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FLAMMABLE GAS TANK SAFETY PROGRAM TECHNICAL BASIS FOR GAS SAMPLING & MONITORING

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ENGINEERING DATA TRANSMITTAL

Page 1 of 2

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1	/	Cog. Mgr. GD Johnson		4/17/95		SH Rifaey	(See 2nd sheet)		T4-07	1	/
1	/	QA DC Board	Dan Board	9-5-95							
1	/	Safety MN Islam	(See 2nd sheet)								
		Env.									
1	1	EJ Lipke		4/25/95							
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1		QA DC Board									
1	1	Safety for MN Islam		4/5/95							
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7. Abstract

Flammable gases are generated in radioactive liquids. Twenty-five high level radioactive liquid waste storage tanks located underground at the Hanford Site are on a Flammable Gas Watch List because they contain waste which tends to retain the gases generated in it until rather large quantities are available for sudden release to the tank head space; if a tank is full it has little dome space, and a flammable concentration of gases could be produced--even if the tank is ventilated. If the waste has no tendency to retain gas generated in it then a continual flammable gas concentration in the tank dome space is established by the gas production rate and the tank ventilation rate (or breathing rate for unventilated tanks); this is also a potential problem for Flammable Gas Watch List tanks, and perhaps other Hanford tanks too.

All Flammable Gas Watch List tanks will be fitted with Standard Hydrogen Monitoring Systems so that their behavior can be observed. In some cases, such as tank 241-SY-101, the data gathered from such observations will indicate that tank conditions need to be mitigated so that gas release events are either eliminated or rendered harmless. For example, a mixer pump was installed in tank 241-SY-101; operating the pump stirs the waste, replacing the large gas release events with small releases of gas that are kept below twenty-five percent of the lower flammability limit by the ventilation system.

The concentration of hydrogen measured in Hanford waste tanks is greater than that of any other flammable gas. Hydrogen levels measured with a Standard Hydrogen Monitoring System in excess of 0.6 volume percent will cause Westinghouse Hanford Company to consider actions which will decrease the amount of flammable gas in the tank.

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FLAMMABLE GAS TANK SAFETY PROGRAM: TECHNICAL BASIS FOR GAS ANALYSIS AND MONITORING

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Flammable Gas Tank Safety Program: Technical Basis for Gas Analysis and Monitoring

ABSTRACT

Flammable gases are generated in radioactive liquids. Twenty-five high level radioactive liquid waste storage tanks located underground at the Hanford Site are on a Flammable Gas Watch List because they contain waste which generates, and in some cases, retains the gases until rather large quantities are available for sudden release to the tank head space. If a tank is full it has little dome space, and a flammable concentration of gases could be produced—even if the tank is ventilated. Thus steady-state, episodic or sporadic concentrations of flammable gas in a tank dome space above 25% of the lower fallmability limit would result in the tank being placed on the Watch List.

All Flammable Gas Watch List tanks will be fitted with Standard Hydrogen Monitoring Systems so that their behavior can be observed. In some cases, such as tank 241-SY-101, the data gathered from such observations will indicate that tank conditions need to be mitigated so that gas release events are either eliminated or rendered harmless. For example, a mixer pump was installed in tank 241-SY-101; operating the pump stirs the waste, replacing the large gas release events with more frequent, smaller releases of gas that are kept below twenty-five percent of the lower flammability limit by the ventilation system.

The concentration of hydrogen measured in Hanford waste tanks is greater than that of any other flammable gas. ***Hydrogen levels measured with a Standard Hydrogen Monitoring System in excess of 0.625 volume percent will cause Westinghouse Hanford Company to consider actions which will decrease the amount of flammable gas retained in the tank.***

1.0 INTRODUCTION: THE FLAMMABLE GAS PROBLEM AT THE HANFORD TANK FARMS

This study concerns the amount of flammable gas (hydrogen being an example) contained in tanks which can store about one million gallons of radioactive liquid waste. How and why hydrogen levels are being measured in these tanks is discussed herein. With respect to the latter, the purpose of taking these measurements is to (1) ensure human health and safety and (2) protect the federal government's investment in the waste storage tanks, thereby ensuring that the waste continues to be isolated from the environment.

The tendency for high level radioactive liquid waste stored in Hanford tanks such as 241-SY-101 to generate, retain, and episodically release large amounts of hydrogen gas (Babad *et al.* 1991) was recognized as a serious problem by 1979. But this problem did not receive adequate attention prior to 1990; for example, combustion of hydrogen mixed with the oxidizer nitrous oxide, a gas mixture measured in tank 241-SY-101, was not considered in the original Safety Analysis Report (Raymond 1989) of worst-case accidents. An investigation of the flammable gas problem at the Hanford tank farms in 1990 (U.S. DOE 1990)[1] resulted in an Unreviewed Safety Question and a Flammable Gas Watch List which now includes twenty-five Hanford waste tanks. As a result of these events, several hydrogen detectors were selected and tested at tank 241-SY-101 (Wilkins 1993), and a design emerged by 1992, the Standard Hydrogen Monitoring System.

The presence of flammable gas mixtures in Hanford high-level radioactive liquid waste storage tanks is a current safety concern, and that is why twenty-five tanks are on the Flammable Gas Watch List. The basis for monitoring hydrogen in Flammable Gas Watch List tanks with Standard Hydrogen Monitoring Systems is given here. Data

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[1]: An excellent overview of the state of neglect at the Hanford tank farms which lead to the flammable gas problem that this document addresses.

obtained with these systems will provide valuable information on the gases. This information could also be useful for other work such as waste retrieval and pretreatment.

The primary hazards associated with low concentrations of gas are toxicity and combustion. Combustible,[2] or flammable gases, are often encountered in industrial processes. Regular inspection of storage facilities, proper work controls and procedures, and adequate ventilation ensure that dangerous accumulations of gas are either avoided or dealt with promptly. Protection of hazardous areas from explosions has been a concern since the industrial revolution. Passive methods emphasize preventing an ignition source from reaching flammable gases, and have been used historically; the supposition being that a flammable gas mixture is present.

There are two reasons requiring the timely detection of flammable gases (Marais 1989):

(1) To ensure the safety of personnel,

and

(2) to ensure the safe operation of monitoring equipment (even though it may be intrinsically safe).

For example, the failure to detect methane in a timely manner resulted in one-hundred and ninety-six deaths in South African mines between 1974 and 1987 (Marais 1989); presumably there was a commensurate loss in

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[2]: *Combustion* is a chemical reaction that liberates energy:

Fuel + Oxidizer → Products + Energy.

Here, the *fuel* is a flammable gas such as hydrogen (H_2), methane (CH_4), and ammonia (NH_3), and the *oxidizer* is oxygen (O_2) or nitrous oxide (N_2O). Examples are (Los Alamos National Laboratory 1994):

$$H_2 + 0.5O_2 \rightarrow H_2O + 241\ \mathrm{kJ/mol_{fuel}};$$
$$H_2 + N_2O \rightarrow H_2O + N_2 + 324\ \mathrm{kJ/mol_{fuel}};$$
$$NH_3 + 0.75O_2 \rightarrow 1.5H_2O + 0.5N_2 + 317\ \mathrm{kJ/mol_{fuel}};$$
$$NH_3 + 1.5N_2O \rightarrow 1.5H_2O + 2N_2 + 442\ \mathrm{kJ/mol_{fuel}};$$
$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 + 798\ \mathrm{kJ/mol_{fuel}};$$
$$CH_4 + 4N_2O \rightarrow 2H_2O + CO_2 + 4N_2 + 1130\ \mathrm{kJ/mol_{fuel}}.$$

The energy is released faster during an explosion than a burn. These reactions also need a little energy (*ignition energy*, such as a spark) to initiate the reaction.

equipment, production, and profits.

Flammable gas is generated by radioactive waste and can be released from the waste to the tank dome space where the flammability problem is posed. In order for a flammable gas to burn it must be mixed with an oxidizer and provided energy to start the chemical reaction. Since an oxidizer is required for combustion, a pure flammable gas will not burn; there is consequently an *upper flammability limit*. Similarly, a dilute mixture of flammable gas and an oxidizer will not burn; there is a *lower flammability limit*. Table 1 gives values of the lower flammability limit in terms of the volume percent of gas in air for a selection of flammable gases. **The National Fire Protection Association (NFPA 69) recommends that processes be controlled so that flammable gas concentrations are less than twenty-five percent of the lower flammability limit**, precluding combustion with a safety factor of four. Use of flammable gas monitors and/or detectors are required in order to meet with this recommendation.

Department of Energy orders (DOE 5480.4) require that Hanford waste tanks be operated within National Fire Protection Association guidelines: the tanks must therefore have flammable gas concentrations that are less than twenty-five percent of the lower flammability limit within the dome space and associated ducting and ventilation system. Compliance with this guideline may require *active measures* such as ventilation system upgrades and/or a form of *mitigation* such as waste agitation, pumping, heating, or dilution.

Table 1. Lower Flammability Limits for Common Gases (from CRC Handbook)

Gas	Minimum Concentration (vol. %) in Air Capable of Supporting Combustion
Hydrogen	4
Ammonia	8
Methane	5
Acetylene	2.5
Butane	2
Acetone	2.6
Butene-1 (2)	1.7 (1.8)
n-Butyl alcohol	1.5
Carbon Monoxide	12.5

Prior to mixer pump installation and operation waste stored in tank 241-SY-101 has, upon at least three occasions, suddenly produced a flammable gas mixture ($[H_2] > 4\%$) in the tank dome space; most of the rest of the gas release events observed in this tank produced hydrogen levels in excess of twenty-five percent of the lower flammability limit. All Flammable Gas Watch List tanks will have Standard Hydrogen Monitoring Systems installed on them to determine if they also exhibit this type of behavior and, consequently, require some form of mitigation, like the mixing pump in tank 241-SY-101. This monitoring should also find other tanks with high steady-state hydrogen levels. (In addition, the *Safety Screening DQO* will provide information about flammable gases in Hanford tanks that are not on the Flammable Gas Watch List.)

Flammable Gas Watch List tanks will also be *core sampled* (McDuffie 1994). This activity results in actual samples of waste being extracted from the tanks for laboratory analysis; chemical and radionuclide inventories, the distribution of material between solid and liquid phases, as well as physical (*e.g.* density) and material (particularly rheological) properties will be determined. Core sampling supports other programs such as mitigation and waste retrieval, in addition to providing information which should enhance our understanding of gas retention and generation by the waste.

If Standard Hydrogen Monitoring Systems measure a hydrogen concentration larger than 0.625 volume percent in a Flammable Gas Watch List tank, then the behavior of this tank will be evaluated and further actions will be considered. These evaluations may include characterization of all flammable gases in the tank, the temperature profile of its waste, and the waste surface level history. Evaluation and analysis could lead to a recommendation to mitigate the tank, so that flammable gases are maintained at levels less than twenty-five percent of the lower flammability limit. The basis for the action level of 0.625 vol% hydrogen is provided in Appendix B.

2.0 DECISIONS TO BE MADE

The paramount decision is whether the gas mixture in the tank headspace exceeds (or can exceed) a concentration which requires an action in order to comply with Department of Energy Order 5480.4. Possible actions, depending on the severity of the problem or probable risk of the situation, are as follows for cases where actual or predicted flammable gas concentrations might exceed twenty-five percent of the lower flammability limit:

(1) Accept the situation but continue monitoring the tank.

(2) Enhance monitoring and oversight, *e.g.* install additional gas monitoring equipment.

(3) Mitigation, such as, active ventilation or operating a mixer pump in the tank, as is the case for tank 241-SY-101.

(4) Control worker access to the tank farm; change worker safety controls; set up an evacuation alarm system.

If a Flammable Gas Watch List tank is found to have flammable gas levels less than twenty-five percent of the lower flammability limit in the dome space or ventilation ducting, then it could be removed from the Watch List. Criteria for removing tanks from the Flammable Gas Watch List are presently under development.

3.0 INPUTS TO THE DECISION PROCESS

Characterization of the Flammable Gas Watch List tanks is primarily directed towards two goals: **(1)** evaluate hazards in the tanks attributable to flammable gases, and **(2)** determine corrective actions ("mitigation").[3] This study concerns the collection of data which supports the former goal; (1) the data are the inputs. Flammable gas can be detected in tank dome spaces by Standard Hydrogen Monitoring Systems, and in other accessible air spaces by *combustible gas meters*. The waste itself can be sampled with the *Retained Gas Sampling System* (Wootan *et al.* 1994) and the *Void Meter* (Borgonovi *et al.* 1994).

Three elements are required for combustion: **(1)** a fuel, **(2)** an oxidizer, and **(3)** an ignition source. For Hanford waste storage tanks, the oxidizers are nitrous oxide and atmospheric oxygen, and the primary fuel of concern is hydrogen, although ammonia and methane may also be present. Table 2 shows which gases might be found in Hanford waste tanks. **The amounts of fuel and oxidizer gases in Flammable Gas Watch List tanks are the primary inputs to the decision process.** Tank equipment (Van Vleet 1994a, 1994b) that could act as an ignition source is a secondary matter which will not be considered further here.

Information required to evaluate the flammable gas Safety Issue is a determination of whether at any time during storage the air space in a given tank could support combustion, should an ignition source be present. This will depend on how much flammable gas (hydrogen ammonia, methane, nitrous oxide) is released from the waste, availability of oxidizer, how much volume is available for gas to occupy, and the ventilation flow rate (or breathing rate for unventilated tanks). Factors which affect the gas release rate from the waste are not easily assessed, but they include waste properties (*e.g.* does the waste tend to retain gas generated in it?) and the rate that gas is generated in the waste; the gas generation rate in the waste is primarily associated with the radionuclide inventory, and it is also

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[3]: Data requirements for the Hydrogen Mitigation Program are given in several reports: Ashby *et al.* (1992), Babad *et al.* (1992), and Lentsch (1992). Mitigation concepts involve either physical or chemical treatments, such as mixing the waste with a jet pump, sonic agitation, and heating and dilution. Each of these mitigation possibilities has its own set of data requirements, some exclusive, and others very general.

influenced by waste chemistry. Thus, there will be information in addition to the flammable gas concentration in the Watch List tanks feeding into the decision process.

Table 2. Estimated Slurry-Gas Composition in Tank 241-SY-101
(Los Alamos National Laboratory 1994)

Gas	**Conservative Estimate** (Volume Percent)
Hydrogen	29
Nitrous Oxide	24
Ammonia	11
Nitrogen	33
Methane	< 1
Others (*e.g.* carbon monoxide)	< 1
Water Vapor	2

Both historical and current "operational" data from the Hanford tank farms will be used to evaluate the behavior of Flammable Gas Watch List tanks, along with the data obtained from the Standard Hydrogen Monitoring Systems. Examples of "operational" data are as follows.

Ventilation flow rates (for actively ventilated tanks).

Breathing rates (for passively ventilated tanks).

Annulus ventilation flow rates (for double-shell tanks).

Waste temperatures.

Pressures and temperatures in tank dome spaces.

Barometric pressure.

Ambient air temperature, humidity, and wind velocity.

The waste surface level and volume of the tank dome space.

Liquid observation well liquid height (single-shell tanks).

The appearance of the waste surface and tank interior indicated by in-tank videos.

Historical tank data (waste composition, temperatures, waste levels, etc)

4.0 STUDY BOUNDARIES

The spatial and temporal boundaries of this study are given here. The spatial boundary relates to the twenty-five Flammable Gas Watch List tanks, which are a subset of the one-hundred and seventy-seven high level radioactive liquid waste storage tanks at the Hanford 200 Area. This boundary can also be viewed as the part of each Flammable Gas Watch List tank where the flammability problem is posed: the *total gas space* (or just "air space") in the tank. The temporal boundary concerns the amount of time that any tank poses a flammability problem. The time frame of this study must therefore be from the present to the time that the waste is retrieved from the tanks for disposal.

Nuclear fuel reprocessing occurred in the 200 Area of the Hanford Site and this is where waste disposal facilities, such as the tank farms, are located. Hanford radioactive liquid waste largely resides in the one-hundred and seventy-seven underground storage tanks; they are either older single-shell tanks or newer double-shell tanks. These tanks, with their resident wastes, are unique chemical systems, no two of which are quite the same. Tank farms comprised of double-shell tanks are equipped with active ventilation systems that exhaust gas in the dome spaces of all the tanks. Some tank farms comprised of single-shell tanks also have active ventilation systems, but others are passive only; breathing is due to atmospheric pressure changes and natural circulation.

Radioactive liquid waste produces hydrogen from the interaction of ionizing radiation and water (*radiolysis*). If the waste contains organic chelating agents then additional hydrogen gas, as well as nitrous oxide and ammonia, can be produced by thermal and radiolytic decomposition of these organics. Twenty-five Hanford waste storage tanks are on a Flammable Gas Watch List because their waste is suspected of retaining hydrogen gas. The ability to retain large amounts of gas appears to be a feature unique to some Hanford waste: Waste properties are affected by chemical processing and evaporation such that a dense, highly viscous material with a yield strength resulted (Mahoney and Trent 1994); gas generated in this type of waste tends to be retained, increasing the waste volume until buoyancy forces are sufficient to displace the waste resulting in a release. After being released from the waste, the gas is transported through the free tank volume and is either exhausted by the active ventilation system or, if the tank is passively ventilated, the gas is dispersed by diffusion and convection then exhausted through any openings in the tank.

Because hydrogen is produced by the radiolysis of water, it is possible for any tank containing radioactive liquid waste to have hydrogen in free spaces, such as that above the waste surface level. Westinghouse Hanford Company has therefore developed criteria (Hopkins 1994) to assess which tanks should be placed on the Flammable Gas Watch List.

The following tanks are currently on the *Flammable Gas Watch List*:[4]

Double-Shell	Single-Shell
241-AN-103, 104, 105	241-A-101
241-AW-101	241-AX-101, 103
241-SY-101, 103	241-S-102, 111, 112
	241-SX-101, 102, 103, 104, 105, 106, 109
	241-T-110
	241-U-103, 105, 107, 108, 109

These tanks either exhibit episodic gas release events similar (but of much lessor magnitude) to those in tank 241-SY-101, or have the potential to exhibit such releases.[5] The flammability problem is posed in the *air space* (which is the volume in a tank that is available for gases) and ventilation system of a Flammable Gas Watch List tank; the smaller the air space the greater the concentration potential for a given slurry gas release volume.

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[4]: Brager (1994) provides a great deal of information on all of these tanks. See Anderson (1990) and Husa *et al.* (1993) for general information about the Hanford tank farms. Note: tanks 241-AX-103 and 241-SX-109 are interim stabilized. Tank 241-SX-109 is on the Flammable Gas Watch List because it shares the ventilation system with the other SX Farm tanks on the watch list, and unlike tank 241-SX-109 (because it is interim stabilized), these other tanks could have a flammable gas problem.

[5]: The Flammable Gas Watch List initially included tank 241-SY-101 and other tanks containing either similar waste materials, or tanks which exhibited slurry growth, episodic surface level drops, or pressure bumps.

Tank 241-SY-101 is an active chemical reactor: Prior to operation of the mixer pump, large gas release events occurred at a frequency of 100 ± 10 days; resulting hydrogen levels were usually greater than twenty-five percent of the lower flammability limit, the waste surface level decreased by several inches due to gas release and the tank pressure increased; see Table 3. Also, these gas release events produced significant waste motion: tank contents turned upside down.[6] Other double-shell Flammable Gas Watch List tanks exhibit somewhat similar behavior, but the gas release events are not as "dramatic." For example, Table 4 shows waste surface level drops for the AN Tank Farm. This table suggest that the gas release events which appear to occur in the AN tanks transpire over days; gas release events in tank 241-SY-101, on the other hand, lasted less than one hour. Another important difference between the behavior exhibited by tank 241-SY-101 and the other Flammable Gas Watch List tanks is shown by Table 5: while the gas release events in tank 241-SY-101 were periodic, those exhibited by many of the other tanks may be better described as sporadic, the waste behavior of tank 241-AN-105 being an example.

Figure 1 shows the effect of a *gas release event* on the hydrogen level in the ventilation system at tank 241-AW-101, as measured by a Standard Hydrogen Monitoring System.[7] In this case the initial, steady state hydrogen level of less than 1000 ppm (0.1%) increased ten*fold* to almost 9000 ppm (0.9%). In contrast, the gas release event in tank 241-SY-101 prior to the mixer pump operation resulted in an increase in H_2 concentration from steady data level of 0.015% to a peak value of 2.8%, an increase of almost 200 times. See Figure 2 (June 26, 1993 gas release event tank 241-SY-101).

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[6]: Video tapes of some gas release events in tank 241-SY-101 are available. Videos of gas release events in the other Flammable Gas Watch List tanks may also be available in the future.

[7]: A Standard Hydrogen Monitoring System was placed at tank 241-AW-101 on September 28, 1994. This tank had a gas release event from October 1 - 4, 1994. The slurry gas was estimated to be 70% H_2, with the remainder being most likely some combination of nitrogen, nitrous oxide, and ammonia. Another gas release event occurred in this tank on February 22, 1995; the peak hydrogen level was 0.625%, and the pressure increased by 0.1 inch water gauge.

Table 3. Summary of Gas Release Events in Tank 241-SY-101
(Reynolds 1994) (Prior to mixer pump installation)

Date	Δp (in. H_2O)	$p_{max.}$ (in. H_2O)	Maximum H_2 Level (vol. %)	Waste Surface Level Decrease (inches)
4/90	2.3	0.1	3.5	9.3
8/90	0.3	-2.0	1.2	5.2
10/90	5.2	2.3	4.7	10.0
2/91	0.4	-2.0	0.6	5.0
5/91	3.3	0.2	0.5	7.2
8/91	0.3	-3.0	0.4	6.0
12/91	10	6.8	5.3	13.0
4/92	0.6	-2.0	1.5	7.2
9/92	7.7	5.4	5.0	9.4
2/93	1.1	-0.1	2.8	8.5
6/93	3.4	0.9	2.8	9.3

Table 4. Likely Gas Release Events at the AN Tank Farm

Tank	Date	Waste Surface Level Drop (inches)	Duration (days)	Largest 1-day Surface Level Drop (inches)
103	May 1992	3.0	5	2.5
	Sep. 1992	1.5	15	0.8
	Jan. 1994	0.9	1	0.9
	Aug. 1994	1.0	2	0.9
104	Apr. 1990	1.4	2	0.9
	May 1990	1.7	3	0.7
	Jan. 1991	1.4	2	1.0
	May 1991	3.1	5	1.6
	May 1992	0.8	5	0.7
	Apr. 1993	0.8	2	0.6
	Aug. 1993	1.4	4	1.0
	July 1994	0.9	1	0.9
105	Dec. 1991	2.1	18	0.7
	Apr. 1992	1.2	3	0.7
	Sep. 1992	1.0	1	1.0
	Jan. 1993	0.9	1	0.9
	May 1994	2.9	7	1.1

Figure 1. Gas Release Event in Tank 241-AW-101

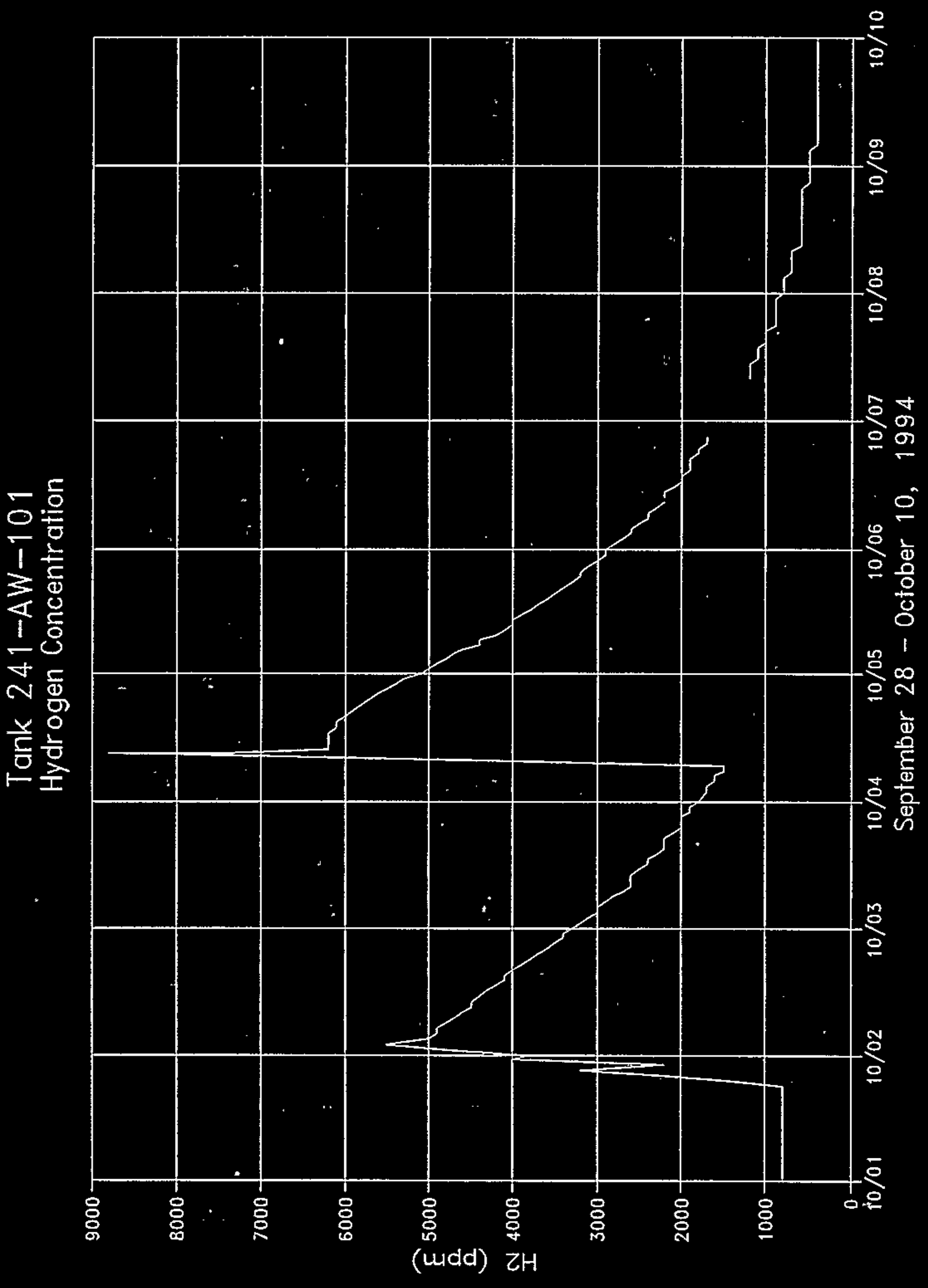

Figure 2. Tank 241-SY-101 Surface Level
FIC, Radar Gauge, and Manual Tape

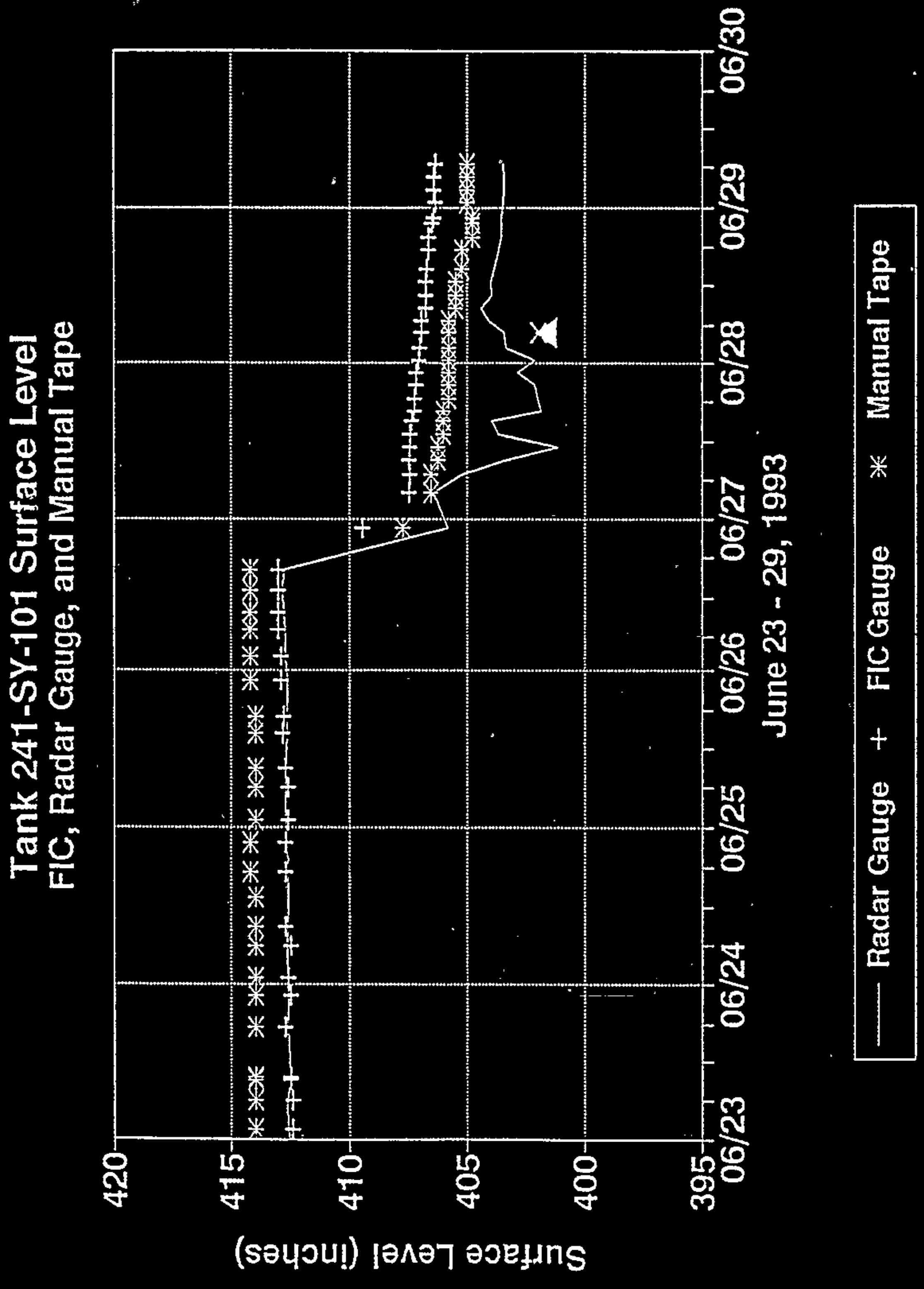

Table 5. Time Intervals Between the Large Surface Level Drops in Tank 241-AN-105

Date	Waste Surface Level Drop (inches)	Time Since Prior Gas Release Event (days)
Dec. 1991	2.1	1432
April 1992	1.2	130
Sep. 1992	1.0	166
Jan. 1993	0.9	118
May 1994	2.9	480

In order to comply with Department of Energy Order 5480.4, flammable gas levels must be monitored at all Flammable Gas Watch List tanks. Standard Hydrogen Monitoring Systems will be used to detect flammable gas (hydrogen) in Hanford waste tanks. These systems will take continuous measurements from a single location in a tank. Resulting data can be used in a gas transport analysis to estimate the spatial-temporal distribution of flammable gas in the tank farm, *e.g.* Wood (1994); sampling multiple locations may therefore not be necessary in general. The relationship between the concentration of a particular specie in a gas mixture at one location and time to that at another location and/or time is discussed next.

A brief description of gas transport theory is given in the following box. This theory provides a local, mathematical description for the *balance law* of a conserved quantity, which is

rate of accumulation = rate of entry — rate of departure

where the rates refer to one gas specie (*e.g.* H_2, NH_3, or N_2O) at some particular (and small) region in a tank's air space. Analysis of this statement produces a differential equation. A global description for the gas concentration results from either an analytical solution to the differential equation (*e.g.* integration) or a numerical solution to it. If the gas of interest can be regarded as mixed into the air well, as could be the case if gas is released in a slow, continuous manner from the waste, then the balance law expressed as

$$dV_{gas}/dt = g - (g + Q)V_{gas}/V_{air}$$

provides an adequate description; here, V_{gas} is the volume occupied by this gas, g is its release rate from the waste (m^3/s), Q is the flow rate (ventilation or breathing) in the tank (m^3/s), and V_{air} is the volume in the tank available for gas (Estey 1992). This rate has no spatial or temporal dependency, and can be easily solved for V_{gas}:

$$V_{gas} = V_{air}[1 - \exp\{-t(g + Q)/V_{air}\}]g/(g + Q);$$

if

$$t >> V_{air}/(g + Q),$$

then $V_{gas} \approx V_{air}g/(g + Q)$ is the volume of gas present in the tank at the *steady state*. Finally, parameters which describe the spatial domains of each Flammable Gas Watch List tank are summarized by Tables 6 and 7.

Gas Transport

Standard Hydrogen Monitoring Systems will only measure the hydrogen concentration at a single location in a tank. Gas concentrations can, however, be both spatially and temporally dependent (Hirano 1984). Let C_i denote the concentration (moles per unit volume) of gas specie i, *e.g.* i = H_2, NH_3, N_2O; then if there are no chemical reactions, *mass balance* gives the ***local*** *rate of change* of C_i in the tank dome space above the waste surface level as

$$\partial C_i/\partial t = P_i - \nabla \bullet \mathbf{J}_i - \nabla \bullet (C_i\mathbf{v}), \qquad (1)$$

where P_i is the release rate of species i from the waste,

$$\mathbf{J}_i = -D_i\nabla C_i \qquad (2)$$

is the flux of species i, which has a diffusivity of D_i, and

$$\mathbf{v} = C^{-1}\textstyle\sum_i C_i\mathbf{v}_i \qquad (3)$$

is the *barycentric velocity* of the mixture, where $C = \sum_i C_i = (C_{H_2} + C_{NH_3} + \ldots + C_{N_2O})$, and $\mathbf{v}_i$ is the velocity of species i. Given enough time the mixture will attain a *steady state* concentration defined by $\partial C_i/\partial t = 0$, which gives

$$\nabla \bullet \mathbf{J}_i + \nabla \bullet (C_i\mathbf{v}) = P_i, \qquad (4)$$

or with $\mathbf{J}_i = -D_i\nabla C_i$,

$$-D_i\nabla^2 C_i + \nabla \bullet (C_i\mathbf{v}) = P_i,$$

assuming that the diffusivity D_i is not spatially dependent, *i.e.* is not influenced by the other species.

Solutions of equation (1) give the concentration of i, C_i, as a function of both position and time, $C_i = C_i(x,y,z,t)$, while solutions of equation (4) have only a spatial dependency, $C_i = C_i(x,y,z)$. Analyses based upon equation (1) can be used to estimate the spatial-temporal distribution of gas from measurements taken at a single location (Wood 1994). Thus, **data obtained with Standard Hydrogen Monitoring Systems can be used to evaluate the flow of a flammable gas mixture throughout the ventilation system of a tank.**

Table 6. Flammable Gas Watch List, Single-Shell Tank Parameters

Tank	Usable Depth (ft.)	Waste Level (ft.)	Dome Volume (ft.^{3})	Total Gas Space (ft.^{3})	*Gas Space ÷ Waste Volume*
101-A	30.3	28.8	27,412	34,168	0.27
101-AX	30.3	23.2	27,412	58,852	0.57
102-S	23	17	30,694	57,201	0.76
111-S	23	17	30,694	57,422	0.77
112-S	23	16.4	30,694	59,999	0.83
101-SX	30.3	14.3	27,412	97,951	1.55
102-SX	30.3	17.1	27,412	85,801	1.14
103-SX	30.3	20.2	27,412	71,996	0.81
104-SX	30.3	19.8	27,412	74,020	0.85
105-SX	30.3	21.4	27,412	66,657	0.7
106-SX	30.3	17.2	27,412	85,323	1.12
110-T	16	12.3	27,412	43,721	0.8
103-U	16	13.9	27,412	36,745	0.6
105-U	16	12.5	27,412	42,967	0.78
107-U	16	12	27,412	61,413	1.16
108-U	16	13.9	27,412	36,690	0.6
109-U	16	13.7	27,412	37,426	0.62

Table 7. Flammable Gas Watch List, Double-Shell Tank Parameters

Tank	Usable Depth (ft.)	Waste Level (ft.)	Dome Volume (ft.^{3})	Total Gas Space (ft.^{3})	*Gas Space ÷ Waste Volume*
101-SY	35.2	34.2	33,010	37,540	0.25
103-SY	35.2	22.8	33,010	87,644	0.87
101-AW	35.2	34	33,010	38,127	0.25
103-AN	35.2	28.9	33,010	60,843	0.48
104-AN	35.2	32.4	33,010	45,417	0.32
105-AN	35.2	34.3	33,010	37,023	0.21

5.0 THE DECISION RULE

This study is being undertaken to assess to what extent flammable gases occupy the air spaces in Hanford Flammable Gas Watch List tanks. The decision rule given here pertains to the concentration of hydrogen that a Standard Hydrogen Monitoring System measures in each Flammable Gas Watch List tank: If the measured concentration of hydrogen exceeds 0.6 volume percent in any Flammable Gas Watch List tank, then a decision will have to be made about how the tank is to be dealt with.

The parameters of interest are the concentrations of all flammable gases in each of the Flammable Gas Watch List tanks. When the concentrations of flammable gases in a tank are measured the lower flammability limit can be estimated, as follows. The lower flammability limit of a gas mixture is dependent on a number of factors such as the types of gases (flammable, inflammable, and oxidizers) in the mixture, the geometry of the combustion chamber, the energy of the ignition source, and the temperature. The combustibility of a mixture can be approximated by *LeChatelier's law*: the mixture is estimated to be at its lower flammability limit (LFL) when

$$\sum \left\{ \frac{y_i}{LFL_i} \right\} = 1.0 \qquad (1)$$

where y_i = volume (or mole) fraction of flammable gas i, and LFL_i = lower flammability limit of this gas in air, with the same units as y_i (Table 1 gives LFL_i for gases in air).[8] The air space in tanks which comply with DOE Order 5480.4 contain gases such that the fraction in equation (1) is less than the value 0.25; *e.g.* for H_2 in air $[H_2]/4\% = 0.25$, which gives $[H_2] = 1\%$; similarly, for a more general mixture, $[H_2]/4\% + [NH_3]/8\% + [CH_4]/5\% + ... = 0.25$.

The composition of the gases in tank 241-SY-101 (Table 2) indicates that

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[8]: Studies were conducted by the U.S. Bureau of Mines (Cashdollar 1992) to evaluate flammability limits for gas mixtures found in tank 241-SY-101. Further information is to be obtained, especially on the effects of higher concentrations of ammonia and nitrous oxide, in work funded this fiscal year.

the lower flammability limit is dominated by hydrogen, even though other gases are evolved by the waste stored in this tank. In order to account for these other gases, **the initial flammable gas criteria for the Hanford Tank Farms will be 0.625% H_2.** If a Standard Hydrogen Monitoring System measures a hydrogen level greater than this, then the tank's behavior will be studied further; if hydrogen levels do not exceed 0.625%, then monitoring data will continue to be collected but additional formal evaluation will not be required. Using $[H_2] = 0.625\%$ instead of $[H_2] = 1\%$ will assure that, given the present state of knowledge about gases in the tank farms, tanks with a potential flammability problem are thoroughly evaluated.[9] The "decision logic" is shown in Figure 2; it means that if measured hydrogen levels ever exceed 0.625%, then:

(1) tank conditions will be noted,

(2) determine reportability per WHC-IP-0482, Volume II, Section 4.6.2

(3) monitors for methane, ammonia, and any other appreciable combustible components found in grab samples will be installed at the tank,

(4) Engineering will evaluate all tank data and recommend any further action;

(5) a formal evaluation will then be prepared, and

(6) the Department of Energy will be notified of a recommendation on the need to, or not to, mitigate the tank.

The last decision block, "Is Flammable Gas Level >25% LFL?" is considered after an evaluation is made for the other potential flammable gases (e.g., methane, ammonia). If the set point of 0.625% H_2 is exceeded, an automatic grab sample is taken and an analysis will be conducted for other gases. Results of this analysis will then be used to estimate the LFL of the mixture.

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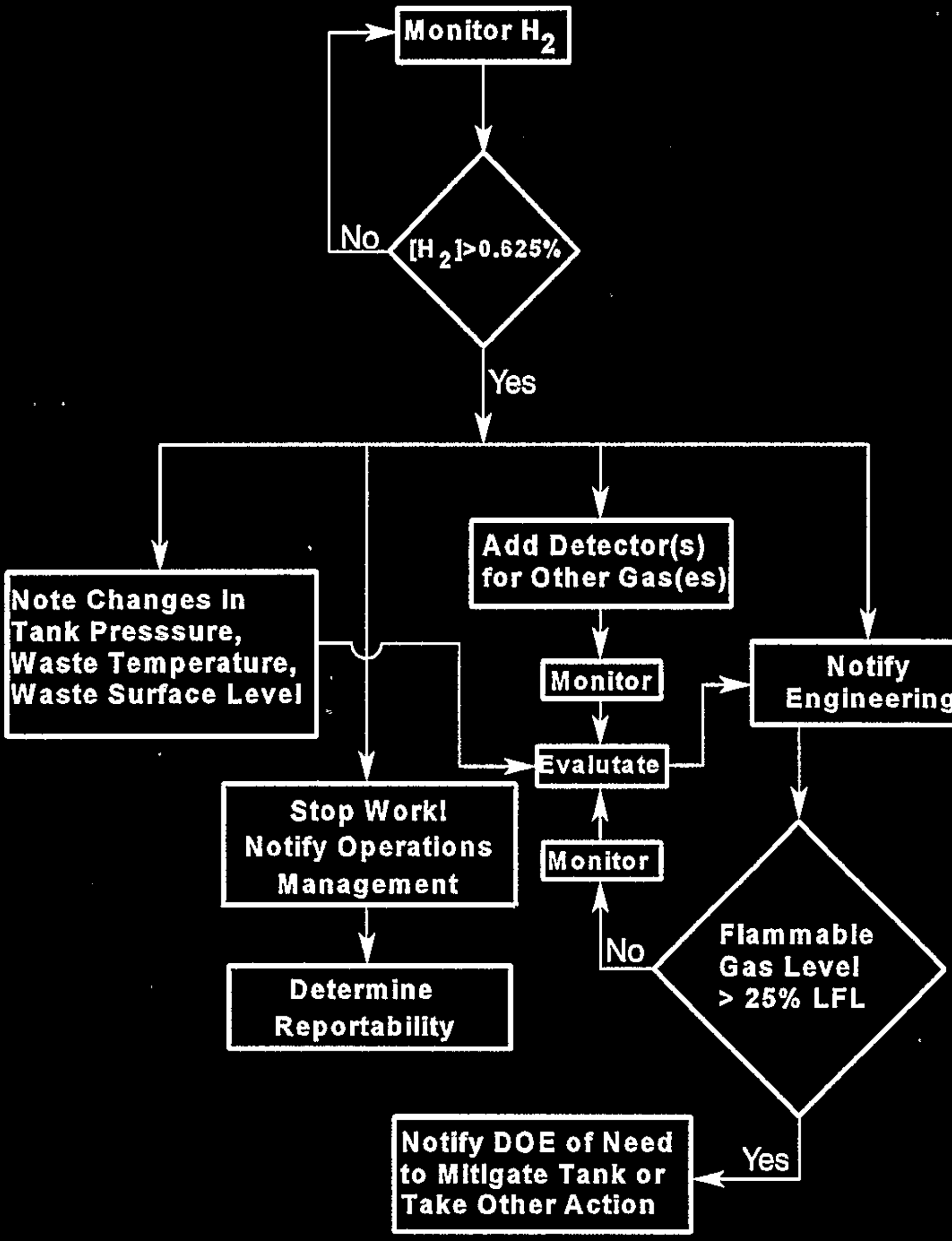
[9]: The value of 0.625% H_2 will be a control limit for performing work at the Hanford Tank Farms; see the latest revision of the *Accelerated Safety Assessment* for further discussion about this value.

Figure 2. Decision Logic for Flammable Gas Watch List Tanks



6.0 DECISION ERRORS

Mixtures of flammable gases could exist in the air spaces of Flammable Gas Watch List tanks at concentrations which could, hypothetically, range from zero to one-hundred percent. This entire range of values is of interest, but practically speaking, only values near twenty-five percent of the lower flammability limit will be monitored; other values can be estimated by conducting temporal-spatial analyses of gas mixing in the tank.

There are two decision errors: **(1)** A tank with hydrogen levels in excess of 0.625% H_2 is not discovered, and therefore is not evaluated. **(2)** A tank without a real flammable gas problem is assumed to have one and resources are allocated to address the non-problem. The consequences of making these errors are:

(1) If the hydrogen concentration is greater than 0.625%, but a Standard Hydrogen Monitoring System indicates that it is less than 0.625%, then additional instrumentation would not be added, other gases might not be detected, and mitigation, if required, might not be done.

This concern has been addressed: each Standard Hydrogen Monitoring System has two hydrogen detectors plus a grab sample capability. In addition, other supporting data (*e.g.* waste surface level and waste temperature) will be used as independent indicators of tank behavior. Gas monitoring for routine tank farm work will, furthermore, always be performed, and information gathered from this activity will be made available to the Test Review Group.

(2) If hydrogen levels are actually less than 0.625%, and if there are no other flammable gases in the tank, but monitoring indicates that hydrogen levels are greater than 0.625%, then unnecessary instrumentation would be installed, and extra costs would result.

These instruments would indicate that in fact there is no problem with the tank, and therefore could be reused elsewhere; only the labor costs would be lost. Incorrectly proceeding with mitigation, even for a short period of time, could, on the other hand, be an expensive undertaking, the costs of which might not be largely recoverable.

7.0 DESIGN OPTIMIZATION FOR FLAMMABLE GAS MONITORING

The objective of this study is to identify every tank which has concentrations of flammable gases near 25% LFL or greater so that it can be evaluated and a prudent course of action developed. A resource-effective data collection system has been designed to fulfill this objective. This was done under the constraint of the potential threat to personnel and equipment safety from the presence of flammable gases in the tank farms.

Because flammable gases pose an immediate threat to personnel and equipment, Flammable Gas Watch List tanks will be continuously monitored for hydrogen, from at least one location, until the behavior observed indicates that other actions are required. Further actions could involve sampling multiple locations in a tank (requiring installation of an additional Standard Hydrogen Monitoring System), and the utilization of monitors for additional flammable gases (ammonia, methane), and oxidizers (nitrous oxide).

Standard Hydrogen Monitoring Systems have been installed at all Flammable Gas Watch List tanks. These systems include climate-controlled cabinets for monitoring equipment. The Standard Hydrogen Monitoring System instruments are intrinsically safe (Schneider 1992): *i.e.* their operation does not provide energy which, in a flammable environment, would be an ignition source. They are relatively inexpensive to construct and install and can be operated by plant personnel (Raymond 1995) after a brief shake-down period. The hydrogen monitors which they contain have been tested (Schneider 1993) to assure that other gases (*e.g.* ammonia and methane) which may be in the tanks do not interfere with their ability to measure hydrogen. Table 8 illustrates some of the Westinghouse Hanford Company deliberations which have contributed to the Standard Hydrogen Monitoring System design.

The *Standard Hydrogen Monitoring System*, Figure 3, consists of a cabinet with piping and instrumentation which supports two on-line hydrogen detectors and a "grab sampler." Whittaker electrochemical cells are currently used for measuring hydrogen, but other detectors can also be installed into these cabinets. Also, several different kinds of detectors were tested at tank 241-SY-101 (Wilkins 1993). **The Whittaker is a hydrogen**

detector,[10] not an analytical tool; its detection threshold is about 100 ppm H_2 and its advertised accuracy is ±0.2% H_2. Other gases are measured by taking grab samples with the Standard Hydrogen Monitoring System; grab samples are analyzed with a high resolution gas chromatograph/mass spectrometer (an analytical instrument) located at the Pacific Northwest Laboratory. The Standard Hydrogen Monitoring System therefore allows for both instantaneous, continuous, gross measurements of the hydrogen concentration, and precise "snap-shots" of the gas concentrations in Hanford waste tanks. A Standard Hydrogen Monitoring System has been monitoring flammable gases in tank 241-SY-101 for over two years; therefore, gas levels in this tank are baselined (composition and release rates are well known). Since the Standard Hydrogen Monitoring System is already field tested at tank 241-SY-101 it offers a credible means to monitor hydrogen levels in the other Flammable Gas Watch List tanks.

Comparison of Whittaker data with grab sampler data suggests that the Whittakers are capable of H_2 detection below 100 ppm. Recent data obtained from operation of the Standard Hydrogen Monitoring Systems are shown below.

HYDROGEN CONCENTRATION, ppm

TANK	WHITTAKER	GAS CHROMATOGRAPH	GRAB SAMPLE
103-SY	0 - 25	---	20 - 40
101-AW	491		362
103-AN	66		68
104-AN	87	60	66
105-AN	321		124

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[10]: The different types of flammable gas detectors are described by King (1983) and Curry (1990); Walsh (1992) discusses optical techniques and Azad *et al.* (1992) discusses solid-state sensors. The only optical method capable of detecting H_2 is Raman Scattering, and it can also detect the other gases of interest in the Hanford waste tanks; this is a viable technology for on-line flammable gas monitoring at the Hanford tank farms (Suhre 1991). Westinghouse Hanford Company has also solicited information about commercial solid-state hydrogen detectors (Pyke 1990).

The grab samples represent a number of samples for each tank; there were generally 7-10 grab sampling events with duplicate samples taken each time. These results illustrate the ability of the Whittaker hydrogen monitors to consistently detect hydrogen at concentrations below 400 ppm. Testing for interference with other gases (Schneider 1993) conducted with H_2 concentrations ranging from 100 ppm to 30,000 ppm (3%), demonstrated a lack of sensitivity to other gases (ammonia, methane, and nitrous oxide) and a wide range of sensitivity. Detection at 6250 ppm (25% of LFL) is well within the range of Whittaker cells.

Standard Hydrogen Monitoring Systems will be installed on tank exhaust piping at the double-shell tanks. Many single-shell tank farms do not have ventilation systems; they are often only passively ventilated. In this case probes will be inserted into risers to permit gas sampling with the Standard Hydrogen Monitoring System.

Detector:	Electrochem. Cell	Solid State Metal Oxide	Solid State Metal Ins.	Optical	Catalytic Bead	Thermal Conductivity
Operating Temp. Range	70-120°F	—40-190°F			—40-140°F	32-125°F
Operating Relative Humidity		0-90%			5-95%	0-100%
Temperature Stability	±0.001% of reading/°F from calibration temperature	Not affected by slow changes in temperature			±0.01% of reading/°F from calibration temperature	No effect within ±20°F of calibration point
Accuracy	0-10% H_2: ±0.2% > 10% H_2: ±2% of full scale	±5% of full scale	±10% of full scale		±5% of full scale	±1% of full scale
Range	0-50% H_2 & ppm	0-8% H_2 & ppm	0-100% H_2 & ppm	0-5% H_2	0-4% H_2	0.25-5% H_2
Intrinsically Safe?	Yes*	Yes*	Yes*	Yes*	Yes*	No
Response Time	< 120 s	%H_2 range: < 15 s ppm H_2 range: < 30 s	< 90 s	90 s	30 s	50 s
Lifetime	1-3 years	5-10 years	1 year		3 years	Unlimited
Repeatability	±0.1% of full scale	±0.1% of reading			±3% of full scale	
Calibration Frequency	90 days	60 days			60 days	7 days
Cost	$7K for cell & electronics; $3K for replacement cell	$1K for cell & electronics; $300 for replacement cell				$2.2K
Development Required?	No	No	Yes	Yes	No	No
Poisons	sulfur compounds	none			Lead, silicones, halogenated hydrocarbons, chlorine & sulfur compounds	sulfur compounds
Interfering Gases	ammonia @ 0.01 atm	acetone (2:1) acetylene (2:1) diethylamine (1:1) n-propanol (1:1) trichloroethylene (25:1) ethylene (1.3:1) benzene (3:1) butane (20:1) carbon monoxide (25:1) methane (20,000:1) propylene (2:1)			hydrocarbons	helium water (7:1)

Table 8. Design Considerations for Standard Hydrogen Monitoring System

* Intrinsically safe because of engineered barriers.

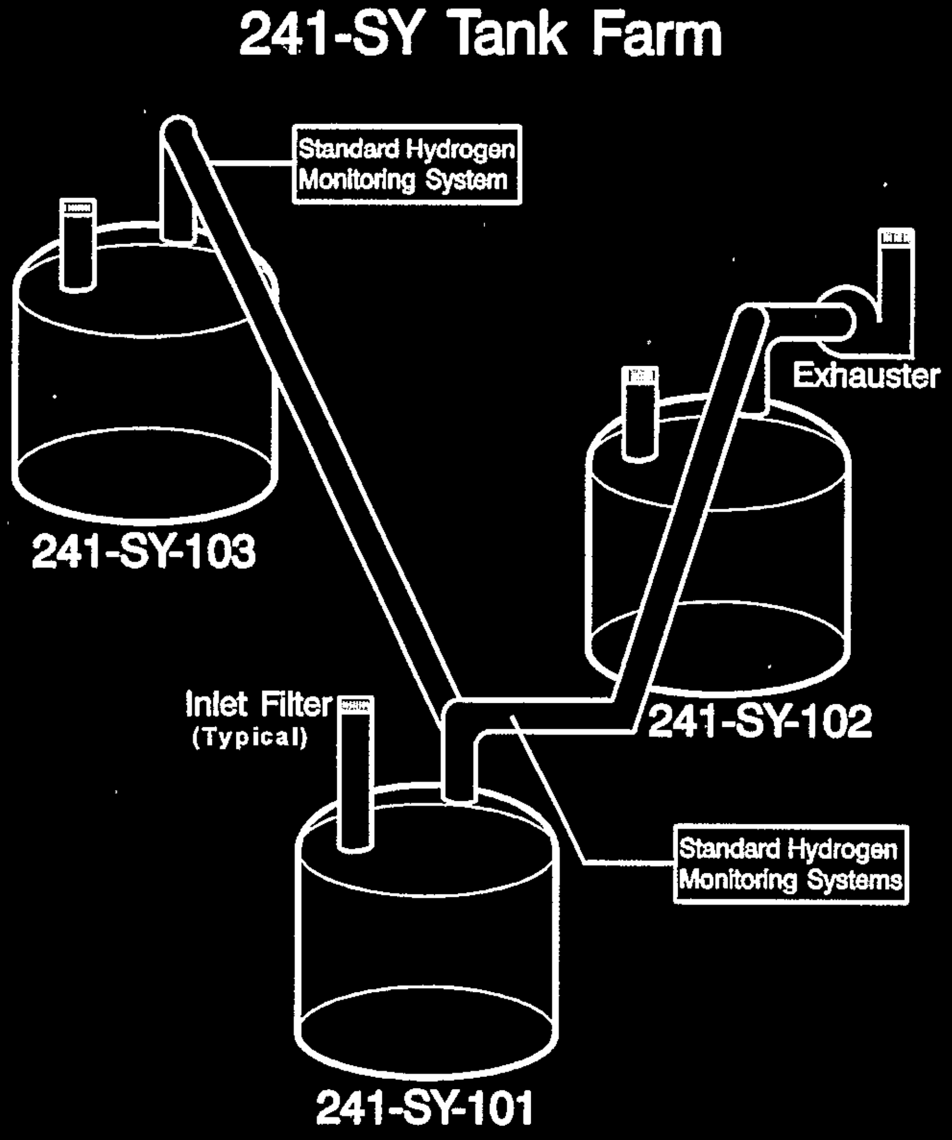

Figure 3. a) A schematic of the 241-SY Tank Farm is shown which emphasizes the ventilation system (inlet filters, exhauster, and piping between the three tanks) and the Standard Hydrogen Monitoring Systems. Tank 241-SY-102 is not on the Flammable Gas Watch List and, therefore, does not have a Standard Hydrogen Monitoring System.

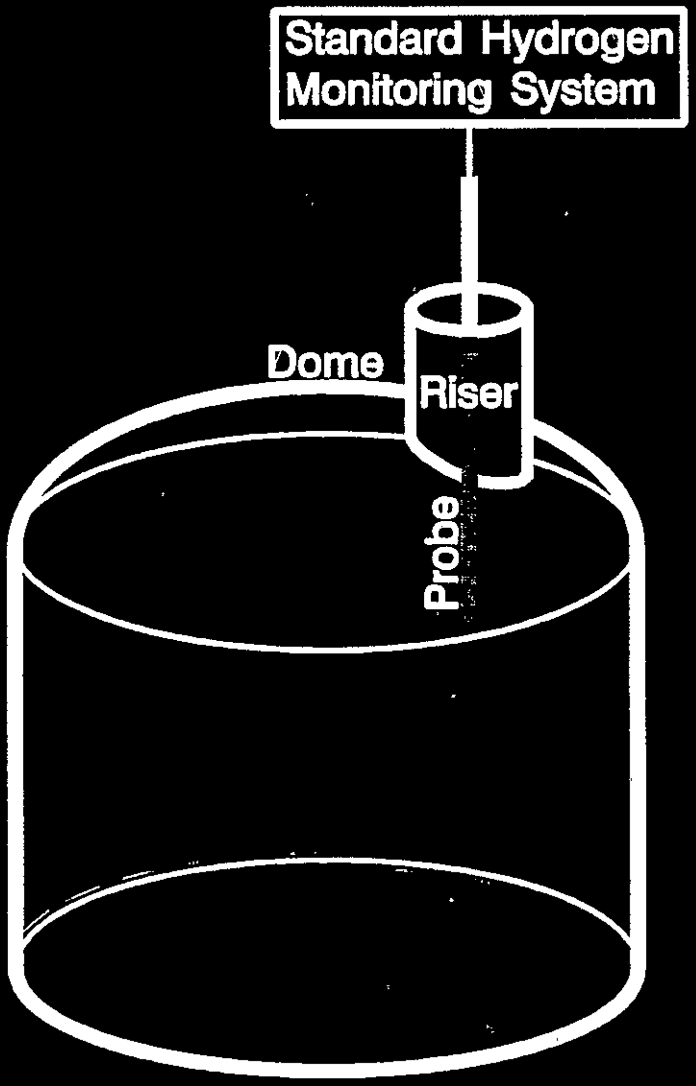

Figure 3 (continued). **b)** Schematic of Hanford single-shell tank that does not have a ventilation system. In this case the Standard Hydrogen Monitoring System is connected to a probe which is inserted into a riser. Risers connect the tank dome space to ground level. (All single-and double-shell Hanford radioactive liquid waste storage tanks are located underground.)

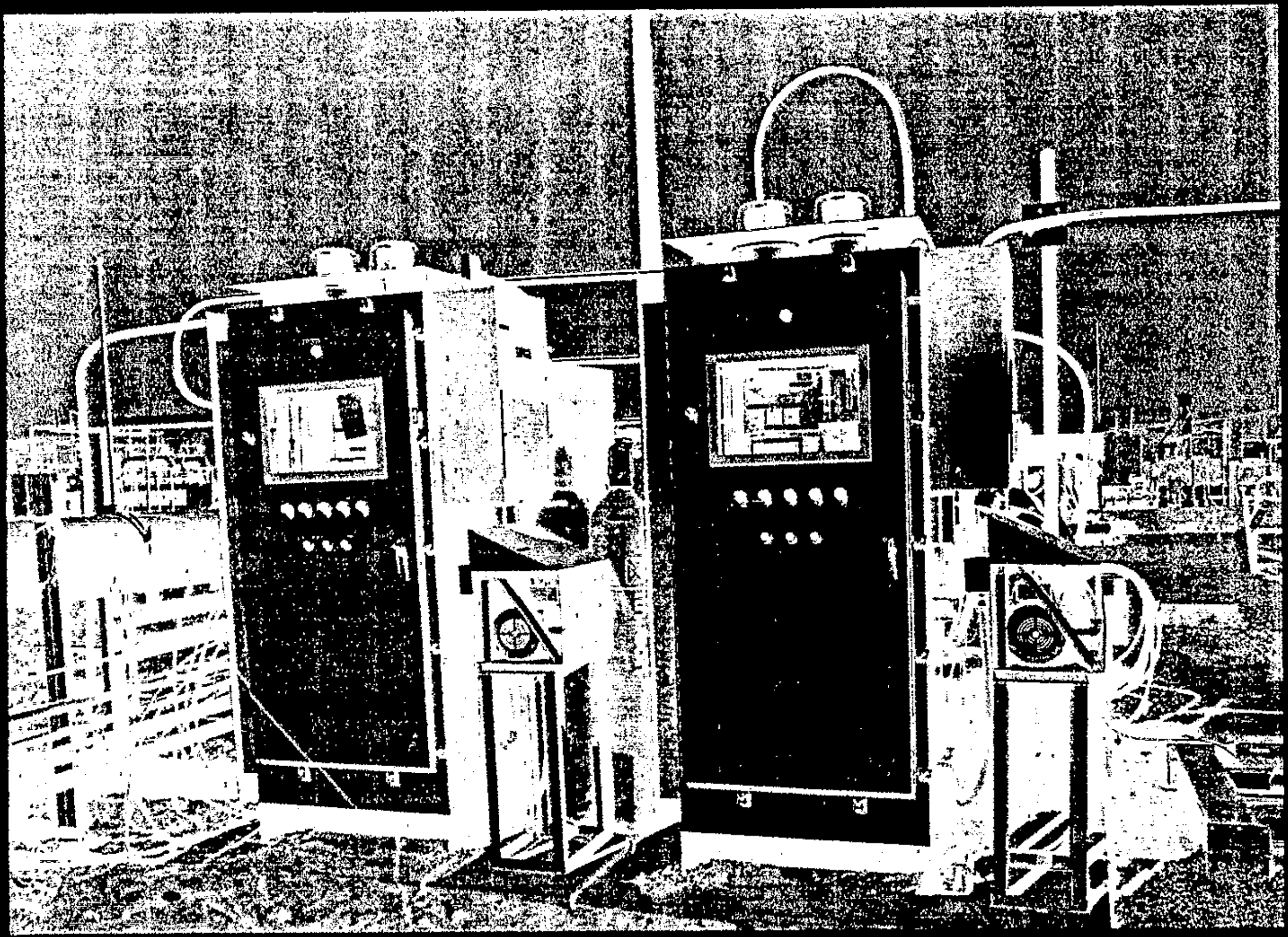

Figure 3. c) Two Standard Hydrogen Monitoring Systems are shown on top of tank 241-SY-101, located in the 200-West Area of the Hanford Site.

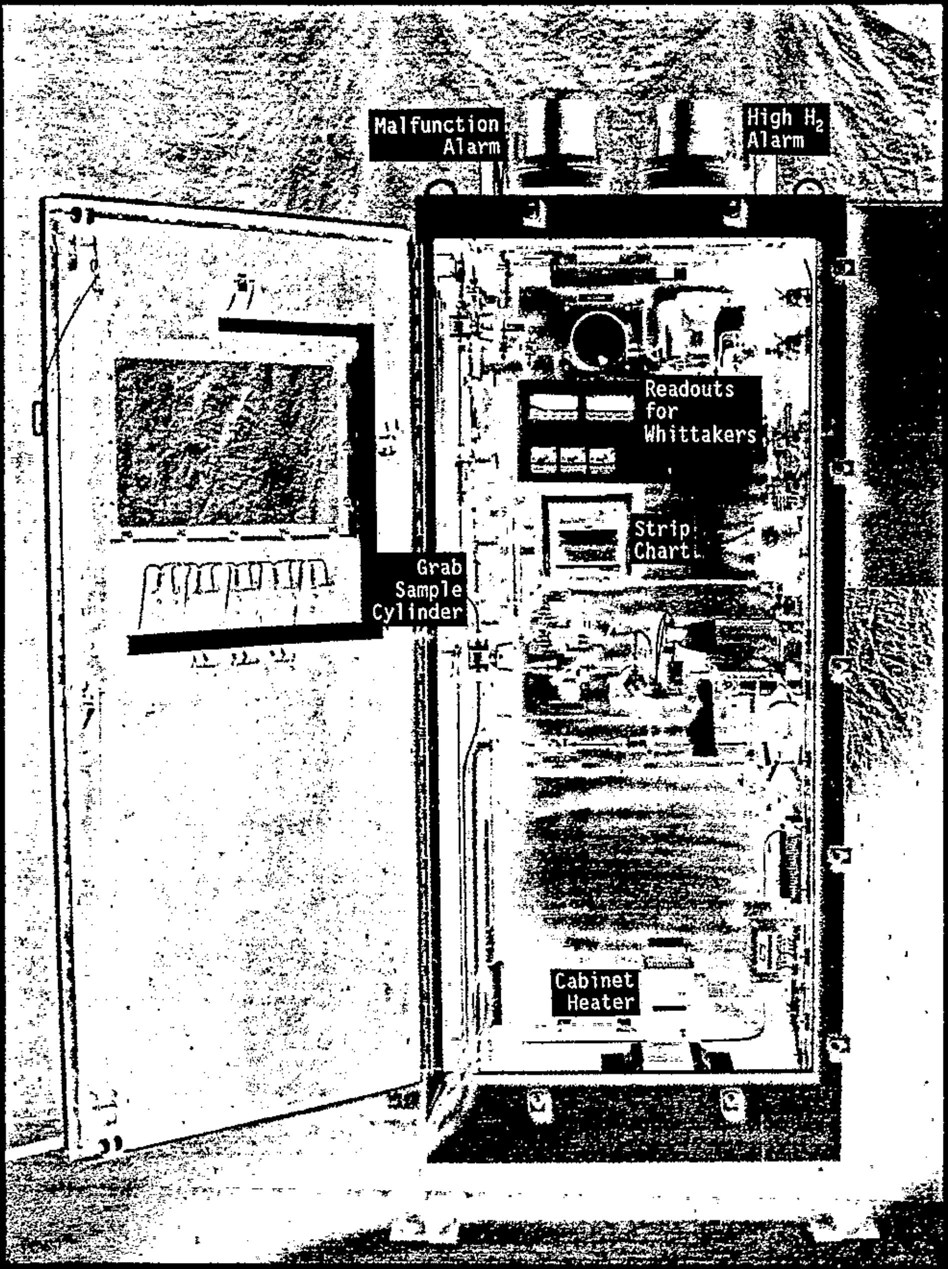

Figure 3 (continued). **d)** This is an interior view of a Standard Hydrogen Monitoring System cabinet. The cabinet is heated during the winter and alarms if either a high hydrogen level is measured or equipment malfunctions. Whittaker electrochemical cells measure hydrogen levels; measurements are displayed electronically and recorded on a strip chart. Grab samples of gas from the tank can also be taken with the Standard Hydrogen Monitoring System.

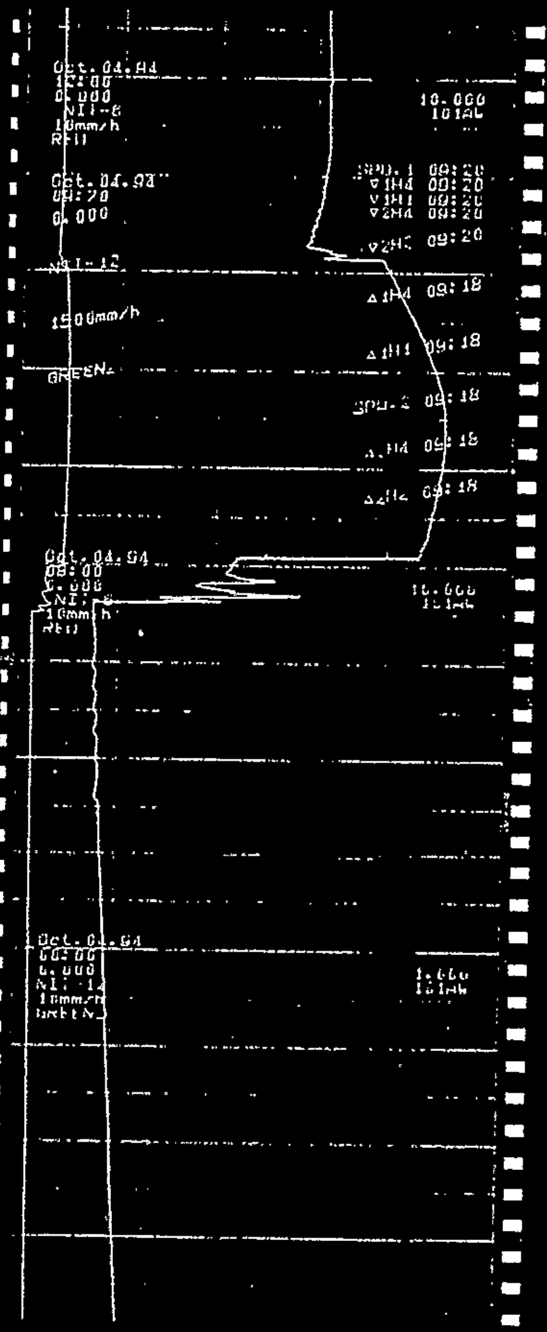

Figure 3 (continued). e) Output of the Whittaker hydrogen sensors in a Standard Hydrogen Monitoring System is recorded on a strip chart. The strip chart shown here was taken from a Standard Hydrogen Monitoring System above tank 241-AW-101, located in the 200-East Area of the Hanford Site. On October 4, 1994, this tank had an episodic gas release event which produced a concentration of 0.9% hydrogen in the tank dome space, as shown by the strip chart.

7.1 RELIABILITY OF FLAMMABLE GAS MONITORING

What is the probability that a Standard Hydrogen Monitoring System will determine that the hydrogen concentration in a tank exceeds some preset value? (This value relates only to the lower flammability limit, and is, consequently, on the order of a few tenths of a percent, as opposed to parts per million.)

Assume that the hydrogen concentration exceeds the value with a constant frequency of $1/\tau$ (τ could be, for example, the period of time between gas release events in the tank). Assume further that the probability for the Standard Hydrogen Monitoring System to operate properly when it is required to make the measurement is π; and that conversely, the probability that it does not operate properly is $1 - \pi$. Now the probability, $p(t)$, that the Standard Hydrogen Monitoring System measures the correct hydrogen concentration at the first time, t, that it is supposed to, $t = \tau_1 = \tau$, is $p(t = \tau_1) = \pi$. Since the probability that the system does not work correctly is $1 - \pi$, the probability that the correct hydrogen concentration is measured at the second event (following a failure to make the correct measurement at time $t = \tau_1$) is $p(t = \tau_2) = \pi(1 - \pi)$, the second event occurring at time $t = \tau_2 = 2\tau$. Similarly for the event occurring at time $t = \tau_3 = 3\tau$, $p(t = \tau_3) = \pi(1 - \pi)^2$, because the monitoring system works the third time after failing to work the first two times. Therefore, the *probability distribution function* for a Standard Hydrogen Monitoring System that correctly identifies a tank as one that exceeds some reoccurring hydrogen level (the events occurring with frequency $1/\tau$) after period $t = \tau_n = n\tau$ is

$$p(t = \tau_n) = \pi(1 - \pi)^{n-1}, \qquad (2)$$

because the system works the n'th time after (n — 1) prior failures.[11] The probability that a Standard Hydrogen Monitoring System has correctly characterized a tank after n periods is given by the *cumulative probability*

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[11]: Developed with Dale N. Anderson of the Pacific Northwest Laboratory, Richland, Washington.

function, $F(t)$, which is just the sum of all the probabilities $p(t)$ up to time t:

$$F(t) = p(t = \tau_1) + p(t = \tau_2) + \ldots + p(t = \tau_n),$$

$$= \pi + \pi(1 - \pi) + \ldots + \pi(1 - \pi)^{n-1}.$$

Of course,

$$F(t \longrightarrow \infty) = \textstyle\sum_{n=1\ldots\infty} p(t = \tau_n) = 1;$$

which means that unless $\pi = 0$ the system will eventually work.

Equation (2) is shown on Figure 4, where the question—For how many periods must a Standard Hydrogen Monitoring System with "reliability" π be operated until the <u>cumulative probability</u> is 0.95 ($F(\tau_n) = 0.95$) that a (reoccurring, with frequency $1/\tau$) hazardous hydrogen level will be properly identified?—is addressed. If the system works 90% of the time ($\pi = 0.9$), then $F \geq 0.95$ after only two periods ($t = 2\tau$); if its "reliability" is $\pi = 0.7$, then $F \geq 0.95$ after three periods ($t = 3\tau$); and for $\pi = 0.5$, then $F \geq 0.95$ after five periods ($t = 5\tau$).

Standard Hydrogen Monitoring Systems contain two hydrogen detectors and a grab sampling capability, and they will be subject to routine maintenance and design improvements. These systems should therefore have a reliability greater than fifty-percent, and they will be operated for several years. Flammable Gas Watch List tanks having hydrogen levels in excess of 0.625% should therefore eventually be identified.

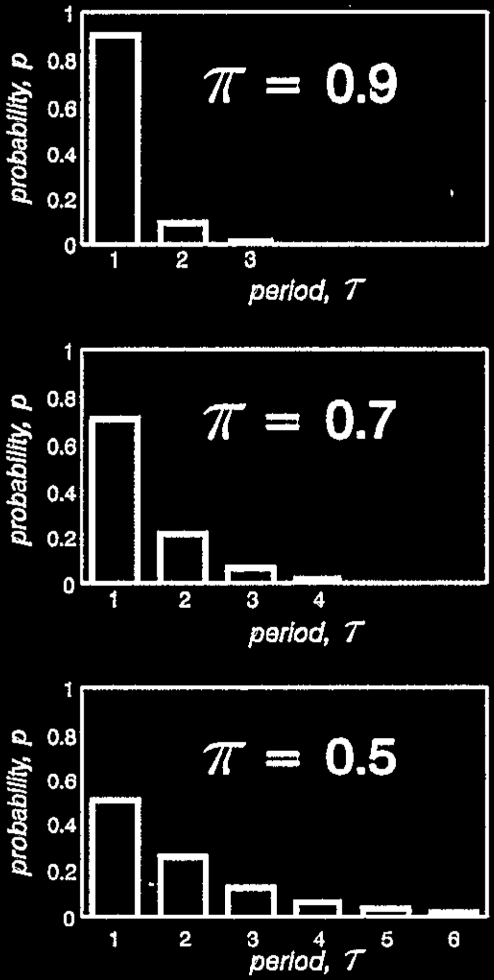

Figure 4. The probability distribution function,

$$p(t = \tau_n) = \pi(1 - \pi)^{n-1},$$

is shown here for three different values of Standard Hydrogen Monitoring System "reliability," π: $\pi = 0.9$, $\pi = 0.7$, $\pi = 0.5$. For each of these three cases the vertical axis gives the value of $p(\tau)$ for the discrete values of τ shown on the horizontal axis.

8.0 DISCUSSION

The presence of flammable gases in the Hanford tank farms has been identified as a Safety Issue (U.S. DOE 1990). Hydrogen gas is produced by water in containers of radioactive solutions; so there are always concerns about accumulation of hydrogen in the vapor spaces of reactor vessels, fuel storage systems, and radioactive waste storage tanks. This concern should be taken into account in designing ventilation systems for such equipment; see, for example, the National Fire Protection Association 69, *Standard on Explosion Prevention Systems*. **The flammable gas Safety Issue at the Hanford tank farms is primarily associated with episodic gas release events like those which occurred in tank 241-SY-101** (Simpson *et al.* 1993). **Unique waste properties are responsible for this peculiar behavior, as follows.**

The ten meter tank depth, chemical makeup of the waste streams, waste evaporation campaigns, and chemical and physical reactions, have generally resulted in a multiphase waste media being stored in the Hanford double-shell tanks.[12] Solids settle at the bottom of a tank, a dense, fluid slurry exists in the lower regions of a tank, a less dense liquid floats on top of the slurry, and a crust floats on the very top of the waste. Flammable gases are generated in any part of the waste in which there are radionuclides or reactants which produce these gases. But gas is probably only retained in

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[12]: Tanks that are likely to have a flammable gas problem are those which contain complexant concentrate, double-shell slurry, or double-shell slurry feed, because waste comprised of these process streams is suspected of having a tendency to retain gas generated in it. *Double-shell slurry* resulted from concentrating radioactive liquid waste from fuel reprocessing operations in an evaporator; this waste exceeds the sodium aluminate saturation boundary (of 0.6 molar hydroxide) and is considered a solid. *Double-shell slurry feed* was evaporated but not so much as to exceed the sodium hydroxide saturation boundary. *Complexant concentrate* is similar, but it also contains significant organic complexant levels. Waste materials resulting from these streams have specific gravities greater than about 1.4. The origin of Hanford waste is briefly discussed in the Appendix.

the lower depths of the tank: there the slurry has a yield strength so that gas bubbles are trapped, and at the very bottom of the tank settled solids can also trap bubbles. During a gas release event gas bubbles are transported from the lower regions of the waste to the waste surface level. Gas bubbles are dispersed to the dome space at the waste surface level, where the resulting gas plume begins to disperse by diffusion and convection and the gas is transported throughout the tank ventilation system. See Allemann *et al.* (1991, 1993) and Pasamehmetoglu *et al.* (1994) for presentations of the physics and chemistry of gas release events.

The manner in which gas is retained in Hanford waste has not yet been ascertained, but several mechanisms are possible: gas can be dissolved in the liquid phase (Allemann 1994), adsorbed on solids, trapped inside collections of solid particles, or trapped as bubbles in fluid media. With respect to the last of these, buoyant forces will make a gas bubble rise in a fluid. Therefore, if a waste slurry retains bubbles of gas being generated in it, then additional forces must exist on the bubbles to hold them in place. Such forces likely include surface tension, gravitational forces acting on particles to which bubbles are attached, and resistive forces from the yield strength of the medium. See Gauglitz *et al.* (1994a) for discussion about gas bubble retention mechanisms, and Gauglitz *et al.* (1994b) for discussion of the effects that gas has on slurry viscosity.

The mixture of gases (*e.g.* hydrogen, ammonia and nitrous oxide) produced in the waste stored in Hanford high level radioactive liquid waste storage tanks[13] is called *slurry gas*. Slurry gas is only detectable in the tank dome space if it is released by the waste. In some cases there may be tanks generating gas but not releasing very much of it: Some of the Flammable Gas Watch List tanks, especially those in the 241-U Tank Farm, have

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[13]: Ammonia and nitrous oxide are largely produced by reduction of nitrite ion in the presence of organic compounds. Laboratory studies suggest that lesser amounts of methane and carbon monoxide could also be produced, particularly at elevated temperatures. See, for example, Ashby *et al.* (1994) for a discussion of laboratory tests conducted to determine how flammable gases are produced in Hanford waste.

exhibited slurry growth over the period of time since their final fillings; *slurry growth* is a gradual increase in waste volume not associated with waste transfers. It is generally assumed that this slurry growth is due to the buildup (retention) of trapped gas in the waste, but the waste volume could also be increased by the production of a low density phase, such as a foam. The waste surface level in fifteen single-shell tanks varies in accordance with the atmospheric pressure, suggesting the presence of a trapped gas in the waste.

Steady-state, episodic, or sporadic concentrations of flammable gas in a tank dome space above twenty-five percent of the lower flammability limit qualifies any Hanford high-level radioactive liquid waste storage tank for the Flammable Gas Watch List.[14] The presence of a "permanent" gas phase comprised of flammable species in tank waste does not constitute an immediate safety concern because there is no means to ignite gas below the waste surface. When the waste is retrieved for final disposal, however, a gas phase in the waste could be released, and this would be a safety concern.

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[14]: Since continuous gas monitoring is not, and may not be made available for all Hanford tanks, additional criteria were developed; see Hopkins (1994) for full details.

Gas Generation in Radioactive Waste

The isotopes Cs-137 and Sr-90 are the dominant radionuclides in Hanford high level radioactive liquid waste storage tanks; their half-lives are about thirty years. Considering an average of all this waste, the radioisotope concentration is about 1 curie per liter, or about 10^{-4} moles per liter (10^{-4} M).

Radioactive decay releases energy, which can generate heat (e.g. 0.43 $W/g_{Cs\text{-}137}$ for Cs-137 and 0.92 $W/g_{Sr\text{-}90}$ for Sr-90), or break down molecules such as water. With respect to the latter, the G-value, G, is a measure for the production of H_2 molecules associated with the deposition of 100 eV of energy in a particular material (Meisel et al. 1991):

$$\underline{G} \equiv (\text{molecules of } H_2)/(100 \text{ eV}).$$

The G-value can be converted to a production rate, say $\underline{P}_{rad.}$:

$$\underline{P}_{rad.}(\text{ft.}^3 \text{ of } H_2 \text{ per kW-day}) = 800\underline{G}.$$

For pure water $\underline{G}$ = 0.45 molecules of H_2/100 eV. G-values are not easily calculated for Hanford waste because the radionuclide inventories are not accurately known and they are affected by chemicals such as organics, nitrite and nitrate (Hopkins 1994). There are other sources of hydrogen such as thermolysis ($\underline{P}_{therm.}$), chemical reactions ($\underline{P}_{chem.}$), and corrosion ($\underline{P}_{corr.}$), so the total production rate of hydrogen gas is (Hopkins 1994)

$$\underline{P}_{H_2} = \underline{P}_{rad.} + \underline{P}_{therm.} + \underline{P}_{chem.} + \underline{P}_{corr.}.$$

9.0 SUMMARY

Decaying radioisotopes emit ionizing radiation which can convert water molecules into hydrogen gas. Thus, hydrogen is generated in radioactive liquid waste. Hydrogen is flammable in air at concentrations greater than four volume percent, which is the lower flammability limit. This is a generic concern for the design and operation of radioactive liquid waste containers. The National Fire Protection Association recommends that flammable gas concentrations be maintained at levels less than twenty-five percent of the lower flammability limit (which is one percent for hydrogen in air). Other flammable gases, such as ammonia, nitrous oxide, and methane, can also be produced by chemical reactions in the waste. Hydrogen is, however, the dominant flammable gas measured in Hanford waste tanks to date.

Waste containers can be ventilated to maintain flammable gas concentrations at levels less than twenty-five percent of the lower flammability limit. Some Hanford double-shell tanks contain waste which tends to retain the gas generated in it until large amounts are released to the tank dome space. Tank 241-SY-101 is the most notable example of this behavior; it has upon at least three occasions released flammable mixtures of hydrogen and nitrous oxide to the tank dome space, the gas release rate was much faster than what the ventilation system could handle resulting in a short term increase in tank pressure. A mixing pump was installed into this tank to stir the waste so that gas is released to the dome space more frequently and in small amounts which are accommodated by the ventilation system; flammable gas concentrations no longer exceed twenty-five percent of the lower flammability limit in the vapor space.

Six double-shell and nineteen single-shell tanks at the Hanford Site are on a Flammable Gas Watch List because they contain waste which tends to generate and retain the flammable gas(es) generated in the waste. Gas generated in waste can be transported through the waste to the waste surface level continually, as it is generated, or very rapidly, after being accumulated in the lower depths of tank. The marked difference between these two types of behavior must be attributable to the rheology of the waste material. After being released from the waste surface, gas is transported through the dome space into the ventilation system and exhausted; in the case of the passively ventilated single-shell tanks, "breathing" occurs through openings, such as risers with HEPA filters, in the tank. Flammable gas release from the waste and its subsequent transport inside the tank and the ventilation system is a Safety Issue at the Hanford tank farms when concentrations approach the LFL. **This document gives the technical basis for an evaluation of this Safety Issue which involves hydrogen monitoring.**

Department of Energy Orders require that Hanford facilities comply with National Fire Protection Association guidelines; flammable gases can therefore not be present in excess of twenty-five percent of the lower flammability limit. All Flammable Gas Watch List tanks will be fitted with Standard Hydrogen Monitoring Systems to determine if hydrogen levels ever exceed 0.625 volume percent. The value 0.625% is less than the twenty-five percent of the lower flammability limit for hydrogen in air because other gases, like the oxidizer nitrous oxide, may be present, and they could reduce the lower flammability limit. In the event that a Flammable Gas Watch List tank is found to have hydrogen levels in excess of 0.625%, other flammable gases will be monitored, and the behavior of the tank evaluated, in order to determine whether the tank needs to be mitigated.

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11.0 APPENDIX A:
Hanford High-Level Radioactive Liquid Waste

Radioactive wastes produced by reprocessing irradiated uranium fuel slugs have been stored as alkaline slurries in underground storage tanks at the Hanford site since 1944. Fuel elements were irradiated in plutonium production reactors located along the Columbia river; these elements were cylindrical slugs originally clad (or coated) with aluminum and later clad with zirconium. Some of the uranium in the fuel was converted to plutonium during irradiation in these reactors. Plutonium was separated from the other materials comprising the fuel by *reprocessing* the fuel in the 200 Area of the Hanford Site. Brevick *et al.* (1994) briefly review reprocessing at Hanford, and give the current state of knowledge about the high level radioactive liquid waste stored in the tank farms.

Irradiated fuel slugs were subjected to four chemical processing operations over the years (Anderson 1990): **(1)** bismuth phosphate ($BiPO_4$), **(2)** tributyl phosphate, **(3)** REDOX, and **(4)** PUREX.

Bismuth Phosphate Process

Both the T and B plants ran the $BiPO_4$ process. *Alkaline coating removal waste* was combined with *first-cycle decontamination waste* for storage; the resulting composition is

$NaAlO_2$	1.2 M
NaOH	1.0 M
$NaNO_3$	0.6 M
$NaNO_2$	0.9 M
Na_2SiO_3	0.02 M
Pu	0.4%
U	0.4%
SpG	1.19

Metal waste contained all of the uranium, 90% of the fission products, and about 1% of the plutonium. This waste was neutralized with 50% caustic and then treated with an excess of sodium carbonate. The waste stream is

U	0.5 lb/gal
OH	0.71 M
CO_3	2.4 M
NO_3	2.7 M
PO_4	1.4 M
Na	4.8 M
Pu	1%
SpG	1.86

Second decontamination-cycle waste was combined with *canyon cell drainage waste*:

$BiPO_4$	0.08 M
LaF	< 0.01 M
KOH	0.45 M
KNO_3	0.01 M
$NaNO_3$	0.34 M
$Cr(NO_3)_3$	< 0.01 M
NaF	0.03 M
$Mn(NO_3)_2$	0.02 M
NH_4NO_3	0.01 M
Pu	1%

Metal waste from the $BiPO_4$ process was also sent to the Uranium Recovery Plant.

Redox Process

Aluminum clad fuel was declad in a boiling solution of sodium nitrate by adding 50% caustic. The resultant salt waste had a composition of

$NaAlO_2$	1.2 M
NaOH	1.0 M
$NaNO_3$	0.6 M
$NaNO_2$	0.9 M
Na_2SiO_3	0.02 M
Pu	0.4%
U	0.4%
SpG	1.19

Zirconium-clad fuel was declad in a boiling ammonium nitrate-ammonium fluoride mixture. The resulting solution was neutralized with 50% caustic, and contained up to 40% slurryable solids:

$ZrO_2 \cdot 2H_2O$	0.1 M
NaF	0.7 M
$NaNO_3$	0.02 M
KF	0.01 M
U	0.001 lb/gal
Pu	0.001 lb/gal
SpG	1.1

REDOX waste was the high-level component of the process waste:

$NaAlO_2$	1.2 M
NaOH	0.69 M
$NaNO_3$	4.83 M
Na_2CrO_7	0.066 M
$Cr(OH)_3$	0.045 M
$Na_2(SO_4)$	0.031 M
$Fe(OH)_3$	0.016 M
Pu	0.04%
U	0.05%
SpG	1.29

PUREX Process

Aluminum clad fuel was declad in a boiling solution of sodium nitrate by adding 50% caustic:

$NaAlO_2$	1.2 M
NaOH	1.0 M
$NaNO_3$	0.6 M
$NaNO_2$	0.9 M
Na_2SiO_3	0.02 M
Pu	0.4%
U	0.4%
SpG	1.19

Zirconium-clad fuel was declad in a boiling ammonium nitrate-ammonium fluoride mixture. The resulting solution was neutralized with 50% caustic, and contained up to 40% slurryable solids:

$ZrO_2 \cdot 2H_2O$	0.1 M
NaF	0.7 M
$NaNO_3$	0.02 M
KF	0.01 M
U	0.001 lb/gal
Pu	0.001 lb/gal
SpG	1.1

Organic wash waste and *neutralized PUREX Plant acid waste* streams also resulted from operation of PUREX; these are, respectively

$NaNO_3$	0.04 M
Na_2CO_3	0.13 M
MnO_2	0.004 M
U	0.0003 lb/gal
Fe	0.4 M
Na	1.4 M
NO_3	1.3 M
SO_4	0.9 M
PO_4	0.02 M
Al	0.15 M

Finally, two thorium campaigns were run in PUREX, producing the following waste stream:

KF	0.12 M
$NaAl(OH)_2$	0.34 M
$NaNO_3$	2.57 M
KNO_3	0.014 M
Na_3PO_4	0.09 M
Fe	0.025 M
SO_4	0.05 M
NaOH	0.05 M

Fission products such as Sr-90 and Cs-137 were present in all of these waste streams, but at concentrations much lower than the species listed here. Jungfleisch (1984) estimates chemical and radionuclide inventories for the Hanford Tank Farms by considering the waste processing history; Van Vleet (1993) gives the limited core sampling data that is available for some tanks.

Tank 241-SY-101 received double-shell slurry, complexed concentrate, and water as feed from 1977 to 1988. The estimated composition of this waste is (Babad *et al.* 1991)

NaOH	3.22 M
$NaAlO_2$	1.90 M
$NaNO_2$	3.28 M
$NaNO_3$	4.23 M
Na_2CO_3	0.62 M
Na_2SO_4	0.12 M
Na_3PO_4	0.19 M
Pu	713 g
Sr-90	2×10^5 Ci
Cs-137	3×10^6 Ci
TOC[15]	26 g/L
H_2O	595,000 gal

Since the waste from these process streams have been stored inside the tanks for quite some time now, it has had the opportunity to react, and has therefore changed form, *i.e.* it has *aged*. Thus, accurate, present-day knowledge of the waste stored in the Hanford Tank Farms is not generally available; it will not be available until the waste is sampled and analyzed, *i.e. characterized*. Tank 241-SY-101 is an exception: the waste in this tank has been sampled several times; see, for example, Herting (1992) for full details. All Flammable Gas Watch List tanks will in the future be similarly characterized.

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[15]: Total Organic Carbon.

12.0 APPENDIX B

CONSERVATIVE ESTIMATE OF SLURRY GAS COMPOSITION AND LOWER FLAMMABLE LIMIT IN THE SINGLE-SHELL FLAMMABLE GAS WATCH LIST TANKS

PREPARED BY R. J. VAN VLEET

1.0 INTRODUCTION

This document discusses hypothetical slurry gas mixtures. One of these is a slurry gas totally composed of hydrogen. This is probably not physically possible since vapor space sampling of other tanks has shown that ammonia is present in the dome spaces of double- and single-shell tanks. It is therefore reasonable to expect that some proportion of the gas mixture will be ammonia. A second hypothetical mixture is a slurry gas mixture used for tank 101-SY. It was chosen since it has been well characterized. The mixture includes hydrogen, nitrous oxide, methane, carbon monoxide, and ammonia. However, the lower flammability for this mixture has not been measured. The U.S. Bureau of Mines has done extensive testing with hydrogen/oxygen and hydrogen/air mixtures. This yields a lower flammability limit of 4 volume percent. Limited testing was performed by the U.S. Bureau of Mines for hydrogen/nitrous oxide. Again, depending on the interpretation of the data, the lower flammability limit is around 4 volume percent. More extensive testing of gas mixtures will be performed during fiscal year 1995.

2.0 GAS COMPOSITION

The composition of the mixture is important. If the mixture is pure hydrogen, then it takes a relatively small ignition source to ignite the mixture. However, it is only when the hydrogen concentration becomes larger (~6 %) that combustion is rapid and complete. Mixing in other gases (such as ammonia) raises the lower flammability limit. It also requires the size of the ignition source to increase. In addition, ignition of mixtures at the lower flammable limit will still be lean burns and are often incomplete. The energetics of the mixture is also another issue. Of the three gases of concern in tank 101-SY, methane is the most energetic on a per mole basis, followed by ammonia, then hydrogen. However, the amount of oxidizer required for combustion varies. Therefore, the most "bang for the buck" would come from assuming the released gas was all methane. However, it is physically unrealistic to expect 100 % methane being produced.

2.1 DERIVATION OF SLURRY GAS COMPOSITION

Only one tank, tank 101-SY, has had the slurry gas composition measured. The data began to be collected from tank 101-SY in April 1990. Instruments used to collect the data included online mass spectrometers, gas chromatographs, electrochemical cells, Fourier transform and infrared spectrometer. Furthermore, grab samples were taken and analyzed at a laboratory.

These data, have been used to develop a best-estimate and conservative estimate for the gas composition of the slurry gas released in tank 101-SY. The conservative estimate is obtained by maximizing the fuel and toxicological gas content of the mixture within the uncertainty bounds of the measured data (LANL, 1994). The information on slurry gas composition is given in the following table (LANL, 1994, Appendix C, Table C-5). The data in this table have been adjusted to take into consideration the effect of the waste temperature from whence the gas is released. This composition of gas is more energetic (about 8.8 %) than the composition computed using the Event I dome space temperatures (LANL, 1994, Appendix C, Table C-3).

Table A1. Estimates of Gas Composition at 327 K[1].

Gas	Best Estimate (%)	Conservative Estimate (%)
Hydrogen	26.66	28.42
Nitrous Oxide	22.66	24.16
Ammonia	16.53	22.15
Nitrogen	30.40	21.23
Methane	0.33	0.48
Others[2]	0.25	0.50
Water Vapor	3.07	3.07

[1] This temperature is the maximum temperature in the non-convecting layer of tank 101-SY.

[2] "Others" is assumed to represent carbon monoxide.

This slurry gas composition is considered conservative for tank 101-SY. As more data become available for the gas compositions from the other tanks on the flammable gas watch list, the analysis will be changed appropriately.

For instance, tank 101-AW had a gas release event on October 1 through October 4, 1994. The standard hydrogen monitor had been installed on tank 101-AW on September 28. The peak hydrogen concentration in the dome space was 0.88 % (i.e., the dome space was non-flammable). Calculations show that the slurry gas had to have approximately 70 % hydrogen in it to give the observed concentration. The remainder of the gas is thought to have been ammonia and/or nitrous oxide. Section 3 of this appendix will discuss the energetics of different slurry gas compositions.

2.2 CONSERVATISMS ASSOCIATED WITH THE SLURRY GAS COMPOSITION

The ammonia fraction in the release gases is assumed to be a constant. Inherent in this assumption is that all the ammonia comes out with the released bubbles of slurry gas. In the case of ammonia, this assumption is clearly incorrect since ammonia is highly soluble and there is potentially a significant mass-transfer contribution to the release. However, it is considered conservative to use a constant ammonia fraction. This is because both the mass-transfer contribution and the gas bubble contribution are proportional to the size of the gas release. The use of a constant ammonia fraction also adds conservatism by maximizing the fuel and toxicological gas content within the uncertainty bounds of the measure data. Additional information on the use of a constant ammonia fraction can be found in Appendix C and Appendix AZ of the tank 101-SY mixer pump safety assessment (LANL, 1994).

The amount of minor gases is reported, from the measured data, as being 0.5 % of the noncondensible gases. In this analysis, it will be used as 0.5 % of the total released gas (both condensible and non-condensible gases). Furthermore, methane was originally included as one of the minor gases, whereas in this analysis, the methane will be treated separately. Finally, the gases assumed to be in the minor gas category are assumed to be flammable and are represented as carbon monoxide.

The methane used in this analysis was measured in the gas composition of the tank 101-SY gas release event called Event I. The Fourier transform infrared spectrometer is not calibrated extensively for methane and the methane data must be analyzed by hand. For Event I, one frame from the Fourier transform infrared spectrometer gave a methane concentration of 378 ppm. Methane was also measured in the Fourier transform infrared spectra on the August 27, 1993, event at 88 and 35 ppm in two different frames and the September 17, 1993, event at 13 (in one frame) and 4 ppm (in six frames). The Event I data gives a methane/nitrous oxide ratio of 0.0145 with an uncertainty estimate of 20%. The other data points give methane/nitrous oxide ratios of 0.012 and 0.01. Because of the limited number of data points and because the

Fourier transform infrared spectrometer methane calibration is not as good as the ammonia calibration, a more conservative uncertainty of 35% is applied. Thus, the ratio of methane/nitrous oxide is obtained as 0.02. For this analysis, this ratio yields a conservative estimate of 0.48 % methane in the released gas.

3.0 ENERGETICS

As mentioned earlier, the fuel in the slurry gas composition has been maximized within the uncertainty of the measured data uncertainty. This section will develop a model for calculating the equivalent fuel content for different slurry gas compositions. This is done by calculating the equivalent internal energy of the combustion for the mixture and uses the following assumptions:

- The combustion process can be approximated as a constant volume process.
- The only combustion products are water, nitrogen, and carbon dioxide (i.e., combustion is complete).
- The available nitrous oxide is consumed first, the remainder of the burn uses oxygen (or air) as an oxidizer.
- The reactants and products behave as an ideal gas mixture.

The following table provide the combustion reactions of interest and the associated energies of combustion. The internal energy, u_{RP}, for an ideal gas mixture is calculated as

$$u_{RP} = h_{RP} - RT(n_P - n_R)$$

where h_{RP} is the enthalpy of combustion, R is the ideal gas constant, T is the temperature of the dome space after mixing (307 K), n_P is the number of moles of products, and n_R is the number of moles of reactants. It is assumed that water is in the vapor state.

Table A2. Combustion Reactions and Associated Internal Energies

Reaction	u_{RP} (kJ/mole of fuel)
$H_2 + 0.5\ O_2 \rightarrow H_2O$	-240.55
$H_2 + N_2O \rightarrow H_2O + N_2$	-323.80
$NH_3 + 0.75\ O_2 \rightarrow 1.5\ H_2O + 0.5\ N_2$	-317.44
$NH_3 + 1.5\ N_2O \rightarrow 1.5\ H_2O + 2\ N_2$	-442.45
$CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$	-798.31
$CH_4 + 4\ N_2O \rightarrow 2\ H_2O + CO_2 + 4\ N_2$	-1,132.10
$CO + 0.5\ O_2 \rightarrow CO_2$	-281.72
$CO + N_2O \rightarrow CO_2 + N_2$	-365.04

Using these energies, the equivalent fuel in terms of volume of hydrogen burning in air can be calculated. First, however, the fraction of the fuel that is oxidized by nitrous oxide is given by

$$\eta = \frac{F(N_2O)}{F(H_2) + 1.5F(NH_3) + 4F(CH_4) + F(CO)}$$

Then, using the internal energies from Table A2, the equivalent fuel can be calculated using the following equation.

$$Fuel_{EQUIV} = F(H_2)[R_1\eta + (1-\eta)] + F(NH_3)[R_2\eta + R_3(1-\eta)] +$$
$$F(CH_4)[R_4\eta + R_5(1-\eta)] + F(CO)[R_6\eta + R_7(1-\eta)]$$

where

$$R_1 = \frac{-323.80}{-240.55} = 1.35$$

$$R_2 = \frac{-442.45}{-240.55} = 1.84$$

$$R_3 = \frac{-317.44}{-240.55} = 1.32$$

$$R_4 = \frac{-1{,}132.10}{-240.55} = 4.71$$

$$R_5 = \frac{-798.31}{-240.55} = 3.32$$

$$R_6 = \frac{-365.04}{-240.55} = 1.52$$

$$R_7 = \frac{-281.72}{-240.55} = 1.17$$

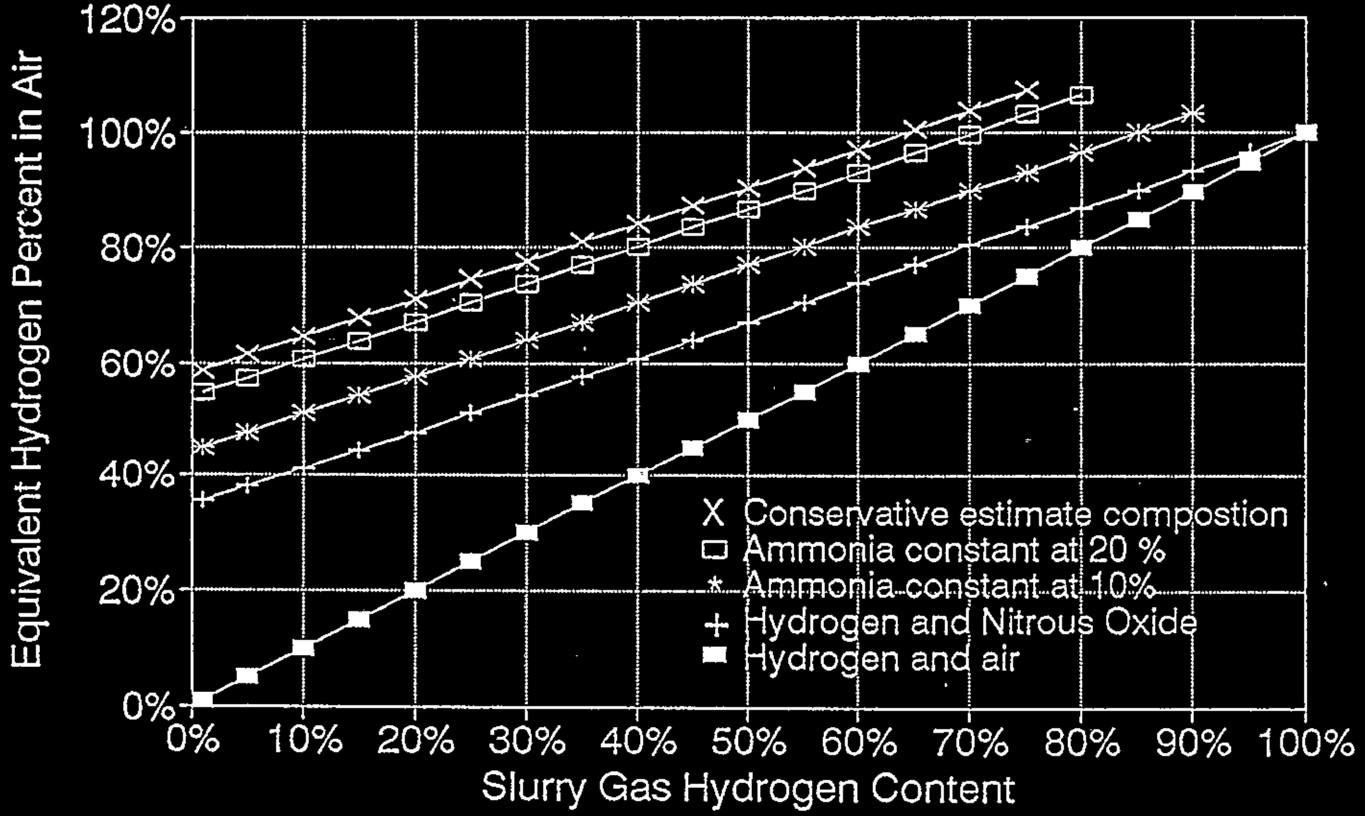
The use of equivalent fuel allows comparison of varying slurry gas compositions. Figure A1 shows curves for various slurry gas mixtures.

One curve shows hydrogen with air; a second curve of hydrogen with nitrous oxide; a third curve with hydrogen, nitrous oxide, and 10 % ammonia; a fourth curve with hydrogen, nitrous oxide, and 20 % ammonia; and a fifth curve representing the conservative mixture from Table A1 (with the exception that the hydrogen is allowed to vary from 0 to 77 % and nitrous oxide is used to account for the remainder of the slurry gas). Note: 77 % is the maximum the hydrogen value can be if the ammonia is at 22.15 %, the methane is at 0.48 %, and the carbon monoxide is at 0.5 %).

For example, if the slurry gas was composed of 30 % hydrogen (the rest of the slurry gas mixture was inert gases) and there is not another oxidizer (no nitrous oxide) then the bottom curve would show that 30 % hydrogen translates into 30 % hydrogen burning in air. This case is intuitively obvious. The conservative estimate curve on Figure A1 uses nitrous oxide as the remainder of the slurry gas, i.e., after the hydrogen, ammonia, methane and carbon monoxide are accounted for, the remainder is taken as nitrous oxide. This makes the conservative estimate curve in Figure A1 slightly more energetic than what was calculated for tank 101-SY (LANL 1994). For example, if the conservative slurry gas concentrations from Table A1 are used (hydrogen at 28.42 %, ammonia at 22.15 %, methane at 0.48 %, carbon monoxide at 0.5 %), the remainder (48.45 %) will be nitrous oxide. This mixture is equivalent to 76.6 % hydrogen in air (see Figure A1) [c.f., with 68.2 % hydrogen in air (LANL 1994)]. Another way of interpreting the chart is that it gives the energy liberated by burning one mole of the mixture (with whatever oxidizer is present). That is, for the first example, the energy liberated is (0.3)(240.55) kJ/mole or 72.2 kJ/mole and for the second example is (0.766)(240.55) kJ/mole or 184 kJ/mole.

Figure A1 shows that the conservative estimate (i.e., based upon tank 101-SY) is more energetic than any of the other compositions shown on the graph. Until better data from the other flammable gas watch list tanks are available, the conservative estimate will be used for determining consequences.

Figure A1. Equivalent Energetics in Terms of Hydrogen in Air for Slurry Gas Mixtures.



4.0 LOWER FLAMMABLE LIMIT

4.1 BACKGROUND

The lower flammable limit of a mixture depends upon a number of parameters. These include the number and types of gases, the number and types of oxidizers, the geometry of the situation, the energetics of the ignition source, etc. For this document, the following assumptions will be made.

- LeChatelier's law applies.
- Measured lower flammable limits are the same in the tank environment as they are in the laboratory.
- The mixture of gases does not change the ignition temperature or the energy required to ignite the mixture (as compared to hydrogen).

LeChatelier's law allows a lower flammable limit to be calculated if one knows the fraction of each flammable gas present in the mixture (i.e., the flammable gases are normalized and any other gases are ignored) and the lower flammable limit for each of those constituents. For example, the conservative mixture reported in Table A1 contains at least seven constituents. However, only four are flammable. These are hydrogen at 28.42 %, ammonia at 22.15 %, methane at 0.48 % and others (modeled as carbon monoxide) at 0.5 %. The fraction of hydrogen is 28.42/(28.42 + 22.15 + 0.48 + 0.5) or 0.5513. Likewise the fractions for ammonia, methane, and carbon monoxide are 0.4296, 0.0093, and 0.0097, respectively.

The following table (Table A3) gives the lower flammable limit for the flammable gases in air/oxygen (Coward and Jones) and nitrous oxide (Hertzberg and Zlochower).

Table A3. Lower Flammable Limits in Various Oxidizers

Gas	Lower Flammable Limit	
	Air/Oxygen	Nitrous Oxide
Hydrogen	3.5^1	1.8
Ammonia	8.0^2	2.0
Methane	5.0	0.8
Carbon Monoxide	12.5	---

[1] This is the lower flammable limit at T = 400 K.

[2] This is the lower flammable limit for upward flame propagation.

LeChatelier's law (Coward and Jones) is

$$LFL_{mixture} = \frac{1}{\frac{f_1}{LFL_1} + \frac{f_2}{LFL_2} + \cdots + \frac{f_n}{LFL_n}}$$

where LFL is the lower flammable limit of the particular gas and f is the normalized fraction of the particular flammable gas. Thus, for the slurry gas conservative estimate (see Table A1), the lower flammable limit in air is 4.68 % while in nitrous oxide it is 1.86 %. However, this is for one particular mixture of slurry gases.

4.2 OPERATING LIMITS FOR IN-TANK ACTIVITIES

Since the standard hydrogen monitoring system measures for only one gas, e.g., hydrogen, appropriate limits must be set for in-tank activities. To do this, some assumptions must be made on potential slurry gas compositions and on oxidizers. The following assumptions will be used:

- The slurry gas will contain four flammable gases. Ammonia will be a constant at 22.15 %, methane a constant at 0.48 %, and carbon monoxide a constant at 0.5 %. Hydrogen will be allowed to vary from 0 to 77 %.

- The maximum amount of nitrous oxide available for combustion is bounded by tank 101-SY. That is, we will assume that the volume available for the released gas to mix in is only the hemispherical portion (no credit is taken for the cylindrical volume above the waste). This volume is 950 m^3. The maximum expected gas release event from tank 101-SY is 263 m^3 of slurry gas. Of this, 24.16 % is nitrous oxide. Thus, the amount of oxidizer that will be nitrous oxide is given by (0.2416)(263/950) or 6.7 %.

The limited literature available on burns in air/oxygen with nitrous oxide indicates that the lower flammable limit is linear function depending only on the amount of nitrous oxide versus air/oxygen (i.e., a simple weighted average). Figure A2 presents the lower flammable limit of slurry gas compositions with 93.3 % air and 6.7 % nitrous oxide.

Current operating experience with tank 101-SY and tank 101-AW would indicate that the percent hydrogen in the slurry gas mixture can range from 28 % to 70 %. Over this range, the lower flammable limit ranges from approximately 4.5 to 3.87 %. Of this, the hydrogen contribution to the lower flammable limit would yield concentrations in the tank ranging from approximately 2.5 to 3.0 % (see Figure A2). Hydrogen is the only flammable gas measured by the Whittaker electrochemical cells in the standard hydrogen monitoring cabinets. To conduct activities safely in a tank, a limit must be chosen that will cause activities to cease before there is any problem with flammability. The National Fire Protection Association, Inc., indicates that 25 % of the lower flammable limit is the cut off for stopping activities. For the currently known situation the safety limit should be (0.25)(2.5 %) or 0.625 % (6,250 ppm) for hydrogen. If additional monitoring is added for ammonia, a limit for ammonia would be (0.25)(0.86 %) or 0.215 % (2,150 ppm).

5.0 CONCLUSIONS

To operate safely, an analysis was performed to determine a conservative estimate of slurry gas composition. This slurry gas composition was shown to be more energetic than a few other mixtures. The lower flammable limit was developed over a range of hydrogen concentrations using the conservative slurry gas composition. An operating limit of 6,250 ppm hydrogen is set for in-tank activities. Additionally, for future contingencies, an operating limit of 2,150 ppm of ammonia was developed. As more data are obtained from the tanks, the information on slurry gas compositions, lower flammable limits, and operating limits may change.

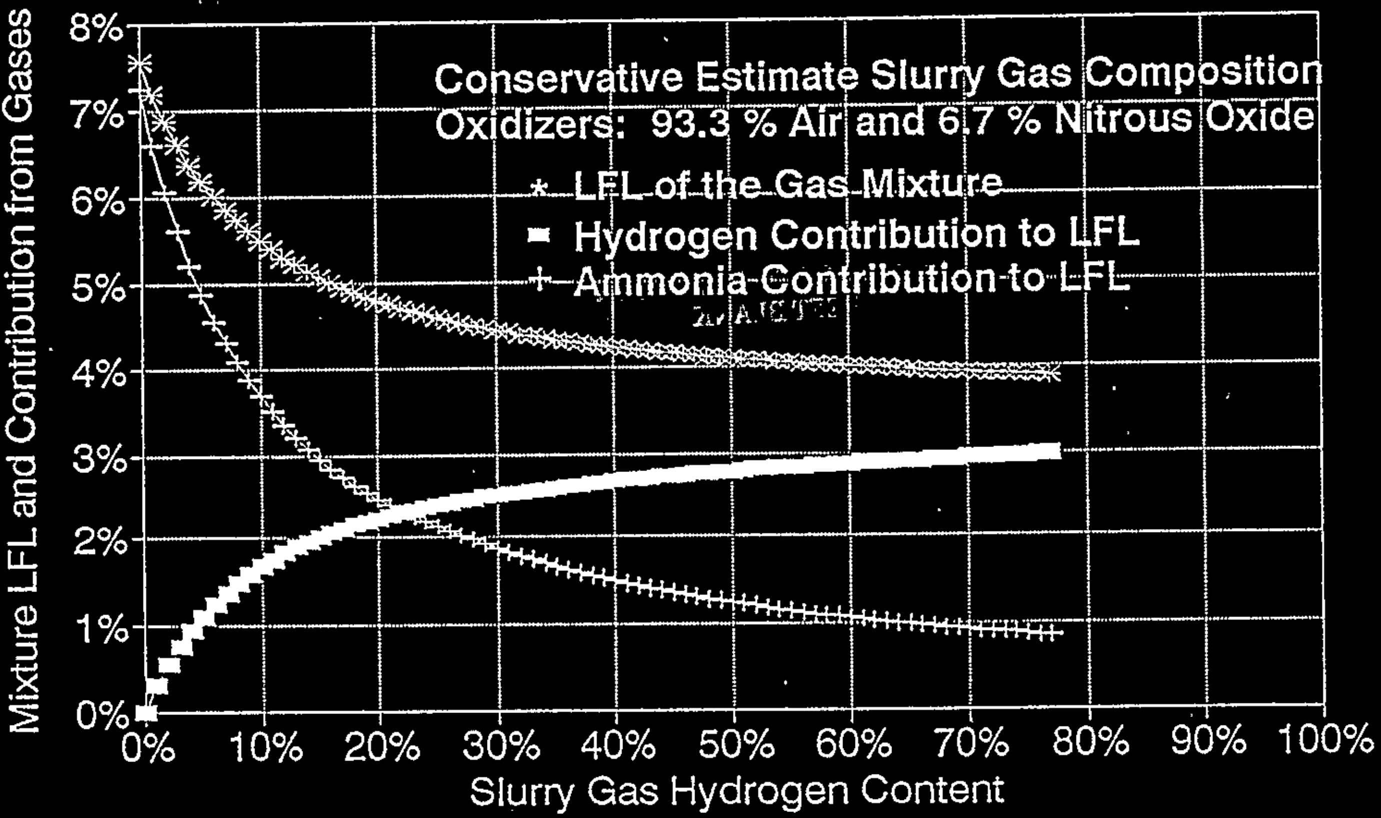
6.0 REFERENCES

Coward, H. F., and G. W. Jones, 1952, *Limits of Flammability of Gases and Vapors*, Bulletin 503, Bureau of Mines, Pittsburgh, Pennsylvania.

Hertzberg, M., and I. A. Zlochower, 1993, *Explosibility of Nitrous Oxide Gas: The Effect of H-Atom-Bearing Impurities*, 25th International Symposium on Combustion, University of California, Irvine, California.

Los Alamos National Laboratory, 1994, *A Safety Assessment for Proposed Pump Mixing Operations to Mitigate Episodic Gas Releases in Tank 241-SY-101: Hanford Site, Richland, Washington*, LA-UR-92-3196, Rev. 13, Los Alamos, New Mexico.

Figure A2. LFL as a Function of the Best Estimate Slurry Gas Composition and 2 Oxidizers



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