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Hanford Tank Safety Project

Minutes of the Tank Waste Science Panel Meeting September 13-14, 1990

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,
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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.

**Minutes of the
Tank Waste Science Panel Meeting
September 13-14, 1990**

Compiled by
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February 1991

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

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Preface

This document contains the minutes for the September 13-14, 1990 meeting of the Tank Waste Science Panel. The objective of this document is to provide an accurate recapitulation of the proceedings so that the diverse views of the Science Panel members can be documented. The content of this document has been reviewed by each of the Panel members to assure its accuracy. Editorial comments are clearly marked in the text and are provided only for clarification. Because of this philosophy, this document may contain provocative statements, opinions which may run counter to facts, facts which are presented out of the context of the tank chemistry and physics, and information that may later be shown as incorrect. These meeting minutes, like the previous minutes and those which will follow, are intended to chronicle the Science Panel activities and progress toward the understanding chemical and physical mechanisms that are taking place in the waste tanks at Hanford.

Summary

The third meeting of the Tank Waste Science Panel was held September 13-14, 1990. Science Panel members were briefed on the August 5, 1990, gas release from tank 241-101-SY (commonly denoted 101-SY), synthetic waste experiments to investigate gas generation and crust behavior in the tank, computer simulations of the thermal behavior of the waste in the tank, and calculations of gas generation based on radiolytic chemistry in alkaline solutions. Data from tanks 103-SY and 103-AN were presented, but it was decided not to divert attention from tank 101-SY at this time by taking additional samples from 103-SY or 103-AN.

Science Panel members recommended that multiple groups begin a concerted experimental effort to understand the chemical and physical mechanisms involved in the tank. This understanding, along with the tank model, can then be used to determine the effectiveness of a particular mitigation method before using the method in tank 101-SY.

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Minutes of the Tank Waste Science Panel Meeting September 13-14, 1990

Introduction

The third meeting of the Tank Waste Science Panel (Science Panel) was held September 13-14, 1990, at the Registry Hotel, Denver, Colorado. The objectives of this meeting were to review the activities of the panel members since the last meeting, agree on the content of the report *Chemical and Physical Processes in Tank 101-SY: A Preliminary Report*, and provide a suggested study plan for work needed to determine the chemical and physical mechanisms in tank 101-SY.

Day One of the Meeting

The first day of the meeting consisted primarily of presentations on the latest gas release event and work performed at Westinghouse Hanford Company (WHC), Argonne National Laboratory (ANL), and Pacific Northwest Laboratory (PNL).^(a) These presentations were preceded by a discussion of how Science Panel reports should be written.

Science Panel Reports

The Science Panel discussed the recent reviews that have been held at Hanford related to the sampling of tank 101-SY. L. G. (Larry) Morgan and T. H. (Thom) Dunning, Jr. talked about their interactions with two of the review teams and suggested changes in the way the Science Panel reports are written. For the purpose of clarity to all those who might read the Science Panel reports, Science Panel members should assume that the reader has only a limited technical knowledge and that his/her knowledge of the wastes at the Hanford Site and of the tank issues is limited. Therefore, the information in the Science Panel reports needs to be referenced or a complete discussion needs to be provided so that the reader can understand the document. When decisions or recommendations are made, the basis of the decision or recommendation needs to be fully discussed, including a discussion of the alternatives. Further, it should be assumed that all of our reports will become publicly available either through the normal Department of Energy (DOE) clearance process or the Freedom of Information Act. It was Larry's and Thom's opinion that all of the Science Panel publications are likely to receive significant scrutiny.

August 5, 1990, Gas Release Event

D. A. (Dan) Reynolds presented the latest information on the August 5, 1990, gas release event from tank 101-SY. This event was more closely monitored than the previous events, so more information was available on the thermal response of the tank contents. Attachment A contains the visual material Dan presented. The thermal profiles (pages A.1 to A.4) in the tank indicate the same thermal behavior before the release as had been noted in the past. Data taken during the event, however, indicate that the temperature just under the crust increased dramatically from approximately 125°F to about 137°F for about 2 hours after the gas release started (pages A.1 and A.2). Dan interpreted these data to indicate that a mass of hot solution from the bottom of the tank had been brought up under the crust. The thermal

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

behavior was not believed to indicate that hot gases were being trapped under the crust and slowly released, rather the solution under the crust in the location of the thermocouple was probably hot.

The temperature of the solution just under the crust had two maxima as a function of time; they corresponded to the two maxima in the hydrogen release data (page A.5). However, the second maximum in the temperature was greater than the first whereas the first maximum in the hydrogen release was greater than the second. [Actual flow rates have never been measured during these gas release events.](a)

The initial interpretation of the thermal data suggested that the second maximum was due to a larger volume of waste. Since a larger volume of waste would suggest a larger volume of hydrogen, the data appeared to be contradictory. It was pointed out by one of the Science Panel members that the waste under the crust after the first release probably resulted from the mixing of a relatively cool waste with a hot waste. The temperature of the waste under the crust after the second release would be the result of the mixing of a relatively hot waste from the bottom with the waste already present and heated from the first release event. Thus, the apparent contradiction of the thermal data and the hydrogen release data has a plausible explanation.

A question was raised concerning the possibility of an exothermic reaction between the bottom of the crust and the waste from the bottom of the tank. An exothermic reaction could also explain the increase in the temperature under the crust as well as the "turn over" of hot fluids from the bottom of the tank. Dan said that he had thought of this possibility as well and could not discount it on the basis of available information. However, he stated that it was his belief that this was not a probable explanation.

From the thermal profiles in the tank, it would appear that the bottom 50 in. or so of waste was not involved in the "turn over." This conclusion was reached because the temperature indicated by the bottom three thermocouples at 4 in., 28 in., and 52 in. did not register a change in temperature during the gas release event. W. J. (Bill) Thomson and D. S. (Don) Trent indicated they believe the bottom portion of the sludge layer did not "turn over" during the event of April 19, 1990.

Part of the discussion by the Science Panel members centered on the thermal gradient in the crust. Don Trent compared the thermal gradients in the crust between this event and the last. He indicated there was a substantial difference in the crust thermal gradient between the August 5, 1990, event and the April 19, 1990, event. There was no conjecture as to the meaning of this difference. Don also requested information on the temperature above the crust (e.g., in the tank plenum). This information, along with the thermal gradient in the crust, is needed to perform heat balance calculations especially since the air flow rate through the tank plenum was greater during this event than the last event, 600 cfm versus about 450 cfm.

Synthetic Waste Experiments at Westinghouse

Following the discussion of the August 5, 1990, gas release event, Dan turned his attention to the experiments that D. L. (Dan) Herting of WHC has been doing with synthetic waste. Dan Herting has two experiments running. In one experiment, he has placed synthetic waste in a beaker at about 100°C. The waste separates into three layers - a crust, a clear solution, and a sludge - in one to two weeks. Into this system he placed a small glass micro-pipette with one end below the crust and the other above and

(a) [] = editorial comments

connected to a helium gas supply. Above the solution was a helium detector. By very slowly bubbling helium under the crust, he was able to grow a bubble that caused the crust to bulge. During the time the bulge was growing, no helium was detected. Eventually, the bulge broke and helium was detected. After breaking, the crust readily healed and no helium gas was found using the helium detector. This cycle repeated about every 12 minutes. It was stated that Dan Herting does not believe that these experiments replicate the mechanism that is taking place in the tank, but the indication is that the crust could fracture to release the gases coming from the bottom of the tank and then quickly heal.

In another experiment, Dan Herting placed synthetic waste in a sealed system (page A.7). In this experiment, the pressure increase was monitored as a function of time and samples of the gas were taken on about a two to three week basis. As the experiment is allowed to run, the pressure increased in the system. Initially, the rate appeared to be linear. However, the latest data (at the date of this meeting) suggested that the rate was decreasing as a function of time, indicating that the reactants are being consumed by the gas generation reactions. The experiments have been running for about six weeks. During the sampling of the gas above the waste, the pressure decreased from about 600 torr to about 400 torr as he withdrew the gas from the vessel. Also during sampling, Dan Herting noticed that the gas trapped in the solids at the bottom was released as the pressure decreased and the solids were stirred as a result. To extend these experiments, Dan Herting would like to perform experiments with two-carbon organic molecules that are likely decomposition products of the organic complexants originally in the waste.

During 1984, when C. (Cal) Delegard was still at Rockwell Hanford Company (later Westinghouse Hanford Company), Dan Reynolds and Cal Delegard investigated the thermodynamics of the electrical half-cell reactions for the various compounds in tank 101-SY (pages A.8 to A.10). Since there were no data on the half-cell reaction for ethylenediamine, he substituted ethyl alcohol. These six half-cell reactions could be combined to give reactions from which the known gases evolving from tank 101-SY could be generated. Combining these reactions into an overall reaction permitted Dan and Cal to calculate a negative Gibbs Free Energy of reaction. A negative reaction free energy indicates that the reaction has the potential to proceed in the direction shown, i.e., the gases observed coming from the tank could come from the decomposition of the organic complexants in the waste. These estimates of the free energies of reaction are just estimates and may not be used for much else other than to indicate possible reactions. The results are no better than the data upon which they are based. E. C. (Gene) Ashby indicated that it is not the Gibbs Free Energy of reaction that is important in these reactions but the free energy of the activated complex for the rate limiting step of the reaction. How large the free energy of formation of the activated complex is depends on the composition of the activated complex - something that should be identified through the proposed research.

Dan Reynolds also provided a short bibliography of information that might be related to this project (page A.11). Dan suggested that since some of these authors have already performed work similar to that which is needed for the proposed studies, they might be interested in performing some work for the Science Panel. In particular, T. J. Meyer has experience in interpreting the information obtained from experiments performed with ¹⁵N-labeled chemicals. Gene Ashby indicated that Tom Meyer has a large and excellent group at the University of North Carolina.

Research at Argonne National Laboratory

At ANL, E. P. (Phil) Horwitz has been using some of his Basic Energy Science funding to perform some preliminary experiments on the source of gases from the synthetic waste. One of his coworkers suggested that the source of the hydrogen was from a Meerwein-Ponndorf-Verley reduction/Oppenauer oxidation (page B.2). However, Phil believes that this proposed mechanism is not correct, particularly because it is inconsistent with the data from Cal Delegard's previous studies.

Data from the literature suggest that all of the organic complexant in these solutions would be combined as a metal complexant (page B.3). However, the actual species that exist under the conditions of the waste solutions are unknown. Also, it appears from the same data that the metal species are predominantly in the form $M(OH)_4$, where "M" stands for a metal such as aluminum or iron.

Phil and his coworkers performed their experiments in a glass apparatus, shown schematically in the handout (page B.4), that was being used in their other work. The material was stirred because they were interested in the kinetics of the reactions and not in the physical reproduction of the waste tank. In the one experiment reported (page B.5), they observed hydrogen and nitrous oxide. Using nuclear magnetic resonance to determine the changes in the organic compounds, they were able to determine that the HEDTA had been significantly altered during the reaction and by more than predicted based solely on the hydrogen production. Two additional experiments were performed in which the gas analyses had not yet been performed because their mass spectrometer broke. The nuclear magnetic resonance results indicate that the HEDTA spectrum did not change after prolonged reaction; substituting sodium formate for HEDTA yielded no reaction.

Phil mentioned that one of the first experiments was performed without stirring. In this experiment, a crust was quickly formed, but gas generation was not measured.

TEMPEST Simulations at PNL

D. S. (Don) Trent performed simulations of the thermal behavior of the waste in tank 101-SY using the computer code TEMPEST and making some assumptions about the physical properties of the waste. He began with an existing thermal model that is currently coded into TEMPEST and some estimated values for thermal properties of the materials in and around the tank, such as thermal conductivity of the liquid and solids, heat generation, etc. Don made estimates of the thermal conductivity for the liquid waste, crust, waste solids, cement, and underlying soil. The viscosity and density of the liquid were also estimated as a function of temperature and the thermal power output of the waste. The crust was assumed to be a poor insulator with no power output; the next 200 in. of waste was assumed to have zero power output and was freely convecting; the next 150 in. was nonconvecting and contained all of the power for heating the waste; the bottom 50 in. was assumed to be a nonconvecting no-power-output sludge - a poor insulator. The tank walls were assumed to be good insulators. Using these assumptions, Don was able to calculate the thermal profile of tank 101-SY just before a gas release. This condition was assumed for this calculation to be the steady-state condition so that transients need not be considered and less dependence would be placed on parameters for which no estimates were available.

Using the resulting estimates, Don was also able to calculate an estimate of the flow patterns and behavior in the freely convecting portion of the tank - the upper 200 in. His calculations indicated that the flow velocities were on the order of 1 ft/min and the thermal gradients driving this flow was on the

order of 0.5°F. Furthermore, the pattern appeared to be a random one, i.e., there was no repeat cycle nor did the system evolve to a set convection pattern. Rather, the flow patterns changed as a function of time. His calculations showed dramatic changes over the period of about 3 hours. [One should remember the caveats under which these calculations were performed; see previous paragraph.]

As a result of this work, Don indicated the need for the following data from the samples that are eventually taken from the tank:

- thermal conductivity of the solids, crust, and liquids in the tank
- densities of the liquids in the tank and the change in density as a function of the temperature
- rheological properties, in particular the shear stress as a function of the shear rate, for the liquids and slurries in the tank
- measurements of the solids content of the slurries at the various depths in the tank and the size distributions of the suspended particles.

These properties need to be measured for the waste in tank 101-SY in order to have a credible analytical model of the tank. In the meantime, these values can be estimated, but in the final analysis the estimates will have to be evaluated using data from the samples taken from the tank.

Radiolytic Chemistry

E. J. (Ed) Hart presented the results of his investigation of the radiation chemistry in alkaline solutions. He stated that above a pH of about 4, the generation of H_2O_2 , H , OH , and $(\text{H} + e_{\text{aq}}^-)$ are essentially constant, as is the decomposition of H_2O . Above pH 9, H atoms are converted to e_{aq}^- . Above a pH of 12, the OH free radical and H_2O_2 dissociate into O^- and HO_2^- , respectively. Consequently, at pH values greater than 14, the dominant free radicals are e_{aq}^- and O^- ; the dominant molecular products are H_2 and HO_2^- . The absence of the H atom and the OH radical greatly simplifies the mechanism of water radiolysis and reduces the number of reactions from 39 (page C.1) to 19 (Table 1). The sole products of e_{aq}^- and O^- reactions are H_2 , HO_2^- , O_2 , and O_2^- .

R. M. (Dick) Wallace presented the results of his calculations on the possible radiolytic source of H_2 gas (page D.1). From his calculations, Dick suggested that the power generated in tank 101-SY is about $5.9 \cdot 10^7$ J/h based solely on the ^{137}Cs concentration. [Dick used a concentration of 0.8 Ci/L and the actual should be about 0.6 Ci/L.] He used the value for $G(\text{H}_2)$ of water (0.45) to calculate the production of H_2 , then the gas production rate is about 68 mol/d (page D.1). However, at the Savannah River Plant a value for $G(\text{H}_2)$ of 0.06 is used because of the NO_3^- and NO_2^- in their process. This value leads to a gas production of about 8.8 mol/d (page D.1). The estimated gas generation rate calculated by Carothers (WHC) is about 37 mol/d. Thus, Dick came to the conclusion that, using the currently available values for $G(\text{H}_2)$, one can bracket the H_2 production of the waste tank. He also pointed out the need for radiolysis experiments and the importance of understanding the radiolytic generation of gases in tank 101-SY.

Dick mentioned that although NO_2^- has been added to solutions at Savannah River Plant to repress the generation of H_2 , the presence of organics causes $G(\text{H}_2)$ to increase. These data were collected for the tetraphenylborate organic species that are used at the Savannah River Plant and not the organics that are present in tank 101-SY.

TABLE 1. Important Radiolysis Reactions in Alkaline Solutions

Reaction #	Reaction	Reaction Rate, k (mol ⁻¹ · s ⁻¹)
1	$\text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$	$1.4 \cdot 10^{10}$
2	$\text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^- \xrightarrow{2\text{H}_2\text{O}} 2\text{OH}^- + \text{H}_2$	$3.0 \cdot 10^9$
3	$\text{e}_{\text{aq}}^- + \text{O}^- \xrightarrow{\text{H}_2\text{O}} 2\text{OH}^-$	$1.5 \cdot 10^{10}$
4	$\text{e}_{\text{aq}}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{HO}_2^- + \text{OH}^-$	$1.2 \cdot 10^{10}$
5	$\text{e}_{\text{aq}}^- + \text{HO}_2^- \xrightarrow{\text{H}_2\text{O}} \text{O}^- + \text{OH}^- + \text{H}_2\text{O}$	$3.5 \cdot 10^9$
6	$\text{e}_{\text{aq}}^- + \text{O}_2 \xrightarrow{\text{H}_2\text{O}} \text{O}_2^- + \text{H}_2\text{O}$	$2.0 \cdot 10^{10}$
7	$\text{O}^- + \text{O}^- \rightarrow \text{O}_2^{2-}$	$9.0 \cdot 10^8$
8	$\text{O}^- + \text{O}_2^- \rightarrow \text{O}_3^{2-}$	$3.5 \cdot 10^8$
9	$\text{O}^- + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}_2^-$	$3.5 \cdot 10^8$
10	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^-$	$2.0 \cdot 10^6$
11	$\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$	$2.0 \cdot 10^8$
12	$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$	$5.0 \cdot 10^8$
13	$\text{HO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^-$	$5.7 \cdot 10^4$
14	$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	$2.6 \cdot 10^{-5}$
15	$\text{H}_2\text{O} + \text{O}_2^- \rightarrow \text{HO}_2^- + \text{OH}^-$	$1.0 \cdot 10^8$
16	$\text{H}_2\text{O} + \text{O}_3^- \rightarrow \text{O}_2 + 2\text{OH}^-$	$1.0 \cdot 10^8$
17	$\text{H}_2\text{O} + \text{O}^{2-} \rightarrow 2\text{OH}^-$	$1.0 \cdot 10^8$
18	$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	$1.4 \cdot 10^{11}$
19	$\text{O} + \text{OH}^- \rightarrow \text{HO}_2^{2-}$	$5 \cdot 10^4$

The above discussion points out the critical need for radiolysis research on these solutions. There is a paucity of data on the effects of radiolysis on solutions containing high concentrations of NaNO_3 , NaNO_2 , NaOH , NaAlO_2 , mixtures of these chemicals, and organic complexants.

General Discussion

After the presentations described above, the Science Panel members discussed several general topics. The subject of the approach that is being taken at Westinghouse Hanford Company (WHC) was discussed. One question asked was "Is anything being done?" The fear was that the only activity was associated with response to the various committees that were visiting Hanford. Panel members questioned whether anything was being done to address some of the questions raised, or suggestions made, by the Science Panel. It was pointed out that some steps had been taken in response to the suggestions made by the Science Panel. However, these actions have not been communicated to the Science Panel. Staff at WHC have been busy making presentations to the various review groups that have been visiting the Hanford Site. It was the hope of several of the Science Panel members that the staff at the Department of Energy recognize the level of effort that will be needed to obtain a scientific basis for managing the tank wastes.

There was some discussion about the length of time it takes for the information generated at the Science Panel meetings to reach people within the WHC. It was recognized that information needs to be transmitted to WHC as soon as possible. However, it must be recognized by the staff at WHC that a reasoned and disciplined approach to solving the problems that exist in the waste tanks is critically needed. In fact, one Science Panel member suggested that Dr. W. R. Wiley go on written record recommending the need for a reasoned and disciplined scientific approach rather than a "quick [engineering] fix" to the waste tank problems.

There was some discussion concerning the material that is handed out at these meetings or sent to the Science Panel members. It was agreed that this material is to be kept within the confines of the work members are doing and not to be disseminated outside of the Science Panel. In general, this is because the material is either not appropriately cleared or is of such a tentative nature that it could be misleading without the appropriate caveats.

A question was asked about the lower limit of detection for the gases known to be emitted during a gas release event. Between events it is believed that these same gases are being emitted but are below the detection limit of the instruments currently in use. One of the Science Panel members has estimated the concentration of H_2 gas in the off-gas between gas release events at about 30 ppm. Therefore, to reliably measure 30 ppm, an instrument with a detection limit of about 1 ppm is needed. Such an instrument does not appear to have been installed at tank 101-SY. Knowing if the gases are constantly evolving is a key part of determining the mechanism by which the gases are released.

There was also some discussion concerning the composition of the crust on the waste in tank 101-SY. There is the question about the analogy between the crust on the waste in tank 101-SY and the crusts in other tanks. According to one of the Science Panel members, there is a possibility that the organometallic complex (i.e., Al-HEDTA) may also be complexed by CO_2 . This species might be expected to contribute to the formation of crust but from the underside. If this is the case, the composition of the crust is likely to be quite different from top to bottom. [However, the composition of the crust would be expected to vary from top to bottom simply because of the thickness (estimated).]

Discussion/Review of the Preliminary Report

Prior to the meeting, a draft copy of the document *Chemical and Physical Processes in Tank 101-SY: A Preliminary Report* had been distributed to the Science Panel members. This report is being written to document the progress in the understanding of the chemical and physical processes by the Science Panel members. One of the first suggestions was to use a different format for the report. It was suggested that much of the background material be eliminated from the Introduction. Instead, the purpose of the Tank Waste Science Panel, what the purpose of the report is, etc., should be stated in the Introduction. The background material should be relegated to another section, such as a section entitled "Background." There needs to be an Executive Summary in which the hypotheses and recommendations are listed. It should also be emphasized that a logical experimental program is expected to produce the information needed to solve the problems associated with tank 101-SY.

There was a suggestion to rewrite the chemistry section. Thom Dunning requested that W. W. (Wally) Schulz coordinate the rewriting of the chemistry section. This will be accomplished with the assistance of Gene Ashby, Ed Hart, and Dick Wallace. The latter two will essentially provide the information needed to write the radiation chemistry section. This section will contain much more information than in previous versions of the report.

Because of the high visibility for the reports that will come from the Science Panel and the expected ultimate wide distribution, the reports should describe technical details thoroughly and provide extensive referencing. More detail is needed because of the wide variety of disciplines for the people who will be reading/reviewing these documents.

Day Two of the Meeting

On the second day of the meeting J. (John) Tseng (DOE/HQ), R. L. (Ron) Gerton (DOE/RL), G. D. (Jerry) Johnson (WHC), and R. (Ray) Daniels (SAIC) were in attendance. These visitors had been invited to see how the Science Panel conducted business and for Mr. Tseng to indicate the importance of the mission to the Science Panel.

Presentation of Data from Tanks 103-SY and 103-AN

During the second day of the meeting, Jerry Johnson gave a presentation on the data that have been obtained on tanks 103-SY and 103-AN. These data included pictures of the cores taken from these tanks, chemical analyses of selected core segments, and waste levels. The waste level in tank 103-SY rises and falls at about the same frequency as tank 101-SY, but not to the same magnitude as tank 101-SY. No analyses of the gases from these tanks have been obtained. Tank 103-SY contains more "double shell slurry" than does tank 101-SY and much less "complex concentrate". Samples from these two tanks were not archived. This data package exclusive of the pictures of the core samples was provided to Larry Morgan and is too voluminous to attach to these minutes. The data package will be distributed to the Science Panel members as a separate transmittal.

One of the Science Panel members asked Jerry if there were plans to sample tank 103-SY and how would a request to do so be received. Jerry's response was that there were no plans to sample tank 103-SY. Ron Gerton was quick to reply that safety had priority and if there was a need to obtain data from tank 103-SY, the request would receive attention. It was pointed out the entire SY tank farm is on

Class "A" safety status so that any actions to be taken in tank 103-SY would require the same level of scrutiny as actions to be carried out in tank 101-SY. This would mean that sampling tank 103-SY would not progress any faster than the current sampling schedule for tank 101-SY.

In the discussion that followed, the Science Panel members decided it was probably inappropriate to divert attention from tank 101-SY at this time. In part, the reason stems from the differences between the compositions of the two wastes. If data were to be collected from a new sample of either tank 103-SY or tank 103-AN, there would always be the question about the correlation between the data from these tanks and tank 101-SY. In addition, when the core sample was obtained from tank 103-SY no analysis of the crust was made and, thus, the safety related question would still exist. The general consensus was that samples taken from other tanks would dilute the effort to develop methods of organic analyses and of other chemical and physical analyses and the development of these methods must not be delayed. Even if a sample from any of the tanks were available today, the determination of the organic species that is needed could not be done because the methods have not yet been fully developed. It was also the consensus that the major problems exist with the waste in tank 101-SY. Solving the chemical and physical puzzles that exist in tank 101-SY gives us a better chance of solving similar problems that may exist in other tanks at the Hanford Site.

After the discussion on the data from the other tanks, the Science Panel members discussed the current state of the organic analytical method development. The Science Panel members would like to see what progress has been made and why the methods developed by A. P. Toste at PNL are not available and why they cannot be used. [It turns out that these methods can be used but they are very lengthy and there may be some question about the ability to obtain knowledge about all of the organics. However, the method could be used if needed.] In particular, the Science Panel members wanted to know what methods are being developed to quantitate the concentrations of EDTA, HEDTA, and glycolic acid. One of the Science Panel members strongly suggested the use of high performance liquid chromatography (HPLC) rather than the method of esterification used by Toste.

Current Understanding of the Chemical Mechanisms

Three Science Panel members - Gene Ashby, Phil Horwitz, and Dick Wallace - were asked to summarize the current understanding of the chemical mechanisms. This was mainly done for the visitors, but also as a review for the Science Panel members.

Gene Ashby presented the work he and his colleagues at Georgia Institute of Technology have done. This material is summarized above and in the Attachment (pages E.1 to E.6). The presentation was a positive one in which Gene indicated that the mechanism can be solved. However, the problem will require the expertise and integration of several chemistry specialties. To date four areas of chemistry have been identified - solution inorganic chemistry, mechanistic organic chemistry, kinetics, and radiation chemistry. As in past discussions, Gene made a strong recommendation for the involvement of multiple groups. This approach would necessitate overlapping work, but this would act as an internal check to make sure that the work will stand up to peer review. This work will take about 2 to 3 years of concerted effort, but a lot of useful information will be available in about 6 months.

Gene related his experience with a company with a new process that was not completely understood. When first approached by the company representatives, Gene indicated that a three year effort would be required to understand the chemical mechanisms involved in the process. The company representatives found this unacceptable and proceeded to build the plant. The process did not work from the start and

the plant was not in production for about two years while company engineers tried various remedies to get the plant running. The company then decided to do the preliminary studies suggested earlier, and in six months Gene and his coworkers were able to provide the information that was needed for the plant to operate successfully.

In a sense, this is what has happened at the Hanford Site for tank 101-SY. A problem with this tank was noted in the early 1980's; several engineering fixes were attempted; insufficient funding was provided to understand the chemical and physical processes taking place in the tank. Now, there is a lot of public and political attention being paid to this problem and now is the time to take a reasoned and disciplined approach to the problem. With the correct approach, the chemical and physical processes taking place in tank 101-SY will be understood and the correct remedial action will be taken to address the safety issues that exist with tank 101-SY.

Gene had in the past suggested that the tank be purged with an inert gas, e.g. nitrogen, to prevent unwanted reactions in the waste and to prevent H_2 build up. In this presentation, he suggested that about 30 spargers be used to stir and inert the tank atmosphere. While Gene asserts that portable N_2 units can be purchased commercially and placed near the tank, members of the WHC staff have considered this option and it does not appear to be as easy as Gene suggests. In the WHC study, something on the order of one 70 000 gallon tank truck of liquid N_2 per day would be needed to maintain a N_2 atmosphere in the tank. ["Air lancing" was carried out in tank 101-SY with the result that the waste volume increased. It has been found (see Phil Horwitz data) that O_2 is needed for the reactions. The point of sparging with N_2 is to stir the waste while at the same time halting unwanted reactions by excluding O_2 .]

Gene was asked by one of the Science Panel members that if a contract were to be placed at Georgia Tech today how soon could work start. Gene indicated that work would start immediately. The bulk of the work would be carried out by post doctoral staff who would be hired. Gene felt that this problem is a national emergency and needed prompt and professional attention; this work is too important to have graduate students working on it.

The next presenter was Phil Horwitz from ANL. Phil stated at the start that he agreed with Gene in the need to start this work immediately and with the approach that Gene suggested. He also agreed that this effort should include a critical number of people and should be carried out at three or four different laboratories in order to get the work done quickly, efficiently, and credibly. Phil agreed with Gene that purging the tank with N_2 should be done to reduce the H_2 gas concentration. Phil believes that the major contribution to the H_2 gas generation is radiolysis.

Both Phil Horwitz's and Dick Wallace's presentation were the same as described in earlier sections of this report and the handouts associated with each section. In closing, it was iterated that the chemical mechanisms and the radiation chemistry can be understood in sufficient detail to allow one to propose remedial actions that will stand the scrutiny of peer review.

Current Understanding of the Physical Mechanisms

Two presenters talked about the physical mechanisms in tank 101-SY as they are understood today. These presenters were W. J. (Bill) Thomson from Washington State University and D. S. (Don) Trent from PNL. Don Trent's presentation was the same as that described above and is not repeated here.

Bill felt that the frequency of the gas release indicated there is a critical bubble size phenomenon rather than density that causes the roll over of the waste in the tank. Calculations at PNL suggest that a density change in the waste at the bottom of the tank due to gas generation could not be used to explain the roll over. However, the data suggest that the gas released during an episodic event originates deep within the waste. Therefore, one is led to believe that the cause for roll over is due to a critical bubble size coupled with an event that triggers mass release.

In order to decipher the physical mechanisms underlying the episodic release of gases from tank 101-SY the following items need to be understood:

- Thermo-physical mechanisms need to be understood through a combination of modeling and laboratory measurements.
- Are all gases trapped? This can be measured in samples taken from the tank.
- Do gases nucleate on the solids in the waste? This should be measured in laboratory experiments.
- What initiates the roll over in the tank - critical bubble size or density difference? This can be modeled and/or measured in the laboratory.
- What is the particle size distribution and solids concentration? This should be measured in the samples taken from the tank.
- What is the importance of the CO₂ gas complexing with the amine-containing organics? This can be measured in the crust samples taken from the tank and in laboratory experiments.
- What is the role of the crust during the gas release events? This can be measured in the crust samples taken from the tank and estimated from modeling efforts.
- What is the total amount of gas generated both continuously and during an event? This can be measured by taking samples of the tank atmosphere and installing a pitot tube in the ventilation system.

These needs point toward the research that should be done. The research areas were listed by Bill as:

- modeling in the areas of thermo-fluid dynamics in the tank and dynamic pressurization in the tank dome and ventilation system
- laboratory efforts using appropriately sized vessels in which the solid-fluid system, bubble formation, bubble behavior, effects of pressure, and effects of heat generation can be measured.

It is important to understand that both chemical and physical mechanisms are needed and both need to be carefully studied. The chemical mechanisms will be used to provide the rate of gas generation and the mixture of gases generated as a function of time. This information must be used in the physical model in order to calculate the time until a gas release event and the behavior of the gas bubbles. Once understood, the combination of the chemical and physical mechanisms can be used along with the tank model to determine the effectiveness of a particular mitigation method before using the method in tank 101-SY.

Bill further indicated that the classic pilot-scale method for mocking the waste tank will not yield the required results. This problem requires accurate measurements that may not be achieved by the classical method due to instrument constraints.

General Discussion

In the discussion that followed the presentations, several needs and suggestions were discussed. It was again emphasized that there is an immediate need to have total flow measurements in the tank ventilation system. This should be achievable through the use of a pitot tube inserted into the tank vent. Accurate gas analyses should be obtained to the lowest possible detection limit. The Science Panel members estimate that the steady state H_2 concentration is about 30 ppm. This is below the limit currently quoted for the mass spectrometer. One of the Science Panel members indicated that it should be easy to detect about 1 ppm H_2 in the gases coming from tank 101-SY.

There was some discussion about using one of the lances that were used during the air and water and steam lancing campaigns to obtain liquid and perhaps solid samples. One Science Panel member suggested the method used in the oil industry to obtain samples or to pump from a particular stratum in a well. This is done by inserting a packer system by which a particular stratum can be isolated. A packer system would consist of two inflatable balloons on a sampling tube. This system would be placed inside of the lance which has holes at various depths in the tank. The packer system would be lowered until the balloons were located on either side of one of the holes in the lance. By inflating the balloons, the hole would be isolated. The material that flowed into the lance through the hole could then be sampled. Gas samples could also be obtained in a similar manner at various depths in the tank.

Nondestructive testing equipment also needs to be developed in order to determine some of the properties of the waste in the tank. Using such devices, it should be possible to determine the behavior of the crust during a gas release event, the density of the waste as a function of depth, and other physical measurements.

The preliminary document, *Chemical and Physical Processes in Tank 101-SY: A Preliminary Report*, should be submitted to the Science Panel members for final review by the end of October 1990. Wally Schulz and Bill Thomson were requested to reformat the chemistry section and the physical mechanisms section, respectively. These reports should be sent to Thom Dunning by the end of September 1990.

Attachment A

Visual Material on August 5, 1990, Gas Release Event

Temperature Profiles

August 5, 1990 -- 101-SY

241-SY-101 Nitrous Oxide and Hydrogen Released

August 5, 1990

BATTELLE
Pacific Northwest Laboratory

Date Aug. 6, 1990
To S.G. Metcalf
From M.W. Goheen
Subject SY-101 Tank Samples

August 5, 1990 Tank 101-SY Gas Release Event
Grab Sample Mass Spec Results

Sample Identification

	PN-13	PN-14	PN-15	PN-16	PN-17	PN-18	PN-19	PN-20	PN-21	PN-22
Carbon dioxide	0.03	0.04	0.06	0.07	0.10	0.04	0.04	0.02	0.02	0.03
Argon	0.91	0.91	0.91	0.92	0.92	0.93	0.92	0.92	0.93	0.94
Oxygen	21.60	20.40	20.40	20.40	20.40	20.50	20.60	20.40	20.70	20.80
Nitrogen	77.40	77.00	77.30	77.10	77.10	77.20	77.20	77.50	77.80	78.00
Carbon monoxide	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Helium	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hydrogen	<0.01	0.93	0.78	0.89	0.82	0.75	0.71	0.63	0.29	0.14
Methane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Nitrous oxide		0.71	0.59	0.66	0.57	0.56	0.54	0.52	0.26	0.11
Other nitrogen oxides		0.01	<0.01	0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01

Sample time

N₂O/H₂

0655 " 0707 " 0718 " 0730 " 0745 " 0756 " 0820 1010 1210
0.763 0.756 0.742 0.695 0.747 0.761 0.825 0.877 0.736

note!
Precision level 1 to 2 percent

1.0 = 2.4%

avg = .7747

SE = .0033

75% CI = .0442

112 = 56.3%

avg N₂O = 43.7%

UCL H₂ = 55.0%

N₂O = 45.0%

112 = 57.5%

1. CI H₂ = 40.2%

75% N₂O = 40.2%

A.6

M.W. Goheen
Staff Scientist

Test Apparatus

Figure 1

REACTION 1) PLUS TWO REACTION 2)

REACTIONS 1), 3), AND 4)

REACTIONS 6) AND REACTION 2)

	<u>G_f Products</u>	<u>G_f Reactants</u>
OXALATE	-322.2	
NITROUS OXIDE	124.50	
HYDROXIDE	-225.54	
WATER	-170.07	
ETHANOL		-86.88
NITRITE		-77.0
SUM	<u>-593.31</u>	<u>-163.88</u>

$$\underline{G_f \text{ Reaction}} = \underline{G_f \text{ Products}} + \underline{G_f \text{ Reactants}}$$

$$-429.43 \text{ kcal/oxn.} = -593.31 - (-163.88)$$

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Cameroon Lake

C. Stager, "Silent Death from Cameroon's Killer Lake", Nat. Geog., 1987, Sept., 404-420

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G. W. Kling, M. A. Clark, H. R. Compton, J. D. Devine, W. C. Evans, A. M. Humphrey, E. J. Koenigsberg, J. P. Lockwood, M. L. Tuttle, G. N. Wagner, "The 1986 Lake Nyos Gas Disaster in Cameroon, West Africa", Science, 1987, 230, 169-175

H. Sigurdsson, "A Dead Chief's Revenge?", Nat. Hist., 1987, 8, 44-49

Attachment B

Visual Material on Research at ANL

PRELIMINARY EXPERIMENTS ON H₂ GENERATION IN 101-SY

B.1 KEN NASH, PAUL RICKERT, RALPH GATRONE, AND PHIL HORWITZ

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY

PROPOSED MECHANISM FOR H₂ GENERATION

The proposed mechanism is based upon the Meerwein-Ponndorf-Verley Reduction (Oppenauer Oxidation). These reactions are reversible redox reactions which convert an alcohol into a carbonyl group in the presence of aluminum alkoxides.

A.L. Wilds, Organic Reactions 2, 178 (1944), C.H. Snyder, M. Micklus, J. Org. Chem. 35, 264 (1970), R. Monicagli, J. Organometal. Chem. 50, C15 (1973).

C. Djerassi, Organic Reactions 6, 207 (1951), E.W. Warnhoff, J. Org. Chem. 28, 1431 (1963).

Al Species - 2.3 M (Al), 0.35 M HEDTA

Temperature = 120 °C, Time = 48 hr

Solution		Comment
NaAlO ₂	2.27M	H ₂ and N ₂ O detected in evolved gas. H ₂ evolved was 0.6 mole% of HEDTA concentration. ¹ H NMR indicates alteration of HEDTA with a peak at 8.8ppm appearing. NMR indicates greater decomposition than shown by H ₂ generation.
NaOH	3.49M	
NaNO ₂	3.55M	
NaNO ₃	3.89M	
Na ₂ CO ₃	0.31M	
HEDTA	0.35M	

Temperature = 120 °C, Time = 112 hr

Solution		Comment
NaAlO ₂	2.27M	Gas analysis is on hold due to breakdown of instrument. NMR indicates no change in the HEDTA spectrum.
NaOH	3.49M	
Na ₂ CO ₃	0.31M	
HEDTA	0.35M	

Temperature = 120 C, Time = 27 hr

Solution		Comment
NaOH	3.49M	Gas analysis is on hold due to breakdown of instrument. NMR indicates no change in the formic acid spectrum.
Na Formate	0.35M	

Attachment C

**Visual Material on Radiation Chemistry
in Alkaline Solutions**

Table 1. Reactions in irradiated water^{a) b) c)}

1: $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	$k(1) = 6.0 \times 10^9$
2: $\text{OH} + \text{e}_{\text{aq}}^- \rightarrow \text{OH}^- + \text{H}_2\text{O}$	$k(2) = 2.5 \times 10^{10}$
3: $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$	$k(3) = 2.5 \times 10^{10}$
4: $\text{OH} + \text{O}^- \rightarrow \text{HO}_2^-$	$k(4) = 1.8 \times 10^{10}$
5: $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_3$	$k(5) = 7.9 \times 10^9$
6: $\text{OH} + \text{O}_2^- \rightarrow \text{OH}^- + \text{O}_2$	$k(6) = 1.0 \times 10^{10}$
7: $\text{OH} + \text{O}_3^- \rightarrow \text{HO}_2 + \text{O}_2^-$	$k(7) = 8.5 \times 10^9$
8: $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2^- + \text{H}^+$	$k(8) = 2.7 \times 10^7$
9: $\text{OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2^-$	$k(9) = 7.5 \times 10^9$
10: $\text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O}$	$k(10) = 1.4 \times 10^{10}$
11: $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$k(11) = 4.0 \times 10^7$
12: $\text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^- \rightarrow 2\text{OH}^- + \text{H}_2$	$k(12) = 6.0 \times 10^9$
13: $\text{e}_{\text{aq}}^- + \text{H} \rightarrow \text{OH}^- + \text{H}_2$	$k(13) = 2.0 \times 10^{10}$
14: $\text{e}_{\text{aq}}^- + \text{O}^- \rightarrow 2\text{OH}^-$	$k(14) = 1.5 \times 10^{10}$
15: $\text{e}_{\text{aq}}^- + \text{O}_2^- \rightarrow \text{HO}_2^- + \text{OH}^-$	$k(15) = 1.2 \times 10^{10}$
16: $\text{e}_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^- + \text{H}_2\text{O}$	$k(16) = 1.6 \times 10^{10}$
17: $\text{e}_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{O}^- + \text{OH}^- + \text{H}_2\text{O}$	$k(17) = 3.5 \times 10^9$
18: $\text{e}_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H} + \text{H}_2\text{O}$	$k(18) = 2.2 \times 10^{10}$
19: $\text{e}_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}_2\text{O}$	$k(19) = 2.0 \times 10^{10}$
20: $\text{H} + \text{H} \rightarrow \text{H}_2$	$k(20) = 5.0 \times 10^9$
21: $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	$k(21) = 2.0 \times 10^{10}$
22: $\text{H} + \text{O}_2^- \rightarrow \text{HO}_2^-$	$k(22) = 2.0 \times 10^{10}$
23: $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O}$	$k(23) = 6.0 \times 10^7$
24: $\text{H} + \text{OH}^- \rightarrow \text{e}_{\text{aq}}^-$	$k(24) = 1.5 \times 10^7$
25: $\text{H} + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}^+$	$k(25) = 2.0 \times 10^{10}$
26: $\text{H} + \text{O}^- \rightarrow \text{OH}^-$	$k(26) = 2.0 \times 10^{10}$
27: $\text{O}^- + \text{O}^- \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O}_2 + 2\text{OH}^-$	$k(27) = 9.0 \times 10^8$
28: $\text{O}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{O}_2 + 2\text{OH}^-$	$k(28) = 6.0 \times 10^8$
29: $\text{O}^- + \text{O}_3^- \rightarrow 2\text{O}_2^-$	$k(29) = 7.0 \times 10^8$
30: $\text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^- + \text{H}_2\text{O}$	$k(30) = 5.0 \times 10^8$
31: $\text{O}^- + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}_2^-$	$k(31) = 3.5 \times 10^8$
32: $\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^-$	$k(32) = 2.0 \times 10^6$
33: $\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$	$k(33) = 3.0 \times 10^9$
34: $\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$	$k(34) = 2.0 \times 10^8$
35: $\text{HO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$	$k(35) = 7.5 \times 10^5$
36: $\text{HO}_2 + \text{O}_2^- \rightarrow \text{O}_2 + \text{HO}_2^-$	$k(36) = 1.0 \times 10^8$
37: $\text{H}_2\text{O}_3 \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$k(37) = 2.1^{\text{d)}$
38: $\text{O}_3^- \rightarrow \text{O}^- + \text{O}_2$	$k(38) = 3.3 \times 10^3$
39: $\text{O}_3^- + \text{H}^+ \rightarrow \text{OH} + \text{O}_2$	$k(39) = 9.0 \times 10^{10}$

a) Dependent on the type of reaction, the rate constant is given as $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ or s^{-1} ; for two identical reactants the rate constant is given as $1 k$.

b) Reactions are taken from ref. [1–4, 10] and the rate constants are chosen from the NBS-tables [18–20].

c) Equilibrium reactions with water are taken into account in the computation but omitted in the Table.

d) The value of $k(37)$ is pH dependent.

Fig. 2. Formation of radiolytic products in air-free pure water following a 100 Gy electron pulse delivered in 1×10^{-6} second.

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Fig. 5. Depletion of oxygen by irradiation in the presence of surplus hydrogen. Dose rate: 1 Gy per second.

Table 2. Main reactions in the radiolysis of neutral aqueous solution of $\text{CO}_2\text{-HCO}_3^-\text{-CO}_3^{2-}$ ^{a) b)}

40: $\text{OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O}$	$k(40) = 8.0 \times 10^6$
41: $\text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^- + \text{OH}^-$	$k(41) = 4.0 \times 10^8$
42: $\text{CO}_3^- + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-} + \text{CO}_2$	$k(42) = 7.0 \times 10^6$
43: $\text{H}_2\text{O} + \text{CO}_3^{2-} \rightarrow \text{HO}_2^- + \text{OH}^- + \text{CO}_2$	$k(43) = 0.2$
44: $\text{H}_2\text{O}_2 + \text{CO}_3^- \rightarrow \text{CO}_3^{2-} + \text{O}_2^- + 2\text{H}^+$	$k(44) = 4.3 \times 10^5$
45: $\text{HO}_2^- + \text{CO}_3^- \rightarrow \text{CO}_3^{2-} + \text{O}_2^- + \text{H}^+$	$k(45) = 3.0 \times 10^7$
46: $\text{e}_{\text{aq}}^- + \text{CO}_2 \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$	$k(46) = 7.7 \times 10^9$
47: $\text{H} + \text{CO}_2 \rightarrow \text{CO}_2^- + \text{H}^+$	$k(47) = 1.0 \times 10^6$
48: $\text{H} + \text{HCO}_3^- \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$	$k(48) = 3.4 \times 10^4$
49: $\text{CO}_2^- + \text{CO}_2 \rightarrow \text{C}_2\text{O}_4^{2-}$	$k(49) = 4.0 \times 10^8$
50: $\text{CO}_2^- + \text{HCO}_3^- \rightarrow \text{HCO}_3^- + \text{CO}_3^-$	$k(50) = 2.0 \times 10^3$
51: $\text{HCO}_3^- + \text{CO}_3^- \rightarrow \text{HCO}_3^- + \text{CO}_2^-$	$k(51) = 1.0 \times 10^5$
52: $\text{OH} + \text{HCO}_2^- \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$	$k(52) = 3.0 \times 10^9$
53: $\text{H} + \text{HCO}_2^- \rightarrow \text{CO}_2^- + \text{H}_2$	$k(53) = 2.2 \times 10^8$
54: $\text{OH} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{OH}^- + \text{C}_2\text{O}_4^-$	$k(54) = 8.0 \times 10^6$
55: $\text{e}_{\text{aq}}^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O}$	$k(55) = 3.0 \times 10^7$
56: $\text{CO}_2^- + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^-$	$k(56) = 2.0 \times 10^9$
57: $\text{O}_2^- + \text{CO}_3^- \rightarrow \text{CO}_3^{2-} + \text{O}_2$	$k(57) = 4.0 \times 10^8$

a) Dependent on the type of reaction, the rate constant is given as $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ or s^{-1} ; for two identical reactants the rate constant is given as $1 k$.

b) Reactions and some rate constants are taken from refs. [25, 27].

at low steady-state concentrations. For example, if hydrogen ($1 \times 10^{-5} \text{mol dm}^{-3}$) is initially present in deaerated water, the steady-state concentrations of oxygen and hydrogen peroxide are reached after a dose of 20 Gy and maintained at very low concentrations (1×10^{-12} and $1 \times 10^{-8} \text{mol dm}^{-3}$) respectively (Fig. 5).

Carbon dioxide

Under radiation, carbon dioxide dissolved in water yields formic and oxalic acid, in addition to hydrogen peroxide, molecular hydrogen and oxygen. Also polymeric material is formed at large doses [25, 26].

Dissolved CO_2 is in equilibrium with HCO_3^- and CO_3^{2-} and the concentration ratios depend on the pH of the water. All species participate in the reaction mechanism, and for computer simulation we have taken the reactions (eqs. 40–57) given in Table 2 in addition to the reactions in pure water (Table 1).

Attachment D

Visual Material on Possible Source of H₂ Gas

ESTIMATE OF H₂ GENERATION BY RADIOLYSIS

Cs-137 Activity = 0.818 Ci/L

Cs-137 Power = 0.005 Watts/Ci

Cs-137 in tank = 0.00409 Watts/L

0.0155 Watts/gal

Total Power = 1.65E+04 Watts

5.93E+07 Joules/Hr

5.62E+04 BTU/Hr

<u>G(H₂)</u>	<u>Moles/Hr</u>	<u>Moles/Day</u>
-------------------------	-----------------	------------------

0.06	0.369	8.85
------	-------	------

0.46	2.83	67.8
------	------	------

Estimate from last event (Carothers)		36.6
---	--	------

H₂ AND O₂ YIELDS FROM NaNO₃ SOLUTIONS

NaNO ₃ M	G(H ₂)	G(O ₂)
0.0012	0.42	*****
0.079	0.39	*****
0.15	0.24	*****
0.51	0.15	*****
1.00	0.096	0.21
2.00	0.059	0.31
3.00	0.042	0.42
4.00	0.038	0.50
5.00	0.035	0.56
6.00	0.029	0.63
7.00	0.025	0.70

H. A. Mahlman, J. Phys. Chem. 64, 936 (1961)

TABLE I

Radiolytic G-Values for Nitrate Destruction and Nitrite Production

<u>Sample</u>	<u>Total [Na⁺] (molar)</u>	<u>G (molecules/100eV)</u>	
		<u>-NO₃⁻</u>	<u>NO₂⁻</u>
Dilute salt solution (no organic present)	.22	.28	.33
Partially washed precipitate (9.4 wt % KTPB)	1.6	1.3	1.9
Unwashed precipitate (9.4 wt % KTPB)	3.3	3.1	3.2

TABLE II

Composition of Simulated 10 Weight % KTPB Slurries

<u>Component</u>			<u>Concentration</u>		<u>"Washed"</u>	
			<u>"Unwashed"</u>	<u>"Partially Washed"</u>	<u>Low OH⁻</u>	<u>High OH⁻</u>
Solids:	KTPB	9.4 wt %		9.4	10.	9.0
Solution:	Na ⁺	3.5 molar		1.7	.20	.68
	NO ₃ ⁻	1.82		.89	.10	.089
	NO ₂ ⁻	.58		.30	.030	.026
	OH ⁻	1.13		.56	.065	.57

FIGURE 1

**Changes in Nitrate and Nitrite Concentrations
Dilute Salt Solution (no KTPB)**

FIGURE 2

Changes in Nitrate and Nitrite Concentrations
Washed Precipitate (0.20 M Na^+ , low pH)

FIGURE 4

Changes in Nitrate and Nitrite Concentrations
Partially Washed Precipitate (1.7 M Na^+)

FIGURE 5

Changes in Nitrate and Nitrite Concentrations
Unwashed Precipitate (3.5 M Na⁺)

FIGURE 3

Changes in Nitrate and Nitrite Concentrations
Washed Precipitate (pH>13)

Irradiation of NO₂ without NO₃ Present

No writing under insert. D.H.C.

These results indicate NO₂⁻ is not affected by radiation—that is, it does not go away.

Avg: 0.0914 ± 0.0027 (13%)

However, this may be significantly lower than the initial NO₂⁻ by 87%. This may reflect some loss.

1 yr storage =

1.45 × 10⁸ rads

PERFORMER

Darrel D. Walker

DATE

10/9/86

TESTED BY

NTT

D.9

Page No. TITLE Results From p 14-21 DATE 10/9/86
 Book No. PURPOSE 10% KTPB 1 Yr = 1.45×10^8 Rad

Loss of NO₂- w/ no NO₃-

NO writing under insert, LSCW

no G-values at the higher NO₂⁻ concentrations agree well, but third expt is off. Could be due to expt error since only points shown, or could be due to higher wt% KTPB, or other reason. It should be repeated at a lower KTPB content with dose increments ~~at~~ to give more non-zero points

ITER Barrel D. Walker

D.10

DATE 10/9/86

Attachment E

Visual Material on Chemical Mechanisms

Suggested Experimental Program to Determine the Chemistry Proceeding in Tank

101-SY

In order to provide a solution to the problem of gas evolution in tank 101-SY, it is important to understand the chemistry that leads to gas formation and hence what might be done to prevent it. There are several factors which are considered crucial to an understanding of this chemistry. In order to investigate these factors it is suggested that reactions of simulated slurry be studied with respect to:

- (1) product identification
- (2) source of carbon, hydrogen and nitrogen in the formation of CO_2 , H_2 , N_2O and NH_3 .
- (3) stoichiometry of the reactions
- (4) kinetics of the reactions
- (5) key intermediates formed in the reactions
- (6) chemical nature of the crust
- (7) effect of actinide and transition metal catalysis on evolution of gases and other product formation
- (8) effect of radiation on all of the above

(1) Product Identification

It is important to determine all of the products formed in the reaction of simulated slurry and how the product ratio may vary with time (monitoring studies).

Simulated Slurry	$\xrightarrow{100^{\circ}\text{C}}$	gas	+	non-gaseous products
NaAlO ₂		volume		HPLC
NaOH		gc/MS		gc/MS of non-volatiles
NaNO ₂				
NaNO ₃				
Na ₂ CO ₃				
*HEDTA				

(*investigate other complexing agents separately)

The determination of degradation products are important in identifying the pathways of reactions.

Experiments to be carried out:

- (a) NaOH-NaNO₃ at typical tank concentrations
- (b) NaOH-NaNO₃-NaAlO₂ at typical tank concentrations
- (c) NaOH-NaNO₂ at typical tank concentrations
- (d) NaOH-NaNO₂-NaAlO₂ at typical tank concentrations
- (e) NaOH-NaNO₃-NaNO₂-NaAlO₂ at typical tank concentrations

Chelating/Complexing Agents^a and Their Degradation Products in Nuclear Wastes

Chelating/Complexing Agents:

Degradation Products:

Chemical Form Detected by GC and GC-MS:

a) Identified as methyl esters:

b) Identified as Intramolecular lactone:

c) Identified as Intramolecular lactam:

d) Identified as dehydrated dimethyl ester

e) Identified as lactone and dimethyl ester

(2) Possible mechanistic origin of CO_2 , H_2 , N_2O and NH_3 .

(3) Stoichiometry of Reaction

Determination necessary for kinetic studies and to understand the mechanism of reaction.

(4) Kinetics

Kinetics carried out were pseudo first order initial rate studies based solely on gas evolution without any consideration for the intermediate formed in solution for the production of products. Initial kinetic studies were very helpful but far from complete.

(5) Isolation of Key Intermediates Formed in the Reaction

If, as anticipated, the thermal reactions are catalyzed by Al(III), investigation of the nature of the species in solution would be desirable. One would specifically seek for evidence of complexation with NO_3^- , NO_2^- , or the various complexing carboxylate anions. Use of ^{27}Al , ^{13}C , ^{15}N and ^1H NMR would be helpful in "in situ" detection of intermediates.

(6) Nature of the Crust

The chemical composition of the crust is very important. If predominantly carbonate, the "in situ" formation of CO_2 is suggested providing evidence for decarboxylation. The formation of crust from simulated slurry will be studied as the composition of crust varies with time.

We propose to investigate the formation of solid when gaseous CO_2 is formed in situ by radiation decomposition of some chosen carboxylic acid in the mixture; temperature gradient to be maintained as best as possible. High intensity Co-60 gamma-ray source to be used for irradiation. Exact composition and concentrations would be based on results from "thermal reactions" and "radiolysis reactions". CO_2 can also trap the amines in solution thereby placing organics in the crust.

(7) Effect of Metal Catalysis

It is not unreasonable that some or all of the reactions leading to decomposition products are metal catalyzed reactions. The rates of the reactions suggested in (1) will be determined in the presence of metal known to exist in tank 101-SY for comparison with those in the absence of the metals.

(8) Effect of Radiation

A large fraction of the reactions performed to understand the nature of the "thermal reactions" would be repeated in the presence of a high intensity radiation source. It might be anticipated that a much larger variety of products would be formed, so that the analytical part of the experimentation would be more extensive. The number of experiments would probably be smaller since it will not be so necessary to use the large variety of concentrations required to establish the kinetics of the "thermal reactions".

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