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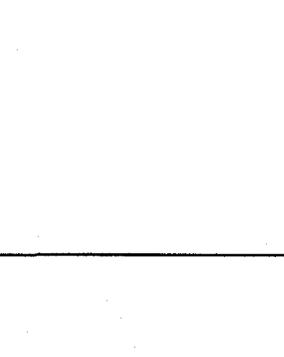
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7. Abstract

A strategy for resolution of the Flammable Gas Safety Issue is presented. An understanding of the processes for gas generation, retention and release of flammable gas mixture is needed to support resolution of the safety issue. Resolution of the USQ is also discussed. Finally, a summary of mitigation approaches is provided.

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Strategy for Resolution of the Flammable Gas Safety Issue

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1.0 INTRODUCTION

The purpose of this document is to provide the general strategy for resolution of the flammable gas safety issue; it is not a detailed description of program activities, budgets and schedules. Details of the program activities have been issued (Johnson and Sherwood, 1994) and the information pertaining to budgets is provided in the FY 1995-1997 Multi-Year Work Plan for Tank Waste Remediation System (TWRS) (Program Element 1.1.1.2.02.). The key element in this strategy is to provide an understanding of the behavior of each of the Flammable Gas Watch List tanks. While a review of historical information does provide some insight, it is necessary to gather current information about the gases, behavior and nature of the waste, and about the control systems that maintain and monitor the waste. Analysis of this information will enable TWRS to determine the best approach to place any tank in a safe condition, if it is found to be in an unsafe state.

2.0 DESCRIPTION OF THE SAFETY ISSUE

2.1 The Unreviewed Safety Question

A flammable gas issue was declared an Unreviewed Safety Question (USQ) in March 1990. The original statement (Daugherty, 1990) said, in part, "Recent Westinghouse reviews of the tank vapor space flammability identified that the gas under the crust is potentially flammable because nitrous oxide (N₂O) and hydrogen can create flammable mixtures. This is considered an Unreviewed Safety Question." Subsequently, the U.S. Department of Energy, Richland Operations sent a notification (Lawrence, 1990) to the U.S. Department of Energy, Headquarters, which stated in part "DOE-RL has determined that the matter of hydrogen and nitrous oxide evolution within the material in certain waste tanks and subsequent hypothetical ignition is an Unreviewed Safety Question." This statement of the USQ involved 22 of the 23 original tanks on the Flammable Gas Watch List. Tank 109-SX was the exception because, although it does not retain or release flammable gases, six Flammable Gas Watch List tanks vent through it.

The then-existing safety analysis report (Koontz, 1986) did include a reference to hydrogen generation but concluded a hydrogen explosion was not a credible event. The analytical and experimental efforts initiated as a result of the declaration of the flammable gas USQ were expanded to also consider the generation of other flammable gases, principally ammonia and methane.

2.2 The Watch List

In November of 1990, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," Public Law 101-510, Section 3137, became effective. Section 3137 specifically addresses the issues concerning waste tanks by requiring the following actions:

- Identify those tanks that "may have a serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure..."
- Ensure that "continuous monitoring to detect a release or excessive temperature or pressure..." is being carried out
- "...develop action plans to respond to excessive temperature or pressure or a release from any tank identified..."
- Restrict additions of high-level nuclear wastes to the identified tanks unless no safer alternative exists or the serious potential for a release of high-level nuclear waste is no longer a threat.

Because of this law, several watch lists were developed: flammable gas, ferrocyanide, organic salt, and high-heat load. A total of 56 tanks, both single shell and double shell, currently comprise these watch lists.

The Flammable Gas Watch List consists of 25 tanks; tanks 241-AW-101 and 241-U-107 were added since the original list was compiled. Six of the 25 tanks are double-shell: 241-SY-101, 241-SY-103, 241-AN-103, 241-AN-104, 241-AN-105, and 241-AW-101. These tanks all exhibit episodic releases of gas, i.e., a period of growth where the surface levels rise because gases are retained, then a relatively quick release (several minutes to several days).

There are nineteen single-shell tanks on the Flammable Gas Watch List. They are tanks 241-A-101, 241-AX-101, 241-AX-103, 241-S-102, 241-S-111, 241-S-112, 241-SX-101, 241-SX-102, 241-SX-103, 241-SX-104, 241-SX-105, 241-SX-106, 241-SX-109, 241-T-110, 241-U-103, 241-U-105, 241-U-107, 241-U-108, and 241-U-109. The single shell tanks were placed on the watch list because (a) the tank currently shows slurry growth, or (b) the tank showed slurry growth at sometime in the past, or (c) waste taken from a given tank may have given rise to slurry growth and/or GREs in a double shell tank after the transfer or after processing in the evaporator. Tank 241-SX-109 is on this list only because the other six SX-Farm Flammable Gas Watch List tanks vent through it.

A detailed report on the historical tank data and chemical information pertaining to each of the Flammable Gas Watch List tanks has been recently issued (Brager, 1994).

2.3 Safety Issues

Twenty three safety issues relating to the Hanford Site Tank Farm Facilities were identified as a result of preparing a plan in response to Section 3137 of Public Law 101-510 (Wilson, 1991). These Safety Issues were sorted into three categories:

- Priority 1 - Issues and/or situations that contain most of the necessary conditions that could lead to worker (onsite) or offsite radiation exposure through an uncontrolled release of radioactive waste.
- Priority 2 - Issues and/or situations that present (or contain) some of the necessary conditions that could lead to an uncontrolled release of radioactive waste under extreme assumptions.
- Priority 3 - Issues and/or situations that could lead to the future release of fission products if the tanks are viewed as intermediate storage (5-30 years) of high-level nuclear waste, i.e., corrosion and/or leakage, operating practices, buried single wall transfer lines.

The Flammable Gas Safety Issue was identified to be a Priority 1 safety issue.

2.4 Method to Identify Flammable Gas Watch List Tanks

Tanks that were originally identified to be "flammable gas tanks" were considered to pose a problem because of observed changes in the waste surface level, such as sudden drops or a continuous increase in level, or by engineering judgement. This judgement related to the process history of the evaporators and the transfer of waste between the tanks. Early studies showed that certain types of waste exhibited a continuous increase in level which was named "slurry growth" (Jansky, 1985). This occurred in the single shell tanks. In some cases the transfer of waste from the single shell tanks to double shell tanks lead to slurry growth and/or postulated gas release events. Some of the single shell tanks were thus considered to be part of the safety issue, even though current records could not provide evidence of behavior indicative of gas production and release. This was done on purpose to be conservative in the identification of potential problem tanks.

Recently, more definitive criteria were developed for evaluation of any tank that might be considered to have a flammable gas concern (Hopkins, 1994). This document developed ways by which gas generated in tank waste might cause a release of waste to the environment. The gas could exist in the dome space of a tank because of a steady state release or an episodic release; episodic releases could be either a large release that involved the whole dome volume in a short time or it would involve a local "plume" that might be confined to some local part of the waste surface. Release to the environment was a result of either ignition of a gas mixture or by direct over pressurization (without ignition) of tank components. Hopkins provided logic diagrams and algorithms for determining if criteria were exceeded; thus, if any of the criteria are exceeded then the tank will be added to the Flammable Gas Watch List.

3.0 KEY PHENOMENA RESPONSIBLE FOR THE SAFETY ISSUE

A key feature for the flammable gas safety issue has been the behavior of the waste surface. Gas generated within the waste is trapped and causes an increase in the waste volume which is reflected by an increase in the waste level. Figure 1 shows this increase in the waste surface level for single shell tank 241-U-107. To date this rise has been postulated to be due to entrapped gas. In some tanks the gas is suddenly released which results in a rapid decrease in the waste level. This behavior is called a gas release event (GRE). Tank 241-SY-101 has been the most notable tank to exhibit this type of behavior which is illustrated in Figure 2. The large GREs for this tank have been essentially eliminated by use of a mixer pump which causes a nearly continuous release of gas.

Thus, the key phenomena for the flammable gas safety issue are the generation of gas and the retention of gas. Understanding the mechanisms for these processes is a prerequisite for final resolution of the safety issue.

Release of gas into the dome space of a tank, either as a steady state or episodic release, will not be a problem if the tank ventilation system sweeps the gas out so that concentrations of concern are never obtained. Many of the single shell tanks only have a passive ventilation system; these systems have not been rigorously analyzed for their capability under high gas loading situations.

3.1 Gas Generation

Historically, the tanks considered primary flammable gas safety issue tanks have been those that contain complexant concentrate, double-shell slurry, or double-shell slurry feed, 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.

Gas generation chemistry of Hanford Site waste material has been studied at Westinghouse Hanford Company (and its predecessor Hanford Site contractors), Argonne National Laboratories, Georgia Institute of Technology, and Pacific Northwest Laboratory. 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 carbon monoxide), especially at elevated temperatures (> 90 C). 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.

Direct measurements of the gas from GREs in tank 241-SY-101 show that the nominal composition of the gas is: 29 % (by volume) hydrogen, 24 % nitrous oxide, 33 % nitrogen, 11 % ammonia, 2 % water vapor, less than 1 % methane, and less than 1 % other gases (Sullivan, 1994). Limited information obtained for other flammable gas double shell tanks (Wilkins, 1995) would indicate that 103-SY may be similar to 101-SY. Data for 101-AW, 103-AN, 104-AN and 105-AN have shown that the ratio of hydrogen to nitrous oxide is much higher than that found for the SY tanks. With little oxidizer present, different mitigation approaches, if needed, might be employed. If there is very little oxidizer in the gas mixture, then inerting the dome space is an option.

3.2 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 the 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 in tank waste layers are underway by the Hydrogen Mitigation Program; once proven to be effective methods the waste sampling DQO (McDuffie, 1995) will be revised to incorporate these devices.

4.0 METHODS FOR EVALUATION OF THE NATURE OF FLAMMABLE GASES

The Flammable Gas Safety Issue involves both the released gas and the stored gas in the Hanford high level waste tanks. Department of Energy orders (DOE 5480.4) require that nuclear facilities, such as the high level waste tanks at Hanford, be operated within National Fire Protection Association (NFPA) guidelines, namely, the tank dome spaces and associated connections must have flammable gas levels that are less than 25% of the lower flammability limit (LFL). Therefore, the major focus of the program at this time is to install gas monitoring equipment for each tank of concern.

4.1 Evaluation of Released Gases in Tanks

Westinghouse Hanford Company has designed, built and installed Standard Hydrogen Monitoring Systems (SHMS) on six double shell tanks. Current efforts are directed at installation of this equipment on 19 single shell tanks (this work will be completed by the end of April, 1995). Each SHMS consists of a cabinet with piping, a pump, and instrumentation which supports two on-line hydrogen detectors and a system for taking "grab samples". The hydrogen detectors are Whittaker electrochemical cells; one is set to cover the range of 50 to 5000 ppm and the other for 0.1 to 8% hydrogen. Other gases are measured by taking grab samples and analyzing the gas with a high resolution mass spectrometer in the laboratory. Each SHMS is also equipped with appropriate piping and fittings so that other types of gas monitors can be utilized. For example, a gas chromatograph is being field tested at one of the double shell tanks and a photo-acoustical infrared detector has been used to monitor ammonia.

Wood's (1994a) analysis indicates that there is good mixing of the gas during steady state release conditions in tank 241-SY-101, and his analysis for the AN and AW tanks (Wood, 1994b) also show gas plumes are dispersed in a short time, even though the ventilation flow rates are much lower than 101-SY. Thus the approach for the SHMS installation is to place them so as to monitor the gas at the ventilation header.

Many single shell tanks do not have active ventilation systems; they often have only a passive ventilation system. In this case probes will be inserted through risers into the tank dome space to permit sampling in the air space above the waste. Recently an analysis was conducted to predict hydrogen concentrations in single shell tanks that were *not* on the flammable gas watch list over time as a function of generation rates and tank ventilation rates (Graves, 1994). None of these passively ventilated tanks had calculated hydrogen concentrations above the LFL. A similar type of analysis was reported for the SSTs that are on the flammable gas watch list (Van Vleet, 1994b). In this analysis two tanks had the potential to be above the LFL at steady state. Confirmation of these analyses must await for the results obtained with the on-line gas monitors; such information will be available by the end of April, 1995.

4.2 Evaluation of Retained Gases

A proper assessment of the amount and nature of retained gases within the waste is required to assess the hazards associated with GREs. Safety analyses, by nature, must be conservative to ensure that imposed work controls provide an adequate margin of safety for people both on and off-site. Evaluation of the retained gases has been accomplished to date by detailed modeling and analysis of the behavior of the waste. This work has primarily been centered on tank 101-SY, because it is the worst case flammable gas tank due to the large episodic gas releases. Gases are generated throughout the entire waste volume in 101-SY, but are retained only in the lower portion of the tank. The accumulation of gas in the lower part of the tank causes an increase in waste volume and a reduction in the density of this lower, "slurry" layer. The axial temperature profile of the waste reflects this behavior. The upper portion of the waste shows a nearly uniform temperature, indicating that convection is occurring; the lower part shows a parabolic temperature profile indicative of heat removal by conduction. As the density of the lower layer decreases it eventually reaches a point of instability and this material then rises to the top of the tank with an attendant release of gas. Shortly after such a gas release the temperature of the waste becomes nearly uniform from top to bottom. With time the solids settle and gas accumulates and the whole process is repeated.

Estimates of the amount of retained gas come from an analysis of the situation just described (Alleman, et. al., 1993). Data used in the analysis include changes in the waste surface level and temperature, pressure and increase in flow rate during the GRE and physical properties of the waste. The first type of analyses used an approach based on the maximum historical surface level drop, which calculated the amount of gas that corresponded to the change in the surface level. The approach described by Alleman was termed the "neutral buoyancy model". Later modeling efforts became more detailed and used the Rayleigh-Taylor Instability model (Sullivan, 1994). These methods have been applied to the double shell tanks that are on the flammable gas watch list (Spore, 1994). Analysis of the behavior of single shell flammable gas tanks is difficult because there are much fewer data for these tanks as compared to the double shell tanks. Thus, the detailed analyses can not be conducted. Preliminary evaluations were done using the maximum historical surface level drop method (Nichols, 1994).

Certainly, the best choice for assessing the retained gas would be via direct measurement within the waste. Efforts are underway to develop equipment for in-situ analyses. One, which has been used recently in 101-SY, is called a "void fraction" instrument (McWethy, 1994). The device captures a known volume of waste and then compresses it. The results provide a measurement of the amount of gas bubbles held in the waste. Another item under development is the "Retained Gas Sampler". In this case a volume of waste will be captured in a gas tight container, removed from the tank, and sent to a laboratory for analysis (Webb, 1994). This analysis will provide information both the amount and composition of the gas mixture; it will also be able to assess the amount of dissolved gases.

It was mentioned earlier that evaluation of retained gas requires information about the physical properties of the waste. Measurements of the physical properties of actual waste samples in the laboratory have not yielded reliable data. Thus, equipment has been prepared for in-situ evaluation of the rheological properties (viscosity, yield strength) of the waste (Shepard, 1994).

It should be noted that until procedures utilizing these devices have been proven to be effective, reliable methods, the evaluation of retained gases will continue to be done by analysis of tank data.

4.3 Equipment Upgrades

In many cases tank instrumentation is old or even not working. In order to ensure that proper evaluations of tank behavior are made it will be necessary to upgrade tank instrumentation. Efforts underway include installation of new surface level measuring equipment, repair or replacement of tank waste thermocouples, addition of pressure measurement devices to single shell tanks, and upgrading the ventilation systems of double shell tanks to ensure that proper flow is being provided to Flammable Gas Watch List tanks. Other types of instruments are being employed as a result of work controls imposed by the safety assessments; an example is in-tank television cameras. Efforts are also underway to obtain an intrinsically safe portable exhauster for use at single shell tanks when waste intrusive activities are conducted.

5.0 RESOLUTION OF THE UNREVIEWED SAFETY QUESTION

Resolution of the USQ requires (a) evaluation of the hazards, including definition of the consequences of postulated events, (b) establishing work controls to prevent initiation of postulated events, (c) updating the facility authorization basis, and (d) obtaining DOE approval for (c).

5.1 Data Needs

In order to perform the requisite hazards analyses some information is needed about the flammable gases. Primary data needed for these analyses are: composition of the gas mixture, volume of gas released in known or postulated events, flammability of the gas mixture, rate of release of the gas, and information on various radiological and toxicological species contained in the waste. Secondary data include such things as physical properties of the waste, and tank parameters for waste surface level and surface level changes, waste temperatures, dome space pressures and ventilation rates. These data have been obtained for tank 101-SY, and they are being used in analyses of the other tanks until such information is actually obtained. For example, the conservative estimate, used for safety analyses, for the composition of the released gas in 101-SY is: 31.4% hydrogen, 26.7% nitrous oxide, 15.0 % ammonia, 23.5% nitrogen, 0.5% methane, 2.4% water vapor and 0.5% other gases (Sullivan, 1994).

5.2 Safety Analyses

Detailed safety evaluations were required for work activities at tank 101-SY, and approval from the Department of Energy (DOE) was needed prior to conducting the work. Each one of the safety analyses provided explicit work controls. An summary of these safety analyses and evaluation of tank behavior was provided by Simpson (1993). Considerable effort was required to prepare and implement a mitigation method for tank 101-SY. Sullivan (1994) provided the extensive safety analyses for installation and operation of a mixer pump, which was approved by DOE. The first three steps for closure of the USQ for 101-SY have been completed and the request for approval of the revised authorization basis has been submitted to DOE for approval.

The safety basis for conducting work activities in the other double shell and single shell tanks on the Flammable Gas Watch List has been developed (Van Vleet, 1994a, 1994b). These documents analyzed the various hazards associated with proposed work activities, calculated consequences at receptor locations required by WHC-CM-4-46 (Nonreactor Facility Safety Analysis Manual) and developed the appropriate work controls. The information provided in these reports will be used to update the Hanford Site Tank Farm Facilities Interim Safety Basis (Leach, 1993).

5.3 Remaining Issues

Resolution of the USQ for all of the flammable gas watch list tanks will not occur until some knowledge has been obtained about the nature of the gas mixture in the dome space of each tank. Once the data have been obtained an evaluation will be conducted to ascertain if the existing safety basis bounds the noted condition. If there are no surprises then Westinghouse Hanford Company will submit the appropriate documentation to DOE for closure of the USQ. If the safety basis does not bound the particular tank conditions or the planned activities for the tank, then additional analyses and measurements will be required. Current program plans call for closing the USQ for double shell tanks by tank farm since the tanks are inter-connected to a common ventilation system and any interactions between tanks must be addressed. This also applies to the SX single shell tanks, because of the cascaded arrangement of the ventilation lines. Remaining single shell tanks can be addressed individually or as selected groups, depending upon availability of gas monitoring data.

Retention of gas in the waste stored in single shell tanks is not as well understood as the situation for double shell tanks. It has been assumed that the slurry growth in the single shell tanks is due to trapped gas. Some of the single shell tanks have shown significant slurry growth, but have not had any recent gas release events as indicated by a sudden drop in waste surface level. One explanation is that the "salt cake" has become porous and the gas escapes slowly but the salt cake does not collapse thus leaving no indication of any decrease in the waste surface level. Analyses are being conducted to look at all available data to improve the understanding of the waste behavior in the 19 single shell flammable gas tanks.

One other issue is associated with the work done for tank 101-SY. Some documents have assumed that the hazards and consequences analyzed for this tank "bound" the other flammable gas tanks. This may not be the case, as details on such things as radionuclide content, toxicological concerns, dome collapse, etc., may not yield results (consequences) that are less severe than what is found for tank 101-SY. In addition, analyses conducted for 101-SY did not consider the role of passive ventilation and the flow of gases through porous media, both of which are needed for understanding the behavior of single shell tanks. However, there is agreement that the general methodology used to analyze 101-SY should be applied to the other tanks.

6.0 RESOLUTION OF THE SAFETY ISSUE

Resolution of the safety issue will require evaluation of the tank conditions relating to the distribution of gas both in the dome space and within the waste. Once evaluated, the tanks must be controlled to ensure safe operation. Control of the facility must ensure that release to the environment via either ignition of the gas or by direct over pressurization of tank components by the gas release does not occur. Thus, it is necessary to establish monitoring criteria, methods for implementing the monitoring, and some actions, or decisions, based on the results of the monitoring. If the results indicate that mitigation is required, then the appropriate approach must be selected and put in place.

6.1 Monitoring Criteria

Criteria need to be set for evaluation of the gas in the dome space of each tank as well as for the gas that may be stored within the waste. Department of Energy orders (DOE 5480.4) require that waste tanks be operated within the guidelines established by the NFPA. The NFPA recommends that processes be controlled so that flammable gas concentrations remain below 25% of the lower flammability limit (LFL); therefore, management efforts must provide assurance that the tank dome spaces be kept below 25% of the LFL. This is assumed to apply to the gas that exists in the dome space on a continuous basis as well as that gas that is, or could be, release suddenly at widely spaced intervals (earlier noted as a "GRE").

6.2 Dome Space Monitoring

Requirements for monitoring the dome spaces of tanks were developed through the Data Quality Objectives process (Sherwood and McDuffie, 1995). Flammability tests have been conducted on gas mixtures believed to represent the major species found in tank 101-SY (Jo, 1992). Results showed that the LFL for a hydrogen in a mixture of air and nitrous oxide was 4% (by volume). Thus 25% of the LFL is 1% hydrogen. However, WHC has adopted a more conservative value in order to account for minor variations in the LFL due to effects of temperature, ignition energy and the effects of other gases such as ammonia and methane. The action limit thus selected is 0.6% hydrogen (see Appendix A for a description of the basis for this limit). Figure 3 presents the logic diagram for flammable gas monitoring. The four main actions required if an action limit is exceeded are:

- 1) Stop work at the affected tank.
- 2) Issue an Unusual Occurrence Report.
- 3) Have a technical review group analyze all available data to determine if the tank needs to be mitigated.
- 4) Add additional equipment for monitoring other gases that might be considered to be "fuels", e.g., ammonia and methane.

In developing the criteria for placing tanks on the Flammable Gas Watch List (Hopkins, 1994) there was one variation in the way gas could enter the dome space. Modes most obviously covered by the gas monitors are the steady state emission of gas and the episodic releases. The variation is for a local gas plume that exceeds the LFL criteria, but if mixed with the dome space would not pose a problem. To date this event has only been considered for safety analyses. As described in Section 4, the dome spaces of double shell tanks are expected to be well mixed. Appendix A of the document for the basis for tank characterization (Meacham, 1995) shows that the tank dome spaces for single shell tanks are also well mixed; this is based on detailed computer modeling of the tanks coupled with limited sampling data. Additional analyses are still being conducted in this area, and until they are completed, no additional criteria will be established. However, it should be noted that the 25% of the LFL criteria selected by the NFPA was conservatively chosen in order to account for variations in measurement errors such as variability of measuring and data transmission devices, bias in such devices and deviations in determination of the LFL.

6.3 Evaluation of Stored Gas

Evaluation of the stored gas must provide a limit that is consistent with that used for the dome space, as just described in Section 6.2. Thus, the amount of stored gas that is considered to be releasable must be less than the amount that, when promptly mixed within the air in the dome space, yields a hydrogen concentration greater than 0.6 vol %. If the dome space never exceeds 0.6% and if the stored gas amount never exceeds the critical volume, then there is no flammability concern.

The amount of stored gas might be determined by relating the change in the waste surface level to changes in atmospheric pressure. Correlations between these parameters have been noticed for several of the single shell tanks. Analysis of these data should lead to an estimate of the gas content of the waste; results of these ongoing analyses will be available in the later part of FY-95.

There is one variation on the stored gas that also needs to be addressed, namely that of a pressure pulse without ignition of the gas. The HEPA filters on the tanks have an operating limit of + 10 in. WG. If the pressure exceeds this value there is a chance that the filter seal will be breached and then there is an open pathway to the environment. Thus, the evaluation of stored gas must also consider the case of a pressure pulse that could fail the HEPAs. This has been discussed in more detail in Hopkins (1994). The criterion developed by Hopkins was to set the limit at 25% of the pressure that would cause a serious release to the environment.

As with the logic diagram given for gas monitoring, if the criteria are exceeded then the action would be to have a technical review group evaluate the data to determine if mitigation is required.

6.4 Remaining Issues

While some insight has been developed on the retention and release of flammable gases in double shell tanks, little is known about the processes occurring within the waste in single shell tanks. In-situ measurements discussed in Section 4 may not work in the single shell tanks where the waste is expected to be more viscous with a higher solids content as opposed to the slurry in double shell tanks. Rather than trying to characterize the gases within the waste in single shell tanks, it may be more cost effective to proceed with Interim Stabilization, once the safety basis has been established. After the remaining liquid has been removed, the generation of gases might be significantly reduced, since it is believed that the majority of the gases are generated in the liquid phase of the waste.

Another issue concerns ventilation of the single shell tanks. Preliminary analyses have shown that passive ventilation may not be sufficient to keep the dome space less than 25% of the LFL for hydrogen in some single shell tanks. However, these analyses use many assumptions, including the gas generation rate which can have a wide range of values. The best source of data will come from the results of the Standard Hydrogen Monitoring Systems which will be available in April, 1995.

The behavior of soluble gases such as ammonia is receiving much attention in both laboratory evaluations and safety analyses. There is a possibility that a gas release event might be enhanced by release of the gas in solution because a change in the local environment of the waste. Release of the ammonia would alter the LFL and would pose an additional toxicological concern. More work is needed to fully understand the behavior of ammonia in these waste tanks.

Finally, all of the waste tanks are experiencing ongoing chemical reactions, e.g., organic chelating agents are degrading into many products with the result of gases being generated (Ashby, 1994). Thus, evaluation of tank chemistry today may not represent the waste in the future, say 10 or 20 years from now. Radioactive decay continues with an attendant cooling of the waste; this could lead to higher viscosity and strength, which in turn, would probably lead to greater retention of gas.

7.0 IMPLEMENTATION OF MITIGATION APPROACHES

Tanks with flammable gas concentrations in the dome space or vent header exhaust that exceed 25 % of the LFL will probably require mitigation because of DOE Order 5480.4 requirements. However, as noted in Section 6 the monitoring limit will be 0.6% hydrogen which is less than the value corresponding to 25 % of the LFL. Also, any tanks with a stored gas inventory in the waste that could exceed the criteria given in Section 6 may also be candidates for mitigation. Alternatively, waivers to DOE order 5480.4 may be requested if the risks posed by tank conditions are analyzed and found to be acceptable. The same type of tank data are required, whether tanks are mitigated or waivers are requested. The gas concentration, flow rate, composition, and retained gas inventory are needed to support either approach.

7.1 Mitigation Options

Various options have been evaluated for mitigation of flammable gas tanks. A total of 22 different options were evaluated (Babad, 1992) for use at tank 241-SY-101. The four highest rated options for elimination of episodic gas releases in 101-SY were:

- Mixing the waste with a pump
- Diluting the waste
- Heating the waste
- Sonic/Ultrasonic agitation of the waste.

A plan to evaluate these later four options was formulated by a team from WHC, LANL, and PNL (Lentsch, 1992). Mixing with a pump was selected for testing in tank 241-SY-101. Testing has been completed and mixing has been shown to successfully mitigate this tank (Allemann, 1994 and Stewart, 1994a).

An evaluation of all four mitigation options listed above has been completed (Stewart, 1994b). Mixing was determined to be a safe and effective option. Dilution requires further work and the dilution ratio is unknown. Heating also requires further work and is less attractive than dilution. Sonic agitation requires extensive prototype testing of first-of-a-kind equipment.

Only mixing and dilution are viable mitigation concepts at this time to deal with the episodic releases. An assessment of dilution indicates that a dilution ratio of 1:1 (diluent:waste) will likely mitigate tank 101-SY (Hudson, 1995). Hot cell tests to determine the effects of dilution on the waste behavior for tanks 101-SY and 103-SY are currently underway and scheduled to be completed in 1995.

The Multi-Year Program Plan currently assumes that all six double shell Flammable Gas Watch List tanks will require mitigation, and that mitigation will be with mixer pumps. Mitigation by dilution is more attractive operationally because it is passive, but it requires utilization of reserve

tank capacity or construction of new tanks, as well as inter-tank and possibly cross-site transfer of waste.

As data are collected from the gas monitoring equipment and analyzed, other types of mitigation may be feasible. For instance, the episodic releases may release only small volumes of gas and thus an increase in the ventilation rate may be able to keep the tank at hydrogen concentrations well below the criteria given in Section 6. Also as discussed earlier, a significant change in the gas composition might suggest a different approach for mitigation. If the gas composition was high in hydrogen, but very low in oxidizers (nitrous oxide) then inerting with nitrogen or argon may prove to be effective.

Many of the single shell tanks on the Flammable Gas Watch List have passive ventilation systems. If results of gas monitoring activities reveal an unacceptable concentration of flammable gases, then one of the first approaches for mitigating these tanks might involve the addition of additional ventilation capacity.

7.2 Mitigation Data Needs

The decision on which tanks require mitigation hinges on the flammable gas release rates and retained gas inventories. The following are the minimum necessary data required to make a decision about mitigation:

- Amount and composition of released gas
- Ventilation flow rate
- Waste surface level history
- Tank vertical temperature profile

Several years of data may be required to demonstrate that a tank does not require mitigation, because of the erratic nature of the episodic gas release events. (A decision to mitigate might be made earlier if a large gas release occurred.) These data will be needed until the tank contents are retrieved, because of the potential that gas retention and generation may change as the tanks cool.

Additional data would be useful for the design of equipment and preparation of safety and environmental assessments to avoid unnecessary conservatism in a mitigation technique:

- Radionuclides and hazardous chemicals in the waste
- Waste physical properties (density, solids content, shear strength, viscosity)
- Retained gas inventory and composition

Data requirements for waste sample analyses have been defined via the Data Quality Objectives process (McDuffie, 1995). The basis for determination of when waste samples are needed is the same basis for actions as described in

Section 6. Waste samples would be obtained if mitigation is needed because of:

- a) The dome space gas concentration exceeded 0.6% hydrogen, or
- b) The amount of stored gas that is releasable would produce a flammable gas concentration greater than 0.6% hydrogen, or
- c) The amount of stored gas that is releasable would develop a pressure greater than 25% of the value needed to cause a serious release.

It would be desirable to use the in-situ methods discussed in Section 4 prior to retrieving waste samples, however this should not be implemented on a routine basis until the devices have been proven to be effective. It is expected that results with these items will be obtained during FY 1995.

If dilution is selected as a mitigation option in the future instead of mixing, then dilution tests on representative core samples of actual waste from each tank would be required to determine the required dilution ratio to achieve a steady state release of flammable gases.

In summary, the need for mitigation will have to be considered on a tank-by-tank basis. Collection of data is needed for the items discussed in this report. Results of the gas monitoring activity and the in-situ measurements with the voidmeter, ball rheometer, retained gas sampler, and in some cases, core sample data will provide the basis for understanding the gas retention and release; then, proper evaluations of mitigation approaches, if needed, can be conducted.

8.0 SUMMARY

Criteria have been established for monitoring Flammable Gas Watch List tanks and decision points were identified as to when an evaluation is needed to consider implementing mitigative actions. If mitigation is not necessary, or cost effective, then the action is to continue diligent monitoring. The basic questions boils down to: "How long do the tanks need to be monitored before they can be removed from the watch list?", or "How long do mitigative actions needed to be implemented before the tank is removed from the watch list?". The answer to the second question is that the mitigative actions for double shell tanks will have to remain in place until the contents are retrieved. In the case of single shell tanks, this process would have to be in place at least until the tanks have been Interim Stabilized, and in some cases, maybe until retrieval.

For tanks that do not require mitigation, monitoring will still have to be conducted long enough to ensure that there are no major episodic releases of gas or that sufficient knowledge was obtained about the waste to ensure that there are no significant amounts of releasible gas stored in the waste. The episodic releases of gas in double shell tanks has shown a rather varied time period between events; for tank 241-AN-105, the GRE periods have ranged from 130 to 1432 days. Monitoring would have to be conducted for a number of years in order to ensure, with any certainty, that the safety issue no longer exists.

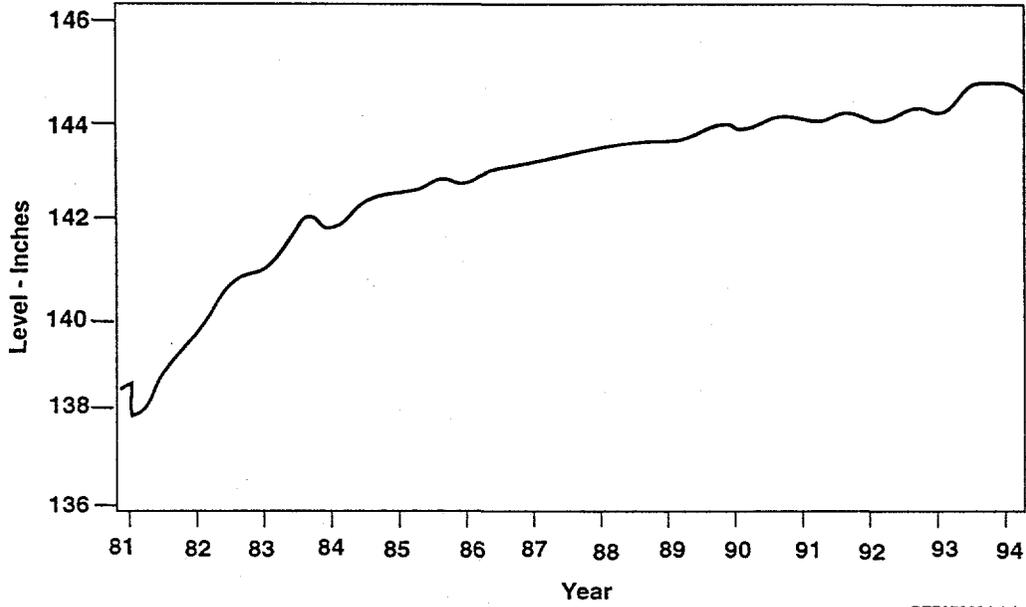
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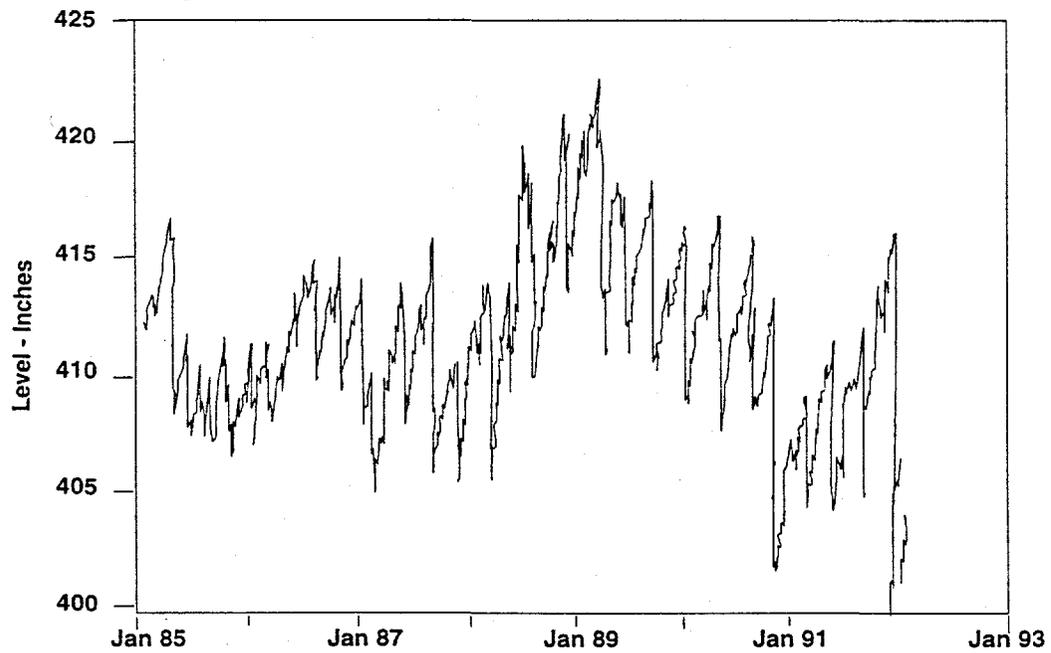
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Figure 1. Tank 107-U Surface Level Readings.



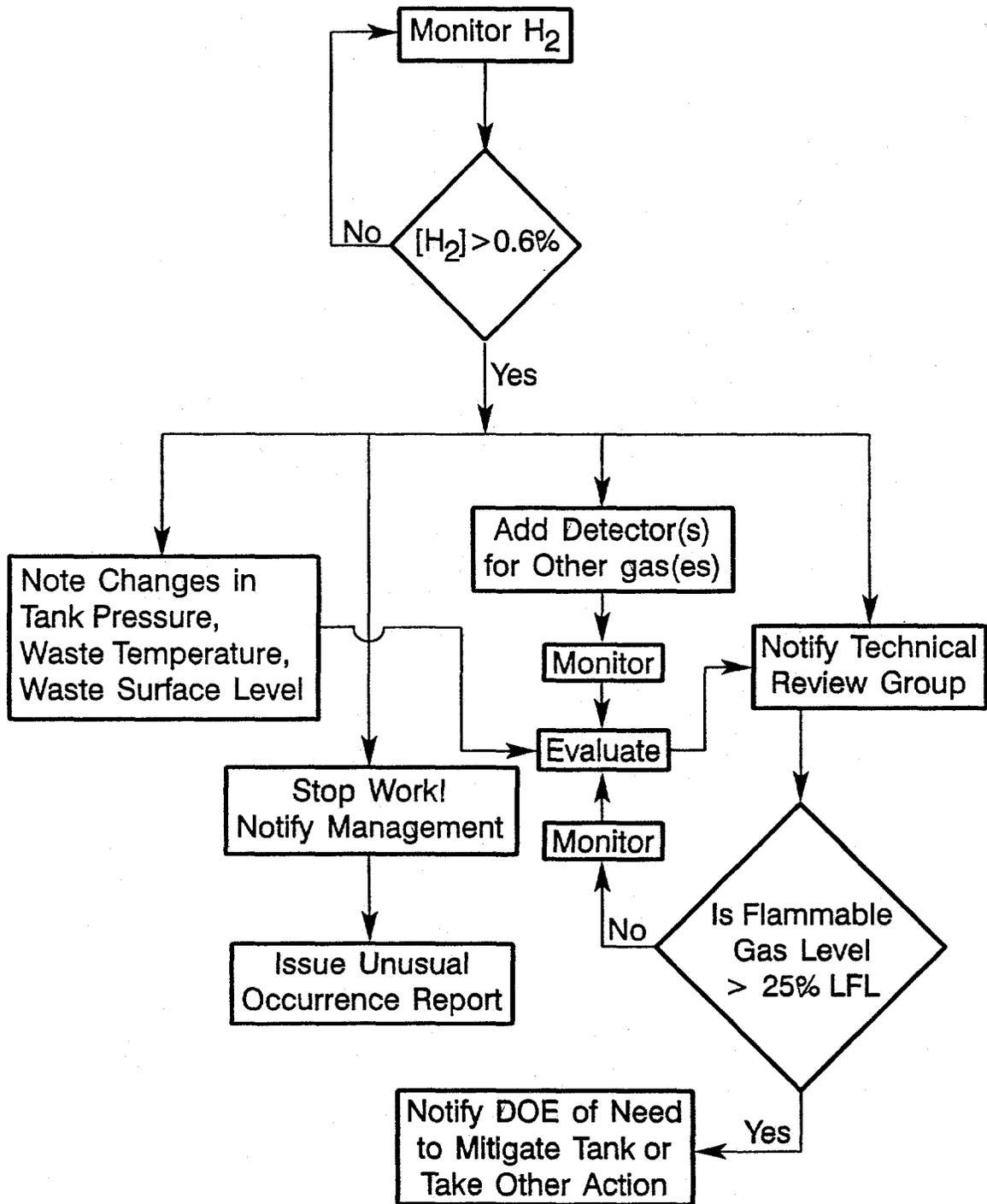
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Figure 2. Tank 241-SY-101 Surface Level Readings.



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Figure 3. Decision Logic for Flammable Gas Watch List Tanks.



APPENDIX A

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

PREPARED BY R. J. VAN VLEET

1.0 INTRODUCTION

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

2.0 GAS COMPOSITION

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

2.1 DERIVATION OF SLURRY GAS COMPOSITION

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

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

Table A1. Estimates of Gas Composition at 327 K¹.

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

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

²"Others" is assumed to represent carbon monoxide.

This slurry gas composition is considered conservative for tank 101-SY. As more data become available for the gas compositions from the other tanks on the flammable gas watch list, the analysis will be changed appropriately. For instance, tank 101-AW had a gas release event on October 1 through October 4. The standard hydrogen monitor had been installed on tank 101-AW on September 28. The peak hydrogen concentration in the dome space was 0.88 % (i.e., the dome space was non-flammable). Calculations show that the slurry gas had to have approximately 70 % hydrogen in it to give the observed concentration. The remainder of the gas is thought to have been ammonia

and/or nitrous oxide. Section 3 of this appendix will discuss the energetics of different slurry gas compositions.

2.2 CONSERVATISMS ASSOCIATED WITH THE SLURRY GAS COMPOSITION

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

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

The methane used in this analysis was measured in the gas composition of the tank 101-SY gas release event called Event I. The Fourier transform infrared spectrometer is not calibrated extensively for methane and the methane data must be analyzed by hand. For Event I, one frame from the Fourier transform infrared spectrometer gave a methane concentration of 378 ppm. Methane was also measured in the Fourier transform infrared spectra on the August 27, 1993, event at 88 and 35 ppm in two different frames and the September 17, 1993, event at 13 (in one frame) and 4 ppm (in six frames). The Event I data gives a methane/nitrous oxide ratio of 0.0145 with an uncertainty estimate of 20 %. The other data points give methane/nitrous oxide ratios of 0.012 and 0.01. Because of the limited number of data points and because the Fourier transform infrared spectrometer methane calibration is not as good as the ammonia calibration, a more conservative uncertainty of 35 % is applied. Thus, the ratio of methane/nitrous oxide is obtained as 0.02. For this analysis, this ratio yields a conservative estimate of 0.48 % methane in the released gas.

3.0 ENERGETICS

As mentioned earlier, the fuel in the slurry gas composition has been maximized within the uncertainty of the measured data uncertainty. This section will develop a model for calculating the equivalent fuel content for different slurry gas compositions. This is done by calculating the equivalent

internal energy of the combustion for the mixture and uses the following assumptions:

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

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

$$u_{RP} = h_{RP} - RT(n_p - n_r)$$

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

Table A2. Combustion Reactions and Associated Internal Energies

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

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

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

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

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

where

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

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

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

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

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

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

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

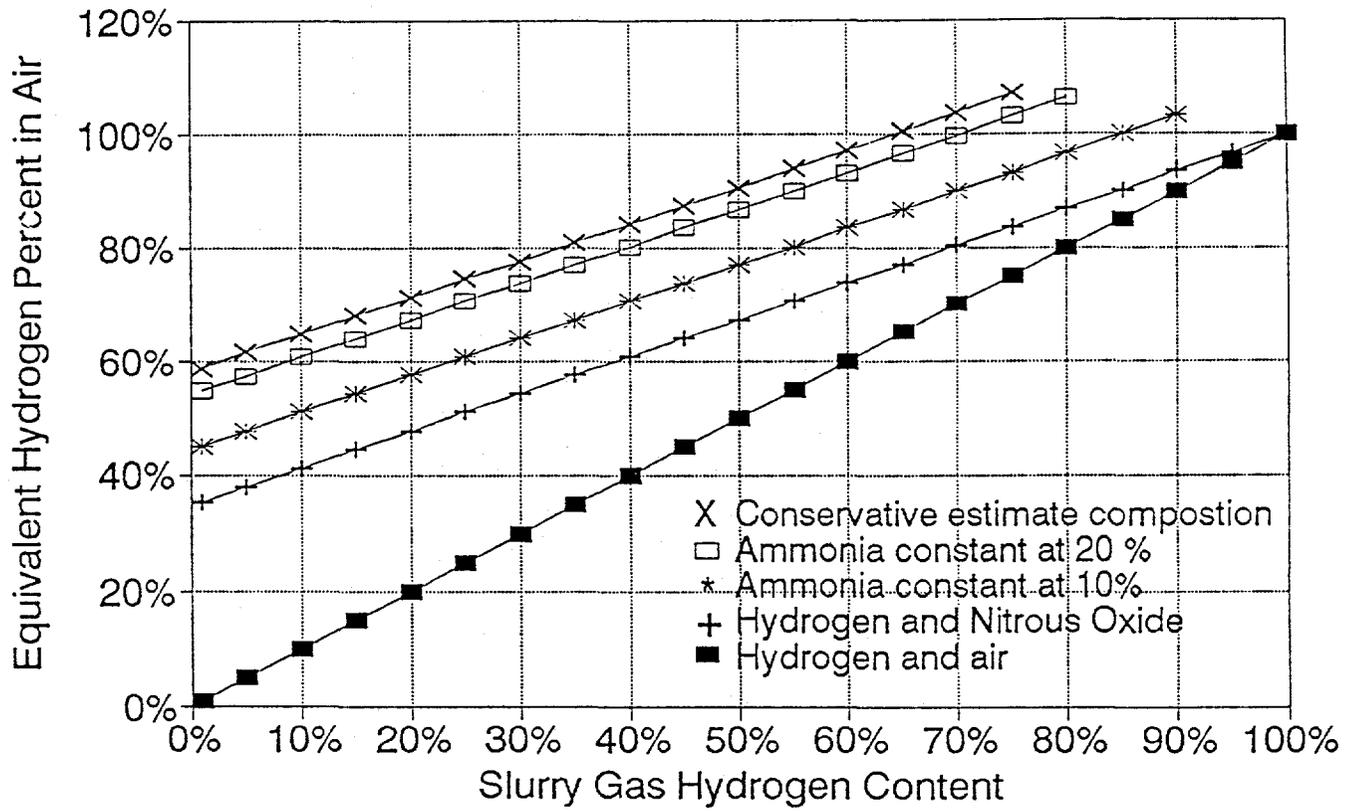
The use of equivalent fuel allows comparison of varying slurry gas compositions. Figure A1 shows curves for various slurry gas mixtures. One curve shows hydrogen with air; a second curve of hydrogen with nitrous oxide; a third curve with hydrogen, nitrous oxide, and 10 % ammonia; a fourth curve

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

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

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

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



4.0 LOWER FLAMMABLE LIMIT

4.1 BACKGROUND

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

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

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

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

Table A3. Lower Flammable Limits in Various Oxidizers

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

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

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

LeChatelier's law (Coward and Jones) is

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

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

4.2 OPERATING LIMITS FOR IN-TANK ACTIVITIES

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

- The slurry gas will contain four flammable gases. Ammonia will be a constant at 22.15 %, methane a constant at 0.48 %, and carbon monoxide a constant at 0.5 %. Hydrogen will be allowed to vary from 0 to 77 %.
- The maximum amount of nitrous oxide available for combustion is bounded by tank 101-SY. That is, we will assume that the volume available for the released gas to mix in is only the hemispherical portion (no credit is taken for the cylindrical volume above the waste). This volume is 950 m³. The maximum expected gas release event from tank 101-SY is 263 m³ of slurry gas. Of this, 24.16 % is nitrous oxide. Thus, the amount of oxidizer that will be nitrous oxide is given by (0.2416)(263/950) or 6.7 %.

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

Current operating experience with tank 101-SY and tank 101-AW would indicate that the percent hydrogen in the slurry gas mixture can range from 28 % to 70 %. Over this range, the lower flammable limit ranges from approximately 4.5 to 3.87 %. Of this, the hydrogen contribution to the lower flammable limit would yield concentrations in the tank ranging from approximately 2.5 to 3.0 % (see Figure A2). Hydrogen is the only flammable gas measured by the Whittaker electrochemical cells in the standard hydrogen monitoring cabinets. To

conduct activities safely in a tank, a limit must be chosen that will cause activities to cease before there is any problem with flammability. The National Fire Protection Association, Inc., indicates that 25 % of the lower flammable limit is the cut off for stopping activities. For the currently known situation the safety limit should be $(0.25)(2.5 \%)$ or 0.625% (6,250 ppm) for hydrogen. If additional monitoring is added for ammonia, a limit for ammonia would be $(0.25)(0.86 \%)$ or 0.215% (2,150 ppm).

5.0 CONCLUSIONS

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

6.0 REFERENCES

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

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

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

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

