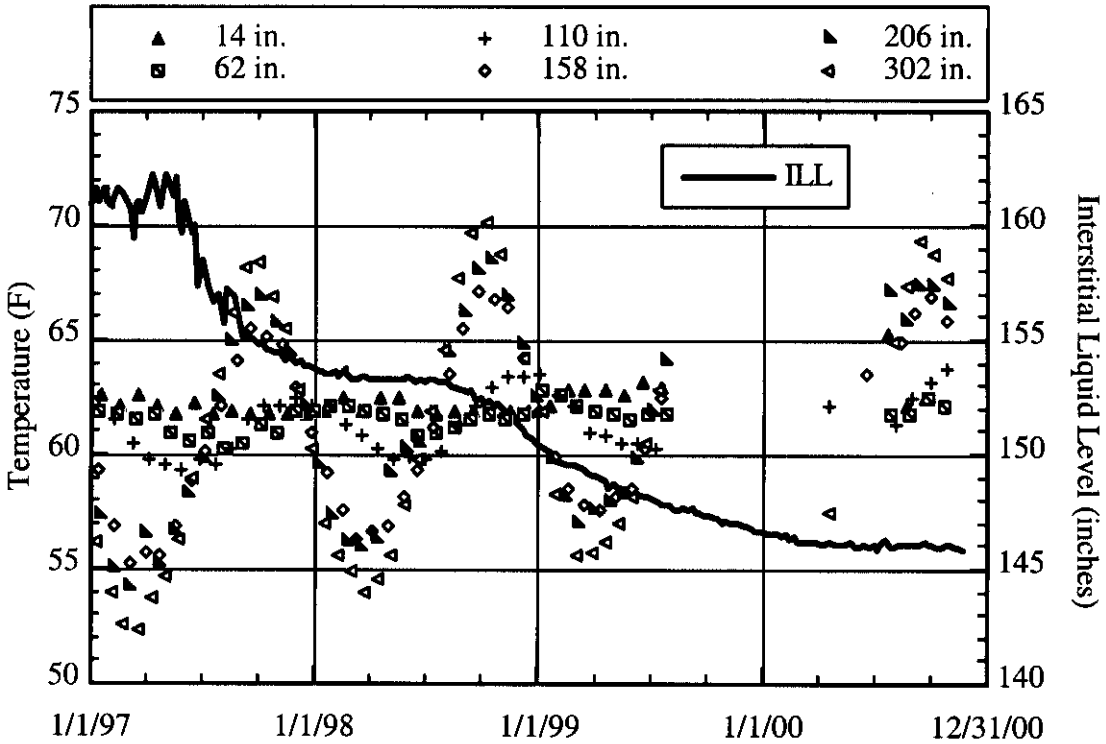


Figure 4-59. Tank 241-T-110 Waste Temperature History

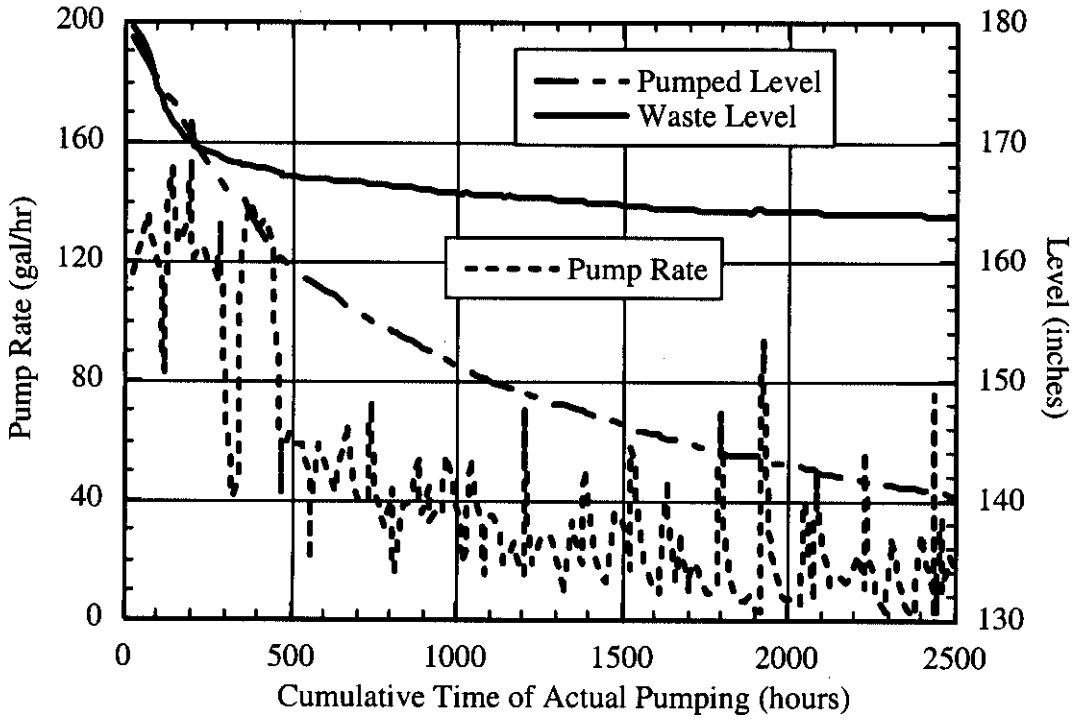


Figure 4-60. Tank 241-U-103 Saltwell Pumping History

RGS in 1997 was 0.19. The BPE and neutron log estimates are 0.13 and 0.15, respectively. A gas fraction over 0.4 was found with the RGS at 125 inches in Riser 7, which is at the 30-ft radius. The 1997 and 1998 neutron logs indicate that most of the gas is below 100 inches, however.

The level history and neutron logs for tank U-103 are shown in Figures 4-61 and 4-62, respectively. The waste level and ILL remained essentially constant from 1990 until the start of pumping. Removal of liquid dropped the surface level 17 inches from 180 to 163 inches, about half of the 39-inch equivalent depth of liquid removed (see Figure 4-60), probably a result of the ENRAF™ being near the tank wall. The ILL is reported to have dropped 118 inches during pumping. However, inspection of the 2000 neutron log indicates that this choice of ILL is quite subjective. The neutron log clearly shows most of the liquid was removed from above the 100-inch level. The neutron profile below 90 inches is essentially unchanged.

The density and yield stress profiles from the 1996 core samples and the 1997, neutron log are given in Figure 4-63. The density was approximately uniform at about 1.76 g/mL below about 150 inches. The lower densities above this level are consistent with a high liquid fraction. The yield stress increases with depth to about 100 inches where it becomes relatively uniform at around 1,000 Pa. The high strength coincides with the low neutron count (drier waste) below 100 inches. One sample at 48 inches had a very low strength and density indicative of an almost-liquid layer.

Risers 2 and 7 are near the periphery at about 30-ft radius while Riser 13 contains the saltwell in the center of the tank (see Figure 2-18). The close correspondence of the density and yield stress from these locations indicates that the waste in tank U-103 was relatively uniform laterally before pumping. The measured waste level, waste upper surface indicated by the neutron log, and the top of the three core samples were similar in elevation indicating a relatively flat waste surface.

All of the U-Farm tanks are quite cool, and tank U-103 is no exception. The temperature history in Figure 4-64 is qualitatively similar to that of tank T-110, where the annual temperature cycle brackets the more constant temperature in the lower part of the waste. Also, like tank T-110, saltwell pumping had little effect on the temperature pattern in the waste. The temperatures in tank U-103 prior to pumping were essentially constant about an annual variation of 2 to 3 °F in the range of 84 to 86 °F below 117 inches. The thermocouple at 165 inches showed a seasonal cycle amplitude of about 8 °F in close phase with the headspace variation represented by the 261-inch thermocouple.

4.1.16 Tank 241-U-105 Waste Configuration

Tank U-105 contains noncomplexed saltcake, like tank U-103. Also, like tank U-103, this tank has been saltwell pumped. Pumping from December 11, 1999, to May 11, 2000, removed 91 kgal, 11 kgal more than the initial estimate of drainable liquid. The saltwell pumping history, shown in Figure 4-65, is also similar to that of tank U-103, except that the waste level follows the pumped level more closely. Prior to pumping, the average retained gas volume fraction was estimated to range from 0.09 to 0.15 based on the BPE method and the neutron log, respectively. At the 30-ft radius of the LOW, the gas was apparently held from 80 to 130 inches.

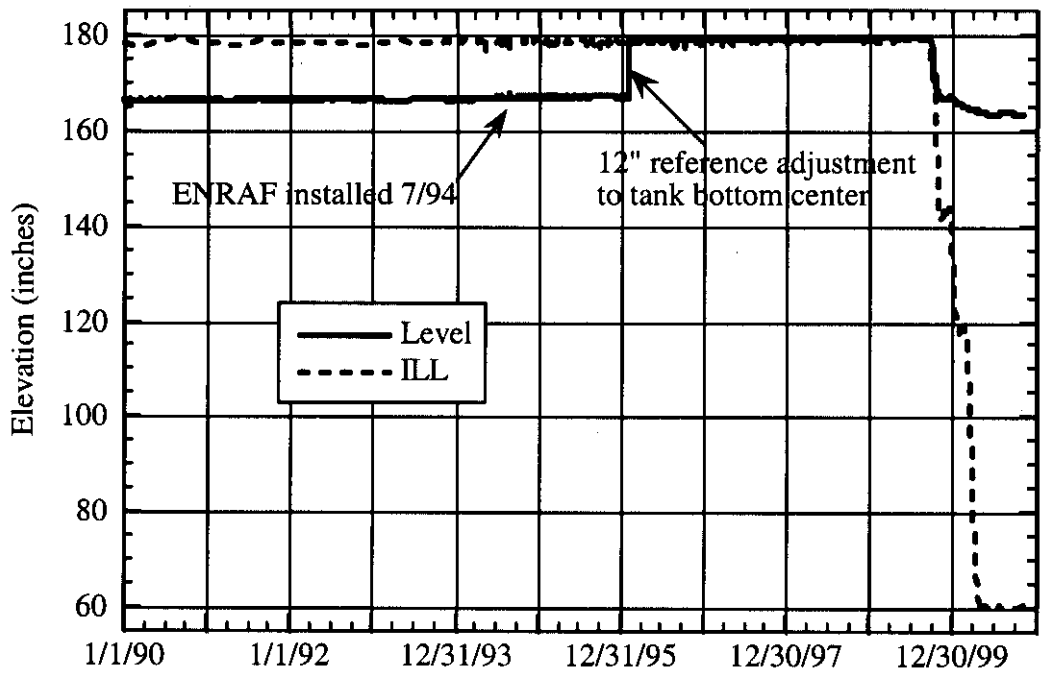


Figure 4-61. Tank 241-U-103 Waste Level and Interstitial Liquid Level History

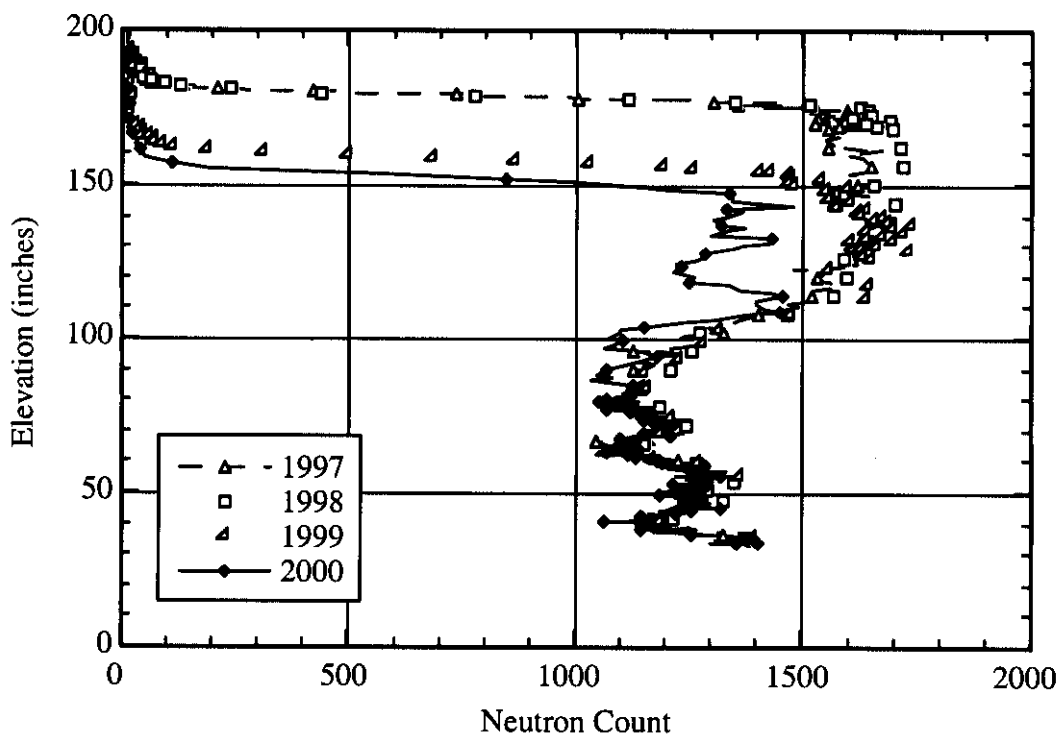


Figure 4-62. Tank 241-U-103 Neutron Logs

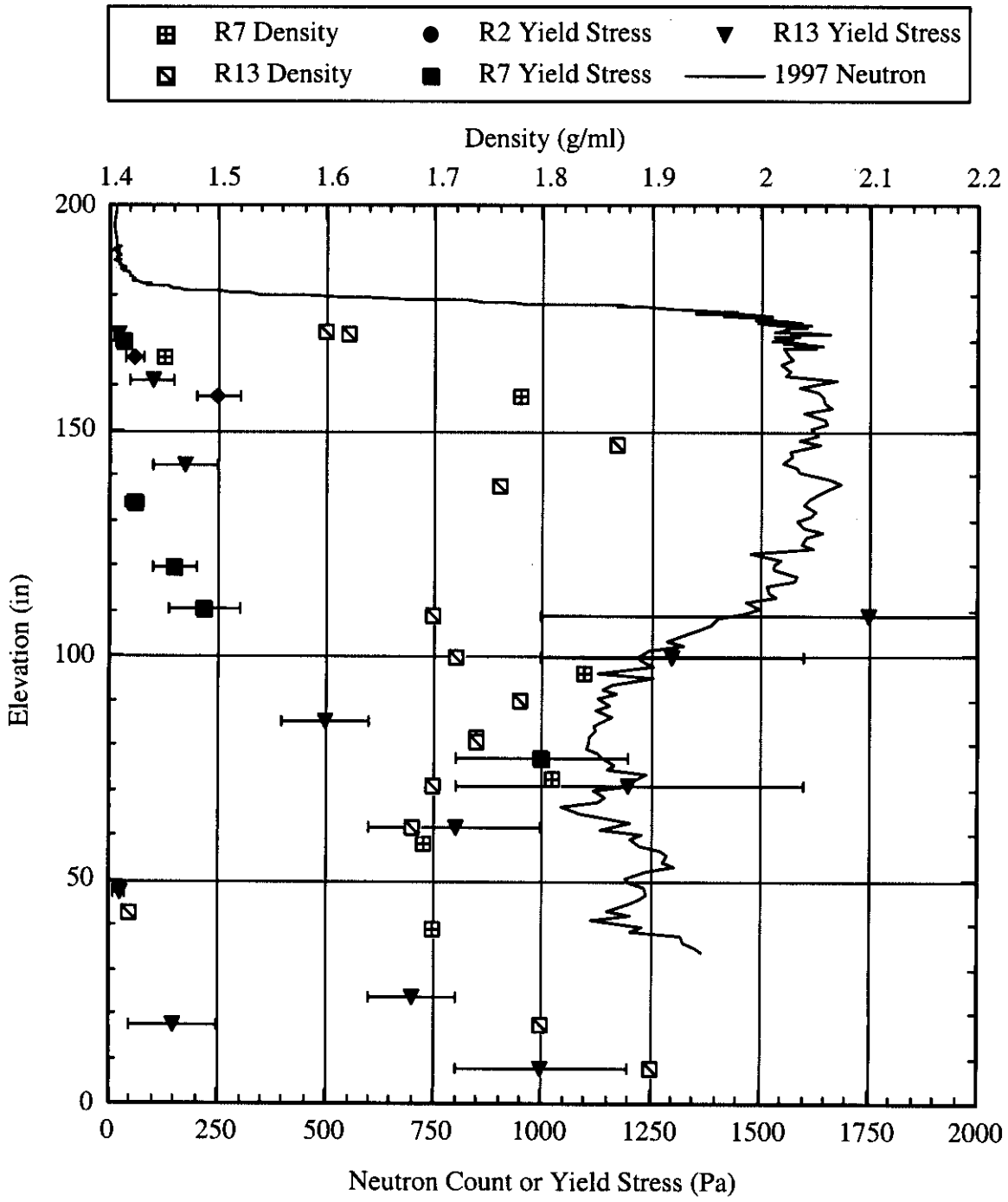


Figure 4-63. Tank 241-U-103 Strength and Density Profile

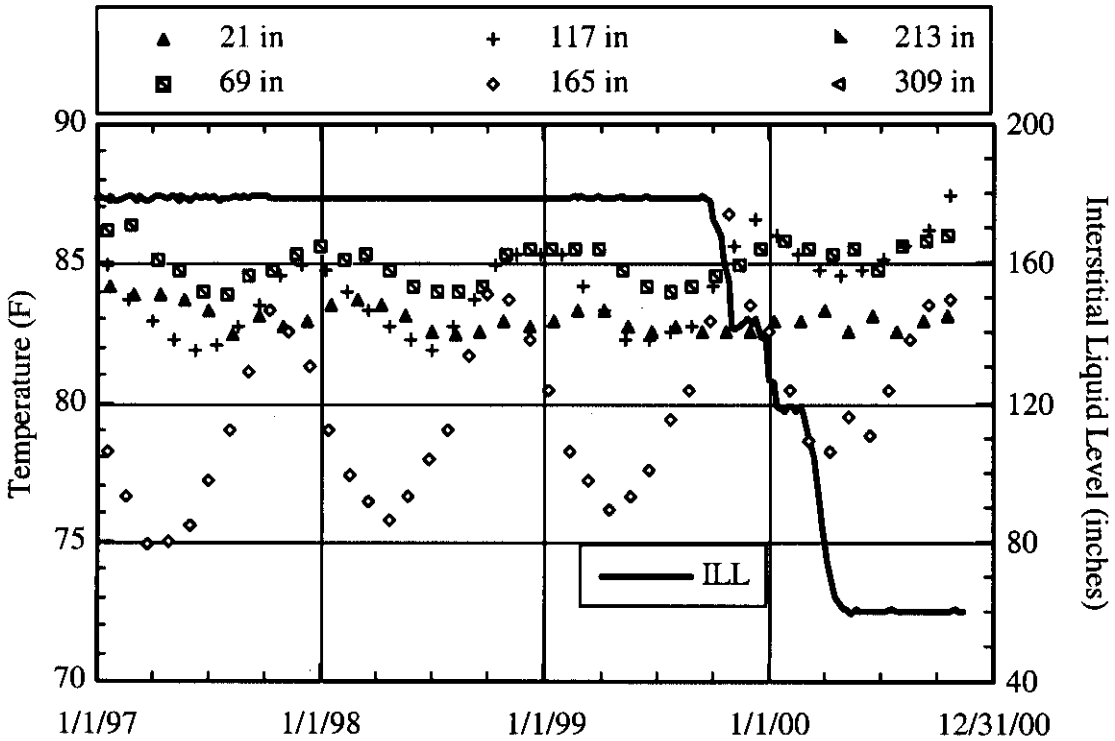


Figure 4-64. Tank 241-U-103 Waste Temperature History

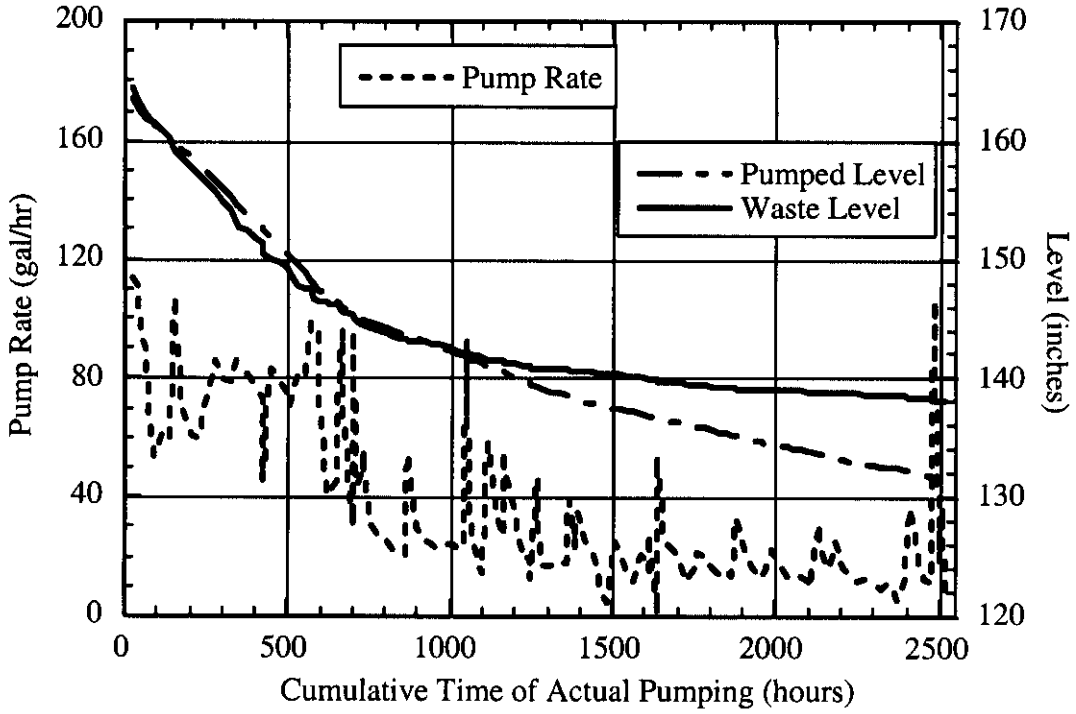


Figure 4-65. Tank 241-U-105 Saltwell Pumping History

The level history in Figure 4-66 shows the waste level and ILL rising very gradually at a constant rate of about 1/3-inch per year. Saltwell pumping abruptly dropped the waste level in the first two months of 2000 as supernatant was removed. Draining of interstitial liquid caused the ILL to continue dropping over the next three months until the end of pumping in May. Pumping reduced the waste level below Riser 8, over 30 ft from the tank center, by 25 inches to its current 138 inches compared to 33 inches equivalent depth of liquid pumped. The ILL measured in Riser 19, also at the 30-ft radius, fell by 72 inches to 93 inches. The neutron logs in Figure 4-67 indicate that the waste surface around the LOW subsided by about 20 inches. The neutron profile below the current ILL did not change significantly.

Figure 4-68 presents the density profile from 1996 core samples. Risers 2 and 7 are at the 30-ft radius while Riser 20 is nearer the center at about the 18-ft radius (see Figure 2-19). The densities measured from each of these cores correspond quite closely indicating the waste properties are relatively uniform laterally. The density increases with depth from about 1.6 g/mL near the top to just over 1.8 g/mL at the tank bottom. The average density is about 1.7 g/mL.

The waste temperature history, shown in Figure 4-69, shows almost exactly the same behavior, and nearly the same temperatures, as in tank U-103. Apparently, there was some exposure of warmer liquid in the early stages of saltwell pumping that caused a spike in the upper three thermocouples. After recovering from this spike, the temperature at the 165-inch thermocouple matches that of the headspace on the 261-inch thermocouple. The average temperature of the waste below 117 inches is 86 to 88 °F with a 2 to 4 °F annual swing.

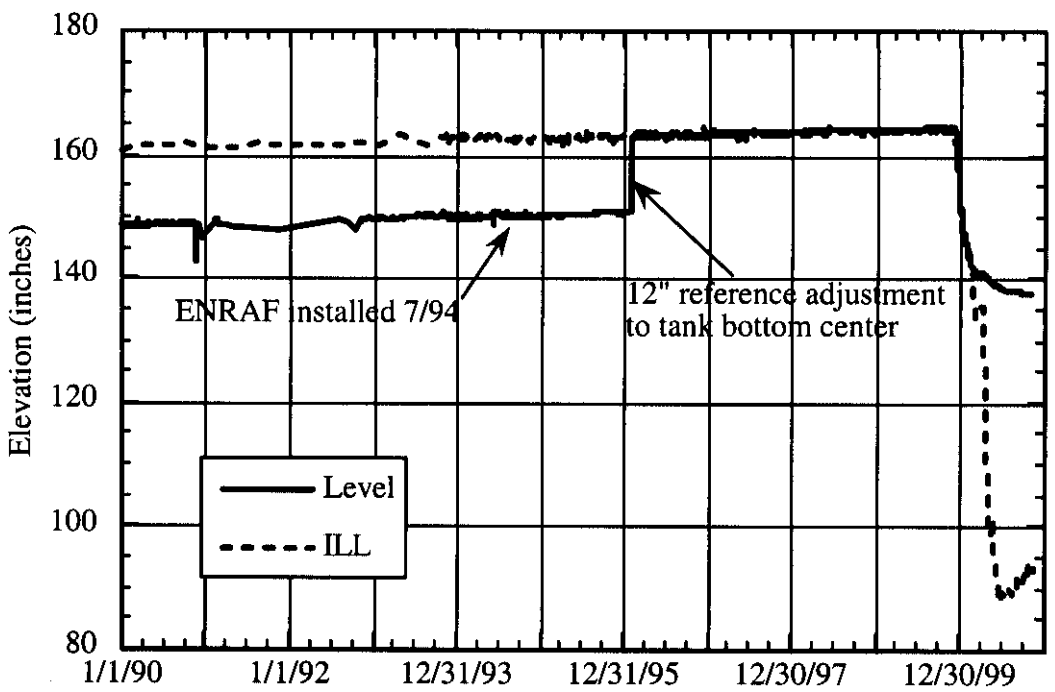


Figure 4-66. Tank 241-U-105 Waste Level and Interstitial Liquid Level History

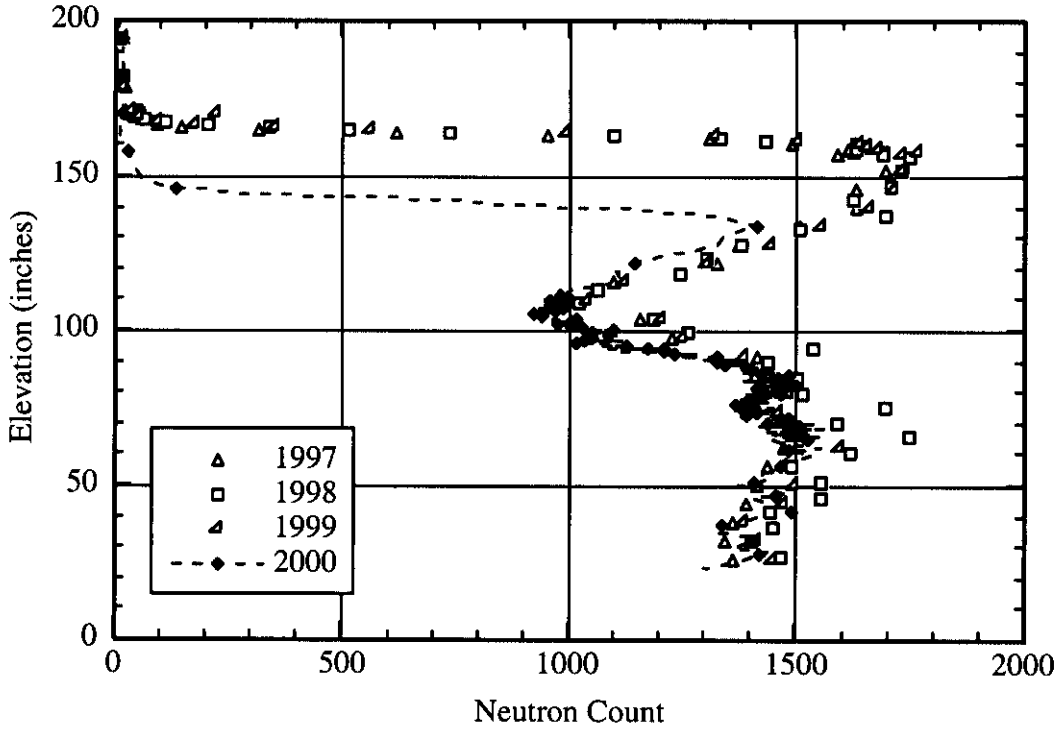


Figure 4-67. Tank 241-U-105 Neutron Logs

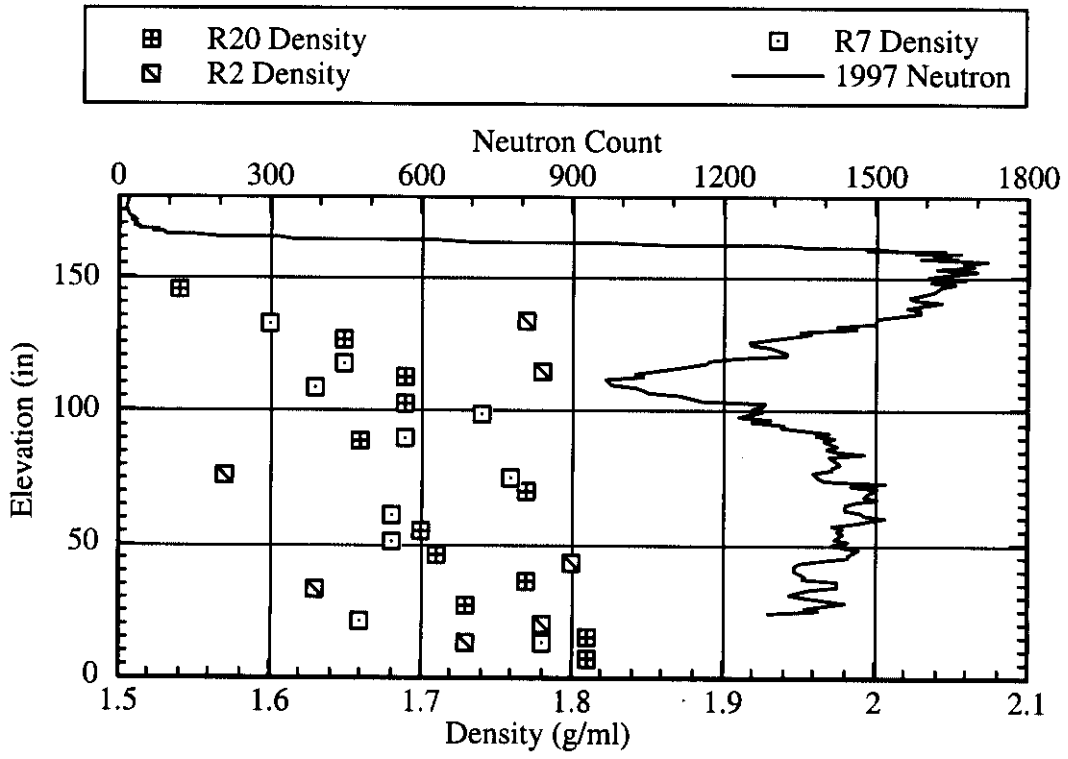


Figure 4-68. Tank 241-U-105 Density Profile

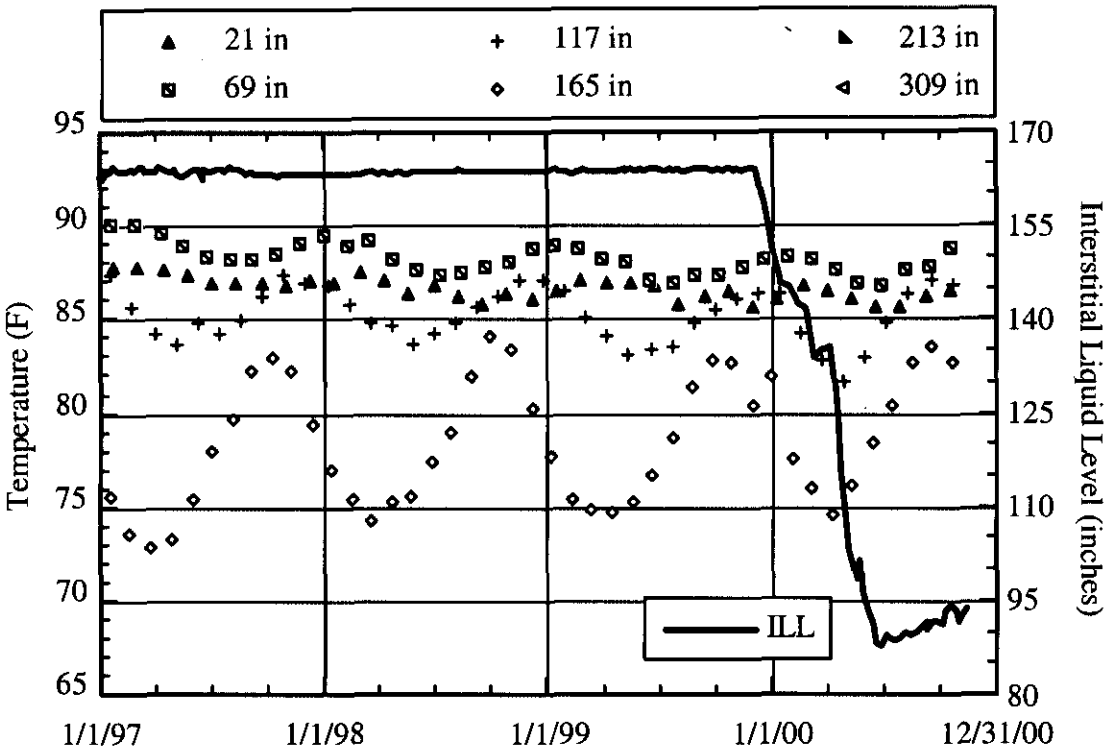


Figure 4-69. Tank 241-U-105 Waste Temperature History

4.1.17 Tank 241-U-107 Waste Configuration

Tank U-107 contains saltcake, and it is the only U-Farm Watch List with waste concentrated to classify as DSSF. The current waste level is 156 inches, which may include on the order of 24 inches of supernatant. Tank U-107 has not yet been saltwell pumped. The BPE method and the neutron log estimate the retained gas volume fraction at 0.08 to 0.11, respectively.

The waste level in tank U-107, which corresponds to the ILL, has been rising at a rate of about 0.1 inch per year, as shown in Figure 4-70. The sudden, 12-inch jump in surface level is assumed to be a change in reference from the sidewall bottom to center bottom. Photographs taken in 1988 show the entire surface to be covered with liquid with numerous small clumps of apparently floating material.

The neutron logs given in Figure 4-71 show a high count above about 130 inches that is consistent with supernatant or very high liquid fraction. Below the supernatant, from 100 to 130 inches, is a region of low count, which may indicate retained gas. The neutron profiles of all of U-Farm Watch List tanks were similar prior to pumping. Figure 4-72 compares the 1997 logs by shifting the profile for each tank by 500 count units on the abscissa. Except for tank U-103, each tank has a prominent high-count layer on top of a region with a lower count. The U-tanks have also responded similarly to saltwell pumping. The 2000 neutron logs for tanks U-103, U-105, and U-109 are compared in Figure 4-73 with each profile shifted by 500 count units, as in the prior figure. The overall shape of the profile is approximately preserved with a more highly saturated layer above a less saturated one. The lower 60 to 80 inches are essentially unchanged.

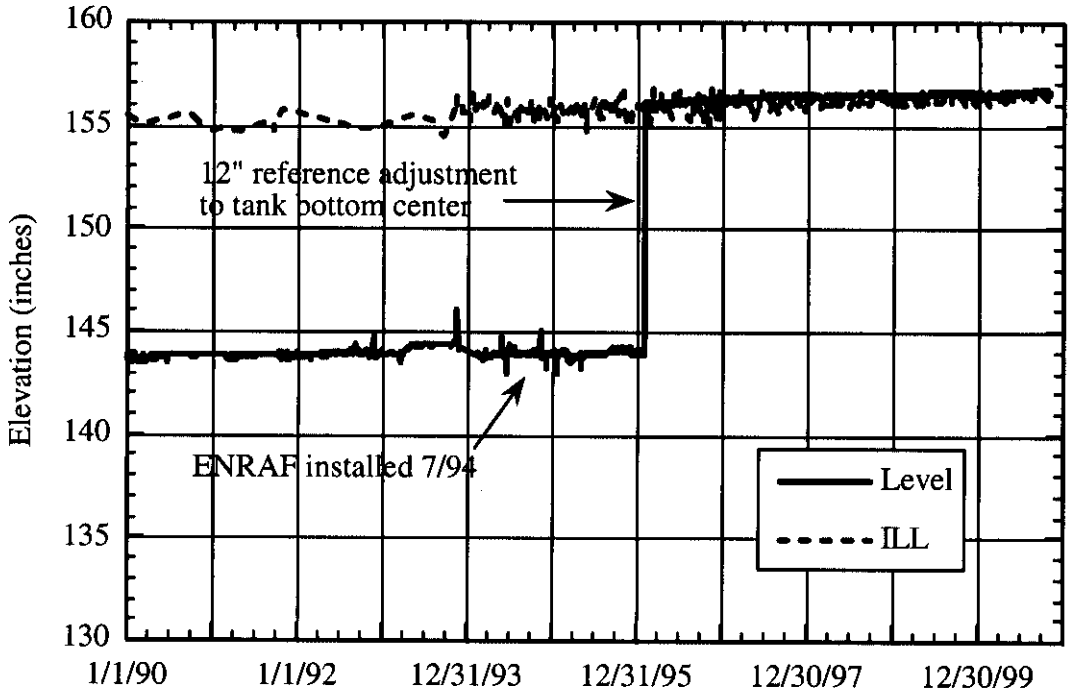


Figure 4-70. Tank 241-U-107 Waste Level and Interstitial Liquid Level History

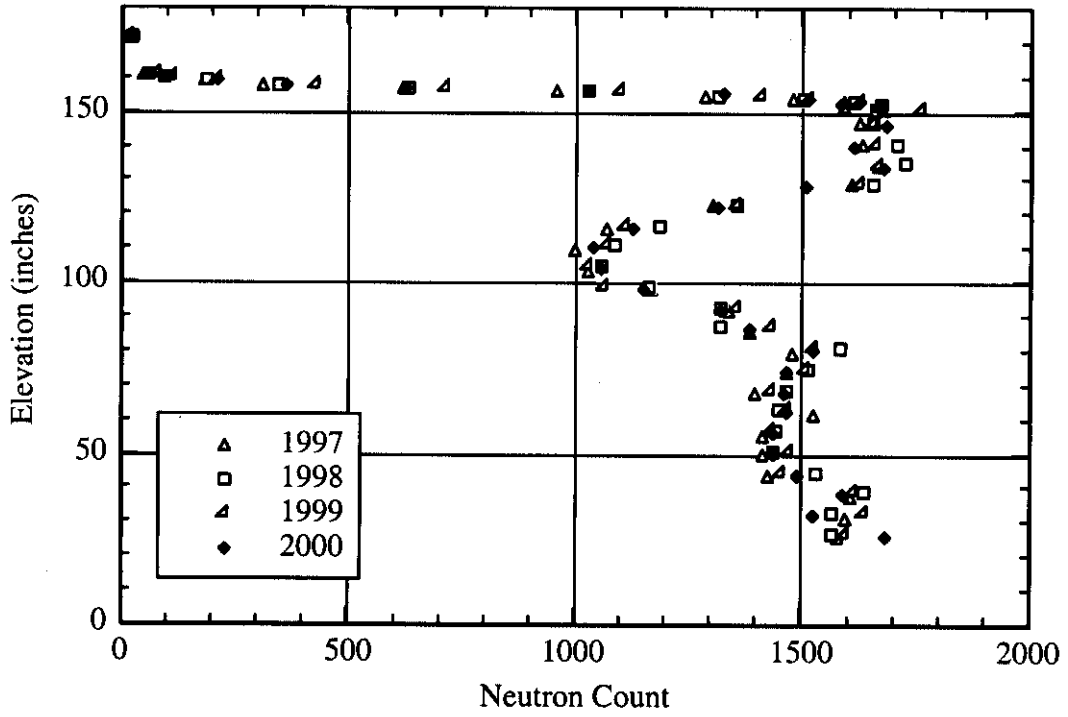


Figure 4-71. Tank 241-U-107 Neutron Logs

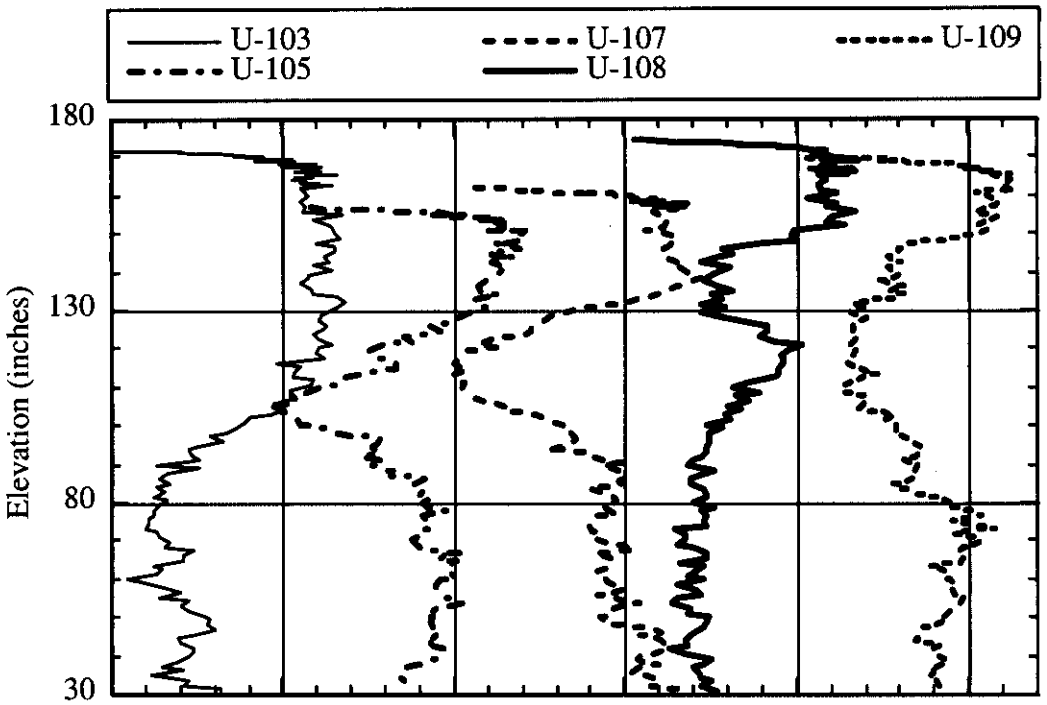


Figure 4-72. Tank 241-U-Farm Neutron Profile Comparison

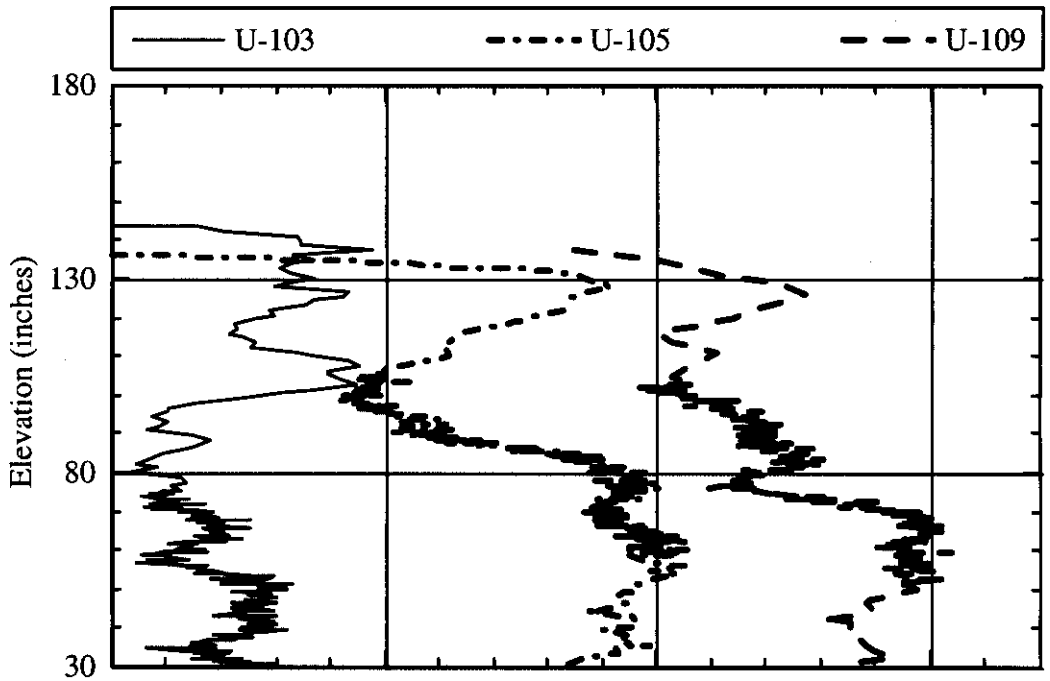


Figure 4-73. Tank 241-U-Farm Post-Pumping Neutron Profile Comparison

The density and yield stress profiles developed from 1996 and 1998 core samples are shown in Figure 4-74. The densities from the three different risers are quite consistent. All three risers are at 27- to 30-ft radii and are separated by approximately 90 degrees around the tank (see Figure 2-20). The low density of ~1.45 g/mL above 100 inches indicates a high water content in this layer. Below about 100 inches, the density appears to increase with depth from ~1.6 g/mL to ~1.8 g/mL. The yield stress behaves similarly.

The upper wet layer has a very low, but non-zero, strength of 30 to 50 Pa, including the two high-density samples seen in Figure 4-74. The yield stress generally increases with depth, although with considerable scatter, from ~100 Pa to 400 to 600 Pa below 80 inches. Tank U-107 waste is significantly weaker than that of tank U-103 prior to pumping. It must be emphasized again that all these samples are from near the periphery of the tank and do not provide information about the central region.

The temperature profile for tank U-107 is shown in Figure 4-75. Tank U-107 is the second coolest Watch List SST with a peak temperature of only 78 °F. However, since the thermocouple tree is out at about the 32-ft radius, the central temperatures could be somewhat higher. During the annual cycle, the headspace temperature actually exceeds the temperature at the 22-inch thermocouple. Within the annual cycle of 2 to 5 °F, the waste temperature up to 118 inches is fairly uniform varying between 73 and 78 °F.

4.1.18 Tank 241-U-108 Waste Configuration

The waste in tank U-108 is similar to that of tank U-105 being noncomplexed saltcake. The waste conditions in tank U-108 also match those in tank U-105 prior to pumping. Tank U-108 has not been saltwell pumped. The retained gas volume fraction is estimated at 0.12 by the BPE method and 0.19 from the neutron log.

The waste level history, neutron logs, density profile and waste temperature history are given in Figures 4-76, 4-77, 4-78, and 4-79, respectively. The tank has a waste level of 179 inches of which roughly 18 inches may be supernatant. The waste level and ILL have been essentially constant since 1990, except for the level reference adjustment in early 1996. The shape of the neutron logs has been discussed in conjunction with tank U-107 in Section 4.1.17. The densities are relatively uniform within the variability of the data from the three risers, which are all at about the same radius.

The temperature history is similar to that of tank U-105 prior to pumping with a slight decreasing trend exhibited by the thermocouples below 69 inches. The waste temperature in the lower half of the tank ranges from 82 to 87 °F with an annual cycle of 2 to 4 °F. The temperature spikes in early January 2000 are attributed to failure of a cooling fan in the instrument cabinet that contains the thermocouple reference junctions. Tanks U-108 and U-109 share the same cabinet, and a similar disturbance occurs at the same time in the tank U-109 temperature history (see Figure 4-84).

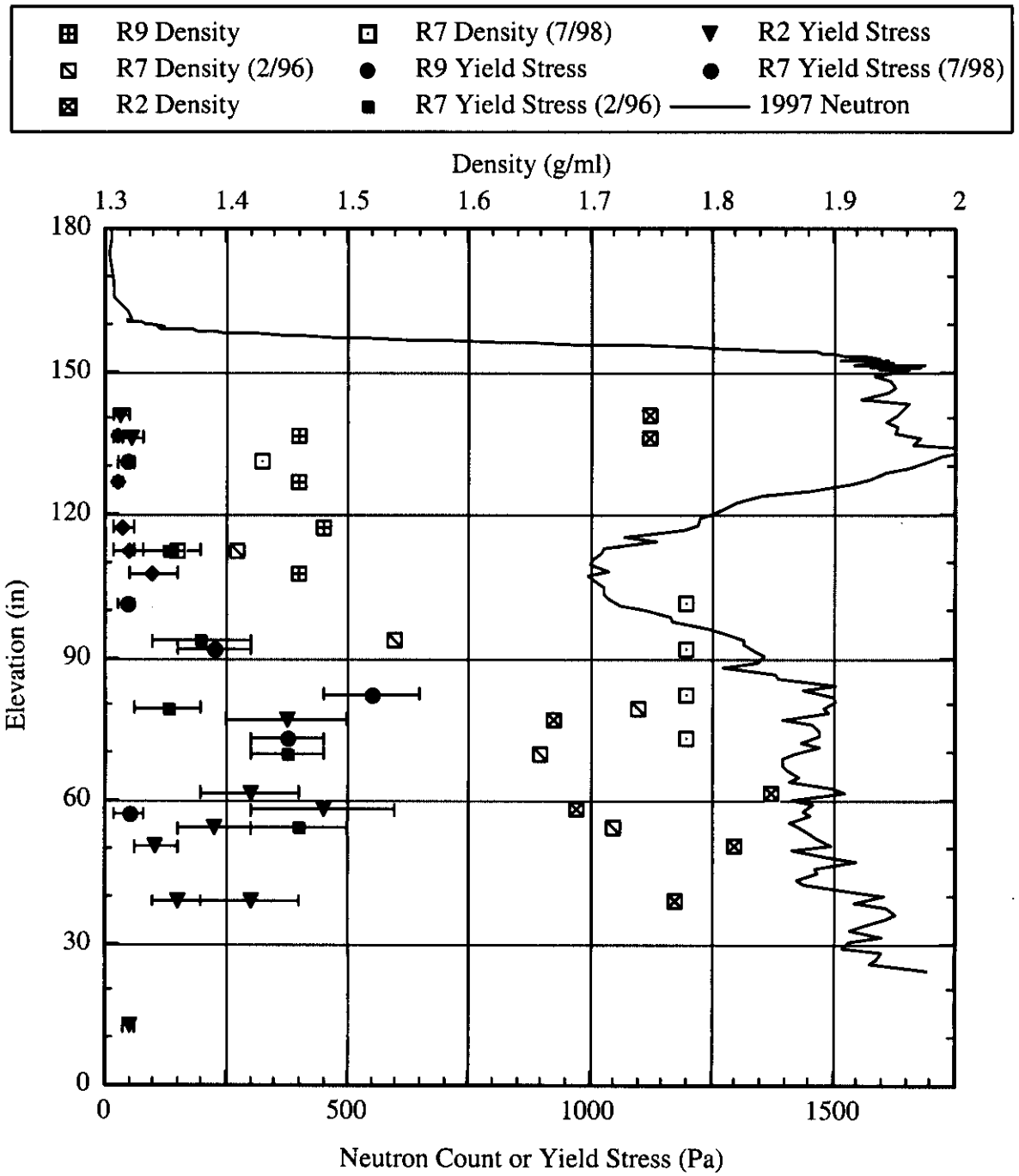


Figure 4-74. Tank 241-U-107 Strength and Density Profile

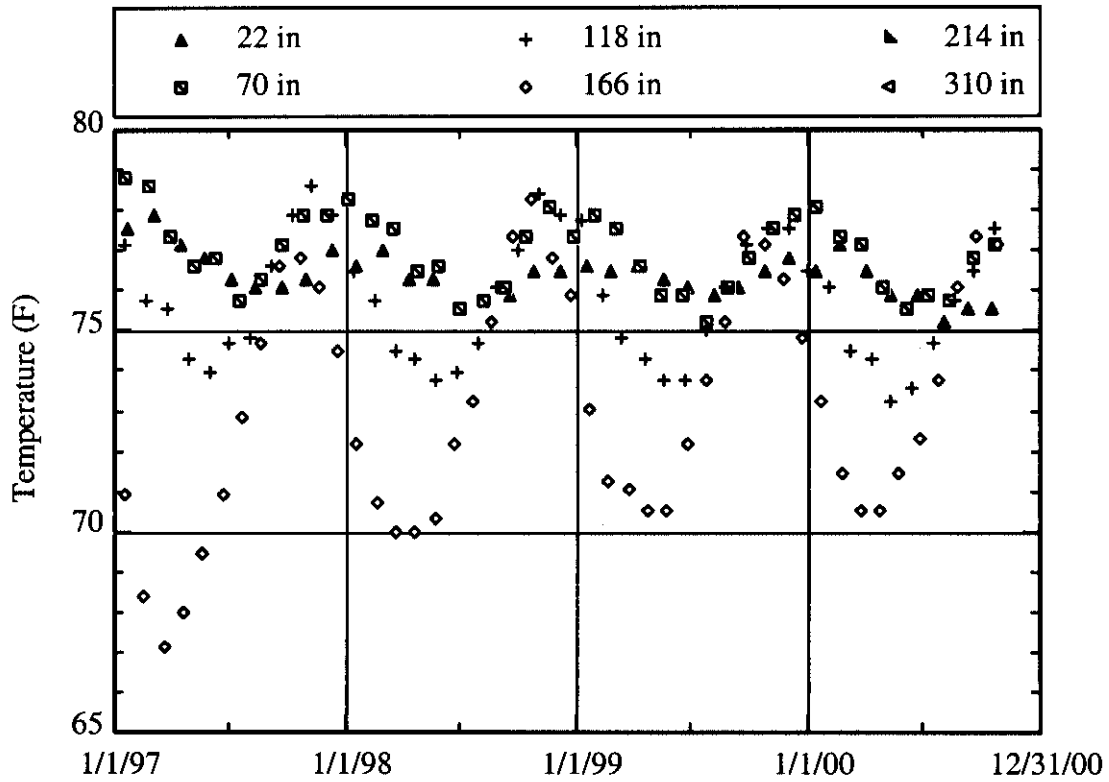


Figure 4-75. Tank 241-U-107 Waste Temperature History

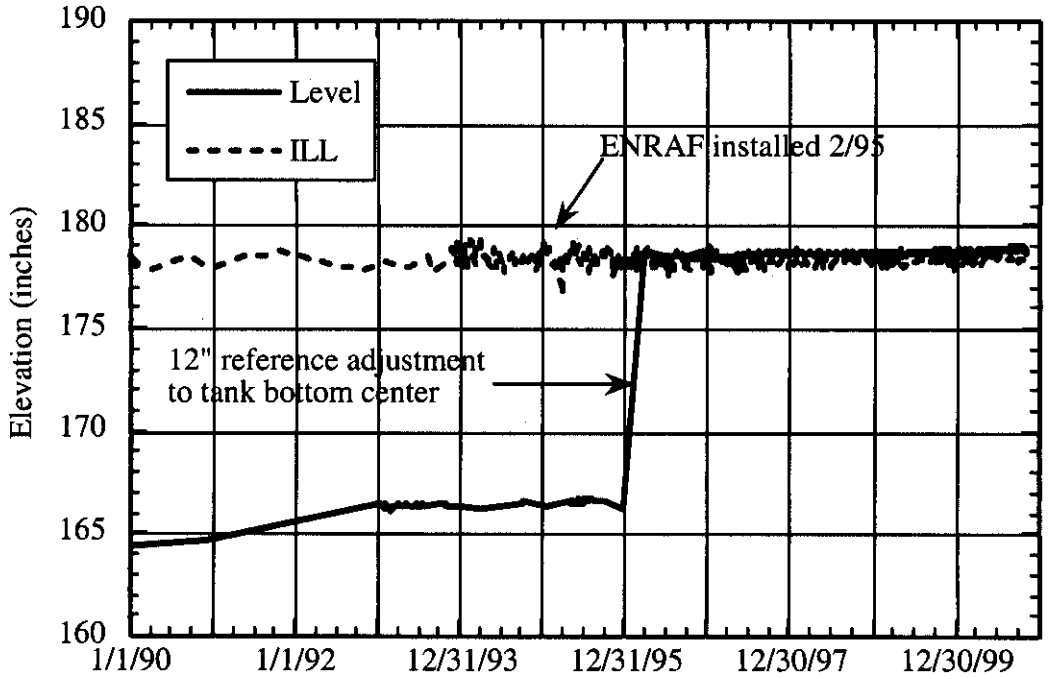


Figure 4-76. Tank 241-U-108 Waste Level and Interstitial Liquid Level History

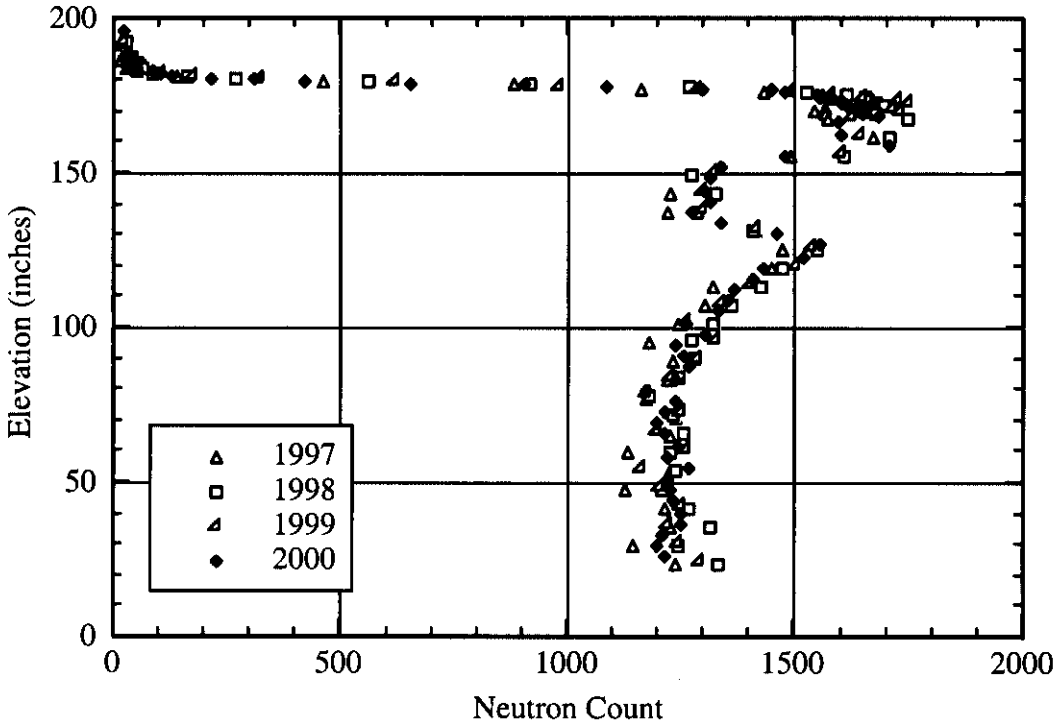


Figure 4-77. Tank 241-U-108 Neutron Logs

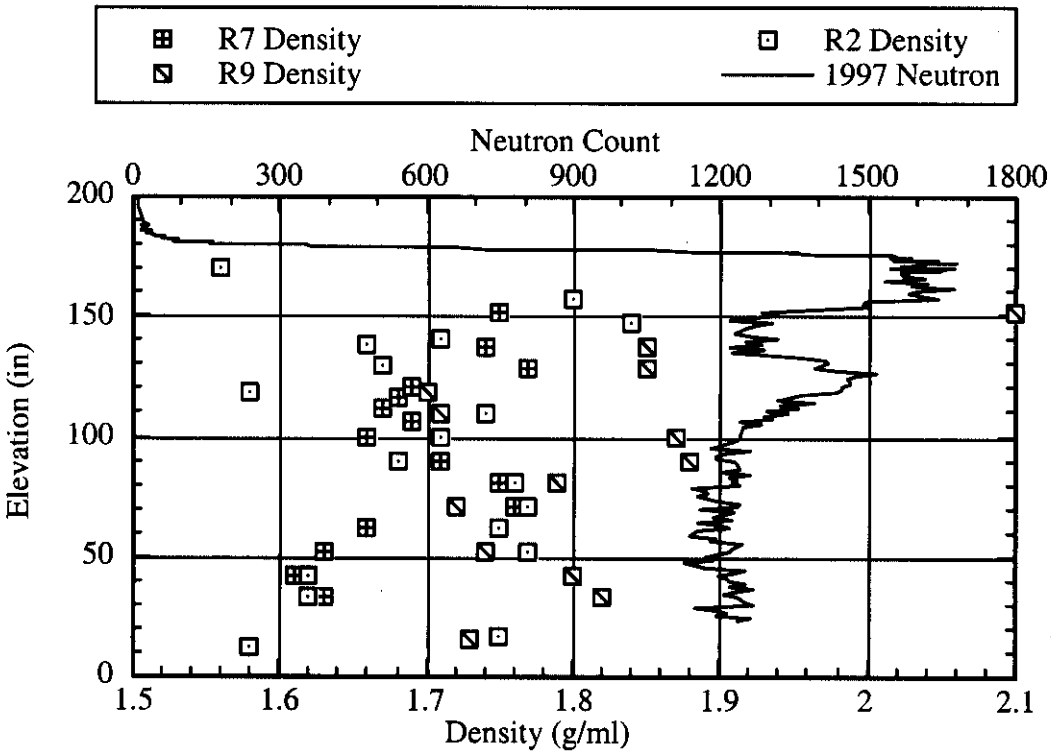


Figure 4-78. Tank-241-U-108 Density Profile

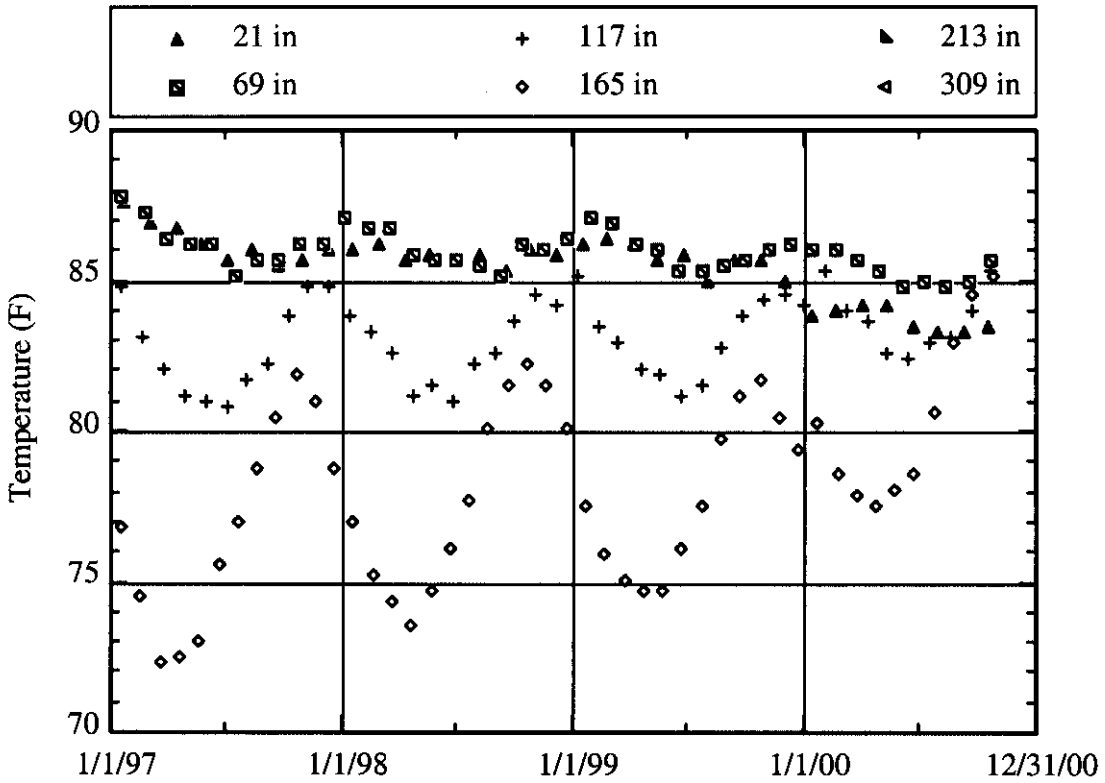


Figure 4-79. Tank 241-U-108 Waste Temperature History

4.1.19 Tank 241-U-109 Waste Configuration

Tank U-109 contains noncomplexed saltcake like most of the other U-Farm tanks. Saltwell pumping began in tank U-109 March 30, 2000, and is still in progress. Pumping to-date has removed 74 kgal (or 75%) of the projected 99 kgal of drainable liquid in the tank. The saltwell pumping history is shown in Figure 4-80. The average retained gas volume fraction measured by the RGS in 1998 core samples was 0.22, ranging from 0.2 at 140 inches to 0.3 at the bottom. The average gas volume fraction is estimated at 0.08 by the BPE method and 0.12 from the neutron log.

The waste level history and neutron logs are shown in Figures 4-81 and 4-82, respectively. The waste level and ILL have been essentially constant for the 10 years prior to pumping, except for the 12-inch waste level reference adjustment in early 1996. The waste level is still dropping with continued pumping. The large drop in ILL may be somewhat misleading in that much of the waste above the current ILL is still very wet, as indicated in Figure 4-82. Photographs taken in 1988 show much of the waste surface covered with supernatant. The level gauge at the 31-ft radius and the LOW is at about 27 ft (see Figure 2-22). There are no measurements or core samples from the central part of the tank.

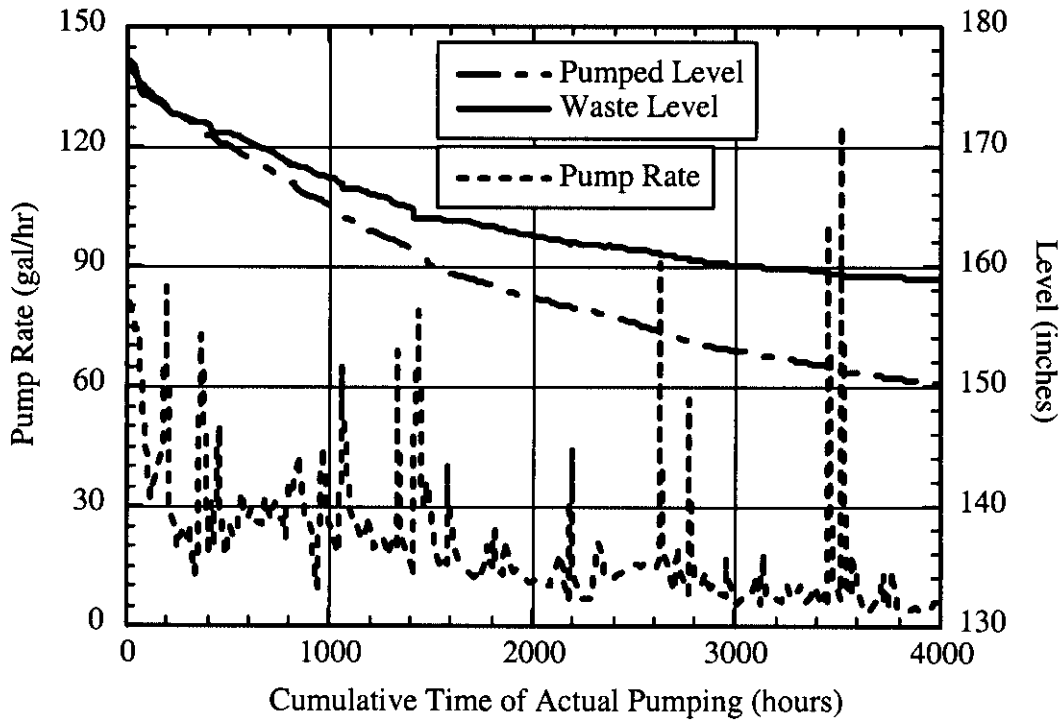


Figure 4-80. Tank 241-U-109 Saltwell Pumping History

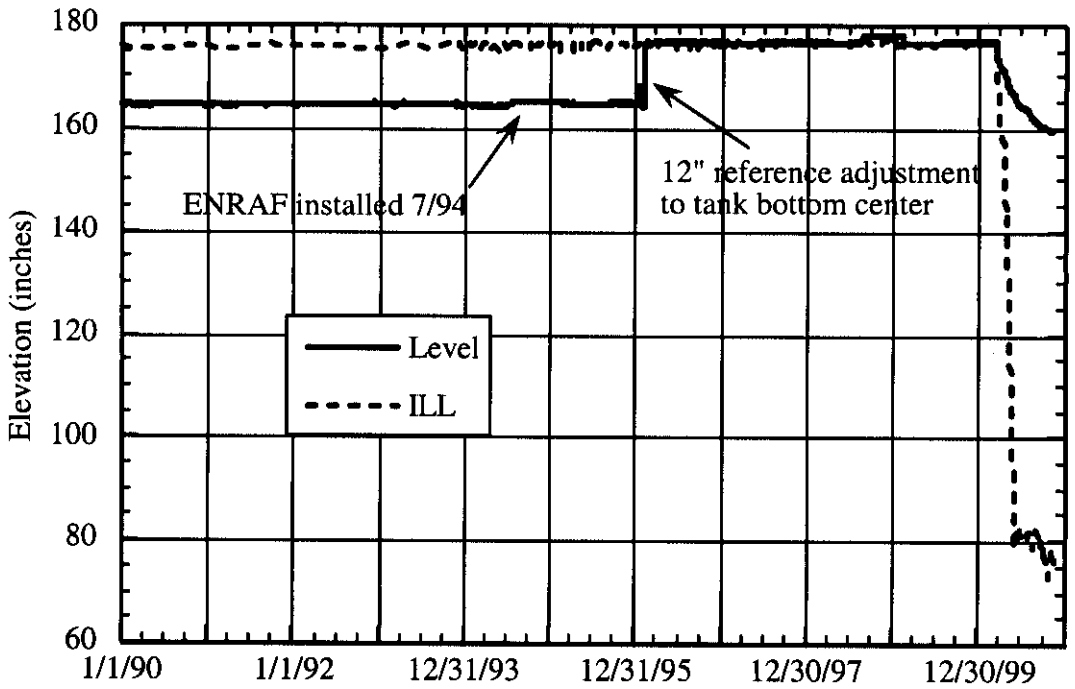


Figure 4-81. Tank 241-U-109 Waste Level and Interstitial Liquid Level History

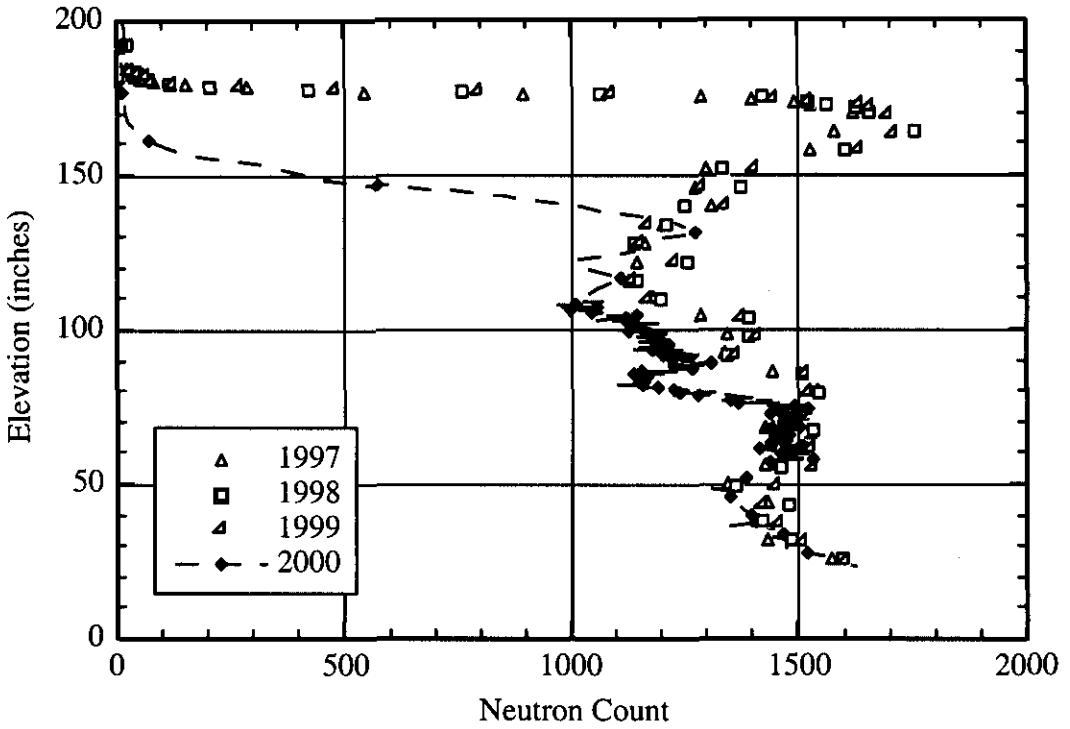


Figure 4-82. Tank 241-U-109 Neutron Logs

The yield stress and density profiles from the 1996 and 1998 cores in Figure 4-83 show a relatively uniform density averaging about 1.7 g/mL from top to bottom. All of the cores were taken from at least the 27-ft radius, and none represents the central part of the tank.

The temperature history, which is shown in Figure 4-84, is very similar to that of tanks U-105 and U-108, prior to pumping. Saltwell pumping has not had a significant effect on the temperature profile. The waste temperature in the lower half of the tank ranges from 78 to 84 °F with an annual cycle of 2 to 4 °F. The unexplained temperature spikes visible on all thermocouples in the waste in January 2000 are very similar to those observed in tank U-108.

4.2 WASTE CONFIGURATION SUMMARY

The waste configurations in the 19 SSTs on the Flammable Gas Watch List vary widely and are changing rapidly due to saltwell pumping. A snapshot of the evolving waste configuration in the 19 tanks is listed in Table 4-1. The table includes the current waste level and ILL (with the drop in each due to pumping), supernatant depth prior to pumping, the initial estimated drainable liquid volume (and volume of liquid pumped) and the current peak waste temperature. Table 4-2 summarizes the liquid and bulk solids density and yield stress range from core samples obtained prior to pumping. Configurations include the deep, unique solid-over-liquid of tanks A-101 to AX-101, the very shallow tank AX-103, the cold tank T-110, and the hot tank SX-105. After saltwell pumping has been completed, the tanks will have had their waste level reduced from 1 ft (T-Farm) to 15 ft (tank A-101).

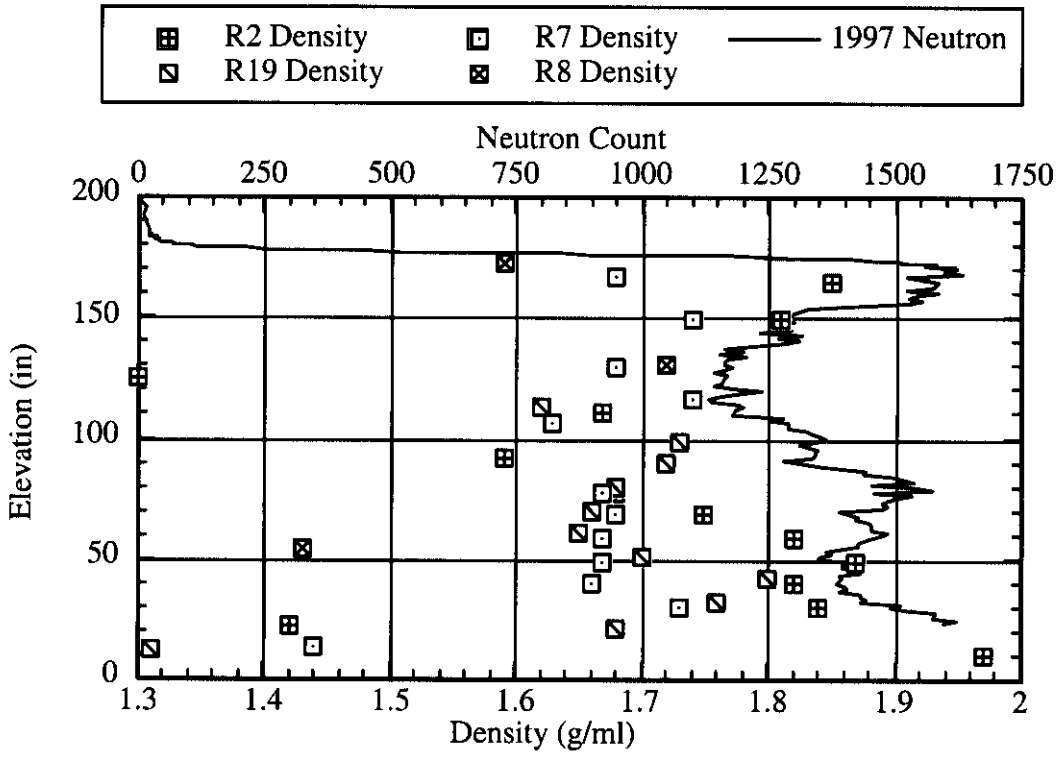


Figure 4-83. Tank 241-U-109 Density Profile

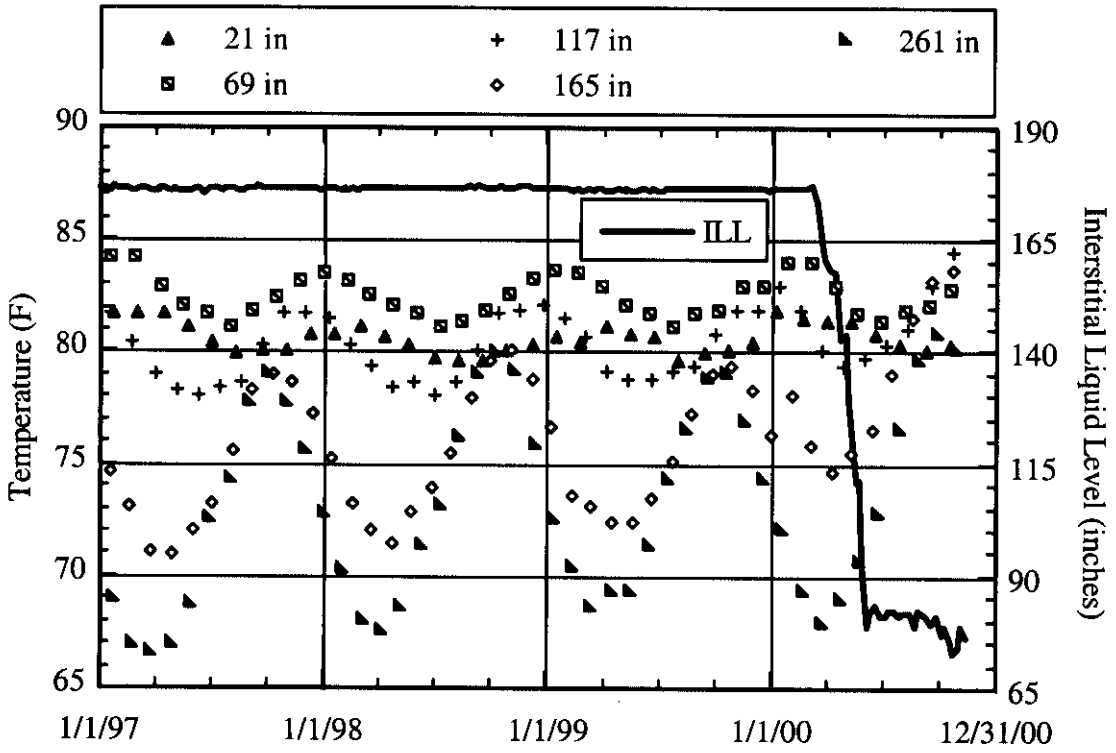


Figure 4-84. Tank 241-U-109 Waste Temperature History

Table 4-1. Waste Configuration Summary as of December 2000

Tank	Waste Level (in.) [a]	ILL (in.)[a]	Supernatant (in.)	Est. Drainable Liq. (kgal) [b]	Peak Temp(°F)
A-101	337 [5]	353 [7]	179 [c]	587 [18]	143
AX-101	266 [12]	264 [d] [8]	138 [c]	444 [9]	128
AX-103	38	-	-	-	108
S-102	169 [36]	169 [36]	-	99 [68]	99
S-111	204	203	~ 12	132 [0]	88
S-112	189	123	-	70 [0]	84
SX-101	166	167	~ 6	99 [0]	130
SX-102	192	193	~ 24	116 [0]	139
SX-103	219 [15]	227 [8]	-	132 [39]	157
SX-104	168 [50]	95 [120] [e]	-	144 [125]	138
SX-105	155 [84]	135 [3] [f]	-	141 [132]	162
SX-106	104 [94]	72 [123] [g]	-	283 [160]	98
SX-109	96	-	-	n/a	135
T-110	147 [12]	146 [15]	-	41 [34]	63
U-103	163 [17]	60 [118]	-	99 [108]	87
U-105	138 [26]	93 [72] [h]	-	80 [91]	88
U-107	156	156	~ 24	115 [0]	78
U-108	179	178	~ 18	124 [0]	86
U-109	159 [18]	79 [98]	-	99 [72]	84

Notes:

(a) The number in brackets is the drop resulting from saltwell pumping to December 2000.

(b) The number in brackets is the volume of liquid removed by saltwell pumping.

(c) The free liquid in tanks A-101 and AX-101 is beneath the solids layer. "Supernatant" inferred from initial depth and volume of liquid pumped. Supernatant in other tanks inferred from neutron logs.

(d) In tank AX-101 the gamma log shows an ILL of 127 inches while the neutron log indicates 264 inches.

(e) The ILL in tank SX-104 was only 73 inches immediately after pumping and recovered 22 inches to the current 95-inch level in about six months.

(f) The last available ILL reading for tank SX-105 was August 15, 2000.

(g) The ILL in tank SX-106 was 60 inches immediately after pumping and recovered 12 inches in about eleven months.

(h) The ILL in tank U-105 was 88 inches immediately after pumping and has recovered 5 inches in the last five months.

est. = estimated

Table 4-2. Waste Densities and Yield Stress

Tank	Density (kg/m^3)		Yield Stress (Pa) [a]
	Liquid	Bulk Solid	
A-101	1489 ± 28	1678 ± 51	200 - 700
AX-101	1561 ± 94	1683 ± 50	
AX-103	no sample		
S-102	1359 ± 70	1684 ± 136	50 - 1000
S-111	1359 ± 10	1648 ± 112	
S-112	no sample		
SX-101	1500 ± 49	1726 ± 140	
SX-102	1450 ± 29	1737 ± 105	
SX-103	1478 ± 21	1693 ± 172	
SX-104	1471 ± 17	N/A	
SX-105	1468 ± 28	N/A	
SX-106	1423 ± 19	1686 ± 57	
SX-109	no sample		
T-110	1064 ± 28	1255 ± 42	
U-103	1422 ± 78	1712 ± 97	20 - 1750
U-105	1462 ± 34	1697 ± 74	
U-107	1422 ± 123	1701 ± 124	30 - 600
U-108	1399 ± 25	1720 ± 77	
U-109	1474 ± 70	1646 ± 144	

(a) Yield stress estimates are given only for tanks where the evaluation described in Section 2.4.1 was performed.

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5.0 GAS GENERATION AND COMPOSITION

The gas generation rate is an important factor in gas retention and frequency of releases. Results of laboratory experiments reveal the effects of changes in dose rate, chemical composition, and temperature on the rates of generation of the various gas species. Based on these data and field measurements, an empirical model for hydrogen generation has been developed that can be used to estimate hydrogen generation rates for future waste states. This model has been used to assess the effect of saltwell pumping on hydrogen generation.

The composition of the gas generated, stored, and released from the waste must be known to determine whether the tank headspace can become flammable following a gas release. While gas generation tests can provide insight on trends in composition, the data most representative of the composition of gas that is actually released are provided by in-situ measurements of the composition of the gas retained in the waste. A comprehensive study of the thermal and radiolytic reactions involved with gas generation by Stock (2000a) provides additional insights as to the sources of the dominant gases. Steady-state headspace gas composition measurements also provide some information, but are affected by transport processes and do not represent the bulk of the stored gas.

This section summarizes the available gas composition measurements, as well as, gas generation data. The theory of gas generation in the Hanford Site tank waste is summarized briefly in Section 5.1. Section 5.2 discusses the results of laboratory gas generation tests on actual tank waste samples, and the gas generation model and field gas generation data are described in Section 5.3. Section 5.4 summarizes gas composition measurements obtained from RGS samples and drill string gas samples, and Section 5.5 covers headspace gas composition measurements. Section 5.6 summarizes the gas generation and composition issue.

5.1 GAS GENERATION THEORY

Based on several years of study of the Hanford Site tank waste characterization and gas composition measurements, Stock (2000a) documented an exhaustive study of the chemistry of flammable gas generation. This section briefly summarizes the conclusions of this work.

Radioactive wastes generate and retain hydrogen, nitrogen, nitrous oxide, ammonia, methane, and other volatile organic compounds. Besides radiolysis of water, radiolytic and chemical oxidation of the organic complexants, phosphate esters and hydrocarbons accelerate the rate of formation of hydrogen. Nitrogen, nitrous oxide, ammonia, methane, and other gases are also produced during oxidation of the organic compounds. The radiolytic and chemical reactions are closely coupled, and the chemistry is complex.

Organic compounds are present in most waste tanks. The wastes contain remnants of the original organic complexants, phosphate esters, and hydrocarbons. Small and large fragments of the original complexants, homologous series of organic compounds derived from the normal paraffin

hydrocarbons, and products of chemical reactions of the phosphate esters have also been identified. The organic waste constituents are slowly oxidizing to common end products including formate, acetate, and oxalate ions. The eventual reaction product is inorganic carbonate ion.

Oxidation of organic compounds and gas formation are initiated by the radioactive decay process, by thermal chemical reactions, and by other chemical reactions that do not involve free radicals. The decay processes produce hydrogen atoms, hydroxyl radicals, nitric oxide, and nitrogen dioxide. Similar radical reagents can also be obtained by thermal reactions. The radiolytic sequence is summarized as follows:

Radiolytic and thermal processes $\rightarrow$ H, OH, NO, NO_2

Organic compounds + reactive free radicals $\rightarrow$ organic free radicals

Organic free radicals + NO and NO_2 $\rightarrow$ reactive organic intermediates

Other chemical processes that do not involve reactive free radicals occur in parallel to produce reactive organic intermediates:

Organic compounds + ionic reagents $\rightarrow$ reactive organic intermediates

The reactive organic intermediates formed in these reactions are transformed into other substances more rapidly than are the compounds from which they were formed. Much of the gas generated in the waste is obtained in these later stages of the chemistry. As noted subsequently, hydrogen is produced during the oxidation of formaldehyde to formate ion and nitrogen-containing gases are by-products of other oxidation reactions.

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

The dominant products of the reactions of the complexants and phosphate esters have been identified. For example, the principal degradation pathway for ethylenediaminetetraacetate (EDTA) ion involves successive loss of two carbon fragments to produce oxalate or formate and carbonate ions. Tributyl phosphate reacts in alkaline solution to produce butanol and dibutylphosphate. A broad array of organic compounds including homologous series of alkanes, alkenes, alcohols, aldehydes and ketones, and nitriles are formed from the original hydrocarbons.

The relative rates of depletion of the principal complexants and phosphate esters have been determined. Among the four original complexants, hydroxyethylethylenediaminetriacetate (HEDTA) ion 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 and oxalate ion. The hydrocarbons react much more slowly than the complexants or tributyl phosphate.

Chemical reactions between the waste constituents and of the reactive organic intermediates produced during radiolytic reactions occur simultaneously. 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 reactions and other related processes have been blended with the initial thermal and radiolytic reactions to provide a comprehensive chemical reaction model that is consistent with the characterization results and laboratory investigations.

Gas formation is a direct consequence of the oxidation of organic molecules. Some hydrogen is formed by hydrogen atom abstraction reactions, but the predominant sources of hydrogen are hydroxide ion-catalyzed oxidation of the intermediate aldehydes, for example, during the conversion of formaldehyde into formate ion. The reactions of the nitroso and nitro compounds yield nitrosyl anion and hydroxylamine. These decompose to form nitrogen, nitrous oxide, and ammonia. Ammonia is also formed by the hydrolysis of nitriles and amides that are formed by the oxidation of the original complexants. Many volatile and some not-so-volatile organic compounds are found in the tank headspaces and in the retained gas. The gases contain methane and lesser amounts of other low molecular weight organic compounds such as propane, cyclopropane, propene, propanol, acetone, and nitropropane.

The gas generation rates from the radiolytic reactions have an exponential dependence on the temperature, like the thermal reactions, because the gases are actually produced in chemical reactions that follow the initial radiolytic reactions. This dependence has been observed in laboratory gas generation tests on several wastes (see Section 5.2) and has been incorporated into an empirical model to predict hydrogen generation rates (see Section 5.3).

5.2 LABORATORY GAS GENERATION TEST RESULTS

While the current in-situ gas composition in the waste has been measured, it is important to understand how the gas compositions might change with temperature, dilution, or on mixing of different wastes. The gas generation tests summarized in this section investigate the effect of temperature and radiation dose on rates at which the main species generated.

Laboratory gas generation tests were performed by measuring the volume of gas produced in a given time by a small waste sample in a small sealed vessel. These tests were particularly challenging because the gas generation rates are very low under tank conditions and the time required to obtain a measurable volume of gas is prohibitively long. To get around this problem, gas generation rates were accelerated by increasing the temperature above 60 °C. Similarly, self-irradiation dose rate in a small sample is much lower than in the tank; therefore, external gamma sources were used to increase the radiolytic gas production sufficiently for it to be measured with reasonable accuracy.

The gas generation rates at elevated temperatures without external irradiation are extrapolated back to tank conditions assuming the standard Arrhenius behavior,

$$Q_T = Ae^{-E_a/RT} \tag{5-1}$$

where:

Q_T is the thermal gas generation rate (mol/kg/day),
A is the pre-exponential constant (mol/kg/day),
E_a is the activation energy (kJ/mol),
R is the gas constant (0.008314 kJ/mol-K), and
T is the temperature (K).
A and E_a are determined fitting Equation 5-1 to the measured gas generation rates.

Similarly, comparing the gas generation rates at several temperatures with and without external irradiation, assuming that radiolytic gas generation is independent of temperature, provides a "G-value" from which the radiolytic contribution can be calculated as:

$$Q_R = 2.488(10^{-8})GR \tag{5-2}$$

where:

Q_R is the radiolytic gas generation rate,
G is the "G-value" in molecules/100 eV and
R is the dose rate (R/hr).

Q_R is determined by subtracting the thermal component calculated by Equation 5-1 from the measured total generation rate with external irradiation.

Laboratory tests have been performed on wastes from the single-shell tanks A-101[10], S-102, S-106, and U-103. Results of the tests on the latter three tanks are summarized in separate subsections below.

5.2.1 Tank 241-S-102 Gas Generation Tests

The details of the procedures and results for high-dose and low-dose tests are given in King et al. (1997) and King and Bryan (1999), respectively. The focus of the gas generation tests on tank S-102 samples was on the effect of temperature and radiation dose on the composition and rate of gas generation. Tests were performed first varying the temperature only. Generation rates of all components increased but the fraction of hydrogen in the gas mixture decreased with temperature. Arrhenius treatment of the rate data gave thermal activation energies, E_a, for the various gases: 91 ± 7 kJ/mol for hydrogen, 79 ± 11 kJ/mol for nitrous oxide, 127 ± 70 kJ/mol for

[10] Results are described in the PNNL letter report TWS98.78, *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste: Status Report*, by S. A. Bryan and C. M. King, September 1998.

nitrogen, and 137 ± 7 kJ/mol for methane. The uncertainties in the activation energies and G-values given here and in the subsequent subsections represent the 95% confidence interval.

The second part of the work exposed the tank S-102 waste samples to a 37,000 rad/hr (^{137}Cs) external gamma source at the same control temperature. The radiolytic G-values for gas generation in molecules/100 eV were 0.017 ± 0.004 for hydrogen, 0.009 ± 0.003 for nitrous oxide, 0.009 ± 0.003 for nitrogen, and 0.0005 ± 0.0002 for methane.

Using the thermal activation energies and radiolytic G-values, the gas generation rates were extrapolated to tank conditions. The tank was at 41 °C (106 °F) and the dose rate in the waste was 207 R/hr. The sum of thermal and radiolytic hydrogen generation rates is 1.0 mol/day, 0.8 scfd. This is about 40% of the 2.2 scfd hydrogen generation rate calculated with Hu's (2000) model shown in Table 5-1. The field measurement of hydrogen generation reported by Hu (2000) was 2.3 scfd.

The composition of the generated gas mixture extrapolated to tank conditions is listed in Table 5-1 along with the composition measured with the RGS. The extrapolated hydrogen fraction was about twice that measured by the RGS.

Table 5-1. Calculated Composition of Gas Generated in Tank 241-S-102

Gas	Mol%	
	Experiment	RGS
Hydrogen	61	33
Nitrous oxide	23	33
Nitrogen	15	32
Methane	1.2	<1

Gas generation experiments are typically run at temperatures and dose rates far higher than tank conditions in order that sufficient volumes of gas are generated to permit accurate measurement within a reasonable time. Then, as above, the measured generation rates are extrapolated to tank temperature and dose rate using the thermal activation energies and G-values obtained from the experimental data. To determine how well this method actually represents tank conditions, a long-term gas generation test was done with tank S-102 waste with the temperature and dose rate more closely matching tank values (King and Bryan 1999). The temperature was maintained at 41 °C (106 °F), which matched the tank temperature, and the dose rate was 286 R/hr, 40% higher than the tank dose rate.

The gas composition in the test vessels was sampled after 40, 77, and 114 days. The amount of gas produced in these tests was small and the quantities of nitrogen, nitrous oxide, and methane could not be measured accurately. However, hydrogen made up 40 to 60% of the gas produced which allowed its rate of formation to be established. Extrapolating only the dose rate from 286 R/hr to the tank value of 207 R/hr using the hydrogen G-value from the short term tests, the

hydrogen generation rate was 0.8 mol/day compared to 1.0 mol/day extrapolated from the short-term, high temperature and dose rate data.

5.2.2 Tank 241- S-106 Gas Generation Tests

Both high- and low-dose tests were also performed on tank S-106 waste. The results are given in King and Bryan (1999).[11] Both hydrogen and methane generation rates appeared to be unusually accelerated by radiation at 120 °C and also appeared to be dose rate dependent at 60 °C. The low-dose rate G-value for hydrogen is three times higher than the high-dose rate G-value at 60 °C and four times higher at 120 °C. The hydrogen G-value appears to be temperature dependent. The high-dose rate G-value at 90 °C was six times higher than the 60 °C G-value. The G-values for nitrogen were assumed not to be dose-rate dependent, and the G-values for nitrous oxide could not be determined.

The data did not allow extrapolation of gas generation rates to tank conditions. The rate of hydrogen generation under tank conditions (25 °C, 177 R/hr) was estimated using the thermal and radiolytic activation parameters for gas generation in actual tank waste. The radiolytic generation rate for hydrogen was determined to be 2.1 (10^{-8}) mol/kg/day, and the thermal rate was determined to be 3.9 (10^{-8}) mol/kg/day. This translates to a total of 0.19 moles of hydrogen generated per day in this tank.

5.2.3 Tank 241-U-103 Gas Generation Tests

The details of the laboratory tests on waste from tank U-103 are described by King and Bryan (1999). The gas generation tests on tank U-103 samples focused first on the effect of temperature on the composition and generation rate. Generation rates of nitrogen, nitrous oxide, methane, and hydrogen increased with temperature and the composition of the product gas mixture also varied with temperature. Thermal activation energies, E_a, for the various gases were: 91 ± 24 kJ/mol for hydrogen, 108 ± 22 kJ/mol for nitrous oxide, 88 ± 34 kJ/mol for nitrogen, and 156 ± 8 kJ/mol for methane. Uncertainties represent a 95% confidence interval.

The second phase of the work focused on the effect of a 36,000-rad/h external gamma source (^{137}Cs) on gas generation at 40, 60, and 90 °C. The best estimates of radiolytic G-values, in molecules per 100 eV, were determined to be: 0.0019 ± 0.0003 for nitrous oxide, 0.012 ± 0.003 for nitrogen, and 0.0022 ± 0.0003 for methane. The hydrogen G-value was temperature-dependent: 0.006 at 40 °C increasing to 0.017 ± 0.004 at 60 °C. Three other tanks studied previously produced temperature-dependent G-values.

The thermal and radiolytic activation parameters obtained above allow the rate of hydrogen generation at tank conditions to be calculated. The tank U-103 waste temperature is 29 °C

[11] The following letter report describes the high-dose rate tests: King, C. M., and S. A. Bryan, 1998, *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste: Status Report*, WS98.77, Pacific Northwest National Laboratory, Richland, Washington.

(84 °F) and the dose rate is 449 R/hr. The 3 (10^6) kg of waste in the tank generates a total of 0.48 moles per day or 0.4 scfd of hydrogen. This is about a factor of five less than the 2.2 scfd calculated with Hu's (2000) model (see Table 5-3), or the 2 scfd estimated by Hu (2000) from headspace measurements. The composition of the total gas mixture at tank conditions extrapolated from the experimental generation rates of hydrogen, nitrous oxide, nitrogen, and methane are summarized along with RGS measurement in Table 5-2. The composition derived from the experiments compares well with that measured by the RGS. If the gas mixture contains 27% hydrogen as given in the table, the total gas generation rate based on Hu's (2000) 2.6 scfd of hydrogen is about 10 scfd.

Table 5-2. Calculated Composition of Gas Generated in Tank 241-U-103

Gas	Mol%	
	Experiment	RGS
Hydrogen	27	23
Nitrous oxide	36	39
Nitrogen	33	36
Methane	4	<1

5.3 GAS GENERATION MODEL

Hydrogen is the major flammable gas observed in the dome space at steady-state. A hydrogen generation rate model was developed and validated by Hu (2000) based on a large body of gas generation data and tank waste characterization data. The rate equations are formulated as a function of physical and chemical properties of tank waste, and are used to estimate the hydrogen generation rate of current waste content, as well as, the newly mixed waste of known waste properties. The model uses a set of semi-empirical rate equations to simulate the hydrogen generation mechanism of thermal chemical reactions, radiolysis of water and organic components, and corrosion processes. Summarized below is the total hydrogen generation rate, HGR, in units of hydrogen yield per kilogram of total waste per day (Hu 2000).

5.3.1 Hydrogen Generation Rate Model Description

The total hydrogen generation rate (HGR) consists of the thermal rate (HGR_{thm}), the radiolysis rate (HGR_{rad}), and the corrosion rate (HGR_{cor}). The HGR is expressed in terms of moles/kg-day.

$$HGR = HGR_{thm} + HGR_{rad} + HGR_{corr} \tag{5-3}$$

Where $HGR_{thm} = a_{thm} \cdot r_f \cdot [TOC] \cdot [Al]^{0.4} \cdot L_f \cdot e^{-(Ethm/RT)}$

$HGR_{rad} = (G_{H2O} + G_{ORG} \cdot L_f) \cdot H_{load} \cdot CF_1$

$HGR_{corr} = R_{corr} \cdot A_{wetted} / M_{tank} \cdot CF_2$

With $G_{ORG} = a_{rad} \cdot e^{(-Erad/RT)} \cdot (r_f \cdot [TOC])$

$G_{H2O} = 0.45 - 0.56 \cdot [NO_3^-]^{1/3} - 0.43 \cdot [NO_2^-]^{1/3}$

And

E_{thm}	is the activation energy for thermal reaction (89.3 kJ/mole)
E_{rad}	is the pre-exponential factor for radiolytic reaction (44.3 kJ/mole)
a_{thm}	is the pre-exponential factor for thermal reaction (2.76E+09 mole/kg/day)
a_{rad}	is the pre-exponential factor for radiolytic reaction (2.49 E+06 H_2/100 eV)
G_{ORG}	is the hydrogen yield per 100eV energy from organic radiolysis
G_{H2O}	is the hydrogen yield per 100eV energy from water radiolysis (G_{H2O} has a minimum value of 0.005 H_2/100 eV)
r_f	is the TOC reactivity coefficient (average value is 0.7 for DSTs and 0.4 for SSTs)
R_{corr}	is the corrosion coefficient [1.83E-08 for DSTs and 3.6E-08 for SSTs (m^3/min/m^2) at 25 °C]
H_{load}	is the heat load (Watt/kg)
L_f	is the liquid weight fraction in the waste.
A_{wetted}	is the wetted surface area of the tank (m^2)
M_{tank}	is the total waste mass (kg) in the tank
CF_1	is the conversion factor to convert the units from (H_2/100eV)(Watts/kg) to (mole/kg/day)
CF_2	is the conversion factor to convert the units from (m^3/kg/min) to (mole/kg/day)

In general, the HGR due to chemical reaction follows Arrhenius behavior, and the rate from radiolysis is proportional to the radiation dose. In addition, the HGRs from radiation effects in tank waste samples have been observed to be temperature-dependent (King and Bryan 1999). The analysis of all available gas generation data (Hu 2000) shows that this temperature-dependent reaction follows Arrhenius behavior, which can result from a multi-step degradation of organic compounds, initiated by radiolysis and followed by thermal reactions. The water radiolysis rate is assumed to be temperature-independent, with the G-value reduced by scavenging effects.

The numerical values in the equations are established by the analysis of gas generation kinetic data from waste samples with the aid of tank field surveillance data and tank waste characterization data. The reactivity coefficient, r_f, was used to adjust for differences in reactivity of TOC among tanks.

5.3.2 Effect of Saltwell Pumping on Gas Generation

The majority of drainable liquid has been or soon will be removed by saltwell pumping from 17 of the 19 SSTs on the Flammable Gas Watch List. These 17 tanks are listed in Table 5-3, along with the saltwell pumping status of each. Because gas generation occurs predominantly in the waste liquid phase, the gas generation rate in an SST is decreased by the removal of drainable liquid. As a comparison, calculations to estimate the hydrogen generation rates prior to and after the saltwell pumping activities were carried out using the hydrogen generation rate model described in Section 5.3.1.

Table 5-3 also lists the estimated total liquid inventories of each tank before and after saltwell pumping. The estimated pre-pumping liquid inventories were based on core sample analyses. The estimated post-pumping liquid inventories were calculated by subtracting the actual (or anticipated) pumpable liquid in each tank (Fort 2000) from the estimated pre-pumping liquid inventories. These liquid inventories were then used with Equation 5-3 to estimate the hydrogen generation rates before and after saltwell pumping. As described above, the hydrogen is generated by thermolysis, radiolysis, and corrosion. Assuming the chemical species concentrations in the waste are the same before and after saltwell pumping, the thermolysis rates and radiolysis rates are calculated by using the generation rates per unit volume waste (Hu et al. 2000) multiplied by the liquid inventories.

The corrosion rates prior to the saltwell pumping are also taken from Hu et al. (2000). The post-pumping corrosion rates decreased from the rates prior to pumping, because of the decreased contribution of the wetted area, which is reduced because of removal of the supernatant. It is assumed that the solid waste of the solid layer will remain on the tank liner surface, keeping it wet for an extended period of time, even though part of the interstitial liquid is pumped out. The calculated total generation rates before and after saltwell pumping for 17 tanks are given in Table 5-3.

The hydrogen generation rates are expected to decrease roughly in proportion to the fraction of liquid removed, unless the generation rate is already quite low. As shown in the table, for tanks where pumping has been finished, the post-pumping hydrogen generation rate is 66% to 100% of the pre-pumping rate. The most significant change is expected to occur in tank A-101, with an anticipated decrease in hydrogen generation rate from 18.6 to 3.6 cubic feet per day. This tank has a relatively high hydrogen generation rate and has a large amount of liquid to be removed. Very little change in the estimated hydrogen generation rates is predicted for the cooler, drier tanks (e.g., tanks S-112 and T-110), in part because corrosion is thought to be the dominant hydrogen source in these tanks, which is less dependent on liquid volume, and in part because the decrease in total liquid inventory is relatively small.

The results in Table 5-3 give only the change in hydrogen generation resulting from saltwell pumping. Neither the amount of gas released during the actual pumping process nor the volume of gas that might eventually accumulate after pumping is considered here. Refer to Sections 6.0 and 7.0 for a full discussion of gas retention and release as affected by saltwell pumping.

Table 5-3. Estimated Hydrogen Generation Rates Before and After Saltwell Pumping

Tank	Saltwell Pumping Status	Pre-pumping		Post-pumping		Post- /Pre-Pumping Generation Rate
		Total Liquid Inventory (kgal)	Hydrogen Generation Rate (ft^3/day)	Total Liquid Inventory (kgal)	Hydrogen Generation Rate (ft^3/day)	
A-101	In Progress	795	18.5	208	3.6	0.19
AX-101	In Progress	602	5.6	158	1.5	0.27
S-102	In Progress	177	2.2	34.4	1.6	0.73
S-111	Not Started	363	1.5	231	1.3	0.87
S-112	Not Started	393	1.7	323	1.6	0.94
SX-101	In Progress	253	1.7	154	1.6	0.94
SX-102	Not Started	416	3.8	300	2.9	0.76
SX-103	In Progress	450	8.0	318	5.9	0.74
SX-104	Finished	371	6.2	246	4.8	0.77
SX-105	In Progress	489	13.7	348	10.2	0.74
SX-106	Finished	433	2.1	273	1.4	0.66
T-110	Finished	368	1.3	334	1.3	1.0
U-103	Finished	337	2.2	229	1.8	0.82
U-105	Finished	234	2.0	143	1.5	0.74
U-107	Not Started	311	1.3	196	1.2	0.93
U-108	Not Started	368	1.8	244	1.6	0.89
U-109	In Progress	233	1.5	115	1.4	0.93

5.4 GAS COMPOSITION MEASUREMENTS

The RGS is the only instrument in use that provides a means of obtaining waste gas composition measurements on actual tank waste. It is the primary method for determining the composition of the retained gas. The RGS system was described in Section 2.6, and gas compositions obtained with the RGS are summarized in Section 5.4.1. Gas compositions derived from core drill string gas samples are discussed in Section 5.4.2. Headspace gas compositions measurements are described in Section 5.5.

5.4.1 Retained Gas Sampler (RGS) Gas Compositions

Retained Gas Sampler data are available for the Flammable Gas Watch List SSTs A-101, AX-101, S-102, S-111, SX-106, U-103, and U-109 (Mahoney 2000). Retained Gas Sampler measurements were also made in the non-Flammable Gas Watch List SSTs BY-109 and S-106. The average gas compositions calculated from local RGS measurements in the SSTs are summarized in Table 5-4.

The gases that are retained in the solid layers of the waste often have higher hydrogen contents than the gases that are retained in liquid waste. This is particularly noticeable in tank A-101. The composition of the gases in the liquid wastes compare more closely to that of the gases that are generated in laboratory tests than the compositions of the gas retained in the solid layers. These observations imply that the composition of the gases that have been retained in solid layers have changed during years of residence, becoming richer in hydrogen as a consequence of slow decomposition reactions or subtle differences in migration rates of the various gas species through the solid-liquid matrix.

Table 5-4. Retained Gas Sampler Gas Compositions (mol%)

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
BY-109 [(b)]	50 ± 6	29 ± 5	18 ± 3	1.4 ± 0.6	< 1	< 1
S-102	33 ± 3	32 ± 4	33 ± 3	1.1 ± 0.4	< 1	< 1
S-106 [(c)]	63 ± 6	25 ± 4	11 ± 1	< 1	< 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
U-103	23 ± 1	36 ± 2	39 ± 2	< 1	< 1	< 1
U-109	25 ± 3	46 ± 8	27 ± 4	1.2 ± 0.5	< 1	< 1

Notes:

(a) From only one sample in tank AX-101.
(b) The RGS samples were taken only from below the ILL.
(c) There was no RGS sample from the supernatant in tank S-106.

5.4.2 Gas Composition from Drill String Samples

Drill string samples are occasionally taken during the process of waste core sampling activities. In this process, a sampler is introduced to the waste by means of a drill string, a hollow tube extending from the drilling truck above ground level down into the waste to the level of the last segment extracted. In some cases, the process is temporarily halted and gases from the waste may accumulate within the hollow drill string. Sampling of the drill string for gases is a normal work control. If high readings for flammable gas were noted, the field crews took grab samples for additional analysis.

Siciliano (1998) analyzed the drill string data that had been obtained over a several year period. His analysis had to account for the use of argon or nitrogen purge gases that were used in the drill string, as well as, for in-leakage of air. In most cases the analysis by Siciliano provided values for hydrogen and nitrous oxide that were in reasonable agreement with the RGS results shown in Table 5-4.

5.5 HEADSPACE GAS COMPOSITION

Monitoring and sampling of tank headspaces have provided considerable information about the composition of gas emerging from the waste. The SSTs on the Flammable Gas Watch List have had instrumentation for continuous monitoring of flammable gases since April 1995 (McCain 2000), and hundreds of headspace and ventilation system grab samples have been collected and analyzed. The following subsections discuss the types of data that have been collected and what each contributes to the current understanding of gas composition in the Flammable Gas Watch List SSTs.

5.5.1 Standard Hydrogen Monitoring System Headspace Monitoring Data

Hydrogen concentrations have been monitored in the 19 Flammable Gas Watch List SSTs and 11 other SSTs with dedicated SHMSs. (Refer to Section 2.3 for a complete description of the SHMSs instrumentation.) Each SHMS is equipped with two Whittaker™ electrochemical cell hydrogen monitors (one to measure concentrations between 0 and 10,000 ppmv, the other to measure concentrations up to 100,000 ppmv), data logging and transmitting equipment, and the ability to automatically collect samples for laboratory analyses in the event of a large GRE. Eight of the SHMSs on SSTs are also equipped with a gas chromatograph – a thermal conductivity detector (GC-TCD) system that measures hydrogen, methane, and nitrous oxide. Hydrogen measurements by the GC-TCDs are not entirely redundant with the Whittaker™ monitor measurements, because the GC-TCDs undergo daily calibration checks and are more accurate. In addition, three of the SHMSs on Flammable Gas Watch List SSTs and four on other tanks are equipped with photo-acoustic infrared multi-gas analyzers, which monitor headspace ammonia concentrations.

Headspace monitoring data indicate that hydrogen concentrations in the Flammable Gas Watch List SSTs stay well below 25% of the LFL. Table 5-6 lists the maximum hydrogen concentration observed in each of the 19 Flammable Gas Watch List SSTs and the date these maximums were observed (McCain 2000). Because the maximum concentrations were generally measured with Whittaker™ electrochemical cell monitors (tank A-101 being the exception), values less than about 1,000 ppmv should be considered approximate.[12] It is pertinent to note that saltwell pumping operations have been completed without the spontaneous release of significant amounts

[12] Whittaker™ electrochemical cells measure hydrogen gas with an absolute accuracy of 2,000 ppmv and a resolution of 50 ppmv (Schneider 1996). Although they generally agree with independent measurements (e.g., the GC-TCD) much better than advertised accuracy of 2,000 ppmv implies, baseline drift on the order of several hundred ppmv is not uncommon.

of hydrogen into the dome space for four tanks (SX-104, SX-106, T-110, and U-105). However, the two highest hydrogen concentrations listed in Table 5-6, observed in tanks U-103 and U-109, are both associated with gas releases induced by the removal of liquids from these tanks. Excluding these two values, the maximum hydrogen concentrations are all below 10% of the LFL of hydrogen in air.

Table 5-5. Maximum Hydrogen Concentrations Measured by Standard Hydrogen Monitoring System Instrumentation

Tank	Maximum H_2 Concentration (ppmv)	Date of Maximum Concentration	Notes
A-101	837	2/7/1999	E+ [1], GRE [2]
AX-101	540	12/10/1996	GRE
AX-103	3,880	11/22/1996	
S-102	3,780	5/20/1996	
S-111	1,270	12/14/1995	GRE
S-112	490	8/22/1995	
SX-101	400	8/22/1995	
SX-102	740	11/12/1996	
SX-103	640	2/12/1995	E+
SX-104	580	8/22/1995	
SX-105	710	12/28/1996	GRE
SX-106	560	8/17/1997	
SX-109	890	12/15/1999	
T-110	500	8/31/1999	
U-103	4,870	11/2/1999	SWP [3]
U-105	3,680	10/24/1996	E+
U-107	1,900	12/28/1996	GRE
U-108	3,280	2/25/1996	
U-109	4,930	3/23/2000	SWP

[1] E+ in the Notes column indicates the tank has a SHMS E+ gas monitor.

[2] GRE in the Notes column indicates the maximum was associated with a GRE.

[3] SWP in the Notes column indicates the maximum was associated with the saltwell pumping removal of drainable liquid from the tank.

Ammonia monitoring in the Flammable Gas Watch List SSTs has been limited by instrument reliability problems, and hampered by the condensation of moisture in the lines (particularly in cold weather), which affects the ammonia in the sample stream. The ammonia monitors have also been out of service for extended periods on several of the tanks. The highest reported ammonia concentration in any SST was about 5,200 ppmv observed in tank U-105 after the removal of drainable liquid waste by saltwell pumping. Table 5-7 lists the maximum ammonia concentrations in the 3 Flammable Gas Watch List SSTs equipped with ammonia monitors.

Table 5-6. Maximum Ammonia Concentrations Measured by Photo-Acoustic Monitors

Tank	Max. Ammonia Concentration (ppmv)	Date(s) of Maximum Concentration	Notes
A-101	1,400	6/2/00	
SX-103	1,470	8/22/98	
U-105	5,200	8/24/00	After SWP

The SHMS GC-TCDs on SSTs provide the only methane and nitrous oxide monitoring data. Although methane is produced by the waste, it is not a major waste gas, and has been observed only at relatively low concentrations in the headspaces. Tank U-105 has had the highest methane concentrations, as monitored by SHMSs, with a maximum concentration of around 60 ppmv, or approximately 0.12% of the LFL of methane in air. Maximum observed nitrous oxide concentrations are listed in Table 5-8. The highest reported nitrous oxide concentration, in tank U-105, was observed during saltwell pumping of this tank.

Table 5-7. Maximum Nitrous Oxide Concentrations Measured by Gas Chromatograph – Thermal Conductivity Detector (GC-TCD) Monitors

Tank	Max. N_2O Concentration (ppmv)	Date(s) of Maximum Concentration	Notes
A-101	221	10/28/00	
SX-103	184	10/28/00	
U-105	4,930	2/15/00	During SWP

The composition of gases released may be different during GREs than in the steady-state. In tank A-101, for example, the gases released by GREs are evidently richer in hydrogen than gases released by non-GRE mechanisms. This is illustrated by the hydrogen and nitrous oxide concentrations for calendar year 1999 for tank A-101 that are plotted in Figure 5-1. The ratio of hydrogen to nitrous oxide headspace concentrations exhibits a dramatic rise with each GRE. This suggests that much of the nitrous oxide in this tank is released via non-GRE mechanisms. During 1999, the ratio of hydrogen to nitrous oxide in the tank A-101 headspace ranged from about 1.2 (after a lull in GRE activity in October) to 7.3 (during the February 6th GRE). The gas release behavior of tank A-101 is discussed in detail by Stock (2000b).

Headspace gas concentrations are affected by seasonal changes in waste temperature. This is illustrated in Figure 5-2, where the tank U-105 headspace ammonia, nitrous oxide, and hydrogen concentrations have been plotted alongside the headspace temperature for a 1-year period. The headspace temperature, thought to be about 1 or 2 degrees cooler than the waste surface at all times, exhibits a characteristic sinusoidal behavior, with high and low temperatures lagging about three months behind ambient seasonal high and low temperature periods. As illustrated in Figure 5-2, in tank U-105 all three monitored gases appear to track with the headspace temperature.

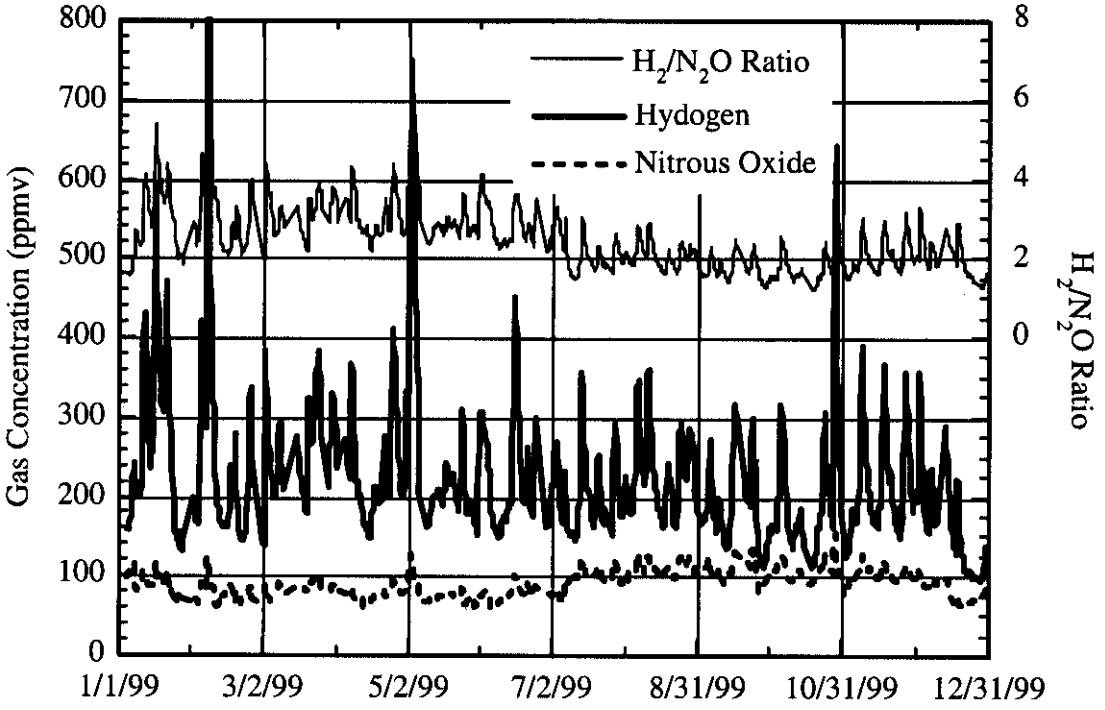


Figure 5-1. Headspace Hydrogen and Nitrous Oxide Concentrations in Tank 241-A-101 during 1999

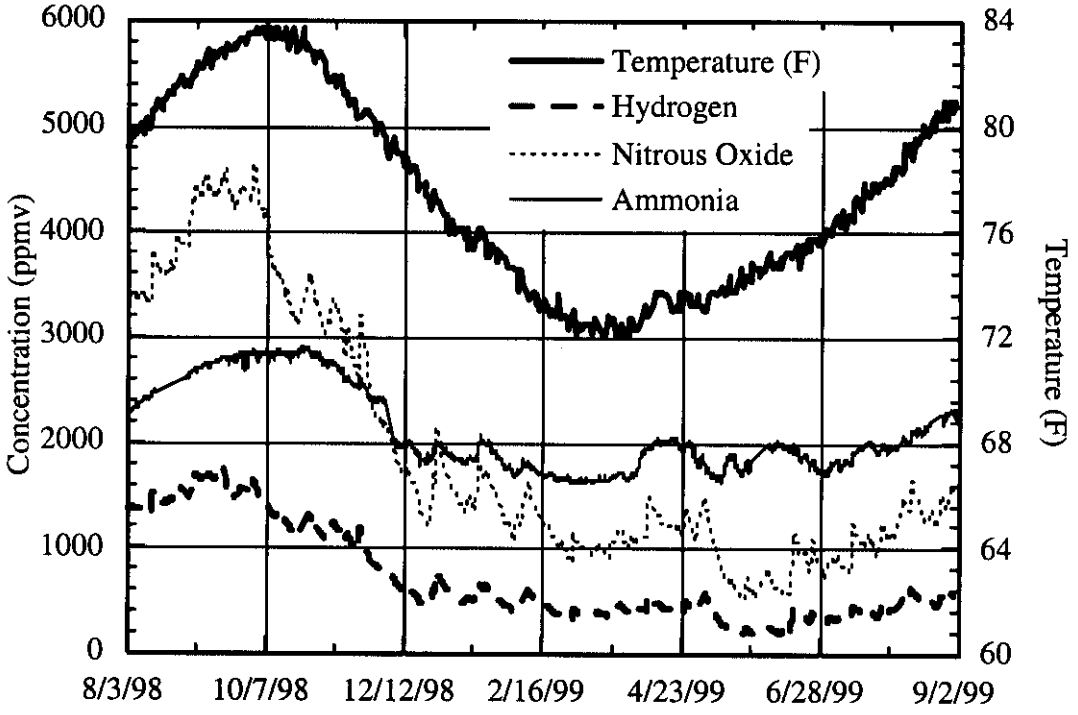


Figure 5-2. Headspace Gas Concentrations and Temperature in Tank 241-U-105

5.5.2 Standard Hydrogen Monitoring System Cabinet Grab Samples

Periodically, gas samples are collected from the SHMSs for laboratory analysis as a quality assurance measure. Grab samples are also collected automatically when a high-level alarm is activated. Samples are analyzed by mass spectrometry. McCain (2000) describes the sampling system and the analytical method. Table 5-9 lists the average and maximum hydrogen concentrations reported in SHMS grab samples for each of the 19 Flammable Gas Watch List SSTs.

The hydrogen averages given in Table 5-8 were calculated using the reported lower detection limits of the instrumentation for conditions where no hydrogen was detected in the sample. For some samples, this could potentially bias the average to a slightly high value. The average hydrogen to nitrous oxide ratio includes only samples for which both hydrogen and nitrous oxide concentrations were above detection limits, and "U" is entered when no samples from a given tank met that criterion. All of the maximum hydrogen concentrations listed in Table 5-8 were from scheduled quality assurance grab samples (i.e., none were collected because of high-level alarms). Maximum hydrogen concentrations determined from SHMS grab samples are lower than determined from continuous monitoring (see Table 5-5) with the exception of results for tank A-101.[13]

Table 5-8. Standard Hydrogen Monitoring System Grab Sample Summary

Tank	Number of Samples	Average Hydrogen (ppmv)	Maximum Hydrogen (ppmv)	Average H_2 to N_2O Ratio
A-101	16	801	1,540	4.8
AX-101	19	48	100	9.6
AX-103	9	26	36	1.1
S-102	12	568	760	1.3
S-111	21	81	330	7.3
S-112	22	25	43	6.9
SX-101	26	9	33	3.6
SX-102	19	17	42	3.5
SX-103	24	27	66	4.2
SX-104	30	9	28	U
SX-105	32	21	98	4.3
SX-106	27	38	160	3.0
SX-109	20	18	69	4.0
T-110	21	9	21	U
U-103	21	575	840	0.7
U-105	18	611	1,550	0.4
U-107	24	390	690	0.8
U-108	29	379	1,060	1.0
U-109	20	386	630	0.8

[13] The maximum hydrogen concentration in tank A-101 SHMS grab samples was reported for a sample collected in August 1995, when no monitoring data were available. The average hydrogen concentration for tank A-101 given in Table 5-5 is also skewed by 10 samples collected in July and August of 1995 when the hydrogen concentration was unusually high.

5.5.3 SUMMA™ Canister and Sorbent Trap Samples

Gas concentrations have been measured in each of the Flammable Gas Watch List SSTs using SUMMA™[14] canister and sorbent trap sampling methods and laboratory analyses. The SSTs were sampled with multiple sampling devices from the central portion of the headspace during a single sampling event, with the exception of tank S-102, which was also sampled five additional times to examine temporal effects (Huckaby et al. 1997a). Huckaby et al. (1996) give an overview of the sampling and analysis methods.

Average headspace hydrogen, nitrous oxide, and ammonia concentration results for each tank are listed in Table 5-9, along with the sampling date. As would be expected, the actively ventilated tanks (all the SX-Farm tanks listed, exclusively) tend to have lower headspace gas concentrations. The concentrations listed in Table 5-9 are thought to accurately indicate the headspace compositions on the specified sampling dates. However, variations in the composition of the tank headspaces due to ventilation rate changes and seasonal effects can range widely. The February 1995 sampling of the tank U-105 headspace, for example, found the headspace concentrations of hydrogen, nitrous oxide, and ammonia to be < 49, 154, and 325 ppmv, respectively, while the SHMS-E+ monitoring data showed their concentrations in 1999 were above 4,000, 1,500, and 2,500 ppmv, respectively, for extended periods (see Figure 5-2).

Table 5-9. SUMMA™ Canister and Sorbent Trap Sample Waste Gas Results

Tank	Sample Date	Hydrogen (ppmv)	Nitrous oxide (ppmv)	Ammonia (ppmv)
A-101	6/8/95	758	218	754
AX-101	6/15/95	103	< 12.6	42
AX-103	6/21/95	< 98	24	42
S-102	Various[(1)]	769	717	602
S-111	3/21/95	391	48	122
S-112	7/11/95	< 25	< 25	89
SX-101	7/21/95	< 25	< 25	3.8
SX-102	7/19/95	< 25	< 25	16
SX-103	3/23/95	< 23	< 23	77
SX-104	7/25/95	< 25	< 25	25
SX-105	7/26/95	< 25	< 25	28
SX-106	3/24/95	< 98	14	179
SX-109	8/1/95	< 25	< 25	17
T-110	8/31/95	< 25	< 25	108
U-103	2/15/95	555	878	730
U-105	2/24/95	< 49	154	325
U-107	2/17/95	500	701	453
U-108	8/29/95	522	612	692
U-109	8/10/95	748	868	577

[(1)] Tank S-102 was sampled on 3/14/95, 1/26/96, 4/4/96, 9/19/96, 12/19/96, and 2/11/97. The concentrations listed for tank S-102 are the averages of the 6 sampling event results.

[14]SUMMA is a trademark of Moletrics, Inc., Cleveland, Ohio.

5.6 SUMMARY OF GAS GENERATION AND COMPOSITION

The data on gas generation rates and gas composition indicate that gas generation rates in the Flammable Gas Watch List SSTs are quite low, on the order of several cubic feet per day, and the resulting steady-state headspace flammable gas concentrations are not hazardous, even under passive ventilation. Laboratory tests have provided information on the dependence of the generation rates of hydrogen and some other gases (nitrogen, nitrous oxide, and methane) on temperature and dose rate. This has enabled the development of a general empirical model that can evaluate the effect of operations like saltwell pumping on the hydrogen generation rate. Calculations presented in this section show that saltwell pumping can be expected to reduce the hydrogen generation rate in proportion to the ratio of the volume of liquid removed to the initial volume present.

The waste gas composition has been measured by the RGS in nine SSTs of which seven are on the Flammable Gas Watch List. The waste gas generally contains 20 to 70% hydrogen. The gas compositions measured in the tank headspaces indicate that the gas being released from the waste in the steady-state is generally much leaner in hydrogen than the retained gas, primarily because nitrous oxide and ammonia are much more soluble than hydrogen and are released primarily by evaporation from the liquid.

Headspace gas composition data provide information on the mechanisms and rates of gas release by the waste and its removal by ventilation. The data clearly indicate that existing ventilation has been adequate to prevent any significant accumulation of flammable gases in the headspaces of the SSTs. Waste gases released in small spontaneous events have been quickly diluted within the headspace to well below 25% of the LFL. The headspace gas concentrations are observed to fluctuate with time, principally due to changes in passive ventilation rates and flow paths, but also because of seasonal changes in waste tank temperatures.

The data and observations on gas generation, retained gas composition, and headspace gas composition and concentration indicate that the SSTs have not presented a flammable gas hazard during steady-state interim storage. Neither intrusive activities such as core sampling nor saltwell pumping operations have resulted in flammable gas concentrations above 25% of the LFL.

6.0 GAS RETENTION AND DISTRIBUTION

Gas is generated molecule-by-molecule 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. The dominant mechanism for ammonia release is evaporation from a stirred liquid surface. Evaporation also contributes to release of nitrous oxide. But since ammonia has a very high flammability limit (16% in air), it is more a toxicological than a flammability hazard. Bubbles are the most important mode of gas retention and release concerning flammability.

Gas retention in SSTs on the Flammable Gas Watch List has been investigated by several methods over the last several years. Gas retention tests have been performed on waste samples from several tanks, and the RGS has measured the local gas fraction in those that were believed to contain the largest volume of retained gas. The total stored gas volume has also been estimated for applicable tanks using the BPE method and integration of neutron logs. At the same time, some of these tanks have been or are being saltwell pumped which releases a large fraction of the originally stored gas and significantly alters the waste configuration.

The basic understanding of gas retention based on experimental and observational data is summarized in Section 6.1. The results of gas retention tests on SST waste samples are discussed in Section 6.2. The RGS gas fraction data are given in Section 6.3, and the gas volume estimates obtained using the BPE method and by integration of the neutron logs are discussed in Section 6.4. Changes in retained gas volume over the last few years are described in Section 6.5, and a summary of the gas retention status of each tank is provided in Section 6.6.

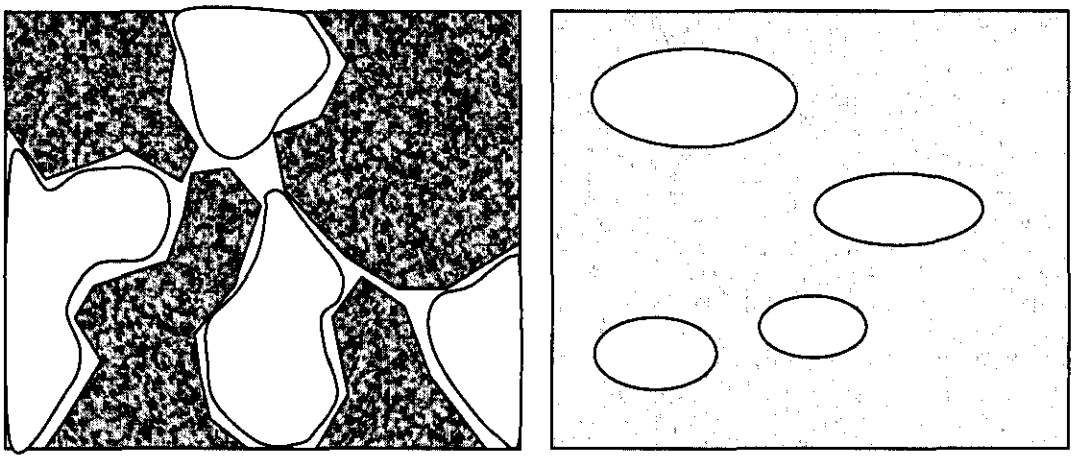
6.1 GAS RETENTION THEORY

The principal mechanisms of bubble retention can be grouped into three categories: bubbles retained by direct attachment to particles (e.g., armored bubbles, attached bubbles, agglomerates, etc.), bubbles retained between particles by capillary forces, and bubbles retained by the strength of the surrounding waste. In sediment layers, bubble retention is dominated by the waste strength and capillary forces; direct attachment of bubbles to particles plays a minor role. Gas release occurs on failure of the gas retention mechanism. Since bubbles rise freely in a fluid, a liquid cannot retain bubbles, except those in transit through the layer, and can only store dissolved gas. The two dominant bubble retention mechanisms are discussed below.

6.1.1 Bubble Retention by Capillary Forces

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 6-1.



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

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

Figure 6-1. Bubbles Retained by Capillary Forces and Waste Strength

Whether a bubble is held by yield strength or capillary force depends on a Bond number criterion developed by Gauglitz et al. (1994, 1995, and 1996). This dimensionless group 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:

$$N_{Bo} = \frac{\Delta\rho g H_S D_p}{4\sigma} + \frac{\tau_y D_p}{4\sigma}\left(\frac{A_2}{A_1}\right) \tag{6-1}$$

where:

- H_S = the height of the lithostatic column above the bubble
- D_P = the mean pore diameter through which a bubble must pass to escape retention. Assumed to be represented by the particle diameter.
- $\Delta\rho$ = the difference between solid and liquid density
- σ = the surface tension
- τ_y = the yield stress
- A = A_2/A_1 is a ratio related to how the yield stress resists bubble expansion; it was estimated at 2.8 by Gauglitz et al. (1995).
- g = gravitation constant

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. 1996). 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, which a pore-filling bubble can attain before percolating is expressed as:

$$\Delta h = 4\sigma/\rho_L g D_p \tag{6-2}$$

where:

σ = the surface tension and
ρ_L = the liquid density.
g = gravitation constant

Pore-filling bubbles, although they may represent a considerable gas volume, are not a 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.

6.1.2 Bubble Retention by Waste Strength

If a bubble is retained by the strength of the waste, as determined by the Bond number in Equation 6-1, 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 before they begin to assume a dendritic shape is given by:

$$D_b < \frac{\sigma}{\tau_y} \tag{6-3}$$

where:

τ_y = the yield stress,
σ = is the surface tension,
D_b = 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[15] can be derived in terms of a critical gravity-yield number, Y_G (Chhabra and Uhler 1986). The resulting limiting diameter is expressed as:

$$D_b < \frac{\tau_y}{\rho_w g Y_G} \tag{6-4}$$

where:

τ_y = the yield stress,
ρ_W = the bulk waste density,
g = the acceleration of gravity.

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

The combined criteria of Equations 6-3 and 6-4 limit the round bubble diameter to 0.5 to 1 cm for nominal Hanford Site waste properties as illustrated in Figure 6-2. This size is essentially constant over the range of tank waste properties and is quite consistent with observations of bubbles in waste samples and simulants. A single round bubble large enough to contain a hazardous amount of gas simply cannot exist.

[15] A Bingham fluid is one where the shear stress must exceed a limiting value , the yield stress, τ_y, for flow to occur.

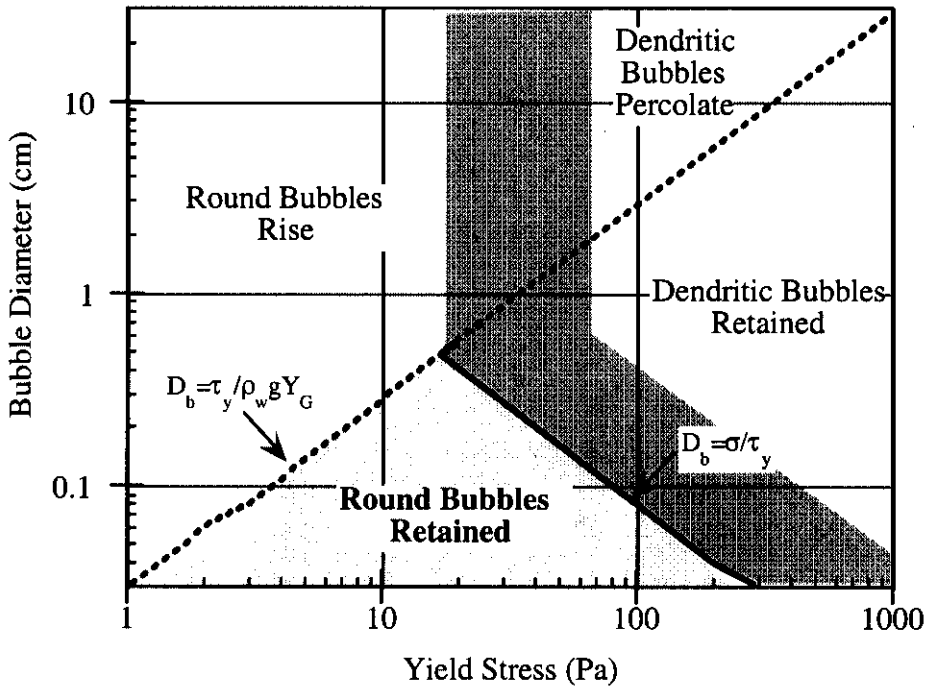


Figure 6-2. Limiting Bubble Size in Single-Shell Tank Waste

Equation 6-4 also gives the limiting height of dendritic particle-displacing bubbles. At the limiting size, any further increase in the vertical hydrostatic pressure difference pinches off the bottom of the bubble and pushes the top of the bubble upward in a manner similar to migration of pore-filling bubbles. However, motion of particle-displacing bubbles is much faster since it does not require liquid flow through a porous medium. If the waste is moderately strong, the bubbles do not collapse completely and dendritic bubble networks form to provide continuous gas release (Gauglitz et al. 1996). Therefore, a relatively weak waste is more likely to exhibit measurable spontaneous releases. This kind of "percolation" of dendritic, particle displacing bubbles is believed to be the primary mechanism for the small spontaneous releases observed in the headspace gas monitoring data on SSTs (see Section 7.0).

It is possible for gas releases to occur while individual bubbles remain confined within the waste. This can happen in tanks with a deep layer of supernatant liquid when a portion 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 headspace. This kind of gas release requires a relatively deep layer of supernatant, which is not present in the SSTs. Only five of the DSTs (AN-103, AN-104, AN-105, AW-101, and SY-103) currently exhibit buoyancy driven GREs. (A summary of the behavior of these DSTs is given in Hedengren et al. (2000).)

6.1.3 Effect of Waste Configuration on Gas Retention

Besides physical properties, gas retention depends on the waste composition or type and the waste layering or configuration. The waste types and configurations common to SSTs were introduced in Section 4.0. The characteristics of gas retention and release in the main waste configurations of interest in SSTs, wet solids and pumped, are discussed below.

6.1.3.1 Wet Sediment Configuration

Most of the SSTs that retain a significant volume of gas consist entirely of a liquid-saturated solid matrix with little or no supernatant liquid. In the saltcake waste type, assuming 30-micron particles, Equation 6-1 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 saltcake waste type have the highest gas fraction and deepest waste; therefore, they account for most of the total retained gas volume.

The characteristics of 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. This is consistent with headspace gas monitoring data which show these tanks typically release on the order of 1 to 2 cubic meters (30 to 70 scf) 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 (see Section 7.0).

6.1.3.2 Pumped Configuration

In tanks that have been saltwell pumped, the ILL is usually 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 6-1 with the density difference set equal to the solid density, only one meter of unsaturated saltcake 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 make it difficult to remove interstitial liquid from sludge effectively by pumping from a single well.

Gas release from the region containing pore-filling bubbles should be slow. But, as the gas exits into regions with lower lithostatic loads, the gas may again displace particles. The particle-displacing bubble region may then exhibit small spontaneous releases as if from an unpumped tank. The only potential mechanism for a significant gas release from a pumped tank might be a sudden waste subsidence months or years after saltwell pumping is completed. The removal of

the interstitial liquid greatly increases the lithostatic load on the particle column. Apparently, the continued slow migration of liquid eventually leads to a failure and compaction of the column. Any gas still trapped in liquid saturated waste in the subsiding region would be subject to release. While no such gas releases have yet been observed, craters and depressions on the surface of pumped tanks clearly show subsidence has occurred.

6.2 RESULTS OF GAS RETENTION TESTS ON SINGLE-SHELL TANK WASTE

Experimental studies have been performed on waste samples and simulants to gain insight on the mechanisms for gas retention. Tests were first done on simulants chosen to mimic the behavior of waste in SSTs (Gauglitz et al. 1994, 1995). Single-shell tank wastes have a wide range of physical properties that range from clay-like, plastic sludges to hard saltcake. Most of the work was done on fine particle simulants composed of bentonite clay and water. Glass beads and sand in water were used in early tests. The results quantified how the simulants retained gas in the form of a map of bubble configuration as a function of waste strength, lithostatic load, and particle size. Additionally, the tests indicated how bubbles are released.

Additional tests were then conducted to confirm that the behavior observed in the simulants also occurred in the waste. The tests were performed by placing an actual waste sample into a transparent vessel and allowing it to settle. It was then irradiated with cesium gamma source to generate a small amount of gas within the sample. The test chamber was then evacuated in a controlled manner to nucleate additional bubbles and to expand existing bubbles. Bubble growth and release are monitored with a video camera during de-pressurization. This method also determines a maximum retained gas fraction in each test.

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 Gauglitz et al. (1996), Rassat et al. (1997), and Rassat et al. (1998). The balance of this section summarizes the tests on SST wastes.

6.2.1 Tank 241-S-102 Gas Retention Tests

Tests with waste samples from the DST SY-103 showed that a buoyancy-like gas release mechanism occurred at close to the predicted neutral buoyancy gas fraction, if sufficient supernatant liquid were present in the sample. The buoyancy-dominated release occurred at an indicated gas fraction of 9 to 12%. In samples with little supernatant, the apparent gas fraction grew to 30% (Gauglitz et al. 1996).

This same behavior was observed in tank S-102 wastes. The samples included granular saltcake, a stiff sludge-like material, and a soft, weak sludge. None of the samples had excess supernatant liquid, and the maximum indicated gas fractions ranging from 20 to 50% exceeded the neutral buoyancy point.

An important observation from tank S-102 studies is that the soft sludge sample, which appeared to be considerably weaker than the stiff sludge sample, retained about 10% more gas at maximum growth (33% compared to 20% for the stiff sludge). Furthermore, the somewhat more granular saltcake samples held even more gas (50% at maximum growth). These results were consistent with observations of bentonite clays of varying strength. In particular, tank S-102 stiff sludge sample developed a connected path structure whereby gas was continuously released. The softer sludge sample experienced several rapid partial releases as paths opened and closed. These results and those of additional simulant studies show that the maximum gas retention occurs in materials of moderate strength and that very weak and very strong wastes do not retain as much gas.

6.2.2 Gas Retention Tests on Tanks 241-A-101, 241-S-106, and 241-U-103 Wastes

The gas retention tests on tanks A-101, S-106, and U-103 wastes were performed in a single study (Rassat et al. 1998) and are reported together. These SSTs were selected on the basis of waste type, indications of significant gas retention (i.e., RGS measurements; see Section 6.3), and sample availability.

- Tank A-101 is of interest because of its unusual inverted configuration with solids on top and liquid on the bottom. The waste is a highly concentrated saltcake classified as DSSF. The waste sample was recovered from the RGS extractor.
- Tank S-106 waste is predominantly saltcake of the noncomplexed type (does not contain high concentrations of organic complexants). The barometric pressure response and cumulative waste level rise in this tank indicated a very high retained gas volume.
- Tank U-103 also contains noncomplexed waste but is reported to contain a significant fraction of finer-grained salt slurry. The RGS found one segment with a gas fraction approaching 40% in this tank.

The tests were conducted near the measured tank temperatures with tanks S-106 and U-103 at 26 to 30 °C and tank A-101 at 53 °C. Unlike previous tests, the samples were not pre-irradiated since it was shown that sufficient gas was present in the samples without pre-irradiation to attain maximum retention under a vacuum.

The retained bubble shapes and gas retention profiles in all three wastes were consistent with those observed in earlier studies in the bentonite clay simulant with a yield stress on the order of 50 Pa. Visual observations of the samples as they were being poured into the retention test vessels also suggest their strengths were less than 100 Pa. As discussed in Section 6.2.1, this strength range should result in a relatively high gas retention.

The maximum retained gas fraction ranged from 30 to 51% in the four samples tested: 40% in tank A-101, 51% in tank S-106, 30% in the tank U-103 upper composite, and 42% in the tank U-103 middle composite. All of these values are much higher than the predicted neutral

buoyancy values as expected since very little supernatant was present. A very large and rapid gas release was observed in tank S-106 sample when the gas fraction dropped from the maximum 51% to 30%. This is consistent with the behavior of relatively weak waste (<50 Pa). The gas fraction then increased slightly for the remainder of the test. The gas releases from tanks A-101 and U-103 samples were characteristic of somewhat stronger material (~70 Pa) where the releases were smaller and more gradual.

The bubble shape was also consistent with the observed strength of the waste as determined from prior studies with simulants and other waste samples. Bubbles remained approximately spherical until coalescence above 30% gas fraction created larger dendritic shaped bubbles.

6.2.3 Summary of Gas Retention Test Results

The results of these tests have repeatedly confirmed that actual waste samples and the various simulants all behave basically as predicted by the bubble retention theory outlined in Section 6.1. This indicates that the mechanisms of bubble retention are determined mainly by the physical properties of the waste and not by the chemistry (except to the extent it influences the physical characteristics). Relatively weak, wet waste is capable of retaining a significant volume of gas and can release large fractions of it suddenly. This can occur only at higher void fractions than that found in the SSTs, and there is no evidence of this behavior having occurred in the tanks. Stiff wastes develop connected pathways that allow gas to escape continuously and limit gas retention. This suggests that removing liquid from waste by saltwell pumping is an effective method for reducing retained gas volume and the potential for spontaneous gas releases. The post-pumping gas monitoring data tend to confirm this effect (see Section 7.0).

6.3 RETAINED GAS SAMPLER GAS RETENTION MEASUREMENTS

Retained Gas Sampler samples were obtained from tanks A-101, AX-101, BY-109, S-102, S-106, SX-106, U-103, and U-109 during 1996 - 1998. Tanks were selected because of evidence of significant gas retention and to provide samples from farms with tanks on the Flammable Gas Watch List. Tanks BY-109 and S-106 are not Flammable Gas Watch List tanks, because of special features that may cast some light on interpretation of data for Flammable Gas Watch List tanks. The average gas volume fraction and total retained gas volume for each tank was determined from local gas volume fraction data measured with the RGS. The data are presented in Section 6.3.1, and the calculated gas inventories are summarized in Section 6.3.2. Tanks A-101, AX-101, S-102, S-106, S-111, SX-106, U-103, and U-109 have all undergone saltwell pumping since the RGS data were taken, and the gas fraction distributions and gas volume estimates made prior to pumping no longer apply to these tanks.

6.3.1 Retained Gas Fraction Measurements

High gas volume fractions were measured in several SSTs, consistent with the inability of SST nonconvective layers to undergo buoyant gas releases that would reduce the average gas volume fraction to the values typical in DSTs. The highest gas volume fraction measured in an SST RGS sample was 42 vol% in a sample taken near the top of the waste in tank U-103. This measured void was about equal to the maximum gas volume fraction of 43 vol% that was measured in laboratory gas-retention tests carried out with a composite sample from the middle of tank U-103 (as summarized in Section 6.2). Tanks SX-106, S-102, and U-109 also contained waste samples with more than 30 vol% gas. The maximum gas volume fractions measured in tank S-102 samples were roughly consistent with the maximum gas volume fractions found in laboratory gas-retention tests with waste samples from tank S-102 (Gauglitz et al. 1996; Rassat et al. 1998).

Plots of the local gas volume fractions measured by the RGS in SSTs between 1996 and 1998 are shown in Figures 6-3 through 6-11. The plot legends show each riser of an RGS core sample. The "error bars" are sized to show the core segment length of 19 in. and do not indicate uncertainty.

There were not enough data for any SST to show whether the shapes of the void profiles differed significantly between risers. However, there does seem to have been some difference in profiles between the tanks. The gas fractions in tanks A-101 and S-111 increased monotonically with depth in the solid layer. Both of these tanks had maximum measured gas volume fractions of less than 25 vol%. A parabolic profile, similar to that seen in DSTs, is suggested (but not proven) by the measurements made in tank SX-106. Tank SX-106 had a deeper supernatant layer than any of the other RGS-sampled SSTs and, in this regard, had a waste configuration more similar to the DSTs. Other tanks that also had gas volume fractions greater than 30 vol%, but did not contain any significant amount of supernatant, showed no apparent pattern in gas volume fraction. This group of tanks included tanks S-102, U-103, and U-109.

The plots include notes on composition variation in cases where substantial variation was present. There is no recognizable relationship between the waste composition and the gas volume fraction.

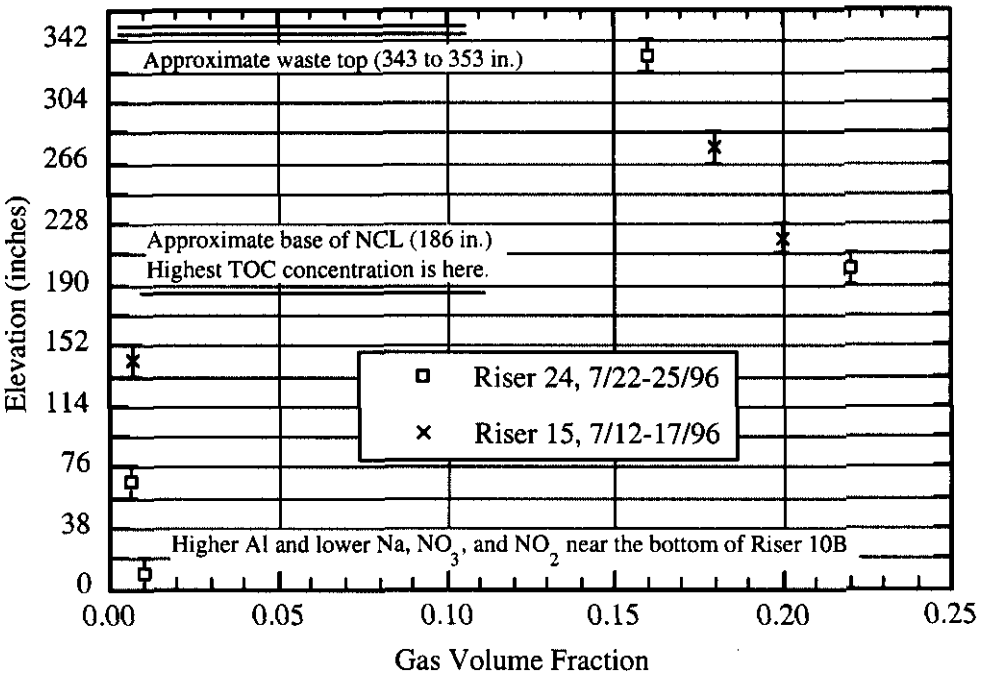


Figure 6-3. Tank 241-A-101 Void Profile (1996 Data)

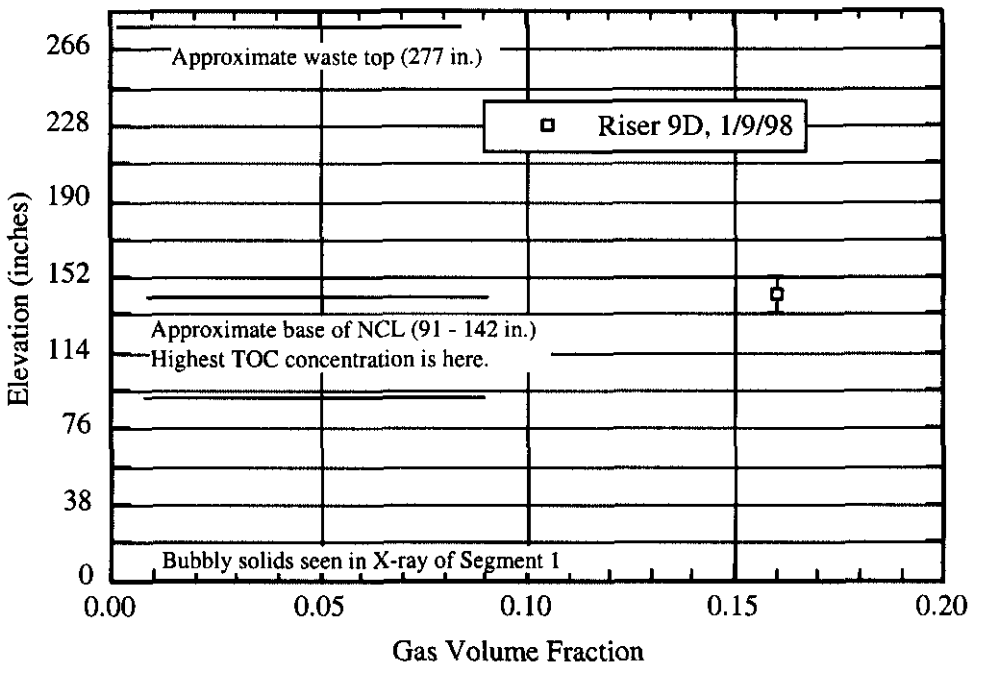


Figure 6-4. Tank 241-AX-101 Void Profile (1998 Data)

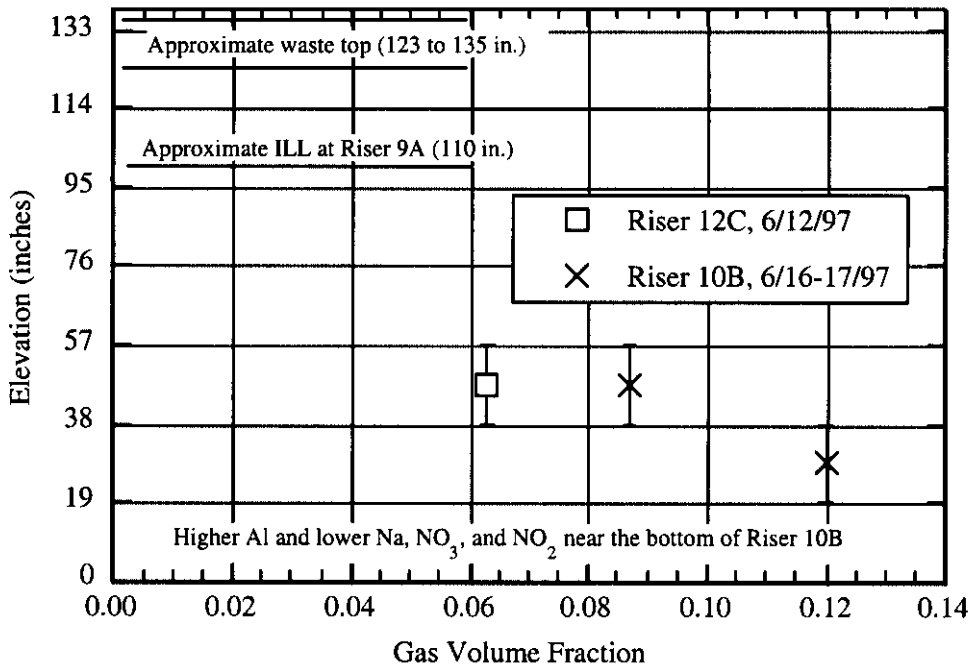


Figure 6-5. Tank 241-BY-109 Void Profile (1997 Data)

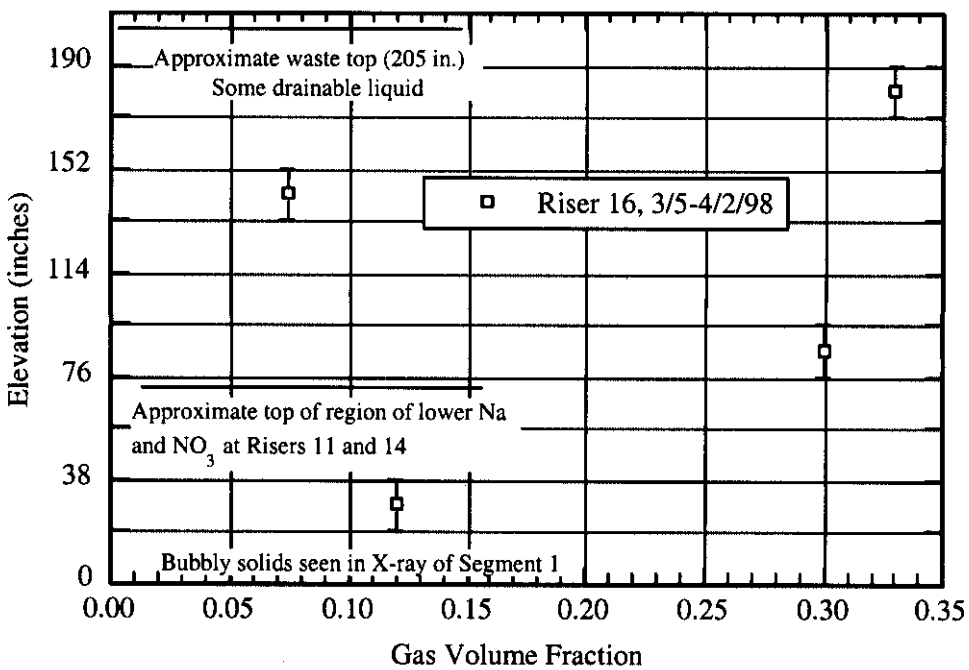


Figure 6-6. Tank 241-S-102 Void Profile (1998 Data)

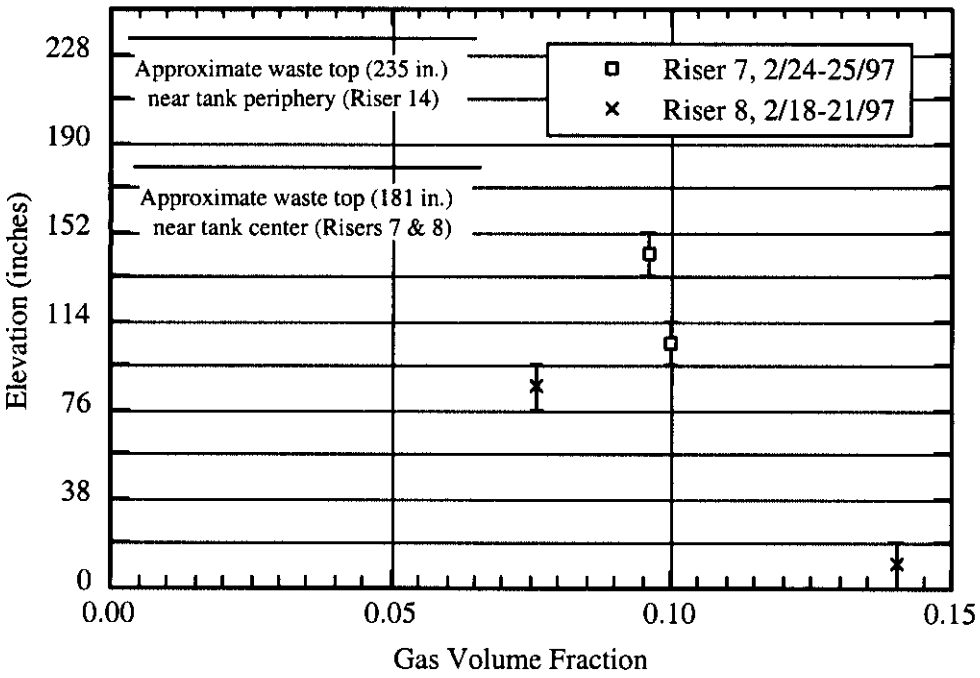


Figure 6-7. Tank 241- S-106 Void Profile (1997 Data)

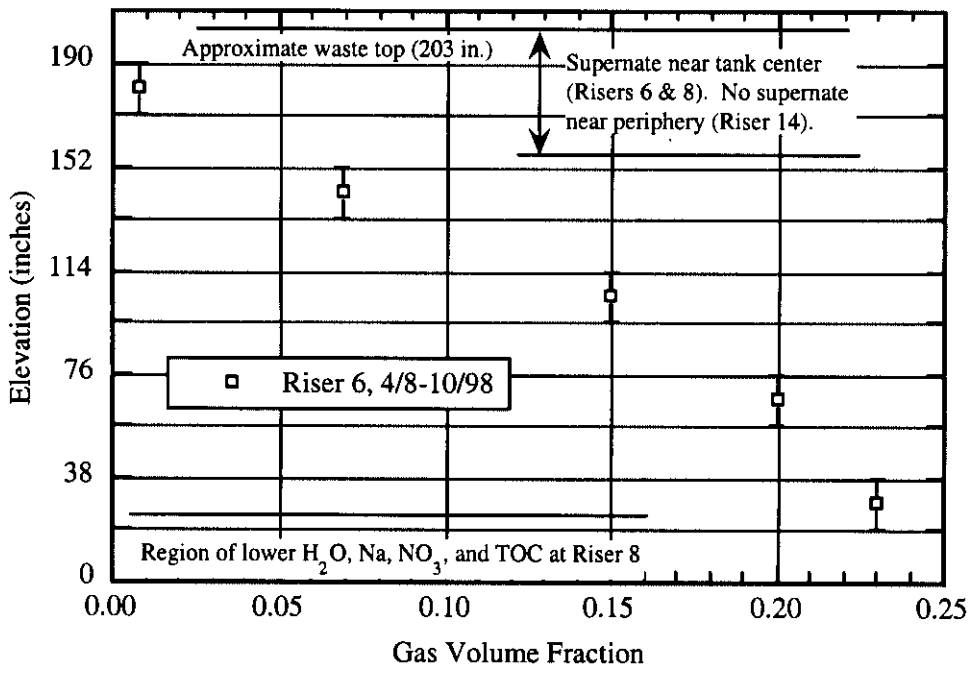


Figure 6-8. Tank 241-S-111 Void Profile (1998 Data)

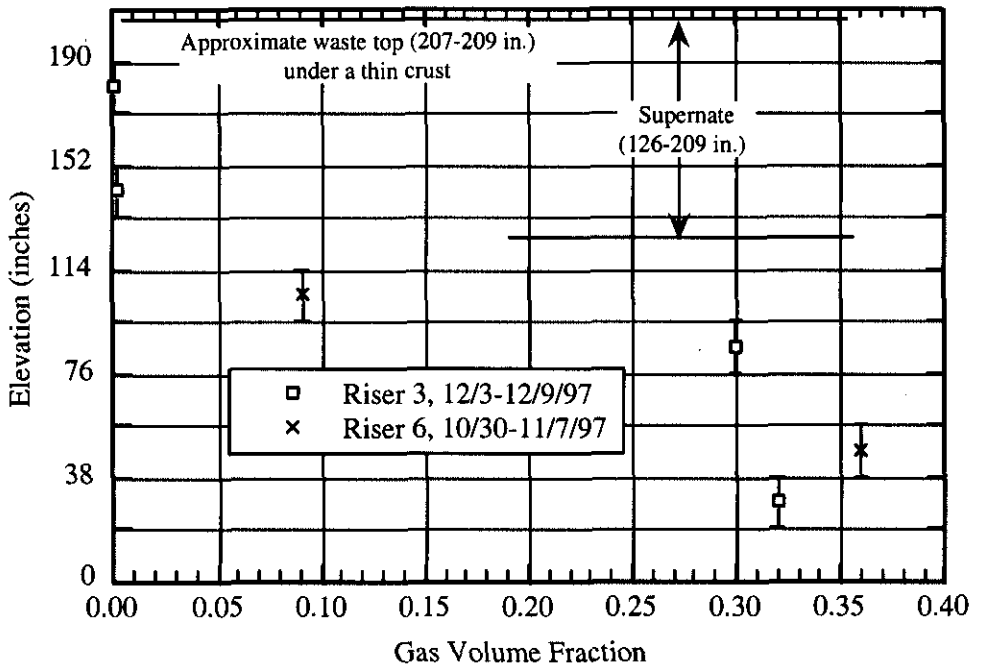


Figure 6-9. Tank 241-SX-106 Void Profile (1997 Data)

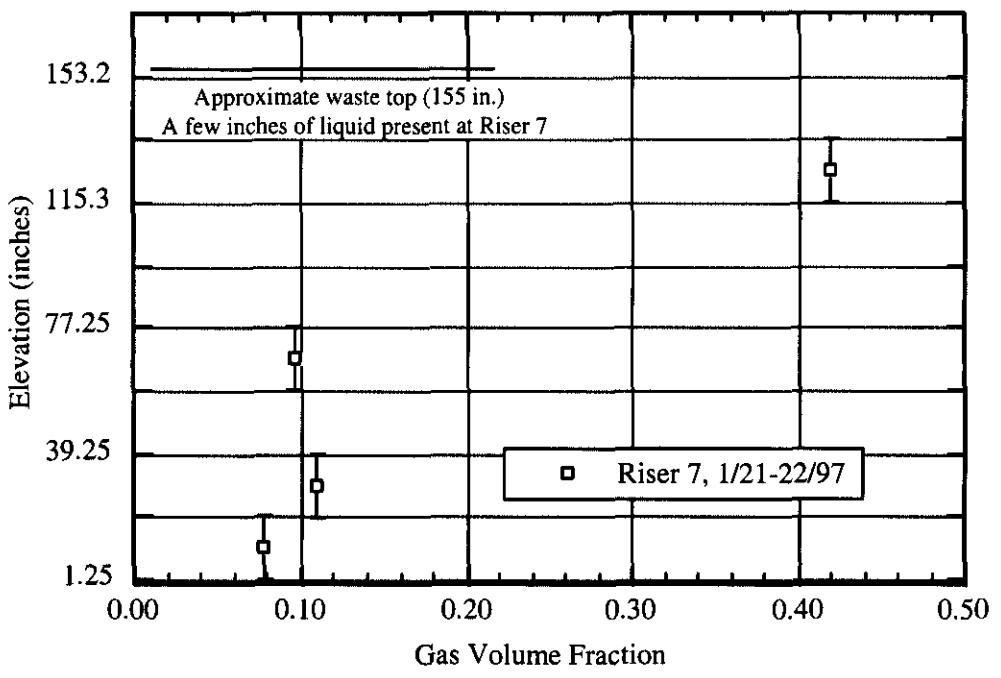


Figure 6-10. Tank 241-U-103 Void Profile (1997 Data)

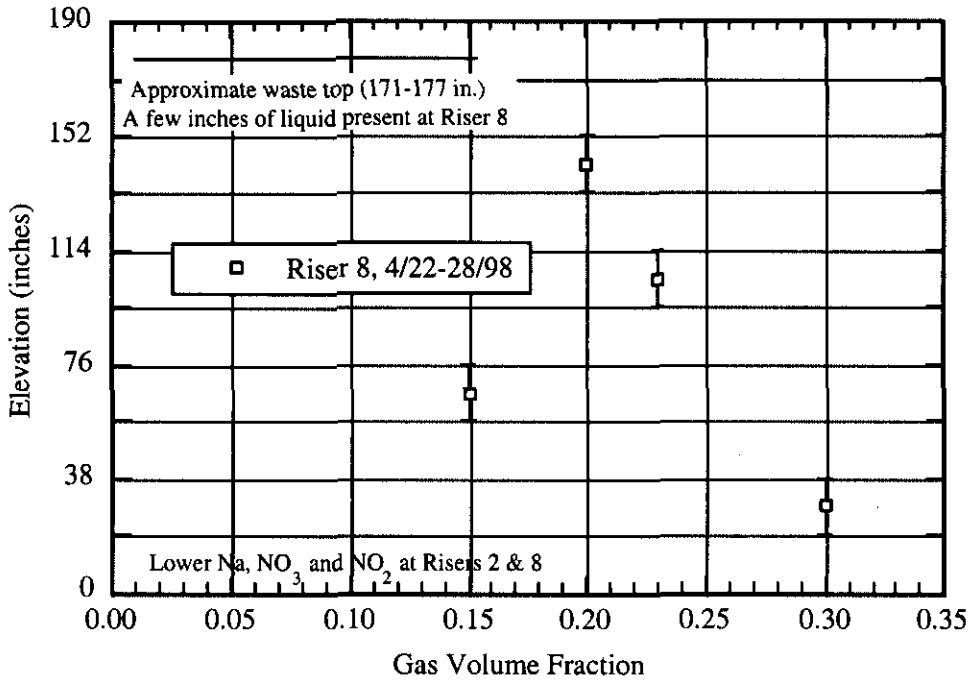


Figure 6-11. Tank 241-U-109 Void Profile (1998 Data)

6.3.2 Calculated Retained Gas Inventory from Retained Gas Sampler Data

This section summarizes the retained gas volumes and other quantities of interest calculated from RGS measurements in the nine SSTs that were sampled with RGS system. The average gas volume fraction and retained gas volume for these tanks have been calculated from the local RGS void fraction data shown in Section 6.3.1.

The data reduction model and the uncertainty are described in Mahoney et al. (1999). The total gas volume is calculated as the sum of non-supernatant layers represented by an RGS core segment. The boundary between layers is the midpoint of the vertical distance between segment centers. Given the average void fraction, α_i, in a layer i, the in-situ gas volume held in the layer is calculated by:

$$V_i = \alpha_i A H_i \tag{6-5}$$

where:

H_i = the layer thickness and
A = the tank area.

The gas volume corrected to standard temperature and pressure is then given by:

$$\hat{V}_i = V_i \frac{p_i}{\hat{p}} \frac{\hat{T}}{T_i} \tag{6-6}$$

where:

p_i and T_i are the average pressure and temperature in the layer, respectively, and $\hat{p}$ and $\hat{T}$ are standard atmospheric pressure (101.32 kPa) and temperature (298 K), respectively.

The product of temperature and pressure ratios [coefficient of V_i in Equation 6-6] is termed the "effective pressure ratio." Table 6-1 gives the calculated void fractions and gas volumes for all nine tanks using the RGS data set. Because of the small number of RGS samples in a tank, there is a high uncertainty in the representativeness of the average, and it is not possible to formally quantify it. For this reason, a ± 50% uncertainty is assigned to the average void fraction and the gas volumes derived from it.

Table 6-1. Retained Gas Volume for Single-Shell Tanks from Retained Gas Sampler Data

Tank [a]	Waste Depth [b] (cm)	Mean Gas Fraction	In-Situ Gas Volume [c] (m^3)	Effective Pressure Ratio	Standard Gas Volume (m^3)
A-101*	412 ± 15	0.18 ± 0.09	304 ± 160	1.18	358 ± 180
AX-101*	355 ± 15	0.17 ± 0.08 [d]	247 ± 120	1.14	282 ± 140
BY-109	279 ± 8 [e]	0.094 ± 0.05	108 ± 50	1.20	130 ± 65
S-102*	519 ± 9	0.26 ± 0.13	554 ± 280	1.20	663 ± 332
S-106	411 ± 48 [f]	0.10 ± 0.05	168 ± 84	1.32	223 ± 111
S-111*	505 ± 10	0.15 ± 0.08	310 ± 155	1.42	440 ± 220
SX-106*	320 ± 24	0.26 ± 0.13	340 ± 170	1.43	487 ± 240
U-103*	394 ± 16	0.19 ± 0.10	307 ± 150	1.19	365 ± 180
U-109*	432 ± 19	0.22 ± 0.11	390 ± 195	1.28	500 ± 250

Notes:

(a) Asterisk indicates the tank is on the Flammable Gas Watch List.
(b) Waste depth at the time of RGS sampling. Does not include any supernatant.
(c) Volume does not consider the effect of the dished tank bottom as was done in Mahoney (2000)
(d) Only one RGS sample was taken in tank AX-101. Uncertainty may be higher than the assigned ± 50%.
(e) The ILL in tank BY-109 is well below the surface. RGS samples were taken only below the ILL. The waste depth tabulated for tank BY-109 is actually the ILL.
(f) The uncertainty in waste depth in tank S-106, at the time of RGS sampling, is taken to be the depth of the supernatant layer, 48 cm, since solids extended more than a meter above the supernatant at the periphery.

6.4 OTHER ESTIMATES OF RETAINED GAS VOLUME

The RGS was designed to measure the composition and volume fraction of retained gas but only produces a few data points in a tank. Although gas fractions measured in each RGS segment are relatively accurate, it is doubtful whether these few measurements represent the entire tank. Two additional methods are described in this section that can estimate the retained gas volume more globally. Section 6.4.1 describes the Barometric Pressure Effect method and Section 6.4.2 explains how a rough estimate of the gas fraction can be obtained from neutron logs.

6.4.1 Gas Volume from Barometric Pressure Effects

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). Only the salient equations are summarized here. The BPE in-situ gas volume is calculated by:

$$V_G = -Ap_{BPE}\frac{dL}{dp_0} \tag{6-7}$$

where the effective pressure for barometric pressure response is defined by:

$$\frac{1}{p_{BPE}} = \sum_{i=1}^{N}\left[\frac{f_i}{p_i}\right] \tag{6-8}$$

and f_i is the fraction of the total in-situ gas stored in layer i:

$$f_i = \frac{A\alpha_i H_i}{V_G} \tag{6-9}$$

To determine the in-situ gas volume accurately, the BPE model requires sensitive and frequent level measurements over a sufficient period of time to establish a good level-pressure correlation. It also requires an estimate of the vertical distribution of gas. The uncertainty of the BPE model is estimated to be ± 10 to 50% of the in-situ volume.

The tank conditions where the BPE model can be applied are listed in Hedengren et al. (2000). The waste must be liquid-saturated and relatively uniform laterally. The BPE cannot be applied in tanks that have had liquid removed by saltwell pumping. Some SSTs have a "jelly donut" configuration (see Section 4.0) where the outer waste is dryer and stronger than the mobile wet waste in the middle. Tanks where the level is measured near the center may have "amplified" dL/dP values, such that the BPE method overestimates gas. The BPE method may underestimate those with level measurements near the periphery.

The BPE volume estimates prior to saltwell pumping are given in Table 6-2 for the set of SSTs including those on the Flammable Gas Watch List plus additional SSTs for which BPE estimates were possible. Single-shell tanks that are not on the Flammable Gas Watch List are included to give a more complete picture of the gas retained in the Hanford Site SSTs. The BPE estimates for tanks with RGS data (tanks A-101, BY-109, S-102, S-106, S-111, U-103, and U-109) use the measured barometric pressure response with the effective pressure and pressure ratio calculated from the gas distribution derived in the RGS data using Equations 6-6 and 6-9. The other tanks used an effective pressure based on the relative gas distribution implied by neutron probe profiles.

Table 6-2. Barometric Pressure Effect Gas Volume Estimates in Single-Shell Tanks

Tank [(a)]	p_{BPE} (atm)	dL/dP (cm/kPa)	In-situ (m^3)	P_{EFF} (atm)	Standard (m^3)
A-101*	1.30 ± 0.07	-0.46 ± 0.041	250 ± 28	1.18	295 ± 33
AX-101*	ALCs hold crust near ENRAF™ in place, no BPE calculation performed.				
AX-103*	Waste level ~ 40 inches, no BPE calculation performed.				
S-101	1.20 ± 0.05	-0.17 ± 0.01	83 ± 5	1.13	94 ± 6
S-102*	1.26 ± 0.06	-0.44 ± 0.03	228 ± 20	1.20	273 ± 22
S-103	1.22 ± 0.05	-0.29 ± 0.02	145 ± 14	1.21	175 ± 17
S-106	1.45 ± 0.11	-0.69 ± 0.13	414 ± 90	1.32	547 ± 120
S-107	1.39 ± 0.09	-0.074 ± 0.04	43 ± 24	1.33	57 ± 32
S-111*	1.45 ± 0.11	-0.48 ± 0.05	288 ± 44	1.42	410 ± 62
S-112*	ILL is 65 in. below waste surface, no BPE calculation performed.				
SX-101*	dL/dP data inconsistent				
SX-102*	dL/dP data inconsistent				
SX-103*	dL/dP data inconsistent				
SX-104*	No apparent dL/dP correlation				
SX-105*	dL/dP data inconsistent				
SX-106*	1.50 ± 0.12	-0.36 ± 0.05	224 ± 39	1.43	320 ± 56
SX-109*	Waste level ~ 95 inches, no BPE calculation performed.				
T-110*	No apparent dL/dP correlation				
U-103*	1.20 ± 0.05	-0.42 ± 0.12	210 ± 63	1.19	250 ± 75
U-105*	1.35 ± 0.08	-0.27 ± 0.11	151 ± 62	1.32	200 ± 82
U-106	1.19 ± 0.05	-0.07 ± 0.01	35 ± 16	1.19	42 ± 19
U-107*	1.21 ± 0.05	-0.23 ± 0.06	117 ± 31	1.21	140 ± 38
U-108*	1.41 ± 0.10	-0.35 ± 0.06	205 ± 40	1.39	285 ± 56
U-109*	1.28 ± 0.07	-0.28 ± 0.08	148 ± 45	1.28	190 ± 58

(a) Asterisk indicates tank is on the Flammable Gas Watch List

The set of tanks, SX-101, SX-102, SX-103, and SX-105, were found to have such widely varying barometric pressure responses that no meaningful estimate of gas volume could be made. In the U-Farm tanks, the ENRAF™ is near the tank wall (32-ft radius) and could be suspected of registering less than the full response of the waste to barometric pressure. However, the surface photographs of the U-tanks show a liquid layer over most of the surface and, therefore, the BPE results for these tanks are considered acceptable. The BPE volume of tank S-106 far exceeds the volume derived from the RGS data. This may be due to a much more pronounced "jelly donut" configuration in tank S-106 than the other RGS-sampled SSTs. The ENRAF™ is near the tank center; therefore, the barometric pressure response may be considerably amplified in this tank.

6.4.2 Gas Volume Estimated from Neutron Logs

Another alternative method for estimating stored gas volume is based on the neutron count profiles measured in the LOWs using the new LOW Surveillance System described in Section 2.8. This method is based on the two major assumptions that the neutron count is reduced mainly by the presence of retained gas and not by variation in the composition of the solid and liquid waste. It is also assumed that the maximum count on the neutron log is a gas-free layer that can be used as the reference count for gas volume fraction estimates.

The in-situ gas volume is calculated from the neutron log by finding the 90th percentile count rate, N_{90}, and treating it as the count rate for the gas-free waste. Then the local gas volume fraction at each point in the profile is calculated simply as:

$$\alpha_i = 1 - N_i / N_{90} \tag{6-10}$$

where:

α_i is the local gas fraction at probe position i, and
N_i is the local count rate.

The average gas volume fraction is then found by integrating the gas fraction profile over the wetted waste depth, from the ILL to the bottom, using Simpson's Rule. It should be noted that this method, like the RGS, gives a gas inventory for the area at a particular riser, which may not represent the average over the whole tank.

Figure 6-12 shows a sample gas fraction profile for tank SX-106, together with RGS data (shown as black squares). While the two sets of data do not agree point-for-point, both show that the void is near zero in the supernatant layer and both indicate the same peak value. The figure also shows the average gas fractions found by the BPE method (heavy black line) and by neutron log integration (dashed line).

Neutron log integration can be applied to any tank that contains an LOW. It depends on two major assumptions. The first is that the maximum count rate in the tank is found in a liquid-saturated region with no retained gas. This will hold true in any tank with a liquid layer more than a few inches thick. In a tank where there is no distinct liquid layer, all the waste may be

gassy to some extent. In this case, the neutron log will systematically underestimate the gas fraction because the measured N_{90} contains void and, therefore, underestimates the true gas-free count rate.

The effect of variation in the composition of the solid and liquid waste on the neutron count depends primarily on the variation in the density of hydrogen atoms in the waste. Hydrogen atoms are found in the greatest density in water and also in hydroxides of low-molecular-weight metals, typically $Al(OH)_3$. Other common waste constituents, such as $NaNO_3$, also slow neutrons, but much less effectively. Major variations in the amount of water and hydroxide in the liquid and solid part of the waste are, therefore, a potential source of error in using the neutron logs to determine the gas fraction. But, the uncertainty introduced by chemistry variation cannot be estimated *a priori*. To represent all these factors, a ± 50% uncertainty is applied to all gas volumes estimated via this method as was done for the RGS gas volumes.

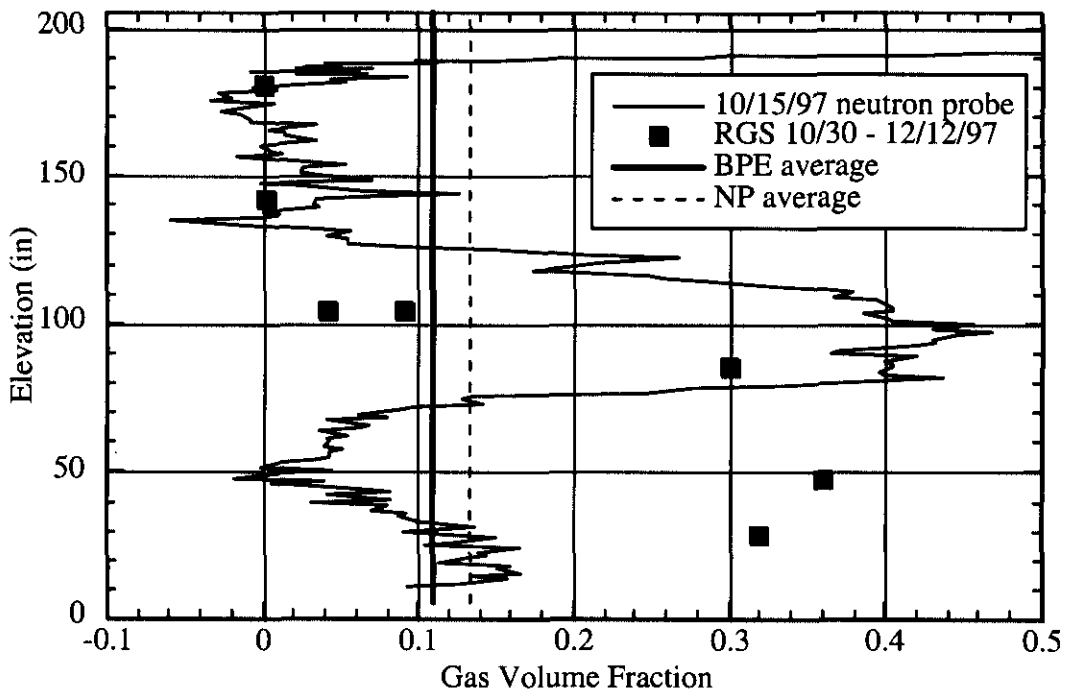


Figure 6-12. Tank 241-SX-106 Void Profile from Neutron Probe

Table 6-3 gives the average void fractions and gas volumes obtained from neutron log integration for a number of SSTs, including some that are not on the Flammable Gas Watch List. Each of the gas fractions in the table derived from neutron logs is the average over five logs measured in 1997 through 1998. The ILL is the value in December 1997. The effective pressure ratio is taken from RGS measurements, where available or derived from the gas distribution implied by the neutron profile. The standard deviation of the gas fraction over five profiles was always 1 vol% or less. The neutron log integration results appear to be as consistent with BPE and RGS results as they are with each other.

Table 6-3. Average Gas Fraction and Gas Volume Estimates from Neutron Logs

Tank [a]	Avg. Gas Fraction [b]	ILL (cm)	In-Situ Gas Volume (m^3)	P_{EFF} (atm)	Standard Gas Volume (m^3)
A-101*	0.073	914	274 ± 135	1.18	323 ± 160
AX-101*	0.080	691	230 ± 110	1.14	260 ± 130
AX-103*	No neutron log available				
BY-109	0.12	279	140 ± 68	1.20	168 ± 84
S-101	0.036	411	60 ± 30	1.13	68 ± 34
S-102*	0.064	492	130 ± 65	1.20	155 ± 80
S-103	0.12	268	130 ± 65	1.21	157 ± 80
S-106	0.14	460	264 ± 130	1.32	350 ± 175
S-109	0.094	361	140 ± 70	1.20	170 ± 85
S-111*	0.077	516	160 ± 80	1.42	230 ± 114
S-112*	0.086	120	40 ± 20	1.15	46 ± 23
SX-101*	0.048	411	80 ± 40	1.16	94 ± 47
SX-102*	0.072	491	145 ± 70	1.19	170 ± 85
SX-103*	0.24 [c]	600	*591*	1.33	*786*
SX-104*	0.079	550	180 ± 90	1.40	250 ± 125
SX-105*	0.055	606	140 ± 70	1.29	180 ± 90
SX-106*	0.13	503	270 ± 135	1.43	386 ± 190
SX-109*	No neutron log available				
T-110*	0.027	371	40 ± 20	1.20	50 ± 25
U-102	0.11	371	170 ± 85	1.32	220 ± 110
U-103*	0.15	452	280 ± 140	1.19	330 ± 160
U-105*	0.15	417	260 ± 130	1.32	340 ± 170
U-106	0.048	229	45 ± 20	1.19	50 ± 25
U-107*	0.11	397	180 ± 90	1.21	220 ± 110
U-108*	0.19	452	350 ± 175	1.39	490 ± 240
U-109*	0.12	450	220 ± 110	1.28	284 ± 140
U-111	0.087	332	120± 60	1.34	160 ± 80

Notes:

(a) Asterisk indicates the tank is on the Flammable Gas Watch List.
(b) Averaged below the ILL. For tanks A-101 and AX-101 the average includes the liquid layer.
(c) The neutron log suggests a region of low liquid content in tank SX-103 at the LOW riser between 50 and 120 in. elevation. The high implied gas fraction is considered to be anomalous.

6.5 CHANGES IN RETAINED GAS VOLUME WITH TIME

The gas volume estimates developed from RGS data represent tanks conditions at the time of sampling in 1996 through 1998. It is possible that the gas volume may have changed in the several years since. The most precise indicator of long-term net gas retention or release is the waste level. Based on the essentially constant waste level and ILL shown in the plots provided in Section 4.1, there has been no significant change in the retained gas volume in the tanks that have not been pumped.

This conclusion is supported by the absence of distinct trends in the response of waste level to barometric pressure fluctuations (dL/dP). The SSTs of interest for which three or more full years of dL/dP data were available are tanks S-103, S-106, S-107, S-111, SX-106, U-103, U-105, U-106, U-107, and U-109. The dL/dP values for these tanks are given in Table 6-4. The only tank for which any trend is apparent is tank S-111; the dL/dP has been decreasing. However, the apparent trend is within the uncertainty of the data and is contradicted by the waste surface level trend, which shows (if anything) a slight increase. The BPE method is not sensitive enough to capture such a small change in volume.

Although it is not possible to quantify very accurately, the saltwell pumping process releases a significant fraction of the retained gas in a tank. As discussed in Section 7.2, an estimate of the hydrogen release rate during pumping is made for tank S-106. Approximate integration of the hydrogen release rate over the pumping period indicates a total hydrogen release of 100 ± 30 m^3 for a total release of 160 ± 40 m^3 using 63 vol% hydrogen as measured by the RGS (see Section 5.4.1). This volume ranges from 30% of the 547 m^3 standard volume calculated with the BPE method to 46% of the 350 m^3 of the volume estimated from the neutron logs or 70% of the 223 m^3 determined from the RGS data. It could be said that on the order of half of the retained gas volume in tank S-106 was released by saltwell pumping. Similar fractions could be expected in other tanks.

Table 6-4. Multi-year Barometric Pressure Response Trends in Some Single-Shell Tanks

Tank	dL/dP (cm/kPa) by calendar years			
	1996	1997	1998	1999
S-103	-0.30±0.05	-0.29±0.03	-0.29±0.02	N/A
S-106	-0.72±0.20	-0.62±0.14	-0.69±0.13	N/A
S-107	-0.09±0.02	-0.10±0.02	-0.08±0.03	-0.07±0.04
S-111	-0.52±0.08	-0.48±0.05	-0.49±0.09	-0.45±0.10
SX-106	-0.30±0.05	-0.36±0.06	-0.36±0.05	N/A
U-103	-0.39±0.06	-0.39±0.06	-0.42±0.12	N/A
U-105	-0.30±0.05	-0.27±0.07	-0.27±0.11	-0.27±0.04
U-106	-0.07±0.03	-0.06±0.08	-0.03±0.03	-0.08±0.06
U-107	-0.24±0.03	-0.21±0.05	-0.24±0.04	-0.23±0.06
U-109	-0.32±0.11	-0.29±0.09	-0.29±0.08	-0.28±0.08

6.6 SUMMARY OF GAS RETENTION IN SINGLE-SHELL TANKS

The experience with DSTs showed that the data from the Void Fraction Instrument (VFI) provides the best estimates of the retained gas volume in the waste (Hedengren et al. 2000; Barker et al. 1999). However, the VFI could not be operated in SSTs because of their higher waste strength. The only actual in-situ gas fraction measurements available are data from one to six RGS segments per tank for several SSTs. Since the uncertainty of gas volume estimates from such sparse data is high, other equally uncertain gas volume estimates from application of the BPE method and integration of neutron logs must also be considered. The best estimate of the retained gas volume is determined by engineering judgement based on the preponderance of data from these sources and available ancillary evidence such as cumulative waste level rise and gas release history. The pre-saltwell pumping retained gas volumes and the overall best estimate are summarized in Table 6-5.

Table 6-5. Summary of Best Estimate Retained Gas Volumes [(a)]

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		260 ± 130	270 ± 100	In progress
AX-103	No gas volume estimate available				
S-102	663 ± 332	273 ± 22	155 ± 80	215 ± 60	In progress
S-111	440 ± 220	410 ± 62	230 ± 114	360 ± 85	
S-112			46 ± 23	46 ± 23	
SX-101			94 ± 47	94 ± 47	In progress
SX-102			170 ± 85	170 ± 85	
SX-103	No gas volume estimate available				
SX-104			250 ± 125	250 ± 125	Completed
SX-105			180 ± 90	180 ± 90	In progress
SX-106	487 ± 240	320 ± 56	386 ± 190	400 ± 100	Completed
SX-109	No gas volume estimate available				
T-110			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

(a) RGS and BPE volume estimates are given only where data was available for the calculation.

The table shows that most of the SSTs on the Flammable Gas Watch List contain 100 to 300 cubic meters of gas, more than most of the DSTs. However, the gas volumes are not growing, and there is no known mechanism for, or evidence that any large fraction of this gas can be released suddenly (Johnson et al. 1997). Saltwell pumping appears to reduce retained gas

volumes and the propensity for spontaneous releases. The remainder of this section discusses the gas retention status, including the progress and effects of saltwell pumping, and rationale for the best estimate of the gas volume in each of the tanks.

Tank 241-A-101: In tank A-101 gas is retained in the floating solids layer in this tank. Although the waste level and ILL have been dropping 0.2 to 0.3 in. per year, this tank has had the most frequent spontaneous GREs of the SSTs. There have been 57 small GREs (maximum hydrogen concentration was 837 ppm) recorded since the SHMS-E+ was installed in February 1998; most were associated with a drop in barometric pressure (McCain 2000).

The gas fraction measured by the RGS ranged from 0.16 to 0.22, increasing monotonically with depth. Estimates of gas volume from all three sources (RGS, BPE, and neutron logs) all agree quite closely. The best estimate of 325 ± 80 cubic meters (11,500 ± 3,000 scf) is taken as the average of the three.

Saltwell pumping has barely started and has not yet affected the gas volume. Since the gas is in the floating layer, it is anticipated that only a small fraction of the gas will be released until after the liquid layer is removed as was the experience with the somewhat similar waste configuration in tank SY-101 (Mahoney et al. 2000).

Tank 241-AX-101: This tank has a floating solids layer like tank A-101 in which the retained gas resides. The waste level has been essentially constant, and the ILL has been dropping at about 0.5 in. per year since 1990. Nine GREs with a peak hydrogen concentration of 540 ppm have been recorded on the tank's SHMS-B since 1996.

Only one RGS segment was obtained in this tank with a gas fraction of 0.16. Assuming that the gas distribution is as smooth and regular as that of tank A-101, this value can be used to represent the average gas fraction for the floating layer. The retained gas volume calculated from this assumed average gas fraction matches that obtained from the neutron logs very closely; therefore, the best estimate of 270 ± 100 cubic meters (9,500 ± 3,500 scf) is taken as the average of the two. Since the ENRAF™ level gauge in tank AX-101 is near several airlift circulators which locally restricts waste response to barometric pressure, no BPE calculation can be made.

Like tank A-101, saltwell pumping has thus far had a minor effect. Except for the potential effects of waste disturbance as the floating layer descends around the airlift circulators, the greater part of the gas release is expected to occur after the liquid layer is removed.

Tank 241-AX-103: There are only about 40 inches of waste in this tank. The waste level has been decreasing over the last ten years; therefore, gas is not accumulating. No gas releases have been observed in the SHMS-B data since the system was installed in March 1995, because the sampling line was plugged. There are no other data available from which to estimate the retained gas volume.

Tank 241-S-102: Prior to saltwell pumping, the waste level and ILL in this tank were high and had been growing about 1/2 inch per year. Because of this level rise rate and early BPE estimates, tank S-102 was suspected of having a very large retained gas volume. However, no spontaneous gas releases have been recorded on its SHMS since it was installed in 1995.

The four RGS gas fractions obtained in 1998 alternated between about 0.1 and 0.3 with an average of 0.26. This average gas fraction corresponds to a standard gas volume of 663 ± 332 cubic meters. However, the estimate from the BPE method was only 273 ± 22 cubic meters, and the volume derived by integrating the neutron logs was 155 ± 80 cubic meters. The high RGS volume is discounted because there were only four RGS measurements in a single riser and these were widely scattered. The low neutron log value of 155 ± 80 cubic meters is supported by the cumulative level rise of 10 inches since 1981 (Whitney 1995) which corresponds to a gas accumulation of 125 cubic meters at a pressure of 1.2 atm. The best estimate of 215 ± 60 cubic meters (7,600 ± 2,100 scf) is the average of the neutron integration and the BPE result.

This retained gas volume estimate is obsolete because pumping is well underway in tank S-102. The waste level has already fallen by over 30 inches, and the November 2000 neutron log indicates the waste had been affected down to the 120-inch elevation. While it is not possible to accurately calculate the gas release from saltwell pumping with the SHMS-B data, the hydrogen concentration has been as high as 2,500 ppm during the pumping period indicating retained gas was released (see Appendix A of McCain 2000).

Tank 241-S-111: This tank has not been saltwell pumped and is very wet with approximately a meter of supernatant. The waste level is close to 205 inches and has been growing very gradually (< 0.2 in. per year) since 1990. Tank S-111 has been one of the more active tanks in terms of spontaneous GREs. Thirteen have been recorded on its SHMS-B since it was installed in March 1995. The maximum headspace hydrogen concentration was 1,670 ppm.

The five RGS segments obtained from a single riser (Riser 6) in October 1998 showed a parabolic gas fraction profile increasing from 0.01 at the 190-inch elevation to 0.23 at 38 inches with an average gas fraction of 0.15. The gas volumes obtained with the BPE calculation and integration of the neutron logs overlap that of the RGS within their uncertainties; therefore, the best estimate is taken to be the average of 360 ± 85 cubic meters (12,700 ± 3,000 scf).

Tank 241-S-112: Tank S-112 was saltwell pumped in 1978. The waste surface appears dry with a deep, irregular depression around the saltwell screen. Since 1981, the waste surface level has subsided about five inches while the ILL has increased about 10 inches (Whitney 1995). The increase in ILL is probably a result of liquid drainage from subsaturated solids above but might also indicate gas accumulation. The ILL is currently more than 60 inches below the waste surface, and the November 2000 neutron log indicates very little liquid above it. No GREs have been recorded since the SHMS-B was installed in 1995. Neutron log integration yields a retained gas volume estimate of 46 ± 23 cubic meters (1,600 ± 800 scf). If the rise in ILL were assumed to be the result of gas accumulation, the recorded 10-inch rise would indicate 54 cubic meters of gas assuming a porosity of 0.4 and a gas pressure of 1.3 atm.

Tank 241-SX-101: This tank contains about 167 inches of waste. Except for a recent rise attributed to water addition while installing a saltwell screen, the ILL has been decreasing steadily since 1990 (the waste level was in intrusion mode until 1998). No GREs have been recorded on the SHMS-B since it was installed in March 1995. The retained gas volume estimate from the neutron log is 94 ± 47 cubic meters (3,300 ± 1,700 scf). The BPE method yielded erratic results and was not considered useable. Saltwell pumping had not yet affected the gas retention data at the time of this writing, December 2000, but will shortly make retained gas estimates obsolete.

Tank 241-SX-102: Both the waste level and ILL have decreased about 10 inches, to the current level of 193 inches since 1981 (Whitney 1995). No GREs have been recorded since the SHMS-B was installed in March 1995. The retained gas volume estimate from the neutron log is 170 ± 85 cubic meters (6,000 ± 3,000 scf). The BPE method yielded erratic results, and was not considered useable.

Tank 241-SX-103: The waste level and ILL in tank SX-103 were about 234 inches before saltwell pumping began October 26, 2000. The waste level had decreased 15 inches and the ILL 9 inches since 1981 (Whitney 1995). Ten spontaneous GREs were recorded on the tank SX-103 SHMS-B since it was installed in March 1995 with a maximum hydrogen concentration of 640 ppm (McCain 2000).

As in all SX-tanks except tank SX-106, the BPE results are erratic and unusable, and only the neutron log is available for a gas volume estimate. However, the neutron log appears to have an anomalously low count that would indicate gas fractions locally approaching 0.50 with an average of 0.27. The corresponding high retained gas volume approaching 800 cubic meters (28,000 scf) is discounted based on the long-term decline in waste level. In any event, any discussion of retained gas volume is made obsolete by the progress of saltwell pumping.

Tank 241-SX-104: This tank was saltwell pumped from July 1998 to July 1999 and was declared interim stabilized April 26, 2000. Prior to pumping the neutron logs indicated a retained gas volume of 250 ± 125 cubic meters (8,800 ± 4,400 scf). No BPE or RGS data were available. Three very small (200 ppm peak hydrogen concentration) spontaneous GREs were observed from December 1995 to November 1996.

Pumping removed 125 kgal and dropped the waste level by 50 inches to 168 inches and the ILL by 120 inches to 95 inches. The waste surface appears to be dry, and there are cracks and shelves typical of drying and subsidence (Hanlon 2000). The November 1999 and 2000 neutron logs show most of the liquid removed down to about 100 inches. No spontaneous GREs were recorded on the tank's SHMS-B during the year following pumping.

Tank 241-SX-105: Saltwell pumping began in tank SX-105 August 8, 2000, and 132 kgal of liquid have been removed as of December 2000. The waste level has dropped 84 inches to 155 inches. No neutron logs are available that show the effect of pumping on the ILL or liquid distribution. The pre-pumping retained gas volume estimated from the neutron logs was 180 ± 90 cubic meters (6,400 ± 3,200 scf) and is now obsolete.

Tank 241-SX-106: Pumping began in tank SX-106 October 7, 1998, and ended December 21, 1999. The tank was declared interim stabilized on May 5, 2000. The waste level is smooth and dry with no appearance of standing water. The waste slopes down from the wall to a large depression in the center of the tank. A second depression surrounds the saltwell screen (Hanlon 2000). Pumping removed 160 kgal of liquid and dropped the waste level 94 inches to 104 inches. The November 2000 neutron log shows that the ILL decreased 123 inches to 72 inches with pumping and a considerable fraction of the liquid was removed above the ILL. No spontaneous GREs have been recorded on the tank's SHMS-B since the end of pumping.

Retained Gas Sampler measurements in 1997 showed a parabolic gas fraction profile under a 2-m layer of supernatant. The gas fraction peaked at 0.36 with an average of 0.26. The BPE and neutron estimates were similar to that of the RGS, and the best estimate was taken as the average of 400 ± 100 cubic meters (14,000 ± 3,500 scf). However, this estimate is now obsolete.

Tank 241-SX-109: There are only about 96 inches of waste in this tank. In a 1986 photograph, the waste surface was highly irregular with large mounds of waste encasing the exposed portions of the airlift circulators. The waste level has been approximately constant over the last ten years; therefore, gas is not accumulating. McCain (2000) reports one small GRE from SHMS-B data in December 11, 1995, with a peak hydrogen concentration of 100 ppm. There are no other data available from which to estimate the retained gas volume.

Tank 241-T-110: This tank was saltwell pumped in 1983 and again in 1997 and 1998. Photographs of the waste surface in 1984 showed a cracked waste surface with the appearance of drying mud. The post-pumping BPE calculation showed no retained gas detectable, and the 2000 neutron log indicates a small gas volume of 50 ± 25 cubic meters (1,800 ± 900 scf).

Tank 241-U-103: Saltwell pumping began in tank U-103 on September 26, 1999, and ended May 11, 2000. The tank was declared interim stabilized on September 11, 2000. The waste surface appears dry and shows cracks apparently due to drying and subsidence. The surface slopes from the wall down to two depressions in the middle of the tank where there is a small pool of liquid estimated to contain about 500 gallons (Hanlon 2000).

Pumping removed 99 kgal of liquid, which reduced the waste level 17 inches to 160 inches. The ILL decreased by 118 inches to 60 inches although a relatively high liquid fraction appears to reside between 100 and 140 inches. During pumping, headspace hydrogen concentrations rose once to almost 5,000 ppm and twice to over 3,000 ppm (McCain 2000). While it is not possible to compute the actual volume of gas released during pumping from the SHMS-B data, these concentrations indicate that a significant fraction of retained gas was released. There have been no spontaneous gas releases recorded after pumping ceased.

Prior to pumping, seventeen small GREs were recorded on the SHMS-B, with a maximum hydrogen concentration of 1,670 ppm. In 1997 the RGS found one segment near the top of the waste with a gas fraction of 0.42. However, three more segments at lower elevations showed gas fractions of only 0.10, making the average gas fraction 0.19. The BPE and neutron estimates of retained gas volume agreed with the RGS within their uncertainties ,and the best estimate of 315 ± 80 cubic meters (11,000 ± 2,800 scf) was taken as the average of the three. This gas volume estimate is obsolete.

Tank 241-U-105: Saltwell pumping began in tank U-105 on December 11, 1999, and ended July 13, 2000, removing 91 kgal of liquid. The tank is currently under evaluation for interim stabilization. As a result of pumping, the waste level was lowered 26 inches to 138 inches, and the ILL decreased 72 inches to 93 inches. The top 20 inches of the waste is still relatively wet, however. During pumping the headspace hydrogen concentration rose to about 1,600 ppm and nitrous oxide to almost 5,000 ppm. No estimate of the gas release volume has been made.

Prior to pumping, nineteen GREs were recorded on the SHMS (SHMS-B March 1995 to May 1998, SHMS-E+ May 1998 to present). The maximum hydrogen concentration was 1,440 ppm. The pre-pumping retained gas volume estimate of 270 ± 90 cubic meters (9,500 ±3,200 scf), which was taken as the average of the BPE and neutron integration values, is obsolete.

Tank 241-U-107: The waste level and ILL in tank U-107 are at 157 inches, of which the upper 20 inches are probably supernatant. Both levels have risen very gradually (< 0.2 in. per year) since 1990. Fourteen small spontaneous GREs have been recorded by the tank's SHMS-B since March 1995. The maximum hydrogen concentration was 1,900 ppm. The best estimate of the retained gas volume, 180 ± 60 cubic meters (6,400 ± 2,000 scf), is taken as the average of the BPE calculation and neutron log integration. The waste level has risen 6 inches since 1981 (Whitney 1995), which would indicate a gas accumulation of 75 cubic meters at 1 atm, assuming an in-situ pressure of 1.2 atm.

Tank 241-U-108: The waste level and ILL in tank U-108 are at 179 inches, of which the upper 20 inches are probably supernatant. Both levels have been essentially constant since 1990. Fourteen small spontaneous GREs have been recorded by the tank's SHMS-B since March 1995. The maximum hydrogen concentration was 1,530 ppm.

The BPE calculation of retained gas volume is 285 ± 56 cubic meters and the neutron log integration gives 490 ± 240 cubic meters. The average of 390 ± 120 cubic meters (13,800 ± 4,200 scf) is taken as the best estimate. The waste level has risen only three inches since 1981, indicating a gas accumulation of 44 cubic meters, if the in-situ pressure were 1.39 atm.

Tank 241-U-109: Saltwell pumping began in tank U-109 March 11, 2000, and is still underway. As of December 2000, 72 kgal of liquid has been removed, of which possibly 55 kgal was supernatant. Pumping has lowered the liquid level 18 inches to 159 inches, and the ILL 98 inches to 79 inches. The headspace hydrogen concentration rose to over 4,500 ppm immediately after initiation of pumping and remained in the range from 3,000 to 4,500 ppm for about two months. While no accurate estimate of the gas release volume can been made with the SHMS-B data, this indicates a significant fraction of the retained gas has been released.

In 1998 the four RGS segments recorded gas fractions from 0.15 to 0.30, generally increasing with depth, with an average gas fraction of 0.22. This gives a relatively high retained gas volume of 500 ± 250 cubic meters. The BPE calculation and neutron log integration gave gas volume estimates of 190 ± 58 and 284 ± 140 cubic meters, respectively, which overlap the RGS value within their mutual uncertainties. The best estimate of 320 ± 90 cubic meters (11,300 ± 3,500 scf) was taken as the average of the three. This gas volume estimate is obsolete.

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7.0 SPONTANEOUS AND INDUCED GAS RELEASE BEHAVIOR

Many of the SSTs on the Flammable Gas Watch List store a significant volume (200 to 400 m^3, see Section 6.0) of flammable gas, and some occasionally release a small volume of it into the tank headspace. Gas releases can also be induced by physically disturbing the waste (e.g., by core sampling, etc.) and by saltwell pumping. A GRE is characterized by an increase in measured headspace hydrogen concentration to a peak at least 100 ppm above the steady-state value over several hours or days followed by a more gradual decrease back to the steady-state concentration. This return to steady-state concentration in SSTs is influenced primarily by the passive (or active) ventilation flow rate through the tank headspace.

Hydrogen gas measurements in SSTs from 1995 to the present (McCain 2000) show that headspace hydrogen concentrations during GREs have not created flammable gas mixtures. The gas releases induced by saltwell pumping have not 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. The LFL for hydrogen is 40,000 ppm.

This section summarizes the gas releases observed in the SHMS data in terms of volume, duration, frequency, and their trends. Section 7.1 discusses the methods used to quantify gas releases and limitations associated with these methods. The spontaneous gas release histories and trends are summarized in Section 7.2. Induced gas releases are discussed in Section 7.3, and a summary is given in Section 7.4.

7.1 METHODS USED TO QUANTIFY GAS RELEASES

Gas release volumes are estimated from the measured concentration of hydrogen in the tank headspace by two methods. The first provides the lower bound based on the peak hydrogen concentration, and the second gives a best estimate by integrating the hydrogen concentration transient. The total gas release volume can be estimated by dividing the hydrogen release by the hydrogen fraction in the stored gas (i.e., as measured by the RGS). However, because the hydrogen fraction is known only for the nine SSTs sampled with the RGS, only the hydrogen release volumes are given in this section. Waste surface level drop analysis has also been used to quantify gas releases and was the only method available prior to SHMS installation. However, it is only applicable to larger releases of tens of cubic meters associated with a few of the DSTs,[16] and none of the GREs considered in this section of this report are based on level drops.

[16] The early waste level histories of some SSTs show the "sawtooth" level rises and abrupt drops associated with buoyant displacements in DSTs. However, these occurred when the tanks contained deep supernatant layers and the liquid-over-solid waste configuration of typical DSTs. None of the SSTs now have that configuration as discussed in Section 6.0.

7.1.1 Lower Bound Estimate

A lower bound estimate of the volume of hydrogen released can be determined from the following equation:

$$V_R = V_{HS}\left([H_2]_{Peak} - [H_2]_{Base}\right) \tag{7-1}$$

where:

V_R = volume of hydrogen released,
V_{HS} = tank headspace volume,
$[H_2]_{Peak}$ = peak hydrogen concentration, and
$[H_2]_{Base}$ = steady-state hydrogen concentration before the GRE.

Assuming a well-mixed headspace and zero ventilation rate, a volume of no less than exactly the peak hydrogen concentration times the headspace volume is required to achieve that concentration. A larger release actually occurs because headspace ventilation (passive or active) reduces the peak measured concentration somewhat and gas release continues at a low rate long after the peak concentration occurs.

This method is subject to the potential error of a local plume of released gas causing a spurious concentration spike. However, since releases in SSTs are typically several days long and the mixing time in the tank headspaces is on the order of a few hours, it is reasonable to assume a well-mixed headspace.

In order to keep a consistent basis and to avoid errors resulting from very noisy SHMS-B data, the lower bound estimate is used for all hydrogen release volumes in this section.

7.1.2 Integrated Exhaust Hydrogen Concentration

The hydrogen signature of a gas release shows a fairly sharp rise from a steady-state concentration followed by an approximately exponential decrease back to the steady-state concentration. The volume of hydrogen released can be calculated by integrating the transient concentration by means of a two-step process. The first step estimates the vent flow rate during the GRE with the following equation:

$$Q_V = \frac{V_{HS}}{t_p - t_0} \ln \frac{[H_2]_p}{[H_2]_0} \tag{7-2}$$

where:

Q_V = estimated ventilation rate,
$[H_2]_p$ = peak hydrogen concentration,
$[H_2]_0$ = steady-state concentration (post release),

t_p = time of peak concentration,
t_0 = time of return to steady-state concentration, and
V_{HS} = headspace volume of the tank.

This equation assumes that the headspace is well mixed, that the hydrogen concentration decays at an exponential rate, and that the release rate is zero after the peak concentration.

The second step calculates the actual release volume by numerically integrating the measured headspace hydrogen concentration (in terms of concentration versus time) above the steady-state value from event initiation through return to steady-state. The total release volume is the product of the integral and the estimated ventilation rate from Equation 7-2.

This estimation of hydrogen gas release volumes is sensitive to the selected starting point of the release, the SHMS baseline offset and calibration, the magnitude of the SHMS concentration peak, and any drift that may occur in the SHMS calibration over the period of several months. This results in uncertainties on the order of 2 to 3 times the calculated value of the release. The hydrogen release volumes documented by McCain (2000) were computed with this method.

7.2 SPONTANEOUS GAS RELEASES

Since the initiation of SHMS monitoring in SSTs in 1995, 204 spontaneous GREs have been observed. Tank A-101 accounts for 28% of these observations, and the tanks in U-Farm account for another 39% of the GREs. The data given in Table 3-7 of McCain (2000) is summarized in Table 7-1 for the SSTs on the Flammable Gas Watch List and Table 7-2 for the non-Watch List SSTs with SHMS installed. Hydrogen release volumes in the table are computed using Equation 7-1. Uncertainties are shown when three or more GREs occurred and represent one standard deviation. None of the GREs listed include those induced by saltwell pumping.

The mechanism by which the small spontaneous gas releases occur in SSTs is not known. As described in Section 6.1, upward motion of pore-filling or particle-displacing bubbles by "percolation" is a probable explanation. In a pore-filling bubble, this is believed to occur when the bubble grows to the point that hydrostatic pressure difference exceeds surface tension forces holding the bubble in the throat between pores. Similarly, particle-displacing bubbles are thought to percolate when they grow such that hydrostatic pressure difference exceeds the waste strength, pinches off the bottom of the bubble, and pushes the top of the bubble upward.

Table 7-1. Spontaneous Gas Release Event Summary for Flammable Gas Watch List Tanks [a]

Tank	#GREs	Date of Last GRE	Duration (days)	Time to Peak (days)	Average $[H_2]$ (ppm)	Release Volume (m^3)	Max. $[H_2]$ (ppm)	SWP Start Date	SHMS Type, Date, Removal
A-101	57 [b]	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
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) GRE data are provided only for tanks where at least one GRE has been recorded.
(b) Only data since 11/97 are included for tank A-101.

Table 7-2. Spontaneous Gas Release Event Summary for Non-Watch List Tanks [a]

Tank	#GREs	Date of Last GRE	Duration (days)	Time to Peak (days)	Average $[H_2]$ (ppm)	Release Volume (m^3)	Max. $[H_2]$ (ppm)	Saltwell Pumping Start Date	SHMS Type, Date, Removal
B-111	0								E+ 5/00
BY-103	4	10/26/99	5 ± 3	1.6 ± 1	290 ± 140	0.6 ± 0.4	490	1997	B 7/95
BY-105	1	1/19/99	6	0.7	310	0.6	310		E+ 3/98
BY-106	4	8/13/98	3 ± 1	1.1 ± 0.6	520 ± 200	0.6 ± 0.1	780		D 7/95
BY-109	3	8/30/99	9 ± 8	3 ± 3	660 ± 630	1.6 ± 1.2	1,390	1997	D 7/95, Removed 2/00
S-101	1	9/16/98	3	1	700	0.3	700		E 3/98, Standby 2/00
S-106	0							4/16/99	E+ 3/98
S-107	0								B 3/98, Standby 2/00
S-109	0							9/23/00	E+ 3/98, Standby 2/00
U-102	2	5/2/99	3.3	1	510	0.5	760	1/20/00	B 3/98
Average			5 ± 4	1.6 ± 1.6	470 ± 300	0.7 ± 0.7			

(a) GRE data are provided only for tanks where at least one GRE has been recorded.

Saltwell pumping is expected to alter a tank's gas release behavior. Percolation of particle-displacing bubbles should be much faster since it does not involve flow of liquid through the porous medium. This implies that waste where gas is stored primarily in the form of particle-displacing bubbles should exhibit more and faster spontaneous gas releases than waste that stores gas as pore-filling bubbles. If saltwell pumping increases the lithostatic load in the waste such that all gas is retained as pore-filling bubbles, tanks should have slower and fewer gas releases after pumping than before. However, as the gas migrates into regions with lower lithostatic loads, the gas may again displace particles. The particle-displacing bubble region may then exhibit small spontaneous releases as if from an unpumped tank.

The monitoring data are somewhat inconclusive on the effect of saltwell pumping on spontaneous gas release behavior. Tank S-112, which was pumped in 1978-1980, and tank T-110, which was pumped in 1997, have had no spontaneous releases since pumping ended. More recent saltwell pumping also appears to have stopped gas releases in tanks SX-106, SX-104, U-103, and U-105. However, tanks BY-103 and BY-109, which were pumped in 1985, have had several spontaneous releases since SHMS were installed in 1995 that are indistinguishable from those of unpumped tanks. At the same time, tanks S-102 and S-106 that store the largest volumes of gas (see Section 6.0), have shown no spontaneous releases at all, before or after pumping.

Although the release mechanisms are not completely understood, 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) is shown in Figure 7-1. The median hydrogen release volume is about 0.5 cubic meters, and the 99.9 percentile release is only 3 cubic meters. The Watch List and non-Watch List tanks have essentially the same distribution.

The cumulative distribution of the time to peak hydrogen concentration is shown in Figure 7-2. The median time to peak is about one day, and many releases require several days to reach the peak concentration. The shortest time to peak, recorded in five GREs, was about four hours. The total release durations given by McCain (2000) are about five times the time to peak. There is no correlation between release size and duration.

Gas releases are becoming fewer, and their duration appears to be decreasing. To investigate the trends, tanks were chosen that had SHMS since 1995 and have not been saltwell pumped. Data from tank A-101 was excluded because it represents only the last two years of the period and the large number of small releases from this tank would dominate the other tanks. The remaining data represent 82 of the 204 total GREs recorded. The trends of time to peak and lower bound hydrogen release volume are plotted in Figure 7-3. The hydrogen release volume appears to be steady while the time to peak has decreased by a factor of about 2 in five years.

A definite grouping of the GREs in the winter months can be seen in Figure 7-3. The gas release mechanisms are apparently sensitive to the void fraction such that most of the spontaneous releases occur during periods of large barometric pressure swings in the fall and winter. This is clearly illustrated in Figure 7-4 that shows the number of GREs in each 3-month period since June 1995 for the same 84-GRE data set used to establish trends in Figure 7-3. The greatest

number of GREs occurs in the six months from September through February. It is also clear that the GRE frequency is decreasing. This result may be slightly skewed since 1996 had 50% more day-to-day pressure swings exceeding 0.25 in.-Hg than the average of the other years. However, the number of pressure swings increases from 1997 through 1999, which is opposite the trend in GRE occurrence.

This and the trend of decreasing GRE duration may be the result of the general cooling trend observed in essentially all of the tanks (see Section 4.0). The DSTs that have cooled also show a marked change in GRE behavior (Hedengren et al. 2000).

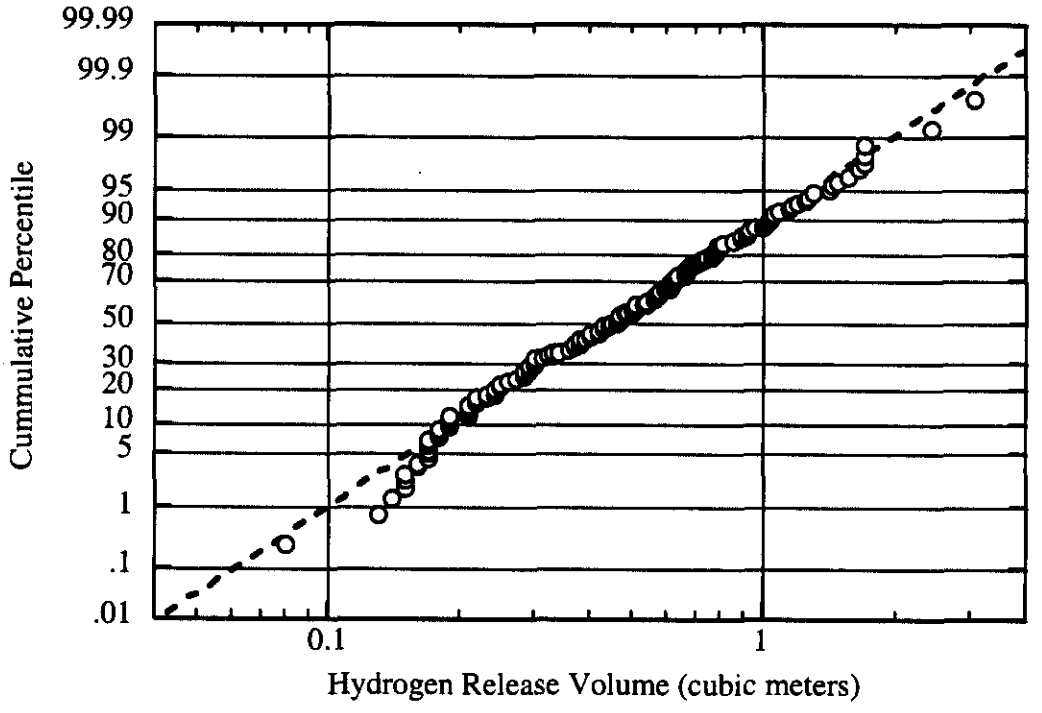

Figure 7-1. Cumulative Distribution of Single-Shell Tank Hydrogen Release Volume

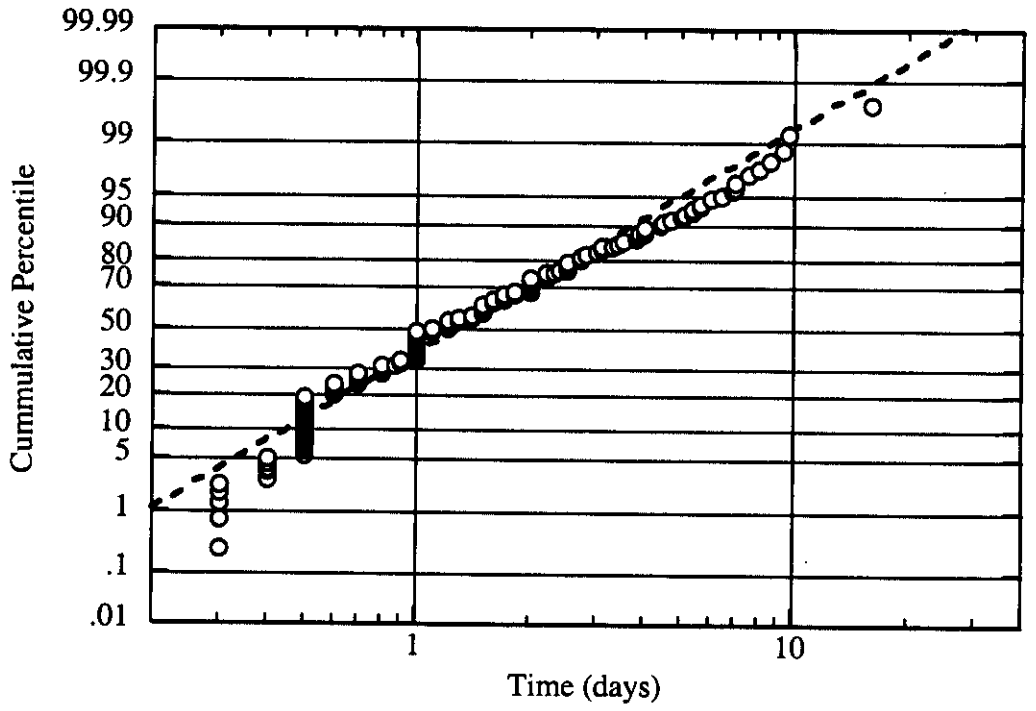

Figure 7-2. Cumulative Distribution of Time-to-Peak Hydrogen Concentration

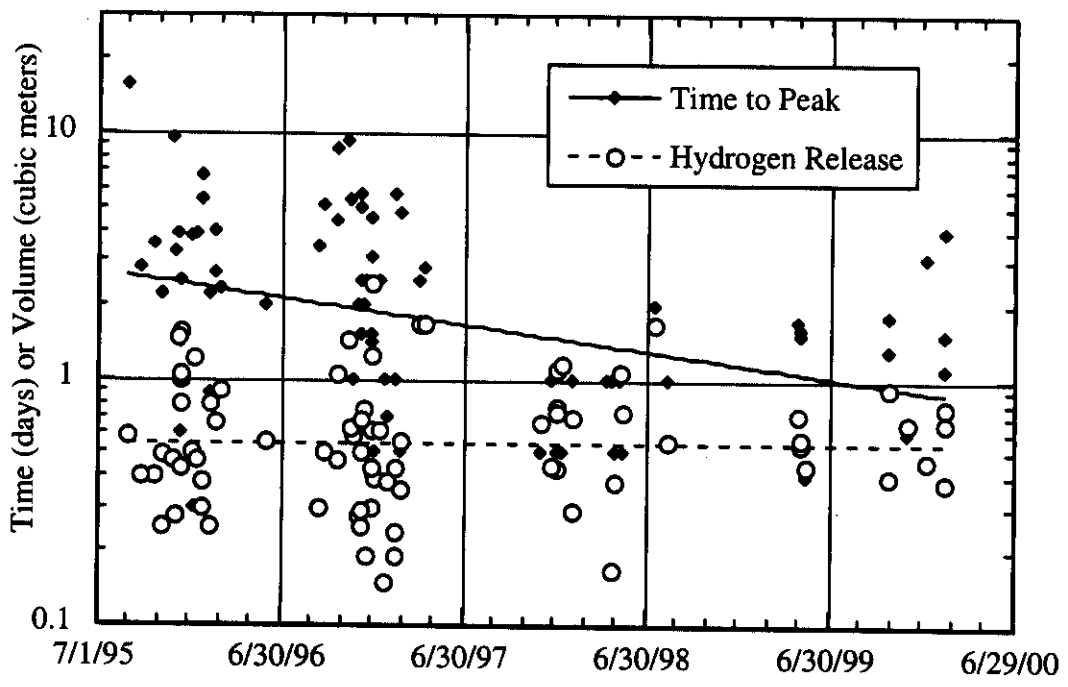

Figure 7-3. Trend of Single-Shell Tank Hydrogen Release Volume and Time-to-Peak Hydrogen Concentration

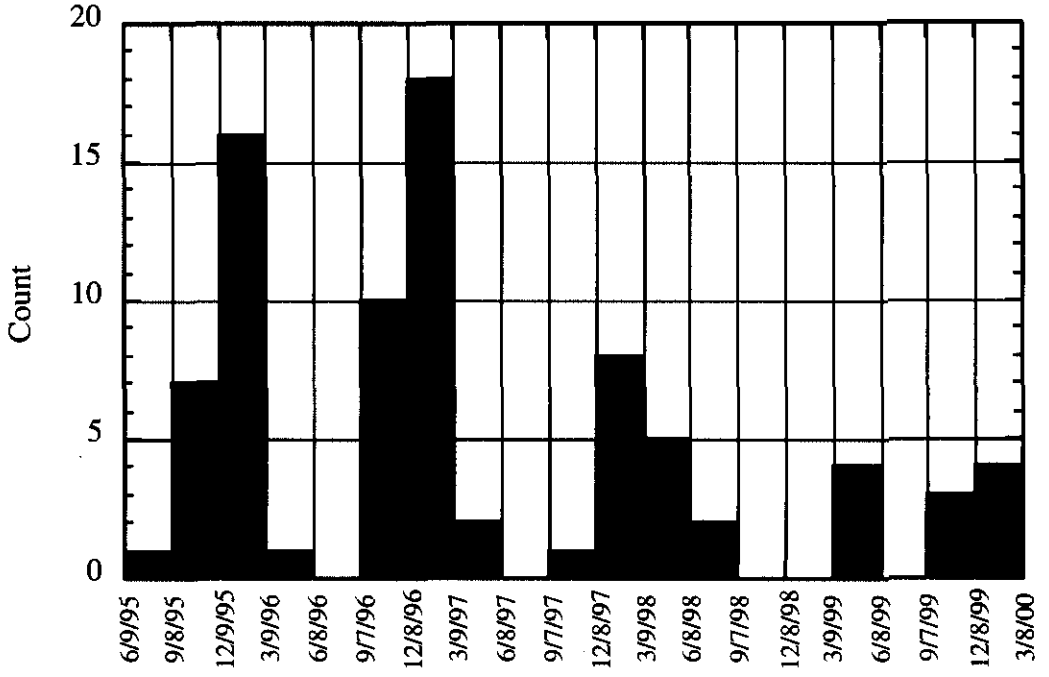

Figure 7-4. Single-Shell Tank Gas Release Event Frequency Trend

7.3 INDUCED GAS RELEASES

Local waste disturbing activities in the SSTs such as equipment installation and core sampling that disrupt a small fraction of the total waste volume, occasionally result in a temporary increase in dome space hydrogen concentration. The highest hydrogen concentrations occur during saltwell pumping, which represents a global disturbance of the entire waste volume. Gas releases induced by local waste disturbing activities are summarized in Section 7.3.1. The gas releases associated with saltwell pumping are described in Section 7.3.2.

Retrieval of the waste from SSTs can also be expected to release much of the gas remaining in the waste. However, there are many different methods currently being considered for retrieval that will release gas in different ways that will need to be considered in planning the operations. Sluicing of tank C-106 is the only SST retrieval operation that has been accomplished recently (Cuta et al. 2000) with the benefit of gas monitoring. But since this case was unique, it is of limited value in assessing possible releases from other SSTs during retrieval. For these reasons, gas releases induced by retrieval are not discussed further.

7.3.1 Gas Releases Induced by Local Waste Disturbances

If a volume of waste containing retained gas is locally disrupted, some gas will be released from the volume actually disturbed. There is no known mechanism whereby a local disturbance can "trigger" a large, global release. Gas releases observed as a result of local waste disturbances have generally been barely detectable, and none have approached 25% of the LFL. A 1996 informal study of 77 waste intrusive activities in 47 separate SSTs showed three probable and two possible releases of gas associated with the waste disturbance. The "possible" releases were identified from surface level changes, while the "probable" releases were detected with headspace gas monitoring equipment. The study then examined gas releases from an additional 61 sampling events and four additional LOW installations. These measurements were made using a hand-held combustible gas meter at the riser level before the drill string was flushed after the sample had been removed. A measurable rise in the hydrogen concentration resulting from a local disturbance occurred in only three SSTs.

7.3.2 Saltwell Pumping Induced Gas Releases

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 dome space. Both of these effects result in bubble growth, which may cause either bubble disengagement or percolation gas release (see Section 6.1). Gas in particle-displacing bubbles too small to release by these mechanisms may be released when the liquid eventually drains away from around them (Peurrung et al. 1997). However, even after the bulk liquid has been drained away, some gas may remain trapped between particles in small, pore-filling bubbles surrounded by liquid held by capillary forces. Gases in this condition can eventually be released when the entrapping liquid evaporates or gradually drains away.

The qualitative correlation between saltwell pumping and gas releases is well established by headspace monitoring data. This is illustrated in Figure 7-5, 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. Headspace ventilation rates, determined from a coincident tracer gas study, were used with the headspace nitrous oxide concentrations to estimate the release rates shown (Peurrung and Huckaby 2000).

The data in Figure 7-5 suggest a definite relationship between saltwell pumping and gas release rates. Although pumping activities do not always lead to a gas release, there appears to be about a one-day or more lag between pumping activities and the corresponding gas release. The correlation between pumping and gas releases is evident from headspace monitoring data in other tanks being saltwell pumped (Caley et al. 1996, Huckaby et al. 1999, Peurrung and Huckaby 2000, Watrous et al. 2000), but as with tank U-105, the timing and magnitude of gas releases are apparently also subject to a variety of other factors.

Available headspace gas monitoring data suggest that the highest induced gas release rates occur shortly after the onset of saltwell pumping, when the liquid drains rapidly and pumping rates tend to be high.[17] This is illustrated in Figure 7-6, where the estimated hydrogen release rate[18] has been plotted above the pumping rate of tank S-106. Much of the liquid being pumped in this initial period consists of supernatant and the fluid from the region immediately surrounding the saltwell screen, which responds quickly to pumping. During the initial phase, the starting and stopping of the saltwell pump may cause the gas release rates to rise and fall rapidly, as shown in Figure 7-5 for tank U-105.

Continued pumping exhausts the supernatant and depletes the region near the saltwell screen of liquid, and the drainage rate tends to decrease. Gas release rates decline correspondingly, as indicated for tank S-106 in Figure 7-6. In this second phase of pumping, the liquid saturation interface profile rises gradually from a low point at the saltwell to some higher level near the tank wall. The majority of liquid being pumped during this phase comes from the regions away from the saltwell screen. A temporary cessation in pumping has little immediate effect on the drainage rate far from the saltwell, and the response of the gas release rate is correspondingly damped.

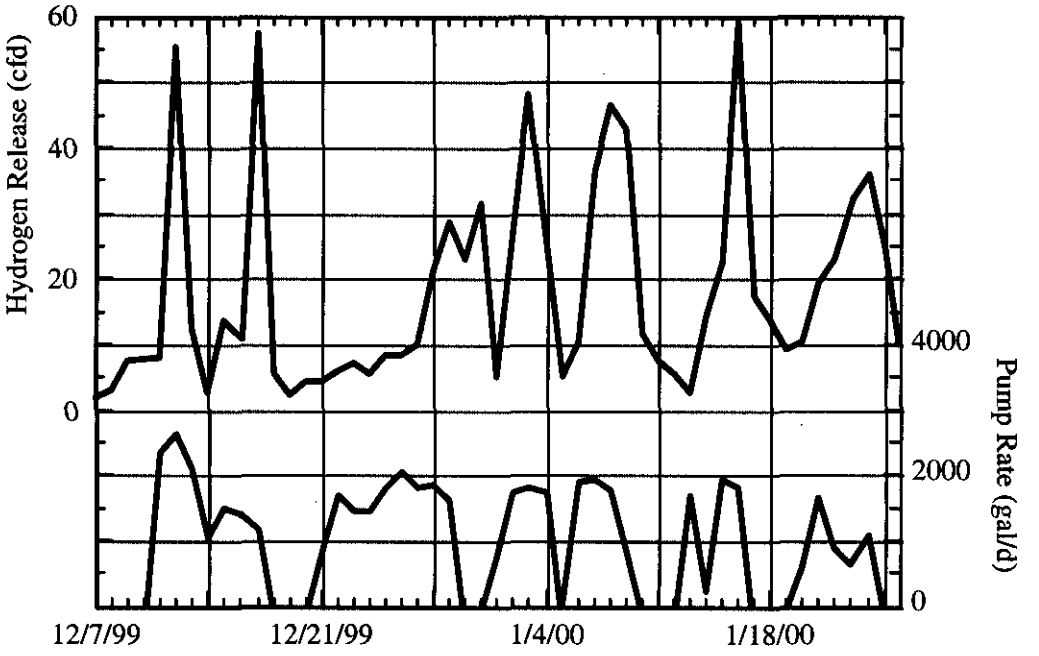

Figure 7-5. Tank 241-U-105 Hydrogen Release and Saltwell Pumping Rates

[17] This generalization may not apply to tanks A-101 or AX-101 because the liquid that would be pumped first is beneath the gas retaining layer.

[18] The hydrogen release rate was calculated from hourly hydrogen concentration data and an average ventilation rate determined from tracer gas studies. The negative gas release rates indicated in Figure 7-5 are not physically reasonable and indicate that the actual ventilation rate at those times was considerably higher than the 9.1 ft^3/min used in calculations.

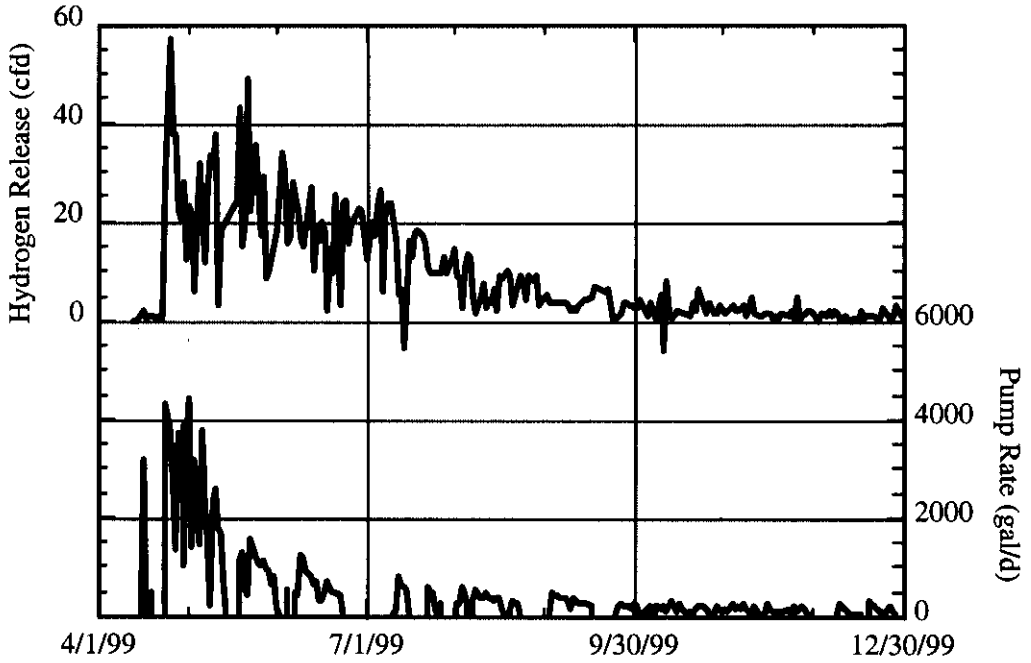

Figure 7-6. Tank 241-S-106 Estimated Hydrogen Release Rate and Pumping Rate

Pumping is stopped when the drainage rate drops below a prescribed level. However, drainage continues from the outer regions of the waste toward the saltwell screen, as well as, from the upper regions of the waste that had not drained completely. This continues to release trapped gases, albeit slowly. The headspace hydrogen and nitrous oxide concentrations in tank S-106, for example, appear to have been significantly higher for months after saltwell pumping was stopped than they were before it was started (Peurrung and Huckaby 2000).

Because of its relatively high solubility in the liquid wastes, headspace ammonia concentrations are not expected to rise and fall as pumping is started and stopped (Peurrung et al. 1997). Unlike hydrogen and nitrous oxide, which reside mainly as trapped bubbles and migrate rapidly to the waste surface once released, ammonia resides mainly (dissolved) in the aqueous solution and evolves into the gas phase by evaporation. Consequently, wherever the waste itself remains wet, there is a reservoir of ammonia that releases ammonia vapor to the headspace as mass transport allows. Saltwell pumping did not apparently affect the ammonia vapor concentration in tank U-105 until the supernatant was removed, at which time the increased wetted surface area (associated with the exposed porous waste surface) resulted in a rapid rise in the headspace ammonia concentration (Peurrung and Huckaby 2000).

A concern in saltwell pumping is the potential for flammable gas accumulation in the pump pit during operation. Accordingly, flammable gas monitoring of the pump pit is required during saltwell pumping. Data from pump pit monitoring has been evaluated by Watrous et al. (2000) by comparison to concurrent headspace concentrations. While the hand-held flammable gas monitors typically gave readings in %LFL much higher than the corresponding headspace

hydrogen concentrations, both measures followed the same trends. Three grab samples of the pump pit atmosphere analyzed by a gas chromatograph showed that the actual hydrogen concentration closely matched that of the dome space. None of the samples from the pump pit or headspace exceeded 25% of the LFL.

7.4 SUMMARY OF GAS RELEASE BEHAVIOR IN SINGLE-SHELL TANKS

No mechanism for large gas releases from SSTs is known nor have any been observed in the current waste configuration (Stewart et al. 1996). Small spontaneous gas releases have been observed in many SSTs since headspace gas monitoring equipment was installed in 1995. All 204 observed releases were less than 5 cubic meters, with the median less than one cubic meter. They are also relatively slow. The median time to peak hydrogen concentration was about one day; the minimum was about four hours. The highest hydrogen concentration observed in any spontaneous release was 2,190 ppm, about 5% of the LFL for hydrogen. Spontaneous gas releases appear to be decreasing in duration and frequency but not in volume. No significant gas releases have been observed during local waste disturbing activities.

The highest hydrogen concentrations are observed during saltwell pumping. The highest hydrogen gas concentration measured by SHMS in an 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 in 1999. Releases generally, but not always, follow pumping rate. Pumping releases a moderate fraction of the stored gas. The small spontaneous releases typical of unpumped SSTs continued after pumping in at least two tanks, although they appeared to have ceased in several other pumped tanks.

The sum of gas release experience in the SSTs in the last five years shows that the demonstrable flammable gas release hazard is negligible and the trend is of decreasing hazard. Saltwell pumping does not significantly increase the hazard while in progress, and reduces the hazard when complete.

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8.0 HEADSPACE DYNAMICS AND FLAMMABLE GAS CONCENTRATIONS

Gases are normally released from the waste to the tank headspace in a gradual, essentially steady manner. As discussed in Section 7.0, some tanks also spontaneously release additional gas episodically over periods of a few hours or days. Waste intrusion (e.g., core sampling, sluicing, saltwell pumping) can induce gas releases with a period roughly corresponding to the period of the disturbance. In each case, the gases from the waste are mixed within the tank headspace and removed by either active or passive ventilation. The relatively small gas release volumes in comparison to the much larger tank headspace and the slow release rates compared to even natural ventilation rates effectively prevent headspace gas concentrations from approaching flammability.

This section describes the phenomena of headspace mixing and breathing. Section 8.1 discusses headspace mixing and presents the results of analyses and experiments that quantify the rate and degree of mixing. Section 8.2 describes the phenomena affecting passive headspace breathing and provides breathing rates measured in tracer studies. An overall summary is given in Section 8.3.

8.1 HEADSPACE MIXING AND UNIFORMITY

This section discusses the rates at which gases released by the waste are mixed within the tank headspace and removed by ventilation. The discussion of waste gas mixing in the tank headspace is divided into two subsections. First, the scenario of a gradual, essentially steady release of gases by the waste is discussed, and second, the scenario of a hypothetical sudden, episodic release of a large quantity of gas is discussed.

8.1.1 Mixing of Gradually Released Waste Gases

Various studies employing numerical modeling and semi-empirical relationships have concluded that thermally induced convection causes rapid mixing of gases in the tank headspace (Claybrook and Wood 1994, Postma et al. 1994, Epstein 1995). Radioactive decay of the waste results in waste surface temperatures that are higher than the temperatures of the tank dome and the ground above the dome. Air is warmed by the waste surface and rises, displaced by descending air cooled by contact with the tank dome. This thermally induced convection mixes gases both vertically and horizontally. The studies indicate that transport and mixing of gases within the convection zone is generally very rapid compared with average gas release rates and that concentration gradients within the convection zone are small.

Between the convection zone and the waste surface is a very thin boundary layer region where mixing occurs by molecular diffusion. It is in this region that fuel and oxidant concentrations may both be sufficient to satisfy combustibility criteria. However, this region represents a very small fraction of the headspace, and releases of waste gases are almost certainly not distributed uniformly across the waste surface (i.e., only very small regions at the waste surface might be

combustible). Epstein (1995) estimated this boundary layer to be on the order of 1.5 to 2.5 cm thick when the waste surface was only 1.4 °C warmer than the dome space in a typical tank. Larger differences between the waste and dome space temperatures would produce more vigorous convection and result in even thinner boundary layer regions.

Tracer gases were used to examine headspace mixing rates in tank S-102 (Huckaby et al. 1997a). A three-dimensional numerical model was used to predict the time-dependent concentrations of tracer gases injected into tank S-102 headspace. Two tracer gases, helium and sulfur hexafluoride, were injected into the headspace, and headspace samples were collected from a point about 4-m away at intervals of 15, 30, and 60-min after injection. Significant levels of both tracers were found in the 15-min samples, and both tracers were essentially at their final concentrations in the 60-min samples. The observed changes in tracer concentrations clearly indicated rapid convective mixing.

The dominance of thermal convection in the headspace of SSTs is further supported by tests performed on tanks C-103 and C-111 (Huckaby and Story 1994; Huckaby 1994), which showed that the gases and vapors in these tank headspaces were not vertically stratified. However, for tanks with very low heat-generation rates, it has been suggested that there may be periods of the year when the ground temperature above the tank is warmer than the waste itself, a situation that does not induce thermal convection. Under these conditions, molecular diffusion and convection associated with tank ventilation continue to mix headspace constituents, but arguably at rates too slow to maintain a homogeneous distribution.

To determine whether composition does vary significantly with location in a cool tank, the headspaces of three waste tanks, selected primarily on the basis of their low waste temperatures, were sampled at different horizontal and vertical locations during that part of the year when thermally induced convection would be minimized (Huckaby et al. 1997b). Headspace composition data from two risers at three elevations in tanks B-103, TY-103, and U-112 were examined for possible differences by standard analysis of variance (ANOVA) methods. The ANOVA study concluded that these tank headspaces are essentially homogeneous. No statistically significant stratification of denser vapors (e.g., carbon tetrachloride, dodecane) or lighter gases (e.g., ammonia, hydrogen) was detected in any of the three tanks. Although the data from three tanks do not prove that no tank headspace ever stratifies at any time of year, the tanks and sampling dates were selected to maximize the possibility of observing stratification. Furthermore, the only tanks in which stratification may be an issue are the coolest tanks, which tend to have the smallest rates of flammable gas generation.

8.1.2 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). The only tank known to release enough gas to raise the entire headspace above the LFL was the DST SY-101,

prior to the installation of the mixing pump. 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).

The main issues concerning plume releases are how long a plume remains flammable and what gas volume is flammable, at any given time. Plume volume, plume composition, release duration, release velocity, headspace convection flows, and headspace geometry each affect the size and duration of any flammable regions. Because it is not practical to collect detailed measurements of actual plume releases, convection flows, etc., the dispersion of plumes under various conditions has been simulated by scale experiments and with numerical models. To a large degree, the results of these studies have been validated by comparison with actual tank data.

8.1.2.1 Plume Dispersion Mechanisms

Dispersion of a plume into its surroundings occurs due to diffusion and turbulent mixing. In the waste tanks, plume dispersion is also accelerated by ambient convective turbulence in the headspace. The buoyancy associated with the temperature and composition of the plume produces a negative radial pressure gradient. The resulting inflow causes the plume to entrain surrounding air as it rises and dilutes the flammable gas concentration. The effect of buoyancy is illustrated in the results of a computational modeling study shown in Figure 8-1, where the hydrogen concentration profile is approximately one minute after the simulated release of 6,400 scf of gas containing 40% hydrogen over an area of 16-ft radius (Antoniak and Recknagle 1997). As it rises, the radial inflow pulls air in toward the center of the narrowing column of rising gases, and the average hydrogen concentration is rapidly reduced as the plume ingests this air.

Epstein and Burelbach (1998) examined the behavior of buoyant plumes using laboratory experiments where fresh water was forced through a porous plate upward into a salt-water solution of higher density. The dimensions of the fresh water plume as it rose and mixed with the brine were visible because of the refractive index differences. Epstein and Burelbach observed that most of the mixing occurred within the mixing layer rather than in the plume itself. This is an important result because it implies dilution of the plume occurs relatively close to the waste surface. Epstein and Burelbach (1998) derived a semi-empirical model for the height of the mixing layer (that portion of the plume immediately above the release area that necks down due to headspace air inflow). Their equation for mixing layer height is plotted (thick line) as a function of radius in Figure 8-1 for the same conditions as the numerical simulation depicted in the figure. As indicated in the figure, both the empirical and numerical model predict approximately the same behavior of the mixing layer.

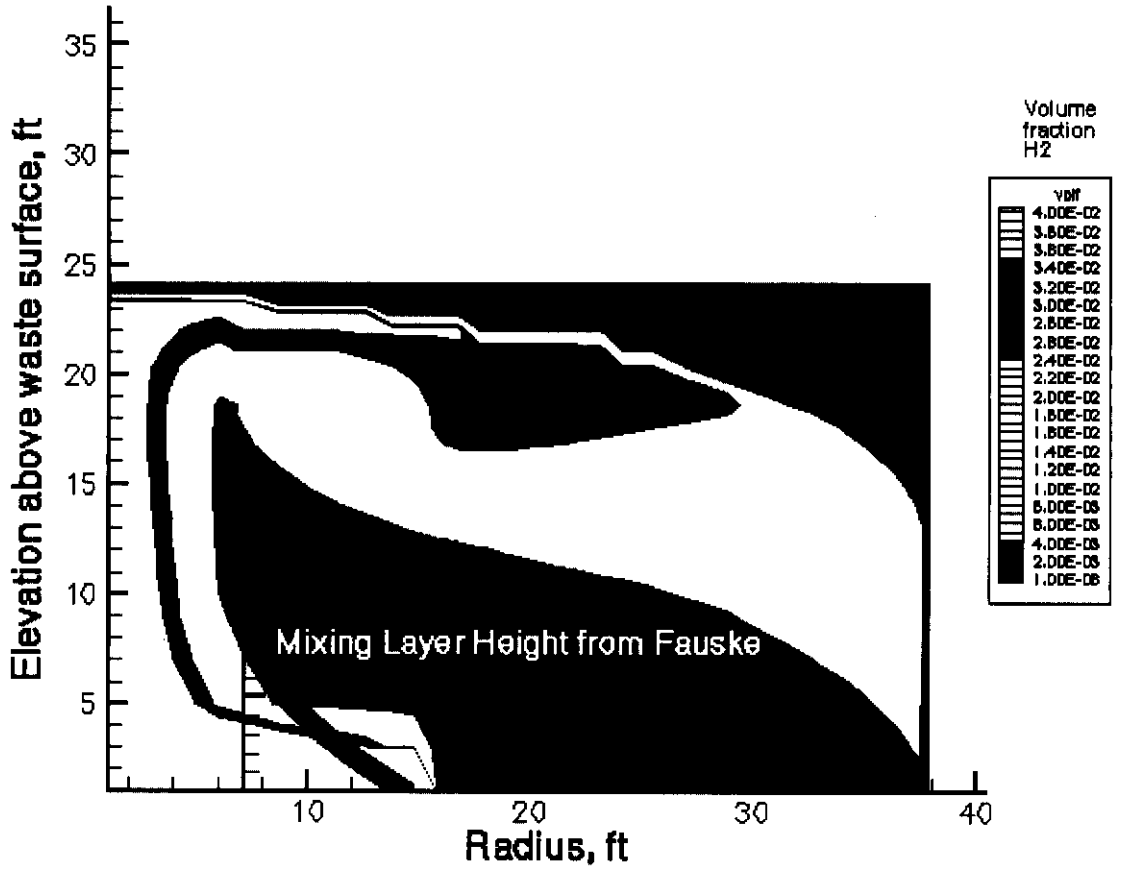

Figure 8-1. Plume H_2 Concentration Contours for a Release Containing 40 mol% H_2.

Long-term dilution of the plume by means of ventilation air inflow typically occurs over time scales of many hours or days, and can be considered almost independently of the initial mixing processes described above. Once it is well mixed, the headspace concentration of H_2 follows an exponential decay curve almost exactly (Antoniak and Recknagle 1995).

8.1.2.2 Numerical Simulations of Plumes

The parameter space affecting plume releases and concentrations is enormous. Besides the composition and temperature of the release gas, the release area and flow rate are also important. A fast local release (from only a small portion of the crust surface) was expected to behave different from a slow global release (uniform over the entire crust surface) of the same total volume. The location of the release (near the tank center versus near the tank wall) is also believed to affect mixing behavior.

Computational modeling using the TEMPEST code (Trent and Eyler 1993) developed at the Pacific Northwest Laboratory was applied to study these complex, combined effects efficiently over a period of several years. A 3-dimensional, transient model was created to simulate plume releases in both DSTs and SSTs. The TEMPEST model was qualified by simulating a well-instrumented thermal plume experiment reported in the literature. The TEMPEST results were found to match the test data reasonably well, usually predicting somewhat slower mixing than what was observed (Antoniak and Recknagle 1996a). This evaluation and the qualitative comparison of the brine-water plume studies shown in Figure 8-1 supports the conclusion that the TEMPEST modeling approach, even with its inevitable assumptions and simplifications, correctly captures plume physics.

The first series of simulations (Antoniak and Recknagle 1995) was performed to determine the peak headspace hydrogen concentrations corresponding to measured concentrations in tank exhaust flow during gas releases. The simulations showed that plume mixing was rapid in all cases. Hydrogen concentration gradients in the dome were not large (e.g., the peak headspace hydrogen concentration differed from the exhaust concentration by about 10 percent), and decreased after the release ended. The calculated exhaust hydrogen concentration transient followed the expected exponential decay and matched measured concentration history quite well. A tank-wide, uniform release rapidly became essentially fully mixed, while a local release required about 2 hours to be fully mixed. Inflow ventilation air temperature was found to affect hydrogen concentrations to a small extent. The released hydrogen took somewhat longer to mix with the headspace atmosphere with cold inlet air (20 °F) than with hot inlet air (120 °F). But in both cases the headspace was nearly completely mixed within 2 hours after the release ended.

The releases in the above simulations consisted entirely of hydrogen. The next round of simulations (Antoniak and Recknagle 1996a) examined the behavior of a much more dense mixture of 40 mol% hydrogen and 60 mol% nitrous oxide. Additional simulations with varying release locations and areas again showed rapid mixing of the tank headspace within an hour or so after the release was over. The use of the heavier mixed gases resulted in significantly lower concentrations for the same volume of hydrogen released.

The effect of a pre-existing passive or forced ventilation flow field on plume dispersion was also addressed (Antoniak and Recknagle 1996b). Simulations of a plume containing 50 mol% hydrogen, 50 mol% air released in a tank with and without forced ventilation showed a negligible difference in mixing time or degree.

The latest study (Antoniak and Recknagle 1997) examined a broad parametric range of release volumes and durations. Release volumes ranged from 100 to 6,400 scf of gas containing 40 mol% hydrogen and 60 mol% air. The 6,400-scf release was chosen to be just sufficient to bring the entire headspace to the LFL for hydrogen, if instantaneously and completely mixed with the headspace volume. Release areas ranged from 1 to 64 ft^2 according to the volume such that the total release time was either 10 or 100 minutes. This range was intended to cover both the small, slow releases observed in SSTs as well as the larger, faster ones in DSTs. A conservative 2 °F temperature gradient between the waste surface and the dome was assumed to drive the natural convection within the headspace.

The results of the parametric studies were consistent with the earlier results, and with tracer gas experiments. Except for the largest (6,400 ft^3) plumes, flammable conditions existed only during the actual release of the plume from the waste. Long-duration releases (again, except for the 6,400 ft^3 plume) never become flammable, within the resolution of the TEMPEST model (2 to 12 ft^3 depending on the release area). The 6,400-scf plume, when released over 10 minutes created a stratified layer with a peak flammable volume of 32,000 ft^3 that decayed exponentially down to zero in a little over two hours. The same plume released over 100 minutes created a peak flammable volume of only 95 ft^3 at the very end of the release.

8.1.2.3 Conclusions

Plume release simulations have been run that encompassed a broad range of parameters. The results indicate that all flammable gas plume-type releases that fall within historical SST volume ranges of up to a few cubic meters (see Section 7.0) will create flammable concentrations in a part of the headspace only during the actual release itself, and the volume that is flammable will be very small. Mixing in tank headspaces is so rapid that the flammable volume goes to zero as soon as the release ends. For hypothetical very large releases of many thousands of cubic feet of gas containing 40 to 60% hydrogen, flammable gas concentrations can theoretically persist for several hours in a stratified layer after the release ends.

8.2 HEADSPACE VENTILATION RATES

Headspace ventilation serves to prevent the build-up of flammable gases released by the waste. Exhausters are used to provide active ventilation of 15 of the 149 SSTs. The remaining 134 SSTs are passively ventilated to the atmosphere via risers equipped with high efficiency particulate air (HEPA) filters.

8.2.1 Actively Ventilated Tanks

The actively ventilated tanks are listed in Table 8-1 with nominal ventilation rates and calculated headspace volumes. Waste tank ventilation rates are, in general, not easily determined because several tanks are connected to each exhauster, and much of the ventilation piping is below grade and inaccessible for direct measurements. Ventilation rates also tend to vary with time because of small changes in system performance (e.g., changes in the flow resistance of HEPA inlet filters). Tanks C-105 and C-106 ventilation rates are estimates of Huckaby et al. (1998). The waste in tank C-106 was removed by sluicing in 1998-1999 (Cuta et al. 2000). The earlier estimate of its ventilation rate is obsolete and forced ventilation may be terminated in the near future. The ventilation rates for the SX-Farm tanks are based on an additive flow through the 3-tank cascades and an estimated 50-ft^3/min flow through each filtered breather riser.

Antoniak and Recknagle (1995) determined that the rate at which a gas species is removed by ventilation is first-order with respect to the concentration, which may be expressed as:

$$C = C_0 \exp\{-v(t - t_0)/V\} \tag{8-1}$$

where:

C is the gas concentration at any time t,
C_0 is the gas concentration at t_0, and
V and v are the headspace volume and ventilation rate, respectively.

That the gas concentration is observed to follow a first-order rate equation implies that the concentration of the gas in the vented air is the headspace average at any given time, and that the mixing rate is high compared to the ventilation rate. Table 8-1 includes the "release half-life," defined here to be the time that it would take for the concentration of a gas species in the headspace to be reduced by a factor of 2. From Equation 8-1, it follows that

$$t_{1/2} = \frac{V}{v}\ln(2) \tag{8-2}$$

Table 8-1. Ventilation Rates of Actively Ventilated Tanks

Tank [(a)]	Type	Ventilation Rate (ft^3/min)	Headspace Volume (ft^3)	Release Half-life (hr)
SX-110	SST	50	162,300	37.5
SX-107	SST	50	156,700	36.2
SX-114	SST	50	146,400	33.8
SX-101*	SST	50	109,700	25.3
C-105	SST	50	96,400	22.3
SX-104*	SST	50	88,600	20.5
SX-108	SST	100	159,000	18.4
SX-111	SST	100	153,900	17.8
SX-112	SST	150	158,300	12.2
SX-102*	SST	100	98,000	11.3
SX-109*	SST	150	138,000	10.6
SX-105*	SST	100	79,300	9.2
SX-106*	SST	150	98,700	7.6
SX-103*	SST	150	83,500	6.4
C-106	SST	350	83,800	2.8

(a) Asterisk Indicates the tank is on the Flammable Gas Watch List

The release half-life allows a qualitative comparison of the headspace/ventilation systems of different tanks. It should be noted that the longer release half-lives are mostly associated with larger tank headspace volumes, which would require greater volumes of flammable gases to reach the LFL. Tanks are shown sorted by descending release half-life in Table 8-1 to highlight this correlation.

8.2.2 Passively Ventilated Tanks

Various phenomena induce the exchange of air between the waste tank headspaces and the atmosphere even when no mechanical exhauster is used. Barometric pressure fluctuations create pressure gradients between the headspaces and the atmosphere; ventilation risers can act as venturis in the wind and draw air out of the risers; and buoyant warm air from the headspaces can move up through ventilation risers or air pathways in pits, to be replaced by cool air via other pathways. The roles that these and other phenomena play in determining the passive ventilation rate of a headspace depend on the local meteorology at any given time, certain physical parameters of the system (e.g., headspace and ventilation system temperatures), as well as, the configuration of the system (i.e., headspace size, ventilation system components, and connections to other tanks). Current understanding of these phenomena and conditions is insufficient to allow tank passive ventilation rates to be reliably predicted *a priori*; however, passive ventilation rate data are available for a few tanks, and provide insight into the likely ventilation rates of others. The data that are available show ventilation rates are generally much higher than the very small barometric breathing rate of 0.45 percent of the headspace volume per day derived from an analysis of barometric pressure variations (Crippen 1993).

Huckaby et al. (1998) used a tracer gas method to measure the passive ventilation rates of 13 tanks. The method involved injecting helium into the headspace and periodically sampling the headspace to determine the helium concentration as a function of time. The ventilation rate between any pair of samples was then determined from the observed helium concentrations using Equation 8-1. 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 8-2. Values listed in Table 8-2 indicate the widely varying ventilation rates observed in different tanks.

Tracer gas was also used to measure ventilation rates during saltwell pumping of tanks S-106 and U-105 (Peurrung and Huckaby 2000). These tanks were equipped with gas chromatographs that measured the helium tracer concentration at approximately 10-min intervals, providing information about the variations in ventilation rate on a much smaller time scale than the grab-sample methods used in previous tracer work. The high precision of the tracer gas measurements (on the order of 1 to 2 percent for most measurements) and relatively rapid changes in tracer concentration (tracer gas concentration could drop by 10 to 20 percent per day) allowed the calculation of ventilation rates for periods as short as several hours. Results indicated no significant diurnal trends; i.e., ventilation rate fluctuations do not appear to be correlated with time of day. Ventilation rate measurements were conducted for a total of about

50 days in tank S-106. The ventilation rate was observed to be about 9.1 ft^3/min, with a standard deviation (based on 50 1-day measurements) of 4.5 ft^3/min. The tracer gas in tank U-105 was monitored for about 101 days, during which the average ventilation rate was calculated to be 3.9 ft^3/min, with a standard deviation (based on 101 1-day measurements) of 1.3 ft^3/min.

Of the tanks that have had ventilation rates measured with a tracer gas, tank C-107 exhibited the lowest average ventilation rate. This was unexpected because it is the hottest passively ventilated tank, and buoyancy forces associated with the headspace-atmosphere temperature difference were expected to result in above average ventilation rates in this tank. The low ventilation rate of this tank is apparently due to its lack of significant leak paths; it has no pump or sluicing pits, few risers from which to leak, and its cascade line connection to tank C-108 may be plugged (Huckaby and Bratzel 1995). Although it has a filtered ventilation riser (as do all SSTs), it may lack a second inlet/outlet and thus lacks the ability to establish continuous in- and out-flows.

The passive ventilation rates of the waste tanks appear to depend most heavily on the number and size of pathways available for air exchange. High ventilation rates were measured in 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. The relatively low ventilation rates measured in S-, TX-, and U-Farms are consistent with the lack of large inter-tank connections (the only 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. The 16-ft^3/min ventilation rate of tank BY-105 was the highest observed average ventilation rate among tanks that do not have large inter-tank connections.

Although local meteorology is thought to have a strong influence on variations in the ventilation rates of the passively ventilated tanks, no definitive correlations between the average ventilation rates measured with tracer studies and data from the Hanford Meteorological Station were established. Furthermore, a yearlong study of tank U-103 indicated only a moderate correlation between measured ventilation rates and seasonal effects (Huckaby et al. 1998). The correlation 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. For lack of evidence to the contrary and in lieu of a more complete data set, the average ventilation rates of individual tanks are assumed to not vary with seasonal changes.

It is expected that in future years the passive ventilation rates will decrease with efforts to decrease fugitive air emissions (e.g., replacement of riser gaskets, sealing pit covers), and as the waste itself cools (i.e., thermal buoyancy forces that enhance ventilation diminish).

Table 8-2. Average Ventilation Rates for Selected Tanks.

Tank [a]	Tracer Gas	Time Period	Average Ventilation Rate, v	
			ft^3/min	m^3/h
A-101*	He	Jul 9 - Jul 15, 1997	10	17
AX-102	He	Aug 28 - Sep 8, 1997	16	28
AX-103*	He	Feb 28 - Mar 3, 1997	25	42
BY-105	He	Apr 17 - May 8, 1997	16	27
C-107	He	Feb 21 - Mar 21, 1997	1.1	1.9
S-102*	He	Sep 24, 1996 - Feb 11, 1997	2.2	3.8
TX-104	He	Jan 14 - Feb 12, 1997	3.5	5.9
U-102	He	Jan 9 - Mar 24, 1998	2.1	3.5
U-103*	SF_6 and He	Feb 27 - Oct 22, 1997	1.7	3.0
U-103*	He	Nov 18, 1997 – Jan 8, 1998	2.3	4.0
U-103*	He	Jan 8 - Mar 24, 1998	$0.9 < v < 6.6$	$1.5 < v < 11$
U-105*	He	Jul 15 - Aug 13, 1997	5.0	8.5
U-106	He	Jan 9 - Mar 24, 1998	1.3	2.2
U-111	He	Jan 9 - Mar 24, 1998	1.9	3.2

(a) Asterisk indicates the tank is on the Flammable Gas Watch List.

8.3 SUMMARY OF HEADSPACE FLAMMABILITY

The dilution of gases released from the waste by mixing within the tanks' headspaces and removal of the gas by forced or natural ventilation prevent hazardous flammable regions from developing in the tank headspace during steady state or following episodic releases. Extensive sampling and monitoring of the Flammable Gas Watch List SSTs for the principal flammable species have demonstrated this. The highest observed concentrations of hydrogen, ammonia, methane, and the total non-methane organic vapors in each of the Flammable Gas Watch List SSTs is listed in Table 8-3, along with the calculated percentage of lower flammability limit (% LFL) in air using LeChatelier's rule (Mahoney et al. 2000). The hydrogen concentrations listed in the table are generally the maximum observed value from years of continuous monitoring (the only exception is the maximum hydrogen concentration in tank A-101, which was measured in a SHMS grab sample before the SHMS monitoring instruments were operational). Many of the other values in the table were obtained from samples collected at essentially random times.

Based on the values listed in Table 8-3, hydrogen is the highest contributor to flammability in each of the Flammable Gas Watch List SSTs. Ammonia is generally the second highest contributor, although the observed ammonia concentrations are so low in several tanks that their

contribution to flammability is lower than that of the near-ambient air levels of methane.[19] The flammability contribution of organic gases and vapors is negligible.

Table 8-3. Maximum Observed Concentrations of Flammable Species

Tank	Hydrogen[(1)]		Ammonia[(2)]		Methane[(3)]		Total Non-methane Organic Vapors[(4)]		Total % of LFL[(5)]
	Max. Conc. (ppmv)	% of LFL	Max. Conc. (ppmv)	% of LFL	Max. Conc. (ppmv)	% of LFL	Max. Conc. (mg/m^3)	% of LFL	
A-101	1,540	3.9	1,400	0.9	14	0.028	26	0.06	4.9
AX-101	540	1.4	42	0.03	3	0.006	1.1	0.003	1.4
AX-103	3,880	9.7	42	0.03	3	0.006	0.52	0.001	9.7
S-102	3,780	9.5	797	0.5	17	0.034	28	0.07	10.1
S-111	1,270	3.2	122	0.08	6	0.012	2	0.005	3.3
S-112	490	1.2	89	0.06	5	0.010	8.2	0.02	1.3
SX-101	400	1.0	3.8	0.003	2	0.004	0.99	0.002	1.0
SX-102	740	1.9	16	0.01	3	0.006	1.2	0.003	1.9
SX-103	640	1.6	1,470	1.0	3	0.006	0.78	0.002	2.6
SX-104	580	1.5	25	0.02	11	0.022	1.2	0.003	1.5
SX-105	710	1.8	28	0.02	4	0.008	2	0.005	1.8
SX-106	560	1.4	179	0.12	9	0.018	2.3	0.005	1.5
SX-109	890	2.2	17	0.01	2	0.004	0.82	0.002	2.2
T-110	500	1.3	108	0.07	5	0.010	1.1	0.003	1.3
U-103	4,870	12	730	0.5	22	0.044	11	0.03	12.7
U-105	3,680	9.2	5,200	3.5	60	0.12	3.1	0.007	12.8
U-107	1,900	4.8	453	0.3	17	0.034	16	0.04	5.1
U-108	3,280	8.2	692	0.5	20	0.040	12	0.03	8.7
U-109	4,930	12	577	0.4	14	0.028	9.2	0.02	12.8

Notes:

(1) Hydrogen LFL = 40,000 ppmv. Tank A-101 result is from SHMS grab sample (McCain 2000), all other hydrogen results are from SHMS monitoring instrumentation (see Table 5-5).

(2) Ammonia LFL = 150,000 ppmv. Tanks A-101, SX-103, and U-105 results are from SHMS monitoring instrumentation (see Table 5-5), all other ammonia results are from sorbent trap vapor samples (see Table 5-9).

(3) Methane LFL = 50,000 ppmv. All methane results are from SHMS grab samples (McCain 2000).

(4) Total non-methane organic vapor LFL = 42,000 mg/m^3 (the LFL of propane). All organic vapor results are from sorbent trap or SUMMA canister vapor samples (see Table 5-9).

(5) Total % of LFL is sum of individual component % of LFL, by Le Chatelier's law. **Note:** The total may be based on individual gas concentrations measured on different dates.

[19] Methane is present in ambient air (from natural sources) at about 2 ppmv.

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9.0 OVERALL SUMMARY AND CONCLUSIONS

The configurations of the wastes in the nineteen SSTs on the Flammable Gas Watch List are undergoing change as liquid is removed by saltwell pumping. These tanks, which have a rather wide variety of waste, have been monitored before, during, and after saltwell pumping operations. The results from measurements of headspace hydrogen concentrations, waste temperatures, levels, and liquid content coupled with data about the chemical compositions of the wastes, the volumes and compositions of the gas retained in the waste prior to saltwell pumping, and physical models describing hydrogen generation and the gas retention and release mechanisms provide a reasonable basis from which conclusions can be drawn.

The waste configuration in each of these tanks was stable, prior to saltwell pumping. The wastes were cooling slowly, except in tanks whose temperatures were already near ambient. The waste levels are nearly constant, and the configuration and dimensions of waste layering was not changing.

Saltwell pumping is causing major changes to the waste configuration, decreasing the amount of liquid and lowering the interstitial liquid level. Neutron logs indicate that liquid remaining in the unsaturated zone after pumping drains slowly leaving a considerable volume of interstitial liquid above the final ILL for several years. Saltwell pumping can lead to subsidence of the waste creating a pronounced surface concavity as has occurred in tank S-112, which was pumped over twenty years ago. Such a subsidence may be accompanied by a gas release. However, SHMS data for periods after saltwell pumping have not shown any significant gas releases.

The data from the RGS, BPE calculations, and integration of the neutron logs show that 50 to 400 cubic meters of gas was retained in each of the nineteen tanks prior to pumping. Ten of the tanks had more than 200 cubic meters. The RGS data indicate the gas retained in the solid-liquid matrix contains up to 70-vol% hydrogen. Most of the tanks contain enough gas to exceed the LFL, if all of it were promptly released into the headspace. However, only a sudden, violent disturbance to the entire waste volume would cause such a release.

Spontaneous and induced gas releases have been monitored before, during, and after saltwell pumping. The volumes of gas released in spontaneous events from the tanks on the Flammable Gas Watch List have been less than 3 cubic meters and the maximum headspace hydrogen concentration was 2,190 ppm (only 5.5% of the LFL of 40,000 ppm). These gas releases are slow; several hours to several days are required. These results are compatible with models that have been developed to describe the physical factors governing gas bubble retention and release.

Retained gas is also released from the waste during saltwell pumping as liquid is withdrawn. Gas releases approximately correlate with the pumping rate with about a day lag. The individual releases resulting from saltwell pumping have been only slightly larger than spontaneous releases. The maximum hydrogen concentration recorded during saltwell pumping was 7,200 ppm (18% of the LFL). Calculations performed for one tank indicate that 25 to 50% of the retained gas inventory may be released during saltwell pumping.

The model for the hydrogen generation rate indicates that removal of interstitial and supernatant liquid from the waste will decrease the rate of hydrogen generation in SSTs on the Flammable Gas Watch List by 10 to 25%. A much larger decrease can be expected in tanks A-101 and AX-101 because they contain a much higher volume of drainable liquid.

Although 25 to 50% of the retained gas is released during saltwell pumping and the gas generation rate decreases as a result of liquid removal, sufficient gas may still be retained in some tanks after pumping that, if all of it were promptly released into the headspace, the LFL would be exceeded. Like the unpumped tanks, however, only a hypothetical violent, tank-wide waste disturbance could cause such a large release.

In conclusion, the work during the past ten years has provided a realistic understanding of the factors governing the generation, retention, and release of gas in SST wastes. Monitoring and study of the behavior of these wastes indicate that they contain significant volumes of gas with a high concentration of hydrogen. However, spontaneous and induced releases of this gas have been sufficiently small and slow that passive ventilation has mitigated the hazard. No new, unforeseen hazards have been identified. Overall, the SSTs on the Flammable Gas Watch List do not present an unmanageable hazard.

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APPENDIX A

INFORMATION ON TANKS 241-S-103 AND 241-S-106

Figure A-1. Tank 241-S-103 Sample and Monitoring Risers A-4

Figure A-2. Tank 241-S-103 Saltwell Pumping History A-5

Figure A-3. Tank 241-S-103 Waste Level and Interstitial Liquid Level History A-5

Figure A-4. Tank 241-S-103 Neutron Logs A-6

Figure A-5. Tank 241-S-103 Waste Temperature History A-7

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Figure A-8. Tank 241-S-106 Waste Level and Interstitial Liquid Level History A-10

Figure A-9. Tank 241-S-106 Neutron Logs A-10

Figure A-10. Tank 241-S-106 Density Profile A-11

Figure A-11. Tank 241-S-106 Waste Temperature History A-11

APPENDIX A

INFORMATION ON TANKS 241-S-103 AND 241-S-106

Tanks S-103 and S-106 are not on the Flammable Gas Watch List but share many of the characteristics of those that are. Various aspects of these two tanks are discussed in several sections of the report, and it is useful to have the same kind of background information provided for the other tanks. These data are given in this appendix to avoid confusion with those on the watch list.

Both of these tanks were included in an evaluation that was performed in 1996 (*Evaluation of Recommendation for Addition of Tanks to the Flammable Gas Watch List*, WHC-SD-WM-ER-594, Rev. 0), and it was concluded that no additional tanks should be added to the Watch List at that time. The main reasons for this conclusion that pertained to tanks S-103 and S-106 were: (1) the data were highly variable and lack the precision and accuracy necessary to make estimates of retained gas, and (2) the physical mechanism responsible for a large spontaneous release of gas was not supported by data or conceptual physical models.

Each tank is covered in its own section: Tank S-103 in A.1 and Tank S-106 in A.2. Each section covers the tank history, installed instrumentation, and waste configuration data.

A.1 TANK 241-S-103 DESCRIPTION

Tank S-103 was constructed between 1950 and 1951, and is located in the 200 West area. The tank has a design capacity of 2,869 kL (758 kgal), and is the third tank in a cascade series of three tanks including tanks S-101 and S-102. The tank entered service in the fourth quarter of 1953. It received Reduction Oxidation (REDOX) process waste (R1) from the fourth quarter of 1953 until the fourth quarter of 1973. REDOX waste was the high-level component of the process waste. From the fourth quarter of 1973 until the second quarter of 1976, the tank received bottoms and recycle streams from the 242-S-Evaporator/Crystallizer. In the fourth quarter of 1976, the tank was used as a low-heat evaporator dump tank containing evaporator feed waste. Between the second quarter of 1978 and the fourth quarter of 1980, tank S-103 was classified as having non-complexed, partial neutralized feed, and double-shell slurry feed wastes. The tank was declared inactive in 1980, and was partial isolated in December 1982. The tank was saltwell pumped in 1999 and was declared interim stabilized on April 18, 2000.

Tank S-103 presently contains 897 kL (237 kgal) of double-shell slurry feed. Waste volume calculations show 170 kL (45 kgal) of drainable interstitial liquid remaining in the tank of which approximately 148 kL (39 kgal) is estimated to be pumpable.

A.1.1 Tank 241-S-103 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure A-1. Currently, the waste level is measured by an ENRAF™ buoyancy gauge system located in riser 3, which was installed in May 1994. Vertical temperature measurements are taken from a single thermocouple tree mounted in Riser 4, which is monitored and recorded through the TMACS system. Riser 2 accommodates a liquid observation well. Tank S-103 does not have headspace gas monitoring equipment. In September 1998, liquid grab samples were taken from Riser 5, which now contains a saltwell screen and pump.

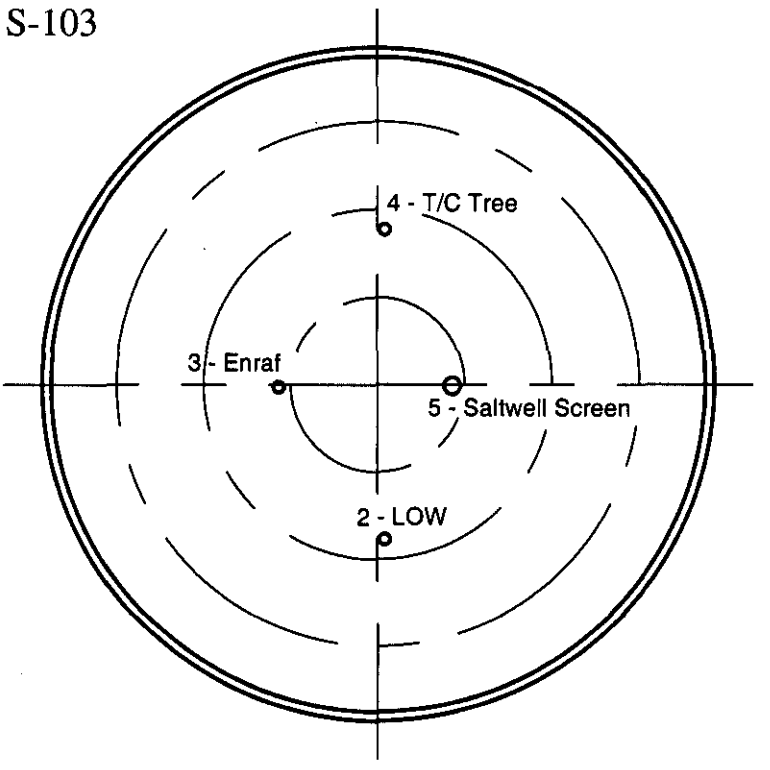

Figure A-1. Tank 241-S-103 Sample and Monitoring Risers

A.1.2 Tank 241-S-103 Waste Configuration

The waste in tank S-103 is classified as double-shell slurry feed, as is tank S-102. The waste level is currently 94 inches, and the ILL is just over 92 inches. The tank was saltwell pumped between June 4, 1999, and January 4, 2000, during which 28 kgal out of an initially estimated 52 kgal of drainable liquid were removed. The saltwell pumping history in tank S-103 is summarized in Figure A-2. The retained gas volume fraction prior to pumping was 0.12 based on the neutron logs and 0.14 via the BPE method.

The waste levels and neutron logs for tank S-103 are shown in Figures A-3 and A-4, respectively. Prior to pumping, the level was rising at less than 1/2 inch per year while the ILL was constant. During pumping, the ILL dropped about 13 inches while the surface level dropped 12 inches. The neutron logs show that most of the liquid was removed from the upper 15 inches of the waste column. However, the region below about 85 inches did not change significantly.

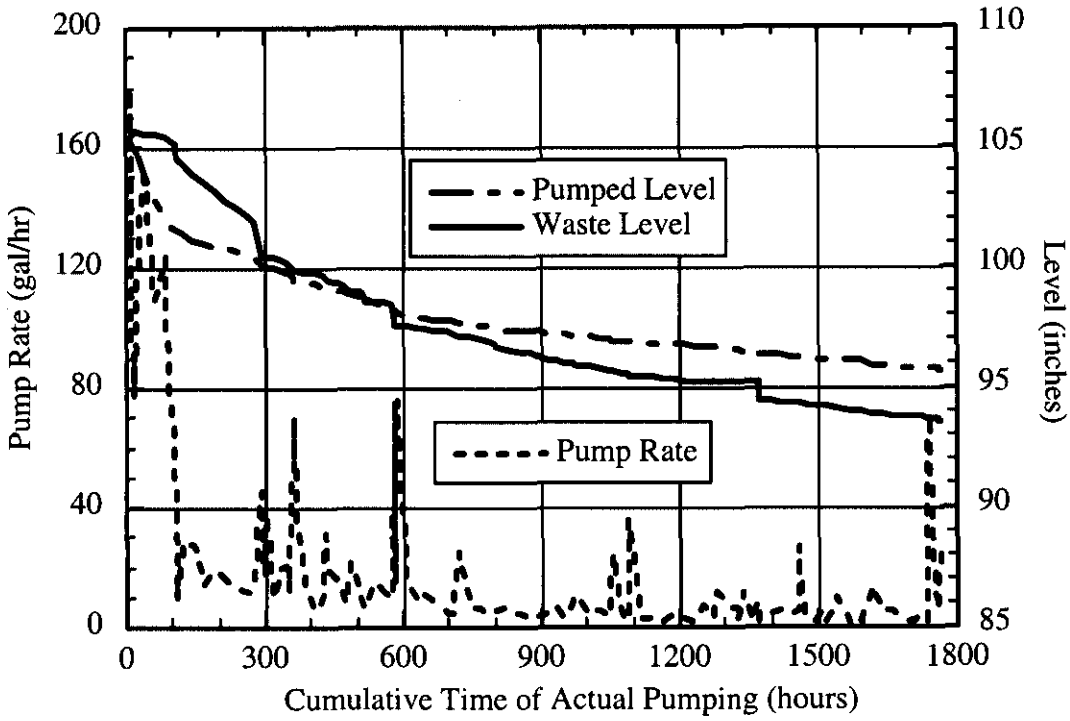

Figure A-2. Tank 241-S-103 Saltwell Pumping History

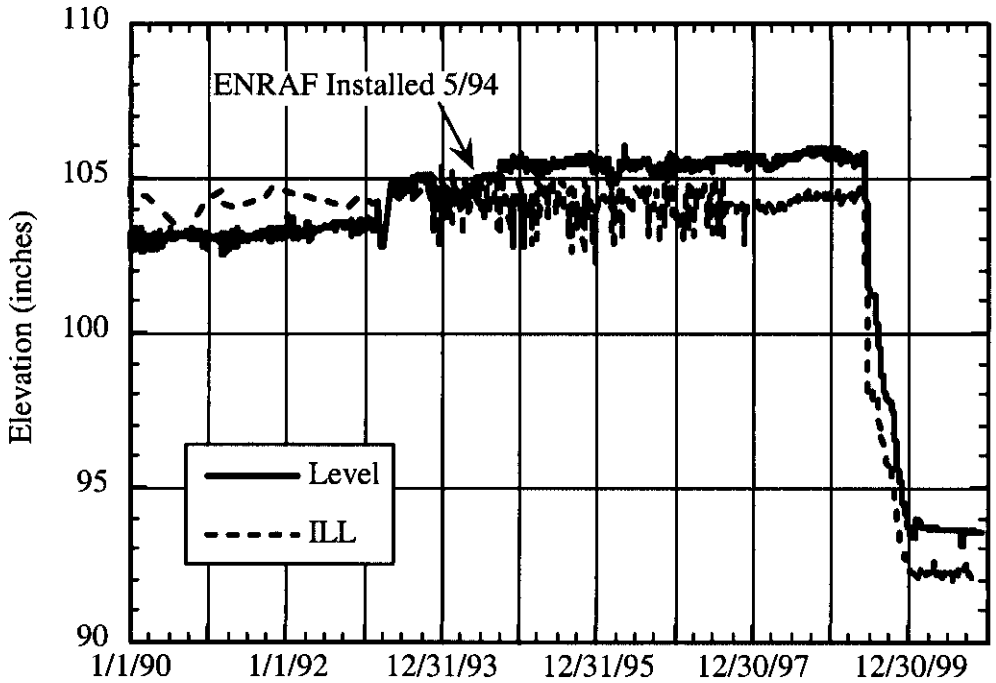

Figure A-3. Tank 241-S-103 Waste Level and Interstitial Liquid Level History

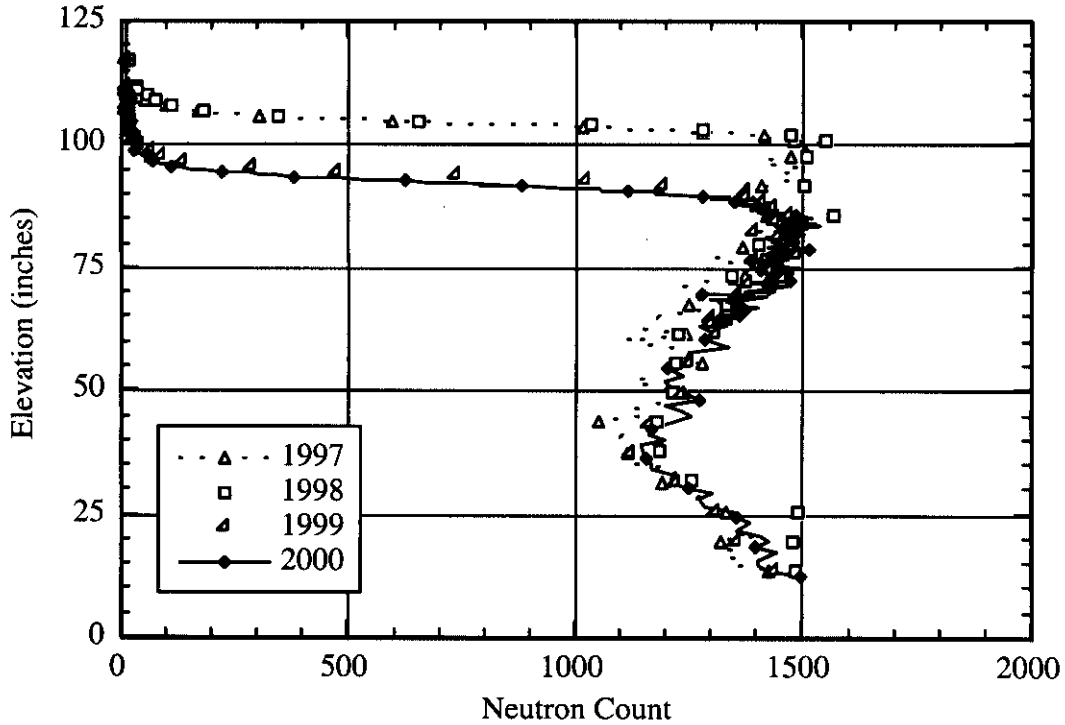

Figure A-4. Tank 241-S-103 Neutron Logs

The waste temperature history given in Figure A-5 shows that the waste temperature was approximately constant prior to pumping with an annual cycle of 2 to 5 °F. Pumping had no dramatic effect on temperatures. The waste temperatures range from 94 to 100 °F.

A.2 TANK 241-S-106 DESCRIPTION

Tank S-106, constructed during 1950 and 1951, is third in a cascade series of three tanks beginning with tanks S-104 and S-105, each tank set one foot lower in elevation from the preceding tank. This tank was filled with waste from the reduction-oxidation (REDOX) facility from the second quarter of 1953 until the third quarter of 1953. The tank received REDOX cladding waste (CWR) in 1955, and evaporator bottoms from the 242-S Evaporator via tank S-102 from 1973 to 1975. The tank was removed from service in 1976 and was partially isolated in 1982. A liquid observation well was installed in December 1980, and a jet pump was installed in 1983. From 1983 to 1984, 378 kL (99.8 kgal) of liquid was pumped from the tank. Tank S-106 has an operating capacity of 2,870 kL (758 kgal) and presently contains an estimated 1,813 kL (479 kgal) of non-complexed waste. The tank is not on the Watch List.

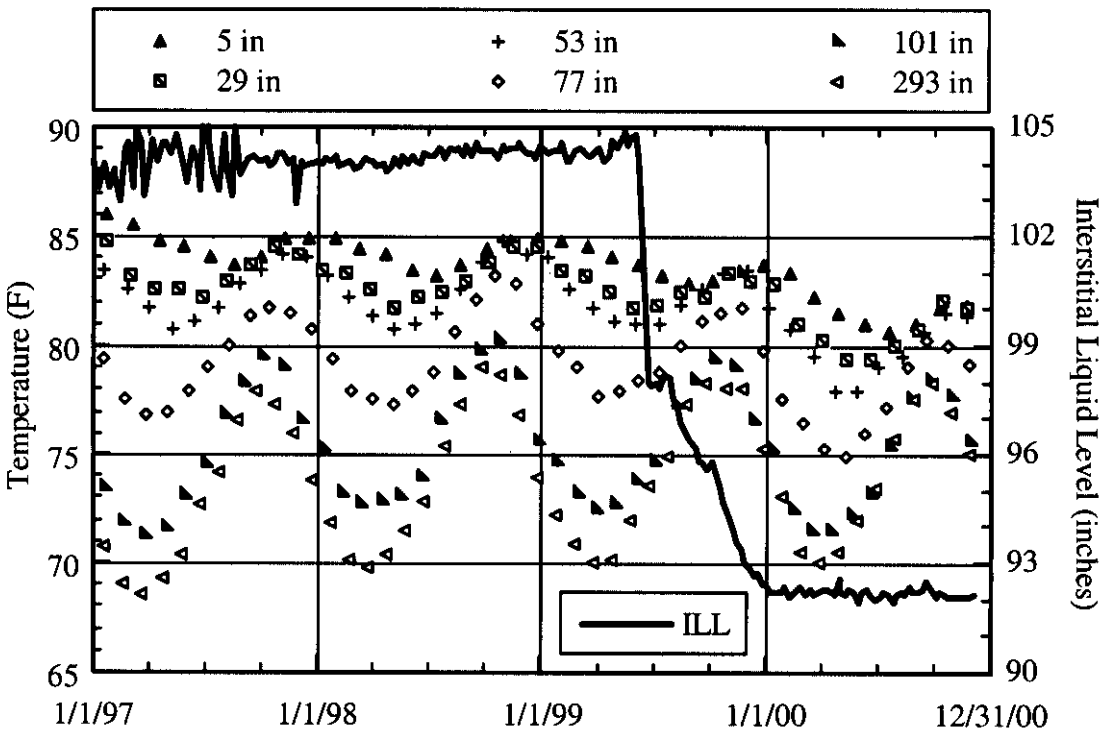

Figure A-5. Tank 241-S-103 Waste Temperature History

A.2.1 Tank 241-S-106 Monitoring and Sampling

The placement of major in-tank instrumentation is shown in Figure A-6. The waste surface level was measured by a manual tape until June 1981 and by a Food Instrument Corporation (FIC) gauge until June 1994 when the current ENRAF™ buoyancy gauge system was installed in Riser 3. Vertical temperature measurements are taken from a single thermocouple tree in Riser 2, with 14 thermocouples, which are monitored and recorded through the TMACS system. Riser 4 accommodates a liquid observation well, and Riser 5 contains a saltwell screen and pump.

Push core sample and RGS measurements were obtained from Risers 7 and 8 in February and March 1997. A SHMS E+ gas monitoring system was installed March 1998.

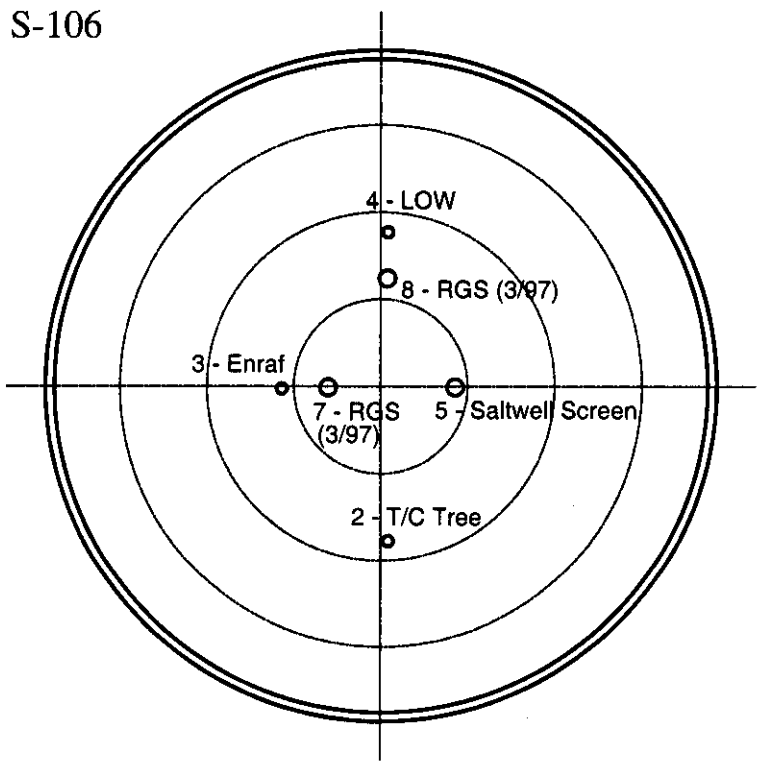

Figure A-6 Tank 241-S-106 Sample and Monitoring Risers

A.2.2 Tank 241-S-106 Waste Configuration

Tank S-106 waste is saltcake classified as non-complexed, like tanks S-111 and S-112. Saltwell pumping began April 16, 1999, and ended January 6, 2000. The tank is currently being evaluated for interim stabilization. Pumping removed 109 kgal of liquid, which is considerably

more than the initial estimate of 76 kgal of drainable liquid. The saltwell pumping history in tank S-106 is summarized in Figure A-7. The retained gas volume fraction based on RGS measurements prior to pumping was 0.10. The BPE method indicated a gas fraction of 0.23 while the neutron logs imply 0.14.

The waste levels and neutron logs for tank S-106 are shown in Figures A-8 and A-9, respectively. Prior to pumping, the waste level was rising by about 1 inch per year, which represents an accumulated gas volume fraction of about 0.10, consistent with RGS measurements above. This level rise rate is higher than any of the Watch List tanks. During pumping, the ILL dropped to 159 inches, but recovered 17 inches to its current level after about a year liquid in the unsaturated region continued to drain slowly. Saltwell pumping released one-third to one-half of the stored gas in the tank. The neutron logs show the result of a very successful saltwell pumping campaign. A significant fraction of the liquid was removed from the entire waste column above about 30 inches. The waste density profile is shown in Figure A-10 along with the 1997 neutron profile. The low densities above the 100-inch level indicate a high liquid content.

The waste temperature history is given in Figure A-11. Tank S-106 is a relatively cool tank with a peak temperature of about 76 °F. The temperatures were essentially constant prior to pumping, ranging from 70 to 80 °F with an annual cycle of 1 to 6 °F. The temperatures have decreased about 4 °F since saltwell pumping with approximately the same annual cycle amplitude.

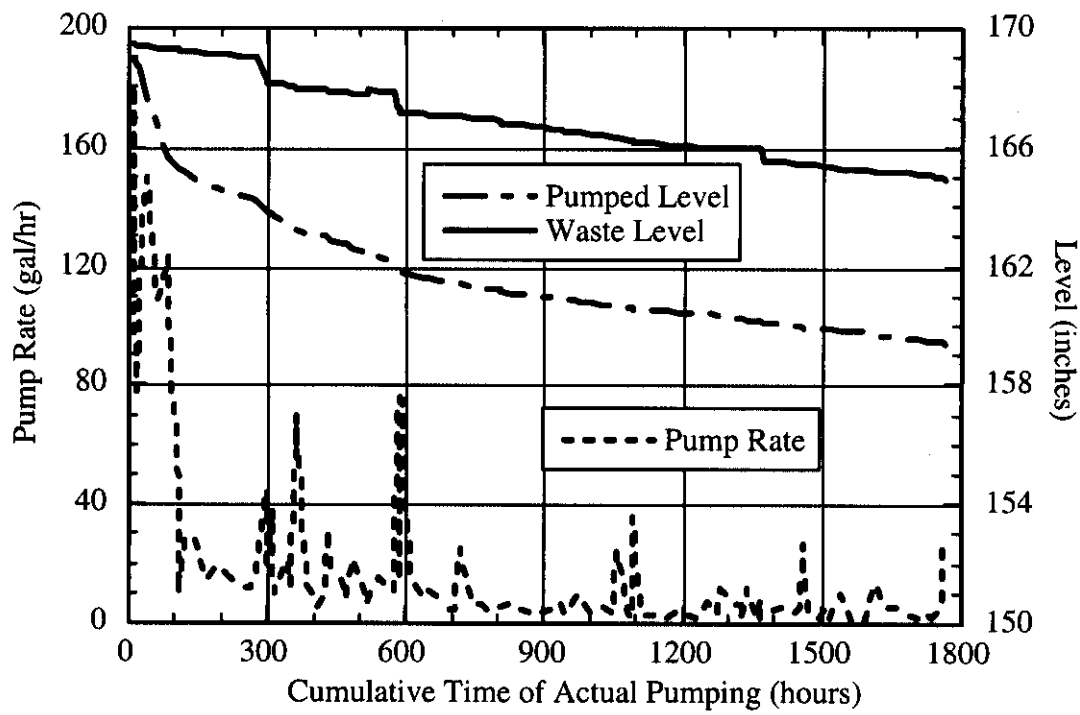

Figure A-7. Tank 241-S-106 Saltwell Pumping History

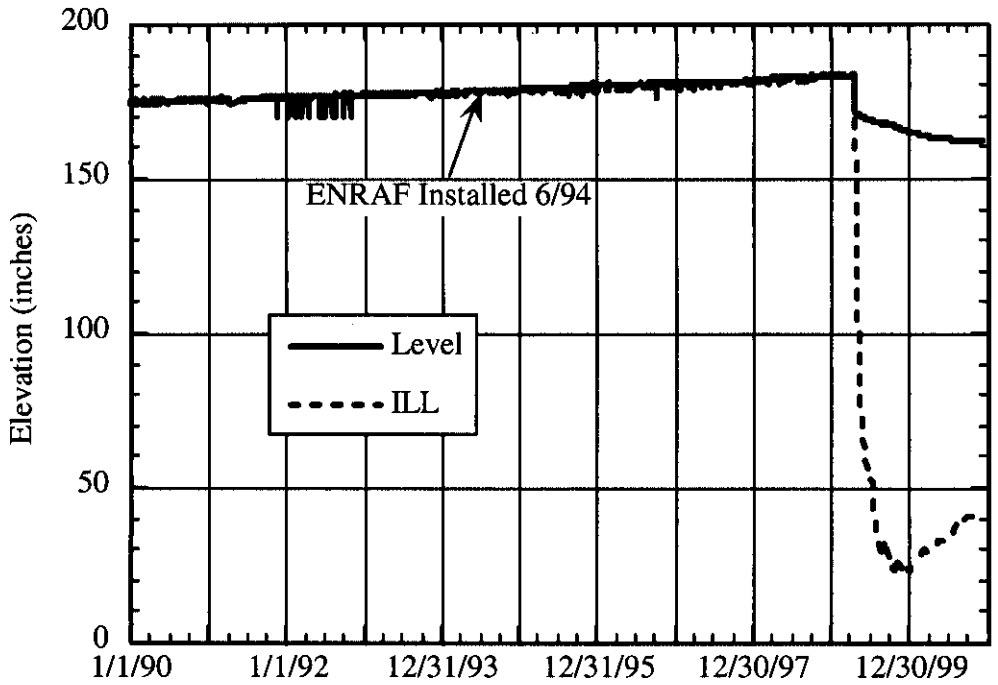

Figure A-8. Tank 241-S-106 Waste Level and Interstitial Liquid Level History

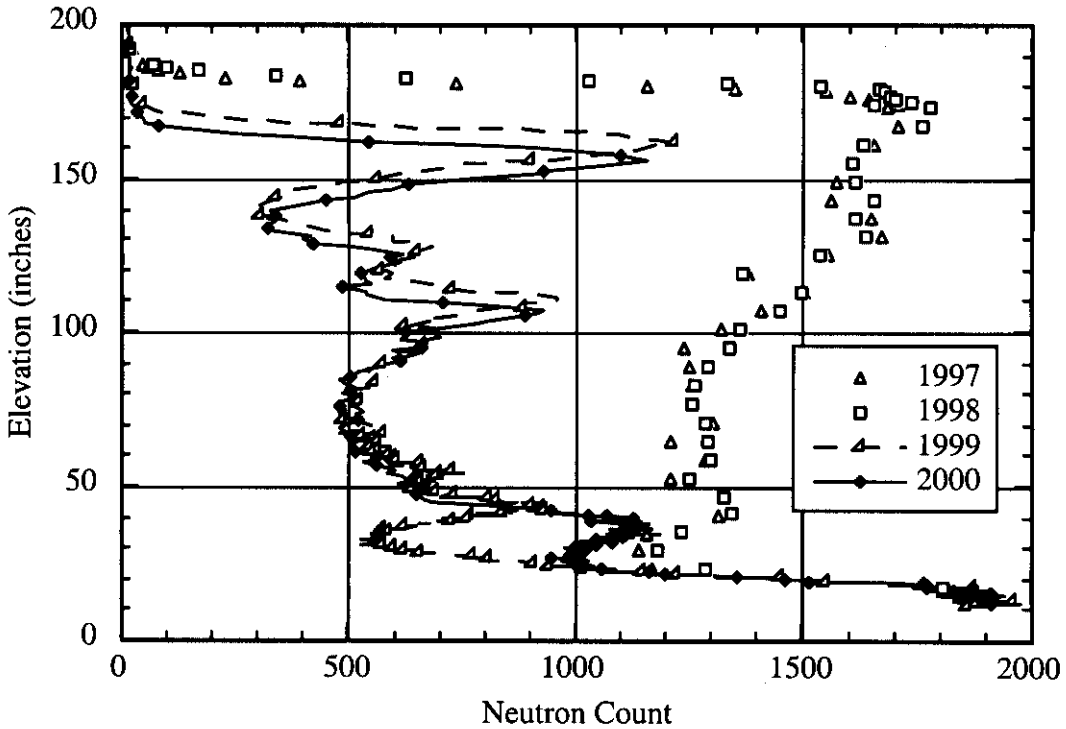

Figure A-9. Tank 241-S-106 Neutron Logs

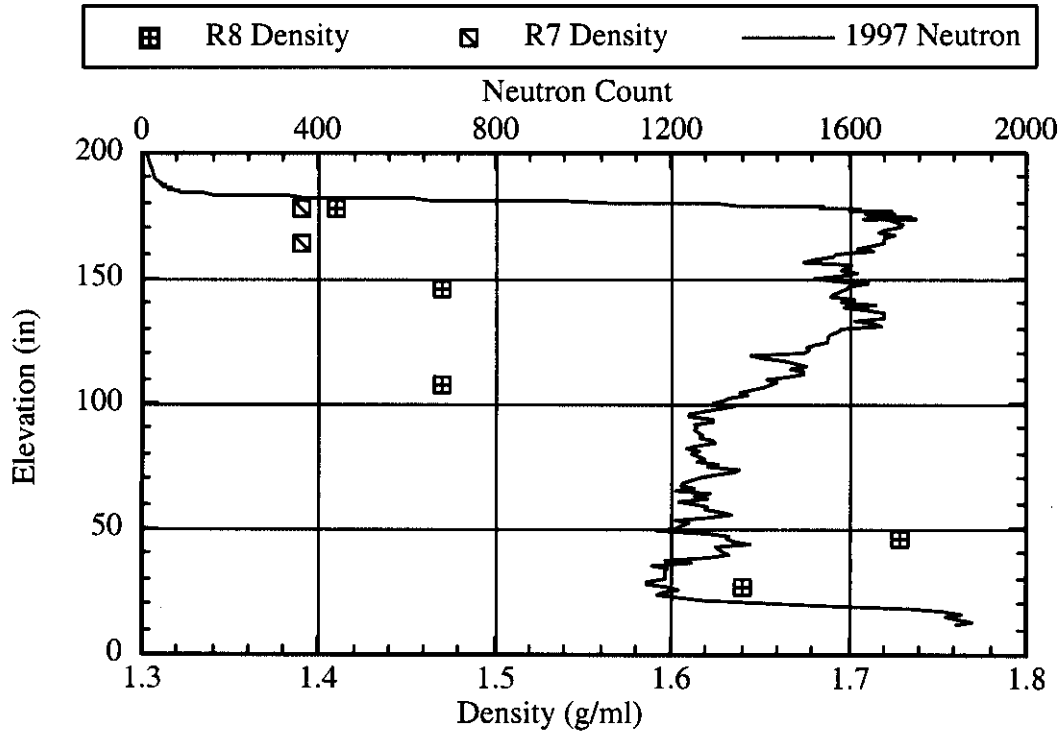

Figure A-10. Tank 241-S-106 Density Profile

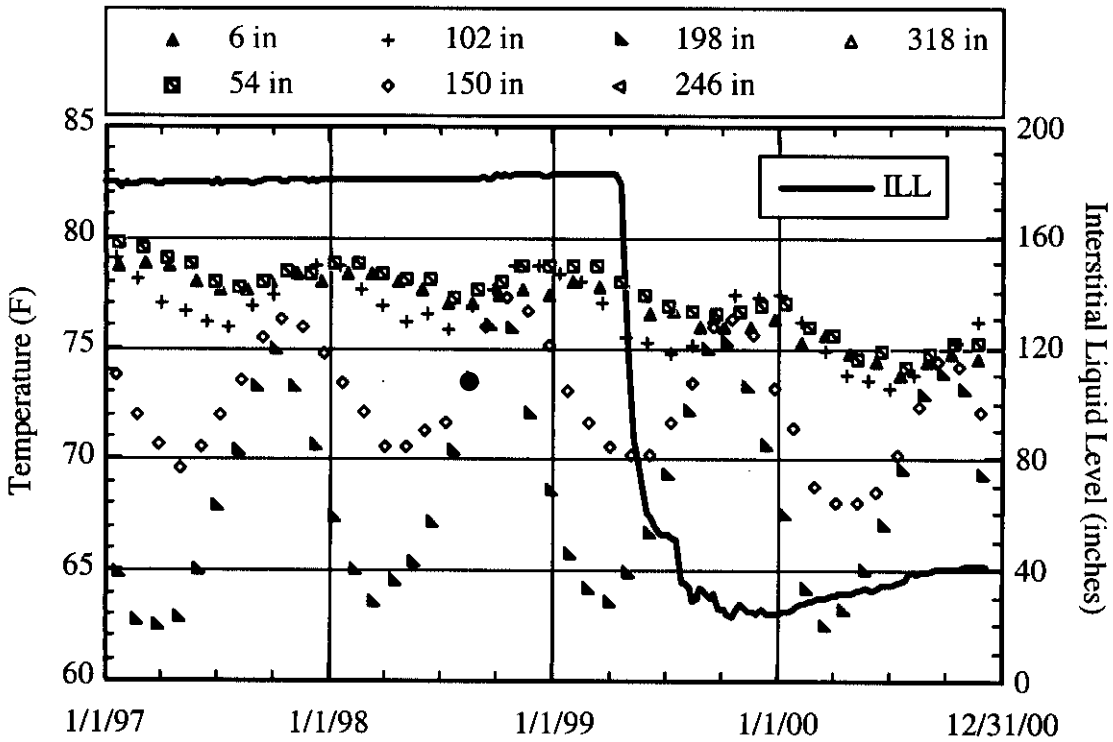

Figure A-11. Tank 241-S-106 Waste Temperature History

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