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FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES (DQO) PROCESS REV 1 (WHC-SD-WM-DQO-004)		ECN No. 165852

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1. ECN 165852

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Changes:

1. Changed some wording to comply with Characterization Program suggestions.
2. More words to emphasize that knowledge gained from current core samples can be used to modify later core sampling.
3. Moved some supporting material from the body of the report to an appendix.
4. Provided for analysis of drainable liquids recovered from cores.
5. Added the analytes ^{3}H, Ba, B, Bi, Si.
6. Added section on use of historical data.
7. Added attachment.

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Conceptual Design Report	[]	Installation Procedure	[]	Component Index	[]
Equipment Spec.	[]	Maintenance Procedure	[]	ASME Coded Item	[]
Const. Spec.	[]	Engineering Procedure	[]	Human Factor Consideration	[]
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Vendor Information	[]	Operating Procedure	[]	Electric Circuit Schedule	[]
OM Manual	[]	Operational Safety Requirement	[]	ICRS Procedure	[]
FSAR/SAR	[]	IEFD Drawing	[]	Process Control Manual/Plan	[]
Safety Equipment List	[]	Cell Arrangement Drawing	[]	Process Flow Chart	[]
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Cog. Mgr. D. G. Baide DGBaide	4/28/95	QA	
QA		Safety	
Safety		Design	
Environ.		Environ.	
Other J. P. Sloughter	5-1-95	Other	
Program Mgr. G. D. Johnson GDJohnson	4-28-95		
Programs N. G. McDuffie GDJ for NGM	4-28-95		
		DEPARTMENT OF ENERGY	
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APPROVED FOR PUBLIC RELEASE

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Name: M. D. LeClair

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7. Abstract

This document represents the application of the Data Quality Objectives (DQO) process to the Flammable Gas Tank Safety Issue at the Hanford Site. The product of this effort is a list of data required from tank core sample analysis to support resolution of this issue.

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(2) Title

FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES (DQO) PROCESS

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Flammable Gas Tank Safety Program: Data Requirements for Core Sample Analysis Developed Through the Data Quality Objectives (DQO) Process

Lead Author - N. G. McDuffie

MASTER

FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES (DQO) PROCESS

ABSTRACT

A Data Quality Objectives (DQO) process was applied to the Flammable Gas Tank Safety Issue at the Hanford Site. The main product from this data quality objectives process was a list of data requirements for the analysis of core samples from the double-shell tanks. Information from core samples is required to support evaluations of chemical mechanisms for gas production and release and to support tank behavior models needed for making safety analyses and developing mitigation methods. Results from these evaluations will be used to provide the basis for making decisions on mitigation and safe storage. Research and development studies in support of these decisions will be documented by separate test plans. These test plans will be submitted along with the applicable DQO's for allocation of material from the core samples. Where applicable, historical data will be used so that the number of analyses can be minimized. A separate DQO will be prepared to cover the primary issue of "flammability" for the watch list tanks. The DQO's will be reviewed routinely to optimize the sampling and analysis processes and to minimize cost of ultimate mitigation of the flammable gas safety issues.

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1.0 INTRODUCTION

Statement of the Issue

The release of flammable gases into the dome space of Tank 241-SY-101 (SY-101) and other waste tanks at the Hanford Site is a top priority safety issue. Periodic releases of these gases has resulted, in a few instances, in concentrations above the lower flammability limit (LFL) for hydrogen and other contained fuels. Such venting of gases is expected to keep recurring until some form of mitigation or retrieval action is taken.

Understanding the Issue

Insufficient knowledge has been obtained about the processes occurring within the waste that generate, retain and release the gases. Collecting information about the basic chemical and physical properties of the waste is one of the first steps needed to gain knowledge about the behavior of the waste. This information, coupled with laboratory and modeling activities, will help to provide the basis for making decisions about the magnitude of the safety issue.

Closure of the Issue

As an understanding of the behavior of the waste is developed, various mitigation methods can be devised to maintain the tanks in a safe condition. These mitigation methods may involve mechanical processes, chemical treatment, or a combination of both. A mixer pump has been installed in Tank SY-101 to mitigate the flammable gas safety issue in that tank. Thorough reviews of successes for this operation will allow projections for possible pump applications in the other double-shell tanks on the Flammable Gas Watch List. These projections can include evaluations of direct mitigation without complete characterization, a process that could save the costs of detailed characterization.

Scope of this Data Quality Objectives Document

This Data Quality Objectives (DQO) document was prepared for the Flammable Gas Tank Safety Program. The scope of this activity was to summarize the analytical needs for core sampling activities of the Flammable Gas Watch List tanks. Data from the core samples are needed to provide an understanding of the tank contents so that: (a) insight may be obtained on the mechanisms for gas generation, retention and release, (b) models of the waste behavior can be developed to support safety analysis and development of mitigation methods, (c) compositions of simulants for waste studies can be developed, and (d) modeling of the release of gases, and subsequent potential for ignition in the dome space, can be done to support hazard analyses. Special tests on the waste samples will be needed to evaluate gas generation, gas solubility and the effects of heating and dilution on waste behavior. Test plans will be prepared for these activities. These test plans will incorporate statements, and justifications, of requirements for samples of tank core material over and above the requirements for laboratory analysis supporting this and other DQO's. The product for the core sampling DQO is a list of data requirements.

As an understanding is developed, it may be possible to specify decisions that can be made on the basis of core sample results. Once this is accomplished, then this DQO will be revised to incorporate the requisite decisions.

Data of various types are required to evaluate safety issues arising from the presence of flammable gas mixtures in Hanford Site tanks, as well as to support mitigation of hazards disclosed through such evaluations. The primary categories of applicable data are:

1) Physical operating data including in-tank temperature histories, dome pressure data, ventilation flow rates, surface levels, and other data, including video recordings of surface appearances and changes, obtained from specific tanks or groups of tanks.

2) Continuous or repetitive gas analyses obtained from continuous or intermittent gas monitoring systems on tank dome contents, individual tank ventilation exhausts, or tank group exhaust systems.

3) Laboratory gas analyses on grab samples from tank dome spaces, individual tank exhausts, or tank group exhaust systems.

4) Laboratory analyses of auger samples of crust or upper solids.

5) Laboratory analyses of core samples obtained either by push-mode or rotary-mode core sampling procedures.

6) Data obtained from in-tank test procedures (viscosity, yield strength, gas content, differential pressures, sound velocity and attenuation, penetrability, compressibility, and others that may be instituted).

7) Retained gas content and composition obtained from procedures involving retained-gas sampler now under development.

The Data Quality Objectives (DQO) for the Flammable Gas Watch List tank characterization are described in this presentation. The current document is not meant to contain a critical evaluation of data quality requirements for items 1, 2, 3, 4, 6, or 7, above. Item 4 is covered by a separate document (Johnson, 1994), which was prepared separately in order to have it finished in time for the auger sampling of Tank 241-SY-103. The auger sampling DQO's were covered in the same meetings in which the presently-described DQO was developed. A separate DQO is being prepared to cover items 2 and 3.

Background of the DQO Process for This Document

Major expectations of participants in the DQO development exercise were to accomplish the following tasks:

- Identify methods beyond the standard safety-screening (in Babad, 1994) suite that will address the safety problem(s).

- Determine what "level of quality" is needed for each analysis or parameter, including newly developing tests.
- Focus especially on data quality and data requirements for characterization.
- Ensure that data users are aware of laboratory and field measurement capabilities and that data users' requirements are well justified, sufficient, quantitative, and achievable.
- Incorporate secondary user data requirements into the design generated to achieve primary user data requirements.
- Focus on practical and useful analyses needed for specified purposes, using historical data when applicable.
- Generate a sampling and analysis plan that meets the needs of data users (by providing input to the specific Tank Characterization Plans, which will give the detailed plan).

This document provides the data requirements that evolved over the course of the meetings. The DQO planning team fully expects the data requirements and DQO to evolve over time. This approach is consistent with the Tank Waste Remediation System DQO Strategy (Babad et al., 1994) which states, "The identification of data requirements is intended to be an ongoing effort aimed at accommodating gains in information from any source, rather than a one-time data requirements identification activity." Core sampling of the waste will provide supporting data for the Flammable Gas Waste Tank Program decision processes, by providing a better understanding of the mechanisms behind gas releases, periodic and aperiodic. A better understanding of gas release events may lead to modifications of the data requirements, which may become either more or less exacting than those currently accepted.

2.0 THE FLAMMABLE GAS SAFETY ISSUE

Hydrogen gas is produced by radiolysis in most containers of radioactive solutions in water, so there are always concerns about accumulation of hydrogen, a very flammable gas, in vapor spaces of vessels of reactors, fuel storage systems, and radioactive waste storage tanks. These are concerns that are taken into account in designing related ventilation, exhaust, and purge systems for such equipment. Even though the Hanford Flammable Gas Waste Tank Safety Program is mandated to study older storage tanks to ensure that unsafe flammable gas (hydrogen and other flammable constituents) concentrations do not accumulate from non-episodic releases, the primary safety issue for the program is that related to episodic gas release events, noted especially in Tank 241-SY-101 (101-SY). In addition to Tank 101-SY, the Flammable Gas Watch List contains 24 other tanks that either exhibit episodic gas releases like those in 101-SY, but to a lesser extent, or are considered likely to exhibit such releases.

2.1 BASIS FOR WATCH LIST

The Flammable Gas Tank Watch List was initially made up to include Tank 101-SY and any tanks containing materials related to contents of Tank 101-SY or tanks that exhibited slurry growth, episodic level drops, or pressure bumps. On this basis, the list is chosen conservatively, since Tank 101-SY, whose episodic activity is greater than that of any other tank, has exceeded lower flammability limits in the ventilation system in only a few events of very short duration. Another, more general, concern is that many tanks are producing smaller releases of gas containing fuel components mixed with the oxidizer, nitrous oxide. The released volume of gas would be flammable, and would be expected to ignite if a spark source were present in the same space. The probability of such ignition in a closed tank is considered to be very low, but possibly not incredible. Scenarios involving such processes are now under study. Outcomes of these studies could affect subsequent revisions of the Flammable Gas Watch List and related DQO's. Also, as noted above, the general concern about accumulations of flammable gas mixtures in dome spaces and ventilation systems of tanks can lead to establishment of requirements for active ventilation of tanks now only passively ventilated. A separate DQO is being prepared for gas monitoring activities. In addition, the general safety screening process could lead to placement of more tanks on the Flammable Gas Watch List, with requirements of further DQO's.

2.2 CHEMISTRY OF GAS GENERATION

Gas generation chemistry of Hanford Site waste material has been studied at WHC (and its predecessor Hanford Site contractors/managers), Argonne National Laboratories (ANL), Georgia Institute of Technology (GIT), and PNL as well as other laboratories, to a lesser extent. Studies with simulant mixtures show that it is possible to produce flammable gas mixtures even without the presence of radiation. Radiolytic production of hydrogen is aided by the presence of organics and hindered by nitrite and nitrate ions. Chemical degradation of organics to produce hydrogen requires basic conditions (high hydroxide ion concentration), as well as the presence of aluminate in some

form. To a large degree ammonia and nitrous oxide are produced by reduction of nitrite ion in the presence of organic compounds. The relative contribution of purely chemical production of gases as compared to radiolytic production has not yet been determined. Laboratory studies confirm the production of lesser amounts of methane (and some CO), especially at elevated temperatures. Furthermore, chemical and radiolytic chemical studies indicate that organic compounds such as some of the complexants are active in producing gases while more refractory organics, especially formate and oxalate (formic acid and oxalic acid anions) are not effective hydrogen producers under tank conditions. A general conclusion is that in Hanford Site radioactive wastes containing active organics, aluminum and nitrite the potential exists for production of flammable mixtures of hydrogen, ammonia, and nitrous oxide, along with low concentrations of methane and carbon monoxide.

Historically, the tanks considered primary flammable gas safety issue tanks have been those that contain complexant concentrate (CC), double-shell slurry (DSS), or double-shell slurry feed (DSSF), all process streams originally containing relatively high concentrations of organic compounds and relatively concentrated in salts to give combined (solids plus liquids) specific gravities over about 1.4.

2.3 PHYSICS AND PHYSICAL CHEMISTRY OF GAS RETENTION

The physics of gas retention and gas release is not completely understood; however, it is known that the relative densities of solid and liquid phases, as well as shear strength of gas-retaining layers are important factors determining the relative amount of gas retained before gas release can occur. Viscosities of the fluids and slurries are also of importance in the computer models used to simulate rollover activities of the tanks. The actual mode of attachment or trapping of gas in the slurries has not yet been ascertained. Current research is directed toward a better understanding of the physics of gas retention. Also, because sampling and sample handling affect rheological measurements, efforts are directed toward in-situ measurements of viscosity and shear strength. Additionally, in-situ measurements of gas content of tank layers are to be attempted under the Mitigation Program.

2.4 CURRENT UNDERSTANDING OF COMPOSITION OF RELEASED GAS

The current understanding of composition of gas released in gas release events is obtained from studies on Tank 101-SY. This tank is highly instrumented for monitoring of results of flammability mitigation activities, *viz.*, mixing with a pump. However, some uncertainty still exists regarding exact composition of the gas from gas release events, because a major component, nitrogen, has only been measured in a few prior grab samples during gas releases. The composition of the gas is variable. Two of the vapor components, ammonia and nitrous oxide, are appreciably soluble. Their release from solution, as well as release of water vapor, will depend on mass transport rate limitations. Ranges of gas compositions are summarized in Table II. The major flammability concerns are for the gases released during the Gas Release Events (GRE's, Table II.A). Examination of the information therein indicates that ammonia, not hydrogen, is the major flammable gas released from Tank 101-SY if the gas release event cycle time is as high as 180 days (see Table II.B). However,

most of the ammonia is released in the periods between gas release events, when it is diluted by the air purge. The lower flammability limit (LFL) for ammonia in air is much higher than it is for hydrogen in air (15-16 vol.% for ammonia compared to 3.5-4 vol. % for hydrogen). In gases containing high

TABLE I. TANK 101-SY RELEASED GAS COMPOSITIONS

A. GAS RELEASE EVENTS, RELEASED GAS, DRY BASIS, 10,000-13,000 STANDARD CUBIC FOOT RELEASE

COMPONENT	CONTENT, VOLUME %	RATIO: COMPONENT/HYDROGEN
H_2	30-35	1.0
N_2O	25-30	0.7-1.3, av. ~0.8
N_2	20-25	0.6-0.8
NH_3	12-18	0.3-0.6
CH_4	≤1	≤0.03

NOTE: WATER VAPOR(H_2O) CONTENT IS ABOUT 4 VOLUME %.

B. BASELINE BETWEEN GRE'S, CONTENTS IN 550 CFM EXHAUST AIR FLOW

COMPONENT	CONTENT, PPM VOL.	AVERAGE RATIO TO HYDROGEN	APPROX. FT^3/D
H_2	10-18, av. ~18	1.0	15
N_2O	12-40, av. ~22	~1.2	18
NH_3	40-100, av. ~40	~2.2	33

NOTES: METHANE (CH_4) NOT MEASURABLE ABOVE AMBIENT AIR CONCENTRATION LEVELS. NITROUS OXIDE (N_2O) AND AMMONIA (NH_3) CONCENTRATIONS REACH THE HIGHER BOUNDS DURING BAROMETRIC PRESSURE LOWS. TOTAL RELEASES (NOT INCLUDING AMOUNT RELEASED IN GRE) DURING A 180-DAY PERIOD WOULD BE: H_2, 2700 STANDARD CUBIC FEET (SCF); N_2O, 3200 SCF; AND NH_3, 5900 SCF.

concentrations of nitrous oxide relative to ammonia, the LFL for ammonia is reported to be very low, reaching 2.2% in mixture with nitrous oxide alone (Coward and Jones, 1952); however, it is not certain whether an LFL value of less than 15% will apply to any of the multicomponent gas mixtures encountered in Hanford Site tanks. This question is the subject an investigation currently funded by the Flammable Gas Safety Program through Los Alamos National Laboratory.

2.5 THE CURRENT FLAMMABLE GAS SAFETY PROGRAM WATCH LIST

The current Flammable Gas Safety Program watch list contains the following tanks:

241-A-101
241-AN-103, 104, 105
241-AW-101
241-AX-101, 103
241-S-102, 111, 122
241-SX-101, 102, 103, 104, 105, 106, 109
241-SY-101, 103
241-T-110
241-U-103, 105, 107, 108, 109

This list is subject to upgrading, especially during the current safety screening campaign. Vigilance should be maintained to respond to any changes in operations or any new developments in any of the waste tanks that indicate possible flammable gas implications. For example, tanks with high radionuclide contents should be monitored to evaluate flammable gas production. Process and transfer tanks [including the double-contained receiving tanks (DCRT's)] are all prone to some buildup of flammable gas. The current set of flammable gas DQO's should provide guidance in developing logical sequences for evaluation of situations involving waste storage tanks not contained in the watch list.

2.6 OVERLAPPING WASTE TANK SAFETY PROGRAM ISSUES

Several of the Hanford waste tanks are covered by safety concerns under more than one specific program. The flammable gas watch list tanks that are covered by other programs in addition the Flammable Gas Safety Program are as follows, listed by specific program or concern:

ORGANIC SAFETY PROGRAM
241-A-101, 241-S-102, 241-S-111, 241-SX-103, 241-U-103, 241-U-105, and 241-U-107

HIGH-HEAT SAFETY PROGRAM
None currently

FERROCYANIDE SAFETY PROGRAM
None currently

CRITICALITY
All tanks

TANK VAPOR ISSUE RESOLUTION
None currently

Safety screening may establish more overlapping concerns. For tanks covered by more than one safety concern, mutually acceptable data requirements must be established. Data quality objectives reports have been issued for the ferrocyanide (Buck, et al., 1993), high-heat (Wang et al., 1994), and tank vapor issue (Osborne et al., 1994) safety issues, as well as for safety screening all tanks (Babad, 1994). Tank 101-SY releases large quantities of nitrous oxide, and it releases ammonia in concentrations far above limits deemed safe for unprotected workers. Other flammable gas watch list tanks are likely to do the same; thus there is certainly concern for toxic vapor released from the tanks. This must be taken into account for any safety assessments and work controls developed for work in, upon, and around the tanks.

2.7 RELATIONSHIP OF UNREVIEWED SAFETY QUESTIONS TO DQO

An Unreviewed Safety Question (USQ) was declared in March of 1990 (Daugherty, 1990) with the issuance of an Unusual Occurrence Report (UOR). The report stated, in part, "Recent Westinghouse reviews of the tank vapor space flammability identified that the gas under the crust is potentially flammable because nitrous oxide N_2O and hydrogen can create flammable mixtures. This is considered an Unreviewed Safety Question." The existing Safety Analysis Report (SAR) at that time did include the issue of hydrogen generation but did not specifically consider the hazard of a flammable mixture of hydrogen and nitrous oxide within the waste. Later, in May, the Department of Energy issued a letter (Lawrence, 1990), per the requirements of DOE Order 5480.5, that stated "DOE-RL has determined that the matter of hydrogen and nitrous oxide evolution within the material in certain waste tanks and subsequent hypothetical hydrogen ignition is an unreviewed safety question". The references to this letter provided identification of the tanks of concern.

Thus, the USQ was generated initially by a concern over the simultaneous generation of fuel (hydrogen) and an oxidizer (nitrous oxide). However, the extensive analytical and experimental work conducted for tank 241-SY-101 have also shown the need to consider other flammable gases such as ammonia and methane.

Closure of the USQ requires the following steps: (1) analyze the hazards, (2) implement work controls, (3) update the safety basis, (4) close the UOR, and (5) obtain DOE approval. The primary information needed for this process is knowledge of the amount and composition of the gas mixture that is released into the dome space of a given tank. This information is then used to determine if there is a potential for ignition of the gas mixture. Resolution of the USQ does not mean that the basic safety issue has been closed. Closure of the safety issue requires placing a tank in a safe condition by enhancing monitoring and operational controls, or by mitigating the existing situation, or maybe even by remedial actions involving waste

treatment. Thus, closure of the safety issue is facilitated with in-depth knowledge of the waste. At the present time, the only Flammable Gas Watch List (FGWL) tank that has been characterized is 101-SY. The other double shell tanks on the FGWL do exhibit episodic gas releases, but there is little information on the nature of the waste in the current situation. This DQO provides the data requirements for the items that need to be analyzed on double-shell tank core segments (see Section 5.0) in order that the Flammable Gas Tank Safety Program can characterize and understand the nature of the basic problem of gas generation, retention and release.

2.8 RELATIONSHIP OF CHARACTERIZATION TO MITIGATION

Characterization of the flammable gas safety watch list tanks will be directed towards two different primary goals along parallel pathways. These goals are as follows: (1) to evaluate relative hazards in the tanks and (2) to develop an understanding of the chemical and physical processes occurring in the waste and then to determine possible modes for mitigating any safety hazard. Minimization of time at risk, radiation exposure of workers, and expense dictates that the same sampling process should provide data for both goals.

Mitigation of flammable gas safety hazards may be achieved by a rather wide range of alternative actions, depending on the nature and grade of risk. Some of the types of mitigation possibilities and their related data requirements have been presented in reports for the Flammable Gas Mitigation Program (Ashby et al., 1992; Babad et al., 1992; Lentsch, 1992). As indicated in these reports, the mitigation concepts involve either physical or chemical treatments. Each of these mitigation possibilities has its own set of data requirements, some exclusive, and others very general. The general data requirements covered by the current characterization effort are not meant to address all possible alternatives for mitigation. Obviously it is not advisable to obtain data for all of the conceivable modes of mitigation for the tanks, and especially for those that do not require mitigation. Ultimately all of the contents of all tanks will be retrieved for final disposal.

2.9 SUPPORTING OPERATIONAL DATA

Other operating data, historical and current, not covered in the present data quality objectives exercise, may be used in supporting safety analyses of flammable gas watch list tanks. Some of these (provided here for information only) are as follows:

- Tank ventilation flow rates (for actively ventilated tanks).
- Tank annulus ventilation flow rate where available.
- Temperatures in tank contents (and resultant temperature profiles).
- Pressures in tank (generally gauge pressures) dome space.
- Tank breathing rate (for passively ventilated tanks).

- Barometric pressure.
- Temperatures of incoming ventilation air streams, dome spaces, exhaust, etc.
- Ambient air temperature, humidity, wind velocity and direction.
- Surface level of waste in tank.
- Liquid observation well liquid height or depth (single-shell tanks)
- Annulus, tank concrete temperatures.
- Water content or relative humidity of tank exhaust.
- Surface characteristics as indicated by in-tank visualization with video cameras installed in tanks.

2.10 USER GROUPS FOR FLAMMABLE GAS WASTE TANK DATA

Currently the primary user groups for the flammable gas waste tank data are as follows:

WESTINGHOUSE HANFORD COMPANY
- Flammable Gas Safety Program, Tank Waste Remediation System
- Technical Data Analysts (with Numerical Applications, Inc.)
- Computer Modelers
- Safety Analysts
- Design Engineers

PACIFIC NORTHWEST LABORATORIES
- Computer modelers
- Physical modelers
- Data Analysts
- Chemical Groups studying properties and reactions (With assistance from several university scientists)

GEORGIA INSTITUTE OF TECHNOLOGY
- Chemistry Department group studying reactions of simulants

LOS ALAMOS NATIONAL LABORATORY
- Safety Analysts
- Scientists studying mitigation processes
- Physical model developers

2.11 QUESTIONS FOR RESOLVING THE PROBLEM

Data obtained from the flammable gas waste tanks will be used to answer the following questions in regard to the flammability problem:

1) Do the tanks present a real flammability problem (primary question)?

2) What is the composition of the slurry gas?

3) How much slurry growth is related to gas entrapment?

4) Is the level of gas evolution sufficient to cause a radiation or toxic release (with or without ignition) during storage and normal tank operations?

5) If the answer to Question (1) is affirmative, How can the situation be corrected?; What control or mitigation actions are dictated?

It should be noted that this DQO does not address the data needed for the above questions, a separate DQO is being prepared for gas monitoring of the tanks.

Secondary questions related to this DQO are:

6) What conditions are responsible for producing the flammable gas species? Can they be controlled; if so, how?

7) What conditions cause gas retention and subsequent episodic gas release?

8) What would be the on-site and off-site dose consequences from a postulated gas burn?

9) What conditions are to be avoided in filling new waste tanks to prevent flammable gas problems from developing?

10) Are there follow-up data requirements?

2.12 SUPPORTING ANALYTICAL DATA

Initially, core samples are to be taken from the double-shell flammable gas watch list tanks only. Decisions regarding core sampling of the single-shell flammable gas watch list tanks will be made after study of results from the double-shell tanks are studied. Chemical and physical characterization analyses of these core samples are deemed very important in the continuing efforts to understand the flammable gas generation, retention, and release issues related to the secondary questions listed in Section 2.11. These data will provide valuable input to the models being used to predict tank behavior and for verification of the laboratory work on waste simulants.

A related effort is the activity directed to development of a retained gas sampling device and procedure for its use. Successful use of this device should provide knowledge of contents of volatile components retained in tank contents, both in restrained bubbles and in solution or at interfaces. When success is attained, suitability of the device for use in primary safety

decisions can be evaluated. The use will be to provide basic data to predict compositions of tank headspace contents that could be produced under plausible mechanisms for release of retained gas. The decision rules are not expected to be changed to any great extent as a consequence of the related studies. However, this further evaluation will provide for firmer risk assessments for those tanks that have exhibited slurry growth without gas release and for tanks that may have stored large amounts of dissolved gas (especially ammonia), for possible mass-transfer release upon tank mixing. An analysis of potential error in measurements and related error propagation can be performed after trials of the experimental retained gas device(s).

3.0 DECISIONS TO BE MADE

As indicated at the beginning of this document core sample data are needed to understand the chemical and physical processes occurring within the waste. As discussed in Section 2.11, there are questions that need to be answered. These questions are:

- What is the mechanism for gas generation?
- What conditions cause retention and subsequent release of the gas?
- What situations are to be avoided in future operations so as not to create another "flammable gas tank?"
- What are the source terms for dose consequence calculations?

Characterization of the waste is needed in order to answer these questions. Closure of the flammable gas safety issue will require answers to these questions. At this time much information needs to be gathered in order to understand the processes occurring within the waste. This information will be used to develop future decisions for mitigation of the safety issue and for safe storage of the waste. In addition, the data provide key parameters for the models that have been developed for describing the behavior of the tank. Results of the modeling efforts have been required for the various safety analyses.

4.0 INPUTS TO THE FLAMMABLE GAS DECISION PROCESS

As a result of the meetings summarized in Appendix A and based on the experience obtained with tank 241-SY-101 there are a number of analyses needed to answer the questions listed in Section 3.

For an understanding of gas generation:

- Chemical composition of the waste
  - Analyses for major anions(including carbonate), cations, and water.
  - Total organic carbon, organic chelating agents and their decomposition products (on selected samples only), formate and oxalate.

For an understanding of gas retention and release:

- Stratum identification and description
- Density of bulk samples, liquid phase and settled solids
- Rheological properties(viscosity and shear strength)
- Solids content and settling rate
- Solubility of solids

For data to support source term evaluation:

- Radionuclides

Other supporting data:

- Bulk enthalpy characteristics

5.0 DECISION BOUNDARIES

The double shell tanks to be sampled according to this DQO are:

241-AN-103, 104, 105
241-AW-101
241-SY-103

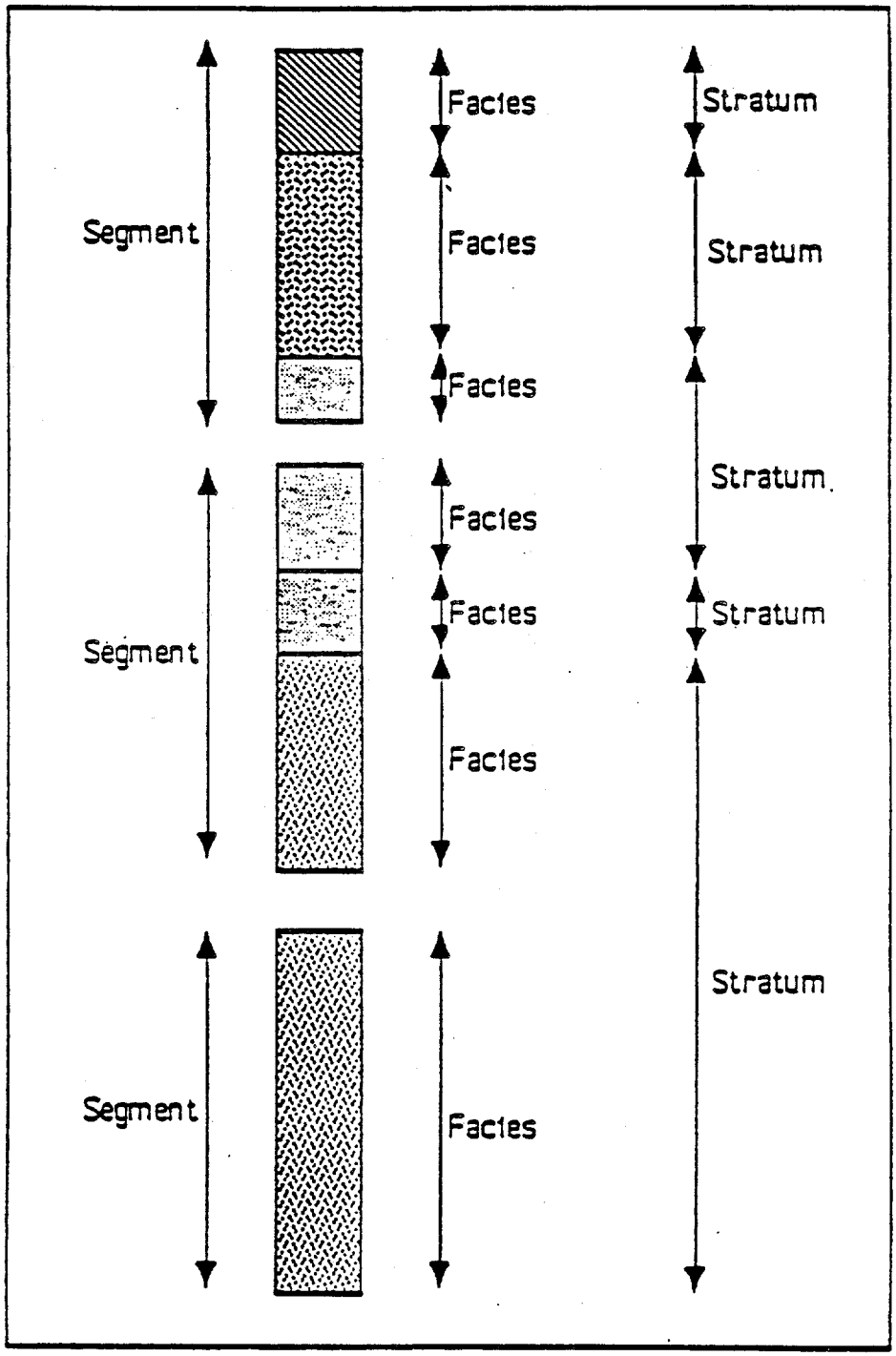
Core sampling of the single shell tanks that are part of the Flammable Gas Watch List is not planned at this time. Efforts for the single shell tanks will first be concentrated on installation and operation of gas monitors. No core drilling of these tanks will be scheduled until it has been determined that gases are being generated in sufficient amounts to be of concern. Exceptions will be made for tanks that have a critical need for other programs, e.g., interim stabilization. This program assumption was stated in the FY-1992 Program Plan (Johnson, 1992), and is still in effect. Tank 241-SY-101 has already been core sampled, and thus is not included in this DQO.

Core samples are to be obtained for the entire depth of the tank. Experience with 241-SY-101 has shown that four layers may exist in the tank. The top of the waste may have crust layer from a few inches to a couple of feet in thickness. The very bottom of the tank has a sludge layer of a few feet. The majority of the tank is comprised of two major layers, a convective layer that is under the crust and a non-convective layer below the convective layer. In Tank 101-SY these two layers were each fairly well defined. However, the analysis plan must allow for analyzing any distinct layer found from the core sampling of any specific tank, without constraints by paradigms developed from 101-SY.

A description of the layers that might be found in core samples is shown in Figure 1 (Jewett, 1992). The core sampling is done by segments, each of which is about 19 inches in length. Two terms need to be defined, namely "facies" and "stratum". A facies is a region of waste, not longer than one segment, having a visually uniform appearance. One core segment may have several facies, but a facies is never larger than one segment. A stratum is generally assumed to represent a horizontal layer of waste in the tank. It may be as small as a facies or it may encompass several consecutive core segments of uniform appearance. The entire core sample from the tanks in question will range from 18 to 22 segments.

For the convective and non-convective regions composite samples will be made from the core segments that comprise each region. If facies or strata are found within each region, then samples must be retained for each facies and each stratum. Details can not be provided for this process since it will have to be determined upon extrusion of the segments in the hot cell facility.

FIGURE 1. SEGMENT-FACIES-STRATUM RELATIONSHIP DIAGRAM



6.0 DECISION RULES

There are no decision rules at this time. The information is needed to provide basic information about the physical and chemical properties of the waste and to support work being done for mechanistic studies, safety analyses, and development of mitigation strategies. However, even though there are no decisions to be made for the current work, it is possible to indicate what those decisions may be once the basic information is obtained.

Section 3.0 listed the four main questions that need to be answered. The first one dealt with the mechanism for gas generation. From current laboratory studies being conducted on simulated waste samples, it is known that the major factors influencing gas production are concentration of certain species, temperature, and radiation dose. Important chemical species are the organic chelating agents and their degradation products, aluminate, nitrite, hydroxide, transition metals, chloride and noble metals. So far 20 major organic species have been identified for 101-SY waste samples. These coupled with the inorganic species present a very complex situation. As the laboratory efforts develop the understanding of the mechanisms that generate hydrogen, nitrogen, nitrous oxide, ammonia and methane, it would be desirable to identify certain species or concentrations of these species such that a decision could be made as to what item would represent the limiting step in the production of gas. Then, the core sampling efforts could be focused for these particular species, However, at this time, the first step is to get an understanding of what is in each tank and how these species play a role in the processes occurring in the waste.

The next item given in Section 3 concerned the entrapment and release of the gases. Again, based on laboratory studies, it is believed that the major reason for gas retention is related to the physical properties. Analysis of waste samples from 101-SY showed that the viscosity was very high and that some segments of the waste actually exhibited a yield strength. In addition the gas can also be trapped because of the hydrostatic pressure. Knowledge of the waste density is needed for determining this pressure at any given depth. Experience with 101-SY waste material showed that the waste contains a large amount of small solid particles. The presence of these particles will greatly influence the physical properties and will also act as sites for gas bubbles. The retention of gas within the waste represents a greater problem than gas generation. Gas generation is not a problem if the gases are released from the waste and if the tank ventilation system can successfully remove them from the tank dome space. Retention of gases, as with tank 101-SY, can lead to large inventories and, when released, present a serious situation. Thus, a basic understanding of gas retention mechanisms may be the most critical item related to the safety issue. As this understanding is developed, it might be possible to specify a given value of solids content, viscosity, or some other property that would indicate that a certain action is needed. However, much work is still needed to develop this information.

The third question in Section 3.0 covered the situation for ensuring that future tank operations would not result in creating the flammability safety issue. It is envisioned that by gaining basic information about the chemical

and physical properties of each of the tanks listed in Section 5.0 that it may be possible to relate this information to the observed tank behavior(i.e., changes in surface level, temperature, type of gases emitted, etc,). This then might show which properties or chemical species have a common link in the observed behavior. For instance, current work indicates that double-shell tank contents having bulk densities somewhat less than 1.4 g/cm^3 do not exhibit episodic releases of gas. However, some tanks containing more dense wastes also do not exhibit episodic releases. Thus more detailed chemical knowledge about the nature of solids formed when wastes are concentrated by evaporation to the higher densities should provide some guidance for control of gas retention and release.

Finally, Section 3.0 indicated that information was needed to evaluate dose consequences. Analysis for various radionuclides will provide the requisite information. Hazard analyses for the various tanks would then indicate the potential for any dose that would exceed established guidelines. Results from these evaluations might be used for establishing new work controls for the various tank activities.

7.0 CONSEQUENCES OF DECISION ERRORS

Since information must be gained in order to make a decision, there is presently no impact of decision errors. As an understanding is developed for the behavior of the tanks, decisions can be established and the DQO then will be updated. However, potential consequences for the items discussed in the previous section can be considered but it should be pointed out that any discussions of decision errors at this time must be considered to be speculative. The complete spectrum of false-negative and false-positive consequences will not be considered, only examples of some will be given.

With respect to decisions that might be established for determination of which species are critical for gas generation it is assumed that the decision would be directed at two situations, one for development of a mitigation method and the other for a process specification for future waste processing operations to ensure that flammable gases would not be generated in sufficient quantity to be of concern. In the case of mitigation an incorrect identification of a particular species, or concentration of such a species, could lead to establishing the wrong process for removal of it from the waste. This would be a severe cost penalty and would still leave the safety issue unresolved. This could also be the case for a waste processing specification(this is the third question); the wrong parameter might be established and the waste might end up producing another flammable gas tank.

Decisions for gas retention might lead to development of a mitigation process. For instance, if the parameter were concerned with viscosity, a decision might be made to dilute the waste so as to reduce the viscosity. Possible consequences of having an error in the analysis, could then lead to excessive generation of additional waste, when, in fact, it would not be needed to mitigate the situation and on the other hand the dilution may not implemented when, in fact, it was needed. Decisions for dealing with the gas retention question might involve several key properties which may then need several related decisions. Consideration of the consequences would thus be an involved process. This can only be developed when all of the data have been analyzed and interpreted.

Consequences of an incorrect analysis for radionuclides could lead to over restrictive work controls in one case and on the other hand an underestimate of the potential dose consequences would lead to an incorrect safety basis for the tanks.

These were only some examples of consequences that might develop for the results of sample analysis for decisions related to the questions given in Section 3.0. Again, as stated earlier, these will have to be developed after the basic understanding of the waste is developed and at that time the DQO will be revised accordingly.

8.0 SAMPLING AND DESIGN OPTIONS

Current data gathering procedures covered under this DQO are for sampling the waste by either the rotary mode or push-mode core sampling. However, it should be noted that the rotary mode core sampling system has not yet been qualified for use in potentially flammable atmospheres.

8.1 CORE ANALYSES

For the double-shell tanks one complete core will be taken. Experience with 101-SY (Herting, 1992a, 1992b) showed little variation for most analyses for the two cores. The core segments will be examined during laboratory extrusion, following procedures developed for Tank 101-SY 'Window E' cores (Jewett, 1992). If visual examination reveals incomplete samples, the Flammable Gas Safety Program representative will decide upon options of retrieving another core from the tank. Also, if distinct stratification, as described in Section 5, is revealed, the Flammable Gas Safety Program will need to determine whether cores from other locations in the tank should be taken (to study inhomogeneity in tank contents). For each core, composites will be made up of discrete distinguishable strata. Where appreciable amounts of drainable liquids are collected, the Flammable Gas Safety Program representative will determine appropriate testing and compositing to be performed with the samples of liquid collected. For guidance, Tank 101-SY is considered to contain four major strata: a bottom sludge layer, a non-convecting lower layer, a convecting middle layer, and a crust layer. The convecting layer is expected to be predominantly drainable liquid; if appreciable solids are found in this layer, they will be analyzed separately, with appropriate compositing determined by the Flammable Gas Safety Program. Laboratory analyses required on the composites (and on individual core segments where indicated) are presented in Table III for physical tests and Table IV for chemical tests. The specific Tank Characterization Plan will provide detailed information for these laboratory tests. Maximum uncertainty bounds are presented as desired accuracy and precision in the tables. In general, these are bounds developed for expected relative percent difference for current laboratory analyses on well-mixed homogeneous samples without sample matrix interferences. Departures beyond these bounds may occur tank samples.

It is necessary to ensure that proper quality assurance requirements are used for the various procedures. This was established for the waste sample analyses performed for tank 101-SY. The same requirements should be used for the analyses described in this DQO. The requirements for duplicate, replicate, blank, spike and blind analyses are given in Table 8-2 of Jewett 1992. There are no regulatory or validation requirements for this DQO.

Core segment samples should be retained until deemed no longer required for (a) rechecking of analyses or (b) future evaluations. Archived samples do undergo deterioration along with contamination from containers. Also, hot-cell space limitations preclude long term archiving of large numbers or volumes of samples. Surplus sample material shall be archived for at least one year after formal reporting of laboratory results, and disposal shall be

executed only with approval of the Waste Tank Safety Program management (see Strong, 1992).

8.2 USE OF HISTORICAL DATA

It is desirable to minimize the number of analyses to be conducted on core samples through the use of prior analyses conducted for the waste tanks. Such data must have been taken at a time as to be applicable to the safety issue. Table V provides a summary for the double tanks in question. For Tank 241-SY-103 the last major addition of waste occurred after the last chemical analysis. No analyses have been conducted since the tank started to exhibit gas release events, thus the full suite of analyses listed in Tables III and IV must be conducted. Tank 241-AW-101 was sampled since the tank started to exhibit gas release events, thus some analyses do not need to be repeated. For the AN tanks, the last analyses were done as part of the evaporator campaign when the tanks received the last addition of waste. It may be possible to use some of these data. Selection of which data can be used from the historical information will be done at the time the Tank Characterization Plan is prepared.

TABLE II. CORE PHYSICAL PROPERTIES DATA REQUIREMENTS

TABLE III. CORE PHYSICAL PROPERTIES DATA REQUIREMENTS

NO.	DATA NAME	PROCEDURE TYPE	TEMP. °C	DESIRED		Reason for Analysis
				ACCUR.	PREC.	
1	STRATUM IDENTIFICATION, DESCRIPTION	VISUAL OBSERVATION OF SEGMENTS DURING EXTRUSION	AMBIENT	NA	NA	ZONE IDENTIFICATION
2	BULK DENSITY	WEIGH & MEASURE VOLUME (VOLUMETRIC FLASK, CALIBR. CENTRIFUGE CONE, OR DIMENSIONS OF SOLIDS)	AMBIENT	10%	10%	BUOYANCY EVALUATIONS, MASS BALANCES
3	VISCOSITY	BOLIN OR HAAKE VISCOMETER, CONE & PLATE AS REQUIRED	40, 65, 90	10%(1)	LOE	MODELING INPUT FOR PUMPING, MIXING
4	SHEAR STRENGTH,(ON EACH SEGMENT, BEFORE MIXING)	VANE TEST	40, 65, 90	10%(2)	LOE	MODELING INPUT
5	VOLUME FRACTION OF CENTRIFUGED SOLIDS	CENTRIFUGED SOLIDS	AMBIENT & 60	LOE	LOE	MATERIAL BALANCES, MODEL INPUT
6	DENSITY, LIQUID FRACTION	WEIGHT/VOLUME MEASUREMENT OR DIGITAL DENSITY METER	AMBIENT	LOE	10%	MATERIAL BALANCES, MODEL INPUT
7	DENSITY, SOLID FRACTION	CALIBR. CENTRIFUGE CONE	AMBIENT	LOE	LOE	MATERIAL BALANCES, MODEL INPUT
8	BULK ENTHALPY CHARACTER.	DSC	20 - 450	LOE	LOE	THERMAL REACTIVITY
9	SOLIDS SETTLING RATE	VISUAL MEASUREMENT	40 & 60	LOE	LOE	MODEL INPUT
10	SOLUBILITY IN 2.5M NaOH	VOLUMETRIC, MASS	40 & 90	LOE	10%	DILUTION EFFECTS
11	SOLUBILITY IN WATER	VOLUMETRIC, MASS	40 & 90	LOE	10%	DILUTION EFFECTS
12	VOLATILES CONTENT*	THERMOGRAVIMETRIC ANALYSIS	20 - 450	LOE	10%	DSC INTERPRETATION, WATER

NOTE: LOE = LEVEL OF EFFORT. TESTS TO BE CONDUCTED ON COMPOSITE SAMPLES OF CRUST, CONVECTING LAYER, NON-CONVECTING LAYER, AND SLUDGE UNLESS OTHERWISE SPECIFIED.

*AS REQUIRED FOR DSC INTERPRETATION, BUT REQUIRED FOR ANY SOLID CRUST SAMPLES.

(1) Instrument to be checked for precision using newtonian fluid viscosity standard.

(2) Instrument to be checked for precision using bentonite test mixture.

TABLE III. CORE CHEMICAL DATA REQUIREMENTS

TABLE IV. CORE CHEMICAL DATA REQUIREMENTS

NO.	DATA NAME	PROCEDURE TYPE	DESIRED		NOTE	REASON FOR ANALYSIS
			ACCUR.	PREC.		
1	TOTAL ORGANIC CARBON (TOC)	DIRECT HOT PERSULFATE METHOD	20%	20%		REACTIVITY
2	FORMATE AND OXALATE CONTENTS	CHROMATOGRAPHIC METHOD	TBD	15%	1	'DEAD' ORGANICS
3	^{137}Cs, ^{90}Sr, ^{241}Am, ^{239}Pu, ^{238}Pu, ^{237}Np, ^{242}Cm, $^{243/244}Cm$, ^{99}Tc, ^{129}I, ^{60}Co, ^{154}Eu, TOTAL ALPHA, TOTAL BETA, (^{63}Ni, if PNL method is ready), ^{3}H (IN $^{3}H_2O$)	APPROPRIATE γ, β, α COUNTS, GAMMA ENERGY ANALYSIS, WITH SEPARATION CHEMISTRY	20%	20%	2	SOURCE TERM ANALYSIS FOR SAFETY EVALUATION
4	Na,Al,Cr,Ca,Fe,K,Ni,Zn,Zr,Ba,Si,B,Bi	INDUCTIVELY COUPLED PLASMA	15%	15%		CHEMICAL DEFINITION
5	TOTAL INORGANIC CARBON (TIC)	ACIDIFICATION OF CARBONATE	15%	15%		CHEMICAL DEFINITION
6	ANIONS: NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-, F^-	ION CHROMATOGRAPHY	20%	20%		CHEMICAL DEFINITION
7	HYDROXIDE ION (OH^-)	TITRATION, pH	10%	10%		CHEMICAL DEFINITION, CORROSION
8	WATER	TGA	LOE	10%		MATERIAL BALANCE
9	Cr(VI)	SPECTROPHOTOMETRIC	20%	20%		CHEMICAL DEFINITION
10	TOTAL URANIUM	LASER FLUORESCENCE	20%	20%		SAFETY ANALYSIS

NOTES: (1) EXPECTED ACCURACY TO BE DETERMINED WITH METHOD DEVELOPMENT

(2) BOTH WATER (ACID, WHERE REQUIRED) DIGEST AND FUSION METHODS TO BE USED (WITH LABORATORY JUDGEMENT)

GENERAL: DESIRED ACCURACY AND PRECISION (RPD) LISTED ARE UPPER LIMITS EXPECTED FOR METHODS NOW IN USE, ALL LIMITED TO NUMBERS ABOVE GIVEN DETECTION LIMIT; TESTS TO BE CONDUCTED ON LAYER COMPOSITES (AS IN TABLE III), UNLESS OTHERWISE SPECIFIED. DETAILED ORGANIC ANALYSIS WILL BE DONE ON A DEVELOPMENT BASIS FOR SELECTED SAMPLES.

TABLE IV. USE OF HISTORICAL DATA

TANK	DATE OF LAST ADDITION OF WASTE	DATE OF LAST CHEMICAL ANALYSIS	START OF GAS RELEASE EVENTS	USE HISTORICAL DATA?
103-SY	1989	1986	1989	NO
101-AW	1986	1990	1986	YES
103-AN	1986	1987	1992	MAYBE
104-AN	1985	1985	1986	MAYBE
105-AN	1985	1985	1987	MAYBE

References: Brager (1994), Reynolds (1994), Wilkins (1994).

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APPENDIX A

DQO DEVELOPMENT PROCESS

The participants in the DQO development process agreed initially that the following groups should be involved: Westinghouse Hanford Company (WHC) and Los Alamos National Laboratories (LANL) safety experts, WHC and Pacific Northwest Laboratories (PNL) computer modelers, PNL laboratory simulant researchers, test plan generators, WHC and PNL laboratory analytical scientists, and appropriate technical experts from WHC and PNL, with facilitation by PNL and Neptune and Company (Neptune).

Consistent with the Tank Waste Remediation System (TWRS) DQO Strategy (Babad et al., 1994) the DQO presented herein is generic (to the Flammable Gas Watch List tanks) in nature. Developing DQO's for a generic problem required an adaptation of the DQO process. The DQO process guidance (USEPA, 1993) focuses on eliciting the input required to develop a statistical design for a specific data collection event in support of a specific decision. Generic DQO's to support decisions for the flammable gas watch list tanks serve different functions, since the decisions are made in a process of logic based on a number of inputs. The DQO presented herein will be reviewed upon completion of each core sampling activity and will be updated accordingly. It is possible that in a number of instances insufficient data will be available to generate a statistical design satisfying the data quality objectives stated in this or other DQO documents. In these cases, a number of critical assumptions must be made, and data quality assessments must be performed to confirm data adequacy for decision making. Then the DQO document serves to guide the design in a qualitative sense during planning, and it can provide guidance for quantitative analysis of data adequacy when data are collected.

Data requirements for the Flammable Gas Watch List tanks were developed in a DQO process with outputs for each step of the process being elicited through a series of meetings. Meetings of WHC and PNL engineers, scientists, and statisticians were facilitated by experienced DQO representatives following the USEPA guidance document (USEPA, 1993). The process was launched with an organizational meeting held by the Flammable Gas Tank Stabilization program manager, the PNL DQO coordinator, a representative from the Tank Waste Remediation System Characterization Program, and a senior level manager involved in this program. In this meeting, the major objectives of the DQO development task were discussed, and the technical experts and stakeholders who needed to be involved were identified. PNL subsequently organized a series of meeting locations and dates and invited each of the identified persons to attend. PNL provided DQO facilitators (Neptune) to assist the WHC program manager in conducting the meetings and documenting the outcomes in appropriate formats. Table V summarizes attendance at the meetings so organized. In addition two separate meetings were held to brainstorm needs in modeling of tank waste behavior and in synthetic and actual waste laboratory studies. These two day-long meetings included scientists and engineers from WHC, PNL and LANL involved in support work for the Flammable Gas Safety

Program. Inputs from these two meetings (see Appendix B) were also used to derive data needs for the program.

TABLE V. DQO PLANNING PARTICIPANTS

PARTICIPANT	ROLE	MEETING DATES					
		Nov 16	Dec 1	Jan 4	Jan 20	Feb 3	Apr 27
Jerry Johnson, WHC	Program Manager	X		X	X	X	X
Harry Babad, WHC	Technical Experts		X				
Don Baker, WHC		X					
Tom Beaver		X					
Alan Brothers, PNL						X	
Joe Brothers, PNL		X		X	X	X	X
George Fox, Technology Applications						X	
Dave Hopkins, WHC				X			X
Rick Johnson, LANL							X
Dennis McCain, WHC							X
Norton McDuffie, WHC		X	X	X	X	X	X
Dan Reynolds, WHC			X	X	X	X	
Fred Riedel, WHC							X
Dave Sherwood, WHC							X
Dan Stepnewski, WHC					X	X	
Eric Straalsund, WHC				X			
Kathryn Tominey, PNL-WSD				X			
Dave Wooten, Technology Applications						X	
Patty Morant, WHC-HASM	Analytical Expert		X	X			X
Rudy Allemann, PNL				X			
Catherine Anderson, PNL				X		X	X
Brent Pulsipher, PNL							X
Randall Ryti, Neptune and Co.	Facilitator/ Statistician		X			X	
John McCann, Neptune and Co.	DQO Process Facilitators			X		X	
Dan Michael, Neptune and Co.			X		X		X
Dean Neptune, Neptune and Co.		X	X	X	X		
Jerry Scott, PNL-Prog. Off.	DQO Logistical Support	X	X				
Paul Turner, PNL-Prog. Off.				X			
Megan Lerchen, WDOEcol	Stakeholders	X					
Gary Rosenwald, DOE-RL		X	X	X		X	

Table V. DQO Planning Participants (continued)

Milt Campbell, Mactec	DOE DQO Oversight						X
Larry Jackson, Mactec				X			
Ken Redus, Mactec			X				
David Schlick, Mactec							X
Steve Krogsrud, WHC	Safety						X
Mohammad Islam, WHC							X

APPENDIX B

SUPPLEMENTAL MEETINGS TO SUPPORT DEVELOPMENT OF THE DQO

I. MEETING ON CHEMICAL MECHANISMS

A meeting was held on November 23, 1993, to evaluate the work being done to determine the mechanisms responsible for gas generation and retention. A historical review was given for the work conducted at WHC, PNL, GIT and ANL to determine the nature of gas generation in synthetic and tank waste samples. Discussions were held as to what type of tests should be done to determine gas retention mechanisms. The effects of gas solubility also needed to be addressed as well as the effect of radiation on the stability of the various gaseous species. The final item discussed at this meeting concerned the type of analyses that needed to be performed on the core samples. In general, the attendees felt that the same analyses that were conducted for tank 101-SY would be needed for the other double shell tanks that are on the Flammable Gas Watch List.

The following list is a summary of the requested items:

- The major anions and cations
- The primary organics that were in the feed material
- The organic products in the waste, including oxalate and formate.
- TOC
- DSC/TGA
- Accountability for C, H, and N.
- % water
- Hydroxide
- Ammonia
- Noble metals
- Polarized Light Microscopy
- % solids
- Physical properties (density, viscosity, yield strength)
- Radionuclides
- Gas content of the waste and gas composition
- Knowledge of surfactants

The following people attended the meeting:

H. Babad, D. L. Herting, C. Delegard, J. C. Person, D. A. Reynolds, S. A. Bryan, D. D. Stepnewski, G. L. Fox, R. J. Van Vleet, L. R. Pederson, G. W. Rosenwald, M. Campbell, N. G. McDuffie, G. D. Johnson

II. MEETING ON MODELING ACTIVITIES

A meeting was held on December 16, 1993 to review the work being done on thermal, gas flow, combustion and waste modeling. The data needs for each type of modeling work are listed below.

a) Thermal Modeling

- Thermal conductivity (may be able to get from synthetic waste)
- Heat Capacity (may be able to get from synthetic waste)
- Density of waste
- Volumetric distribution of heat sources
- Solubility of various species
- Vapor pressure and density of vapor
- Soil thermal conductivity
- System operating parameters
    - Flow rates for dome and annulus
    - Air temperature for dome and annulus
    - Relative humidity
    - Waste temperature
    - Structural temperatures
    - Ventilation system configuration

b) Gas Flow Modeling

- System flow rates
- System configuration
- Psychometric data
- Vapor pressure data
- Gas composition

c) Waste Behavior Modeling

- Distribution of solids in the waste
- Gas content of waste and gas composition
- Distribution of gas in waste
- Viscosity
- Rheogram
- Yield Strength
- Density
- Particle size of solids
- Solubility of gases and solids
- Mechanism for gas retention and release

d) Gas Burn Modeling

- Properties of Crust
  - DSC
  - TGA
  - Adiabatic calorimetry
  - % water
  - Radionuclides
- Gas composition

The following people attended the meeting;

WHC: R. Van Vleet, D. Reynolds, W. Cowley, D. Stepnewski, G. Fox, W. Kencht, K. Sathyanarayana, T. McCall, F. Heard, S. Wood, T. Beaver, N. McDuffie, D. Hopkins, G. Johnson, B. Vonderfecht, R. Graves

PNL: C. Stewart, D. Anderson, Z. Antoniak, D. Trent, T. Michener, R. Allemann, L. Schienbein

LANL: K. Pasamehmetoglu, J. Edwards, B. Lin, J. Spore, R. Nelson

RL: G. Rosenwald

ATTACHMENT A

DETERMINING DATA NEEDS AND THE ATTENDANT DATA QUALITY OBJECTIVES REQUIRED TO SUPPORT SAFETY-RELATED DECISIONS CONCERNING THE GENERATION OF FLAMMABLE GAS IN HANFORD TANK WASTES

D. Wayne Berman
ICF Kaiser Engineers, Inc.

FOREWORD

Any strategy describing the overall approach to safe storage and disposal of waste must identify the problems and decisions requiring characterization data. Requirements for obtaining tank characterization information are developed through the use of the Data Quality Objectives (DQO) Process. The DQO Process addresses each decision or group of related decisions to specify data needs.

The initial attempt at performing the DQO Process to address safety issues revealed points where significant assumptions would be required to proceed. Although the problems and decisions were identified, details of the error tolerances and confidence levels were difficult to develop. Attempts to optimize the data collection for each tank were affected by the limited locations from which samples could be obtained and concerns that samples did not represent overall waste contents. The complexity of sampling made it impossible to design a high-confidence data acquisition scheme based solely on multiple samples, and necessitated review of the overall strategy for obtaining data and resolving issues.

A revised safety strategy was developed for the storage of tank waste, focused on ensuring safe operations over a range of waste materials rather than on characterizing waste in great detail. The revised safety strategy includes several assumptions about the nature of the waste which require verification through additional sample analysis. Should these assumptions be shown to be well founded, the approach to screening the waste for safety issues and resolving those issues is considerably simplified. The following draft of the data requirements, based on the revised safety strategy, has been prepared.

Clearly any assumptions must be addressed before proceeding with the revised safety strategy. The preceding minor revisions to the baseline DQO document were found to be adequate to perform safety analyses in the near term, while specific additional information needs are pursued to verify the assumptions in the revised safety strategy. In addition to resolving the assumptions, the near-term sampling events will obtain information that will support the determination of error tolerances, confidence levels, and optimization schemes in the finalized version of the revised safety strategy DQO. The approach taken in the revised baseline DQO document, simply requesting multiple samples per tank, is the appropriate first step to finalizing the optimization requirements.

The DQO Process is iterative in nature. It is anticipated that the data collected in the near term, based on the revised baseline DQO document, will provide the added information needed to provide complete DQO requirements for longer term characterization. As such, the following revised safety strategy DQO may continue to undergo further development and revision as this added information becomes available. At the appropriate time after the revised safety strategy DQO is completed, the necessary reviews and approvals will be conducted and the document will become the new baseline.

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1 INTRODUCTION

This document provides an analysis of the safety concerns associated with the generation of flammable gases in the wastes currently contained within 177 tanks that are located in the 200 Area of the Hanford reservation. The purpose of the analysis is to identify the data needs and attendant data quality objectives (DQOs)[1] required to support evaluation of the flammable gas concerns primarily to determine whether mitigation is required for specific tanks.

The analysis in this report is based on the data quality objective (DQO) process, which was developed at the U.S. Environmental Protection Agency in the mid-1980's. The DQO *process* is a formalized procedure for designing *cost-effective* studies to provide the data required to support the resolution of problems using the scientific method. By requiring that the precise manner in which data are to be used be defined during planning, the DQO process facilitates design of cost-efficient studies that focus *only* on the collection of data that are both necessary and sufficient for resolving the problem of interest.

The DQO process is typically divided into seven steps:

(1) state the problem;

(2) define the decisions;

(3) identify inputs to each decision;

(4) define the decision boundaries;

(5) define decision rules;

(6) identify acceptable error limits and the attendant data quality objectives; and

(7) optimize the study design.

The process is intended to be iterative; as additional information is developed, the various steps of the process can be refined to further optimize study design.

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[1] Data quality objectives (DQOs) are concise statements indicating the specific level of quality that a *set* of data must achieve to adequately support a particular decision. Depending on circumstances, measures of the quality of a *set* of data may include: precision, accuracy, representativeness, comparability, completeness, and sensitivity.

The remaining sections of this report are organized as follows:

- Chapter 2 is an overview of the issues and concerns associated with flammable gas;
- Chapter 3 describes the technical approach adopted for addressing the flammable gas problem at Hanford;
- Chapter 4 documents the steps of the DQO process as they are applied to each of the subset of specific decisions associated with the flammable gas problem that are the focus of this document; and
- Chapter 5 provides references.

The focus of this document is to define the data needs and attendant DQOs required to address decisions concerning whether specific tanks at Hanford require mitigation of potential safety hazards posed by the generation of flammable gas. Although decisions relating to other aspects of the flammable gas problem (such as those associated with the identification of tanks requiring monitoring for flammable gas, those associated with refinements to the technical approach adopted for this problem, or those required to design, select, and/or implement mitigation options) are also identified in this report, their evaluation using the DQO process (to identify data needs and the attendant DQOs) will be reported in companion documents scheduled to be completed in the near future.

Some of the components of the gas mixtures generated by the wastes in the Hanford tanks are noxious as well as flammable. However, it is beyond the scope of this document to consider issues associated with the toxic effects of the gases produced in the Hanford tanks. Such issues are being evaluated in a companion set of documents, which address the full range of safety-related issues associated with the storing of wastes in the Hanford tanks.

2 THE FLAMMABLE GAS PROBLEM (BACKGROUND)

An overview of the flammable gas problem (with particular focus on those aspects of the problem that contribute to safety concerns) is presented below.

2.1 GAS GENERATION, TRANSPORT, AND RELEASE

The known mechanisms by which flammable gases might be generated in wastes in the Hanford tanks are discussed in the following sub-section. As indicated, both the overall rate of gas generation and the relative contributions from specific mechanisms in particular tanks are primarily determined by the composition of the waste in that tank. In addition to contributing to the overall rate of flammable gas generation, the relative magnitude of the contributions from specific mechanisms determines the overall composition of the gases generated.

Given that the detailed composition of wastes (particularly with respect to components that determine flammable gas generation) varies over broad ranges across tanks, both the rate of gas generation and the relative importance of different generating mechanisms vary from tank to tank. As indicated in Section X.XX, however, knowledge of the precise generation rates of flammable gases is not critical to addressing the specific safety issues that are the focus of this document, although it might help improve the confidence of such decisions. More important for addressing such safety issues is the *composition* of the gases generated in each tank. The need for information concerning the composition of the gases that are generated in a particular tank is addressed further in Section X.XX.

The transport and release of gases (once generated) are discussed in Section 2.1.2. Because, as indicated in Section X.XX, at least some of the tanks at Hanford exhibit behavior indicating significant retention of flammable gases within the waste and some tanks exhibit episodic releases at rates that far exceed the rate of generation of the gases, an understanding of the mechanisms of transport and release of gases within the Hanford wastes is critical for evaluating the specific safety concerns that are addressed in this document.

2.1.1 The Generation of Flammable Gases

Processes potentially contributing to the generation of flammable gases in Hanford tank wastes have been identified based on published studies of the behavior of alkaline metal sludges, the behavior of organic chemicals in such sludges, and the behavior of metal salts, water, and organic chemicals in the kinds of radiation fields found in the Hanford tanks. Based on such studies, the following processes may each contribute to the generation of flammable gases in Hanford tank wastes:

- direct volatilization of the volatile components of organic phases and dissolved phases within the waste;
- radiolysis of water and/or organic chemicals;
- chemical reactions between specific components of the waste;
- thermal degradation of organic chemicals; and/or
- corrosion of the steel liners of the tanks containing the wastes.

Of these, the first mechanism is unlikely to be important in most tanks. Although direct volatilization may have been a major contributor to flammable gas generation when wastes were first introduced into the tanks, most of the wastes have been sitting in the tanks for more than 30 years and the most recent additions of waste to the tanks were completed more than 14 years ago. It is therefore expected that the majority of the volatile organic components of the waste (likely including low molecular weight components of petroleum fuels, lubricants, and/or solvents) have largely been depleted.

There are tanks at Hanford in which a separate organic phase has been observed. To the extent that such a phase consists of volatile organic mixtures (such as petroleum fuels, lubricants, and/or solvents), rather than the less volatile organic complexants and organic phosphates known to have been used at Hanford, direct volatilization may still be an important contributor to flammable gas generation in such tanks. This is true even if the lighter ends of such mixtures have been depleted over time. However, for tanks in which no such organic phase exists, it is unlikely that sufficient quantities of sufficiently volatile organic compounds remain in dissolved phases to represent a major source of flammable gases in the tank. In any case, the potential importance of contributions to flammable gas generation from this process will be adequately addressed as part of the recommended compositional studies of dome-space gases found within the tanks (see Section X.XX).

Radiolysis of water and organic chemicals containing hydrogen potentially represents an important source of hydrogen gas in the Hanford tanks (**Meisel et al. 1993**)[2]. Also depending on the concentration of specific organic components, flammable gases other than hydrogen may be produced by radiolysis.

The initial step in radiolysis typically involves ionization of a target molecule followed by intra-system transfer that may lead to dissociation. The specific orbital from which the electron is initially extracted is a function

[2] Meisel et al. (1993) studied radiolysis reactions in a variety of simulants under a range of conditions designed to represent both the types of wastes found in the Hanford tanks and the physical conditions observed in the tanks.

of both the type of ionizing radiation (the major sources of radiation in the Hanford tanks emit both beta and gamma radiation -- **Meisel et al. 1993**), and the electron density, size, and orientation of the orbital in which the electron resides.

Of the range of chemicals found in the Hanford tanks, "productive" radiolytic reactions most commonly involve either water or the organic compounds that may be present in the waste (**Meisel et al. 1993**). Radiolytic ionization of metal atoms or the inorganic anions in the wastes tend primarily to generate solvated electrons, after the initially formed ions have reacted. Solvated electrons, however, may then proceed to react with various species in processes that may be productive[3].

Following an initial radiolytic ionization of water, the major products formed include atomic hydrogen (H•), hydroxyl radicals (OH•), and various ionic fragments of water (H^+ or OH^+). The latter tend to react rapidly with neutral water to produce primarily H_3O^+. A solvated electron is also produced with each ionization.

As reported by **Meisel et al. (1993)**, hydrogen is generated following radiolysis of water primarily from the reactions of atomic hydrogen (i.e. through recombination) and from the reactions between solvated electrons and either atomic hydrogen or hydronium ions (H_3O^+).

In the absence of organic compounds, the yield of hydrogen gas as a function of radiation dose, "G_{H2}" is reported to be approximately 0.03 molecules per 100 eV (**Meisel et al. 1993**). G_{H2} is also reported to be independent of dose and dose rate. Due to its ability to scavenge atomic hydrogen, this yield is also reportedly reduced as the concentration of nitrite increases.

If organic chemicals are present in the wastes, molecular hydrogen (and, eventually, hydrogen gas) may also be formed from atomic hydrogen by hydrogen abstraction, as indicated in Equation 1.

$$H\bullet + RH \rightarrow H_2 + R\bullet \qquad (1)$$

where:

RH is any organic compound containing hydrogen.

---

3 The term "productive" as used here is intended to indicate reactions or processes that yield new species that are different in composition from their parent compounds. Thus, for example, a process involving a dissociation followed by a recombination that produces the initial parent structure would not be considered productive.

Due to the relatively greater abundance of organic compounds (in tanks where they are known to exist in the waste) than the relatively rare atomic hydrogen or solvated electrons (i.e. the direct products of radiolysis), gas generation via this abstraction reaction tends to dominate radiolytic generation of hydrogen whenever organic compounds are present in the waste. The yield efficiency of hydrogen abstraction from specific organic compounds is approximately proportional to the number of C-H and N-H bonds in the compound. Yield efficiencies for a range of organic compounds over a range of conditions are reported by **Meisel et al. (1993)**.

Production of hydrogen via the direct radiolysis of organic compounds also represents a viable process. In most tanks, however, this is expected to contribute relatively less to the overall production of gas than the direct radiolysis of water and the attendant hydrogen abstraction reactions (**Meisel et al. 1993**).

The most important radiolysis products of the organic complexants that are present in Hanford wastes appear to be organic degradation products that may still contribute to the production of hydrogen through various thermally induced reactions (**Meisel et al. 1993**). Of these, formaldehyde and glyoxalate appear to be the most efficient contributors to hydrogen generation.

As indicated previously, radiolytic yields for hydrogen are reduced by the presence of nitrite (**Meisel et al 1993**). Yields are also reportedly lower in slurries than in solution (potentially due to the hindered mobility of atomic hydrogen, which would favor recombination over the productive reactions that atomic hydrogen tends to undergo). Increases in temperature tend to reduce the differences in the yields observed in slurries and solution, potentially due to the dissolution of some of the solids.

Based on their simulant studies, **Meisel et al. (1993)** report that other gases produced by radiolysis (when organic chemicals are present) include nitrous oxide (N_2O) and ammonia (NH_3). Under varying conditions, yields for production of N_2O are reportedly as much as 10 times that for hydrogen. Yields for ammonia are reportedly extremely low, less than one tenth to one hundredth that of hydrogen under most of the conditions tested. Nitrogen is also reportedly produced (from further breakdown of nitrous oxide), but the yield of this product is reportedly less than a fifth of that for hydrogen over most of the conditions studied.

The complex dependence of the yield of nitrous oxide on temperature and on the concentrations of various components of the simulants (and, presumably, real wastes) suggests that production of this gas is the result of a complex, multi-molecular process involving several intermediates (**Meisel et al. 1993**). Regarding ammonia, it is reported that the yield for this gas increases linearly with temperature.

Very few of the minor constituents of Hanford wastes were shown to affect the radiolytic yields of the various gases (**Meisel et al. 1993**). Among the

exceptions, N_2O production was shown to be significantly reduced in the presence of small amounts of Cr(III).

Given the above, the fractional contribution of radiolysis to the total production of flammable gas in any particular tank depends on the detailed composition of the wastes including, specifically, the moisture content, the concentration of specific organic components, and the concentration of radionuclides (the latter of which defines the strength of the radiation field in the tank). Yields are also dependent to some extent on the physical properties of the wastes; highly viscous wastes or solid matrices hinder the mobility of intermediates and promote unproductive re-combination. Production of some gases also show a dependence on temperature.

It is reported by **Meisel et al. (1993)** that radiolysis (at the present time) accounts for approximately 30% of the hydrogen produced in Tank SY-101 and that most of the production of nitrous oxide can be attributed to radiolysis. Whether such values are representative of other tanks, however, depends on the combination of each of the factors listed above. Whether these fractional contributions from radiolysis will continue in the future in Tank SY-101 also depends on the degree to which conditions in the tank remain stable (with regard to each of the factors listed above). Among the changes that are known to be occurring, for example, is the decay of the radionuclides in the tank. Therefore, the radiation field in the tank is not constant in time.

Despite the potential difficulties in determining specific contributions by specific mechanisms to the overall generation of flammable gas in a tank, the potential impact of the combined contributions from all mechanisms on the safety issues covered *specifically* in this document should be adequately addressed by the recommended compositional studies of dome-space gases found within the tanks (see Section X.XX).

Given the primary constituents of the wastes deposited in the Hanford tanks, a number of chemical reactions are likely occurring and the products of some of the more important of these include hydrogen and other flammable gases. Based on the characteristics of the wastes stored in Hanford tanks and the conditions found in the tanks, the types of reactions likely occurring include:

- alkali catalyzed rearrangements and degradation (particularly of nitrogen and oxygen containing organic species);
- alkali catalyzed nucleophilic substitutions of organic compounds with water;
- oxidation-reduction reactions, particularly those driven by nitrates and nitrites;
- heavy metal catalyzed degradations (through complexation); and

- surface catalyzed degradation.

Because radionuclide decay represents a significant source of heat in most of the Hanford tanks, the temperature of the wastes in many of the Hanford tanks is elevated over ambient temperatures. Elevated temperatures affect chemical reactions in two ways. First, they serve in general to accelerate chemical reactions. In fact, even chemical reactions that are prohibitively slow at ambient temperatures, may contribute significantly to changes in the waste at the elevated temperatures that obtain in some tanks.

Second, elevated temperatures alter the thermodynamic equilibria between reactants and products so that the course of some reactions may be entirely changed when temperatures are elevated. Except for a small number of special cases, this latter effect generally tends to be small over the range of temperatures observed in the Hanford tanks. Among the special cases, however, are systems involving equilibria with ammonia. It is therefore possible that, at least in some tanks, this second effect may be important.

In general, the range of elevated temperatures observed in the Hanford tanks should serve primarily to accelerate the range of reactions already discussed above. Some changes in the overall chemistry that is likely attributable elevated temperatures, however, may include:

Given that the production of hydrogen by displacement with iron from water is exothermic, under the conditions commonly encountered in the Hanford tanks, the corrosion of the steel vessels holding the wastes represent another hydrogen-generating mechanism potentially contributing to the production of flammable gas. However, based on current models of hydrogen generation and the measured rate of corrosion in the tanks, the contribution from this process to the overall rate of production of hydrogen is expected to be small in most of the Hanford tanks. Therefore, because the schemes for addressing safety-related concerns discussed in this document (see Sections X.XX) do not require detailed knowledge of the rate of hydrogen generation in specific tanks, this mechanism is not addressed further in this document.

2.1.2 The Transport and Release of Flammable Gases

Unless gases are generated in the surface layer of a waste, once generated, gases within the wastes in the Hanford tanks tend to remain dissolved within the phases of waste in which they were generated until sufficient gas accumulates so that the equilibrium vapor pressure of the solution exceeds the local hydrostatic pressure of the waste. If sufficient nucleation sites (such as the surface of a solid, a collection of suspended particles, or the interface between two fluids) are present in the waste, the gas may then coalesce to form bubbles. Solutions lacking such nucleation sites, however, may easily become supersaturated before a triggering event initiates bubble formation.

The mechanism of transport of gas at the surface of the waste is slightly different. At a liquid surface (obviously, solids may inhibit and trap gas molecules), dissolved gas molecules migrate to the surface where they will escape from the waste directly. Eventually, a thin layer of enriched air forms over the immediate surface of the waste and a dynamic equilibrium develops between the partial pressure of the gas exerted by this thin layer and the gas dissolved in the waste. The rate of release of gas from the surface will then be determined by the nature of this equilibrium and the rate at which gas migrates into the air away from this thin layer.

Depending on the physical characteristics of the waste, gas bubbles that form in the waste may either migrate upward freely or may be hindered and retained until they are released by some triggering event. Unsaturated, porous solids and liquids (even moderately viscous liquids) may offer some resistance to bubble migration but will generally allow transport. The net gas load in such layers will tend to increase until the mass rate of release of gas by bubbles reaching the surface just equals the rate of generation of gas in the waste. Saturated solids, liquids containing significant concentrations of solid particles (slurries), gels, foams, and highly viscous liquids may effectively hinder bubble migration.

Temperature effects also play an important role in determining the migration of gas within Hanford wastes. Many of the layers of wastes in various tanks generate heat. However, the production of such heat is neither uniform nor is the effect of such heat uniform on the changes it induces in the physical characteristics of the various components of the wastes. Consequently, density gradients frequently form that drive convection. By facilitating the mixing of wastes, convection facilitates the transport of gases to the surface of the wastes.

Layers of waste that effectively trap gas may also effectively restrict convection. The heat capacity of most gases are sufficiently low that, if bubbles are present in a particular layer of waste in sufficient concentration, transport of heat is effectively curtailed. This then suppresses or even halts convection. Thus, the effects of gas retention are complex and highly non-linear.

Because the trapping of gas within a layer of waste effectively lowers the bulk density of that layer, if sufficient gas is trapped within one layer that underlies a second layer in which gas is not effectively trapped, Rayleigh-Taylor instabilities may develop. This is a situation in which an accelerating force is driving a less dense fluid through a more dense fluid and visa versa. Typically, gravity is the accelerating force. Therefore, Rayleigh-Taylor instabilities exist whenever a less dense fluid is overlain by a more dense fluid.

The mechanism by which the interface between two fluids breaks down under Rayleigh-Taylor instability (so that flow is initiated that eventually resolves the instability) has been described for fluids exhibiting certain

types of characteristics under a range of well-defined conditions. However, the characteristics of the wastes in many of the Hanford tanks sometimes fall outside the range of characteristics that have been described to date. Among other things, for example, many of the layers of wastes that contribute to Rayleigh-Taylor instabilities in specific tanks cannot even be characterized as fluids. Therefore, it may be difficult to adequately predict the characteristics of flow in such cases.

The potential significance of the flow that occurs under Rayleigh-Taylor instability conditions in the Hanford tanks is that these are the conditions that describe the episodic releases of gases that has been observed in several tanks. Because the rate of release of gas during such an episodic event can greatly exceed the generation rate of gas in a tank (at least over a short period of time), such events raise particular safety concerns over and above those that may be associated with the more continuous release of gases that is observed in many other tanks.

When gas is released continuously from the waste, at a rate that approaches the generation rate, the concentration of gas within the dome space over the waste will generally increase until the release (generation) rate of the gas just matches the rate at which the gas is exhausted from the tank due to ventilation. When the rate of generation and exhausting of the gas become equal a steady-state is reached and the flammable gas concentrations will be at a maximum (for the case in which release is continuous and episodic releases do not occur).

In tanks that are actively tanks that are actively vented, the ventilation rate is essentially constant so that a stable steady state generally obtains. In tanks that are passively vented, the ventilation rate varies as a function of temperature and barometric pressure so that conditions are not stable. When observed over periods of several days to weeks, however, the ventilation rates in these tanks approach a stable average. Further, given that the generation rates expected to obtain in most of the tanks at Hanford are sufficiently small to require weeks to months to release enough gas to establish a steady state in the dome space, even passively vented tanks can be assumed to achieve a stable steady state.

The steady-state concentration that may obtain in a tank can be predicted easily if both the generation rate of the gas and the ventilation rate of the tank are known. However, because the information required to predict overall generation rates precisely is not generally available for most tanks and the type of sophisticated model required to integrate such information does not currently exist, in practice, it is not practical to predict steady-state concentrations in such a manner. Rather, because the approach to steady-state conditions is sufficiently slow to allow advanced warning of the build up of unsafe concentrations simply by monitoring of dome space concentrations, this is the approach that is being pursued to address this part of the flammable gas problem.

The situation is more complex when episodic releases occur. The rates at which gases are released during episodic events are sufficiently rapid that ventilation rates can be insufficient in some tanks to prevent the creation of unsafe conditions. In fact, episodic releases may be sufficiently large in some tanks to contribute directly to catastrophic effects (see Section X.XX).

Because release rates during episodic events are rapid, monitoring dome space concentrations to provide advanced warning of such are release is clearly inadequate. Therefore, this aspect of the flammable gas problem is currently being handled in an entirely different manner. Currently, simple bounding models have been developed to predict the worst-case magnitude of an episodic release that may occur in a particular tank. Because such models rely on relatively little data and, significantly, require neither knowledge of the generation rates of gases in a tank nor a detailed understanding of the mechanisms associated with gas retention and episodic release, it may be possible to adapt them for evaluation of most tanks. The tradeoff is that they tend to be fairly conservative by overpredicting the magnitude of the largest episodic release that might occur, so that decisions based on such models leave something to be desired.

2.2 SAFETY CONCERNS ASSOCIATED WITH FLAMMABLE GAS GENERATION IN THE HANFORD TANKS

As indicated previously (Section X.XX), flammable gas may be introduced into the air space of a tank by either of two general mechanisms:

(1) in some tanks, the gases that are generated migrate relatively freely within the waste and are released continuously at a rate that ultimately approaches the rate at which they are generated; and/or

(2) in some tanks, the gases that are generated are hindered from free movement within the waste and are retained until sufficient gas is stored to create an unstable condition. Then, periodically, some triggering event occurs that results in an episodic release of gas at a rate that far exceeds the rate of generation of the gas.

The degree to which either (or both) mechanisms contribute to the release of flammable gas in a particular tank at a particular time is a function of the physical characteristics of the waste and the physical conditions in the tank (see Section X.XX).

In those tanks in which gas is predominantly introduced into the tank continuously at a rate approaching the rate of generation of the gas (i.e. Case one above) the primary safety concerns relate to the potential accumulation of flammable gas within the dome space of the tank until the point at which the lower flammability limit (LFL) of the mixture is exceeded.

Once that happens, the introduction of a spark (or other ignition source) into the tank would cause the gas to burn.

The surge in pressure created by combustion of dome-space gas in a tank might then lead to a loss of containment with the consequent venting of part (or all) of the hazardous components in the tank to the environment. Depending on the maximum force of the pressure surge created by the burning gas, loss of containment may occur by: (1) rupturing of the HEPA filter on the tank vent, (2) forcing fugitive emissions through the seams and seals in tank risers and equipment feeds, or (3) structural failure and rupture of the tank itself.

In those tanks in which the predominant mechanism of release of gas to the dome space is via episodic events at rates that far exceed the generation rates of the gas (i.e. case two above), a safety-threatening pressure surge may be created by (1) the direct pressure pulse associated with the episodic release itself, (2) ignition of the flammable gas plume as it is released from the waste (before it has had a chance to mix thoroughly within the dome space of the tank), and/or (3) ignition of the flammable gas, if the LFL is exceeded once the gas released during the episodic event has completely dispersed and mixed within the dome space of the tank.

To adequately address flammable gas safety concerns, it is necessary to:

- identify which of the 177 tanks at Hanford potentially contain wastes that are capable of generating and releasing flammable gas (either continuously or episodically) at sufficient rates to warrant additional evaluation for this problem;

- among those tanks initially identified, determine which of those tanks are actually capable (with an unacceptable probability) of releasing gas continuously at a sufficient rate to allow the LFL (or some other defined fraction of the LFL)[4] to be exceeded;

- among those tanks initially identified, determine which of those tanks are actually capable (with an unacceptable probability) of releasing gas episodically at a sufficient rate to cause:

  - a pressure surge sufficient to rupture the HEPA filter in the tank vent (or force a fugitive release through seams and feeds);

  - a plume of escaping gas of sufficient volume that, if ignited, would cause a pressure surge sufficient to rupture

[4] There is a legal requirement that the dome-spaces of the tanks at Hanford remain below 25% of the LFL for the mixture of flammable gases found within each tank (DOE 1984, NFPA 1992).

the HEPA filter in the tank vent (or force a fugitive release through seams and feeds); and/or

- escape of sufficient gas during one event such that, once the gas becomes dispersed and mixed within the dome space, the LFL (or some other defined fraction of the LFL) would be exceeded.

- for those tanks determined to pose an unacceptable safety risk (i.e. exhibiting one of the above defined conditions), define an appropriate mitigation measure (or set of mitigation options);

- determine the most cost-effective mitigation option for each tank posing an unacceptable safety risk; and

- satisfy data requirements to complete design and implementation of selected mitigation.

Of the above components of the flammable gas safety program, the first of the above bulleted tasks is being completed by defining a set of tanks defined as a watch list for this issue. The manner in which watch list tanks have been identified to date is described in Hopkins (1994). Modifications to the procedure for identifying tanks for placement on the watch list have also been proposed.

Procedures that are required to determine which of the tanks on the watch list potentially require mitigation (i.e. the second and third bulleted tasks above) are the focus of this document. A decision strategy addressing these issues is defined in this document (Section X.XX) and the DQO process is employed to identify the precise data needs and associated DQOs required to support the decisions required to determine which of the tanks on the flammable-gas watch list require mitigation.

Mitigation options are also being developed as part of the flammable gas safety program, but their consideration is beyond the scope of this document. As indicated previously, issues concerning the selection, design, and implementation of mitigation options are also beyond the scope of this document. However, such issues are being actively pursued as part of the flammable gas safety program.

3 TECHNICAL APPROACH TO THE PROBLEMS

Because the flammable gas problem is complex, the critical processes are incompletely understood, and the data required to adequately assess the magnitude of the problem in most tanks is currently unavailable, a multi-faceted approach was adopted for attacking the problem. First, physical and chemical principles were applied based on the conditions known to exist in the tanks and the known characteristics of wastes to develop a general understanding of the problem so that a series of markers could be defined that were highly likely to indicate tanks in which the rates of flammable gas generation and release might pose an unacceptable safety concern.

Tanks exhibiting these markers where then placed on a watch list. Note that, as the understanding of the problem continues to improve, the set of markers employed to define the watch list is being modified. A detailed discussion of watch list criteria is presented in Section X.XX. The set of tanks currently included on the watch list are provided in Table XX. An additional set of tanks that are proposed for addition to the flammable gas watch list based on additional watch list criteria (Section X.XX) are provided in Table XX.

Second, procedures have been implemented for installing and/or upgrading monitoring devices (including thermocouple trees, waste level monitors, and dome-space hydrogen gas monitors) that will provide additional information, that was identified as useful for further identifying and tracking the gas generation and release in specific tanks. Details of this enhanced monitoring program are provided in Section X.XX.

Third, at the same time as the improved monitoring program is being implemented, the mechanisms that have been identified as contributing to the generation (see Section X.XX), retention (see Section X.XX), and release (see Section X.XX) of flammable gases are being further evaluated to identify physical and or chemical constraints that can be used to bound the problem as it is evaluated in specific tanks. Because these models are employed directly in the decision-making process for determining mitigation (the subject of this document), a detailed discussion of the bounding models in current use, their strengths, and their limitations is provided in Section X.XX.

Fourth, various simulant studies and waste sampling and analysis events are being completed to improve the overall understanding of the problem and to provide information for refining and validating models of the critical mechanisms that contribute to gas generation, retention, and release (see Section X.XX)

Fifth, the current, relatively simple, bounding models are being replaced by increasingly sophisticated models that take into account more of the detailed physical and chemical processes that drive gas generation and retention, so that decisions concerning the need for mitigation can be rendered more accurately (see Section X.XX). Note, although it is beyond the scope of this document, a cost-benefit analysis could be performed to determine the most

efficient combination of analysis, modeling, and mitigation for resolving the flammable gas issue. The logic for such an analysis could easily follow the steps of the DQO process.

Finally, schemes for mitigating the flammable gas problem are being developed and evaluated and the data needed to support selection and design of options for specific tanks are being defined (see Section X.XX).

3.1 HISTORY OF THE PROBLEM AT HANFORD

How Problem was Discovered:

- Observations in Hanford Tanks (i.e. SY-101)
- General Knowledge and Experience with Gas Generation in Sludges
- Other

A logic diagram showing the inter-relationship of the decisions associated with the above considerations is provided in Figure XXX.

3.2 TITLE

3.2.1 Overview: it was necessary to address (1) identifying tanks in which problem potentially required consideration (i.e. creation of watch list), (2) among the watch list tanks, determining the need (in specific tanks) for continuous monitoring (and the type of monitoring required), (3) among the watch list tanks, determining the need (in specific tanks) for mitigation, and (4) for those tanks requiring mitigation, to support design/engineering of and select among appropriate mitigation measures. Given that the current understanding of the processes associated with this problem (particularly those contributing to episodic releases) is currently incomplete, additional work is also proposed to support an improvement in the understanding of the problem.

3.2.2 Considerations for Identifying Tanks to be Targeted for Evaluating the Flammable Gas Problem

3.2.2.1 Given the current understanding of the flammable gas problem, it was decided that tanks for which the production of flammable gas is a potential problem (requiring further study, monitoring, and/or mitigation) could be identified by a combination of:

3.2.2.1.1 knowledge of the specific types of wastes in the tank.

3.2.2.1.2 knowledge of the level of the radiation field in the tank.

3.2.2.1.3 observations of certain gaseous components in the gas phase of the tank.

3.2.2.1.4 observations of changes in level of the surface of the waste in the tank (either growth, which might indicate the generation and retention of gas, or a relatively rapid reduction, which might indicate an episodic release of gas).

3.2.2.1.5 observations of pressure bumps in the dome space of the tank (potentially indicating an episodic release of gas).

3.2.2.1.6 observations of certain types of changes in the distribution of temperatures measured as a function of depth within the tank wastes (potentially indicating changes in the conductibility and heat capacity of specific layers of wastes, which in turn might indicate the retention of gas).

3.2.2.1.7 Other

3.2.2.1.8 The above have been used to establish a flammable gas tank watch list.

3.2.3 Considerations for Determining the Need and Type of Monitoring Required in Specific Tanks

3.2.4 Considerations for Determining the Need for Mitigating Specific Tanks

3.2.4.1 Given the current understanding of flammable gas generation in the tanks, it is currently assumed that monitoring of hydrogen gas in the dome space of the tanks would provide an adequate signal of the potential for creation of a mixture exceeding some fraction (i.e. with adequate safety factor) of the lower flammability limit as a warning of the potential that gas generation in a particular tank might

be sufficient to raise safety concerns under steady-state conditions (see below for potential modifications to this scenario). It was also recognized, however, that such monitoring would not provide adequate warning of the potential for an episodic release of gas to produce an unsafe condition in a tank.

3.2.4.2 For episodic releases, no direct monitoring system can currently be identified that can provide adequate, *advanced* warning that a safety criterion might be exceeded due to a episodic release. Consequently, evaluation of this part of the flammable gas safety issue has been addressed by modeling the generation, retention, and release of gas in a waste tank.

Simple, worst-case (bounding) models have been developed initially for this purpose based largely on observations from Tank SY-101). These models provide estimates of the maximum rate of gas generation expected in a tank (based on observed rates in Tank SY-101 and measurement of a small number of waste characteristics in the tanks to which the model is to be extrapolated. Bounding conditions in these models include consideration of whether the undiluted mixture of gases produced in the waste itself exceeds the LFL (non-flammable components are also generated in the waste) and whether the maximum volume of gas produced over the longest period of time expected between episodic releases (if released completely) exceeds the volume required to (1) create a sufficiently large pressure surge to cause a release of material from the tank, (2) if ignited as released, to create a sufficiently large pressure surge to cause a release from the tank, and/or (3) once dispersed and mixed within the dome space to create a concentration that exceeds some defined fraction (i.e. with adequate safety factor) of the LFL. As indicated above, specific types of measurements of the characteristics of wastes in Hanford tanks may be required to support application of this model to tanks other than SY-101. Additional waste measurements, perhaps coupled with gas phase monitoring may also be required to validate this model.

The bounding model indicated above incorporates neither the consideration of the actual chemistry of gas generation nor the physics and chemistry of gas retention. Therefore, numerous opportunities exist for improvement in the model. In fact, more sophisticated models are already under development. However, whether such models offer either increased reliability or an improvement in the ability to distinguish non-problem tanks from those that are truly problems (and therefore increase the cost-effectiveness of the program) remains to be evaluated. As with the simpler model described above, specific types of measurements of the characteristics of wastes in Hanford tanks may be required to support application of the more sophisticated models to conditions in the Hanford tanks. Additional waste measurements, perhaps coupled with gas phase monitoring may also be required to validate such models.

3.2.5 Considerations for Design/Engineering of Mitigation Measures and for Selecting Among Mitigation Measures

3.2.6 Directions for Improving the Understanding of the Problem

3.2.6.1 As the understanding of the conditions contributing to the flammable gas problem improves (including, for example, either improved understanding of the generation or the retention of gases), it will prove useful to re-evaluate the criteria currently employed to identify tanks to be placed on the flammable gas watch list (see Section 2.3.2).

3.2.6.2 One of the issues that still needs to be adequately evaluated is the degree to which hydrogen gas concentrations in the dome space of a tank can be considered to bound the concentrations of other flammable gases that might be produced in specific tanks *under the entire range of conditions and waste characteristics found within the entire tank farm* (see Section 2.3.4.1 above). To the extent that hydrogen gas concentrations cannot be shown to be adequately bounding, equipment may have to be installed for monitoring of additional gas components. Studies may have to be developed to target and address this issue. Among the types of studies that might be appropriate could be a

one-time sampling event (potentially spread out over some defined period of time) to characterize the detailed composition of the flammable gas found in the dome space of a tank.

3.2.6.3 As indicated in Section 2.3.4.2, the bounding model currently being used to evaluate the potential for unacceptable episodic releases to occur in specific tanks may need to be properly validated, particularly to the extent that it may be adapted to tanks other than SY-101. It may therefore be prudent to devise appropriate studies to test and validate the critical components and assumptions of the model.

3.2.6.4 As indicated in Section 2.3.4.2, several models (with increasing levels of sophistication) are also being developed to evaluate the potential for unacceptable episodic releases to occur in specific tanks. These two will need to be validated before they can be applied as part of the formal decision logic that is to be used to determine the need for monitoring and/or mitigation of specific tanks to prevent unacceptable flammable gas releases. Therefore, a series of appropriate studies will have to be devised to test and validate the critical components and assumptions of these models.

3.2.6.5 Other.

3.3 FOCUS OF THIS DOCUMENT

3.3.1 As indicated above, the technical approach adopted for addressing safety concerns associated with the generation of flammable gas in the Hanford tanks is complex (because the problem is not trivial) and numerous parts of the approach may require various types of measurement to support decision making. However, the immediate focus of this DQO document is to address the measurement that is currently required to support the need for mitigation of flammable gas safety issues based on the existing approach to the problem. Therefore, the focus of the remaining sections of this document will be on (1) the monitoring efforts that are required to determine whether flammable gas is generated at a sufficient rate in a particular tank to contribute to the creation of an unsafe condition associated with steady-state conditions in a tank and (2) the monitoring and measurement that may be required to support a bounding evaluation of a

tank (using the existing model) to determine whether conditions in the tank allow for unacceptable episodic releases. Presumably, the finding of a potential problem in a particular tank via either of these routes would result in a decision to mitigate the tank.

Should it be determined that mitigation is required in a particular tank, the next logical step would be to perform an evaluation to select and design the most cost-effective option for mitigation. However, considering the design of any program to provide measurements required to support the design or evaluation of mitigation options is beyond the scope of this document. Such will be the subject of a companion document to be produced in the near future. It is also expected that the sampling and analysis that may be required to support other aspects of the flammable gas program (including, for example, model development and validation) will be addressed in companion documents that will also be developed later, as the need arises.

4 DEFINING DATA NEEDS AND ATTENDANT DQO'S FOR SUPPORTING DECISIONS CONCERNING THE NEED FOR REMEDIATION

It is clear from previous sections of this document that additional measurements of various types will be required to support the mitigation-related decisions associated with flammable gas. Thus a preliminary set of data needs and the attendant DQOs required to support each such decision are identified in this chapter through formal application of the DQO process. To facilitate discussion, the remaining sections of this chapter are also organized in parallel with the seven steps of the DQO process.

In the following sections of this chapter, the DQO process is applied separately to the two general issues that must both be considered to assess the need for mitigation of a particular tank to prevent the development of an unsafe condition due to the generation and release of flammable gas:

- determining whether gas generation rates in a tank are sufficient to cause steady-state flammable gas concentrations to exceed the LFL (or some defined fraction of the LFL) in a tank; and

- determining whether conditions in a tank potentially allow the retention and episodic release of a volume of flammable gas that is sufficient (either with or without ignition) to cause a containment failure that leads to expulsion of hazardous materials from the tank into the environment.

Note, the issues being addressed in this document are a small subset of the issues that are the focus of an integrated program to address flammable gas safety concerns. Also, as more components of the program are completed with time, the understanding of the flammable gas problem continues to improve. However, this report reflects only a snapshot of the *unfinished* program as it currently exists. Consequently, the approaches proposed in this document for addressing mitigation-related decisions may be modified in the future.

4.1 DEFINING DATA NEEDS AND DQO'S TO DETERMINE WHETHER MITIGATION IS NECESSARY TO PREVENT UNACCEPTABLE STEADY STATE CONDITIONS

The primary reason for addressing this consideration separately from the consideration of episodic releases is because tanks may exist at the Hanford site in which flammable gas is generated at sufficient rates to pose this problem but in which conditions are not conducive to gas retention so that episodic releases are not important. This issue should also be addressed, however, when evaluating mitigation options for controlling episodic releases.

Some of the primary mitigation options considered for addressing episodic releases (such as the introduction of a pump to a tank to keep wastes well mixed) will have no impact on the potential for the tank to exceed the LFL (or

an appropriate fraction of the LFL) at steady state. Thus, an additional reason for considering this scenario in this document is to provide a mechanism for determining whether mitigation options that only address episodic releases are adequate for a particular tank or whether other measures alternate options might be more cost-effective.

4.1.1 State the Problem

This step of the DQO process was largely completed in Chapters 2 and 3. As indicated above, the main objective being addressed here is determining whether mitigation is required in any particular tank due to the potential that the generation of flammable gas in that tank is sufficient to produce a steady state concentration exceeding the LFL (or an appropriate fraction thereof).

4.1.2 Define the Decisions

Assuming for the moment that monitoring of hydrogen gas effectively bounds the concentration of all other flammable gas components in the dome space (see Section X.XX), the decision that needs to be determined for this issue is:

> determine whether the *instantaneous* concentration of hydrogen in the dome space of a tank exceeds a target (i.e. the LFL or some pre-defined fraction of the LFL).

Presumably, if it is concluded that this decision is affirmative, then mitigation of the tank would be required; otherwise, no action would be required beyond continued monitoring.

The definition of a target equal to some fraction of the LFL can be seen as a safety mechanism that provides time for response in those cases where some action is deemed appropriate, i.e., where the chance of reaching the LFL after observing a concentration equal to the target is no greater than some acceptably low level. Because there is also a legal requirement that flammable gases in confined spaces be maintained below 25% of the LFL (DOE 1984, NFPA 1992), this might be considered initially as an appropriate target. However, as indicated in Section X.XX, an appropriate target level (which may be less than 25%) needs to be selected to assure that the chance of exceeding the LFL is no greater than acceptable.

Note, as indicated in Section X.XX, there is a need to determine whether monitoring hydrogen gas concentrations does in fact adequately bound contributions to flammable gas concentrations from other flammable components potentially produced in the Hanford tanks (e.g. ammonia, or low molecular weight hydrocarbons). To address this problem, a sampling program is routinely performed in concert with the placement of hydrogen monitors in a tank in which samples of the dome space gas are collected periodically over a

range of 10 weeks for detailed analysis to identify other flammable components that may be important in that tank.

A safety analysis addressing this issue has also been completed (Johnson 1995) and suggests that targeting approximately 15% of the LFL for hydrogen (rather than 25%) may adequately account for contributions from other flammable components. However, because this analysis does not appear to have addressed the true range of variability in gas monitoring in the Hanford tanks, the analysis provided below is designed to determine whether setting an even lower target may be appropriate.

Given the broad range of conditions and waste mixtures observed among the 25 tanks on the flammable gas watch list and the 54 tanks proposed for addition to the watch list (Section X.XX), the available safety analysis also may not have adequately accounted for the full range of gas mixtures potentially encountered among all of the tanks. To the extent that this is so, it may be necessary to install additional monitors to track concentrations of specific components in addition to hydrogen. Even to the extent that this is needed, however, the analysis proposed below is equally applicable to mitigation decisions that might be based on monitoring of gases other than hydrogen.

4.1.3 Identify Inputs to the Decisions

To support the decision(s) defined in above, the only inputs are the real time, continuous measurements of hydrogen concentrations (or other flammable gas components provided by the monitors installed (or to be installed) in each tank of interest. Note, monitoring of gases other than hydrogen will not be addressed further. As indicated above, however, the analysis presented below for hydrogen is *directly* transferable to monitoring of any other flammable gas.

4.1.4 Define the Decision Boundaries

Both spatial and temporal boundaries must be considered.

4.1.4.1 Spatial boundaries

Spatially, the boundaries of the population representing the input to this decision (hydrogen gas concentrations in the dome space) are simply the physical boundaries of the dome space of a particular tank (defined by the inner walls of the tank and the top of the condensed waste). This may be considered a population of point concentrations that has some variability. However, a simplifying assumption that may be reasonably supported is that gas phase transport is sufficiently rapid that the spatial variability of hydrogen gas within the dome space is small relative to temporal variations and can more than likely be ignored.

Also, with the few exceptions discussed below, gradients (to the extent they exist in the air space of a tank) are likely small and relatively localized. Therefore, the spatial component of variability can be ignored; in essence, for any particular point in time, there is only a single relevant concentration. Therefore, monitoring of the dome space concentrations at a single, centralized location would be sufficient and representative of the dome space as a whole.

One additional consideration that must be addressed before dismissing the definition of spatial boundaries, however, is whether the gas monitor is placed in such a location so as to provide an *unbiased* measurement of dome space concentrations. Since monitors are being placed directly into a relatively central portion of the dome space in single shell tanks, this issue can likely be ignored for such tanks.

In double shell tanks, however, monitors are typically installed in the exit vent to the tank. For many tanks, this may not be a problem. Because double shell tanks are actively vented, however, it is important to review the relative locations of entrance and exit vents in the tank to assure that conditions do not arise in which air flow is essentially short-circuited so that air entering the exit vent is significantly diluted relative to dome-space gas.

In still other double shell tanks, exit vents from multiple tanks are interconnected. In such arrays, it is important to assure that the placement of the monitor is sufficiently removed from a particular tank so as to be sampling gas that is not representative of the specific tank of interest. To the extent that any of the problems exist, effort needs to be expended to rectify the problem; non-representative data compromises the ability to support decisions within defined error rates.

4.1.4.2 Temporal boundaries

Temporarily, the boundaries of the population need to be defined based on what is known or suspected about the nature of the time-dependent variation of hydrogen gas in a tank. Even ignoring episodic releases (which are addressed in Section 4.2), various factors may contribute to the temporal variation of steady-state gas concentrations within a tank. These may include, for example:

- variations introduced into ventilation rates due to diurnal temperature variations;
- variations in ventilation rates and tank waste temperatures (affecting generation rates) due to seasonal variations in temperature;

- variations in ventilation rates due to weather-induced changes in ambient barometric pressure;
- effects of inter-connected tanks, especially single-shell tanks with cascade lines; and/or
- role of convection and diffusion

Due to the large contributions to variation in hydrogen concentrations potentially introduced by these temporal factors, a procedure is proposed below for incorporating such variation as part of the total variation of the input measurements required to assess the above decision(s). Thus, factors are considered as part of the process presented below for selecting an appropriate target concentration as a decision criterion useful for assuring (with an acceptably low probability) that the LFL will not be exceeded in the dome space of the tank.

4.1.5 Define Decision Rules

The complete description of a decision rule includes:

- a statement of the hypotheses to be tested to determine each required decision;
- a specified statistical test (or precise rule) by which the data are to be used to support the decision; and
- a specific decision criterion (i.e. the target around which the decision is to be determined).

4.1.5.1 The testable hypotheses

In the context of determining whether the "steady-state" concentration of hydrogen exceeds a defined target concentration (i.e. a defined fraction of the LFL), it is proposed that hypotheses be tested as follows:

$$H_o = C_{H2} < Q$$

and

$$H_a = C_{H2} \geq Q$$

where:

H_o is the null hypothesis;
H_a is the alternate hypothesis; and
Q is the target value (not to be exceeded).

As indicated previously, Q is to be chosen such that, if Q is never exceeded (i.e. that the null hypothesis is never rejected), there is an acceptably small probability that the LFL will be exceeded in the tank for some define period of time into the future. Thus, adequate advanced warning of an event requiring mitigation will be assured. For such an analysis to be useful, however, Q must be selected with adequate consideration both for contributions to error from measurement error and from the contributions to error from temporal variation (see below).

Note that, due to the expected differences in the sources and magnitude of variation in different tanks, it is expected that a different Q will need to be defined for different tanks using the procedure described below.

4.1.5.2 The data evaluation rule

Two options are proposed for the rule to be used to evaluate monitoring data to test the above hypothesis and determine whether a particular tanks requires mitigation. The first is simply to continue monitoring until any point in time at which a monitored concentration exceeds an appropriately defined Q (Section 4.1.5.3). This may work for tanks in which episodic events are not expected to be a significant problem.

For tanks in which episodic releases are anticipated to be a problem, the following rule is preferred:

- once sufficient data are collected (assume a minimum of a month of monitoring, but the minimum amount of data required may depend on the frequency and magnitude of the episodic events that need to be excluded) set up a control chart based on monitoring results from the tank that includes:
  - a line representing the long-term mean concentration (derived by integrating the data);
  - lines representing several upper percentiles of the data (e.g. the 95th and 99th percentile) that are designed to assist with identification and exclusion of excursions that are more likely than not to be attributable to episodic releases. The procedure by which specific percentiles should be chosen may be somewhat ad hoc but should be based on careful, visual inspection of the data[5];

[5] The ability to construct such a control chart is based on the assumption that, given the extended period of time over which wastes have been left in the tanks, dome space concentrations should have had time to equilibrate so that near steady-state conditions should already prevail. The extent to which this assumption is valid may be evaluated by trend analysis. To the extent that intervals during which episodic events occur can be corroborated from independent monitoring devices (such waste level devices), a more formal procedure for their identification and exclusion can be applied.

- update the control chart over regular, extended intervals of time; and

- reject the null hypothesis whenever the mean concentration over some short interval (i.e. hours or days, this will also need to be chosen by inspection) that is derived from data that are not excluded as belonging to an episodic release, exceeds the appropriately defined Q.

4.1.5.3 The decision criterion (defining "Q")

To derive an appropriate target concentration "Q" (for use in the hypothesis testing described above) that assures adequate protectiveness, a physical model of the balance between gas generation and removal from the tank is evaluated by considering the consequences of the inclusion of random variation in the model's parameters. As presented below, however, measurement error is assumed to be nil. If estimates of the degree of uncertainty associated with measurement error becomes available (from the types of analysis recommended in Section 5.1.6.3, such error can be incorporated into the following analysis by allowing the estimates of concentrations employed in the simulations to vary accordingly.

Note that the following procedure may be used for defining an appropriate Q whether or not the monitoring data employed in the analysis has been adjusted to exclude episodic releases.

The following procedure will allow developments of tolerance limit-type statements about the certainty with which one can predict the probability that the LFL will be exceeded (over some period of time into the future) given a monitoring result at the start of the prediction interval that is no larger than some target, "Q."

The physical model assumed for gas generation and removal incorporates a rate of release of the gas from waste that is zero order (in gas concentration) while the venting of the gas from the dome space to the external air is first-order, then

$$dC/dt = (z - v*A)/V \qquad (4.1)$$

where:

C is the dome space concentration of the monitored gas (e.g. hydrogen) (mg/L);
z is the rate of release of gas from the waste in the tank (mg/hr);
v is the first-order rate constant (hr^{-1});
A is the amount of gas in the dome space (mg); and
V is the volume of the dome space (L).

This can be rewritten with the obvious change of variables as

$$dC/dt = f - v*C \qquad (4.2)$$

where:
f is the rate of change in concentration (mg/L-hr).

Equation 4.2 has the solution,

$$C_i = f/v*(1 - e^{-vt}) + C_{i-1}*e^{-vt} \qquad (4.3)$$

where:
t is the time between observation i-1 and i.

Note that to use this form of the equation, it will be necessary to discretize the monitoring data into arbitrarily short time intervals. The selected interval should be short compared to changes in concentrations attributable to the sources of variability of interest.[6]

Although the model presented above is a relatively simple representation of a waste tank, it is likely an adequate representation of a passively (or actively) ventilated tank. However, if other processes or considerations dictate, alternate (more appropriate) differential equations can also be used. It is conceivable that even simpler models (such as assuming that the system has essentially reached steady state) might be appropriate. The subsequent treatment remains essentially the same, no matter if the model of the system is simpler or more complex, although numerical rather than analytical solutions may be required for more complex models.

The solution presented to the proposed model presented above is valid as long as f and v are constant[7]. However, we are interested in exploring the effect of the variability of f and v on the prediction of concentration with time. Therefore, the variability of f and v can be tracked as an "error" or deviation from the deterministic equation as follows:

$$C_i = Chat_i + r_i, \qquad (4.4)$$

where:

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6 It may also be possible to find a solution of to this equation that can tolerate input of a continuous variable, although such a solution is not immediately obvious.

7 Actually, the solution is valid even if v and f are variable, as long as they vary independently of concentration.

$Chat_i$ is set equal to $(f/v*(1 - e^{-vt}) + C_{i-1}*e^{-vt})$, which are the predictions from the model derived above for the relevant differential equation; and

r_i represents a random "error" or deviation from the prediction.

The mean of the r_i's should be zero. However, we may or may not want to treat the r_i's as being independent.

The simpler treatment would be to assume the r_i's are independent. If we assume that they are not (or test for autocorrelation and find that it is likely that there is some) then a time series approach could be used to model the r_i's. Briefly, the time series approach would estimate the lag k autocorrelation coefficients and those would be used to estimate a value of r_i from the values of r_{i-1}, r_{i-2}, etc., rather than assuming that r_i could be picked independently of r_{i-1}, r_{i-2}, etc.

In either case, the following 5 steps describe the process by which the desired probability (tolerance) statements can be derived (in association with a specified value of "Q":

(1) estimate the parameters of the model(s) from the observed data. In the differential equation-based part of the modeling, the parameters to be estimated are f and v. These can be estimated by maximum-likelihood or least squares approaches based on the consecutive pairs of observations, c_0 and c_1, c_1 and c_2, etc. In addition, it is necessary to plot the values estimated for the r_i's to derive an empirical distribution that can be randomly sampled (as described below)[8]. If independence is assumed, then only the variance of the r_i's needs to be estimated (the mean is zero). In the time-series case, we would estimate not only the variance but also the autocorrelation coefficients; maximum likelihood approaches are available for this estimation as well;

(2) with the estimates from Step 1, run many simulations. Each simulation will start with the concentration at an estimated value for Q (i.e. y_*LFL) and follow the time course of concentrations over time for the desired time interval. At each time step, i, along the way, a value for r_i is randomly selected based on either the time series or independence assumption. This is the only thing that varies from one simulation to another. Count up the number of individual simulations for which the LFL is exceeded over the total time interval of the simulation and divide this by

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8 It may also be possible to find a reasonable parametric description of the distribution of r_i's. This would simplify the manner in which values for r_i are chosen in the following simulations.

the total number of simulations run. The result of this step is an estimate of the probability of getting a concentration at or above LFL from our best estimates of the underlying relationship and the degree of variability.

Note that a large number of simulations may be required. If the acceptable probability of exceeding the LFL is about 10^{-6} per year (for example), 10^{7} or more simulations will be required;

(3) to account for uncertainty in the estimates of f, v, and the parameters defining the r_i's, "bootstrap" sampling will be required. Using the best estimates of f and v from Step 1, the observed r_i's (differences between the observed and predicted concentrations) must be calculated and saved. From some starting concentration (e.g., the initial concentration in the original observed data set), one can create a bootstrap sample as follows:

for the next observation, predict the concentration using the differential equation-based model and the best estimates of f and v, then add to that prediction a randomly selected r_i from the saved set of observed r_i's. Continue doing this, creating new observations at each of the time points (accounting for the autocorrelation in the random selection of the r_i's if doing the time series approach -- this could be done by defining weights on the observed r_i's based on the previous selection(s) so that those more likely to be observed next, based on the best estimates of the autocorrelation coefficients, are given greater weight than those less likely to occur next). The end of this process will be a simulated set of concentrations at all of the same time points as the original data set;

(4) repeat Steps 1 and 2 on the simulated data set from Step 3. Each time we will get an estimate of the probability of exceeding the LFL for; and

(5) repeat Steps 3 and 4 a large number of times (say 1000 or more).

Based on the result of the above 5 steps a statement can be constructed such as, "We are 95% certain that the probability of getting a concentration greater than or equal to the LFL after observing a concentration at or below Q is less than x." Here x is the probability not exceeded by more than 5% of the bootstrapped samples (i.e., the 95th percentile of the 1000 bootstrap runs, with respect to the proportion of time the LFL was equaled or exceeded). Of course, other degrees of certainty can be substituted, as desired.

As discussed above, this analysis relates to the determination of reasonable targets for the earlier decision rules. The results will show the probability that the LFL is eventually exceeded, so that the current observations can be judged in the context of what future concentrations might be observed. The

proposed analysis can support the determination of some maximum value of y, for y between 0 and 1, such that the degree of certainty is at least 95% that the probability of exceeding the LFL will be less than 10^{-6}, for example. The selection of the maximum y satisfying that condition reduces the number of times remediation will have to be done.

4.1.6 Identify Acceptable Error Limits and the Attendant Data Quality Objectives

The appropriate data quality objectives that need to be defined for this issue include:

- a tolerance limit (as opposed to an acceptable error rate);
- a sensitivity requirement;
- an accuracy requirement; and
- a representativeness requirement.

4.1.6.1 Defining an appropriate tolerance limit

An appropriate tolerance limit (i.e. an acceptable probability for exceeding the LFL over some period of time) needs to be defined based on the an analysis of the magnitude of the consequences potentially suffered by exceeding the LFL versus the cost of mitigating tanks that cannot be shown to satisfy the tolerance limit. Ideally, this level needs to be defined by consensus among the appropriate decision makers.

4.1.6.2 Defining appropriate sensitivity

The sensitivity required of the monitoring equipment to be used to measure hydrogen concentrations (or the concentrations of other flammable gas components) should ideally be set no higher than one tenth of the target value, "Q." Given the large value at which Q is likely to be set, however, relative to the kinds of concentrations of concern typically required in environmental analyses, it is likely that the sensitivity requirement listed here will be easily surpassed by the equipment in use for monitoring flammable gas.

4.1.6.3 Defining appropriate accuracy

If mitigation-decisions are to be made with some assurance of reliability based on the monitoring data to be collected, it is critical that the monitoring data be designed to achieve a defined accuracy. What is required here is that the monitoring devices be equipped with some type of apparatus

that allows periodic sampling of a reference standard. The known stability of the equipment may be used to establish the required frequency with which calibration standards are to be run (and they may in fact be required only relatively infrequently). In any case, it must be possible to demonstrate that any potential bias introduced by measurement error be shown to be sufficiently small so as to contribute insignificantly to the overall error in determining whether mitigation is required. An appropriate target accuracy will therefore need to be defined.

If measurement error (including bias in this case) cannot be demonstrated to be insignificant, the contribution from such error to the achievable tolerance limit can be addressed formally. What would be required would be periodic measurement of a reference standard at a sufficient frequency to allow estimation of a mean and a standard deviation. Especially is the distribution of such error is amenable to parametric analysis, it may then be incorporated formally into the simulations proposed in Section 4.1.5.3 for deriving an appropriate Q.

4.1.6.4 Defining appropriate representativeness

Although representativeness is a qualitative measure of data quality, it is nonetheless critical that it be considered formally and that the results of its consideration be documented. Given the scenarios presented in Section 4.1.4.1 under which the degree to which monitoring results might be considered to be inadequately representative of overall dome space concentrations, such situations either need to be formally evaluated to demonstrate that representativeness is adequate. Even better, situations in which representativeness might be questioned should be avoided to the extent possible, even if requires creative modification of hardware to allow better placement.

4.1.7 Optimize The Study Design

Based on the current conceptualization of the manner in which the DQO process is to be applied at Hanford, This step of the DQO process is typically considered beyond the scope of a "generic" issues document of this type. Rather, it is supposed to be completed in a test plan for a specific tank. For this issue, however, the manner in which monitoring is to be performed to obtain the required data has already been determined and is being implemented. Given the following, such an approach is considered acceptable for this case:

- the lack of options for developing inputs to this set of decisions;
- the relatively minor expense associated with the installation of hydrogen monitoring devices (in comparison with the cost of implementing mitigation options); and

- the use of a continuous monitoring device that makes irrelevant the consideration of costs associated with the "number of samples" required to achieve a stated error rate.

Thus, optimizing the study design for this issue is focused on assuring adequate protectiveness (by assuring collection of data of adequate quality) rather than finding the most cost-effective option for collecting data. Therefore, the most important lessons of the DQO process as applied to this issue are the specific considerations identified in Sections 5.1.6 that need to be adequately addressed and documented to assure that data collected from the monitoring devices that have been (or will be) installed are providing data of sufficient quality to achieve the desired level of protection for this issue.

Note, as the understanding of the flammable gas problem improves, less conservative but equally protective options for addressing concerns associated with steady-state concentrations of flammable gas in the dome spaces of particular tanks may become apparent.

4.2 DEFINING DATA NEEDS AND DQO'S TO DETERMINE WHETHER MITIGATION IS NECESSARY TO PREVENT UNACCEPTABLE EPISODIC RELEASES

Abrupt reductions in waste levels have been recorded in several of the double-shelled tanks on the flammable gas watch list. Such drops are indicative of an episodic release of gas.

4.2.1 State the Problem

This step of the DQO process was largely completed in Chapters 2 and 3. As indicated above, the main objective being addressed here is determining whether mitigation is required in any particular tank due to the potential for retention and release of flammable gas at a rate that might cause loss of containment of the waste through any of failure modes that have been previously identified (Section X.XX).

4.2.2 Define the Decisions

The discussion provided in Section X.XX indicates that, due to the complexity of this problem and the limitations of current knowledge, decisions relating to the potential for unacceptable episodic releases will be based on a conservative, bounding analysis of the problem. Therefore, what needs to be decided is:

whether the volume of gas that can be *stored* in the waste between episodic releases is sufficient (if released during one event) to: (1) create a pressure pulse that is sufficient to cause a failure

of the HEPA filter in the tank vent (or fugitive emissions from seals and feeds) in the tank, (2) cause vent filter failure (or fugitive emissions) if ignited during release from the waste, or (3) cause dome space concentrations to exceed some pre-defined fraction of the LFL after the gas from the episodic release is completely dispersed and mixed within the dome space.

Because this decision is to be based on a bounding analysis, one need only focus on the smallest (bounding) of the limiting volumes of gas that can be associated with each of the three failure scenarios listed above. If a formal cost-benefit analysis is to be supported, however, it may also be prudent to formulate this decision to address each of the three potential failure modes separately; the magnitude and cost of consequences attributable to each type of failure differ significantly because the mass of hazardous material expected to escape into the environment is expected to vary radically for each type of failure. Even if each failure mode is considered separately, however, the following discussion can be applied in each case.

Note, the decisions defined above are formally designed to determine when mitigation is indicated. However, as indicated below, the state of current knowledge and technology requires that these decisions be addressed using a conservative, bounding model. Such models may be protective but they also frequently indicate a false need for mitigation, which (if followed) is not cost-effective. It is therefore recommended that the action to be taken based on the outcome of the decisions listed above be to initiate a cost-benefit analysis to determine whether further study might better distinguish between true and questionable needs for mitigation in specific tanks and whether such study would be less expensive than simply mitigating all tanks identified as problems by the bounding model. Then, only when a decision to mitigate is supported by the more sophisticated analysis, would design and implementation of mitigation be recommended.

4.2.3 Identify Inputs to the Decisions

The decision identified in the last section (regarding whether sufficient flammable gas can be retained in the waste between episodic releases to support a release that exceeds some pre-defined, minimum volume) can potentially be supported by several combinations of inputs. Not all such options, however, are equally feasible (given the current state of knowledge and technology). The various options also range in costs. Therefore one of the goals of the DQO analysis of this problem should be to identify the most cost-effective of the options available for addressing this issue.

Input options that are potentially applicable to the above decision:

(1) direct monitoring of some physical characteristic of the waste (i.e. waste level) as an indicator of episodic releases. However, because episodic releases potentially occur over time periods that

are too short to allow adequate response, direct monitoring as a predictor of this problems was determined not to provide sufficiently advanced warning of the problem and it is not considered further;

(2) regular, direct measurement of retained gas with a determination as to whether the volume of retained gas exceeds the pre-defined, critical volume. This option is not feasible because no validated method currently exists for providing reliable, representative measurements of retained gas;

(3) one-time measurement of certain physical and chemical properties of the waste to serve as inputs to a sophisticated and reliable model that predicts the time dependence of gas generation, retention, and release followed by a determination from the output of the model whether the maximum volume of gas potentially released at any one time from the waste exceeds the critical volume of interest. This option is not currently feasible because no model capable of supporting the indicated analysis has been developed and validated;

(4) one-time measurement of certain physical and chemical properties of the waste to serve as inputs to a bounding model capable of predicting the upper limit volume of gas that can be retained by the waste before triggering a release. Because a simple model that serves this purpose currently exists (though it remains to be completely validated for tanks other than SY-101), it is potentially feasible to employ this option. However, an additional limitation (addressed below) is the degree to which current measurement procedures can provide representative or at least reliably conservative measurements of the various parameters required to adapt this model to tanks other than SY-101; or

(5) extrapolation of certain physical and chemical properties of the waste from tank SY-101 to other tanks to serve as inputs to a bounding model capable of predicting the upper limit volume of gas that can be retained by the waste before triggering a release. Because a simple model that serves this purpose currently exists (though it remains to be completely validated), it is potentially feasible to employ this option.

Unlike the previous option, this option is immune to the potential problems associated with the measurement of various waste properties in various tanks. It is subject, however, to limitations in the ability to adequately estimate bounding conditions in a tank based on extrapolation of data from Tank SY-101.

The remaining discussion focuses on the last two options listed above (i.e. the only two options that are currently viable).

For the bounding model to be used in this analysis (described in Section X.XX), the required input parameters are:

- the volume of waste in the tank;
- the volume of the dome space in the tank (determined as the difference between the total volume of the tank and the volume of waste);
- the cross-sectional area of the waste (i.e. the inside cross-sectional area of the tank);
- the thickness of the layer of waste in which gas retention occurs. This is termed the non-convecting layer in the model. The thickness of the non-convecting layer is determined by temperature measurements from a vertical thermocouple tree, which are the real inputs for this parameter; and
- the gas-free densities of a specific shallow of waste and a specific deep layer of waste known, respectively as the convecting and the non-convecting layers.

Of these, only the last two are derived by types of measurements that are potentially subject to significant error. The remaining inputs are either determined from design drawings or from a measurement of waste level, which is assumed to be sufficiently accurate to ignore the error associated with its measurement.

The primary difference between the two options being considered for inputs to the decision is that, for one option density measurements are to be derived for a particular tank by extrapolation from Tank SY-101 while, for the other option, density estimates are to be derived by measurement.

Sources of error associated with estimates of density derived by extrapolation relate to the degree with which the types of wastes assumed to reside in Tank SY-101 and the target tank of interest differ from the actual wastes in the tank. They also relate to the degree to which the properties of such wastes vary from the values assigned to them based on the measurements collected in Tank SY-101.

Sources of error associated with estimates of density derived by measurement are subject to the uncertainty potentially introduced by the degree to which the locations from which core samples are collected are not representative of the waste in the tank as a whole; the magnitude of any sampling bias introduced from core sampling; the degree of bias potentially introduced by changes in the character of the sampled waste as the material is extruded,

purged of gas, and handled in preparation for measurement of the density; and the variability inherent in the density measurement.

4.2.4 Define the Decision Boundaries

The boundaries relevant to the decision identified in Section 4.2.2, differ depending on the specific option selected for providing inputs to the decision. For the options considered here, the relevant measurable inputs to the decision are all characteristics of the waste in the tank. Therefore, the spatial boundaries of interest are the boundaries of the volume of waste in the tank (i.e. the inside walls of the tank and the surface of the waste).

Because the bounding model to be employed to support the decision listed in Section 4.2.2 is a time independent model, temporal boundaries do not need to be defined in this case.

4.2.5 Define Decision Rules

The complete description of a decision rule includes:

- a statement of the hypotheses to be tested to determine each required decision;
- a specified statistical test (or precise rule) by which the data are to be used to support the decision; and
- a specific decision criterion (i.e. the target around which the decision is to be determined).

4.2.5.1 The testable hypotheses

The decision regarding the need to mitigate a tank because of the potential for catastrophic episodic release of flammable gases must be based on determinations of the likelihood of such releases occurring. Because such decisions are made under conditions of uncertainty, the possibility of error exists in the decision process. The goal of the decision rule is to specify the options to be taken so as to minimize, to the extent possible, the likelihood of making an error.

Hypothesis testing is a natural framework for considering error rates. Hypothesis tests specify a null hypothesis and an alternative hypothesis that are weighed against one another in light of the evidence. It is natural to define decision rules based on the outcomes of hypothesis tests: if the null hypothesis is rejected in favor of the alternative, then one decision option is selected; if the null hypothesis is not rejected, then the other decision option is selected.

Well-designed statistical procedures specify the maximum value of some types of error. typically, this is the so-called type I error, which is the error made by rejecting the null hypothesis when that hypothesis is in fact correct. Rates of type II error (i.e. failing to reject the null hypothesis when it is false) will then typically vary depending on the degree to which the true condition differs from the condition specified by the null hypothesis. Statistical procedures cannot be designed that universally limit both type I and type II error rates simultaneously. However, it is possible to determine the degree of deviation from the null conditions that ensures an acceptably low probability of making a type II error. Such considerations have traditionally been considered as defining the power of a statistical test, where power is defined as the probability of rejecting the null when it is not true (i.e., it is the inverse of the probability of type II error).

The null and alternative hypotheses that are proposed for determining if mitigation of a particular tank is needed to protect against episodic releases are:

$$H_o = V_g \geq V_{critical}$$

and

$$H_a = V_g < V_{critical}$$

where:

H_o is the null hypothesis;
H_a is the alternate hypothesis;
V_g is the estimated maximum volume of gas that can be retained; and
$V_{critical}$ is the critical maximum volume not to be exceeded.

4.2.5.2 The data evaluation rule

What needs to be resolved in this case is how to estimate values for V_g and how to compare V_g to $V_{critical}$ to derive a conclusion to the decision identified in Section 4.2.2. V_g will be estimated using the modified neutral buoyancy model (MNBM) that was described in Section X.XX. V_g will be estimated as the output of this model based on defined values of the set of inputs defined at the end of Section 4.2.3:

$$V_g = MNBM(\boldsymbol{\theta})$$

where:

$\boldsymbol{\theta}$ is the vector of parameters (i.e. the densities of the NC and C layers of waste, the temperature measurements that define the thickness of the NC layer of waste, and the various parameters

defined primarily from the physical measurements of the tank that are assumed known with virtual certainty).

If all of the parameters comprising $\boldsymbol{\theta}$ were known without error (and if the model was known to be correct), then V_g could be determined without uncertainty and the null hypothesis would be known to be true or false without error, for any given $V_{critical}$. In reality, however, $\boldsymbol{\theta}$ can only be estimated from a finite sample of observations (for density and temperature) so that the comparison of V_g and $V_{critical}$ (i.e., the test of the null hypothesis) will be subject to error. Procedures for setting $V_{critical}$ are defined in Section 4.2.5.3. Procedures for setting acceptable error rates are defined in Section 4.2.6.1.

Depending on whether the distribution of outputs from the model associated with the distribution errors associated with the inputs to the model (i.e. the estimates of the gas free densities for the convective and non-convective layers of waste and the temperature measurements employed to derive the thickness of the non-convective layer) can be adequately described parametrically, one of the following two rules for data evaluation should be employed. Note, that the rules presented below are appropriate for cases in which density estimates are derived from direct measurement in a tank. A different set of rules may need to be developed for estimates that are extrapolated from other tanks.

Assuming that the distribution of V_gs that are associated with the range of errors on density (and temperature) estimates can be described parametrically, average the multiple measurements of each parameter to derive a representative estimate for the waste as a whole and input each averaged estimate into the bounding model. Then employ the appropriate statistical test to complete the comparison between V_g and $V_{critical}$. If, for example, the distribution of V_gs expected as a function of the distribution of errors on density can be shown to be normally or lognormally distributed, a one sample t-test may be used when comparing the resulting V_g to $V_{critical}$.

If the distribution of V_gs expected from the range of errors on density (and temperature) estimates cannot be described parametrically, input each *individual* set of measurements (i.e. each set representing a complete input vector) into the model and derive multiple estimates for V_g (i.e. one estimate for each complete input vector available from the set of measurements). Find the median value of the estimates of V_g and compare the median to $V_{critical}$ using a sign test.

Note that selection of the appropriate evaluation rule may be based on the results of the simulations proposed in Section 4.2.5.3.

4.2.5.3 The decision criterion

To assure adequate protectiveness (i.e. to assure that the null hypothesis will be falsely rejected no more frequently than the acceptable error rate to be defined for this decision), $V_{critical}$ needs to be chosen so as to reflect both the volume of gas that potentially trigger a loss of containment via a particular failure mode (see Section X.XX) and an adequate margin of safety to account for the uncertainty contributed by measurement error.

Values for $V_{failure}$ need to be set based on engineering and fault analysis that are beyond the scope of this document. For example, an engineering analysis is required to determine the specific over-pressure required to cause a HEPA filter to fail.

It is proposed that the following simulation procedure be employed to establish an appropriate safety factor. Such a safety factor would be associated with an assumed fixed number of measurements for each of the input parameters available for the model[9]. In the simulation, we assume that we know the value of $\boldsymbol{\theta}$ (and therefore the value of V_g) as well as the ratio $V_g/V_{critical}$. For various degrees of the measurement uncertainty of the components of $\boldsymbol{\theta}$, some number of sample values of each component can be simulated. These are the values that mimic the actual observations that may be available for the components of $\boldsymbol{\theta}$: each sample value a measure of the true value for that parameter but will deviate from that true value by some random factor related to the difficulty of getting precise measurements. Many sets of simulated parameter observations will be generated within a single simulation. For each set, or iteration, within a simulation, employ the appropriate of the two evaluation rules defined in Section 4.2.5.2 that will be used to render the actual decision with real data:

(1) the sampled values of the components of the parameter vector can be averaged. In that case, each iteration will result in a single estimate of V_g being derived. That single value of V_g can be compared to $V_{critical}$; the null hypothesis would be rejected if $V_g < V_{critical}$, and not rejected otherwise. This option may be preferred if it is expected that the measurements of the components of $\boldsymbol{\theta}$ are not in some way naturally linked to one another, as might be the case if, for example, the thickness measurements are collected independently of the density measurements, and there is no compelling reason to associate one set of density measurements with any particular thickness measurement;

(2) no averaging of parameter values is done. In that case, each of the sets of parameter measurements can be used to estimate a V_g. If, as described above, the measurements of the components of $\boldsymbol{\theta}$ are not linked together naturally, one might consider defining all the possible

[9] Errors can be controlled equally well either by adjusting the safety factor for a fixed number of measurements for each input parameter or by adjusting the number of measurements used in an analysis with a fixed safety factor.

combinations of the measurements. One would then obtain as many values of V_g as the number of combinations. There are two options for handling the output V_g values:

(a) average the V_g values. That average could then be compared to $V_{critical}$ using a one sample t-test, and the null hypothesis would be rejected if and only if the t-test indicated that the calculated average was significantly less than $V_{critical}$[10]; or

(b) retain the individual V_g values. A sign test could then be used to test whether the median V_g was significantly less than $V_{critical}$. If that appeared to be the case, then the null hypothesis would be rejected.

Note that second approach is likely more rigorous because it mimics the precise evaluation rule to be used with real data in this case.

The selection of option a or b within the second procedure depends on what can be deduced about the distribution of the output of the neutral buoyancy model, V_g, as a function of the distributions of the input parameters. If the likely distributions of the inputs are combined by the model in such a way that normal or lognormal distributions might be reasonable representations of the V_g outputs, then option a may be more powerful. If, on the other hand, the output distributions can not be described by normal or lognormal distributions, the nonparametric sign test of option b might be preferred. Tests of the model and the manner in which is transforms the distributions of the input parameters can be performed prior to the initiation of the simulation to suggest the best approach.

In any of these cases, the procedure will result in acceptance or rejection of the null hypothesis for each iteration within a simulation. Determining the overall proportion of the time the null hypothesis is rejected provides an estimate of the probability of rejecting the null, which we know to be the correct or the incorrect choice, depending on the value of $V_g/V_{critical}$. These results give a "power curve" for the test procedures, as a function of the ratio (and of course dependent on the assumed variation and number of measurements of $\boldsymbol{\theta}$).

Given the set up of the null and the alternative hypotheses presented above, failure to reject the null would be consistent with a decision to mitigate the tank in question. Suppose that for a given set of assumptions about the uncertainty and number of measurements for $\boldsymbol{\theta}$, we determine that a ratio, $V_g/V_{critical}$, equal to x (>1) provides an acceptably low probability, P, of rejecting the null. Naturally, if V_g equals $V_{failure}$, we would want to be

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10 The central limit theorem applies in this case because what is being evaluated is the distribution of errors on the average of a set of measurements. Therefore, it is likely that normality can be assumed.

guaranteed that the rejection probability is at most P. Consequently, $V_{critical}$ can be set equal to $V_{failure}/x$, so that for $V_g = V_{failure}$, $V_g/V_{critical} = x$, and the rejection rate will be suitably low.

Of course, for values of V_g just less than $V_{failure}$, such that the defined failure would not in fact be expected to occur, the above procedure will entail an almost equally low probability of rejection and hence a high probability of mitigation. With $V_{critical}$ defined as above, algebraic manipulations can determine the value of a "safety factor," S, such that when $V_g = V_{failure}/S$, the probability of rejecting the null becomes acceptably large. S can be determined to be

$$S = V_{failure}/(V_{critical}*y),$$

where y (<1) is the ratio $V_g/V_{critical}$ that is estimated from the simulation to give the acceptably large probability. Values of V_g between $V_{failure}/S$ and $V_{failure}$ will be those most likely to indicate the need for mitigation when in fact no mitigation is necessary.

The range between $V_{failure}/S$ and $V_{failure}$ can be decreased to the degree that uncertainty about the parameter vector $\boldsymbol{\theta}$ can be decreased. This will occur when more samples relevant to the estimation of $\boldsymbol{\theta}$ are collected. In fact, the simulation procedure described here can be used to estimate the relationship between the number of measurements and the range between $V_{failure}/S$ and $V_{failure}$. That relationship will depend on the number of measurements in two ways. First, as the number of measurements increases, $V_{critical}$ will increase toward $V_{failure}$. Second, the value of y will also be increased toward 1. Both of these effects directly reduce S, as can be determined from the equation above. In this way, one can assess the benefits (and weigh those against the costs) of collecting more samples relevant to the estimation of the values of $\boldsymbol{\theta}$. Of course, the cost of completing mitigation in those cases where it is not actually required also influence the decision whether or not to collect more samples.

4.2.6 Identify Acceptable Error Limits and the Attendant Data Quality Objectives

The appropriate data quality objectives that need to be defined for this issue include:

- acceptable error rates;
- an precision requirement; and
- a representativeness requirement.

Note that accuracy is not critical for this case because measurements are all to be used only in a relative sense: i.e. differences in measured temperatures and differences in measured densities are what is important.

4.2.6.1 Defining appropriate error rates

Acceptable error rates for determining whether mitigation is required to prevent unacceptable episodic releases need to be defined based on the an analysis of the magnitude of the consequences potentially suffered by the target failure mode versus the cost of collecting sufficient data to achieve a desired error rate. Evaluating such tradeoffs are greatly facilitated by the power curves that are proposed to be generated as described in the previous section. It may also be prudent to consider the relative cost-benefit of performing sampling and analysis to determine the need for mitigation (to some defined, acceptable error rate) versus the cost of assuming that a set of tanks are unsafe and proceeding with mitigation.

4.2.6.2 Defining appropriate precision

As intended here, this is the precision of a *set* of measurements rather than what is commonly referred to as analytical precision (or the precision of a single measurement). The precision of a set of measurements is a function of both the underlying analytical precision and the number of measurements in the set.

As indicated in Section 4.2.5.3, there will be a tradeoff (that can be evaluated in terms of optimizing cost) between setting relatively larger safety factors and collecting fewer samples or setting relatively smaller safety factors and collecting a greater number of samples.

4.2.6.3 Defining appropriate representativeness

Although representativeness is a qualitative measure of data quality, it is nonetheless critical that it be considered formally and that the results of its consideration be documented. Given the contributions to error described in the final paragraphs of Section 4.2.2, to adequately address representativeness, the orientation of locations from which samples may be collected in a particular tank, the potential bias associated with the equipment employed for sampling, and the potential bias introduced by the laboratory handling and preparation of the sample must all be evaluated. Costs for modifying procedures (or, for example, adding risers to a tank) need to be compared rigorously against the potential penalty for potential deviations from representativeness in terms of what that does to the achievable error rate for decisions concerning the need for mitigation.

4.2.7 Optimize The Study Design

Based on the current conceptualization of the manner in which the DQO process is to be applied at Hanford, this step of the DQO process is typically considered beyond the scope of a "generic" issues document of this type. Rather, it is supposed to be completed in a test plan for a specific tank.

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