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Hanford Tank Safety Project

Chemical and Physical Processes in Tank 241-SY-101: A Preliminary Report

February 1991

Work Supported by the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
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;
prices available from (615) 576-8401. FTS 626-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

On the cover:

An aerial photograph of the SY waste tank farm under construction (circa 1975) on the Hanford site in southeastern Washington State. Tank 241-SY-101 is the tank in the foreground to the right.

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A Preliminary
Report**

Tank Waste Science Panel

February 1991

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Pacific Northwest Laboratory
Richland, Washington 99352

Foreword

This document, as others that will follow, is being written to chronicle the progress in understanding the physical and chemical processes occurring in Tank 241-SY-101 that lead to gas generation and release. Because these documents are essentially progress reports, topics found to be important in subsequent work may be missing or not fully developed herein; in some cases, work presented here may even, at a later date, be found to be incorrect.

TANK WASTE SCIENCE PANEL

T. H. Dunning, Jr., Pacific Northwest Laboratory, Co-chairman
E. P. Horwitz, Argonne National Laboratory, Co-chairman
D. M. Strachan, Pacific Northwest Laboratory, Executive Secretary

E. C. Ashby, Georgia Institute of Technology
E. J. Hart, Private Consultant
D. A. Reynolds, Westinghouse Hanford Company
W. W. Schulz, Private Consultant
D. D. Siemer, Westinghouse Idaho National Engineering Company
W. J. Thomson, Washington State University
D. S. Trent, Pacific Northwest Laboratory
R. M. Wallace, Westinghouse Savannah River Company

Executive Summary

Over the years since 1942, chemical and radioactive wastes from the processes used to separate plutonium from uranium have been stored in underground tanks at the Hanford Site in south-central Washington. In March 1981 one of the double shell tanks, 241-SY-101 (called 101-SY), began venting large quantities of gas that continues to this day on an 8 to 15 week cycle. Subsequent analyses showed that the gases were composed primarily of hydrogen and nitrous oxide.

Because of the potential for explosion and attendant release of hazardous materials into the environment, Westinghouse Hanford Company and the U.S. Department of Energy realized the need for knowledge about the chemical and physical processes occurring in this tank that lead to generation of the gases and their subsequent release. In June 1990, the Pacific Northwest Laboratory,^(a) with funding from Westinghouse Hanford Company, began assembling a Tank Waste Science Panel of senior chemists, physicists, and engineers to develop a better understanding of the physical and chemical processes occurring in Tank 101-SY. This knowledge is necessary to provide a technically defensible basis for the safety analyses, which will allow the tank contents to be sampled, as well as for the future remediation of the tank and its contents.

Although plausible mechanisms for both gas generation and release were proposed, the Panel concluded that the data available on Tank 101-SY are insufficient to allow the critical chemical and physical processes giving rise to gas formation and release to be unambiguously identified. To provide the needed information the Panel recommends that:

1. Tank 101-SY be physically and chemically characterized as fully as possible and as expeditiously as safety considerations allow.
2. Laboratory studies and modeling efforts be undertaken to understand the chemical and physical processes involved in gas generation and release in Tank 101-SY.

The data needs from these two programs are outlined in this report; a detailed description of the second program is being prepared. Finally, the Panel recommends that:

3. No remediation steps be taken until there is a better understanding of the chemical and physical phenomena occurring in Tank 101-SY.

Premature remediation steps may only serve to compound the problem and create more severe safety problems than presently exist. Furthermore, such steps may change the chemical and physical characteristics of the tank and prevent a true understanding of the phenomena involved. As a consequence, similar problems in other tanks on the site may not be adequately addressed.

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1.0 Introduction

Over the years since 1942, liquid and solid wastes have been accumulated at the Hanford Site in south-central Washington from the various processes used to separate plutonium from uranium and the fission products in spent metallic uranium fuel. A significant quantity of these wastes was pumped to large underground storage tanks consisting of a single steel inner shell with a concrete outer shell. In the early 1970's, a decision was made to remove all liquid waste from these single shell tanks for storage in tanks with double shells. Before sending the wastes to the double shell tanks, the wastes were concentrated using crystallizer-evaporators. The product of this process was a thick slurry, termed "double shell slurry," consisting of a solution high in NaOH, NaNO_3 , NaNO_2 , NaAlO_2 , dissolved organic complexants (EDTA, HEDTA, NTA, HOAcOH, etc.),^(a) and minor concentrations of other salts (sulfates and phosphates). The slurry also contained solids consisting primarily of NaNO_3 , NaNO_2 , and NaAlO_2 . A less dense slurry, termed "complex concentrate," was produced as well; this waste contained about 6 M(olar) organic carbon, again from organic complexants, with salt concentrations that were not as high as in the "double shell slurry."

Shortly after approximately 250,000 gal of double shell slurry were transferred to Tank 241-SY-101 (hereafter referred to as Tank 101-SY) in April 1977, the waste volume began to increase. Later that year, complex concentrate was added to the tank. Three more waste additions were made between 1977 and 1980; the complete fill record of Tank 101-SY is given in Appendix A. During this time period, a crust developed on top of the liquid waste and grew in thickness. In March 1981, the first growth and collapse cycle of the wastes in Tank 101-SY was observed and these cycles have continued more or less regularly since that time, recurring in 8 to 15 weeks. Preliminary chemical analyses indicated that the gases that evolved during the waste volume collapse consisted of H_2 and N_2O , with (perhaps) some NH_3 .

Because of the potential for explosion and attendant release of hazardous materials into the environment, Westinghouse Hanford Company and the U.S. Department of Energy realized the need for knowledge about the chemical and physical processes occurring in this tank that lead to generation of the gases and their episodic release. This knowledge is necessary to provide a technically defensible basis for stabilization and mitigation of the present problem as well as future remediation of the tank and its contents.

In June 1990, the Pacific Northwest Laboratory, with support from Westinghouse Hanford Company, began assembling a panel of senior scientists and engineers to develop a better understanding of the processes involved in Tank 101-SY. The Tank Waste Science Panel includes scientists from the DOE laboratories, the various Westinghouse companies, and universities; it includes experts in theoretical chemistry, separations chemistry, organic chemistry, radiation chemistry, analytical chemistry, nuclear chemistry, chemical engineering, process chemistry, mechanical engineering, and fluid dynamics. Other experts will be added to the Panel as the situation dictates.

(a) The water-soluble chelating agents EDTA, HEDTA, NTA, etc., were used to separate plutonium from uranium and fission products in the various solvent extraction processes; HOAcOH was used as a buffering agent. The names for these chelators are EDTA, ethylenediaminetetraacetic acid; HEDTA N-(2-hydroxyethyl), ethylenediaminetriacetic acid; NTA, nitrilotriacetic acid; and HOAcOH, glycolic acid.

To accomplish its mission the Panel set forth four tasks:

1. Compile the data available on Tank 101-SY pertinent to the formation and subsequent release of the gases.
2. Analyze the available data on Tank 101-SY to establish, if possible, preliminary models of the chemical processes resulting in the formation of H_2 and N_2O and of the physical processes giving rise to the episodic release of the gases.
3. Formulate a research program to address the outstanding issues identified in the analysis of the data on Tank 101-SY.
4. Review the results of the research program on a periodic basis and recommend further work as required.

Task (1) has been completed and a report, "A Survey of Available Information on Gas Generation in Tank 101-SY," has been prepared (Strachan et al. 1990). The present report is the result of the analysis of the data contained in this survey as well as other data that have become available since the survey was completed: Task (2). A companion document is being prepared that outlines in detail the research program needed to address the open issues identified in this analysis: Task (3); a prerelease version of this document has been made available to Westinghouse Hanford Company in order to expedite the initiation of the proposed research activities. Hereafter, the Panel expects to convene every 3 to 6 months to review progress in the research program and to update this report as new knowledge is gained: Task (4).

In Sections 2.0 and 3.0, we review the data available on Tank 101-SY and present plausible mechanisms for both the physical processes leading to the episodic release of the gases (Section 2.0) and the chemical processes giving rise to the gases (Section 3.0). These models with their data needs were used to guide the development of the research programs. In Section 4.0 we present the general recommendations of the Panel, followed by a brief enumeration of the detailed needs in each of the research areas.

2.0 Physical Processes Involved in Gas Evolution

Developing a model of the physical processes leading to the episodic release of gases requires detailed data on the physical properties of the contents of Tank 101-SY, such as thermal conductivities, viscosities, and densities; see Appendix B. In 1986, the contents of the tank were sampled by punching a hole in the crust and inserting a pole with a bottle attached. When the bottle was at the desired sampling level, a rubber stopper was pulled from the bottle and the sample collected. In this manner, samples from three levels (top, 380 in.;^(a) middle, 175 in.; and bottom, 20 in.) were obtained (Mauss 1986; Reynolds 1990). These samples provided information on chemical composition, suspended solids, radionuclides, specific gravity, and viscosity.

The solution viscosities at various levels are different. At the mid-level the solution exhibits Newtonian behavior, i.e., the viscosity is independent of shear rate, whereas at the upper and lower levels the solutions exhibit slightly non-Newtonian rheological properties. The solution density was approximately 1.3 g/cm³ for the samples taken from the middle and upper part of the tank and 1.7 g/cm³ for the sample from the lower part of the tank. Although total organic content in the samples taken from Tank 101-SY has been determined, a detailed analysis of the organic constituents was not attempted. However, the genealogy of the organic species in Tank 101-SY is similar to that of the wastes in Tank 107-AN. Approximately 75% of the organics in Tank 107-AN have been speciated (Strachan et al. 1986). It is reasonable to expect the same organic species to be present in Tank 101-SY, albeit at different concentrations.

The above data, when combined with the following two observations, suggest a plausible model for the episodic gas release in Tank 101-SY. The two relevant observations are:

1. The estimated volume of gas released in the 19 April 1990 event, ~7000 ft³, was significantly larger than the observed decrease in the waste volume in the tank, ~3400 ft³.
2. The temperature profile shows a marked change upon gas release, the profile possessing a pronounced "knee" at ~75 in. from the bottom of the tank before the gas release and a nearly constant profile after the release; see Figure 2.1.

The first observation indicates that, prior to release, the gas in the tank is under pressure, suggesting that it accumulates and is stored near the bottom of the tank, probably trapped by the high concentration of solids found in that region (Mauss 1986). An overburden of 275 to 375 in. of liquid ($\rho = 1.3\text{--}1.7\text{ g/cm}^3$) would be required to provide the 2 atm of pressure needed to compress the gas by the observed factor. The second observation suggests that the gas is generated and stored in a nonconvecting slurry located from 50 to 200 in. above the bottom of the tank; see Figure 2.2. The temperature of this layer increases with time until the buoyancy forces, due to the accumulating gases, overcome the resistance of the slurry to flow. At that point, the waste in the tank "over-turns" and the gas is rapidly released. Thorough mixing of the two layers, induced by the "over-turn" results in the nearly vertical temperature profile observed after the gas release. A more detailed discussion of the model is given in Appendix B.

(a) All distances are measured relative to the bottom of the tank.

Figure 2.1. Temperature Profiles in Tank 101-SY Before and After the 19 April 1990 Gas Release

Estimates of the effective thermal conductivity of the nonconvecting slurry (see Appendix C) indicate that convection currents do exist in this layer but are increasingly hampered by the solids that settle from above after a gas release event, so that the effective thermal conductivity decreases with time. Formation of gas bubbles in this layer would also decrease the effective thermal conductivity. The observation that the frequency of the events is decreasing and the magnitude of the gas release is increasing supports the above hypothesis that gases are trapped as bubbles in the slurry near the bottom of the tank until they reach the volume (size) necessary for buoyancy to overcome the resistance of the slurry to gas flow. It is likely that the solids concentration in this region is slowly increasing with time, forcing the trapped gases to reach a larger volume before being released to the surface.

Finally, analysis of the temperature profiles suggests that there may be a region at the bottom of the tank which consists of a wet sludge that does not contribute substantially to either heat or gas release.

Figure 2.2. Cross Section of Tank 101-SY

The above discussion suggests that the crust does not play a major role in trapping the gases within the tank, although it may act to throttle the gas flow during a release, thereby diluting the H_2 and N_2O in the exhaust. The gases evolved during a release are apparently able to rapidly diffuse through the crust, vent through fissures in the crust, and/or flow between the crust and the tank wall. The latter two mechanisms are supported by pictures of the tank, e.g., the cracks and fissures evident in the crust and the "splashing" evident on the walls in the post-event photographs. The first mechanism was indirectly considered by Strachan (1975a,b), who measured the permeability of synthetic salt cake and synthetic salt cake treated with CO_2 . The measurements made on moist, drained salt cakes indicated that diffusion through the crust should be rapid. Furthermore, Strachan (1975a) measured a pore pressure^(a) of 0.05 atm for the synthetic salt cakes. This measurement would indicate that, before a gas could diffuse through the portion of the crust in contact with the liquid waste in Tank 101-SY, the capillary-held fluid would have to be displaced. Fluid displacement would hinder diffusion of the gases through the crust, at least initially. However, since the gases appear to originate near the bottom of the tank where the pressure is expected to be near 2 atm, the capillary pressure would not be expected to offer much resistance.

(a) The pore pressure is the pressure required to push capillary-held fluids from the pores of the material.

Finally, it should be emphasized that the quoted total quantities of gas released during an event are **only estimates**. The actual gas flow rates during a release have never been measured and the fact that the release is capable of pressurizing the dome space above the crust is an indication that the gas release rates are high enough to overcome the vapor removal by the tank ventilation system. This would indicate that the release rates during an event are greater than the 300 cfm provided by the tank ventilation system. Finally, it seems likely that quantities of H_2 and N_2O are being continuously released at concentrations below the detectability limits of the existing on-line instrumentation (see Section 3.0).

While the above analysis offers a plausible explanation of the physics of the gas release in Tank 101-SY, additional data are clearly needed to verify (or disprove) this hypothesis. Specific data needs are outlined in Section 4.1.

3.0 Radiolytic and Chemical Processes Involved in Gas Generation

Unraveling the chemical reactions that are occurring in Tank 101-SY will be a formidable task since many different inorganic and organic compounds are present. Some of these compounds are in solution, and some exist as solids in the crust and sludge phases of the mixture. Further complicating the chemistry is the fact that some of the compounds react in the absence of radioactive materials, although some reactions are certainly initiated by the radiation emanating from ^{137}Cs , ^{90}Sr , and other fission products that are present in Tank 101-SY. Indeed, some reactions may be catalyzed by a specific metal, either radioactive or non-radioactive, present in the mixture. In spite of the complexity of the system, the Panel believes that the chemical and/or radiolytic processes giving rise to gas production in Tank 101-SY can be deduced through a careful and systematic series of fundamental studies.

As noted above, both radiolytic processes and chemical processes may be contributing to gas generation in Tank 101-SY. In fact, hydrogen gas is produced as a normal product of the radiolysis of water. However, nitrates/nitrites, such as found in Tank 101-SY, are added to aqueous solutions of radioactive materials to suppress hydrogen generation. Important information on the chemical reactions likely to be occurring in Tank 101-SY in the absence of radiation is found in the laboratory studies of Delegard (1980), Jansky and Meissner (1983-4), and Gale (1983a,b). Delegard found that H_2 , N_2O , and N_2 are formed in synthetic slurries containing HEDTA. Following this work, Jansky and Meissner and Gale conducted additional studies of the slurry growth phenomenon in synthetic slurries. They found that glycolic acid (hydroxyacetic acid) also decomposes to yield H_2 and that soluble iron species can cause oxidative decomposition of both HEDTA and glycolic acid.

In the following two sections we present discussions of the mechanisms, both radiolytic and chemical, which may give rise to the generation of H_2 and N_2O in Tank 101-SY. However, gaps in our knowledge of radiolytic and chemical processes under the unusual conditions present in Tank 101-SY prevent definitive identification of the $\text{H}_2/\text{N}_2\text{O}$ sources. Specific data needs are outlined in Section 4.2.

3.1 Processes Involved in H_2 Production

It is likely that a significant fraction of the H_2 currently observed in the gas released from Tank 101-SY results from radiolytic decomposition of water and/or organic material. Calculation of the quantity of H_2 produced from γ -radiolysis by ^{137}Cs is summarized in Table 3.1; the quantity of H_2 that would be produced by ^{90}Sr is an order of magnitude smaller and, thus, is neglected here. The initial loading of ^{137}Cs was taken from the data given in Table 1 of the Survey (Strachan et al. 1990) and corrected for depletion by radioactive decay. Approximately 37 moles of H_2 would need to be produced each day to account for the volume of gas released in the 19 April 1990 event.^(a)

(a) This must be considered a lower bound for it is likely that H_2 is produced throughout the aqueous phase in Tank 101-SY, but the H_2 formed in the convecting layer is continuously released at concentrations too low to detect with the instrumentation presently available on Tank 101-SY.

Table 3.1. Production of Hydrogen in Tank 101-SY by Radiolysis of Water**Radiation Source**

^{137}Cs	Activity	0.818 Ci/L
	Power	0.005 W/Ci
		0.00409 W/L
	Total Power	5.62×10^4 Btu/h

Production of H_2

$G(\text{H}_2)$	Moles H_2 /Day	Comments
0.06	8.85	Nitrate/nitrite solutions
0.46	67.8	Pure water

Calculation of the exact amount of hydrogen that would be generated by radiolytic processes is not possible because the effective $G(\text{H}_2)$ -values^(a) are not known for the liquids and sludges present in Tank 101-SY. As can be seen in Table 3.1, if the tank were composed of pure water, radiolysis of water could account for essentially all of the H_2 produced. However, the aqueous phases in Tank 101-SY contain molar quantities of nitrates/nitrites which reduce the effective G-value from 0.46 to 0.06. This decreases the volume of gas produced to a fraction of that observed. However, the effect of the organic species (HEDTA, EDTA, etc.) in the tank on the effective G-value of the salt solutions is unknown, although experience at the Savannah River Site suggests that the presence of certain organic species can profoundly affect $G(\text{H}_2)$ for a solution containing NO_3^- and/or NO_2^- . Hydrogen generation in Tank 101-SY has also been considered by Gough (1990); he concluded that "a conservative analysis cannot rule out significant gas generation by radiolysis."

Although definitive estimates of the amount of H_2 produced by radiolysis are not possible at this time, it is clear that a complete understanding of gas generation occurring in Tank 101-SY has to take into account the radiolytic decomposition of water and other species present, particularly the organics. In fact, from the data of Delegard (1980), the rate of H_2 generation from the purely chemical oxidation of HEDTA is estimated to be only one-sixth of the rate of H_2 generation actually observed in Tank 101-SY.

A possible chemical mechanism for the production of H_2 in Tank 101-SY is illustrated in Figure 3.1. It involves a chemical reaction similar to the Oppenauer oxidation reaction (Djerassi 1951; Warnhoff 1963). The Oppenauer oxidation reaction converts an alcohol into an aldehyde or ketone utilizing an aluminum alkoxide. The mechanism has been postulated to proceed via formation of an intermediate hydroxyaluminum-alcohol complex which, in the presence of water, decomposes to yield an aldehyde and H_2 . This concept can be applied to conversion of HEDTA to EDTA (the intermediate aldehyde would not be stable), accounting for the formation of H_2 in Tank 101-SY as illustrated in Figure 3.1.

(a) The G-value is the number of molecules of gas produced per 100 eV of radiative energy; it is an empirically determined quantity.

Figure 3.1. Detailed Mechanism for the Oppenauer Oxidation of HEDTA to EDTA

3.2 Processes Involved in N_2O Production

Although nitrous oxide and nitrite ion are the products of radiolysis of nitric oxide in aqueous solution, there is no known mechanism that produces N_2O in irradiated, concentrated solutions containing only nitrate and nitrite. However, Hart (1990) has found that, in the presence of EDTA and citric acid, N_2O forms radiolytically in yields an order of magnitude greater than H_2 . The exact mechanism leading to the production of N_2O is not known. Appendix C lists the principal reactions believed to take place in the strongly basic waste solutions. As shown there, the powerful oxidizers N_2O_4 and N_2O_3 are formed. A possible radiation-induced reaction is:

However, even if energetically allowed, the rate of this reaction has yet to be measured.

Identifying chemical sources of N_2O has also proven difficult. In the series NH_3 , N_2 , N_2O , NO_2^- , and NO_3^- , the oxidation state of nitrogen progresses from -3 to 5. Since all of these nitrogenous species have been observed either in solution or in the off-gas from Tank 101-SY, it is clear that several oxidation reactions are occurring. It remains to be determined which might be involved in the production of N_2O .

As noted above, Delegard (1980) has shown that N_2O is formed in the absence of radiation in solutions containing NaOH , NaNO_3 , NaNO_2 , NaAlO_2 and HEDTA. Since NO_3^- cannot be

N_2O , NO_3^- and NO_2^- must form complexes that facilitate reduction. It is hypothesized, therefore, that NO_3^- and NO_2^- are complexed to $\text{NaAl}(\text{OH})_4$ ($\text{NaAlO}_2 \cdot 2\text{H}_2\text{O}$) in order to 1) provide the optimal configuration for reduction of NO_3^- and 2) provide an intramolecular pathway for the electron transfer. The reaction leading to the proposed complex is:

HEDTA then reacts with this nitro-hydroxyaluminum complex to form the intermediate involved in the electron transfer process. The structure of the key intermediate involving HEDTA is indicated below:

This configuration should facilitate electron transfer from the nitrogen or oxygen atoms to the NO_3^- group, thereby initiating the complex series of reactions leading to N_2O , CO_2 , and ED3A.^(a)

Finally, there is no evidence that the crust at the top of Tank 101-SY plays a major role in the formation of either H_2 or N_2O . Nevertheless, analyses of the solids in the "top" sample from Tank 101-SY (Mauss 1986) suggest the presence of organic material in the crust as well as the expected carbonates, nitrates, etc. Clearly, there is a need to determine the chemical composition of the crust to settle this issue as well as to address safety concerns.

(a) Ethylenediaminetriacetic acid (ED3A) is an organic degradation product detected in Tank 107-AN (Strachan et al. 1986).

4.0 Recommendations

As is clear from the discussions in the preceding two sections, the data available on Tank 101-SY, including the laboratory studies of synthetic slurries, are insufficient to allow the critical chemical and physical processes giving rise to gas formation and release to be unambiguously identified. This knowledge is necessary to provide a technically defensible basis for the safety analysis needed to permit full characterization of the tank, for stabilization and mitigation of the present problem, and for eventual remediation of the tank contents. To provide the needed information the Waste Tank Science Panel recommends that:

Tank 101-SY be physically and chemically characterized as fully as possible and as expeditiously as safety considerations allow. These data are needed to guide the laboratory and modeling efforts necessary to understand the complex physical and chemical processes involved in the tank and to confirm the results of these efforts. It is, however, not sufficient to obtain data from only a single location in the tank; e.g., there is only a single thermocouple tree in Tank 101-SY and the present chemical sampling protocol calls for a single top-to-bottom sample in 19 separate segments. To be statistically significant, data must be collected from a number of different locations in the tank.

Laboratory studies and modeling efforts be undertaken to understand the chemical and physical processes involved in the gas generation and release in Tank 101-SY. It is highly unlikely that the key chemical and physical processes operative in the tank will be determined solely from the tank characterization effort. The situation in Tank 101-SY is far too complex to be effectively addressed by observation alone. An aggressive experimental and computational program must be established to determine the key processes occurring in this tank in a timely fashion.

In addition, the Panel recommends:

No remediation steps be taken until there is a better understanding of the chemical and physical phenomena connected with gas generation and release in Tank 101-SY. Premature remediation steps may only serve to compound the problem and create more severe safety problems than presently exist. For example, if the crust does indeed act as a throttle on the gas release, elimination of the crust could well result in higher concentrations of H_2 and N_2O being released into the head space in tank, increasing the risk of reaching a flammable or explosive mixture. Premature remediation procedures that change the chemical and physical characteristics of the tank could also preclude an understanding of the phenomena involved in Tank 101-SY, and thus delay the solution of similar problems in other tanks on the site.

Detailed data needs are presented in the following two sections. A companion document is being prepared that outlines in detail the research program needed to address the open issues identified in the present analysis.

4.1 Physical Processes Involved in Gas Release

The present data base is too meager to allow definitive answers about the physical processes involved in the episodic gas releases in Tank 101-SY. The Waste Tank Science Panel

recommends that the following actions (listed in order of priority) be taken to provide the scientific data base needed to elucidate the physical processes which lead to the periodic release of H_2 and N_2O .

1. It is essential to accurately measure the *dynamic flow rates* during a gas release event. To date, flow rates in the tank ventilation system have been estimated on the basis of the steady-state flow rates during normal operation. Installation of a centerline pitot tube, together with a knowledge of the usual velocity profile in the riser, would dramatically improve the flow rate estimates.
2. It is essential that suitable instrumentation be installed to permit frequent measurements of the concentrations of H_2 , N_2O , and other important gases in the vent line *between* the release events.
3. It is important to have a knowledge of the *concentrations and particle sizes of the suspended solids* in the slurry. These data would permit better estimates of the settling rates to corroborate the changing gas-release patterns as well as to understand the rheology of the slurry and to verify that the solids are capable of retaining the bubbles until they reach a critical size.
4. It is important to determine the permeability of the crust. In the absence of bona fide permeability measurements, measurements of the *pore size distributions* are needed. Injection of helium under the crust is suggested as one means of obtaining qualitative information on the permeability of the crust *in situ*. In addition, it is recommended that instrumentation be installed so that dynamic pressure measurements can be taken beneath the crust. It is possible that the existing air lance in Tank 101-SY can be modified to obtain these, as well as other, measurements.
5. It is recommended that a data logger be installed on Tank 101-SY so that the temperature profiles can be recorded in a more timely fashion before, during, and after an event. These data can be used in conjunction with the mathematical simulations to help predict the occurrence of future events.

The Tank Waste Science Panel also recommends that modeling efforts and laboratory studies be undertaken to better understand the physics involved in the gas release from Tank 101-SY. The modeling effort should include:

1. Simulation of the unsteady-state temperature profiles as they develop between events. This will provide verification of the "over-turn" hypothesis and indicate what remediation steps (e.g., pumping, mixing, etc.) could be undertaken to reduce or eliminate the episodic nature of the events. These simulations, as well as those in 2 and 3 below, will require detailed information on the rheological properties of the material in the tank, along with the physical properties of the crust.
2. Simulation of the dynamic pressurization and flow rates in the tank during an event. This will allow the throttling effect of the crust to be evaluated, lead to refined estimates of the magnitude of the gas released during an event, corroborate estimates of the permeability of the crust, and allow for an assessment of the safety risks associated with the release of H_2 and N_2O , i.e., the role of dilution of the released gases with the intake air.

3. Simulation of the thermal hydraulics associated with bubble trapping and eventual release. This model will allow for better predictions of the gas release events and could suggest remedial actions.

Finally, laboratory studies need to be undertaken to simulate the entire phenomenon of "over-turn." For example, a fundamental question to be answered is whether the gas release is initiated as a result of bubbles attaining a critical size or as a result of the nonconvecting slurry attaining a critical density. This will require an experimental apparatus in which gases can be generated at an appropriate (i.e., slow) rate and in a model slurry that approximates, as closely as possible, the situation at the bottom of Tank 101-SY. In order to do this properly, an experimental apparatus must be developed that is both safe and credible. Ideally, it would be possible to answer the "what if" questions which will invariably arise out of safety considerations with this apparatus. Therefore, it must be flexible with respect to operating capabilities and be properly instrumented. Because of these requirements, it is important that this **not be done using a conventional pilot plant approach**, but rather, by research engineers using an appropriately sized apparatus.

4.2 Chemical Processes Involved in Gas Generation

Our knowledge of the chemical reactions occurring in Tank 101-SY is also very limited. The Tank Waste Science Panel recommends that the following actions be taken to obtain the data base needed to elucidate the chemistry involved in the generation of H_2 and N_2O . All of these recommendations are considered to be of high priority.

1. Organize and conduct a comprehensive suite of experiments with various simulated "complex concentrate"-type wastes to obtain a sufficiently detailed understanding of the chemical reactions that lead to the production of H_2 , N_2O , and other gases in such wastes. The experiments should include:
 - identification of critical reactants
 - determination of threshold reactant concentrations, if any
 - determination of the reaction stoichiometries, including individual gas generation rates
 - determination of the reaction energetics.

This will require isotopic labeling studies as well as spectroscopic identification of the key intermediates in situ, e.g., by NMR techniques.

2. Determine the concentrations of complexants:
 - HEDTA
 - EDTA
 - glycolic acid

In samples from Tank 101-SY. To perform such analyses, action must be taken to provide (or acquire) the necessary analytical instrumentation, procedures, and analyses.

3. Archive, if necessary, and analyze as quickly as possible samples of wastes from Tank 101-SY for:
 - citric acid
 - oxalic acid
 - degradation products of HEDTA, EDTA, glycolic acid, and citrate.
4. Obtain and analyze representative samples of the "crust" material in Tank 101-SY. The suite of chemical analyses should include not only conventional wet chemistry analyses for cations and anions, but also specialized (e.g., SEM, X-ray diffraction, optical microscopic, microprobe, etc.) microstructural analyses. Sufficient analytical work should be performed to establish the amount and identity of each chemical compound present in the solid crust.
5. Develop a phased experimental plan for establishing what role, if any, radiation plays in the generation of H_2 and N_2O from various organic compounds present in Tank 101-SY. This plan should be scoped to take into account information which will be acquired when Recommendation 2, concerning the nature and concentration of the organic compounds present in Tank 101-SY, is completed.

Appendix A

Fill Record for Tank 101-SY

Appendix A

Fill Record for Tank 101-SY

	Waste 1	Waste 2	Waste 3	Waste 4	Waste 5
Date	Apr 1977	Nov 1977	Jun 1978	Aug 1978	Oct 1980
Volume ^(a)	275.5	365.6	133.3	59.5	231.3
NaOH ^(b)	3.02	2.10	2.11	4.50	3.76
NaAlO ₂	1.46	0.994	0.409	3.28	3.59
NaNO ₂	2.72	1.86	1.10	5.23	5.47
NaNO ₃	2.72	3.44	3.92	4.88	4.95
Na ₂ CO ₃	0.8	0.474	0.932	0.002	0.14
Na ₂ SO ₄	0.07	0.065	0.07	0.805	0.07
Na ₃ PO ₄	0.152	0.148	0.066	0.123	0.30
TOC ^(c)	14.52	26.32	34.27	26.6	18.01
⁹⁰ Sr ^(d)	0.013	0.16	0.074	0.45	0.005
¹³⁷ Cs ^(d)	0.74	1.76	0.28	0.28	1.11

(a) Volumes are in 1000's of gallons.

(b) Concentrations are in moles per liter.

(c) Total organic carbon (TOC) values are in grams of carbon per liter.

(d) Radionuclide concentrations are in curies per liter.

Appendix B

Preliminary Heat Transfer Simulations for Tank 101-SY

Appendix B

Preliminary Heat Transfer Simulations for Tank 101-SY

D. S. Trent

Knowledge of heat transfer in Tank 101-SY is critical to understanding the physical processes leading to a gas release event. Unfortunately, little is known of the physical properties of the waste materials in Tank 101-SY. We performed a number of computer simulations to identify those properties critical to understanding heat transfer in the waste tanks. However, the studies were based on limited information of questionable accuracy and involve a number of engineering assumptions. In addition, the computer model needs further improvement; e.g., the present study assumed that the side of the tank is adiabatic when, in fact, there will be a substantial amount of heat transferred to the annulus and surrounding soil. Thus, the results and conclusions are, at best, tentative.

Comments on Temperature Profile Measurements and Stratification of the Wastes

Temperature data for Tank 101-SY are obtained from a thermocouple (TC) "tree" that extends from the waste tank top to bottom, yielding measurements approximately every 2 ft of depth. Unfortunately, there is only one thermocouple tree in place, which is located approximately halfway from the tank centerline to the tank inner wall. This single-point vertical temperature profile may not be representative of the overall tank. Additional questions concern the TC's calibration and read-out accuracy, and the current vertical orientation of the TC tree. The conclusions drawn below, as well as the computer simulations, are subject to these contingencies.

The temperature profile measured on 16 April 1990, see Figure B.1, suggests that the waste material in Tank 101-SY is stratified. The linear temperature profile at the top and bottom of the tank indicates heat conduction in an immobile medium without substantial heat generation. The parabolic temperature profile near the bottom of the tank indicates conduction in a heat-generating, essentially immobile medium. Finally, the vertical temperature profile near the top of the tank suggests a medium well stirred by natural convection (thermal conductivity alone cannot account for the even temperature distribution - the required conductivity constant would be unreasonably large).

Observing only the thermal data leads to the conclusion that a rapid transient event - the gas release - took place between 16 April 1990 and 23 April 1990 which mixed the material vertically, dramatically changing the temperature profile. The profile measured on 6 July 1990 indicates a slow return to the condition that was observed prior to the gas release episode.

These observations suggest that

1. The top layer, a "crust," is 4 to 5 ft thick.
2. The liquid layer, underlying the crust, is about 14 ft deep and is in continual motion resulting from a "gentle" natural convection process. Heat generation in this region will not change the observed or computed temperature profiles appreciably.

Figure B.1. Temperature Data for Tank 101-SY

3. Below the liquid region is a layer of slurry material that appears to be about 11 ft thick, which is immobile during the period preceding the gas release event but is dramatically mobilized during the event. Some of the heat generated in this layer is effectively "trapped" until the gas release event.
4. The bottom layer, which is possibly 3 to 4 ft thick, appears to be a denser sludge that behaves differently from the slurry layer above. This material does not seem to become mobilized to any great extent during the gas release event. The positive temperature gradient in this layer indicates that heat is being lost to the tank bottom structure, ventilation ducts, and underlying soil. After the gas release event, this layer cools because of the reduced temperature of the overlying material or because it was disturbed by the event. Cooling apparently continues to the point where heat from the warmer tank bottom structure flows back to the bottom layer.

Preliminary Computer Simulation of Heat Transfer in Tank 101-SY

Based on the above data, a two-dimensional simulation model was constructed with material regions as illustrated in Figure B.2. Cylindrical coordinates were used to solve the heat transfer equations for a 30 degree segment of the tank. The boundary temperature at the

Figure B.2. The Two-Dimensional Simulation Model for Tank 101-SY

top surface of the waste crust was taken to be the measured value, the radial boundary condition at the tank wall was assumed adiabatic, and the model extended approximately 30 ft into the soil below the tank where a fixed temperature boundary of 55 °F was assumed.

For quasi-steady state simulation of heat transfer, only the thermal conductivity and volumetric heat generation rate are needed for the immobile slurry. In the liquid region, which we expect to be in motion, estimates of the density and the density changes with temperature

are needed in addition to thermal conductivity, viscosity, and specific heat. The only data available are the liquid density and viscosity (Mauss 1986). The variation of these quantities with temperature is unknown.

Accurate estimates of the physical properties of the liquid region are less important than accurate estimates of the thermal conductivity and volumetric heat generation rate in the immobile slurry. Natural convection is a very efficient heat transport mechanism compared with conduction in the immobile slurry. Thus, as long as natural convection in the liquid region is sufficient to maintain the near vertical temperature profile, the temperature distribution in the tank during quasi-steady state conditions will be governed by the thermal conductivity and volumetric heat generation in the immobile slurry. This will be the case only for quasi-steady state conditions. During and immediately following the gas release event, thermal hydraulic processes will govern physical behavior of the tank.

The simulations were performed with the TEMPEST computer code (Trent and Eyler 1990) using the finite-difference model illustrated in Figure B.2 (including minor changes in the layer dimensions). Results for two of these cases, with the thermal conductivities listed in Table B.1, are illustrated in Figures B.3 and B.4. In case 1, a heat generation rate of 40,000 Btu/hr was used and heat generation was assumed to be distributed uniformly in the immobile slurry region. In case 2, heat generation was distributed in the liquid (27,200 Btu/hr) and in the immobile slurry (12,800 Btu/hr). Thus, for quasi-steady state conditions, both the distribution of heat generation and values of the material thermal conductivity play important roles in establishing the tank thermal regime.

Preliminary Conclusions

The scoping simulations outlined above provide a basis for several preliminary conclusions:

1. Assumptions concerning the material layer configuration (crust, liquid, slurry, and sludge), physical state, and layer thicknesses appear to be reasonable. If this configuration was significantly in error, the thermal measurements could not have been reproduced by computer simulation using plausible estimates of the material properties.
2. Simulation of the thermal regime during quasi-steady state conditions, along with estimates of average material properties, could be improved significantly if the distribution and power of the heat-generating material could be accurately defined.
3. The simulations and temperature measurements suggest that a dense layer of possibly immobile or nearly immobile sludge exists at the bottom of the tank which is perhaps 3 to 4 ft thick. This layer does not appear to participate to any large degree in the dynamics of the gas release event.
4. Computer simulations can greatly improve our understanding of the tank dynamics and thermodynamics and will be of significant benefit for assessment of future remedial action(s). However, this will not only require model improvements, but also a more complete data base including such items as transport properties, thermodynamic properties, solids distribution/particle sizes, and heat generation rates for the materials in the waste tanks.

Table B.1. Thermal Conductivity of Layers in Tank 101-SY for Simulation Studies

Material	Thermal Conductivity, κ (Btu/°F·ft·hr)	
	Case 1	Case 2
Crust	1.5	0.93
Slurry	3.2	0.6
Sludge	0.6	0.6
Concrete	0.54	0.54
Soil	0.20	0.20

Figure B.3. Comparison of Measured and Calculated Temperature Profiles for Tank 101-SY (Case 1)

Figure B.4. Calculated Vertical Temperature Profile for Tank 101-SY (Case 2)

Appendix C

Preliminary Analysis of Temperature Profiles in Tank 101-SY

Appendix C

Preliminary Analysis of Temperature Profiles in Tank 101-SY

W. J. Thomson

Figure 2.1 of the main text shows the temperature profiles measured in Tank 101-SY in April 1990, just before and after the event of 19 April 1990. As noted previously, the material in the tank can be grouped into four distinct layers: **I**, from the bottom of the tank (0 in.) to 50 in., characterized by a linear temperature profile; **II**, from 50 to 200 in., characterized by a parabolic temperature profile; **III**, from 200 to 360 in., characterized by a flat temperature profile; and **IV**, from 360 to 410 in., characterized by a linear temperature profile. As previously noted by Reynolds (1990), flat profiles imply efficient heat transfer (e.g., by convection), while linear or parabolic profiles indicate conduction without and with an energy source. Thus, we may assume that Layer **III** is dominated by convection, Layers **I** and **IV** are conductive regions without an energy source, and Layer **II** is a conductive region with an energy source (see also the discussion in Appendix B).

Layer **IV** is undoubtedly the crust layer. In view of previous measurements of the properties of the bottom of the tank (Mauss 1986), Layer **I** is likely to be a wetted sludge. It is doubtful whether **I** plays a significant part in the gas release event since the temperature at the very bottom of the tank does not change significantly after an event. Consequently, Layer **II** was analyzed in an effort to estimate its "effective" thermal conductivity. Figure C.1 shows the parameters defining the layer.

Referring to Figure C.1, if we assume steady state, one-dimensional conduction, a uniform generation of heat released, Q_v , a constant flux boundary condition at $z = 0$ (q_1), and a constant temperature boundary condition at $z = l_1$ (T_3), then the applicable differential equation is

$$\frac{d^2T}{dz^2} + \frac{Q_v}{k_{eff}} = 0$$

Figure C.1. Parameters Defining Layer II

which can be solved in dimensionless form, together with the two boundary conditions to give

$$\Theta = -1/2 \Lambda_1 (\eta^2 - 1) - \Lambda_2 (\eta - 1)$$

where

$$\Theta = \frac{(T - T_3)}{T_3}, \quad \eta = \frac{z}{l_1},$$

$$\Lambda_1 = \frac{Q_v l_1^2}{k_{eff} T_3} \quad \text{and} \quad \Lambda_2 = -\frac{q_1 l_1}{k_{eff} T_3}$$

In these equations, q_1 , T_3 , and k_{eff} are the constant heat flux at $\eta = 0$, the temperature in Layer III, and the effective thermal conductivity of Layer II, respectively. The magnitude of the heat lost to Layer I relative to that being generated by radioactive decay can be estimated by solving for the point where the temperature is a maximum, $dT/d\eta = 0$, which gives

$$\eta_M = \frac{\Lambda_1}{\Lambda_2} = -\frac{q_1}{Q_v l_1}$$

Since the point at which the temperature is a maximum is very close to Layer I, we can conclude that very little heat is being lost to the bottom of the tank.

Assuming that **all** of the heat released, ~50,000 Btu/hr (James and Sullaway 1988), is generated uniformly throughout the tank, then one-half is delivered to Layer III at $\eta = 1$ and we can numerically differentiate the measured temperature gradient at that point and solve for k_{eff}

$$k_{eff} \frac{\Delta T}{\Delta z} = \frac{25,000}{\frac{\pi}{4} (75)^2}$$

The measured gradient is ~2.9 deg/ft, so

$$k_{eff} = 2.0 \frac{\text{Btu}}{\text{ft} \cdot ^\circ\text{F} \cdot \text{hr}}$$

Since values of the thermal conductivity of brines are on the order of 0.4 Btu/ft•F•hr and sodium aluminate solids would not have substantially higher values than this, we can conclude that the major mode of energy transport in Layer II is by "hampered convection." That is, natural convection currents are hampered by the presence of suspended solids. The temperature profile in this region probably changes with time because the solids concentration increases as they settle from above, which further reduces the convection currents. This is substantiated by the fact that a similar estimate of k_{eff} immediately *after* a gas release gives a value of approximately 30 Btu/ft•F•hr, a value indicative of thermal convection.

Appendix D

Chemical Reactions in Irradiated Alkaline $\text{NO}_3^-/\text{NO}_2^-$ Solutions

Appendix D

Chemical Reactions in Irradiated Alkaline $\text{NO}_3^-/\text{NO}_2^-$ Solutions

E. J. Hart

In molar solutions of nitrate and nitrite ions above pH 14, the principal reactions resulting from radiolysis are as follows:

Number	Reaction	Reaction Rate $k \text{ (M}^{-1}\text{s}^{-1}\text{)}$
(R1)	$\text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$	1.4×10^{10}
(R2)	$e_{\text{aq}}^- + e_{\text{aq}}^- \xrightarrow{2\text{H}_2\text{O}} 2\text{OH}^- + \text{H}_2$	3.0×10^9
(R3)	$e_{\text{aq}}^- + \text{O}^- \xrightarrow{\text{H}_2\text{O}} 2\text{OH}^-$	1.5×10^{10}
(R4)	$e_{\text{aq}}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{HO}_2^- + \text{OH}^-$	1.2×10^{10}
(R5)	$e_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{O}^- + \text{OH}^-$	3.5×10^9
(R6)	$e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^-$	2.0×10^{10}
(R7)	$\text{O}^- + \text{O}^- \rightarrow \text{O}_2^{=}$	9.0×10^8
(R8)	$\text{O}^- + \text{O}_2^- \rightarrow \text{O}_3^{=}$	3.5×10^8
(R9)	$\text{O}^- + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}_2^-$	3.5×10^8
(R10)	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^-$	2.0×10^6
(R11)	$\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$	2.0×10^8
(R12)	$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$	5.0×10^8
(R13)	$\text{HO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^-$	5.7×10^4
(R14)	$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	2.6×10^{-5}
(R15)	$\text{H}_2\text{O} + \text{O}_2^{=} \rightarrow \text{HO}_2^- + \text{OH}^-$	1.0×10^8

(R16)	$\text{H}_2\text{O} + \text{O}_3^- \rightarrow \text{O}_2 + 2\text{OH}^-$	1.0×10^8
(R17)	$\text{H}_2\text{O} + \text{O}^- \rightarrow 2\text{OH}^-$	1.0×10^8
(R18)	$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	1.4×10^{11}
(R19)	$\text{O}^- + \text{NO}_2^- \rightarrow \text{NO}_2 + \text{O}^-$	3.6×10^8
(R20)	$e_{\text{aq}}^- + \text{NO}_3^- \rightarrow \text{NO}_3^-$	9.7×10^9
(R21)	$e_{\text{aq}}^- + \text{NO}_2^- \rightarrow \text{NO}_2^-$	4.1×10^9
(R22)	$\text{O}_2^- + \text{NO}_2^- \rightarrow \text{NO}_2^- + \text{O}_2$	5.0×10^6
(R23)	$\text{O}_2 + \text{NO}_3^- \rightarrow \text{NO}_3^- + \text{O}_2$	2.0×10^8
(R24)	$\text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{NO}_2 + 2\text{OH}^-$	1.0×10^3
(R25)	$\text{H}_2\text{O} + \text{NO}_2^- \rightarrow \text{NO} + 2\text{OH}^-$	1.0×10^3
(R26)	$\text{H}_2\text{O} + \text{N}_2\text{O}_4 \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+$	1.1×10^3
(R27)	$\text{H}_2\text{O} + \text{N}_2\text{O}_3 \rightarrow 2\text{NO}_2^- + 2\text{H}^+$	5.3×10^2
(R28)	$\text{NO}_2 + \text{NO} \rightarrow \text{N}_2\text{O}_3$	1.1×10^9
(R29)	$\text{N}_2\text{O}_3 \rightarrow \text{NO}_2 + \text{NO}$	2.2×10^4
(R30)	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	4.6×10^8
(R31)	$\text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO}_2$	7.0×10^3
(R32)	$\text{O} + \text{OH}^- \rightarrow \text{HO}_2^-$	5.0×10^4
(R33)	$\text{O} + \text{NO}_2^- \rightarrow \text{NO}_3^-$	2.0×10^4
(R34)	$\text{HO}_2^- + \text{R}^\bullet \rightarrow \text{RO}^\bullet + \text{OH}^-$	$\sim 1.0 \times 10^1$

where $\text{R}^\bullet$ is any organic free radical. H_2 , HO_2^- , O_2 and equilibrium NO_2 , N_2O_3 and N_2O_4 are the products of the e_{aq}^- and O^- reactions. However, since N_2O_3 and N_2O_4 reform NO_3^- and NO_2^- , H_2 , HO_2^- , and O_2 are the only stable products left if (R26) and (R27) go to completion. Even the O_2^- and O_2 react in the absence of organic compounds so only the H_2 remains (Hart 1990). In the presence of organic compounds, HO_2^- is consumed in Reaction 34.

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