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Gas Generation and Retention in Tank 101-SY: A Summary of Laboratory Studies, Tank Data, and Information Needs

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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PACIFIC NORTHWEST LABORATORY
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for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
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Available to the public from the National Technical Information Service,
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Summary and Conclusions

As of October 1991, the authors have assembled current information from laboratory studies and from Tank 241-SY-101 (hereafter referred to as Tank 101-SY) characterization efforts to support remediation or mitigation of the safety hazards associated with the operation of the tank. This information combines what was known about the chemistry of the waste in Tank 101-SY at the start of the project (about June 1990) with what has been learned since that time by workers at Argonne National Laboratory, Georgia Institute of Technology, Pacific Northwest Laboratory, and Westinghouse Hanford Company.

Existing data are reviewed for actual Tank 101-SY waste, including waste composition, slurry growth and collapse, and the composition of released gases. The mechanisms by which gases are generated are examined, including thermochemical degradation reactions, radiolytic processes, tank wall corrosion, and microbial action. Quantities of gases produced in laboratory studies are compared with that estimated in the actual tank. Mechanisms responsible for crust growth and gas retention in the wastes are addressed, as are models for gas release. Finally, mitigation/ remediation strategies are considered, with an emphasis on laboratory data that are needed to support further development.

Rate of Slurry Growth in Tank 101-SY: The best estimate, derived from data obtained over a number of years, of slurry growth rates in the actual tank is believed to be 0.11 ± 0.02 inch/day. Consideration of surface level decreases associated with major release events and elapsed times between events yields a lower value (approximately 0.07 inch/day, obtained from an average for six recent release events). The latter approach neglects frequent and minor gas releases, which are known to occur. Slurry growth rates provide a means for estimating the overall rates of gas generation in Tank 101-SY.

Comparison of Laboratory and Actual Tank 101-SY Gas Generation Data: The sum of thermochemical, radiolytic, and tank wall corrosion contributions to hydrogen generation in laboratory studies reasonably agrees with actual tank data. Laboratory studies using simplified synthetic wastes indicate that thermochemical and radiolytic processes each account for approximately one-third of the estimated quantity of hydrogen produced in Tank 101-SY, when scaled to the tank volume and temperature. Tank wall corrosion could contribute possibly as much as one-tenth of the total; however, no direct laboratory measurements of gas production from steel corrosion under relevant conditions have been made. Microbial action is not expected to contribute measurably to gas generation in this hostile environment.

In laboratory studies, estimates of nitrous oxide (N_2O) production are much higher than the quantities indicated in actual tank data. Analyses of gases collected during release events from the actual tank show hydrogen and N_2O to be present in approximately equimolar quantities, while laboratory studies have found N_2O/hydrogen ratios in the range of 5:1 to 10:1. Laboratory

studies show that thermochemical degradation reaction mechanisms appear to produce approximately 5 times more N_2O, and radiolytic processes produce approximately 10 times more N_2O than estimates for Tank 101-SY. The reason for this discrepancy is not known at this time. It could be a result of a relatively high solubility of N_2O in the liquid waste compared with that of hydrogen, which might provide a pathway for enhanced venting of this product from the waste tank. Alternatively, there could be a mechanism by which N_2O is destroyed before it escapes from the waste, although such reactions have not been observed to date under conditions used in laboratory studies.

Crust Growth and Gas Retention: Laboratory studies show that stable, floating crusts are formed by the adherence of gas bubbles to solid particles in response to surface tension forces. The adsorption of organic complexants onto solid surfaces appears to play a key role in gas bubble adsorption, particle flotation, and gas retention in the wastes. Surface tension forces that are responsible for particle flotation also are expected to maintain a high moisture content in the crust. As a result, the flammability of the floating crusts should be low.

Mitigation and Remediation Strategies: Mitigation/remediation strategies are organized into two groups: 1) those aimed at reducing the rate of gas generation, and 2) those aimed at reducing the extent of flammable gas retention. Strategies to reduce the rate of gas generation include removal of cesium, destruction of organics, addition of chemicals to inhibit specific gas generation processes, dilution/concentration of the wastes, lowering of the pH, cooling of the waste, and addition of a mineral-forming agent. Strategies considered to reduce the extent of flammable gas retention include the addition of surfactants, sparging of the non-convecting layer with inert gas, use of ultrasound, waste heating, and waste dilution. For each of these strategies, an attempt was made to identify information needs to support its selection, emphasizing that which can be obtained in laboratory studies. From information presently available, it is not possible to select any particular mitigation/remediation strategy.

Results obtained in laboratory studies utilizing synthetic wastes suggest that some of the mitigation/remediation strategies listed above are not viable options. For example, radiolysis studies show that hydrogen is a primary product; therefore, the use of chemical additives to inhibit its formation is not practical. Nitrous oxide appears to be produced in several steps: thus, the use of a chemical inhibitor is possible, at least in principle. Sufficient unknowns exist to preclude the selection of many other mitigation/remediation strategies at this time.

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1.0 Introduction

Chemical and radioactive wastes from processes used to separate plutonium from uranium are stored in underground tanks at the Hanford Site in Washington state. In March 1981, it was observed that the volume of wastes in Tank 101-SY slowly increased, followed by a rapid decrease and the venting of large quantities of gases. These cycles occurred every 8 to 15 weeks and continue to the present time. Subsequent analyses showed that these gases were composed primarily of hydrogen and nitrous oxide (N_2O). In response to the potential for explosion and release of hazardous materials to the environment, laboratory programs were initiated at Argonne National Laboratory (ANL), Georgia Institute of Technology (GIT), Pacific Northwest Laboratory (PNL), and Westinghouse Hanford Company (WHC), to develop a better understanding of the physical and chemical processes occurring in this waste tank. An aggressive sampling and analysis effort is also under way to characterize the wastes as fully as possible. These efforts will provide a technically defensible basis for safety analyses and future mitigation/remediation of the tank and its contents.

The purpose of this report is to assemble current information obtained from laboratory studies utilizing synthetic wastes and from Tank 101-SY in an effort to support remediation or mitigation of the safety hazards associated with the operation of the tank. The information given here largely is drawn from what has been learned by workers at ANL, GIT, PNL, and WHC.

This document reviews existing data for actual Tank 101-SY waste, including waste composition, slurry growth and collapse, and the composition of released gases. The mechanisms by which gases are generated are examined, including thermochemical degradation reactions, radiolytic processes, tank wall corrosion, and microbial action. Quantities of gases produced in laboratory studies are compared with the quantities estimated in the actual tank. Mechanisms responsible for crust growth and gas retention in the wastes are addressed, as are models for gas release. Finally, mitigation/remediation strategies are considered, with an emphasis on the laboratory data needed to support further development.

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2.0 Review of Existing Tank Data

Available data on the waste composition, gas volume releases, and gas composition are presented in this section.

2.1 Composition of Actual Tank 101-SY Waste

The contents of Tank 101-SY consist of five separate additions made over an approximately 3 1/2-year period starting in April 1977. Water was added over an approximately 4-year period beginning in 1984. The nature, amounts, and times of these five additions are given by Simpson (1984) and are summarized in Table 1. The total initial composition of the waste was estimated from these data by Simpson (1984). He also noted that waste analyses were unavailable for most of the transfers, and that almost all of the waste compositions were based on one analysis of one sample.

To better define the composition of the waste in Tank 101-SY, direct sampling of the wastes was conducted. Three samples were obtained on January 6, 1986, from three different levels in the tank (20, 175, and 380 inches from the bottom of the tank) by the dip or "bottle-on-a-pole" method. These samples were analyzed in early 1986 (Mauss 1986) and provided information on chemical composition, suspended solids, radionuclide concentrations, densities, and viscosity. Although the accuracy of these data is somewhat uncertain (Herting 1991), the results did demonstrate that the waste is heterogeneous. A comprehensive waste sampling and analysis effort is under way at present to more fully characterize the physical and chemical properties of the wastes stored in Tank 101-SY (Crawford 1991; Herting 1991).

Three crust samples were obtained from Tank 101-SY on November 18, 1990, by removing material from three level detectors; analyses of the chemical and radionuclide content of these samples was reported by Herting et al. (1991). The samples varied considerably in physical appearance, ranging from extremely dry to moist, and in color, from yellow to dark brown. All samples were similar in composition to each other and to middle slurry samples obtained in 1986 (Mauss 1986). The major components in all of the samples were sodium salts of nitrate, nitrite, carbonate, aluminate, and organic complexants. The principal differences between the middle slurry samples (Mauss 1986) and recent crust samples (Herting et al. 1991) are the carbonate and hydroxide contents. Carbonate was much higher in the crust sample than in the slurry sample, while the hydroxide content was much lower in the crust sample. These observations are in accordance with the expectations of a caustic material exposed to an atmosphere containing carbon dioxide over a relatively long period.

A detailed chemical analysis of the organic species present in Tank 101-SY has not been performed. Lokken et al. (1986) identified approximately 75 percent of the chemical species based on the total organic content in Tank 107-AN, which represent some of the organics

Table 1. Fill Record for Tank 101-SY

	Addition 1	Addition 2	Addition 3	Addition 4	Addition 5	Addition 6	Total
Date	April 1977	Nov 1977	June 1978	Aug 1978	Oct 1980	Sep 1984 through May 1988	
Volume, gallons	275,500	365,600	133,300	59,500	213,300	8,000	1,073,200
Description	Double Shell Slurry[(d)]	Complexed Concentrate [(e)]	106-SX Complexed Concentrate	111-U Complexed Concentrate	Double Shell Slurry	Water	
$NaOH$[(a)]	3.02	2.10	2.11	4.50	3.76	0	3.22
$NaAlO_2$	1.46	0.994	0.409	3.28	3.59	0	1.90
$NaNO_2$	2.72	1.86	1.10	5.23	5.47	0	3.28
$NaNO_3$	2.72	3.44	3.92	4.88	4.95	0	4.23
Na_2CO_3	0.8	0.474	0.932	0.002	0.14	0	0.62
Na_2SO_4	0.07	0.065	0.07	0.805	0.07	0	0.12
Na_3PO_4	0.152	0.148	0.066	0.123	0.30	0	0.19
TOC[(b)]	14.52	26.32	34.27	26.6	18.01	0	26.24
^{90}Sr[(c)]	0.013	0.16	0.074	0.45	0.005	0	0.051
^{137}Cs[(c)]	0.74	1.76	0.28	0.28	1.11	0	0.73

(a) Concentrations are in moles/liter.
(b) Total organic carbon (TOC) values are in grams of carbon per liter.
(c) Radionuclide concentrations are in Curies per liter.
(d) Double-shell slurry is a concentrated waste produced by the evaporators that contain high concentrations of hydroxide, nitrate, and aluminate.
(e) Complexed concentrate is an evaporator product similar to double-shell slurry, that also contains significant organic complexant concentrations.

originally used in chemical processes and their breakdown products. Chelators (citric acid, HEDTA, EDTA, methane tricarbonic acid, and NTA), chelator fragments (IDA and ED3A were most prevalent), carboxylic acids, alkanes, and phthalate esters were included. Complete identification of all of the organic constituents is a challenging task, because of the complexity of the waste. Considerable effort to further develop analytical procedures is needed to accomplish this task. However, it is assumed that the organic constituents of the waste in Tank 101-SY are similar to the organic constituents of the waste in Tank 107-AN.

2.2 Gas Generation

The volume of gas generated in Tank 101-SY is indicated by the fluctuation of the crust height. Information on gas generation is gathered from crust height measurements and analysis of grab samples.

2.2.1 Crust Height Cycles

Since Tank 101-SY was filled, waste volume readings have been taken using both an automatic Food Instrument Company (FIC) gauge and a manual tape. The FIC gauge and manual tape were used to measure the distance from the top of the tank riser to the surface of the waste. These measurements are the only records in existence of long-term growth and release cycles in this waste tank. These data show considerable fluctuation in the crust height, time between gas releases, and the volume of waste associated with each gas release.

Crust height changes associated with recent major release events are summarized in Table 2 (Babad, Johnson, et al. 1991), as are the times between release events, changes in waste volume, estimates of gas release, peak tank pressures, and peak hydrogen concentrations. Average values for each of these measurements and an associated standard deviation are also included in Table 2. The average decrease in surface level was 7.3 inches with a standard deviation of 2.0 inches for the six events summarized in Table 2, which corresponds to a waste volume change of 2670 ft^3 (368 ft^3 per one inch level change). Assuming that gases released in each event are initially retained in the bottom 18 feet of the tank at a hydrostatic pressure of 2 atm (Tank Waste Science Panel 1991; Reynolds 1991), the mean gas volume released per event was 5340 ft^3. Peak pressures and peak hydrogen concentration readings tended to fluctuate considerably for the six release events listed. Peak pressure readings reflect the relative rate at which gases are released from the wastes; high positive values indicate that the trapped gases were released rapidly. The largest pressure change occurred on October 24, 1990. On that date, the peak hydrogen concentration reached 4.7 percent, which is less than the lower flammability limit (LFL) for hydrogen in air but greater than the LFL value for hydrogen in N_2O. However, air is the primary oxidant in the tank dome.

An estimate of the rate at which gases are generated in Tank 101-SY may be made using the surface level changes and associated elapsed times between events listed in Table 2. Because of the irregularity in surface level changes and times between release events, a reasonable approach

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Table 2. Data Summary for Recent Release Events from Tank 101-SY

Event Date	Number of Days Since Last Event	Change in Surface Level (Inches)	Change in Waste Volume (Cubic Feet)	Volume[(a)] of Gases Released (Cubic Feet)	Peak Pressure[(b)] (Inches Water Gauge)	Peak Hydrogen Concentration (Percent)
January 1990	109	- 7.7	- 2830	5670	Not Measured	Not Measured
April 19, 1990	110	- 8.7	- 3200	6400	+0.10	3.5
August 5, 1990	109	- 5.2	- 1910	3830	-1.96	1.2
October 24, 1990	80	-10.3	- 3790	7580	+2.30	4.7
Feb 13, 1991	110	- 5.0	- 1840	3680	-2.00	0.04
May 16, 1991	92	- 7.0	- 2580	5150	+0.25	0.5
Mean	102	- 7.3	- 2670	5340	-0.26	2.0
Std. Dev. of Mean	13	2.0	730	1470	1.80	2.0
Sum	610	-43.5	-16,010	32,030	Not Applicable	Not Applicable

(a) Gas volumes were calculated from changes in the surface level of the waste assuming that, prior to release, the gases were held in the lower, non-convecting region of the tank at a hydrostatic pressure of 2 atm. Volumes are not corrected for temperature effects.

(b) In normal operation, the tank pressure is maintained at -2.30 inches of water.

might be to average net surface level changes for many events and divide by the total elapsed time rather than rely on one event. The sum of surface level changes for the six most recent release events included in Table 2 (-43.5 inches), divided by the elapsed time between events (610 days), corresponds to a rate of 0.071 ± 0.003 inches per day. The rate was estimated assuming an uncertainty of 0.5 inches in determining the surface level change for each release event, to which an uneven floating crust layer is probably the principal contributor.

Strachan (1991) considered waste surface level data collected from 1984 to the present in detail to more directly determine the kinetics of gas generation in that tank. It was observed that surface level readings increased linearly with time, within a standard deviation of 5 percent or less, in the period between gas release events. This was true for each data set considered. The average rate of increase in the surface level for 12 such data sets collected between March 1984 and December 1989 was 0.11 inch per day with a standard deviation of 0.02 inch per day.

Growth rates calculated by Strachan (1991) are, therefore, approximately 60 percent larger than those calculated from the data of Table 2. Differences may be attributed mainly to the relatively small waste level reductions that occur regularly between the much larger release events. These small releases are excluded when calculating the rate of surface level change from the data of Table 2, but are considered in the approach used by Strachan (1991). Waste volume growth was found to be linear over the entire period between major (>3 inches) decreases in the crust height when the effects of the small surface level changes were mathematically eliminated. It was concluded that the gas generation rate is essentially at steady state, is independent of physical processes (such as the mechanical stirring of the tank during a release event), and is insensitive to the increase in temperature that occurs between events. A rate of surface level increase of 0.11 ± 0.02 inch per day is probably a more realistic assessment than the lower value obtained from major release events (Table 3).

Rates of waste volume growth appeared to be decreasing slowly with time in Tank 101-SY. Strachan (1991) found the decrease in waste volume growth rates to be consistent with radioactive decay of ^{137}Cs ($t_{1/2}$=30.23 years) and ^{90}Sr($t_{1/2}$=28.1 years). At this time, however, the statistical uncertainty in the rates determined from waste volume data are too high to establish whether radioactive decay of these isotopes is the primary controlling factor. From approximately 1985 to 1988, air and water injections were attempted as means to quench the cyclic growth and collapse of waste levels in the tank (Leggett, quoted in Reynolds et al. 1991), although with limited success. Water injection tended to keep the amplitude of the gas release low and the gas release frequency higher than air injection. A more rigorous statistical analysis of available data is required, however, to support this conclusion. Air injection was attempted as a method to sparge gases from the tank and thus limit flammable gas release. This method appeared to raise the waste height baseline on which the cycles were occurring, and therefore, was stopped. Since that time, the waste height baseline has been decreasing to the value observed before the start of the air injections (Leggett, quoted in Reynolds et al. 1991). Strachan (1991) found some evidence for

Table 3. Rates of Surface Level Growth in Tank 101-SY

	Rates (inches/day)	Comments
Average of Six major release events January 1990 - May 1991	0.071 $\pm$ 0.003	Considers only major gas release events, so probably underestimates the true value.
Average of twelve data sets March 1984 - December 1989 (Strachan 1991)	0.11 $\pm$ 0.02	Accounts for minor (<3 inches) gas release events, so is probably the most realistic value.

an enhanced rate of waste volume growth as a result of air injection, but the statistical uncertainty in the data was too high to establish this observation conclusively. These studies are continuing.

2.2.2 Gas Analyses

The composition of gases liberated from Tank 101-SY during periodic release events has been estimated on the basis of mass spectrometric analyses of a series of grab samples taken from the vent line. Sampling and data reduction procedures that were employed are described by Pajunen et al. (1991). Uncertainties in the data are relatively high because of dilution of the liberated gases by a continuous flow of vent gas. Allemann (1991) reviewed the gas composition results for a series of gas releases from April 1990 to February 1991, and concluded that data corresponding to the October 24, 1990, release event are the most promising for an estimate of composition.

The non-condensable fraction of released gases consists of 39 vol% hydrogen, 31 vol% N_2O, and 29 vol% nitrogen, based on data from the October 24, 1990, release (Barker 1991; Allemann 1991) with uncertainties of ± 2 percent. Gas compositions for this release event are listed in Table 4. Mass spectrometric analyses performed at PNL and Westinghouse-Idaho Nuclear Company (WINCO) were in relative agreement for these samples. Trace gases were also reported, the most likely of which is methane at approximately 0.4 vol%. Carbon dioxide and NO_x appear to be low, probably less than 0.01 vol%. Of course, given the relatively high solubility of CO_2 and NO_x in alkaline solutions, these gases will probably not be easily released.

Ammonia may also be present. While its presence is indicated by its odor, it is not easily detected in mass spectrometric analyses (Campbell, quoted in Reynolds et al. 1991). An ammonia concentration of approximately 2000 ppm was measured using a Draeger™ tube during air lancing operations. Organic vapor analyzer (OVA) data obtained recently indicate a probable ammonia concentration of 4 vol% (Babad, Johnson et al. 1991).

Combining the gas compositional data listed in Table 4, with the best estimate of the overall rate of surface level increases, the rates of generation of important gaseous products may be estimated. These are listed in Table 5. Of most interest are those gases generated in the non-convecting slurry, representing the bottom 15 feet of the tank. These gases are believed to be responsible for major release events (Tank Waste Science Panel 1991). An approximately equal volume of wastes comprises the convecting slurry layer in Tank 101-SY. Gases are assumed to be generated in this layer at essentially the same rate as in the lower, non-convecting layer, but because these are expected to be continuously vented to the atmosphere, no contribution to surface level growth is anticipated. The rate of hydrogen generation that contributes to cyclic release events is estimated to be 33 ± 6 moles per day and that of N_2O is estimated to be 27 ± 5 moles per day.

Table 4. Gas Compositions in Tank 101-SY (October 24, 1990 Release Event)

Gas	*Percent by Volume*
H_2	39 ± 2
N_2O	31 ± 2
N_2	29 ± 2
CH_4	0.4
CO_2	<0.01
NO_x	<0.01

Table 5. Estimation of Rates of Gas Generation in Tank 101-SY Based on Slurry Growth Data and Tank Gas Analyses

	Non-Convecting[c] Slurry Layer	Total (Non-Convecting[d] and Convecting Layer)
Rate of Gas Generation[a]	83 ± 15 cubic feet/day	160 ± 30 cubic feet/day
Rate of Hydrogen Generation[b]	32 ± 6 cubic feet/day (33 ± 6 moles/day)	62 ± 12 cubic feet/day (64 ± 12 moles/day)
Rate of Nitrous Oxide Generation[b]	26 ± 5 cubic feet/day (27 ± 5 moles/day)	50 ± 10 cubic feet/day (52 moles/day)
Rate of Nitrogen Generation[b]	25 ± 5 cubic feet/day (26 ± 5 moles/day)	48 ± 10 cubic feet/day (50 ± 10 moles/day)

(a) Assumes a slurry growth rate of 0.11 ± 0.02 inches/day (see Table 3).
(b) Based on gas analyses from the October 24, 1990 event (see Table 4).
(c) The non-convecting slurry is assumed to be contained in the bottom 15 feet of the tank; gas volumes are uncorrected to standard temperature and pressure.
(d) Convecting and non-convecting slurry layers total 29 feet in thickness. Values assume that generation rates are identical in both layers. Gases are not believed to be retained in the convecting layer, however.

3.0 Gas Generation Mechanisms

Four possible mechanisms for gas generation have been considered: thermochemical degradation, radiolytic processes, steel corrosion, and microbial action.

3.1 Thermochemical Degradation

General: All of the gases released from Tank 101-SY have been observed in a series of studies that utilized synthetic double shell slurry wastes in the absence of radiation. Gases that have been observed include N_2O and H_2, the most important gases from a safety aspect, as well as N_2 and minor amounts of CO, CO_2, CH_4, NH_3, and NO_x. While significant progress has been made in determining the chemical reactions responsible for generating these gases, it must be emphasized that the wastes in Tank 101-SY are quite complex and much work remains to be done.

The stoichiometry and rate of gas generation from synthetic wastes has been found to depend on waste composition, most notably nitrite, hydroxide, aluminate, and organic concentrations as well as organic identity. Delegard (1980) reported gas generation occurred with HEDTA but not EDTA. The difference between these two chelating agents is that one of the carboxylate groups (-COOH) of EDTA is replaced by an alcohol group (-CH_2OH). Jansky and Meissner (1984) found similar behavior, reporting significant hydrogen generation when HEDTA and/or glycolic acid (hydroxyacetic acid) was present, but no gases generated in their absence. Delegard (1980) found that elimination of sodium aluminate from the synthetic waste composition substantially reduced the overall gas generation rate, recently corroborated by Ashby (quoted in Strachan 1991). A first order dependence on the hydroxide ion concentration for concentrations below 1.5 M was also reported (Delegard 1980). In these studies, wastes containing no sodium aluminate or no sodium nitrite were found to generate only very small quantities of gas; elimination of oxygen also drastically reduced gas generation rates. Elimination of sodium nitrate actually enhanced the rate of gas generation.

Chemical mechanisms responsible for the generation of gases are not well understood at this time, but considerable progress is being made. Reaction of a nitrate ion with sodium aluminum hydroxide dihydrate in the presence of HEDTA to form a nitro-hydroxyaluminum-HEDTA complex has been described (Tank Waste Science Panel 1991), which leads to the formation of N_2O, H_2, CO_2, and ED3A. A series of mechanisms have been described by Ashby (in Strachan 1991) that may be responsible for the breaking of carbon-carbon and carbon-nitrogen bonds, and the formation of hydrogen, ammonia, and other products. The Oppenauer oxidation mechanism would convert HEDTA to EDTA via an intermediate hydroxyaluminum-alcohol complex, liberating H_2. Cannizzaro-type reaction mechanisms have also been proposed as a means of generating H_2. Verification that these or other mechanisms are correct is being pursued through careful identification of reaction products by NMR and other methods, and through the use of isotopic labels to show the source of the product gases.

Comparison to gas generation in Tank 101-SY: No clear agreement among the synthetic waste studies exists as to the stoichiometry of gases generated from synthetic wastes, particularly for N_2O/H_2 ratios. At least some of this behavior probably arises from the choice of experimental waste compositions and reaction temperatures. While N_2O exceeded the concentration of H_2 by more than a factor of 10 in the presence of sodium nitrite, H_2 exceeded N_2O concentrations by more than a factor of 6 in the absence of sodium nitrite (Delegard 1980). Jansky and Meissner (1984) also found H_2 concentrations to exceed that of N_2O by more than a factor of 10 when sodium nitrite was present. Hart (in Tank Waste Science Panel 1991) found that N_2O/H_2 yields were 10 times that of hydrogen, whereas Bryan et al. (1992) found values typically in the range of 6 to 8. In contrast to these results from synthetic waste studies, gas compositional data obtained from the October 24, 1990 event, given in Table 4, indicate that N_2O and H_2 were present in approximately a 1:1 ratio (Barker 1991; Allemann 1991). It should be noted that the temperatures used in synthetic waste studies are usually 100°C or greater, to accelerate the rates of reaction using small batches of synthetic waste, whereas actual tank temperatures are approximately 60°C; this difference may have a substantial impact on the stoichiometry of gaseous products. Meisel et al. (1991b), for example, found in experiments conducted at room temperature that no gases were formed in the absence of radiation. However, non-negligible generation of H_2 was detected by the same workers at 60°C in the absence of radiation, especially for samples in which prior irradiation generated degradation products that might be expected in the tank.

The quantity of hydrogen generated by thermally driven chemical degradation reactions in synthetic wastes account for perhaps one-third of that generated in the actual tank. A comparison of gas production calculated on the basis of synthetic waste studies and estimates for Tank 101-SY are included in Table 6. Hydrogen generation rates from synthetic wastes that were reported by Bryan et al. (1992) (1.3 mmol over a period of 500 h at 90°C using a 500 mL waste volume) correspond to a rate of approximately 500 moles of hydrogen per day per million gallons of waste. Using an activation energy of 25 kcal/mol (Delegard 1980; Siemers, in Strachan 1991) to adjust this rate to the actual tank temperature of 60°C, a rate of 20 moles of hydrogen per day per million gallons waste is obtained. A similar treatment of N_2O results reported by Bryan et al. (1992) leads to an estimate of 100 moles of N_2O per day per million gallons waste at 60°C. This quantity is approximately twice the estimated rate of generation of this gas from the actual tank.

Ashby (in Strachan 1991) reported an overall rate of gas generation from a reference synthetic waste composition (0.13 mL per h per 100 mL waste volume at 120°C). Concentrations of individual gas components were not identified at the time of the referenced report. Correcting that gas volume to 60°C using an activation energy of 25 kcal/mole yields a gas production rate of 55 moles of gas per day per million gallons waste, a value approximately one-third of that estimated for Tank 101-SY.

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Table 6. Comparison of Gas Generation in Synthetic Waste Studies with Estimates for Tank 101-SY

	Moles H_2/day	Moles N_2O/day	Comments
Thermochemical	20	100	Results of Bryan et al. (1991) were obtained at 90°C and corrected to 60°C using an activation energy of 25 kcal/mol
Radiolytic	21	207	From Meisel et al. (1991b) Hydrogen value includes radiolytically induced thermal generation.
Tank Wall Corrosion	6	Unknown	Calculated from corrosion rates measured by Divine (1985) assuming H_2 is the sole product of trans-oxidation to the ferrous state. No direct observation of gas generation has been made.
Microbial Action	--	--	No estimates are available; probably negligible
Estimates for 101-SY	64	52	Based on a slurry growth rate of 0.11 inches/day (Strachan 1991) and vent gas analyses for the October 24, 1990 event.

It must be emphasized that the above discussion is only an estimate of the quantity of gases that might be produced by thermally driven degradation reactions. Synthetic wastes used in these experiments were considerably less complex than actual wastes; speciation of the organic components in the actual waste has not been performed to date. To accelerate the rate of gas generation in the synthetic waste studies, reaction temperatures in the range of 90 to 120°C were used rather than the actual tank temperature of 60°C, requiring correction of the laboratory data to account for the activation energy. One must be certain that the reaction mechanisms do not change over the temperature range in question if such an estimation is to be valid.

The cause for the discrepancy between N_2O yields estimated from synthetic waste studies and that estimated from actual tank data is not known. Gas releases from Tank 101-SY have been found to contain approximately equimolar quantities of N_2O and H_2, while synthetic waste results generally show N_2O to be present at concentrations 6 to 10 times greater than H_2 (Tables 4 and 6). Considerably more N_2O production is estimated from synthetic waste studies than is indicated by actual release data. One possible explanation involves the solubility of N_2O, which is 20 times greater than that of H_2 in water. This high solubility may provide a means for enhanced transport of this gas through the liquid relative to H_2, and greater continuous release rates from the tank surface. Selective loss of N_2O from reaction vessels was observed by Bryan et al. (1992), who collected gaseous products over water. Monitoring of N_2O and H_2 release from Tank 101-SY between release events would be valuable in establishing whether the above is important.

Unknowns: Continued laboratory studies are needed to obtain a sufficiently detailed understanding of the chemical reactions leading to the production of H_2, N_2O, and other gases. In general, these studies should identify critical reactants; determine threshold reactant concentrations, if any; determine reaction stoichiometries, including individual gas generation rates; and determine reaction energetics.

One of the primary needs is to determine individual organic species that are present in the actual wastes. Results obtained by Lokken et al. (1986) for Tank 107-AN, a related waste, shows remarkable complexity. In addition, not all of the organic components were identified (≈75 percent, based on TOC). A considerable effort in developing analytical methodology is anticipated. In that study, most of the organic degradation products were observed in the synthetic wastes within a matter of months at room temperature.

A large discrepancy exists between N_2O generation rates predicted on the basis of synthetic waste studies and that determined from actual tank data, the cause of which has not been established.

Nitrogen has been observed in both synthetic waste studies and in releases from Tank 101-SY. The source of this product is unknown.

The role of minor and trace elements in gas generation reactions, including the transition and noble metals, has received little attention. Ashby (in Strachan 1991) recently showed that low concentrations of copper enhanced gas generation rates.

3.2 Radiolytic Processes

General: The gases H_2 and O_2 are produced by the radiolysis of water, but when the chemicals present in Tank 101-SY are added, the yields of these gases are markedly altered and other gaseous products result (Meisel et al. 1991a). In addition to H_2, N_2O, which is produced in large yield, and N_2 were also found. Oxygen has been observed in the absence of organic solutes, but is consumed if organics are present. Other gases that are likely to be produced are NH_3 and CO_2.

Other radiolysis products may be important in gas generation. Degradation products of the organic chelators may be important in thermal reactions. For example, the degradation product formaldehyde and other molecules with C-H bonds that are not in the α position to a carbonyl group have been proposed as sources of thermally produced H_2 (Tank Waste Science Panel 1991). Evidence exists that hydrogen peroxide, which is formed in the radiolysis of water, can also form hydrogen in simulated tank systems.

Hydrogen and N_2O are of principal importance with respect to Tank 101-SY. The sources of hydrogen in radiolysis are well known for aqueous solutions containing no organic material. Hydrogen can be formed by the direct dissociation of water as well as by reactions between the primary transient species $H^{\cdot}$ and the solvated electron (e_{aq}^-). Because of the inhomogeneous nature of energy deposition by ionizing radiation, which results in very large local concentrations of these transient species, the latter reactions cannot be reduced to zero at attainable concentrations of scavengers. Direct dissociation of water cannot be affected by added scavengers. Nevertheless, concentrations of NO_2^-, NO_3^-, and OH^- similar to those present in Tank 101-SY do cause great reduction in the radiolytic yield of H_2, and the effects of variation in the concentrations of these ions on the H_2 yield can be predicted. The presence of organics causes an increase in the yield of H_2 due to the reaction of $H^{\cdot}$ atoms to abstract $H^{\cdot}$ from the organic, but the magnitude of this increase is limited by the aforementioned inorganic ions, primarily nitrite ions, that effectively compete for the $H^{\cdot}$ atoms. The effects of other solutes on the H_2 yield can be predicted if the reactivity of the solute with $H^{\cdot}$ atoms is known at high pH. Prior knowledge concerning N_2O is much less complete compared with H_2, and the exact mechanism of N_2O formation is not known; information given below summarizes that state of knowledge.

Comparison to gas generation in Tank 101-SY: Modeling calculations have been performed and experiments conducted using a homogeneous, simulated waste solution (Meisel et al. 1991a). The radiolytic yields (G-values in molecules/100 eV of energy deposited) of gases produced were determined. Yields of H_2 and N_2O have been measured in solutions irradiated at 30 and 60°C that contain 2.12 M NaOH, 0.86 M $NaAlO_2$, 2.22 M $NaNO_2$, and 2.79 M $NaNO_3$ (a solution intended to mimic the tank solution and referred to as solution "P" below) and concentrations of various organics (e.g., EDTA, HEDTA, IDA) in the range of 0.1 to 0.2 M. Nitrogen and O_2

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were also determined, but N_2 was generally not detectable (but see below) and the addition of organics reduced a small $G(O_2)$ from solution "P" to zero. In fact, O_2 initially present in test solutions is consumed when organics are present. The other likely gaseous products that have not yet been confirmed or denied are NH_3 and CO_2.

The yield of H_2 should depend on the concentration of the organic material and its reactivity with the H atom. In line with this finding, the G-values of H_2 show a qualitative correlation with the number of C-H bonds in the additive and a linear dependence on organic concentration. The G-values of H_2 and N_2O are somewhat higher at the higher temperature. For H_2, the increase is in the range of 40 ± 30 percent for a variety of additives and conditions. The variability in yield could be due to differences in activation energy for the hydrogen abstraction reaction. For N_2O, the increases at 60°C are somewhat larger and generally fall in the range of 25 to 100 percent. Because 60°C corresponds to the approximate temperature in Tank 101-SY, the G-values of H_2 and N_2O measured at 60°C will be discussed in the following, unless otherwise noted.

Independent of dose or dose rate, the generation of H_2 occurs with a G-value in the range 0.07 ± 0.02 from solution "P" containing concentrations of the organic chelators and their degradation products chosen to simulate Tank 101-SY wastes. This estimate of G-value is based both on G-values measured when well-controlled additions of organic chelators were made and the G-values measured on a solution that had been pre-irradiated to simulate the effects in Tank 101-SY. Nitrogen was observed with a G-value of 0.13 from pre-irradiated material, but N_2 was not detected from radiolysis of other simulated waste solutions. Generation of N_2O from solution "P" with added organics occurs much more efficiently, having a G-value of about 1, a yield which does not appear to depend on dose or radiation intensity.

From these yields, H_2 and N_2O generation rates of 2.5×10^{-9} and 3.6×10^{-8} moles liter^{-1}min^{-1}, respectively, are determined for synthetic Tank 101-SY wastes. A non-radiolytic yield of H_2 at 60°C of 1.3×10^{-9} moles liter^{-1} min^{-1} has been observed in solution "P" containing 0.17 M IDA; this yield brings the total rate of H_2 generation to 3.8×10^{-9} moles liter^{-1}min^{-1}. Of course, application of these numbers to the tank is an approximation both because it is not clear that this approach is applicable to non-homogeneous phases, and because only the approximate chemical composition of the material in the tank is known; specific organic species present in the waste are unknown. The yield of hydrogen will be strongly dependent on the organic and NO_2^- concentration, but only weakly on the NO_3^- concentration.

From the above measurements, yields of 21 moles per day of H_2 and 207 moles per day of N_2O are predicted (Table 6). To explain the quantity of H_2 generated per day based on slurry growth data (Table 5), an H_2 production rate of approximately 64 moles per day and an N_2O production rate of 52 moles per day are needed. Thus, the measured production rates lead to about one-third the H_2 production observed and about 4 times the N_2O observed. Whether the radiolytic yields from the inhomogeneous phases are sufficiently different to explain these disparities remains to be determined. Hydrogen production from organic radicals catalyzed by particulates

has been mentioned as a possibility in the Argonne National Laboratory survey on the radiation chemistry of synthetic waste (Meisel et al. 1991a).

The large N_2O excess has not been explained from experiments done on homogeneous systems where the total dose is not sufficient to saturate the solutions in N_2O or H_2. One can speculate on physical or chemical mechanisms to explain the discrepancy. A physical mechanism whereby N_2O is continually lost between release events at a much larger rate compared with H_2 is conceivable. Such a speculative mechanism is as follows. If N_2O is adsorbed much more strongly than H_2 on particulate matter, a release event may not appreciably dislodge N_2O relative to H_2. Then, N_2O generated after a release event would escape at a rate closer to its production rate, because its adsorption sites would still be saturated, whereas the H_2 would be less likely to escape in this way because its adsorption sites would have been purged of H_2 during the release event. A similar variant would be that the N_2O is much less strongly bound, or not bound at all to the particles so that almost all of the N_2O escapes during the time between events. This means that the gas measured in an event does not well reflect the total yield of the gas. Another alternative is the chemical reaction of the N_2O with radicals and ions, for example, NO_3^{2-} produced in the solution. A saturated solution of N_2O in solution "P" is approximately 1 mM so radical lifetimes in the millisecond range would make such a mechanism possible. While no evidence of such a mechanism exists in the experimental yields of N_2O as a function of total dose, insufficient dose has been given to test samples to create sufficient N_2O to saturate the solution.

Some information related to the mechanism of N_2O formation has been obtained. Use of sodium glycolate as an organic additive still results in a substantial yield of N_2O despite the fact that there is no nitrogen in glycolate. Also, the use of ^{15}N-labelled glycine as an additive results in N_2O that contains a negligible amount of ^{15}N. These observations show that the nitrogen in N_2O originates from the inorganic constituents, even though the organic is necessary to produce N_2O.

Unknowns: A list of the unknowns related to gas generation in Tank 101-SY follows:

- The concentration of substances in the tank. The nitrite anion is of particular importance because of its ability to inhibit H_2 formation. The concentrations of the various organics are important because they increase H_2 formation.

- The effects of heterogeneity. Many effects of heterogeneity are possible, but the contributions of these to gas production are unknown. Uncertainties include the extent to which direct absorption of energetic radiation by solids affects yields, the effect of reactions at the interfaces, and the catalysis of reactions by particulates.

- The mechanism of radiolytic formation of N_2O. The sequence of inorganic reactions, the identity of the intermediates involved, and the nature of the involvement of the organics is not known.

- The effect of degradation products from the organics and the production of H_2O_2 on the thermal yield of H_2.

- The yields of NH_3 and CO_2.

3.3 Steel Corrosion

General: Hydrogen and other gases may also be produced via corrosion reactions of the double-shell steel tanks. General steel corrosion rates are expected to be very slow in strongly alkaline solutions, less than 0.0005 inch per year (Divine et al. 1985; Mackey and Divine 1986) and probably do not pose a significant structural problem. Given the large size of the Hanford double-shell waste tanks, however, the quantity of gas that theoretically could be produced from such an extent of corrosion is within an order of magnitude of the quantity of gas generation from Tank 101-SY. No direct measurement of gas generation from steel corrosion in the presence of actual or simulated double shell slurry waste has been performed to date.

Tank 101-SY and other double-shell tanks at the Hanford site are constructed of ASTM A-537 Class I carbon steel plate. The nominal composition of this steel is (weight percent) C (<0.24), Cr (<0.25), Cu (<0.35), Mn (0.6-1.4), Mo (<0.08), Ni (<0.25), P (<0.035), S (<0.04), Si (0.13-0.55), with the balance Fe. A closely-related alloy, ASTM A-516, was used in the construction of older, single-shell tanks (Divine et al. 1985).

Divine et al. (1985) performed a series of corrosion tests for ASTM A-537 steel, aiming to simulate conditions present in Hanford double-shell tanks. Major and minor waste components as well as temperature were varied in these tests, with weight loss of steel coupons measured for periods up to one year. From the results of these tests, a predictive equation was developed that allows corrosion rates to be calculated as a function of waste composition and temperature (Divine et al. 1985; Mackey and Divine 1986). The predictive equation describes general corrosion processes; localized and stress corrosion cracking were not observed in the tests. Under conditions expected in actual double shell waste tanks, corrosion rates were less than 0.0005 inch per year. Results of these studies are in good agreement with predictions based on thermochemical data for iron (Pourbaix 1974), where good corrosion resistance is afforded by the formation of passive layers of iron (II) hydroxide or magnetite.

The primary anodic (corrosion) reaction for A-537 steel is believed to be (Divine et al. 1985)

$$2\ OH^- + Fe = Fe(OH)_2 + 2e^- \tag{1}$$

while, in anoxic wastes, the primary cathodic reaction is given by

$$H_2O + e^- = 1/2\ H_2 + OH^-. \tag{2}$$

In oxygenated wastes, oxygen will react with iron to produce iron (II) hydroxide plus water. Of course, in oxygenated wastes, steel should be strongly passive and corrosion rates very low (Pourbaix 1974). Nitrate and nitrite ions are believed to participate, not in the initial iron oxidation, but in conversion of the corrosion products to a higher oxidation state.

$$NO_2^- + Fe(OH)_2 = Fe(OH)_3 + \text{"reduced } NO_2^-\text{"} \quad (3)$$

$$NO_2^- + Fe(OH)_2 = 1/3\ Fe_3O_4 + \text{"reduced } NO_2^-\text{"} \quad (4)$$

Comparison to gas generation in Tank 101-SY: From Equations (1) and (2), the quantity of hydrogen that can be produced by steel corrosion in Tank 101-SY is readily estimated to be 4000 ft^3/year/0.001 inch of corrosion, assuming a tank diameter of 75 feet and a height of 35 feet. This corresponds to a hydrogen production rate of 5.5 ft^3 per day (6 moles/day) if the actual corrosion rate was 0.0005 inch per year, as was concluded by Divine et al. (1985). It is additionally assumed that corrosion proceeds uniformly on the tank walls and bottom in this estimation. A corrosion rate of one-half mil per year could thus account for approximately 10 percent of all hydrogen generated in the tank. Of course, if corrosion was the major mechanism by which hydrogen is produced, it might be expected that other Hanford tanks would behave similarly to Tank 101-SY, which is clearly not the case.

Unknowns: Given that the estimated quantity of hydrogen that can be produced by steel corrosion is within an order of magnitude of that actually produced in Tank 101-SY, this aspect warrants further consideration as a gas source. In earlier studies performed by Divine et al. (1985), while considering a range of pertinent liquid compositions, no attempt was made to identify or directly measure the concentration of any gaseous corrosion products in their assessment of corrosion rates of A-537 steel. It remains to be determined whether all iron oxidation results in the reduction of water to hydrogen, or whether other reduction products such as N_2O are formed.

The effects of radiation were not included in the study by Divine et al. (1985). Radiation effects in steel corrosion need to be assessed under relevant tank conditions.

In the above calculation, it was assumed that the tank walls were in contact with the waste. An interpretation of recent gamma scans in the annulus of Tank 101-SY suggests that the tank walls are coated with a substantial layer of solid material. This material, presumably precipitated because the tank walls are cool relative to the contained wastes, would be expected to substantially reduce the corrosion of the steel. Proof that a passivating, solid material coats the tank walls is not available at present.

Retention of hydrogen generated by tank wall corrosion may be less likely than gases generated within the non-convecting layer. Because gas would be produced in a very localized area near the walls, enhanced escape to the convecting layer may be facilitated.

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3.4 Microbial Action

Because gases being produced in Tank 101-SY are common microbial metabolites and because of the presence of large quantities of organic matter, the possibility exists that some fraction of gas production in this tank is mediated by microorganisms. No experimental investigation has been performed to date to confirm or deny the presence of microorganisms in the Hanford waste tanks. However, Stevens and Frederickson (in Bryan et al. 1992) briefly addressed this issue recently by discussing the types of organisms that might be present and the experiments needed to confirm or reject microorganisms as a cause of gas generation in double-shell tank waste.

Although many components of Tank 101-SY waste are attractive substrates for microorganisms, conditions within the tank appear to present a severe challenge to the tenacity of life. An extended adaption period is usually required before microbial proliferation in such an extreme habitat. The quick onset of gas production, as well as its occurrence above 100°C in simulated waste mixtures, appears to rule out any need to invoke bacterial fermentation as a major cause.

However, until samples of actual waste can be examined for the presence of microorganisms, it is not possible to rule out the possibility of active microbial fermentation. Simple experiments to test these postulates in the double-shell tank wastes are briefly outlined below. If the first test is positive, the remaining experiments should be done. Otherwise, microorganisms can be discounted as a significant cause of chemical reactions in these wastes.

1) **Microscopic Examination of Waste Samples.** If microorganisms do exist in the double-shell tank wastes, they are likely to be in zones where they might be protected from extreme conditions. Such zones might be expected where the waste has separated into phases, such as the crust, bottom sediments, or any less saline layers that may have resulted from water injection. Films along the walls of the tanks could also be potential refugia for microorganisms. Samples obtained from such zones in Tank 101-SY, or similar tanks, should be examined by high-power, phase-contrast, and epifluorescence microscopy. Phase contrast microscopy is simple, and allows observation of living cells, but in the presence of many bacteria-sized particles, interpretation can be difficult. Epifluorescence microscopy allows the use of various fluorescent reagents that bind specifically to living cells.

2) **Sterilization of Active Waste Samples.** If microorganisms are responsible for some component of gas production in active waste subsamples, the gas production rate or its composition should change after sterilizing treatments. An example of such a treatment would be to autoclave three times, on three successive days, with incubation at ambient temperature during intervening periods. Other methods are also possible. Sterilized and non-sterilized samples should be analyzed for differences in gas composition and production.

3) **Transfer of Activity by Inoculation.** If some microbially-mediated reaction is eliminated by the sterilization treatment, it should be possible to transfer this activity from active samples to sterile, inactive waste samples of similar composition. Inactive samples could be obtained from experiment 2) described above, or from preparation of sterilized synthetic waste. A small volume of the active sample should be transferred into the inactive sample. After a suitable incubation period, any microbiological activity present in the first sample should be observed in the second sample. The rate of gas production and the gas composition of inoculated and uninoculated samples should be compared over time.

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4.0 Crust Formation, Gas Retention, and Gas Release

Any proposed mitigation strategy must be based on an understanding of how the crust forms, how gas is retained in the waste, and what causes the gas to be released. Current understanding of these issues is presented here.

4.1 Crust Formation and Gas Retention

General: One of the consequences of gas generation in Tank 101-SY is the growth of a floating crust, which has reached an estimated thickness of approximately 50 inches (Tank Waste Science Panel 1991). A floating crust is believed to be formed when gas bubbles generated in the waste become attached to solid particles in sufficient quantity to overcome the higher density of the solid particles (Bryan et al. 1992). This technology is widely utilized by the mining industry in mineral separation operations. Gas bubble-solid particle combinations without sufficient buoyancy to float to the surface provide a means for gases to be retained elsewhere in the waste, particularly within the non-convecting layer. It is thought that the crust does not play a major role in the trapping of gases within Tank 101-SY, but it may act to somewhat moderate gas flow during a release, thereby diluting hydrogen and N_2O gases in the exhaust (Tank Waste Science Panel 1991).

A gas bubble will tend to become attached to a solid particle immersed in a liquid if the equilibrium contact angle between the solid and liquid is greater than zero (or, at equilibrium, the solid is incompletely wetted by the liquid). To minimize the surface energy of the system, a solid will seek a position at a liquid-gas interface such that the equilibrium contact angle is achieved. Critical conditions for the flotation of solid particles in a less dense liquid phase have been calculated by Huh and Mason (1974). Flotation is favored by poor solids wettability, small solid/liquid density ratios, small particle sizes, and high liquid phase surface tension values.

Organic constituents of the waste are believed to serve an important role in gas retention and floating crust formation, through alteration of the surface chemistry of the particulates by adsorption. Surface adsorption of organic waste components appears to decrease the wettability of the solids, which increases the tendency for adherence to gas bubbles. Bryan et al. (1992) showed that stable, floating crusts could be formed on synthetic wastes by sparging with nitrogen and other gases. Particularly for synthetic waste mixtures containing EDTA and HEDTA, gas bubbles introduced into the wastes became attached to solid particles; these floated to the surface, where they were stable indefinitely. In contrast, a synthetic waste solution containing only inorganic components did not form a stable crust. Rather, within a relatively short time (hours), the inorganic solids fused into a hard mass and could no longer be dispersed by stirring, let alone floated.

Comparison to Tank 101-SY: The composition of the crust formed on synthetic wastes has been found to be quite similar to the overall composition of the solids. Principal solids contained

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within the crust included sodium aluminate, sodium carbonate, sodium carbonate monohydrate, sodium nitrate, and sodium nitrate (Bryan et al. 1992; Strachan 1991), similar to solids identified in actual crust (Herting et al. 1991). Actual crusts appear to be higher in sodium carbonate, perhaps the result of long exposure to air, which contains carbon dioxide.

Synthetic as well as actual crust samples were found to contain substantial amounts of water. High water contents are expected to lower the risk of crust flammability because of the high heats needed to evaporate the water. Moist crust samples, both synthetic and actual, have been found to contain more than 20 wt% water (Bryan et al. 1991; Herting et al. 1991). Dry actual crust samples have been found to contain approximately 10 wt% water (Herting et al. 1991). X-ray diffraction analyses of synthetic crusts have shown the presence of sodium carbonate monohydrate (Bryan et al. 1992; Thomson in Strachan 1991); hydrated forms of sodium aluminate are also expected. In addition, the solids comprising the crust are expected to remain partially wetted by the aqueous solution if the equilibrium solid-liquid contact angle is to be maintained (Bryan et al. 1992).

Unknowns: While it is quite probable that crust growth and gas retention in these wastes are due to the attachment of gas bubbles to solid particles in a manner controlled by surface tension forces, this mechanism has not been conclusively established. Determining the mechanism for gas retention in the wastes is among the most important issues to be addressed by the Tank Waste Safety Program.

4.2 Models for Gas Release

General: Several models have been proposed to explain the mechanism responsible for periodic gas releases from Tank 101-SY. These can be grouped in two classes: those in which gases are held by the crust and those in which gases are held in the non-convecting (sludge) layer (Reynolds 1990; Allemann et al. 1991). From analyses of the data available, Allemann et al. (1991) concluded that the sludge overturn models are most probable. This conclusion is supported by recent video pictures taken during a release that show the crust to have the consistency of loose oatmeal and the gas released as many small bubbles. However, from a historical perspective, a brief review of these crust models is important.

Models based on the assumption that flammable gases are trapped by a relatively impervious crust at the top of the waste tank include the "crust fracture" model and the "crust tilt" model. In the "crust fracture" model, the crust is believed to be in the form of a flat plate that is supported by a flat bubble of gas. This gas bubble is located directly underneath the crust but above the liquid level. As gas gathers in the flat bubble, the crust level is raised. At the time of release, the crust fractures, allowing gases to escape and the crust level to descend, reforming a seal. In the similar "crust tilt" model, rather than fracturing to allow gases to escape, the crust tilts to one side. After releasing the gases, the crust returns to a level position and reforms a gas seal. Recent video pictures taken during a release event are not consistent with such models, however.

A series of models described by Reynolds (1990) are based on the assumption that gases are retained in the non-convecting layer near the bottom of the tank rather than just under the crust. These models include "total sludge buoyancy," "gas supersaturation," "bubble separation from sludge," "local gas bubble," "local buoyancy upset," and "hot liquid release." In these models, it is assumed that the crust offers little resistance to gas release, which is in accordance with an analysis by Thomson (in Strachan 1991). These models are described briefly below (Reynolds, cited in Reynolds et al. 1991):

Total Sludge Buoyancy: Gas formed and retained within the sludge layer achieves sufficient buoyancy to rise, leading to the release of some of the trapped gases. The lifting of the material also relieves the pressure on the gases, resulting in gas expansion and hastened tank rollover. Solids that are brought to the top of the tank resettle to the bottom, where they again inhibit convection currents. Gases formed in the sludge layer make the entire sludge rise, and separation of the bubbles from the solids occurs high in the tank pool.

Gas Supersaturation: Gas collects at the bottom of the tank in a supersaturated condition. Some trigger causes a local or general reduction of pressure, which allows the gas to nucleate into bubbles. These grow rapidly and rise from the sludge and fluid mass.

Bubble Separation from Sludge: Gases that are formed are collected as small bubbles in the thick solid-liquid sludge layer near the bottom of the tank. The bubbles are held by surface adhesion to the solids or by the sludge viscosity and yield strength. The bubbles grow until they can no longer be held by these forces. Some begin to rise; this motion aids and triggers the release of other bubbles. The triggering could be local and progress as a wave across the tank, or it could be at some general level in the waste and progress to other levels. The essence of this model is that the bubbles retained in the sludge layer separate from the waste sludge at the bottom of the tank.

Local Gas Bubble: In this model, gases are assumed to collect in a large bubble under a membrane-like layer of sludge. Eventually the membrane breaks and a large bubble of gas rises from this local part of the tank, passes quickly through the convecting liquid layer, and impacts against the crust.

Local Buoyancy Upset: The hypothesis of this model is that a part of the sludge achieves sufficient buoyancy to suddenly rise, leading to the release of trapped gases. This model is otherwise similar to the Total Sludge Buoyancy model.

Hot Liquid Release: In this model, the formation and release of gas opens pathways for hot liquid to rise from the sludge. The liquid, by being heated, is less dense than the liquid above but has been held down by the cohesive slurry. Cooler liquid from above fills in regions where the hot liquid was. As the liquid rises, it brings some sludge solids with it. These later settle to the bottom again, and begin to recreate the bottom bulge of temperature.

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Comparison to Tank 101-SY: Allemann et al. (1991) concluded that the sludge overturn models most probably represent actual gas release events in the tank. These models include the Total Sludge Buoyancy and Local Buoyancy Upset models. Evidence that an overturn does occur has come from temperature profiles taken at 10-second intervals during the October 24, 1990, gas release event. The pre-release temperature profile showed a temperature bulge near the bottom, which collapsed simultaneously with a buildup of the temperature region just below the temperature gradient of the crust region. Calculations made by Allemann et al. (1991) based on a gross overturn driven by the buoyancy of the amount of gas (estimated from waste level drops and from vent measurements) gave rise times on the order of 50 seconds, which is in close agreement with thermocouple profiles in the tank.

Evidence points to the retention of significant amounts of gas in the waste after a release event (Allemann et al. 1991). This could occur if only a small fraction of the sludge is involved in an overturn, or, if the complete sludge layer is involved, only 25 to 30 percent of the trapped gas is released. In crust growth studies using synthetic wastes, it was concluded that gas bubbles will adhere to solid particles as a result of surface tension forces; because the solids are somewhat hydrophobic as a result of the adsorption of certain organic waste constituents, stability can be gained by displacement of some of the liquid in contact with solid surfaces by gas bubbles (Bryan et al. 1992). Thus, since the surface tension of solids is lowered by attachment to gas bubbles, it is unlikely that detachment of all of the gas will be easily accomplished.

Unknowns: While total sludge buoyancy and local buoyancy upset models appear to most closely represent gas release events in Tank 101-SY (Allemann et al. 1991), unknowns associated with modeling these phenomena are significant. Unknowns include the following:

- What controls the yield stress of the non-convecting layer? Presumably, when the yield stress is exceeded by buoyancy forces, gases are released. Dendritic crystals of sodium nitrite have been suggested to play a key role (Allemann et al. 1991).

- What fraction of gases that are stored in the waste tank are involved in release events? Allemann et al. (1991) have cited evidence that less than one-third of trapped gases are released.

- What is the mechanism for minor gas releases, which occur frequently?

- What is responsible for the slow decrease in the slurry level following a major release event?

5.0 Potential Mitigation Strategies

A number of strategies to reduce or eliminate the hazards associated with the cyclic release of hydrogen and other gases from Tank 101-SY are being developed elsewhere (Babad, Deichman, et al., 1991). Many of these strategies are briefly summarized below from the standpoint of what has been learned from studies involving synthetic wastes and what additional data are needed to support the selection of any of these strategies. Mitigation/remediation strategies are subdivided into two sections: a) methods to decrease the rate of gas generation, and b) methods to decrease gas retention. These are given in Table 7 and described below.

5.1 Methods to Decrease the Rate of Gas Generation

Seven possible strategies for decreasing the rate of gas generation have been considered: 1) removal of cesium, 2) destruction of organic constituents, 3) chemical additives to inhibit specific gas generation pathways, 4) waste dilution or concentration, 5) lowering the pH, 6) adding a mineral-forming agent, and 7) cooling the waste.

5.1.1 Removal of Cesium

Description: Removal of cesium would most probably result in a significant decrease in the generation of flammable gases, both through a reduction in radiolytic reactions and through a substantial decrease in the tank temperature. Several approaches to cesium removal are possible, including the use of ion exchange and solvent extraction methodologies. Cesium removal processes would most probably be performed ex-tank.

Likelihood for Success: The removal of cesium would reduce the radiolytic production of H_2, estimated to account for approximately one-third of the hydrogen generated in the tank. Radioactive decay of ^{137}Cs additionally accounts for approximately 90 percent of the heat generated in the tank, the balance principally due to decay of ^{90}Sr. Thermochemical degradation of organics and possibly steel corrosion will continue to generate flammable gases, but at a much reduced rate. This is probably a high cost option, and may require a long time to implement.

Unknowns: Further studies are needed to more completely assess the reaction pathways responsible for flammable gas generation in Tank 101-SY wastes. The relative contributions of radiolysis, thermochemical reactions, and steel corrosion reactions are not well-established at this time.

The extent of cooling of the tank and associated changes in waste behavior as a result of cesium removal need to be assessed. Substantial cooling of the waste will likely result in major changes in solution rheology. Considerable quantities of dissolved solids will be precipitated. Gas retention/release cycles may continue with a high flammability risk, although at much lower frequencies.

Table 7. Mitigation/Remediation Strategies for Tank 101-SY

Methods to Decrease Gas Generation	*Methods to Decrease Gas Retention*
Removal of cesium, strontium (P)	Inert gas sparging (with mixing) (T)
Destruction of organics (P)	Ultrasonic irradiation (T)
Chemical additives to inhibit specific reaction pathways (P)	Waste heating (T)
Dilution/concentration (P)	Dilution (P)
Lower pH (P)	Surfactant addition (P)
Addition of mineral forming agents (P)	Waste Heating (T)
Waste Cooling (T)	

P denotes strategies that are considered to permanently alter the character of the waste.
T denotes strategies that are considered to cause temporary changes.

5.1.2 Destruction of Organic Waste Constituents

Description: Destruction of organic constituents, believed to be one of the principal sources of flammable gases in Tank 101-SY, may provide a means of mitigating cyclic gas releases. Methods to destroy organics include heating and ozonolysis. The basic concept of the heating approach is to utilize nitrate/nitrite ions present in the waste to oxidize the organics at 200 to 300°C in a pressurized reactor, either in- or ex-tank. Ozone is a powerful oxidizer and will attack organics. Ozone can either be generated and then injected into the waste or it can be formed *in situ* with aeration and ultraviolet light.

Likelihood for Success: Destruction or removal of all organics would significantly reduce the probability of periodic gas releases from the tank. Generation of hydrogen from radiolysis of the waste solution from which the organics were removed would still account for ≈10 percent of the total hydrogen observed in a typical major release event. Thermochemical generation of hydrogen not associated with steel corrosion is expected to be reduced to negligible levels. Generation of hydrogen from steel corrosion reactions would probably not be affected by organic destruction or removal.

The formation of N_2O would probably be eliminated because its production requires the presence of organics, following either thermochemical or radiolytic reaction pathways. Any release of H_2 not accompanied with an oxidant such as N_2O would present a negligible flammability risk because these gases would be quickly diluted in the plenum space. Of course, radiolytic processes lead to the formation of equivalent quantities of oxidants and reductants; if N_2O is not formed, then perhaps O_2 will be generated. Studies indicate that radiolytically generated O_2 is consumed when organics are present.

Destruction of organic waste constituents may also reduce or eliminate gas retention in the waste, even if generated by water radiolysis or steel corrosion. The adsorption of organics on solid particles in the waste is believed to enhance the tendency for gas bubbles to adhere to the solids by lowering their wettability.

Unknowns: Removal of organics may lower the ability of gases to be retained in the waste, even if flammable gases continue to be generated by water radiolysis and/or steel corrosion. It is believed that the adsorption of organic molecules on solid particulates decreases the wettability of those solids, thereby enhancing the tendency for gas bubbles to adhere to the solids. If no organic molecules are present, gas bubbles may not stick to the particles, and be continuously released instead. This mechanism has not ben demonstrated conclusively in either synthetic or actual wastes, however.

Later waste processing activities may be adversely affected by the removal of organic constituents. In preliminary experiments, it was found that the solids in synthetic wastes that contained no organics formed a hard, monolithic mass after standing for a period of several hours, which could not be dispersed by stirring. In contrast, solids in synthetic wastes containing organics such as

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EDTA or HEDTA were easily resuspended by limited stirring. If the solids in the actual waste tank were to form a hard mass rather than remain as relatively easily dispersed particulates, later waste removal for processing would be more difficult.

Even if the rate of flammable gas generation is significantly reduced (e.g. a factor of 10), it is not known whether tank rollover events will continue to occur, albeit at a lower frequency.

5.1.3 Chemical Additives to Inhibit Specific Gas Generation Pathways

Description: Chemical additives may provide a means of reducing the rate at which gases are generated in Tank 101-SY. If the source of flammable gases is reduced, so too will be the frequency of release events. Appropriate additives have yet to be identified to reduce either hydrogen or N_2O, however.

Likelihood for Success: There is little likelihood of finding a chemical additive that can significantly reduce the rate of flammable gas generation, remain stable in a hostile environment, and not significantly complicate later waste processing activities.

It is quite unlikely that an additive will be found that successfully reduces the rate of hydrogen generation in the waste. The H_2 produced by radiolysis in homogeneous solutions is from reactions of primary radiolytic transients with the organic species in solution, which occur on a very rapid time scale. These can only be interfered with by substantial concentrations of additives that are highly reactive with the $H^{\cdot}$ atom. Unless the current NO_2^- concentration in Tank 101-SY is 3 to 10 times less than the assumed ≈3 M level, it is unlikely that any additive would decrease the H_2 yield substantially. The addition of sulfide was suggested; however, no significant effect on hydrogen formation has been found (Meisel et al. 1991b). Perchlorinated aromatics would reduce the H_2 yield by reacting with hydrogen atoms, thereby preventing them from reacting with the other organics, but this idea has not been tested to determine whether substantial reduction could be attained.

The effect of additives on the production of N_2O may be different in principle. Results from studies performed at ANL (Meisel et al. 1991b) indicate that reactions leading to N_2O involve reactions of secondary transient species derived from reactions of the primary species with the inorganic (NO_3^- and NO_2^-) and organic constituents. Because these reactions are slow, a small concentration of an additive could, in theory, interfere with them and substantially reduce the yield of N_2O; however, a search for such appropriate additives has not been made.

Unknowns: Specific chemical additives that can significantly reduce the kinetics of flammable gas generation have yet to be identified. These chemicals should be stable in a hostile environment, function effectively in low concentration, and not complicate later waste processing activities. It is not clear that chemical additives with such properties exist.

Further studies are required to establish the mechanisms by which flammable gases are produced. While good progress has been made, a discrepancy exists between volumes of gases actually generated in Tank 101-SY and volumes estimated as a result of synthetic waste studies. Before any chemicals are added to the tank, it is essential to have established the reaction pathways by which flammable gases are generated, to avoid creating an even larger problem.

Even if the rate of gas generation were to be significantly slowed, it is not known whether a slower rate of gas generation might not lead to larger gas releases when waste rollover events occur. If so, the flammability risk may actually be increased. Hence, the physical mechanism for gas retention and release must also be well understood.

5.1.4 Waste Dilution/Waste Concentration

Description: Dilution of the waste may result in a significant reduction in the rate at which flammable gas is generated. Substantial dilution of a solution having high NO_2^- and NO_3^- concentrations, for example, could reduce the radiolytic yield of hydrogen by ≈60 percent, as long as NO_2^- and NO_3^- concentrations remain high (Meisel et al. 1991a).

Dilution could also dissolve many of the solids. Gas retention via gas bubble adherence to solid particles could be much reduced or even eliminated as a result.

Concentration of the waste by evaporation of part of the water could change the radiolytic yields of H_2 and N_2O. Little can be said about this because the limiting behavior (radiolytic or thermal) for the case where all of the water is removed is not known.

Likelihood for Success: This effect will depend critically on the solubility of both organic and inorganic materials. If the organics present are in quantities above their solubility, dilution will not be useful. Gas retention mechanisms are not clearly understood at this time, so it is not known how dissolution of some of the solids will affect this aspect. Of course, dilution would require additional tank space, of which there is limited amounts at the present time.

Unknowns: The effect on thermally produced H_2 is not well known, although some indications exist in the work of Delegard (1980) and Jansky and Meissner (1984). Likewise, the effect on N_2O generation is not known. Of course, dilution would directly reduce the rate of radiolytic gas generation per unit volume of liquid.

Dilution by deionized water would also be accompanied by a decrease in the pH of the waste, which is expected to enhance the corrosion of the steel tank (Divine et al. 1985; Mackey and Divine 1986). In addition to possibly enhanced hydrogen generation rates, the integrity of the steel could be adversely affected. Dilution of the waste by a sodium hydroxide solution would, of course, maintain the pH of the waste.

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5.1.5 Lower pH

Description: Additions of chemicals to lower the pH of the waste may be a means of reducing the rate of flammable gas generation. The most probable method would be to add nitric acid in the form of a concentrated liquid or by sparging the waste with an acidic gas such as NO_2, SO_2, or CO_2.

Likelihood for Success: In earlier studies by Delegard (1980), the rate of flammable gas generation in synthetic wastes was found to depend directly on the hydroxide concentration in solution up to 1.5 M. If the free hydroxide concentration could be reduced, gas generation rates are expected to be lowered accordingly. However, lowering the pH is not expected to lower radiolytic yields, so gas generation should continue at a significant rate.

Unknowns: The role of hydroxide ion in the mechanism of flammable gas generation needs to be established. Associated questions include the quantity needed to yield a significant rate decrease.

Addition of nitric acid would lower the pH but would also add the oxidizing agent NO_3^- and evolve considerable heat. These effects could lead to increased reaction rates.

Addition of NO_2 would decrease the hydroxide concentration by a reaction that also forms NO_3^- and NO_2^-. Increasing the amounts of these two ions would not be favorable (Meisel et al. 1991a).

Addition of SO_2 would need to be considered very carefully. There is an extensive literature on the very complex reaction of sulfite with nitrite. Almost all the reduction products possible from nitrite (NO, N_2O, N_2, H_3N, $HONH_2$) have been observed depending on the conditions. Use of SO_2 to lower the pH would also have a major impact on the final treatment of this waste as the vitrification process can tolerate only small amounts of sulfate ion.

Addition of CO_2 would decrease the hydroxide concentration through formation of CO_3^{2-}. Sodium carbonate would probably precipitate.

Sufficient decrease of the pH with CO_2 would probably also lead to precipitation of Al(III) in some form. The precipitate could be some form of sodium aluminate, or could be $NaAl(OH)_2CO_3$ (the mineral Dawsonite). However, it is most likely that some form of $Al(OH)_3$ would precipitate, based on the phase diagram given by Barney (1976). The rheological properties of the slurry might change with increasing amounts of Al(III) solids.

The impact of lowered hydroxide content on steel corrosion reactions needs to be addressed. As reported by Divine et al. (1985), high hydroxide concentrations are needed to maintain steel passivity.

Lowered gas production rates may lower the frequency of gas retention/release events, but the hazards associated with each event may not change or even be increased.

5.1.6 Addition of a Mineral-Forming Agent

Description: Additions of a mineral-forming chemical such as silica may be effective in reducing the rate of flammable gas generation through precipitation of alumina compounds. In studies with simulated wastes, compositions containing no sodium aluminate did not generate flammable gases by thermally driven reactions (Delegard 1980).

Likelihood for Success: Hydrated silica is well-known to be effective in the precipitation of aluminum from solution. Addition of this material to the tank would be relatively simple, although extensive mixing would be required. However, the required volume of material probably will exceed the capacity of Tank 101-SY. Because it has not been conclusively established whether dissolved sodium aluminate is necessary in flammable gas generation, the probability for success is difficult to assess. Lowering of the solution concentration of aluminate ions is not expected to lower radiolytic yields, so gas generation should continue at a significant rate.

Unknowns: The role of dissolved aluminate ions in the generation of flammable gases needs to be determined under both thermal and radiolytic conditions. Not all studies have found that dissolved aluminum is needed to generate flammable gases.

5.1.7 Waste Cooling

Description: Cooling of the waste will lower the rates of chemical reactions responsible for the generation of flammable gases. Waste cooling may be accomplished by extending a heat exchanger below the liquid level, by cooling the inlet air into the plenum space, or by cooling the annular space between the tank walls by gas flow.

Likelihood for Success: The rate at which flammable gases are generated will be reduced by cooling. Waste cooling may also promote circulation in the tank, which could lessen the tendency for turnover events. However, cooling will also cause the volume of solids to increase, which may actually increase the severity of turnover events.

Unknowns: Key data needs include the temperature dependence of gas generation reactions and the temperature dependence of solubilities in this high ionic strength, highly alkaline solution.

The impact of waste cooling on gas retention and eventual release is not well understood. While the cooling of upper layers of the waste may promote circulation within the tank, this has not been demonstrated.

It must be shown that waste cooling does not cause flammable gases to buildup to an even higher level prior to release than is occurring now.

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5.2 Methods to Decrease Gas Retention

Four possible strategies for decreasing gas retention have been considered: 1) adding surfactant, 2) inert gas sparging of the non-convecting layer, 3) ultrasonic irradiation, and 4) heating the waste.

5.2.1 Surfactant Addition

Description: The addition of a surfactant is predicated on the hypothesis that the gas is being retained in the waste by surface tension forces. The supposition is that some or all of the solid particles have become coated with a hydrophobic layer, presumably some organic compound that enhances particle-gas bubble adhesion. The gas bubbles eventually grow large enough to float the slurry to the top where the gas is released, creating the gas release event. The added surfactant would act as a depressant to stop the bonding of the gas with the particles and thus allow the gas to be released continuously. The retention phase of the slurry growth cycle would thus be eliminated.

A second theory is that the surface activity of the sludge allows it to gel or "set up" at certain temperatures or concentrations and attain a strength that will trap generated gases. A surfactant might destroy the ability to "set" under the conditions in the tank and allow the gas to be released more or less continuously.

Usually, only a small amount of surfactant is required, perhaps less than 0.5 percent. The surfactant would be added to the tank and allowed to mix by virtue of natural convection, turnover, and diffusion, or perhaps be enhanced by mechanical mixing.

Likelihood for Success: Success of this mitigation approach depends on identification of an appropriate surfactant that could inhibit the retention of gases in the waste. Rather stringent properties are required, including the ability to counter the effects of rather large concentrations of organic waste components and good stability under harsh chemical and radiolytic conditions.

If an appropriate surfactant can be identified, the advantages are significant. The goal of this mitigation strategy is not to eliminate the source of flammable gases, but to prevent their buildup in the waste. Gases would be vented continuously rather than in bursts, thus reducing the flammability hazard to negligible levels. Implementation would require a minimum of equipment and could be quite simply accomplished.

Unknowns: The mechanism by which gases are retained in the waste has yet to be established conclusively.

A surfactant that will be sufficiently active in strongly alkaline solution of high ionic strength has yet to be identified. The surfactant must counter the effects of organic waste constituents, approximately 3 M in total organic carbon.

The surfactant must be stable in a relatively hostile chemical and radiolytic environment. Decomposition behavior needs to be assessed. Because it is expected that relatively small quantities of a surfactant will be required to produce desired results, it is not expected that decomposition reactions will contribute significantly to gas generation kinetics.

An assessment of the potential effects of surfactant addition on later waste processing and disposal activity is needed, although small additions would not be anticipated to cause any significant changes in the treatment of this waste prior to final disposal.

5.2.2 Inert Gas Sparging of the Non-Convecting Layer

Description: Sparging of the waste with an inert gas such as nitrogen or argon is a promising means of diluting flammable gases that are generated within the waste. To be applied continuously at the level of the non-convecting layer, believed to be the source of gases released during tank rollovers, this approach is much more efficient than gas dilution in the plenum space during release events (Reynolds in Strachan 1991). Gas bubbles introduced into the waste are expected to adhere to solid particles in response to a driving force to achieve an equilibrium solid/liquid contact angle (Bryan et al. 1992). Waste mixing in the non-convecting layer, such as jet pumping, would probably be required in combination with inert gas sparging to ensure an optimum distribution of inert gases. Rollovers are expected to occur with greater frequency due to inert gas additions, depending on the rate of inert gas sparging, and the average waste volume may be somewhat increased. Gas releases should be well below the flammability limit using this approach. The risk of implementation is considered low; no impact on later waste processing activities is anticipated unless perhaps the evaporation rate of water were to be substantially increased.

Likelihood of Success: This mitigation scheme has a high likelihood of significantly reducing the flammability hazard of gases released from Tank 101-SY if a means could be devised to uniformly sparge inert gases in the non-convecting layer. The only practical means identified to date is to inject the inert gas upstream of a mixing pump. With such an arrangement, one must then question whether or not the mixing alone, without the gas addition, might be adequate.

There are several attractive features with this mitigation strategy. A relatively simple concept, this scheme would add no chemicals that might become a source of gases. Cyclic rollover/gas release events should become more predictable, although more frequent and with much reduced hydrogen concentrations. If inert gas sparging operations were to be halted at some time after being implemented, no persistent effect on waste composition or behavior is expected. This mitigation scheme should not affect later waste processing operations.

Among the disadvantages of this approach, cyclic waste rollover/gas release events would become more frequent, but the flammability of released gases would be significantly reduced. The average waste volume will likely increase as a result of inert gas sparging, from increased gas bubble trapping by solid particles. In particular, the thickness of the floating crust will be increased.

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Waste mixing by jet pumping, probably required in combination with inert gas sparging, would increase the heat load in the tank, and may enhance gas generation reactions in other ways.

Unknowns: It has not yet been conclusively established that the mechanism of gas retention in Tank 101-SY is the adherence of gas bubbles to solid particles, held in the non-convecting layer by insufficient buoyancy to overcome the shear strength of the waste. Further studies are required to establish that mechanism.

It is not clear that inert gas sparging can be accomplished uniformly within the non-convecting layer, even in combination with waste mixing methods such as jet pumping. If areas of the non-convecting layer are not sparged with inert gases, pockets of flammable gases above the lower flammability limit may be released during rollover events. Development of uniform gas sparging/waste mixing methods in the non-convecting waste layer is needed.

It is not known whether energetic waste mixing activities may enhance the rate of flammable gas generation.

5.2.3 Ultrasonic Irradiation

Description: Ultrasonic irradiation has been suggested as a means of preventing the retention of gases in the non-convecting waste layer. Ultrasonic irradiation is expected to cause gas bubbles that are generated in the waste to be released continuously, thus preventing gas retention/release cycles, or to provide a means to control the gas release time and size .

Likelihood for Success: The ultrasonic irradiation approach seeks to prevent flammable gases from being retained in the waste, rather than to reduce the source of the gases. While ultrasonic irradiation has the potential for removing hydrogen bubbles from the surfaces of particles, this has not been demonstrated. Ultrasound could also increase H_2 production. It is well-known that ultrasonically induced chemistry can reproduce the chemistry that occurs in radiolysis by the production of $H^{\cdot}$ and $OH^{\cdot}$ radicals. The $H^{\cdot}$ formed could increase the production of H_2. Margulis (1974) has reported the formation of significant quantities of nitrite ions and hydrogen peroxide in ultrasonically irradiated nitrate solutions at fairly low intensities.

Unknowns: An important unknown associated with ultrasonic irradiation is the effect on gas generation. Uncertainties exist with regard to the minimum power density required to initiate chemical reactions by ultrasonic irradiation and how to deliver the ultrasound into the waste. If gas generation reactions are significantly accelerated by this approach, there may be no net gain.

It also has not been demonstrated to date that ultrasound is effective in breaking up gas bubble particle combinations, believed to be the means by which gases are retained in the waste.

5.2.4 Waste Heating

Waste heating to less than the boiling temperature at atmospheric pressure may be a means of lowering the retention of gases in the waste. Heating the waste is expected to dissolve some of the solids that are responsible for gas retention, resulting in a continuous rather than episodic release of flammable gases.

Likelihood for Success: Whether waste heating will substantially lower the extent of gas retention and episodic release is not certain. If shown to be effective, a number of engineering options are available to heat the waste above its present temperature. All of the waste mixing options, for example, will lead to some waste heating.

Unknown: It has not been established whether waste heating will indeed lessen the tendency for gas retention and eventual release in Tank 101-SY, let alone how much heating is required. In fact, Barney (1976) indicates that solubilities are not string functions of temperature between 20 and 80°C.

Solubilities of solid phases in the complex waste mixtures as a function of temperature are not well established in this complex waste mixture. Neither are the identity of solid phases responsible for gas retention.

The rate at which flammable gases are generated will increase substantially with increased temperature. The impact of increased gas production on retention and release is not known.

Waste heating will increase the rate of water evaporation. This could overload the current ventilation system.

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