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Evaluation of Hanford High-Level Waste Tank 241-SY-101

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EVALUATION OF HANFORD HIGH-LEVEL WASTE TANK 241-SY-101

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LIST OF TERMS

atm	atmosphere
BD-GRE	buoyant displacement gas release event
CHG	CH2M HILL Hanford Group, Inc.
cfm	cubic feet per minute
dL/dP	change in level versus change in pressure
DOE	U.S. Department of Energy
DOE-ORP	U.S. Department of Energy, Office of River Protection
DOE-RL	U.S. Department of Energy, Richland Operations Office
DSS	double-shell slurry
DST	double-shell tank
EDS	energy-dispersive x-ray spectroscopy
FIC	Food Instrument Corporation
ft	feet
ft^2	square feet
ft^3	cubic feet
ft^3/min	cubic feet per minute
gal	gallons
g	gram(s)
g/mL	grams per milliliter
GRE	gas release event
HEDTA	N-(hydroxyethyl)-ethylenediaminetriacetic acid
HGR	hydrogen generation rate
HLW	high-level waste
in.	inch(es)
J/mole/K	Joule per mole degrees Kelvin
kg	kilogram
kg/m^3	kilograms per cubic meters
kgal	kilogallons
kJ/mole	KiloJoule per mole
kPa	kiloPascals
LANL	Los Alamos National Laboratory
LFL	lower flammability limit
m	meter(s)
m^3	cubic meters
m^3/kg-min	cubic meters per kilogram per minute
mil/yr	mil (0.001 inch) per year
MIT	multifunction instrument tree
mol/m^3-d	mol per cubic meter per day
mole/kg-day	moles per kilogram per day
molecule/100 eV	molecules per 100 electron volts
moles/L	moles per liter
mols	moles
Pa	Pascal

PLM	polarized light microscopy
PNL	Pacific Northwest Laboratory (prior to 1996)
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
psig	pounds per square inch (gauge)
RGS	retained gas sampler
rpm	revolutions per minute
scf	standard cubic feet
scfd	standard cubic feet per day
SEM/EDS	scanning electron microscopy with energy-dispersive x-ray spectroscopy
SpG	specific gravity
SST	single-shell tank
TOC	total organic carbon
VFI	void fraction instrument
vol%	volume percent
USQ	unreviewed safety question
Watt/kg	watts per kilogram
WHC	Westinghouse Hanford Company
wt%	weight percent
%	percent
°C	degrees Celsius
°F	degrees Fahrenheit
K	Kelvin
µg/g	micrograms per gram
µg/mL	micrograms per milliliter
µCi/g	microcuries per gram
µCi/mL	microcuries per milliliter

EVALUATION OF HANFORD HIGH-LEVEL WASTE TANK 241-SY-101

1.0 INTRODUCTION

Between 1977 and 1980, tank 241-SY-101 was filled with waste that was the most concentrated material produced by the evaporators. Subsequent waste additions included concentrated complexant waste containing significant organic complexant concentrations. The waste in 241-SY-101 was observed to generate a flammable mixture of gases, retain the gas mixture within the waste, and spontaneously release large volumes of the gas mixture in what are understood to be buoyant displacement gas release events (BD-GREs). While periodic in nature, the amount and timing of waste gas releases could neither be accurately predicted nor controlled. Three of the largest BD-GREs resulted in the tank domespace exceeding the lower flammability limit (LFL).

In 1990, this behavior was declared an Unreviewed Safety Question (USQ). In order to control waste gas release behavior and reduce the flammability hazard, a mixer pump was installed in 1993. Routine pump operations prevented the buildup and release of large volumes of flammable gas. An unanticipated consequence of mixer pump operations and mitigation of the large gas releases was an excessive growth of a gas-retaining crust on the waste surface. The waste surface change (level rise) caused by accumulation of gas and solids within this crust resulted in declaration of a USQ in 1998. This USQ was revised in 1999 to reflect the results of waste characterization and analysis performed to understand level growth and potential hazards (French 1999).

Between December 18, 1999, and March 15, 2000, a series of waste transfers and water dilution of the remaining 241-SY-101 waste dissolved most of the soluble sodium salts, significantly improving the waste characteristics. The gas generation rate has been reduced by a factor of seven from the pre-dilution value, and none of the numerous instruments now monitoring the 241-SY-101 waste show evidence of significant gas retention. Additionally, waste dilution has eliminated the thick crust. Only a thin layer of floating waste material that poses no hazard remains.

This document summarizes the technical basis to show that tank 241-SY-101 waste characteristics do not now meet the criteria for inclusion on the Flammable Gas Watch List and are similar to other Hanford double-shell tanks (DSTs) that do not exhibit spontaneous GREs. This technical basis supports closure of the surface level rise USQ and resolution of the Flammable Gas Safety Issue for tank 241-SY-101. The information in this report also provides the basis to remove the tank from the Flammable Gas Watch List.

A summary is provided on the understanding of the processes for gas generation, retention, and release. Efforts to mitigate the GREs associated with tank 241-SY-101 and the surface level rise issue are discussed. An overview is provided of the work done to return this tank to normal service. The report closes with the recommendations for closure of the safety issue and removal of the tank from the Watch List.

2.0 THE FLAMMABLE GAS SAFETY ISSUE

All radioactive waste in the Hanford Tank Farms underground storage tanks slowly generates flammable gas: hydrogen, nitrous oxide, ammonia, nitrogen, and traces of methane and other hydrocarbons. The gas is generated by a series of complex chemical reactions involving the thermal and radiological decomposition of organic compounds, radiolysis of water, and corrosion reactions with the metal tank wall. The rate due to water radiolysis can be estimated from the radiation dose, while the chemical reaction and corrosion path requires more knowledge of the waste conditions. The generation rate is so low that tank ventilation is able to keep the flammable gas far below the concentration necessary for ignition. Thus, flammable gas generation alone is not a safety issue in any tank in which the flammable gas is continuously released to the tank domespace and ventilation is maintained.

However, many tanks may contain enough retained gas in the waste to cause worker injury or damage to equipment if a significant fraction of it were suddenly released into the domespace and ignited. Gas releases may be spontaneous or induced by external forces (e.g., earthquakes, saltwell pumping, barometric pressure changes) or by waste intrusion (e.g., core sampling, equipment installation). The potential for such releases and their undesirable consequences constitutes the Flammable Gas Safety Issue. In May 1990, the U.S. Department of Energy, Richland Operation Office (DOE-RL) determined that hydrogen and nitrous oxide buildup in certain waste tanks constituted a USQ (Lawrence 1990). The USQ was applied to tank 241-SY-101 and 22 other tanks at that time. The same tanks defined by the USQ were also included in the Flammable Gas Watch List.

The U.S. Department of Energy (DOE) established a High-Level Waste Tank Working Group to evaluate safety issues at various sites in the United States. Their report (DOE-HQ 1992) provided a definition of a safety issue that provides additional insight. They defined a safety issue as:

> An event or condition that can lead to either:
>
> (1) an uncontrolled release of radionuclides, or exposure to radiation, resulting from operations of the DOE high-level waste storage tank farms that is not (a) within the approved safety envelope (i.e., a USQ), or (b) properly analyzed or mitigated;
>
> (2) or, a loss of primary or secondary containment for high-level radioactive waste.

Figure 2-1 provides a logic diagram of this definition of a safety issue. Resolution would occur when it is shown that the conditions listed on the right side of the figure do not exist.

The approach for resolution of the safety issue centers on the following items:

- Develop an understanding of the processes for gas generation, retention, and release (see Section 4.0)
- Collect data to develop an understanding of the behavior of the waste (see Sections 5.3 to 5.5)
- Assess the potential hazards posed by the presence of flammable gas and potential ignition sources and implement the appropriate controls (see Sections 6.0 and 7.0)
- Develop and implement appropriate means to monitor the tank and mitigate the accumulation and release of unacceptable quantities of flammable gas and the potential ignition sources (see Sections 3.4, 6.0, 7.0, and 8.0)
- Update approved safety envelope (see Section 9.0)
- Close any open USQs (see Sections 6.0 and 9.0).

Completion of these items will constitute resolution of the Flammable Gas Safety Issue.

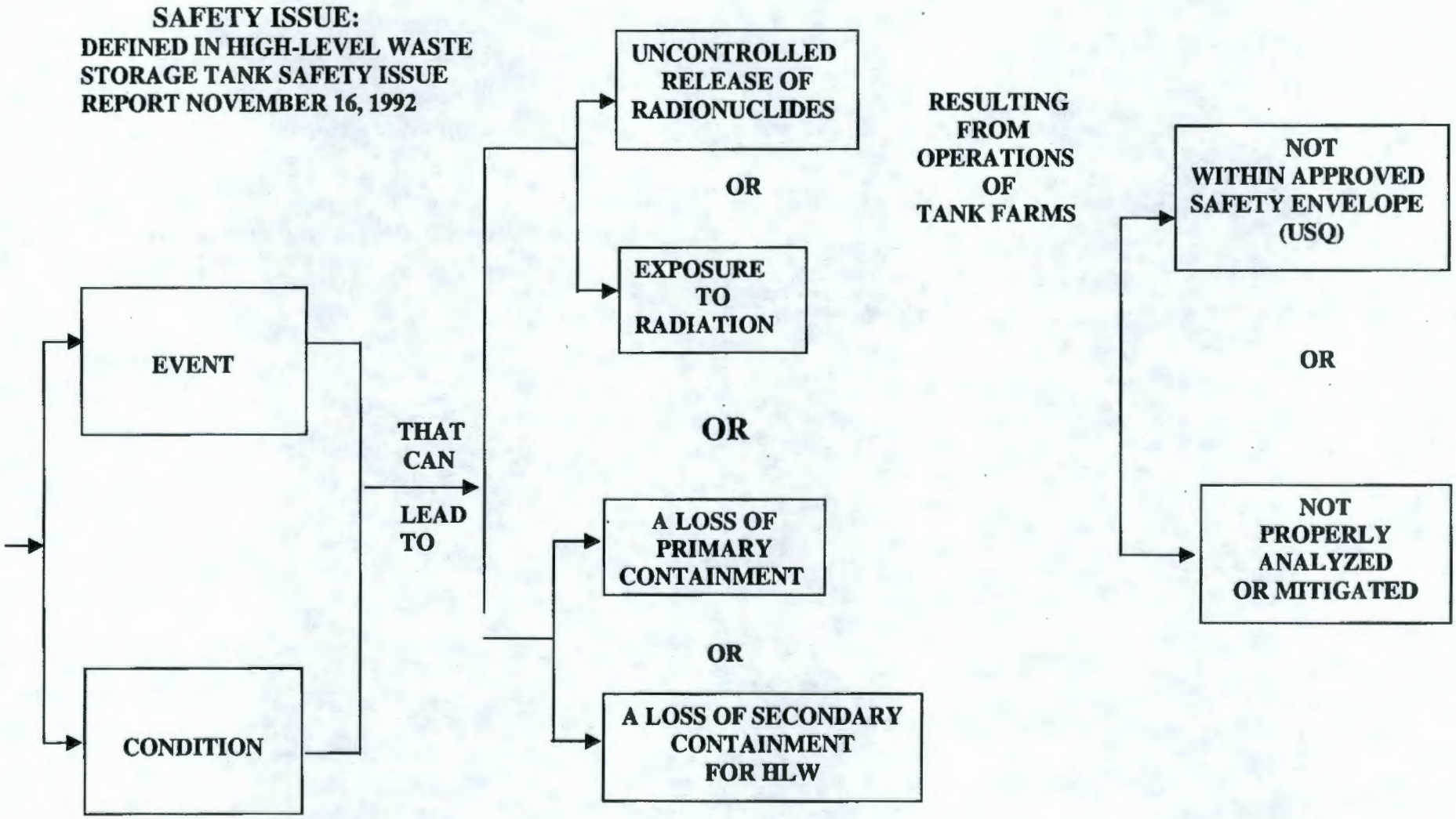

Figure 2-1. Safety Issue Logic Diagram

3.0 THE FLAMMABLE GAS WATCH LIST

3.1 PUBLIC LAW 101-510, SECTION 3137

In November 1990, Public Law 101-510 was passed. Section 3137 (text provided in Appendix A), also referred to as the Wyden Amendment, was part of this law. This section required the Secretary of Energy to identify within 90 days which high-level nuclear waste tanks may have a "serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure." The process by which the tanks were identified was described by Harmon (1991).

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

3.2 REASON FOR ADDING TANK 241-SY-101 TO THE WATCH LIST

The volume of waste in tank 241-SY-101 was first noticed to expand in 1977 when the first double-shell slurry was put into the tank; this phenomenon was called slurry growth. After the last addition to the tank, the waste continued to grow and then dropped several inches during a GRE. Figure 3-1 shows the cyclic behavior of the waste surface over the period of 1988 to 1991. Each of the drops in level was associated with the rapid release of gas to the tank domespace. In some cases the tank domespace was pressure was slightly positive for a short time.

The temperature profile within the waste changed during the events as shown in Figure 3-2. Before the event, the profile showed a higher temperature in the lower part of the tank with essentially a constant temperature in the upper region. The upper region has been called the convective layer as its temperature profile indicates that the heat generated is being transported via a convective process. The lower region was termed the nonconvective layer. A parabolic temperature profile is indicative of heat transport by conduction; it does not indicate whether gas is trapped within the waste. However, in the case of tank 241-SY-101, a significant amount of gas was being retained in this layer. During a GRE, the material from the nonconvective layer is transported to the convective layer. The temperature profile just after an event is also shown in Figure 3-2. The temperature profiles indicate that during a GRE, the material from the lower region was transported to the upper region.

Therefore, this behavior of tank 241-SY-101, the rapid GREs, slight pressurization of the domespace, and the nature of the gas (hydrogen and nitrous oxide) led to the declaration of a USQ and contributed to the passage of Public Law 101-510 (Section 3137) in 1990.

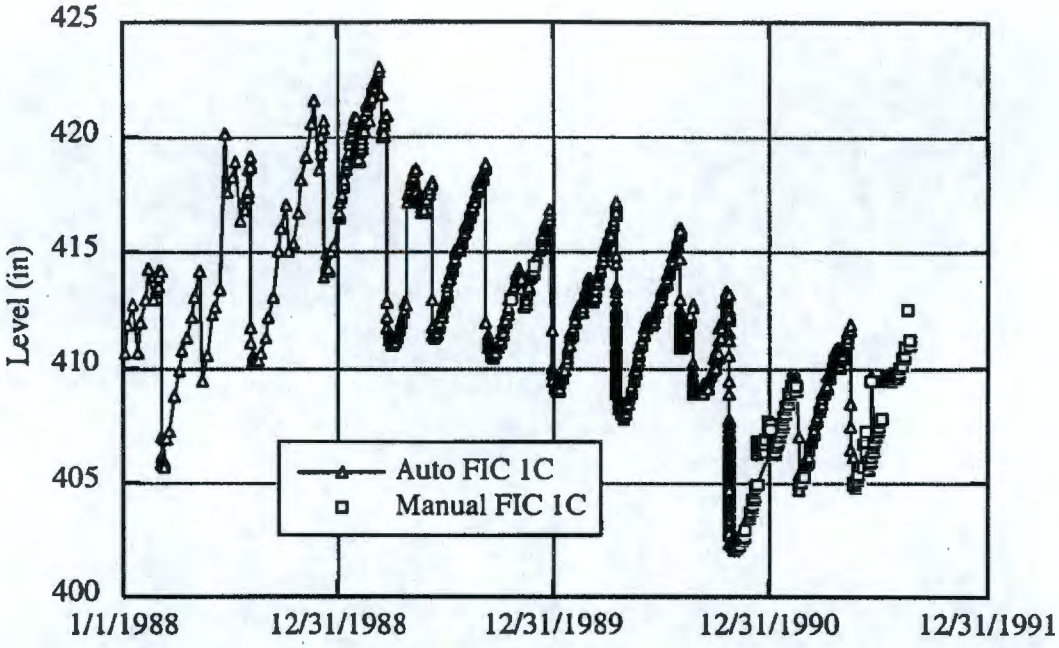

Figure 3-1. Tank 241-SY-101 Surface Level from 1988 to 1991

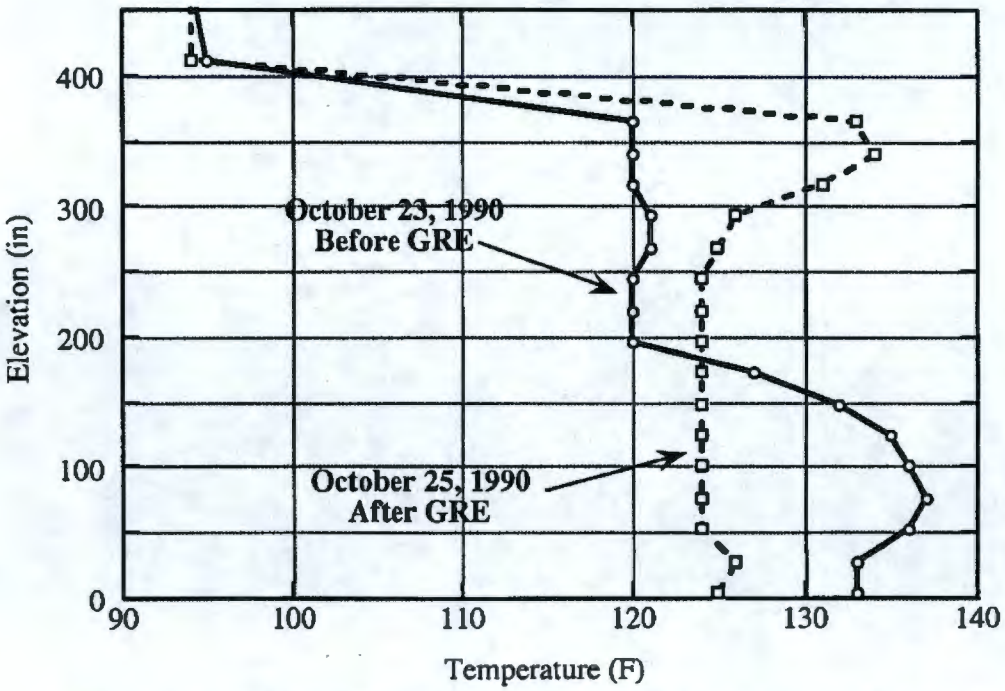

Figure 3-2. Tank 241-SY-101 Temperature Profile Before and After Gas Release Event on October 24, 1999

3.3 CRITERIA FOR FLAMMABLE GAS WATCH LIST TANKS

Criteria for Flammable Gas Watch List tanks were refined in 1997 (Johnson 1997a), and approved by the U.S. Department of Energy (Kinzer 1997). The report states that:

The selection criterion is:

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

The criterion for removal is:

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

In 1997, a document was issued that described the strategy for resolution of the Flammable Gas Safety Issue (Johnson 1997b). Facilitated workshops were used to develop the strategy, and sessions were devoted to interpretation of the Watch List criteria. A conclusion of the workshop was that the selection criterion should be interpreted as meaning "to have significant potential for an unacceptable risk from a spontaneous release of flammable gas."

Also, as a result of the workshops, the criterion for removing a tank from the Watch List was interpreted to mean (1) a tank that cannot spontaneously release enough flammable gas to the domespace "which, if ignited.....tank design limit" has acceptable risk from the perspective of the Watch List, and (2) this acceptable risk will be demonstrated by compliance with DOE orders in implementing an approved authorization basis.

3.4 MONITORING REQUIREMENTS OF PUBLIC LAW 101-510, SECTION 3137

One of the requirements of this law was to implement continuous monitoring to detect a gas release or excessive waste temperature or tank pressure. At the time that the law was enacted, all DSTs were equipped with: (a) thermocouples to measure the waste and tank structure temperatures, (b) pressure sensors in the tank domespace, and (c) continuous air monitors in the tank annulus to detect any leaks. Thus, tank 241-SY-101 was in compliance with the monitoring requirements.

Beginning in 1990, additional instrumentation was added to the tank, including multiple gas monitoring systems, two additional instrument trees for waste and domespace temperatures, a television camera in the domespace, improved waste level measuring instruments, and instruments for measuring the humidity and flow of air through the ventilation system. The gas monitoring systems were set to alarm at 25% of the LFL of hydrogen in air, and controls were established to protect against performing work in a flammable atmosphere. Tank 241-SY-101 became the most intensively monitored tank at the Hanford Site.

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

Analysis of how chemical and physical processes affect the flammable gas issue must embody the cause and effect relationship of generation, retention, and release. Gas generation is the ultimate source of the hazard; gas retention is a measure of the potential hazard; and gas release represents the actual hazard. The understanding of each of these processes for the waste in tank 241-SY-101 is described below.

4.1 GAS GENERATION

Hydrogen, nitrogen, nitrous oxide, and ammonia are found in the domespaces of waste tanks and in bubbles within the wastes (Johnson et al. 1997; Mahoney 2000). Some hydrogen is produced as a byproduct of the corrosion of the steel tank walls, but most hydrogen and the other gases are formed as a consequence of the radiolysis of water and degradation of the organic constituents in the waste. Nitrous oxide and nitrogen are formed principally from the inorganic oxidants as byproducts of the oxidation of the organic constituents. Ammonia is produced from the nitrogen-containing complexants and from the inorganic oxidants. These conclusions are based upon studies of the chemical behavior of the complexants[1] in well-defined reactions by university and national laboratory teams (Stock 2000).

There is a very close relationship between the rate of gas generation and the rate of decomposition of the organic constituents. The widespread distribution of organic compounds has been established by the analysis of core samples and by the analysis of samples from the domespaces. Broadly speaking, information about gas generation, including the influences of chemical constituents, tank temperature, and radiation dose on the rates and products of the ongoing chemical processes is required for the assessment of the behavior of the waste during storage, for the evaluation of monitoring operations, the design of control strategies, and the planning of mitigation operations.

A detailed report (Stock 2000) on the degradation of the various organic compounds and the production of the various gaseous species was recently issued. This report describes how the organic complexants and solvents are oxidized through long sequences of chemical reactions to form volatile compounds, which emerge from the waste, or sodium carboxylates and sodium carbonate, which are retained, as the inorganic oxidants are reduced to form nitrogen-containing gases and hydrogen.

It was shown by Stock (2000) that the radiolysis of water and the subsequent reactions with nitrate and nitrite ions provide the reagents necessary for oxidation of the organic compounds in the waste. The radicals produced in these reactions extract a hydrogen atom or an electron from the organic constituents to initiate chemical transformations. The initial radiolytic processes have negligible activation energies, but the rates of the ensuing

[1] More background on the source of organics in waste is provided in Section 5.1.

chemical reactions are temperature dependent. Other ionic and radical reactions are initiated by ions and radicals formed from inorganic constituents. These reactions, of course, are temperature dependent and have a broad range of activation energies.

The overall gas generation rates are found to be highly sensitive to temperature and also dependent on the concentration of reactant species and radioactive isotopes. Prior to dilution, tank 241-SY-101 waste had both a relatively high temperature and a high concentration of species involved with gas generation. In fact, it had the highest total gas generation rate of all DSTs and single-shell tanks (SSTs) at Hanford.

The temperature dependence of both thermolytic and radiolytic hydrogen generation has been incorporated in an empirical rate equation correlating field measurements of hydrogen generation with waste properties in Hanford tanks developed recently by Hu (2000). In addition to the thermolytic and radiolytic hydrogen generation rates, the total hydrogen generation estimate by Hu (2000) also includes a factor for tank wall corrosion that conservatively assumes a corrosion rate of 0.1 mil/yr and that one mole of hydrogen is generated per mole of iron corrosion. While the established corrosion allowance for these tanks is 1 mil/yr, corrosion rates measured in simulated Hanford wastes under thermal and irradiated conditions show steel corrosion rates on the order of 0.01 mil/yr (Strachan 1994). For Hanford wastes with adequately high pH control, the 0.1 mil/yr assumption is extremely conservative.

The empirical rate equation for hydrogen generation in Hanford waste developed above contains the simulation of thermal reaction, HGR_{thm}, radiolysis of water and organic, HGR_{rad}, and the corrosion process, HGR_{corr}. This rate equation is a function of waste composition (TOC, Al, NO_3^-, NO_2^-), radiation dose, temperature, liquid fraction, and tank wetted area. Both the thermal and radiolysis rates follow Arrhenius behavior with a derived activation energy. The equation for hydrogen generation rate (HGR) in the unit of mole/kg-day can be summarized as follows.

$$HGR = HGR_{thm} + HGR_{rad} + HGR_{corr} \qquad (4\text{-}1)$$

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

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

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

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

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

The values used to calculate the HGR are:

E_{thm} = 89.3 kJ/mole, the activation energy for the thermal reaction
a_{thm} = 2.76E+09 mole/kg-day, pre-exponential factor of the thermal rate
E_{rad} = 44.3 kJ/mole, activation energy in organic radiolysis G
a_{rad} = 2.49 E+06 molecules/100 eV, the pre-exponential term in organic radiolysis G
r_f = 0.7 for DSTs and 0.4 for SSTs (unitless), the TOC reactivity coefficient

R = 8.314 J/mole/K, gas constant
G_{ORG} = generation rate of H_2 from organics, molecules/100 eV
G_{H2O} = generation rate of H_2 from radiolysis, molecules/100 eV
$(G_{H2O})_{sat}$ = 0.005 H_2/100 eV, the default water radiolysis G for high salts
R_{corr} = 6.0E-08 for DSTs and 1.2E-07 for SSTs ($ft^3/min/ft^2$), corrosion coefficient
[TOC] is total organic carbon concentration in the liquid waste (wt%)
[Al] is aluminum concentration in liquid waste (wt%)
$[NO_3^-]$ is the nitrate ion concentration in the liquid waste (moles/L)
$[NO_2^-]$ is the nitrite ion concentration in the liquid waste (moles/L)
H_{load} is total heat load of the tank (Watt/kg)
L_f is the liquid weight fraction in the waste (unitless)
T is the temperature of waste (K)
A_{wetted} is the area of steel exposed to moisture-containing waste (ft^2).
M_{tank} is the total mass in the waste (kg).
CF_1 is the conversion factor from (H_2/100 eV)(Watts/kg) to (mole/kg-day)
CF_2 is the conversion factor from (m^3/kg-min) to (mole/kg-day)

The total gas generation rate can be estimated by dividing the hydrogen generation rate by the hydrogen fraction in the retained gas. However, the hydrogen fraction of the gas currently generated and released is unknown. Prior to remediation, the best estimate of hydrogen fraction in the retained gas was 30% with an uncertainty of ± 5% based on gas generation tests on 241-SY-101 waste (Person 1996), domespace composition following large GREs (LANL 1996), and retained gas sampler (RGS) measurements of retained gas composition (Mahoney 2000).

Since the post-remediation waste temperature and the soluble organic concentration are significantly lower, the gas currently generated should be richer in hydrogen. However, to the extent it can be determined with the gas concentration instruments near their detection limit, the hydrogen-to-nitrous oxide ratio in the domespace has not changed significantly. Therefore, 30% hydrogen in the generated gas is assumed since, (1) it gives a higher total gas generation rate and is, therefore, conservative, (2) the hydrogen-to-nitrous oxide ratio has not changed, and (3) there are no other data available to quantify a higher hydrogen fraction. An uncertainty of ± 50% is ascribed to the calculated gas generation rate.

4.2 GAS RETENTION

Gas retention is the precursor to every GRE, whether spontaneous or induced. The waste in almost every tank contains flammable gas. Most tanks accumulate gas until they reach an equilibrium between generation rate and release rate, and the flammability hazard is controlled by domespace ventilation. If gas continues to accumulate in the waste at even a very low rate, a potentially hazardous gas volume can eventually accumulate.

Retention of relatively insoluble gases (hydrogen, nitrous oxide) in the form of bubbles is most important in terms of flammability. Bubbles can comprise large volumes and can potentially be released quickly. A large mass of soluble gas (almost entirely ammonia) can also be retained in the liquid, but because it is not very flammable, ammonia is a minor contributor to the flammable gas hazard. Ammonia, however, is toxic, and relatively low concentration limits are set to protect on-site personnel. Some gas can be adsorbed on the surfaces of solid particles, but this gas is not a flammability concern because the amount adsorbed is small and cannot be released quickly. Therefore, the discussion of gas retention will focus on insoluble gas in the form of individual bubbles.

A bubble can exist attached to a particle (bubble less than or approximately equal to the size of the particle), surrounded or "armored" by particles (particles somewhat smaller than the bubble), or as a free bubble within a liquid or liquid-solid matrix (bubble is much larger than the particles). Free bubbles are the most important in terms of gas retention and release. Though attached and armored bubbles are responsible for the formation and growth of floating "crust" layers, the gas retained in this way is not easily releasable and, generally, represents a small fraction of the total gas content of a tank. In tank 241-SY-101 prior to dilution, however, armored bubbles or bubbles attached to particles are believed to have comprised the relatively large volume of gas in the mixed slurry created by mixer pump operation (Mahoney et al. 2000; Rassat et al. 2000). Since these small bubbles were not readily releasable, they were not a safety concern but did have an effect on mixer pump performance.

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 internal pressure trying to push them apart. This retention mechanism requires either relatively large particles, 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. Because the particle size is small and the shallow depth of the nonconvective layer and buoyancy of the dense liquid limits the lithostatic load, pore-filling bubbles do not occur in tank 241-SY-101.

When the internal pressure of a bubble is sufficient to push the surrounding particles apart, bubble configuration becomes dominated by the balance of buoyancy 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. This type of bubble is believed to be the dominant retention mechanism in tank 241-SY-101.

There are three important waste types and several configurations of these waste types that affect how gas is retained and released. The three basic waste types are liquid, sludge, and saltcake. Liquid, by definition, is a dilute or concentrated salt solution that contains at most a small fraction of suspended solids. Liquids can retain only dissolved gas in any

significant quantity. Sludge consists of fine, relatively insoluble particles (mostly metal oxides). Saltcake forms by settling of sodium and aluminum salts precipitated from a saturated salt solution by cooling. Saltcake particles are generally larger than sludge particles. A "salt-slurry" waste type, which consists of finer particles than saltcake exists in the DSTs, including tank 241-SY-101. Both sludge and saltcake can retain significant volumes of insoluble gas depending on the waste configuration and properties (e.g., nonconvective layer depth, densities).

Waste configurations are the arrangement of waste types within a tank. The most important configuration for gas retention is "liquid-over-solid," where a relatively deep layer of supernatant liquid overlies a gas-retaining sediment layer. Two other waste configurations were also important in 241-SY-101 prior to remediation: "mixed slurry," in which most of the solid particles are kept in suspension by mixing, and crust, which is a floating layer of gas-bearing solids. Tank 241-SY-101 contained the thickest crust of all the DSTs.

In the liquid-over-solid configuration, which now typifies tank 241-SY-101 waste, the liquid is termed the convective layer because thermally driven convection occurs there, and the settled solids are called the nonconvective layer because the strength of the solids prevents convection. This creates the characteristic temperature profile, with uniform temperatures in the convective layer and a parabolic profile at the bottom in the nonconvective layer, from which the thickness of the layers can be determined nonintrusively.

4.3 GAS RELEASE

The liquid-over-solid waste configuration is subject to possible buoyant displacement gas release. Gas can accumulate in the nonconvective layer until a portion of it becomes buoyant with respect to the convective liquid above. At this point, a portion of the nonconvective layer rises to the surface and releases a large fraction of its gas before falling back to the bottom to begin a new retention-release cycle. Buoyant displacements are the largest and fastest releases known to occur in Hanford tanks, and the largest ones occurred in tank 241-SY-101 prior to mixer pump installation. No other waste configuration is subject to this release mechanism.

Because the nonconvective layer breaks away from its surroundings and initiates a GRE when it becomes buoyant (ignoring the small effect of waste strength), the maximum gas fraction in the nonconvective layer is limited to approximately the neutral buoyancy condition, which is given by:

$$\alpha_{NB} = 1 - \frac{\rho_{CL}}{\rho_{NCL}} \tag{4-2}$$

where: α_{NB} is the maximum gas fraction at neutral buoyancy

ρ_{CL} and ρ_{NCL} are the gas-free densities of the convective and nonconvective layers, respectively.

Equation 4-2 gives neutral buoyancy void fractions of about 0.10 to 0.15 for liquid-over-solid saltcake tanks, including tank 241-SY-101 prior to dilution.

Most tanks apparently achieve a steady-state where gas generation is balanced by a steady, background release so that the neutral buoyant void fraction given by Equation 4-2 is never attained. In a few tanks, however, the background release rate remains less than the generation rate. This allows gas to periodically accumulate to the point of buoyancy and consequent buoyant displacement gas release. The dominant conditions that exacerbate gas retention and increase the probability of buoyant displacements are given below:

- **Deep nonconvective layer**: Increases the volume of gas generated per unit area available for background release thereby increasing the likelihood that generation will exceed the background release.
- **Small neutral buoyancy void fraction** (small difference between convective layer [CL] and nonconvective layer [NCL] density): Less gas is required to accumulate to achieve buoyancy.
- **High gas generation rate**: Increases the likelihood that gas generation will exceed the background release and cause gas to accumulate.

Concentration of the waste by evaporation drives each of these conditions in a hazardous direction. Conversely, dilution drives them all in a direction away from buoyant displacements such that the hazard can be eliminated with sufficient dilution. Specific models and criteria for determining whether or not buoyant displacements can occur are described in Section 8.0.

5.0 HISTORY OF TANK 241-SY-101

5.1 BACKGROUND INFORMATION

Tank 241-SY-101 is a DST in the 241-SY Farm, which is located in the 200 West Area of the Hanford Site. Construction of the tank was completed in 1976, and the first waste put into the tank was from the first double-shell slurry (DSS) campaign using the 242-S Evaporator in 1977. Double-shell slurry is the most concentrated material that the evaporators can produce, and 275,500 gallons were put into tank 241-SY-101. Double-shell slurry is highly viscous because it has been concentrated past the sodium aluminate saturation boundary. Tank 241-SY-101 was filled between 1977 and 1980 in a series of five evaporator campaigns and transfers consisting of DSS and concentrated complexant (CC) waste as listed in Table 5-1 below.

Table 5-1. Tank 241-SY-101 Fill Summary 1977 through 1980

Campaign Type	Waste Type	Feed to Evaporator (gal)	Received in SY-101 (gal)	Volume Reduction Factor
Evaporator	DSS	365,000	275,500	0.25
Evaporator	CC	524,400	365,600	0.30
Transfer	CC	-	133,300	-
Transfer	CC	-	59,500	-
Evaporator	DSS	313,000	231,300	0.26
TOTAL	-	-	1,065,200	-

The CC waste, which is a waste from the cesium/strontium recovery process in the B-Plant, was rich in organic chelators (i.e., ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), and citric and hydroxyacetic acid). The waste, therefore, had a high concentration of organic carbon.

Table 5-1 shows that the volume reduction factor that created tank 241-SY-101 waste was 25 to 30%. Prior to concentration in the evaporator, none of the tank 241-SY-101 evaporator feed wastes exhibited BD-GRE behavior, nor did the waste feeds for tank 241-SY-101 that were not processed through the evaporator experience slurry growth (gas retention) or exhibit BD-GREs.

Water and air lancing was used during the mid-1980s in an attempt to control the gas releases. Lancing was stopped in 1989 when it was determined to not eliminate gas releases and the surface level exceeded the operational limit of 422 inches.

In 1990, the release of large quantities of flammable gases from the waste into the domespace of tank 241-SY-101 was recognized as a situation requiring special attention and control. In April 1990, administrative controls were implemented to control various activities. In May 1990, the DOE-RL determined that hydrogen and nitrous oxide buildup

in certain waste tanks and the possibility of their ignition constituted an USQ (Lawrence 1990). The USQ was applied to tank 241-SY-101 and 22 other tanks at that time. The same tanks defined by the USQ were also included in the Flammable Gas Watch List.

5.2 TANK CHEMISTRY PRIOR TO LEVEL RISE MITIGATION

The first full-depth core sampling of tank 241-SY-101 was conducted in May and December 1991. Additional cores were obtained in November and December 1998 and January 1999. Samples were obtained for the full depth of the waste. Results of these core samples analyses were used to prepare an overall average composition for the tank (Reynolds 1993, Person 1999) which is shown in Table 5-2. Both cores indicated essentially the same waste composition.

Table 5-2. Composition of Tank 241-SY-101 Waste

Analyte	1991 Samples (weight %)	1998/1999 Samples (weight %)
Na^+	20.7	19.3
Al	3.2	3.5
Cr (total)	0.41	0.34
Cr (VI)	0.002	Not analyzed
Ca	0.023	0.011
Fe	0.028	0.022
K^+	0.326	0.354
Ni	0.015	0.014
Zn	0.002	0.0007
NO_3^-	11.7	11.6
NO_2^-	10.5	11.2
OH^-	2.47	2.20
Total organic carbon	1.53	1.17
Total inorganic carbon	0.63	0.57
PO_4^{-3}	0.64	0.45
SO_4^{--}	0.40	0.36
Cl-	0.79	0.94
NH_3/NH_4	0.19	Not analyzed
Water	35.5	37.6

The waste in tank 241-SY-101 has the major components: sodium carbonate, sodium hydroxide, sodium nitrate, sodium nitrite, sodium phosphate, sodium sulfate, numerous organic compounds, and water.

Extensive efforts were conducted to identify the organic compounds. Techniques developed and applied to the tank 241-SY-101 samples included derivatization gas chromatography/mass spectrometry (GC/MS), liquid chromatography (LC), ion

chromatography (IC), and gas chromatography/flame ionization detector (Campbell et al. 1995). Compounds identified were:

Chelators and Fragments

ethylenediaminetetraacetic acid (EDTA)
ethylenediaminetriaacetic acid (ED3A)
nitrosoiminodiacetic acid (NIDA)
nitrilotriacetic acid (NTA)
citric acid (CA)
succinic acid (SA)

Low Molecular Weight Acids

Oxalic
Formic
Acetic

Soluble Organic Carbon

Normal paraffin hydrocarbons (NPH)

HEDTA was not detected, presumably due to its complete degradation to other compounds.

5.3 GENERATION OF FLAMMABLE GASES

An empirical model (Equation 4-1) was developed for estimating the production of gases in the various waste tanks (Hu 2000). The model calculates hydrogen production by thermal, radiolytic, and corrosion processes. For tank 241-SY-101 just prior to the waste transfer and dilution sequence, the calculated rates were:

Thermal: 1.04E-06 mole/kg-day

Radiolytic: 3.83E-06 mole/kg-day

Corrosion: 1.69E-07 mole/kg-day

The results above give a total production for hydrogen of 5.04E-06 mols of gas per kg of waste per day; this is equivalent to 28 scfd. Measured rates for hydrogen, based on the integrated release rate, ranged from 35 scfd prior to mixer pump installation to 22 scfd prior to the waste transfer and dilution sequence. The corresponding total gas generation rate, assuming 29% hydrogen, was 120 to 80 scfd (McCain 2000; Conner and Koreski 1998).

The composition of the gas mixture produced within the waste was estimated based on data collected during several large GREs (LANL 1996) prior to mixer pump installation. In-situ gas composition was also measured with the Retained Gas Sampler (RGS)

(Mahoney 2000) during the 1998/1999 core sampling. The compositions measured in the mixed slurry match the estimated composition more closely than those measured in the crust layer. Table 5-3 provides a summary of this information.

Table 5-3. Tank 241-SY-101 Gas Composition

COMPONENT	ESTIMATED (mole %)	MEASURED	
		Crust (mole %)	Slurry (mole %)
Hydrogen	30	34 ± 4	30 ± 9
Nitrous Oxide	25	20 ± 3	24 ± 7
Ammonia	11	18 ± 4	6.2 ± 1.9
Nitrogen	33	27 ± 5	37 ± 12
Methane	0.4	0.6 ± 0.1	1.4 ± 0.5
Other	0.6	0.4 ± 0.3	1.4 ± 0.5

Notes:

The compositions above are given on a dry basis. LANL (1996) estimated that water made up 2.4% of the overall gas. No explicit uncertainties were provided for the estimated composition.

5.4 GAS RETENTION IN TANK 241-SY-101

Prior to installation of the mixer pump the waste in tank 241-SY-101 retained a very large volume of gas. The safety assessment that was used for mitigation of the GREs (LANL 1996) provided a bounding estimate of the amount of gas retained. The in-situ gas volumes, assuming a neutral buoyancy void fraction of 0.15 in the nonconvective layer, were given in the safety assessment as:

Convective Layer:	2,420 ± 490 ft^3
Nonconvective Layer:	11,400 ± 2350 ft^3
Total In-situ volume:	13,900 ± 2840 ft^3
Total Volume at 1 atm:	27,500 ± 5240 ft^3

The next section will discuss the historic data for the observed gas release events in tank 241-SY-101.

5.5 GAS RELEASES IN TANK 241-SY-101

The nature of the level drops during GREs in tank 241-SY-101 was shown earlier in Figure 3-1. A summary of the major gas releases is provided in Table 5-4. The level drop values in this table are for the amount of change in one day; this is taken to be the "prompt" decrease in waste level. Additional decreases in level usually occurred over several days.

Table 5-4. Gas Release Events in Tank 241-SY-101 Prior to Mitigation

Date	Maximum Measured H_2 Concentration (ppm)	Prompt Waste Level Drop (in.)	Volume Released (ft^3 at one atm)
4/19/90	35,000	9	7,000
8/5/90	12,000	5	4,000
10/24/90	47,000	10	7,700
2/16/91	400	4	3,200
5/16/91	28,000	7	5,400
8/27/91	3800	6	4,400
12/4/91	53,000	12	9,300
4/20/92	14,800	6	4,600
9/3/92	51,200	10	7,600
2/2/93	27,400	9	7,000
6/26/93	34,000	10	7,600

The LFL of hydrogen in air is 4% (40,000 ppm). Therefore, three of the GREs in the 1990 to 1993 time period exceeded the LFL for a short period of time, i.e., less than one hour. It was likely that some earlier GREs also exceeded the LFL. Such situations were unacceptable, and efforts were initiated to mitigate the GREs.

6.0 MITIGATION OF GAS RELEASE EVENTS

In 1991, efforts were initiated to mitigate the large GREs. Mitigation concepts were developed by several working groups and from sources outside of the Hanford Site. A total of 22 approaches were evaluated (Babad et al. 1992). Four concepts (heating, dilution, ultrasonic agitation, and mixing) were selected for further study (Lentsch 1992).

The approach selected for mitigation of the GREs was to mix the waste contents with a jet mixer pump (WHC 1992). A detailed safety assessment was prepared by Los Alamos National Laboratory (LANL 1996) and was approved by DOE. A jet mixer pump, with two opposed jets, was installed on July 3, 1993. Demonstration testing in October through December 1993 mobilized the nonconvective layer and released most of its retained gas. Data showed that mixing had not adversely altered the waste or created any safety issues (Allemann et al. 1994). During February through April 1994, full scale testing was performed to demonstrate long-term control of gas retention by mixer pump operation (Stewart et al. 1994).

One set of these tests showed that the mixer pump jets could excavate settled solids to within a few inches of the tank bottom out to at least 27 ft (within 9 ft of the tank wall) from the tank center when operated at 1,000 rpm for 25 minutes several times in the same direction. After excavating the entire tank during the summer of 1994 by making several runs at each of six jet orientations 30 degrees apart, the Test Review Group (TRG) decided in September 1994 to make 1,000-rpm, 25-minute runs three times a week, with the jets indexed 30 degrees each time. This procedure swept the tank with six runs every two weeks. In July 1995, the TRG amended this procedure to offset the jets 15 degrees on alternate tank sweeps to insure that waste would not accumulate in the area between 30-degree segments. This regular mixer pump operation schedule was maintained with few breaks until mid-December 1999, when the first transfer was performed.

The mixed state of the tank is illustrated by the axial temperature profiles shown in Figure 6-1. The 1993 pre-pump profile shows a bulge at the lower part of the tank. This indicates a deep, 250-inch nonconvective layer that allowed the waste to retain gas. The profile from 1996 after several years of mixing shows a uniform temperature over almost the whole depth of the waste indicating that mixer pump operation prevented the historic deep nonconvective layer from forming.

Figure 6-2 shows the behavior of the waste level before and after insertion of the mixer pump; by late 1994, the GREs had been eliminated. Figure 6-3 shows the hydrogen concentrations in the dome for the last few major GREs and for the period of pump operation up to early 1995; the reduction was due to the fact that operation of the mixer pump released a significant portion of retained gas.

Detailed characterization of the stored gas (void content) was performed by measuring the void with a device called a Void Fraction Instrument (VFI) (Stewart et al. 1995). The results of the measurements are shown in Figure 6-4. The calculated volume of stored gas in tank 241-SY-101 based on the data in Figure 6-4 was 6,900 ft^3 at 1 atm including the crust. A re-evaluation of the safety basis for tank 241-SY-101 showed that the conditions in the tank were such that the amount of gas that could be released and burned in a deflagration would not challenge the structural integrity of the tank (LANL 1996). This analysis also showed, however, that continued operation of the mixer pump was required to prevent buildup of gas within the waste.

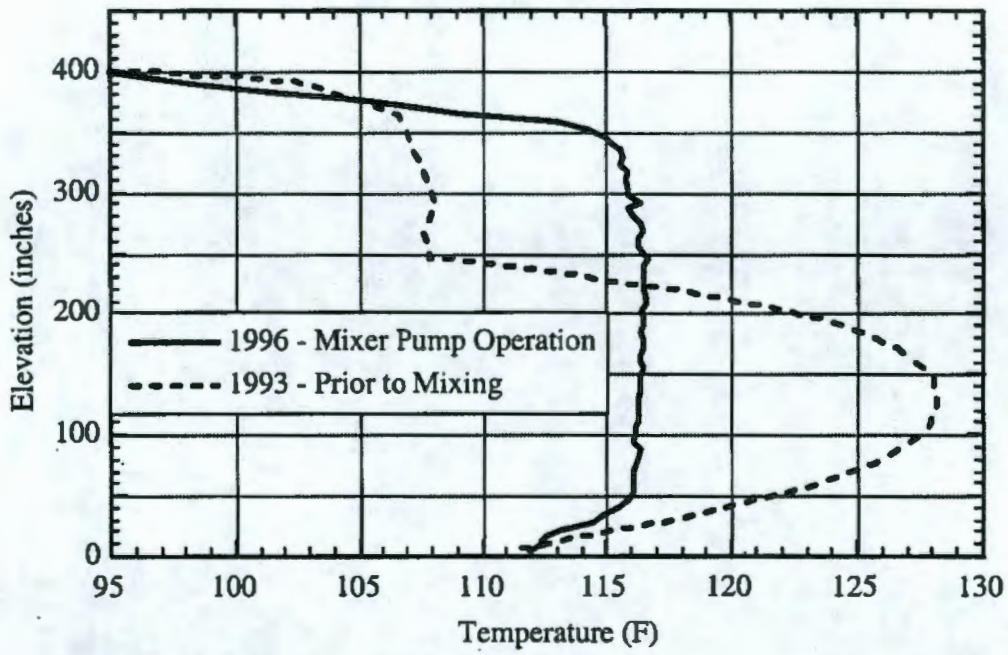

Figure 6-1. Temperature Profiles Before and After Mixer Pump Installation

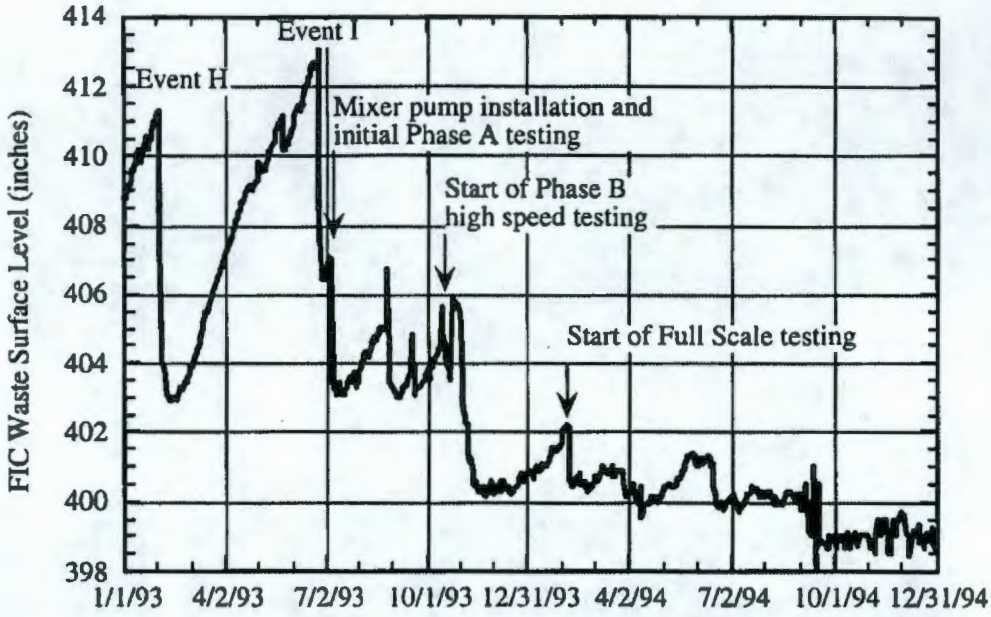

Figure 6-2. Tank 241-SY-101 Surface Level Before and After Mixer Pump Installation

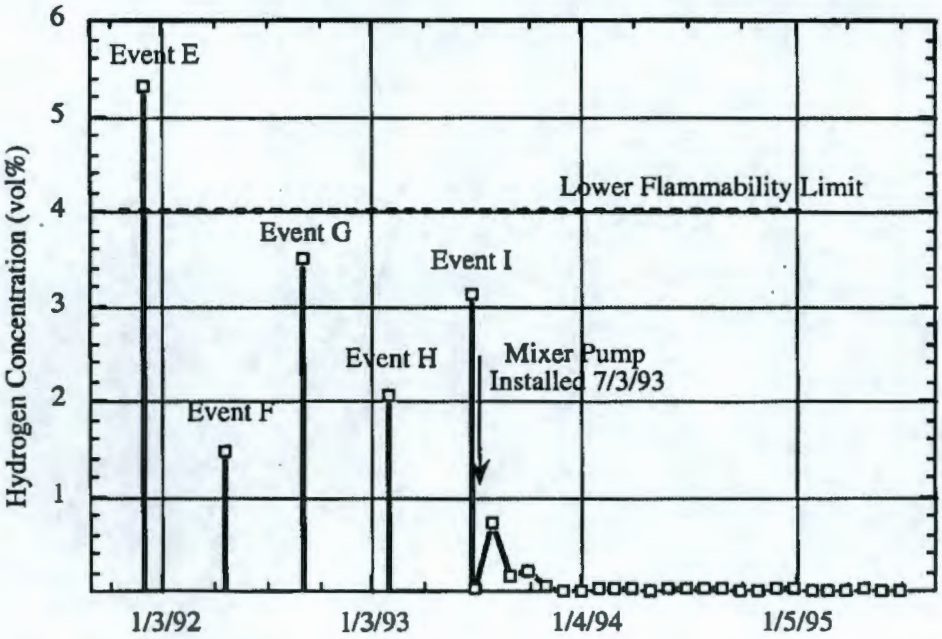

Figure 6-3. Tank 241-SY-101 Peak Hydrogen Concentrations Before and After Mixer Pump Installation

An amendment to the Authorization Basis was prepared for operation of the mixer pump and closure of the USQ. The U.S. Department of Energy, Richland Operation Office (DOE-RL) submitted a request for closure of the USQ for tank 241-SY-101 (Wagoner 1995). The U.S. Department of Energy, Headquarters (DOE-HQ) concurred with the request (Guimond 1996), and DOE-RL closed the Flammable Gas USQ for tank 241-SY-101 (Wagoner 1996).

Once the waste was initially mobilized, the years of routine mixing did not produce any significant changes in the waste chemistry or gas composition. The tank was core sampled in 1998, and the results shown in Table 5-2 are in agreement with the data from 1991. Through use of the RGS, the composition of the gas mixture measured in 1999 (Mahoney 2000) was similar to that given in the safety assessment as shown in Table 5-3.

Though the basic nature of the waste was not effected by mixing, noticeable changes were beginning to occur. A slow but steady increase in the waste level was detected in 1996 that was to become the next major issue in tank 241-SY-101's history. How the surface level rise issue was discovered and dealt with is the subject of the next section.

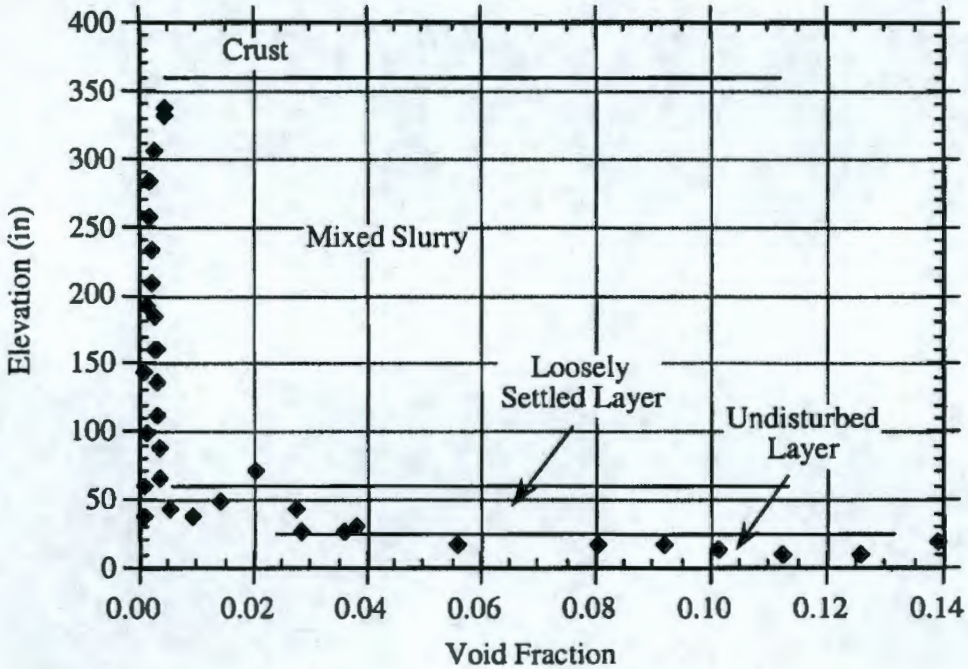

Figure 6-4. Tank 241-SY-101 Void Profile, 1994/1995 Data

7.0 SURFACE LEVEL RISE ISSUE

Mixer pump operation successfully mitigated gas retention in the nonconvective layer and prevented BD-GREs in tank 241-SY-101 by keeping the solids from forming a deep nonconvective layer as discussed in Section 6.0. However, during the period of regular mixer pump operation, absence of the periodic disturbance of the large GREs allowed the floating crust layer to grow by accumulating small bubbles and attached solids from below. This caused an accelerating waste level rise that was first detected in early 1996.

7.1 BACKGROUND

The rise in level since 1995 is shown in Figure 7-1. The waste surface under the level instrument in Riser 1C was flushed regularly with water to remove waste deposits from the level probe. This also dissolved a depression in the crust around the instrument. Because of this, the 1C level was assumed to represent the free liquid level. Since the area under the level instrument in Riser 1A was not flushed, the 1A level was assumed to represent the top of the crust surface. Both level instruments showed a rapidly accelerating level rise from 1996 through the first part of 1999.

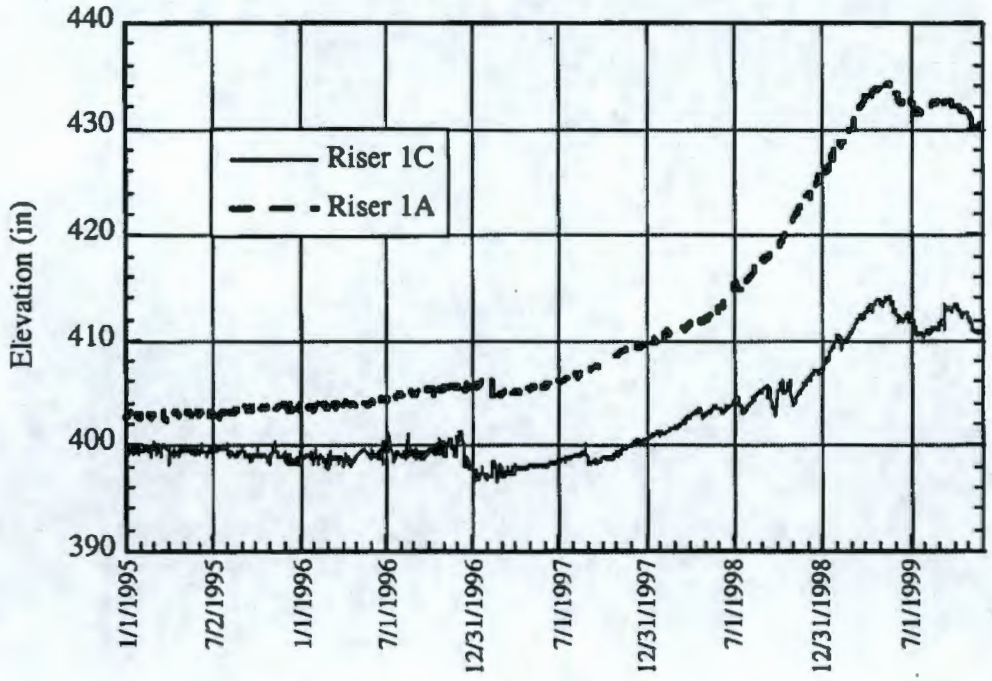

Figure 7-1. Waste Level Rise Since 1995

In November 1997, mixer pump runs were increased to four times per week in an attempt to reduce the rate of level rise. Contrary to expectations, the level rise accelerated slightly. On December 29, 1997, the Tank Waste Remediation System (TWRS) Plant Review Committee (PRC) declared that there was a "discovery" with respect to tank 241-SY-101 because of potential inadequacy in the Authorization Basis (AB). The observed level rise was inconsistent with the basic assumptions of the mixer pump safety assessment (LANL 1996). The rise in waste level was indicative of gas being trapped within the waste according to the assumptions of the safety assessment. Even though the mixer pump was mobilizing solids and preventing GREs, it could not control the level rise. In February 1998 the contractor recommended that a USQ be declared for this condition (Hatch 1998). The DOE-RL concurred with the recommendation and declared the USQ on February 26, 1998 (Kinzer 1998). This USQ was called "the surface level rise USQ."

7.2 EVALUATION OF TANK CONDITIONS

To address the surface level rise USQ, a project team was established to develop and implement options for remediating the unacceptable situation in tank 241-SY-101 (Raymond 1999). The first action of the team was to evaluate the tank conditions and confirm the primary cause of the level rise. Temperature profiles had been used for many years to estimate the thickness of the crust and nonconvective layers. The transition from a uniform temperature, which is characteristic of a convective or mixed fluid, and a linear profile, which indicates conduction in a solid, was taken as the base of the crust. Temperature profiles showed a definite thickening trend in the crust from 1995 through 1999 as shown in Figure 7-2. This pointed to growth of the crust layer as the cause of surface level rise.

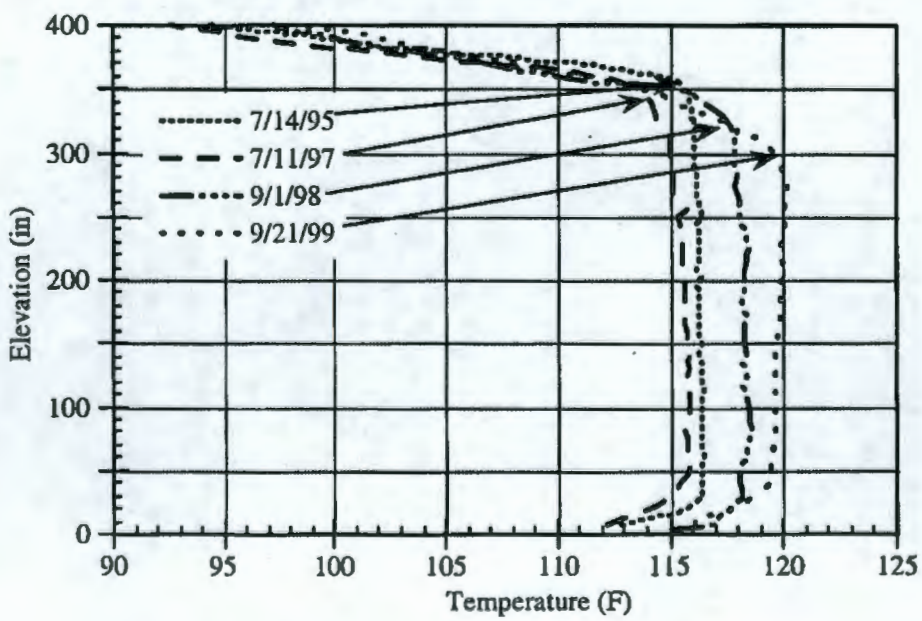

Figure 7-2. Waste Temperature Profile History

Void-fraction measurements were made during the summer of 1998 to confirm that gas was not being accumulated outside the crust layer. The void fraction averaged 0.30 in the crust and 0.013 in the mixed slurry (Stewart et al. 1998). These data give gas volumes (at 1 atm) of 138 m^3 (4,900 ft^3) in the crust and 87 m^3 (3,000 ft^3) in the waste below the crust for a total retained gas volume of 225 m^3 (7,900 ft^3). The crust gas volume had been estimated at 76 m^3 (2,700 ft^3) at 1 atm in 1994/1995. The comparison with VFI results showed the crust had accumulated more than twice its initial gas volume in three years. Retained Gas Sampler (RGS) data were also obtained from tank 241-SY-101 in the winter of 1998/1999. The void fraction from these measurements showed that the crust varied from over 0.5 near the base to 0.2 just below the liquid level; this confirmed the VFI data. The RGS void fractions in the mixed slurry were also consistent with the VFI measurements. The overall conclusion was that gas retention was occurring mainly in the crust layer with very little additional gas accumulation in the mixed slurry or the loosely settled solids layers below.

Gas retention in the crust was tied to a reduction in gas release. The release of gas from tank 241-SY-101 was monitored to determine the effectiveness of mixer-pump operations. Daily total gas-release volumes were calculated by integrating the product of the hydrogen concentration and the vent-header flow rate over time and dividing by an assumed hydrogen fraction of 0.29 in the tank gas. A reduction in the total gas-release rate was observed from the pre-pump installation baseline rate of ~20 m^3 (700 ft^3) per week to ~15 m^3 (540 ft^3) per week from July to September 1998 (Conner and Koreski 1998). If the surface-level rise were caused by gas retention in the crust (assumed to be at 1 atm), the 12-in.-surface-level rise for the last six months of 1998 equated to 4.8 m^3 (170 ft^3) per week of gas accumulation. This matched the deficit in retention and indicated that about 70% of generated gas was released and 30% was retained.

An evaluation of the crust conditions was performed based on past gas retention studies (Rassat et al. 1999). The analysis showed an increase in both the thickness and the "freeboard" of the crust. In the summer of 1998, the crust thickness had increased by about 14 in. to 54 in., but the crust base elevation was lower by only 3 to 4 in. (Stewart et al. 1998). This meant that about 10 more inches of the crust was above the free liquid level than in 1995. This extra buoyancy could only be the result of a higher gas volume fraction in the submerged crust. Figure 7-3 shows the acceleration in the crust thickness and the freeboard increases in 1998. The crust base was inferred from temperature profiles obtained with the multifunction instrument tree (MIT) validation probe and the top of the crust was assumed to be the level measured by the ENRAF[2] in Riser 1A. The liquid level was assumed to be represented by the ENRAF™ level in Riser 1C, which had been flushed with water regularly since 1994 dissolving a hole in the soluble crust. While the flushed plummet should more closely represent the liquid level than an unflushed one, the true liquid level was not known.

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

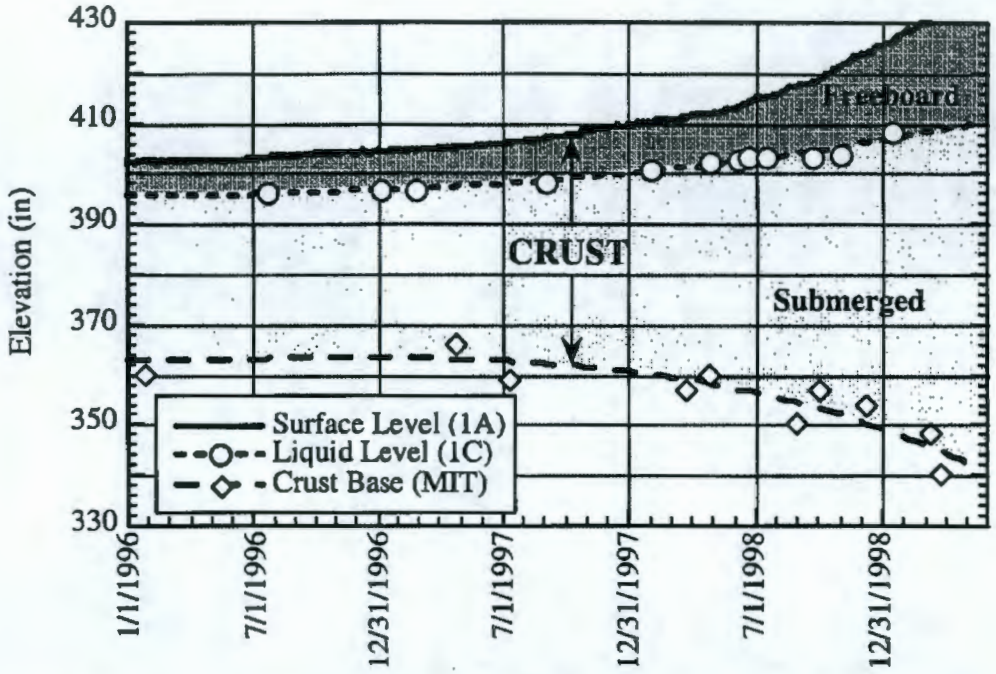

Figure 7-3. Tank 241-SY-101 Crust Growth from 1995 through 1998

In an attempt to gain more information about the crust, a small-bore neutron/gamma probe, similar to that used in the liquid observation wells in SSTs, was developed for use in the tank. The neutron probe uses an americium-beryllium source to emit fast, high-energy neutrons. These neutrons are "moderated" by moisture in the waste and detected by the probe. The probe detection response is a good indicator of water content. The gamma probe detects dissolved cesium within the waste, again providing an indicator of moisture content. The probe was deployed in the two MITs. Each MIT has a central cavity that extends almost to the bottom of the tank through which the probe is designed to pass. The neutron logs provided much information about the layers within the crust. A relatively high neutron count rate indicates the presence of water while a lower count means a lower moisture content. In the case of tank 241-SY-101, the lower counts were taken to indicate the presence of gas. Figure 7-4 shows the evolution of the crust and the increase in thickness between February and December 1999 as indicated by the neutron logs.

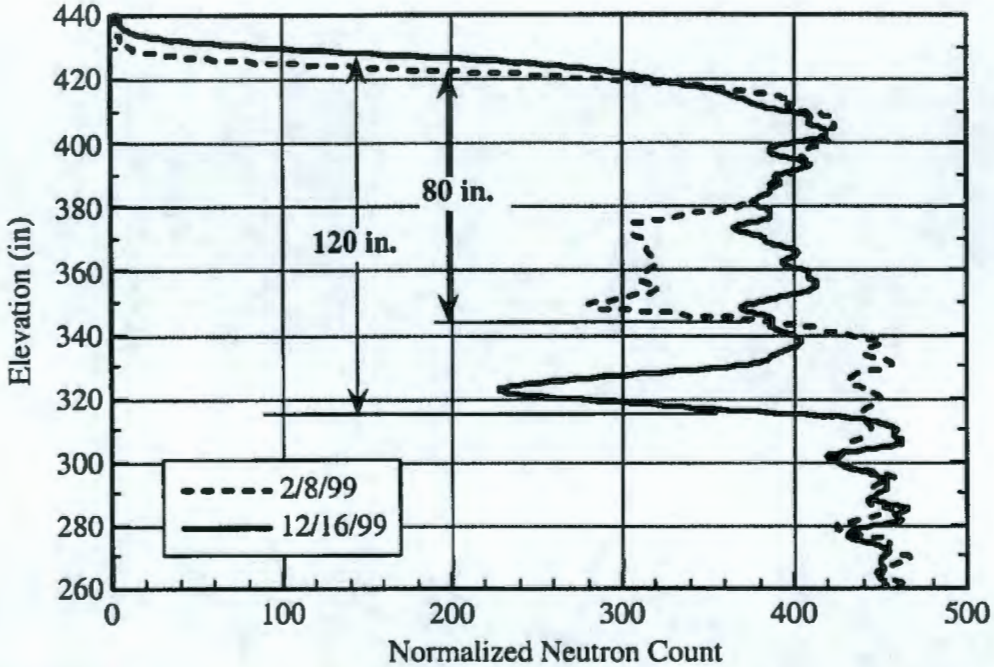

Figure 7-4. Comparison of Neutron Profiles from February and December 1999

Using the neutron probe data coupled with information gained during some intrusive operations, a description of the crust layer as it existed prior to the first transfer and back dilution was developed (Rassat et al. 2000). As it existed then, the crust consisted of four layers as illustrated in Figure 7-5. The bottom layer (312 to 320 in.) was a high-void material termed bubble slurry. Because the neutron count was lower than that recorded when the RGS registered a void fraction over 0.5, its void fraction was estimated to be approaching 0.6. It had a relatively low yield stress, <100 Pa. The middle two-thirds (320 to 400 in.) was called the "paste" layer because of its expected stiff peanut butter or clay consistency. It had a moderate void fraction of ~0.2 and a yield stress of 1,000 to 3,000 Pa. The "wet clay" layer (400 to 412 in.) just below the liquid level had a very low void fraction, estimated at 0.08 by comparing the neutron count with other layers, and was probably very strong. Though there are no direct measurements, its yield stress was assumed to be greater than 3,000 Pa. The top one-sixth (412 to 432 in.) was freeboard, the porous broken material above the liquid level. Individual fragments were quite strong (yield stress was probably greater than 10,000 Pa), but this layer had no strength as a unit.

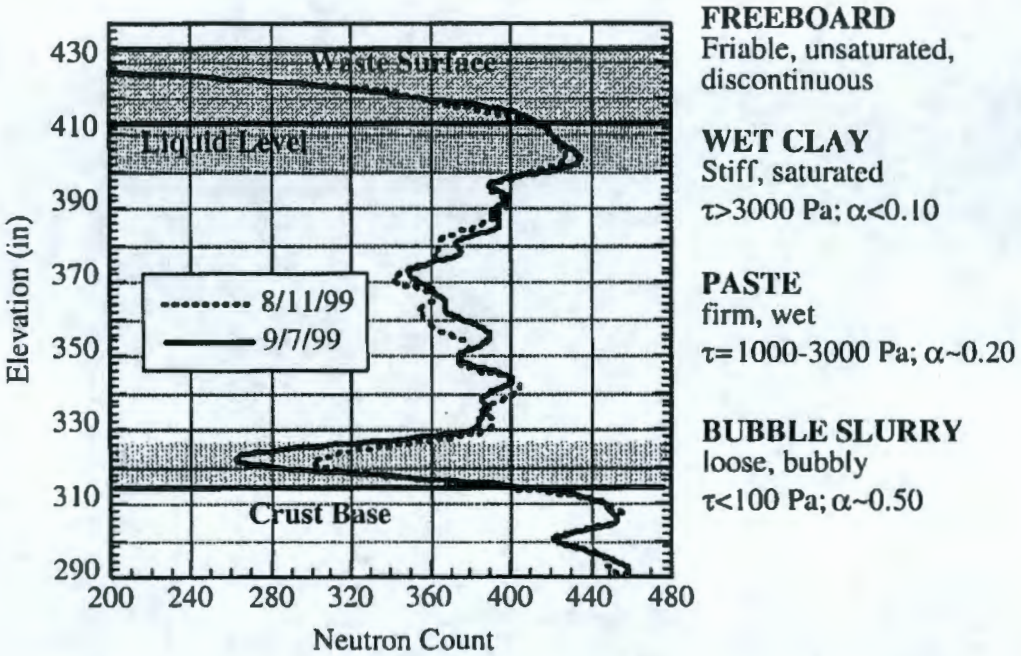

Figure 7-5. Crust Configuration as Indicated by Neutron Profiles

7.3 REMEDIATION OF THE SURFACE LEVEL RISE

The remediation of level rise focused on removing the crust layer and preventing its re-formation. A number of options were evaluated for dealing with the situation in tank 241-SY-101 (Raymond 1998). The option selected was to remediate the level rise by a series of waste transfers from tank 241-SY-101 to tank 241-SY-102 followed by back dilution with water. This approach was selected because the technical likelihood of success was high, the design could be flexible, and an incremental approach could be used that would allow for decisions to be based on actual results. There was high confidence that transfer and dilution of the waste would stop the level rise by dissolving solids, which in turn, would lead to a reduction in gas retention.

Analyses were conducted for dissolution of the crust and release of gas (Rassat et al. 2000) and for postulated hazards during the transfer and back dilution operations (Stewart et al. 2000). A safety basis was prepared to support the operations (Ryan 2000), and a process control plan was used to cover the specific steps of all of the operations for transfer and back dilution (Estey 2000).

The system consisted of a transfer pump, an overground, encased transfer line and drop leg connection at tank 241-SY-102. This system also included a pressurized, heated water supply for in-line dilution of the waste being removed from tank 241-SY-101. The drop leg

in tank 241-SY-102 was used to minimize mixing of tank 241-SY-101 waste with the existing tank 241-SY-102 solids layer and minimize ammonia and volatile organic compounds within the SY-Farm ventilation system.

Three campaigns of transfers followed by back dilutions were accomplished. The first campaign, from December 18 to December 20, 1999, mitigated the immediate level concern by lowering the waste level by almost 15 in. and dissolving a large fraction of the original freeboard. The second transfer and top back dilution, January 25 to 28, 2000, removed the major hazard of level rise by dissolving the crust and releasing most of its stored gas. The subsequent low back dilution from February 21 to February 23 dissolved most of the soluble solids in the slurry and the remaining crust remnants. The third transfer was performed February 27 to March 2, 2000, and the final back dilution was completed on March 15, 2000. Table 7-1 provides a summary of the transfer and back dilution volumes. Since the second and third transfers followed dilutions, they also removed some of the dilution water and less of the original, undiluted waste. The actual contents of the tank after each campaign are listed in the last two columns.

Table 7-1. Tank 241-SY-101 Transfer and Dilution Volumes

(all volumes in gallons)	SY-101 Waste Transferred	Top Back Dilution	Low Back Dilution	Original Waste Left in Tank	Net Water Added to Tank
Campaign #1	89,500	26,000	36,000	974,500	62,000
Campaign #2	240,500	89,500	150,000	744,500	291,000
Campaign #3	286,000	36,500	187,000	539,000	434,000
Cumulative	616,000	152,000	373,000	539,000	434,000

Figure 7-6 shows the changes in waste level during the three transfer and back dilution operations, and Figure 7-7 shows the domespace hydrogen and ammonia concentrations over the same time period. The cumulative gas release calculated from these data, the estimated gas generation rate and the ventilation rate is 14,650 scf (Mahoney et al. 2000). This is very close to the 14,900 scf of gas estimated to be retained in the tank just prior to the first transfer. At the completion of these actions, a neutron probe run was made to see if there was any appreciable crust layer. Results presented in Figure 7-8 show a uniform count rate over the majority of the waste depth; no crust was noted from these examinations.

The surface level rise phenomenon resulted from accumulation of both gas and solids in the crust by bubbles generated in the mixed slurry below. The data show that the crust and the gas it contained no longer exist. Also, the dilution of the waste dissolved most of the soluble solids and, along with the lower temperature, greatly reduced the gas generation rate. The conditions that gave rise to the surface level rise USQ are no longer present in the tank and are not expected to recur. The current conditions and analyses further supporting this conclusion are given in Section 8.0.

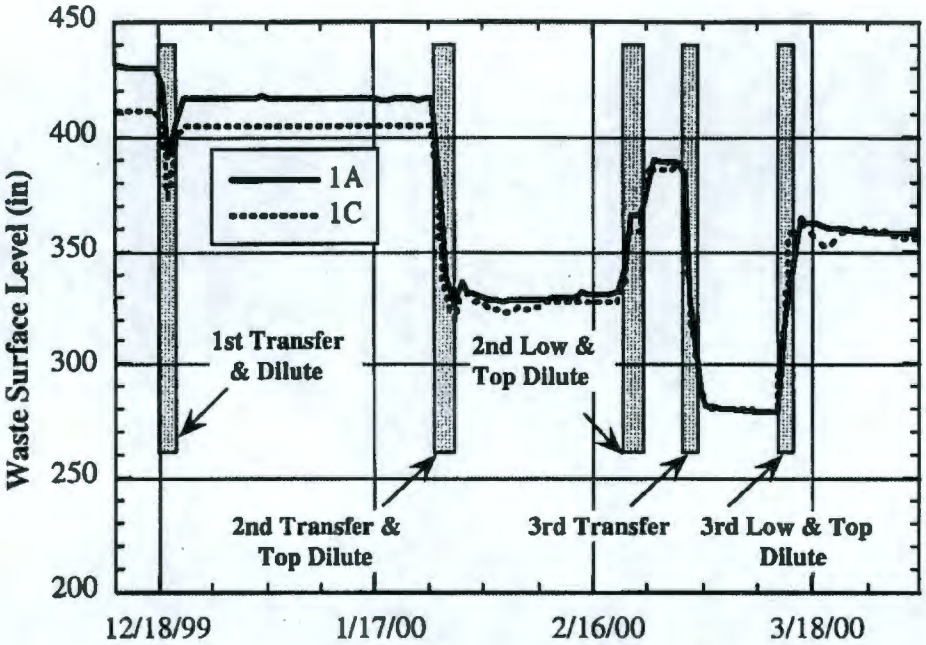

Figure 7-6. Waste Level History During Remediation

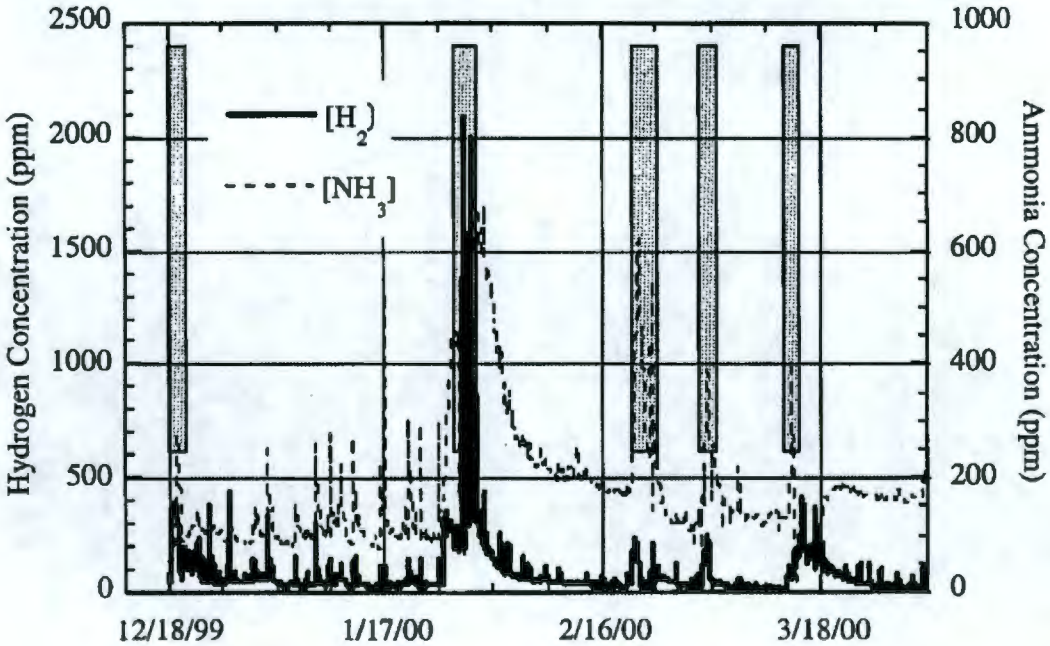

Figure 7-7. Domespace Gas Concentrations During Remediation

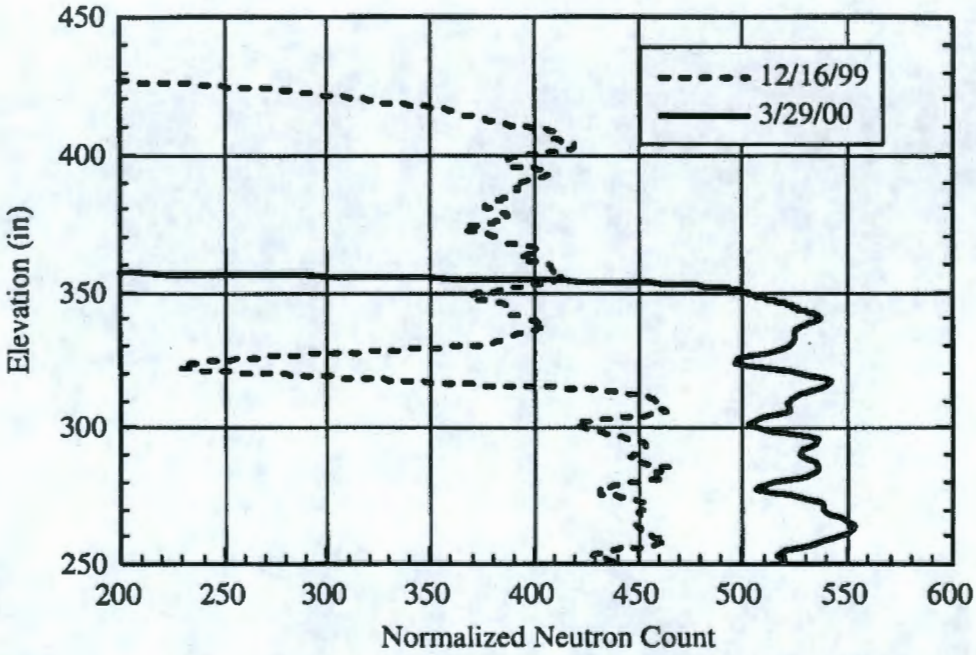

Figure 7-8. Comparison of Neutron Profiles Before and After Remediation Campaigns

8.0 CURRENT CONDITION OF TANK 241-SY-101 SUPPORTING RETURN TO NORMAL SERVICE

The tank 241-SY-101 waste transfer and water dilution volumes were selected such that the waste in tank 241-SY-101 would be similar in concentration to other DST wastes that do not exhibit crust growth (although they may have a crust) and do not exhibit BD-GRE behavior (although there may be some gas retention). Changing the waste conditions to be similar to other non-BD-GRE wastes by diluting with water was determined to be sufficient to resolve the crust growth/level rise issue and also eliminate BD-GREs (Bauer 2000). An evaluation of information available following the transfer and dilution campaigns concludes that the waste conditions have been modified such that crust growth and BD-GRE behaviors have been remediated.

8.1 EVALUATION DATA

Following the transfer and dilution campaigns, the mixer pump was run 31 times between March 17 and April 1, 2000, to complete dissolution by mixing the settled solids with the dilution water and to release the maximum possible gas. Each run was 25 minutes in duration. The discharge nozzle orientation was changed between each run to assure best mixing. As a result, the tank was well mixed from approximately 50 in. (the mixer pump discharge nozzles are about 22 in. off the bottom of the tank) up to near the waste surface. The waste below 50 inches was believed to consist of loosely settled solids easily disturbed by the jet. The mixer pump has not been run since April 1, 2000. Since that time, the waste solids have settled and have been compacting to form distinct convective and nonconvective layers of waste. A thin layer of floating waste material is also present on the waste surface.

The evaluations in this report are based on data available as of October 1, 2000. Available data include normal monitoring of waste level, temperature, and domespace gas concentrations as well as weekly neutron and gamma scans in the MITs. Grab samples were obtained April 3-6, 2000, and again on June 20, 2000, after about 90 days of waste settling. Periodic video scans of the waste surface were performed. The data collected during and subsequent to the evaluation period are summarized in Section 8.1.1 below, and grab sample analyses are given in Section 8.1.2. Temperature effects on solubility are discussed in Section 8.1.3. Evaluations relative to crust growth and BD-GRE behavior are presented in Sections 8.2 and 8.3, respectively.

8.1.1 Data Summary

- *Waste Surface Level:* The surface level initially dropped 3 in., probably due to ongoing dissolution and gas release from solids. Figure 8-1 shows the surface level trend for April through October 2000 compared with a similar six-month period when the tank exhibited BD-GREs (April through October 1990). The surface level trended slightly

downward since mid-May, which indicates negligible gas retention. (Surface level trends are evaluated for evaporation and gas retention in Section 8.3.)

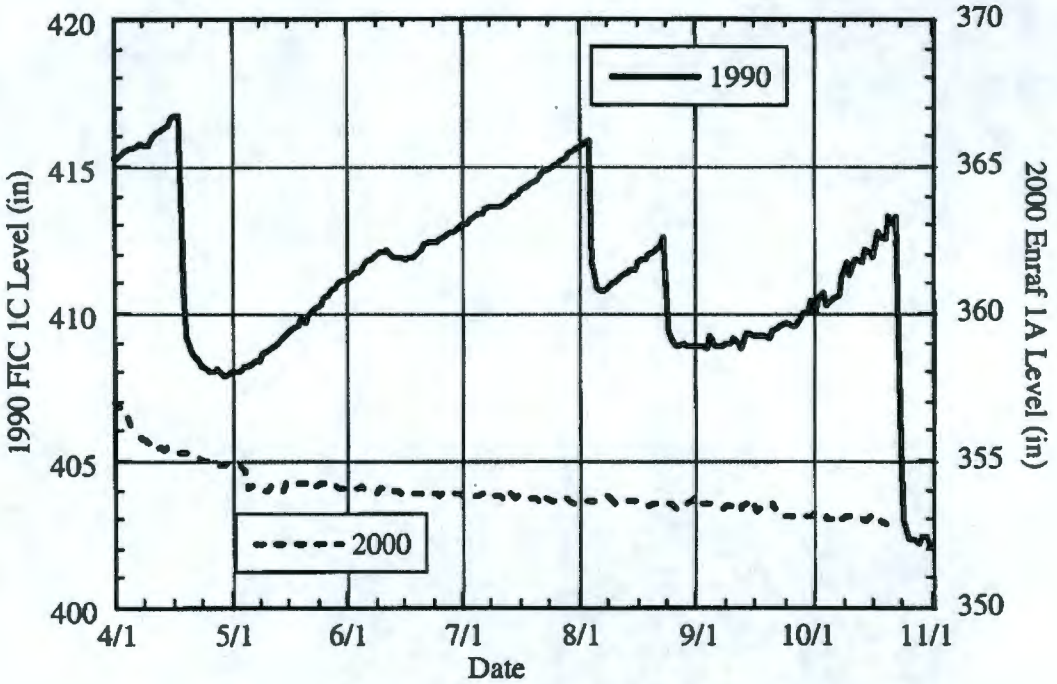

Figure 8-1. Comparison of Waste Level Behavior during April - November 1990 and 2000

- *Gas Concentrations:* Gas concentrations in the tank domespace have dropped to very low levels (< 5 ppm for H_2 and N_2O), which are near the detection threshold of the instrumentation. (Measured gas release rate and concentrations are compared to predicted values as a measure of gas retention in Section 8.3.)

- *Waste Temperature Profile and Trends:* The temperatures show relatively rapid settling in the first few weeks followed by gradually slower compaction of the nonconvective layer. The temperature profile from October 2000 is compared with the temperature profile from before and after a BD-GRE in October 1990 in Figure 8-2. The depth of settled solids is significantly less than the condition when the tank exhibited BD-GREs. (Settling rate and nonconvective layer depth are evaluated in Section 8.3.)

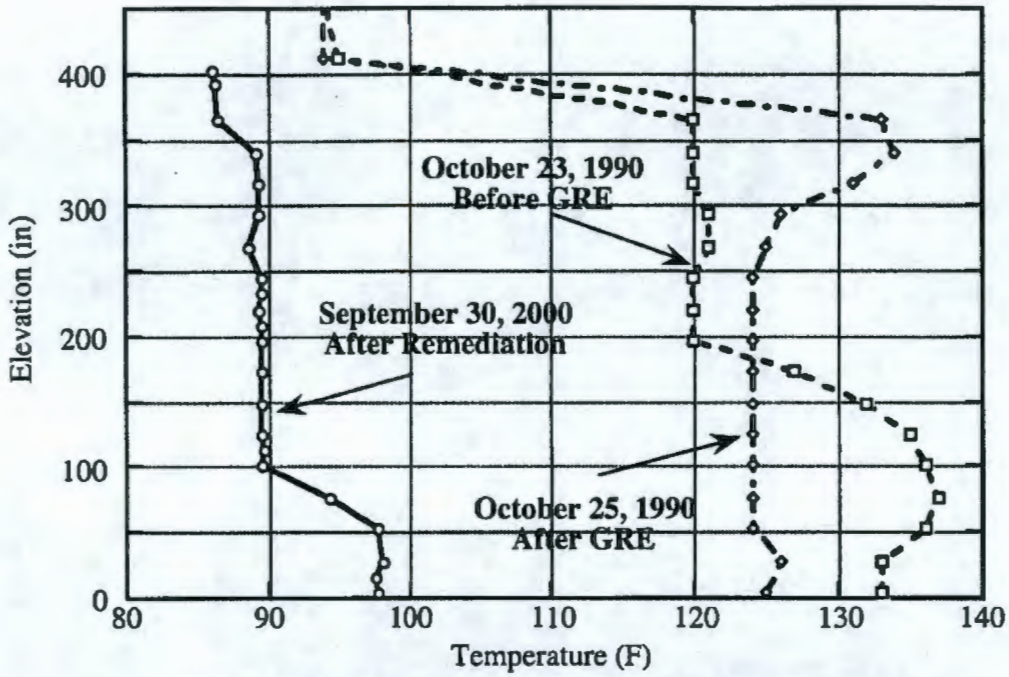

Figure 8-2. Comparison of Temperature Profiles from October 1990 and September 2000

- *Neutron Logs:* No region of low neutron count, indicating reduced water or high void fraction content, was seen near the waste surface. This indicates that the surface layer visible in the tank is thin (estimated to be < 6 in.). A region of slightly reduced water content at the bottom of the profile (below 50 in.) indicates either original, less-diluted waste in this area with lower water content, or more compacted settled solids in this region. (Neutron logs near the waste surface illustrating the thin surface layer are given in Section 8.3.)

- *Gamma Logs:* The liquid/settled solids interface inferred from the gamma logs was very consistent with the temperature profile. A higher gamma count region in the bottom ~50 in. of the settled solids confirms that this layer does not contain significant gas, but rather old (original, undiluted) waste with higher concentrations of gamma emitters. No region of lower or higher gamma counts can be detected near the surface, indicating that the surface layer is thin. (Gamma logs are used to track the nonconvective layer height in Section 8.3.)

- *Video inspection:* The surface layer appears to be less than 6-in. thick and is soft and foamy. Sludge weights and sampling devices penetrated this layer easily. Open pools of liquid were observed in June but had mostly disappeared by mid-July. The largest open liquid area was somewhat greater than 10 ft in diameter, and appeared to be under the vent header riser. (Video frames of the surface layer are shown in Section 8.2.)

- *Grab samples:* Grab samples were taken April 3-6 and again on June 20 from five elevations starting 1-in. below the surface down to 10 in. above the bottom of the tank (the lowest that the sampling apparatus can reach) (Esch 2000a, 2000b). Chemical analysis of the April samples showed the solids to be mainly sodium oxalate and aluminum hydroxide with some sodium phosphate. This composition was confirmed by polarized light microscopy (PLM) and scanning electron microscopy (SEM) which also revealed the size and shape of the particles (Herting 2000a). Only water content and bulk density or specific gravity were obtained for the June 20 samples. The average specific gravity (SpG) of the waste is 1.39. This matches the predicted value of 1.39 (Bauer 2000). (Grab sample analysis results are described in Sections 8.1.2 and 8.1.3. Waste average specific gravity is used to evaluate potential BD-GRE behavior in Section 8.3.)

8.1.2 Grab Sample Analysis Results

Analysis results for the April 3-6 samples are reported in Esch (2000a) and summarized in Table 8-1. The samples contained clear, slightly yellow liquid and varying amounts of gray/brown solids, with the settled solids fraction increasing from 30 to 72 vol% from top to bottom. The centrifuged liquids were fairly homogeneous but increased in density with depth with an average density of 1.33 g/mL. The top sample contained higher concentrations of total organic carbon, which was mainly oxalate. The centrifuged solids had an average density of 1.49 g/mL. The average specific gravity (SpG) of the waste was 1.39.

The centrifuged solids from the five April grab samples were analyzed by PLM and by scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM/EDS) (Herting 2000a).

At least five solid phases were found by the combination of PLM and EDS and are described below in order of relative abundance. Precipitated sodium nitrate and sodium nitrite were not observed in the samples.

- Sodium oxalate, $Na_2C_2O_4$ (~40%), identified by both PLM and SEM/EDS. Crystals were tiny anisotropic needles, roughly 1 x 5 microns, that tended to form agglomerates 100 microns or more in diameter.
- Aluminum hydroxide, $Al(OH)_3$ (~30%), identified by SEM/EDS and observed but not identified by PLM. Crystals were tiny (1 to 5 micron) approximately cubic in shape but are actually anisotropic.
- Sodium phosphate, $Na_3PO_4 \cdot 12H_2O$ (~20%), identified by PLM and SEM/EDS. The crystals were large rod or needles, up to several hundred microns in length.
- Sodium fluoride phosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$ (0 - 10%), identified only by PLM and only in the two deepest samples. This phase appeared as large, 100 micron, angular isotropic crystals.

- Calcium carbonate or calcium oxalate, $CaCO_3$ or CaC_2O_4 (~1%), identified by EDS x-ray spectra only.
- Chromium (~1%) of undetermined species (possibly chromium oxide) was observed with EDS x-ray spectra associated with $Al(OH)_3$ but not with sodium oxalate or sodium phosphate.

The sodium oxalate agglomerations and the long sodium phosphate needles, in conjunction with the tiny aluminum hydroxide crystals should tend to form a weak, widely separated network. PLM and SEM/EDS were also performed on the June 20 samples to determine whether further dissolution or precipitation had occurred. The results were consistent with the April samples (Herting 2000b).

A second set of grab samples was taken on June 20 to confirm the settled conditions of the tank. Only water content and bulk density or specific gravity were obtained for these samples. Analysis results are reported in Esch (2000b) and summarized in Table 8-2. The top sample contained 22% settled solids, apparently from the floating surface layer. Samples from 250 and 115 in. contained 1 to 2% solids. This is consistent with the temperature and gamma profiles, which indicated a nonconvective layer height of 112 in. at the time of sampling. Samples from 75 and 10 in. contained 82 and 100% bulk settled solids with bulk densities of 1.45 and 1.5 g/mL, respectively. After centrifuging, the solids volumes were 6.2%, 48%, and 62% for the top and the two bottom samples.

Table 8-1. Tank 241-SY-101 Grab Sample Results from April 2000

Analyte	Average Centrifuged Solids	Average Centrifuged Liquids	Overall Concentration
Density/Specific Gravity	1.49 g/mL	1.33 g/mL	1.39 g/mL
Water	53.0 wt%	60.9 wt%	59.4 wt%
Hydroxide (OH)	Not analyzed	26,300 µg/mL	1.59 wt%
Nitrate (NO_3)	72,800 µg/g	152,000 µg/mL	10.6 wt%
Nitrite (NO_2)	50,200 µg/g	95,600 µg/mL	6.77 wt%
Phosphate (PO_4)	14,100 µg/g	4940 µg/mL	0.57 wt%
Oxalate (C_2O_4)	66,900 µg/g	not detected	1.30 wt%
Aluminum (Al)	53,400 µg/g	13,400 µg/mL	1.85 wt%
Chromium (Cr)	11,900 µg/g	136 µg/mL	0.24 wt%
Sodium	145,000 µg/g	163,000 µg/mL	12.7 wt%
Total inorganic carbon	3940 µg/g	6870 µg/mL	0.49 wt%
Total organic carbon	18,400 µg/g	6160 µg/mL	0.73 wt%
^{137}Cs	144 µCi/g	262 µCi/mL	187µCi/g
^{90}Sr	41.9 µCi/g	3.73 µCi/mL	10.4µCi/g

Table 8-2. Tank 241-SY-101 Grab Samples Results from June 20, 2000

Analyte	Average Centrifuged Solids in NCL	Bulk Solids in NCL	Average Centrifuged Liquids in CL
Density/Specific Gravity	1.58 g/mL	1.48 g/mL	1.35 g/mL
Water	44.5 wt%	Not analyzed	58.8 wt%

After approximately 2 weeks in the laboratory, additional white precipitate was observed in the samples from 250 and 115 inches. The sample from 250 inches was centrifuged, with 8% centrifuged solids reported. Polarized light microscopy of the solids identified mostly sodium phosphate, with some aluminum hydroxide, sodium oxalate, and sodium fluoride phosphate. The additional precipitation was found by PLM to be mainly sodium phosphate, which is somewhat sensitive to temperature. A discussion of the solubility effects of temperature is presented in Section 8.1.3.

8.1.3 Waste Solubility Evaluation

Approximately 35% by weight of the original undissolved or dry solids in 241-SY-101 prior to the mitigation activities of 1999/2000 was sodium nitrate and sodium nitrite (Hudson et al. 1995). The solubilities of sodium nitrate and nitrite increase from 80 g/100 g water at 10 °C to about 95 g/100 g water at 30 °C, ~1% /°C. However, as discussed in Section 8.1.2, the major constituents of the dry solids are now aluminum hydroxide, sodium phosphate and sodium oxalate.

Comparison of the available solubility data as a function of temperature demonstrates a marked reduction in the effect of temperature on the solids. Solubilities given by Perry (1963) show that sodium oxalate is essentially insoluble with less than 5 g soluble in 100 g of water at 20 °C. Sodium phosphate solubility is somewhat higher, increasing from about 5 g/100 g water at 10 °C to 20 g/100 g water at 30 °C. In fact, a small amount of sodium phosphate precipitated in the June 2000 grab sample bottles when cooled to laboratory temperature.

The solubility of aluminum can depend on both Na^+ and OH^-. The data reported by Barney (1976) are as sodium aluminate, but also, from the dependence on sodium hydroxide concentration, show the equilibrium solid phase to be actually gibbsite instead of sodium aluminate once the sodium hydroxide concentration falls below about 1.5 molar. Barney (1976) reported the aluminum concentration for four temperatures: 20, 40, 60, and 80 °C. The results do not show a trend among these temperatures, from which we infer the

temperature dependence is not steep. Therefore, we do not expect changes in temperature to cause significant changes in the mass of gibbsite.

The tank 241-SY-101 supernatant liquid, in its current state, is undersaturated relative to sodium nitrate and nitrite, and the solubilities of saturated species either have a small dependence on temperature or make up no more than 20% of the solids. These data indicate that no significant precipitation or dissolution (in regards to gas retention and release behavior) should occur with changes in temperature in tank 241-SY-101.

The lack of a temperature effect on the mass of solids in diluted tank 241-SY-101 waste has been confirmed experimentally. Person (1999) found that 30% dilution with water was sufficient to cancel the effect of temperature on the quantity of dry solids in composite samples from 1998 cores, Figure 8-3. These findings are consistent with the earlier results of Tingey et al. (1994). They showed, at higher temperatures, that a dilution of composite samples of the 1991 nonconvective layer cores of between 25 and 54% with 2M NaOH also removed the effect of temperature on the quantity of filtered solids (Figure 8-4). Based on these findings, the current dilution of approximately 80% should be more than sufficient to preclude any precipitation or dissolution of solids with changes in temperature in tank 241-SY-101.

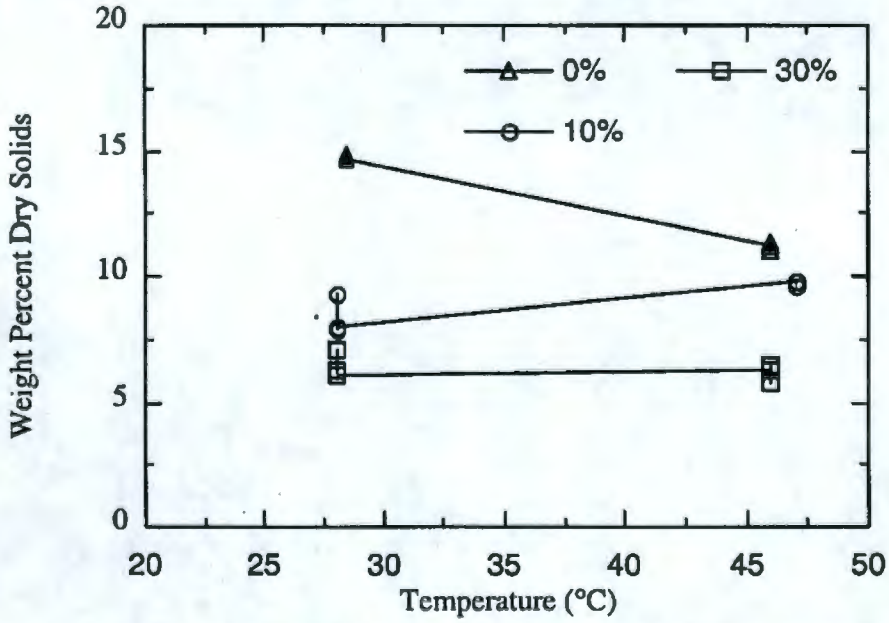

Figure 8-3. Weight Percent of Dry Solids as a function of Temperature at 0, 10, and 30% Dilution With Water (Person 1999)

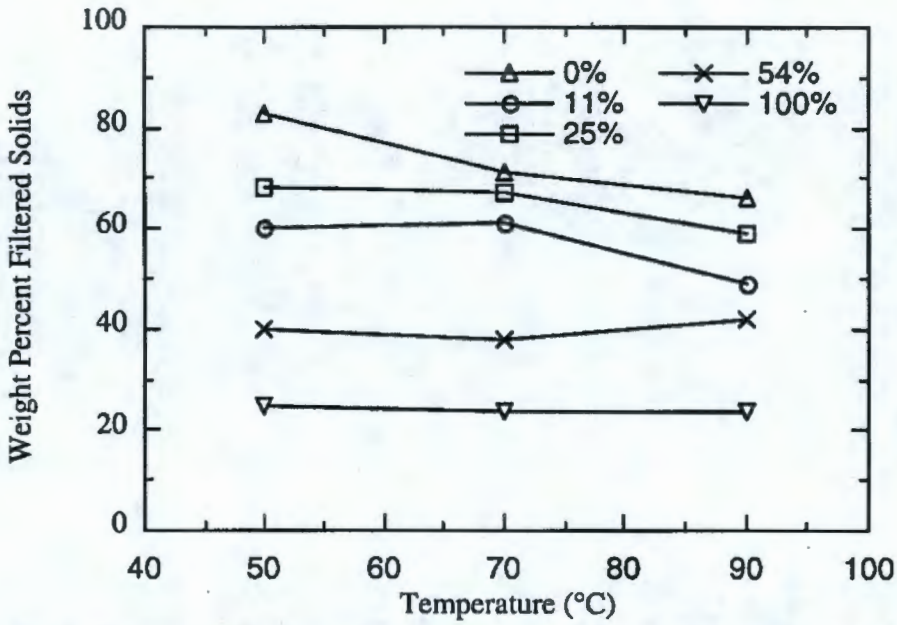

Figure 8-4. Weight Percent of Filtered Solids as a function of Temperature at 0, 11, 25, 54, and 100% Dilution with 2M NaOH (Tingey et al. 1994)

Finally, there have been no identifiable changes in the nonconvective layer depth or crust thickness in any of the other DSTs over the last five years, during which time the waste temperatures have decreased as much as 10 °F with seasonal variations of as much as 3 °F (Hedengren et al. 2000). If the waste configuration in these more concentrated tanks did not change with moderate temperature changes, there is no reason to believe that the more dilute waste in tank 241-SY-101 will be significantly affected by the small temperature changes anticipated in the future.

8.2 EVALUATION FOR CRUST GROWTH

Crust growth remediation is based on diluting the waste to dissolve the soluble salts, particularly sodium nitrate and sodium nitrite. These salt solids were theorized to be the main contributors to crust growth behavior. Following dilution, the thick, strong crust was replaced by a thin layer of scum (floating material composed of solid particles, gas, and entrained liquids). Scum is the terminology used in this report to describe the floating surface layer to differentiate this material from the thick (up to 10 ft thick) and strong (yield strength estimated up to several thousand Pa) "crust" that was present before dilution operations occurred.

Waste samples taken at the surface contained 22% solids, apparently from the surface scum layer. Based on sample analysis, we conclude that the scum is predominately sodium oxalate

and aluminum hydroxide. Sodium oxalate scum is also present in tank 241-AN-107, which is thin and only covers a portion of the waste surface.

Video inspection of the surface indicates a thin scum layer with negligible strength. Sludge weights and grab sample bottles were observed to penetrate this layer easily. Open pools of liquid were observed in May and June 2000 but had mostly disappeared by mid-July 2000. No large pools were visible as late as September. Video frames of the same location of the edge of the pool captured on June 20 and July 25 are shown in Figure 8-5. The largest open liquid area was somewhat greater than 10 ft in diameter, and appeared to be under the vent header riser.

The scum layer is too thin and insubstantial to be measured with available means. The video scans cannot see the portion, if any, below the liquid surface, and there is no clean, vertical cut through the scum across which a height could be measured. The heights of the surface irregularities have been estimated at roughly 2 inches. Neutron and gamma logs near the waste surface obtained on September 28, 2000 are shown in Figure 8-6. The sharp decrease in gamma count at about 347 in. is attenuation by a metal spacer within the MIT. The decreasing neutron and gamma counts from about 350 in. (from the bottom of the tank) upward to the waste surface cannot be distinguished from the Gaussian response of the probes passing through a sharp liquid interface. In any case, the maximum thickness that could be attributed to a floating layer, ignoring the limitations of the measurement, is about 6 inches as shown by the shaded area on the plot. Therefore, the scum layer thickness can be said to be bounded in the range of 2 to 6 inches. The gas content of the scum layer cannot be quantified from any of these data. However, the foamy appearance and lack of strength of the material suggests a high void fraction.

Figure 8-5. Video Frames Showing Scum Layer

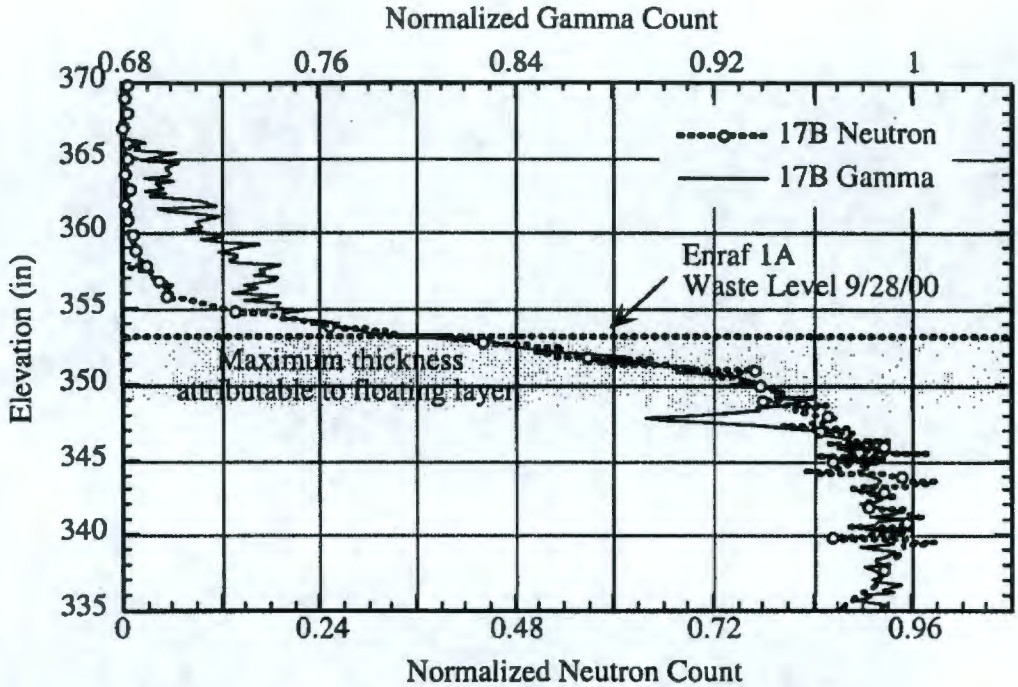

Figure 8-6. Neutron and Gamma Profiles near the Waste Surface

The surface level rise phenomenon resulted from accumulation of both gas and solids in the crust by armored bubbles generated in the mixed waste slurry below. The data show that the crust and the gas it contained no longer exist. The mixer pump is no longer being run to encourage the motion of armored bubbles to the surface. The dilution of the waste with water and the resulting much lower waste temperature, have greatly reduced the gas generation rate. The hydrogen generation rate estimated with the Hu (2000) model is about 4 ± 2 ft^3 per day (which is equivalent to 5 ± 3 ppm at 550 cfm). Results were calculated using the waste temperatures of July 20, 2000. The waste has cooled since then, slightly reducing the generation rate. The hydrogen generation equates to a total gas generation rate of 13 ft^3 per day. This is a factor of 7 less than the 90 ft^3 per day generation rate prior to remediation (Conner and Koreski 2000).

The mechanism for crust growth is also no longer present. Kubic and Beloussov (1999) observed that other DSTs with thick crusts have a high concentration of sodium nitrite and nitrate whose solubility increases with temperature. Double-shell tanks with thin crusts are high in sodium carbonate, sulfate, and oxalate where the solubility is more constant or even decreases with increasing temperature. Since the waste surface is the coldest location, crusts tend to grow there if the solubility of one or more major constituents decreases with decreasing temperatures, i.e., sodium nitrate and sodium nitrite. The grab sample analysis shows the post-remediation solids in the tank to be high in sodium oxalate, sodium phosphate and aluminum hydroxide. Since these are nearly insoluble at the current and projected temperatures, the influence of temperature on solubility in the scum layer should be minimal.

Regardless of how thin and insubstantial the current scum layer is, the concern is that, if a crust were to grow in the future, what hazard would it pose. Not only has the mechanism to form crust been remediated, but also far less mass is available to form crust now that most of the soluble solids have been dissolved. The tank now contains only 100 inches of solids at a volume fraction of about 16%. In the hypothetical case in which this entire mass were to form a crust at the waste surface at the same 35% solids volume fraction and 25% average void fraction as in the 120-inch thick pre-dilution crust, it would produce a layer 64 inches thick that would contain less than 6000 scf of gas. This would be a significantly thick crust and a significant retained gas volume; however, it would be substantially less than that required to be a safety issue. Because all of the solids would be committed to the crust, this hypothetical case would result in a tank condition in which BD-GREs are not possible.

In summary, the conditions that gave rise to crust growth in tank 241-SY-101 are no longer present in the tank, and a thick crust is not expected to recur.

8.3 EVALUATION FOR BUOYANT DISPLACEMENT GAS RELEASE EVENT POTENTIAL

The primary requirement for a BD-GRE is sufficient gas retention to achieve buoyancy. The retained gas volume required for buoyancy is determined by the ratio of the bulk densities of the convective and nonconvective layers. The gas volume fraction required to make the nonconvective layer neutrally buoyant, α_{NB}, is given by Equation 4-2. A BD-GRE actually requires a slightly higher gas volume fraction to offset the waste strength, but the increment is small and can be ignored in practice.

In tanks that exhibit BD-GREs, the waste has been concentrated beyond the solubility limit of the major sodium salts. This has precipitated a relatively deep nonconvective layer and raised the concentration of radionuclides and organic complexants which increases the gas generation rate per unit volume. The process of concentrating the waste also increases the density of the convective layer so a smaller gas volume is required in the nonconvective layer to achieve buoyancy.

Dilution reverses these trends. Dissolution of soluble solids decreases the depth of the nonconvective layer and dilution of the reactants reduces the gas generation rate per unit volume. At the same time, dilution also reduces the density of the convective layer when the waste becomes subsaturated in one or more of the major salts. This results in a larger gas fraction in the nonconvective layer being required for buoyancy, reducing the potential for reaching BD-GRE conditions. A relatively small volume of gas retention is expected in tank 241-SY-101 at the steady-state where gas generation is equal to background gas release. As discussed in the following sections, tank 241-SY-101 conditions are such that no significant gas retention can be detected. Additionally, evaluation of BD-GRE potential using predictive indicators for possible future BD-GRE behavior is provided.

8.3.1 Evaluation of Gas Retention

Gas retention can be detected and the retained gas volume estimated using changes in the waste surface level (Meyer et al. 1997). The current tank 241-SY-101 level data indicate that the waste is not retaining gas. Evaporation, additional solids dissolution and thermal expansion/contraction can effect the measured waste surface level. The largest effect is due to the evaporation of water. The waste level history since May 6, 2000, corrected for evaporation, is shown in Figure 8-7. After about May 16, the corrected level is essentially flat. The corrected level on that date is the same as that of September 30.

The corrected surface level has uncertainty introduced due to the error in the measured humidity. The evaporation correction is based on the difference in water content of the inlet air (measured by the Hanford meteorological station) and the ventilation exhaust stream (measured by a relative humidity probe in the SY-101 exhaust duct). The sensitivity of the evaporation correction to a $\pm 20\%$ variation in measured exhaust relative humidity is also shown in Figure 8-7. The upper curve represents a case where the exhaust relative humidity is 20% greater than measured, and often reaches 100 % relative humidity. The upper curve is considered bounding and would be equivalent to approximately 70 ft^3/month in-situ gas retention, which is insignificant.

Another measure of retained gas volume is the response of waste level to changes in barometric pressure (dL/dP). The current 241-SY-101 waste configuration meets the criteria for applying this method (Meyer et al. 1997; Hedengren et al. 2000). However, this method is not very sensitive, especially during the summer months when barometric pressure swings are minimal, and can only detect significant retained gas volumes. One appreciable pressure swing (1.8 kPa) occurred on June 12, 2000, for which the detection limit was about 2000 ft^3 of retained gas in-situ. The barometric pressure and waste level transients are shown in Figure 8-8, and the pressure-level correlation for this event is shown in Figure 8-9. The correlation indicated a void fraction of 0.03 for an in-situ gas volume of 1,300 ft^3. However, the correlation was very poor, and the calculated gas volume can only be claimed to be below the detection limit of 2,000 ft^3. This is consistent with the conclusion that gas retention is not significant. Three additional pressure swings occurred in September and October 2000, that gave similar indications of negligible gas retention.

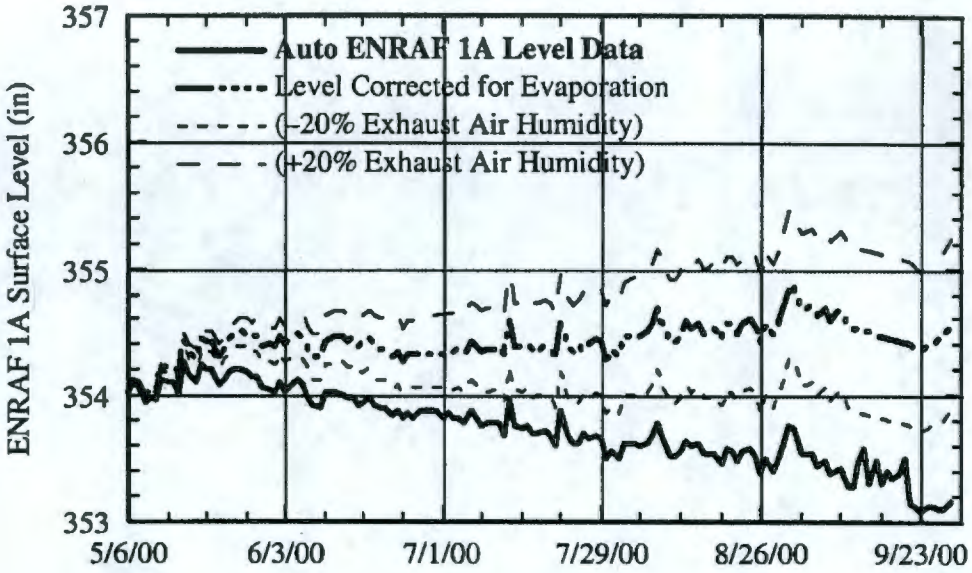

Figure 8-7. Waste Level and Level Drop Due to Measured Evaporation

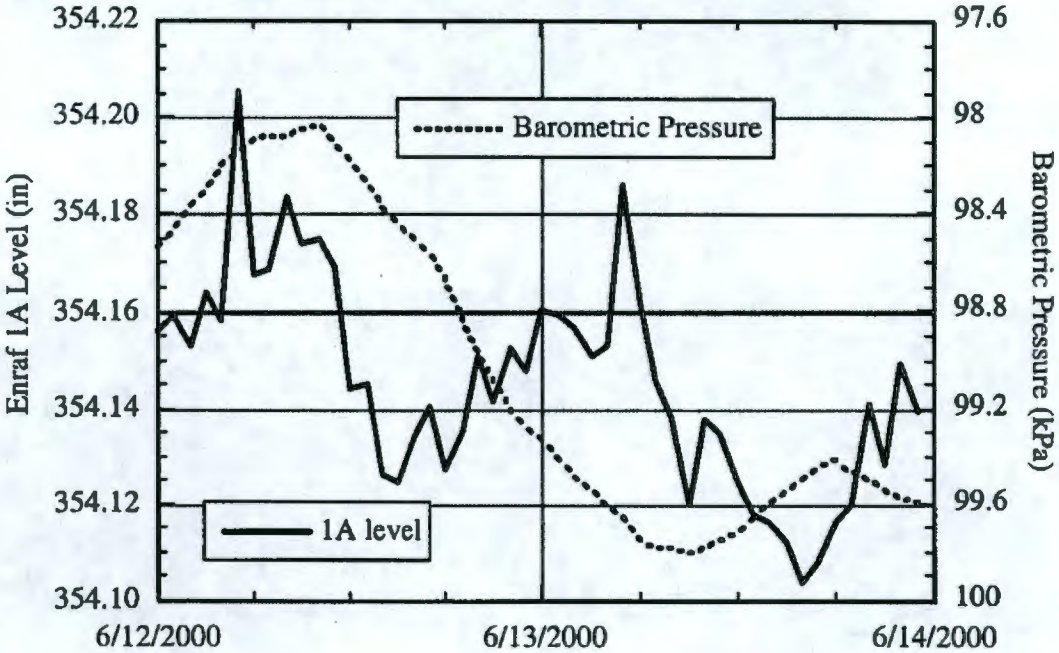

Figure 8-8. Waste Level and Barometric Pressure Transient, June 12-14, 2000

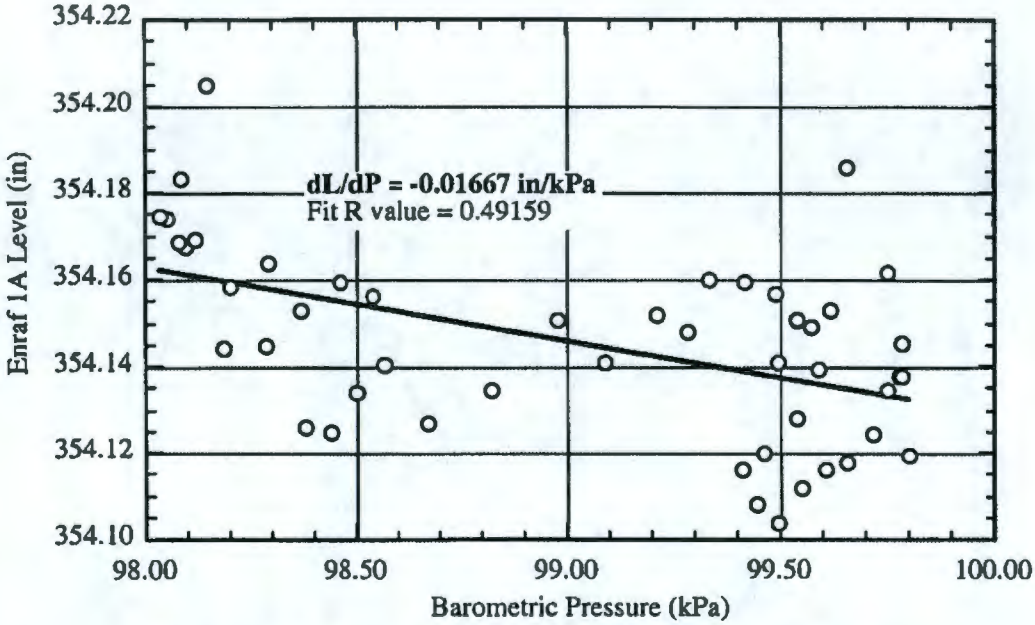

Figure 8-9. Correlation of Level and Barometric Pressure

Gas retention is also indicated if the domespace hydrogen concentration consistently measures less than the domespace hydrogen concentration corresponding to the generation rate. The hydrogen concentration history and the concentration predicted using the Hu (2000) model are shown in Figure 8-10. The average hydrogen concentration is near the detection limit of the gas chromatographs (GCs) where the reading is on the same order as the uncertainty, estimated to be ± 3 ppm. Since late July, however, the domespace hydrogen concentration has increased to as high as 4 ± 3 ppm, which corresponds to a hydrogen release rate of about 3 ± 2 ft^3/day at an average ventilation rate of 550 cfm. As the diluted waste has cooled between April 2 and July 17, 2000, the estimated hydrogen generation rate decreased from 4.8 ± 2 ft^3 per day to 4 ± 2 ft^3 per day (which is equivalent to 5 ± 3 ppm at 550 cfm). Comparison of the domespace concentration and the concentration predicted by the estimated gas generation rate is consistent with the conclusion that gas retention is not significant. At the limits of the uncertainties any gas retention indicated by a difference between release and generation should also be measurable by other methods such as surface level rise. The absence of indications from these primary sources supports the conclusion that gas retention, if occurring, is not significant.

From all of the above data and evaluations, the conclusion is that gas retention is currently negligible. However, even if the waste behavior were to change unexpectedly and begin retaining gas at the maximum rate, gas retention to neutral buoyancy and, therefore, BD-GREs could not occur for almost two years. Based on the convective layer and nonconvective layer density measurements of 1.35 g/mL and 1.48 g/mL, respectively, from the June 20 grab samples, a void fraction of at least 0.09 is required for buoyancy according to Equation 4-2. If the void fraction were to rise to 0.09, the current 100-inch nonconvective

layer depth would increase to 110 inches [$H_{NCL} = H_0/(1-\alpha_{NCL})$ assuming the current void fraction is zero]. This requires retention of about ($V = \alpha_{NCL}H_{NCL}A$) 3,600 ft^3 of gas in-situ at an average 2.1 atm of pressure, or about 7,700 ft^3 at 1 atm. This is less than the Watch List criterion of 8,650 ft^3. If the retained gas is 30% hydrogen, the complete retention of the post-remediation hydrogen generation rate of 4 ft^3/day would require about 600 days to accumulate this volume.

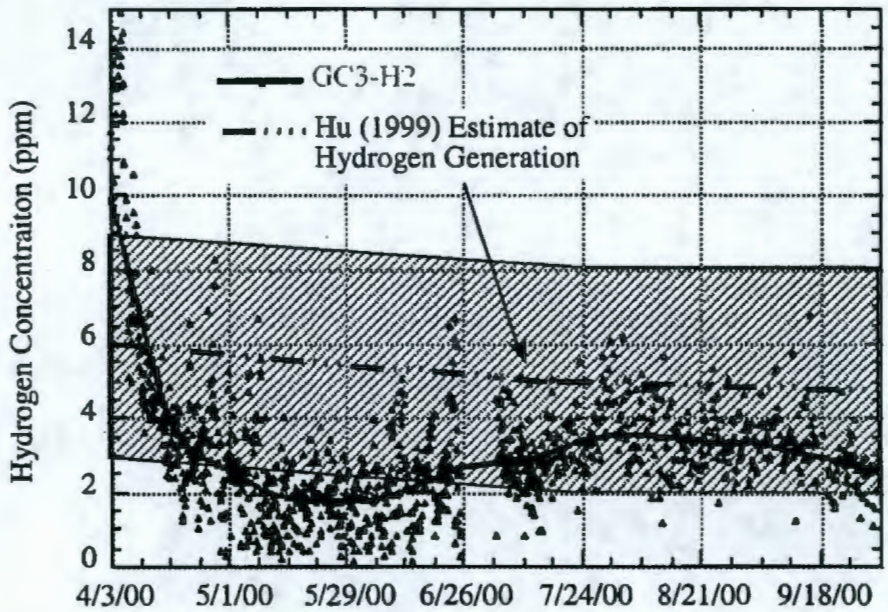

Figure 8-10. Hydrogen Concentration History

8.3.2 Application of Buoyant Displacement Gas Release Event Predictive Indicators

The transfer and back dilution campaigns were planned to change the waste in tank 241-SY-101 to a state that would not be susceptible to BD-GREs. This state was selected by comparing values of groups of physical parameters for DSTs that exhibit BD-GREs and those that do not exhibit BD-GREs. Remediation transfer and dilution volumes were selected such that the predicted parameter values for tank 241-SY-101 matched those typical of non-BD-GRE tanks (Bauer 2000). This section summarizes the parameter groups used and their values for the waste configuration in tank 241-SY-101.

Three parameters or combinations of parameters were used[3] to differentiate BD-GRE tanks from non-BD-GRE tanks as follows:

- **Average Specific Gravity (SpG):** Based on experience from evaporator operations, hundreds of tank-years of waste storage experience at Hanford, and models of waste behavior, average specific gravity of the waste in the tank is used to separate BD-GRE and non-BD-GRE tanks in the waste compatibility criteria used for tank farms operations. Since the application of this criterion to tank farm transfer and evaporator operations, no new BD-GRE tanks have been created. A limit of 1.41 is generally accepted to differentiate BD-GRE and non-BD-GRE tanks (Fowler 2000).

- **SpG_{CL}*H_{NCL}**: The product of the convective layer specific gravity (SpG_{CL}) and the nonconvective layer depth (H_{NCL}) was determined empirically to be a discriminator of BD-GRE behavior (Estey and Guthrie 1996). Physically, a high SpG_{CL} indicates a low neutral buoyancy void fraction, and a large H_{NCL} is associated with increased gas retention. The values are normalized to the value for tank 241-AW-101, the minimum for BD-GRE tanks, to make unity the limit for BD-GRE behavior. Therefore, a value of less than unity is indicative of non-BD-GRE behavior.

- **Buoyancy Ratio**: This is a semi-empirical relation (Meyer and Wells 2000) that estimates the average waste void fraction based on a balance of gas generation and background release. The buoyancy ratio, BR, represents the average nonconvective layer void fraction divided by the neutral buoyancy void fraction. A buoyancy ratio of less than unity indicates that buoyant conditions would not occur. The buoyancy ratio is calculated for steady-state conditions using Equation 8-1.

$$BR = \frac{\alpha_{NCL}}{\alpha_{NB}} = \frac{CH_{NCL}^2}{\rho_{NCL} - \rho_{CL}} \left(\frac{GT}{P} \right)^{1/3} \tag{8-1}$$

where: BR is the buoyancy ratio.
α_{NCL} is the average void fraction in the nonconvective layer,
α_{NB} is the neutral buoyancy void fraction given by Equation 4-2,
C is a dimensional constant (C=863), adjusted so that Equation 8-1 is unity for tank 241-AW-101, the minimum BD-GRE tank,
H_{NCL} is the nonconvective layer depth (m),
ρ_{NCL} and ρ_{CL} are the nonconvective and convective layer densities, (kg/m^3),
G is the molar gas generation rate per unit volume (mol/m^3-d), and
T and P are the nonconvective layer temperature (K) and pressure (Pa).

[3] The concentration criteria of aluminum, sodium, nitrite, and total organic carbon were also applied in the initial evaluation, but proved to be poor discriminators of BD-GRE behavior. Hence, only the physical parameters are used in this assessment

To evaluate the three predictive indicators, data on the waste layer depths, densities, and gas generation rate are needed. The data representing the post-remediation waste configuration are presented in Table 8-3. Two sets of data are shown. The first is the predicted waste configuration for the transfer of 525 kgal and back dilution with 434 kgal of water that was used to plan and execute the transfer and dilution campaigns. The second represents the conditions as of October 1, 2000, determined from data available for this evaluation. The predicted waste configuration and densities are based on the results of dilution tests (Rassat et al. 2000). The predicted gas generation rate was based only on dilution and did not account for temperature change. It was intended to be an upper bound. Uncertainties in the predicted values were determined from a Monte-Carlo simulation and represent the 99% confidence interval.

The convective layer density listed is an average of the centrifuged liquid densities determined from the June 20, 2000 grab sample data, 1.35 g/mL. The nonconvective layer density of 1.50 g/mL is computed from the average bulk density from the June 20 samples, 1.48 g/mL, adjusted for the change in nonconvective layer height. The height has decreased from 112 inches on June 20 to 100 inches as of October 1. The gas generation rate was estimated by applying the Hu (2000) correlation to the temperatures measured on October 1 and chemical composition determined from the grab sample analyses.

Table 8-3. Tank 241-SY-101 Post Remediation Waste Configuration

Parameter		Predicted	October 2000
Layer Depth (in.):	Convective (H_{CL})	270 ± 32	253 ± 6
	Nonconvective (H_{NCL})	64 ± 30	100 ± 3
Layer Density (g/mL):	Convective (SpG_{CL})	1.34 ± 0.06	1.35 ± 0.02
	Nonconvective (SpG_{NCL})	1.60 ± 0.11	1.50 ± 0.04
NCL Pressure (atm)		2.0 ± 0.16	2.0 ± 0.03
NCL Temperature (°F)		89 ± 1	92 ± 1
NCL Solids Volume Fraction		0.30 ± 0.12	0.17 ± 0.02
Gas Generation Rate (scfd)		44 ± 13	13 ± 7
Neutral Buoyancy Void Fraction (α_{NB})		0.16 ± 0.06	0.10 ± 0.03

The most accurate indicators of nonconvective layer depth are the waste temperature profiles and gamma logs. Figure 8-11 shows a close-up of the temperature profiles around the convective and nonconvective layer interface at Risers 17B and 17C. The boundary between the convective and nonconvective layers is quite distinct at about 100 inches as of October 1. This result agrees with the indications of gamma logs in both risers shown in Figure 8-12. The raw gamma counts have been normalized by the count at 150 inches to make the profiles overlay. Gamma radiation in the waste is primarily the result of decay of ^{137}Cs, which is highly soluble and resides mainly in the liquid. The reduced liquid content in the nonconvective layer reduces the gamma count and indicates its depth was about 99 inches for the September 28 log. Thus, the average nonconvective layer height is taken as 100 inches.

Table 8-3 reveals a significant difference between the predicted and current nonconvective layer depth. The nonconvective layer depth estimate in the pre-remediation prediction was based on the assumption that the remaining solids would settle/compact to the same volume fraction they occupied prior to dilution. The post-remediation nonconvective layer has a lower solids volume fraction than the predicted condition assumed. This is the primary source of the difference between the predicted and October 2000 values of the nonconvective layer depth as well as the other parameters related to it.

Based on the PLM and SEM of the April and June grab samples discussed in Section 8.1, the solids consist of about 40 vol% aluminum hydroxide, 30 vol% sodium oxalate and about 20 vol% sodium phosphate. The long, needle-like crystals of sodium phosphate and the weak agglomerations of sodium oxalate crystals explain the low solids volume fraction. No bubbles were observed in PLM of either the April or June grab samples.

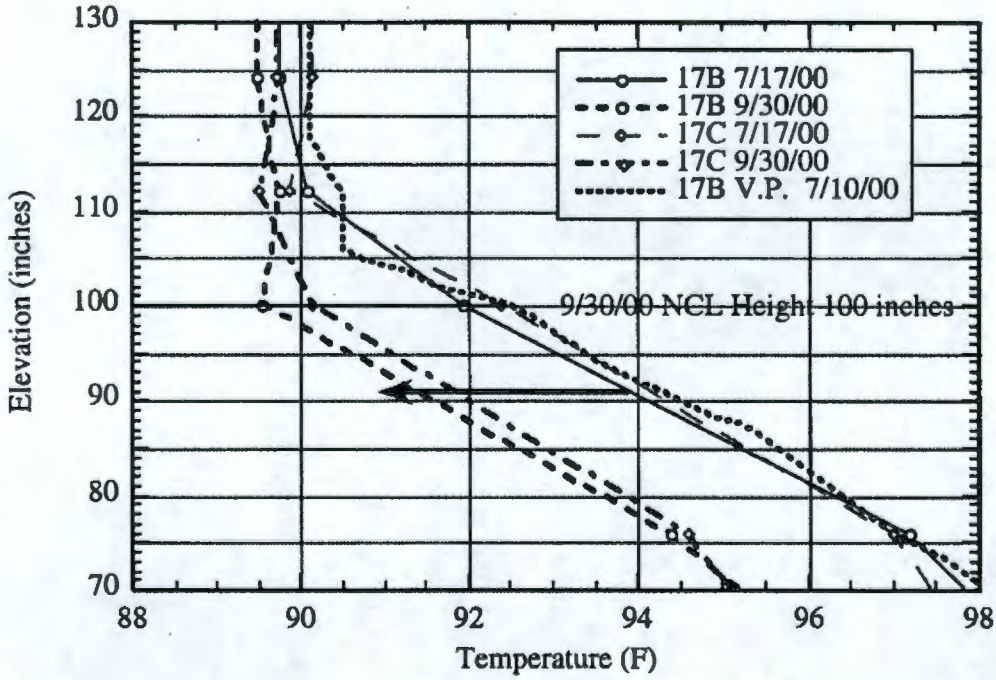

Figure 8-11. Temperature Profiles Near the Top of the Nonconvective Layer

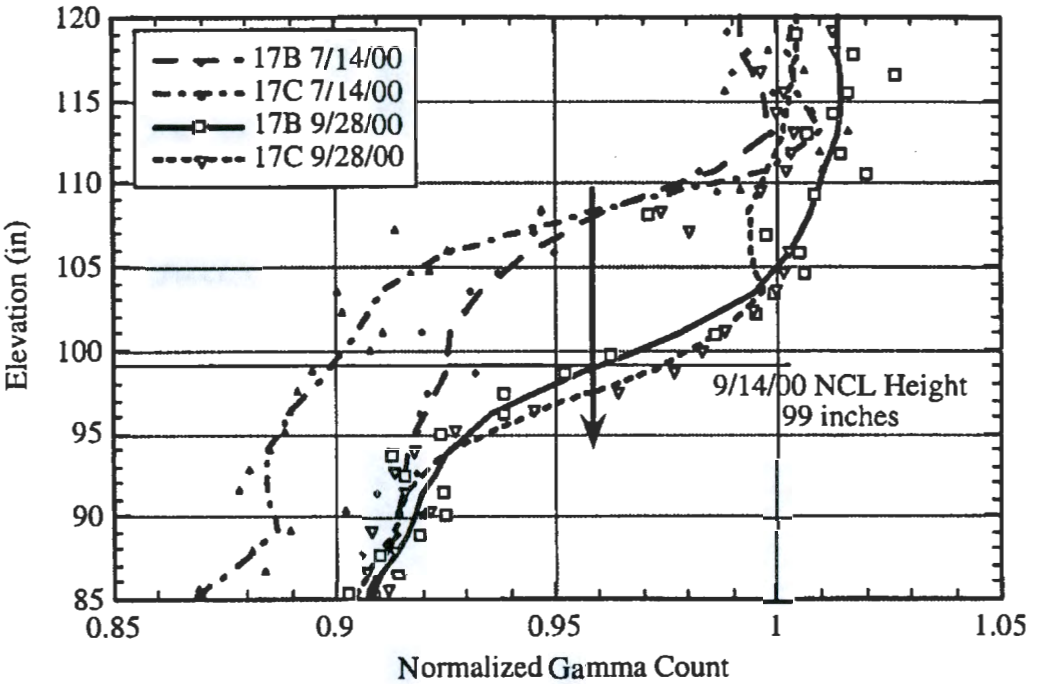

Figure 8-12. Gamma Profiles Near the Top of the Nonconvective Layer

The trend in nonconvective layer depth is shown in Figure 8-13, which includes all the gamma and temperature profile layer thickness indicators through October 1, 2000. The nonconvective layer thickness trend can be projected between the bounds of a constant thickness and a linear fit to the recent data trend as shown in Figure 8-13. The nonconvective layer height as of October 1, 2000 is at 100 inches and may decrease a few more inches. Figure 8-13 also shows the predicted nonconvective layer height of 64 ± 30 inches.

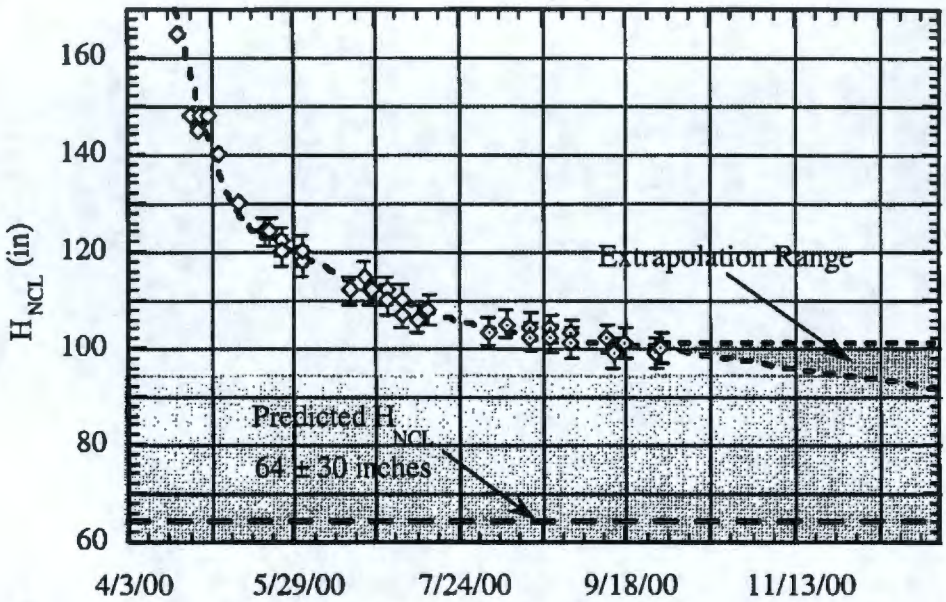

Figure 8-13. Trend of Nonconvective Layer Depth

8.3.3 Results of Evaluation of Buoyant Displacement Gas Release Event Predictive Indicators

The values of the three physical parameters evaluated with the data shown in Table 8-3 are given in Table 8-4, and the results are summarized as follows:

- Average Specific Gravity (SpG): The measured average specific gravity is 1.39 ± 0.02 which is less than the criterion of 1.41, even including the uncertainty, and matches the predicted value of 1.39 ± 0.07.

- $SpG_{CL}*H_{NCL}$: The value as of October 1 was 0.85 ± 0.04 which is less than the criterion of 1.0 accounting for the uncertainty.

- Buoyancy Ratio: As of October 1, the buoyancy ratio was 0.78 ± 0.19. This is also below the criterion of 1.0 including the uncertainty.

Table 8-4. Tank 241-SY-101 Buoyant Displacement Gas Release Event (BD-GRE) Predictive Parameter Values

	SpG_{avg}	$SpG_{CL}*H_{NCL}$ Normalized	Buoyancy Ratio
As Predicted	1.39 ± 0.07	0.54 ± 0.25	0.26 ± 0.19
As of 10/1/00	1.39 ± 0.02	0.85 ± 0.04	0.78 ± 0.19

The values in Table 8-4 show the predicted values for all three parameters are below the threshold indicating potential BD-GREs. These values are compared to the other BD-GRE and non-BD-GRE DSTs in Figures 8-14 through 8-16. In the figures, the squares represent pre-mitigation and predicted conditions in 241-SY-101. The circle is the 241-SY-101 state as of October 1. The triangles show tanks that exhibit BD-GREs, and the diamonds indicate the tanks which do not have BD-GREs (non-BD-GRE tanks) but are closest to the BD-GRE condition being evaluated. The vertical separation on the plots has no significance and is included only to improve clarity.

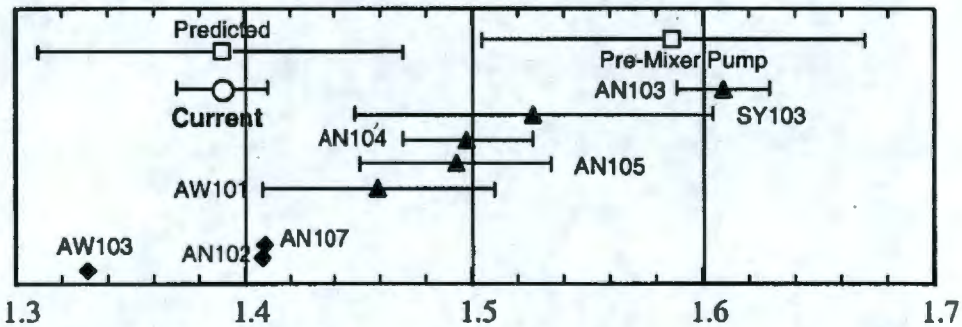

Figure 8-14. Average Specific Gravity for Tank 241-SY-101 and Other Double-Shell Tanks

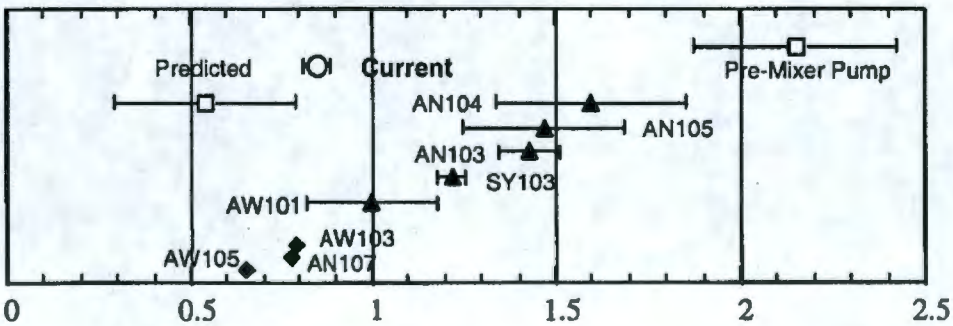

Figure 8-15. $SpG_{CL}*H_{NCL}$ for Tank 241-SY-101 and Other Double-Shell Tanks

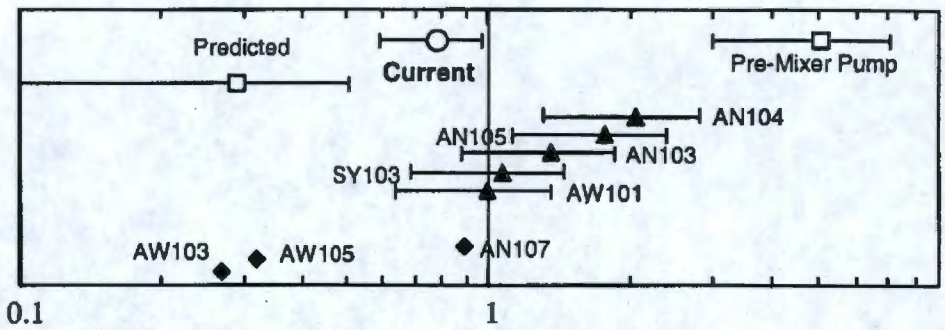

Figure 8-16. Buoyancy Ratio for Tank 241-SY-101 and Other Double-Shell Tanks

8.4 CONCLUSION OF EVALUATION FOR BUOYANT DISPLACEMENT GAS RELEASE EVENT POTENTIAL

The primary requirement for a BD-GRE is sufficient gas retention to achieve buoyancy. Available data and evaluations led to the conclusion that since remediation actions have been completed and the mixer pump has been off, there is no indication of significant gas retention. In addition, analysis of the physical parameters that can correlate observed BD-GRE behavior and non-BD-GRE behavior in other DSTs shows that tank 241-SY-101 meets criteria for non-BD-GRE behavior. It is, therefore, concluded that BD-GRE behavior in tank 241-SY-101 has been remediated.

9.0 RESOLUTION OF THE FLAMMABLE GAS SAFETY ISSUE

Referring to Figure 2-1, resolution of the Safety Issue can occur when it can be shown that the two conditions at the right hand side of the figure no longer exist. These two conditions are:

- "Not within approved safety envelope (USQ)" and
- "Not properly analyzed or mitigated."

The flammable gas USQ was closed for tank 241-SY-101 in 1996 (Wagoner 1996) and for all of the other tanks in 1998 (Wagoner 1998a, Wagoner 1998b). The waste surface change USQ will be closed upon the U.S. Department of Energy, Office of River Protection (DOE-ORP) approval of an Authorization Basis (AB) amendment. This Authorization Basis amendment was submitted in September 2000, and when approved, tank 241-SY-101 will be "within approved safety envelope."

Section 5.0 of this report provided a discussion for the characterization and evaluation of tank 241-SY-101. Section 6.0 covered the efforts taken to mitigate the buoyant displacement GREs. Section 7.0 discussed the level rise issue and the remediation actions. Finally, Section 8.0 showed that, based on evaluation of post-remediation conditions, the tank no longer behaves in an unsafe manner and could be returned to normal service. The waste composition and characteristics have been analyzed and changed such that there is no tendency for crust growth or gas retention sufficient to allow BD-GREs and is, therefore, "properly analyzed and mitigated."

Therefore, the conditions represented by the two blocks at the right hand side of Figure 2-1 will no longer exist, and the Flammable Gas Safety Issue for tank 241-SY-101 can be declared resolved, upon approval of the Authorization Basis amendment.

10.0 REMOVAL OF TANK 241-SY-101 FROM THE WATCH LIST

Section 3.3 provided the DOE-approved criteria for placing a tank on the Watch List and for removal from the Watch List. The criteria were centered on a "containment related tank design limit." Containment is interpreted to mean the portions of the tank system that hold the bulk of the waste. Therefore, containment is provided by the tank's two shells (the primary and secondary shells). Controlling the spread of airborne contamination is confinement. Confinement is provided by the filtered ventilation system. The containment design limit, therefore, is the design strength of the tank shells, in particular the primary shell.

Tank 241-SY-101 can be removed from the Flammable Gas Watch List when it can be shown that there is no credible means by which a volume of gas can be released to the domespace that, if burned, would fail the tank structure. The evaluated failure pressure for the tank structure is about 60 psig. Structural analysis of flammable gas deflagrations in tank 241-SY-101 concluded that structural acceptance criteria (no failure of the leak-tight integrity of the primary or secondary tank liners, no gross structural deformation of the liners, no large liner tears) are met if the burned gas volume is 8,650 scf or less (LANL 1996). Therefore, when the maximum possible gas release in tank 241-SY-101 is (and can be kept) well below 8,650 scf, the tank satisfies the first part of the criterion for removal from the Flammable Gas Watch List.

In Section 7.0 it was shown that the volume of gas released during the three transfer/back dilution remediation campaigns was about the same as estimated to be retained beforehand. In Section 8.0 it was shown that there has been no detectable gas retention since mixer pump operation ceased on April 1, 2000. This was based both on the absence of waste level rise and the approximate match of measured gas release to estimated generation rates. A barometric pressure response evaluation also confirmed that there is currently no significant gas volume stored in the tank. A buoyant displacement gas release would require accumulation of approximately 4,000 cubic feet in-situ to reach the neutral buoyancy void fraction. This would have resulted in over 10 inches of level rise. Since no level rise approaching this magnitude has been observed and the initial gas inventory is negligible, it is clear that BD-GREs cannot occur in tank 241-SY-101 in its state as of October 2000.

The second part of the criterion will be satisfied with the transition of the Authorization Basis for 241-SY-101 to the Final Safety Analysis Report (FSAR) and Technical Safety Requirements (TSRs) as applied to the other non-Flammable Gas Watch List Double-Shell Tanks and when the surface level rise USQ is closed.

Since large gas releases are not possible, there is no potential to create a deflagration or detonation that would exceed the structural limits of the tank. It is recommended to be removed from the Flammable Gas Watch List upon approval of the Authorization Basis amendment.

11.0 SUMMARY AND PATH FORWARD

Tank 241-SY-101 has been the focus of considerable effort to understand and manage the flammable gas hazard and waste behavior. More characterization of the waste in this tank has been performed than for any other tank at the Hanford Site. Episodic gas releases in this tank were sufficiently severe to require a mixer pump to be operated to mitigate the hazard. However, mixer pump operation could not control the development of a large, gas-retaining crust. Therefore, actions were taken to modify the waste conditions to remediate both crust growth and episodic gas releases.

In 1999 and 2000, a series of waste transfers and subsequent water dilutions of the remaining tank 241-SY-101 waste have dissolved most of the soluble waste salts, significantly improving the waste characteristics. The gas generation rate has been significantly reduced, and no gas retention has been observed. Additionally, waste dilution eliminated the thick crust. Only a thin layer of floating solids remains that poses no hazard. The evaluation described in Section 8.2 concludes that crust growth has been remediated.

The potential for future BD-GRE behavior has been assessed as described in Section 8.3. The primary requirement for a BD-GRE is sufficient gas retention to achieve buoyancy. The mixer pump has not been operated since April 1, 2000. Analyses of available data (including waste level, gas monitoring, gamma and neutron scans) conclude that, since remediation actions have been completed and the mixer pump has been off, there is no indication of significant gas retention. In addition, analysis of the physical parameters that can correlate observed BD-GRE behavior and non-BD-GRE behavior in other DSTs (waste average specific gravity, waste nonconvective layer height, and buoyancy ratio) shows that tank 241-SY-101 is similar to other DSTs that do not exhibit BD-GRE behavior. Based on the preponderance of evidence, it is concluded that BD-GRE behavior in tank 241-SY-101 has been remediated.

The safety analysis and controls for tank 241-SY-101 have been updated to reflect the improved waste conditions. An Authorization Basis amendment has been submitted that recommends revision to the *Tank Waste Remediation System Final Safety Analysis Report* (FSAR) (HNF-SD-WM-SAR-067) and *Tank Waste Remediation System Technical Safety Requirements* (TSRs) (HNF-SD-WM-TSR-006) based on the conclusion that dilution of the waste has remediated crust growth and BD-GRE behavior. This evaluation supports, and the Authorization Basis amendment reflects, the recommendation to close the waste surface change USQ.

Upon approval of the Authorization Basis amendment, tank 241-SY-101 will be managed under the safety analysis and controls applicable to other non-BD-GRE DSTs. The safety controls (TSRs) include requirements for ventilation, control of ignition sources, and monitoring for flammable gases. In addition to these flammable gas related safety controls, other monitoring is routinely provided for non-BD-GRE DSTs including monitoring of waste temperatures and waste surface level.

Closure of the surface change USQ and approval of the Authorization Basis amendment resolves the Flammable Gas Safety Issue for 241-SY-101 as described in Section 9.0.

Remediation of gas retention and BD-GREs satisfies the first criterion for removal from the Flammable Gas Watch List as described in Section 10.0. Approval of the Authorization Basis amendment will satisfy the second criterion. Therefore, with approval of the Authorization Basis amendment, tank 241-SY-101 can be removed from the Flammable Gas Watch List.

Following removal from the Flammable Gas Watch List, tank 241-SY-101 will be returned to normal service. Plans are to use 241-SY-101 to receive saltwell wastes from West area tanks beginning in 2002 and to use 241-SY-101 to transfer these wastes cross-site as part of the ongoing interim stabilization and tank farm operations. Should future conditions change with respect to the behavior of the waste, the conditions will be evaluated via the USQ process in accordance with the Authorization Basis.

12.0 REFERENCES

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APPENDIX A

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

NATIONAL DEFENSE AUTHORIZATION ACT FOR FISCAL YEAR 1991

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

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

NATIONAL DEFENSE AUTHORIZATION ACT FOR FISCAL YEAR 1991

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

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

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

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

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