

UNDERSTANDING OF CYCLIC VENTING PHENOMENA IN HANFORD SITE HIGH-LEVEL WASTE TANKS: THE EVALUATION OF TANK 241-SY-101

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ABSTRACT

Tank 241-SY-101 is a double-shell, high-level waste tank located in the 200 West Area on the Hanford Site. This tank contains about one million gallons of concentrated neutralized waste. Shortly after the waste was put in the tank, the waste began to expand because of gas generation. In 1990 this tank was declared to have an unreviewed safety question because of the generation of flammable mixtures of hydrogen and nitrous oxide gas that was periodically released to the tank dome space and ventilation system.

A safety program was established to characterize the waste and released gases and to determine an effective means to prevent the accumulation of those gases in the tank dome space and ventilation system.

Results of the expanded characterization conducted in fiscal year 1991 are presented. Instrumentation placed in the tank helped to provide more detailed information on tank temperatures, gas pressure, gas flow rates, and gas composition.

An extensive laboratory study involving the Westinghouse Hanford Company, Pacific Northwest Laboratory, Argonne National Laboratory, and the Georgia Institute of Technology was initiated to determine the mechanisms responsible for the generation and retention of various gases. These studies evaluate both radiolytic and thermochemical processes. Results of the first series of experiments are described.

INTRODUCTION

Flammable gas generation in Tank 241-SY-101 is a top priority waste tank safety issue at the Hanford Site because peak concentrations above the lower flammability limit (LFL) for hydrogen occur periodically in the tank dome space. This release of gases is expected to keep recurring until some form of remediation is taken. In the unlikely event that an ignition source were present during these periods, a hydrogen burn or explosion might occur with a possible release of nuclear waste to onsite and offsite personnel. In addition, it is likely that a concentration greater than the LFL exists within gas bubbles that are trapped in the waste. Background information on the tank's history is provided.

Administrative and technical controls are in place to restrict activities that could cause undesirable reactions. Non-sparking tools and electrical bonding and grounding techniques are used. So-called "normal" activities for tanks of concern are limited to surveillance. Special safety analysis documents prepared for all work inside the tank are extensively peer reviewed and require U.S. Department of Energy (DOE) approval.

A significant portion of the activities of the Waste Tank Safety Program have been jointly directed at the characterization of the gases that are released from the tank and at the definition of the mechanism(s) for the production of these gases. The purpose of this paper is to provide a summary of (1) the methods used for characterization of the gas release events, (2) the data obtained from the recent gas release events and waste sampling activities, and (3) the results obtained from laboratory studies directed at understanding the mechanisms for the formation and storage of the gases. Such information is aimed at gaining understanding of the mechanisms of gas formation, retention, and release in Tank 241-SY-101 so that mitigation and/or remediation of the tank can be accomplished.

Although 22 other tanks are also suspected of potentially containing smaller accumulations of hydrogen or other flammable gases, this report focuses only on Tank 241-SY-101. There is a significant difference in behavior (e.g., gas release quantity and intensity) between Tank 241-SY-101 and the other 22 tanks. Evidence of gas release, surface level behavior, and knowledge of the other tank contents suggests a much lower likelihood of potentially dangerous gas concentrations in those other tanks.

BACKGROUND INFORMATION ON TANK 241-SY-101

Construction on Tank 241-SY-101 was completed in 1976. The first waste put into the tank was from the first double-shell slurry campaign using the 242-S Evaporator in 1977. Double-shell slurry is the most concentrated material that the evaporators can produce. The degree of evaporation is limited only by the pumpability of the slurry. Tank 241-SY-101 received 2.54 m (100 in.) of this material.

From 1977 to 1980, the tank received complexed concentrate waste, which was placed in the tank at three different times (Table I shows the filling history). A total of 5.16 m (203 in.) of complexant concentrate waste was placed on top of the heavier double-shell slurry. Although other double-shell tanks have also received complexed concentrate, in Tank 241-SY-101 the dynamics of gas release make it our initial primary concern. Complexant concentrate is a waste from the cesium/strontium recovery process in B Plant. It is rich in complexing agents such as ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), citric and glycolic acid (hydroxyacetic acid). These alkali-soluble organics were concentrated with the waste stream.

The volume of waste in Tank 241-SY-101 was first noted to increase in 1977 after the first double-shell slurry was put

TABLE I

Tank 241-SY-101 Contents

| Tank fill Chronology | Cubic meters (gallons) | Substance | Meters (inches) |
|----------------------------|------------------------|-------------------------------------|-----------------|
| April 1977 | 1040 (274,000) | Double-shell slurry ^a | 2.54 (100) |
| November 1977 | 1380 (365,000) | Complexant concentrate ^b | 3.38 (133) |
| June 1978 | 496 (131,000) | 241-SX-106 complexant concentrate | 1.2 (48) |
| August 1978 | 227 (60,000) | 111-U complexant concentrate | .56 (22) |
| November 1980 | 870 (230,000) | Double-shell slurry | 2.1 (84) |
| September 1984 to May 1988 | 30 (8,000) | Water | .08 (3) |
| Totals | 4040 (1,068,000) | | 9.9 (390) |

^a Double-shell slurry is a concentrated waste produced by the evaporator. It is high in hydroxide, nitrate, and aluminate concentration.

^b Complexed concentrate is an evaporator product similar to double-shell slurry (though not as concentrated). It also contains significant organic complexant concentrations.

into the tank. A cycle of growth and collapse began after the last addition in 1980 and continues today.

Figure 1 shows the cycles of the surface level of the tank during the past several years. Water and air lancing was used for a number of years in an attempt to control the gas releases in the tank. Lancing was stopped in 1989 when the ineffectiveness of this operation was noted and the surface level reached 10.8 m (423 in.). This was greater than the 10.7-m (422-in.) operating specification, which is in place to prevent overfilling the tank and overstressing it due to hydrostatic head.

An indication that gas is released is indicated by the pressure increases in the dome space, even though forced ventilation is maintained and the tank operates at negative .08 m (3 in.) water gage pressure. Early laboratory work to identify the cause of the slurry growth phenomena indicated that hydrogen is a major component of the slurry growth gas. Since early 1990, there has been an ongoing vapor sampling

effort(1). Among the gases released from the waste in addition to hydrogen are nitrous oxide, nitrogen, and ammonia.

MONITORING OF TANK 241-SY-101

Identification of the species and amounts of the gases that are released from Tank 241-SY-101 has occurred through the evaluation of data obtained from (1) surface level measurements, (2) tank pressure, (3) flow rate of the ventilation system, and (4) measurement of the gas composition. In addition, significant insight into the venting process has been gained from interpretation of the temperature changes in profiles in the tank during gas buildup and release. Instrumentation used to monitor and characterize the tank is briefly described in the following paragraphs.

Surface Level Measurements, Tank Pressure, and Ventilation Flow Rate

The original purpose of measuring the surface level in the tank was to monitor for leakage of waste tank contents and to ascertain when the tank was filled to the upper limit. Leakage would be indicated by a drop in surface level. In Tank 241-SY-101, an increase in the surface level indicated a "growth" of the slurry caused by entrapment of generated gases.

Gas Composition and Quantity

Gas composition is determined by a number of methods. Some are used on a continual basis and some are used only when an event is thought to be imminent with measurements continuing until some time after the event. The devices and systems used are discussed briefly in the following paragraphs.

A Teledyne* hydrogen monitor is located at the ventilation header. The monitor determines hydrogen based on

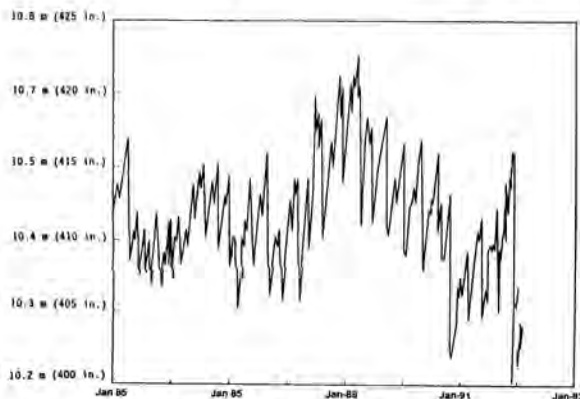


Fig. 1. Tank 241-SY-101 surface level readings.

* Teledyne is a trademark of Teledyne, Inc.

thermal conductivity and provides continuous output to a strip chart recorder and a data logger.

Grab samples are taken from a port in the ventilation system at intervals during each event. They are analyzed by a mass spectrometer and provide information about the gas composition. The ventilation line port also feeds two gas chromatographs (one for hydrogen only, the second for other gases), a cryogenic sampler, and an ammonia detection system. The external instruments are installed and operated for a gas release event. To determine the base concentration of gases evolved between vent cycles, grab samples have been collected periodically and analyzed for hydrogen on a high-sensitivity gas chromatograph.

An organic vapor monitor is installed at the SY tank farm stack approximately one week before an anticipated event. It is a nonspecific monitor that indicates ammonia. The readings appear to correlate well with Drager* tube sampling, which is used at the stack to indicate ammonia.

To better measure gas composition, a gas monitoring system was installed in April 1991. The gas is taken from a sampling tube located in the tank dome space. The gas monitoring system is comprised of four main subsystems: (1) a mass spectrometer for analyzing the gas for its components with atomic mass units between 2 and 100, (2) a hydrogen monitoring unit, (3) a differential pressure transmitter, and (4) a port for obtaining grab samples. Detailed information on the gas monitoring system can be found in WHC-EP-0517(2).

Temperature Measurements

The temperature of the waste is obtained from a single thermocouple (TC) tree that contains 18 Type J thermocouples. Data from this TC tree provide an axial temperature measurement in the waste.

In addition to the TCs in the tank space, a TC and temperature transmitter are located in the ventilation header space. The ventilation temperature data and relative humidity are sent to a Hewlett-Packard** data logger located in the gas monitoring system shelter.

Summary of Typical Gas Release Events

In the spring of 1990, an increased emphasis was placed on the characterization of the gas releases from Tank 241-SY-101. In the past 2 years, these episodic releases have occurred about every 100 days. Table II provides a summary of the events of 1990 and 1991.

It is not the intent of this report to provide a detailed description of each event; rather, selected observations will be presented. Detailed reports are issued for each gas release event and can be made available to the reader. Summary descriptions of gas releases can be found in WHC-EP-0517(2).

Amount of Gas Released in an Event

Using the estimates of gas composition, the flow rate for the ventilation, and the hydrogen release profiles, it is possible to estimate the total amount of gas released in the various events. A summary of the calculations is given in Table III.

The released gas volume can also be calculated from the change in the surface level of the tank. Assuming that the entire surface of the tank waste moves in a uniform manner during an event and that the gas behaves as an ideal gas, the volume of gas was calculated for two cases: (1) the specific gravity of the waste equals 2, and (2) the specific gravity equals 1.6. Table IV presents the results. These values are in general agreement with those in Table III.

In Table IV, the composition of the gas, based solely on mass spectrometer data, was 40% H₂, 32% N₂O, and 28% N₂. J. J. Barker(3) reported that the October 1990 data yielded a composition of 38% H₂, 32% N₂O, and 30% N₂. These two results are in good agreement, considering the difficulties in estimating the constituents in a diluted gas stream. These analyses do not account for the condensable gases (H₂O and NH₃). Ammonia was detected during the October 1990 event and the May 1991 and December 1991 events. Analyses show that, as is expected, water vapor also is present. In consideration of the fact that the trapped gases at the bottom of the waste are under about two atmospheres of pressure and that the total pressure of the mixture is composed of the partial pressure of the various gases, a calculation was made to determine the amount of minor constituents in the released gases. At this point in time, the best estimate for the gas composition is as follows:

| Constituent | Amount |
|--|--------|
| Hydrogen | 36% |
| Nitrogen | 27% |
| Nitrous oxide | 28.5% |
| Water | 4% |
| Ammonia | 4% |
| Others: CO ₂ , CH ₄ , CO | 0.5% |

Continued monitoring of the tank with more sensitive instrumentation will help to improve the knowledge of the specific gases released in the events.

Characterization of Tank 241-SY-101 Waste

In mid-1991 a full-depth core sample, consisting of 22 segments, was obtained from Tank 241-SY-101. Numerous chemical, physical, and radionuclide analyses were conducted on these segments. Observations of the segments showed there were three layers within the waste: a very thin crust, a layer corresponding to the so-called convective region, and a layer containing numerous solids that corresponds to the nonconvective region.

A comparison of the major analytes for each of the two main layers is shown in Table V. The major difference found was in the total organic carbon, which is about 50% higher in the nonconvective region. Nitrite is about 20% lower in the nonconvective region. Chromium was much higher in the nonconvective region, and the chromium is probably associated with the solid particles that were in a much greater

* Drager is a trademark of Dragerwerk AG Lubeck.

** Hewlett-Packard is a trademark of Hewlett-Packard Company.

TABLE II
Periodic Release of Gases

| Event date | Number of days since last event | Change in surface level, meters (inches) | Peak pressure, Pascale gage (inches water gage) | Peak H ₂ conc. (%) |
|-------------------|---------------------------------|--|---|-------------------------------|
| January 1990 | 109 | -0.20 (-7.7) | -- | -- |
| April 19, 1990 | 110 | -0.21 (-8.3) | + 25 (+ 0.1) | 3.5 |
| August 5, 1990 | 109 | -0.13 (-5.2) | -490 (-1.96) | 1.2 |
| October 24, 1990 | 80 | -0.26 (-10.3) | + 575 (+ 2.3) | 4.7 |
| February 13, 1991 | 110 | -0.13 (-5.0) | -500 (-2.0) | 0.04 |
| May 16, 1991 | 82 | -0.18 (-7.2) | + 63 (+ 0.25) | 0.5 |
| August 1991 | -- | ≤ 0.13 (≤ 5) | -708 (-2.83) | 0.56 |
| December 4, 1991 | 97 | -0.33 (-13) | + 2040 (+ 8.16) | 5.0 |

TABLE III
Comparison of Data from Three Gas Release Events

| Date | Crust level change, meters (inches) | Pressure peak, Pascale gage (inches, WG) | H ₂ concentration peak (mol%) | H ₂ gas release ^a , cubic meters (cubic feet) | Total gas release, cubic meters (cubic feet) | Steady-state ventilation flow rate, cubic meters/minute (cubic feet/minute) |
|------------------|-------------------------------------|--|--|---|--|---|
| April 19, 1990 | -0.24 (-9.3) | + 25 (+ 0.1) | 3.5 | 102 (3,600) | 300 (11,000) | 10.5 (371) |
| August 5, 1990 | -0.13 (-5.2) | -490 (-1.96) | 1.2 | 54 (1,900) | 200 (7,000) ^b | 11.8 (417) |
| October 24, 1990 | -0.259 (-10.2) | + 575 (+ 2.3) | 4.7 | 91 (3,200) | 234 (8,400) | 17 (600) |

^aCalculated values.

^bAssumes 27 mol% hydrogen in evolved slurry-growth gas. At 40 mol% hydrogen, total gas amounts to $136 \pm 12.7 \text{ m}^3$ ($4,800 \pm 450 \text{ ft}^3$).

TABLE IV
Gas Volumes for Events

| Date | Drop, meters (inches) | Minimum, cubic meters (cubic feet) | Maximum, cubic meters (cubic feet) |
|---------------|-----------------------|------------------------------------|------------------------------------|
| April 1990 | 0.24 (9.3) | 174 (6,140) | 253 (8,930) |
| August 1990 | 0.13 (5.2) | 96 (3,430) | 133 (4,990) |
| October 1990 | 0.25 (10) | 187 (6,600) | 272 (9,600) |
| February 1991 | 0.13 (5) | 93 (3,300) | 128 (4,800) |
| May 1991 | 0.18 (7.2) | 114 (4,300) | 204 (7,200) |
| August 1991 | 0.13 (5) | 85 (3,000) | 142 (5,000) |

concentration in the lower region. Other analytes (sodium, aluminum, and nitrate) were nearly the same in the two layers.

Perhaps the greatest differences found between the two main layers was in the physical properties. There was a considerable difference in the amount of solids. In the convective region, the solids amounted to about 15 vol%, while in the nonconvective region the solids were about 85 vol%. Finally, a very significant increase in the shear strength was noted for the last segment, i.e., the material on the bottom of the tank.

A comprehensive report on the analyses of the tank waste is being prepared for public release. These data will be used to provide insight on the chemical processes occurring in the waste and will also provide critical data to the modeling activities.

TABLE V

Comparison of Average Composition of Tank Layers (dry wt %)

| Analyte | Convective layer | Nonconvective layer |
|----------------------|------------------|---------------------|
| Nitrate | 10.3 | 10.2 |
| Nitrite | 11.7 | 9.1 |
| Total organic carbon | 1.25 | 1.9 |
| Sodium | 20.1 | 21.2 |
| Aluminum | 3.4 | 3.5 |
| Calcium | 0.012 | 0.036 |
| Chromium | 0.088 | 0.70 |

Summary of Studies Conducted to Determine the Mechanisms for Gas Generation

Possible Mechanisms of Tank Behavior: Work is in progress at Westinghouse Hanford Company, Argonne National Laboratory, the Georgia Institute of Technology, and Pacific Northwest Laboratory to determine the mechanisms of gas generation and release and to develop a thermophysical model of the waste(4).

Based on analysis of the off-gas stream, a mixture of hydrogen, nitrous oxide, and nitrogen gas appears to form as the product of radiolysis and/or the chemical decomposition of the organic chemicals in Tank 241-SY-101. According to our current hypothesis, tank gases appear to be formed continuously in the whole tank, but they appear to be stored preferentially in the nonconvective sludge layer in the bottom portion of the tank. Unknown instabilities trigger a movement of the waste toward the top of the tank, thereby releasing the stored gas.

Before a gas release, the bottom part of the tank shows a profile that has a maximum temperature near the middle of this region. This temperature profile is indicative of a material with a volumetric heat source and in which the heat is dissipated by conduction. The indications are that this layer contains settled solids that do not move. The radioactive decay heats this layer uniformly, but the heat can flow from both the bottom and top of the layer. Hence, those areas are cooler than the center of the layer.

Above this layer is a layer that has a very uniform temperature. This is an indication of a fluid convective heat transfer zone. Heat generated in this zone and transferred to it from

below is the driving force to move the fluid by convection. The convection mixes the layer and keeps the temperature uniform.

After a gas release, the temperature profile is generally uniform from top to bottom, thus indicating a mixing of the two layers in the tank. Indeed, when the temperature profiles are studied more closely, it is common to see the hot material from the bottom rise to the top and lodge there for a short time before dissipating. Figure 2 shows a schematic of what is believed to be happening.

The chemical reactions (involving the organics and assisted by the radiation) appear to be producing gas throughout the tank. In the convective layer, the motion of the fluid brings the gas generated in that layer up to the surface where it can be released. This does not allow the gas to accumulate in the fluid layer. However, in the lower layer, the waste does not move. Most of the gas formed in this layer is retained.

This layer eventually becomes less dense due to the accumulated gas. As the temperature rises in the lower region the accumulated gas expands, further decreasing the density. The increased temperature also decreases the viscosity of the material. Some of the solid material may redissolve in the warmer temperature. Finally, the rate of chemical reaction may also increase.

At some point, the lower level reaches a critical density and becomes buoyant. This causes instability, and the lower region moves or "rolls over" to the top. When this happens, the hydrostatic head decreases, the pressure on the accumulated gas drops, and the bubbles expand. This further increases the buoyancy. The gas releases when it gets to the surface. The size of the cohesive mass of slurry that rises to the tank waste surface is probably dependent on the previous history of various regions of the slurry. From videotapes of the tank surface, one can conclude that large coalesced bubbles release rapidly while smaller bubbles percolate out of the waste more slowly.

Eventually, enough of the accumulated gas is released so that the solids can settle out. The nonconvective layer forms once more on the bottom, and the cycle starts over again.

Gas-Retention Mechanisms

Three possible mechanisms for gas retention have been proposed, and tests to distinguish them are being designed. Understanding of the retention mechanism will help in the design of a mitigation strategy. These mechanisms and the evidence supporting them are described below.

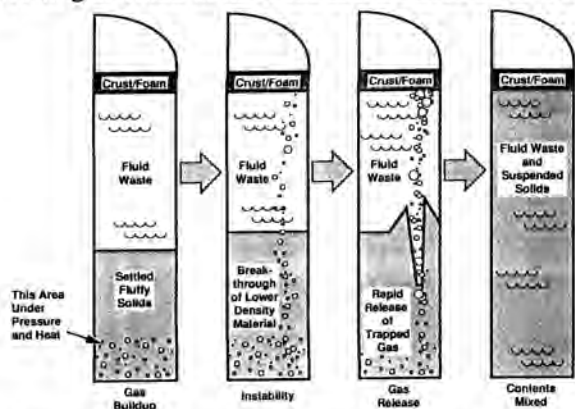


Fig. 2. Postulated mechanism of tank 241-SY-101 venting.

- The mechanical entrapment of gas is within a "pseudo lattice" of solid crystals. The shear strength of the slurry would be related to the gas retention capability.
 - The nature of the crystals in synthetic waste changes markedly when heated to 328-338 K (55 to 65°C).
 - There is a sharp decrease in ultrasound signal attenuation at ~338 K (~65°C).
 - Gas retention within the slurry is very dependent on bubble size.
 - Some bubbles may remain within cohesive "gobs" of slurry and return to the tank bottom as the new nonconvective layer reforms after a vent. Temperature observations following a rollover seem to support this hypothesis.
- Forces associated with surface tension between gas bubbles and the solid crystals trap the gases generated in the nonconvective layer. The presence of organic constituents may be critical to the existence of a hydrophobic surface capable of holding the gas bubbles. A critical element for the effectiveness of a such a mechanism would be the ratio of gas bubble to particle size.
 - Crust formation seems to originate by flotation of the slurry particles and only occurs in the presence of an organic chelator.
 - Bubbles on both actual wastes and the synthetic mixtures appear to be attached to individual crystals.
 - Loss of crystal surface through selective dissolution could aide gas release. (This also supports mechanical entrapment mechanism.)
- Viscous forces may prevent the escape of gas from the settled slurry.
 - Modeling of turnover based on this theory gives plausible results.
 - Slurry viscosity drops rapidly with an increase in "void" (e.g., nonsolid) fraction volume.
- Although EDTA is not reactive under thermal conditions, it leads to gas generation under radiolytic conditions.
- Irradiation of typical waste solutions leads to the generation of as-yet unidentified organic intermediates that greatly increase the rate of thermal decomposition.
- Radiolytic gas generation is insensitive to nitrite compositions above 1.5M and nitrate above 0.5M.
- Formaldehyde, a probable reaction intermediate, is a primary source of hydrogen under thermal conditions. The generation of hydrogen from formaldehyde is enhanced by the presence of caustic.
- Aluminum has been confirmed to be an essential ingredient in the decomposition of organics under both thermal and radiolytic conditions.
- Nitrite ion appears more important than nitrate ion in the production of hydrogen under thermal conditions.
- Radiolysis occurs in localized regions (solvent cells or spurs) where high concentrations of reactive intermediates exist for short periods of time; hence, radical scavenging agents are not effective in stopping gas formation.
- Relative to mechanisms for radiolytic gas generation, differences in sources and type of radiation are calculated to be negligible.

Gas Generation

- The quantity of hydrogen generated by thermally driven chemical degradation reactions in synthetic wastes accounts for perhaps one-third of that generated in the actual tank. The amount of nitrous oxide generated in the synthetic studies far exceeds that found in Tank 241-SY-101. A comparison of gas production calculated on the basis of synthetic waste studies and estimates for Tank 241-SY-101 is included in Table VI.
- The rate of gas generation increases with temperature, indicating a combined radical and thermal gas-generation mechanism.
- The rate of gas generation under radiolytic conditions increases with the number of C-H and N-H bonds. However, N₂ was generally not detected as a radiolysis product. The other likely gaseous products that have not yet been quantified are NH₃ and CO₂, although ammonia gas has been smelled in some experiments.

Problems to be Resolved

No clear correlation exists between the stoichiometry of gases generated from synthetic wastes, particularly for N₂O/H₂ ratios, and those measured in the tank for most organics intermediates tested.

To accelerate the rate of organic chemical decomposition and gas generation in the synthetic waste studies, reaction temperatures in the range of 363 K (90°C) to 393 K (120°C) were used rather than the actual tank temperature of 333 K (60°C), requiring correction of the laboratory data to account for the raised activation energy. If such an extrapolation is

Summary of Mechanistic Knowledge from Synthetic Waste Studies

Details of the thermochemical studies done by the Georgia Institute of Technology on synthetic waste can be found in WHC-EP-0517(2). A description of the work done at the Argonne National Laboratory on radiolytic decomposition of synthetic waste is also reported in that document. The findings from those mechanistic studies, as well as recent data obtained at PNL, are summarized below. Details of Dr. Meisel's work are also being presented at this symposium(5).

Solution Chemistry

- The original chelating agents (EDTA and HEDTA) probably account for only a small fraction of the organic carbon left in Tank 241-SY-101. This serves to focus the analyses of waste toward identification of degradation products.
- To produce hydrogen or nitrous oxide under thermal conditions, organic constituents must be present. Organic constituents enhance gas production under radiolytic conditions.

TABLE VI

Comparison of Gas Generation in Synthetic Waste Studies with Estimates for Tank 241-SY-101

| | Moles H ₂ /day | Moles N ₂ O/day | Comments |
|-------------------------------|---------------------------|----------------------------|---|
| Thermochemical | 20 | 100 | Results at Pacific Northwest Laboratory were obtained at 363 K (90°C) and corrected to 333 K (60°C) using an activation energy of 25 kcal/mol |
| Radiolytic | 21 | 207 | From studies at Argonne National Laboratory |
| Estimates for Tank 241-SY-101 | 64 | 52 | Based on a slurry growth rate of .003 m (0.11 in.)/day(4) and vent gas analyses for the October 24, 1990 event |

valid, one must be certain that the reaction mechanisms do not change over the temperature range in question. Such work is in progress.

The effect of slurries on gas generation needs to be evaluated. The initial sets of experiments were carried out on homogeneous solutions to maximize experimental control. The nature of the effects of heterogeneous media on the reaction pathway is being explored.

The effect of longer reaction times under 2 atmospheres pressure on nitrous oxide production is being studied. This is part of the study to determine why more nitrous oxide is generated in Tank 241-SY-101 than in the synthetic tests performed at atmospheric pressure.

The identification and role of the reaction intermediates (e.g., complexant degradation products) in gas generation must be determined. It can be assumed from first principles of thermodynamics that the materials remaining in Tank 241-SY-101 are less reactive than those consumed; otherwise, they would not accumulate in the waste.

CONCLUSION

The knowledge and understanding of the risks from the cyclic venting of Tank 241-SY-101 have been greatly enhanced because of the sampling and laboratory studies conducted over the last year and a half.

Additional instrumentation for evaluating the composition of the vented gases has led to an estimated composition that is mainly hydrogen, nitrogen, and nitrous oxide. Small amounts of ammonia and water vapor are also present.

The concentration of hydrogen in the exhaust header on top of the tank is above the lower flammability limit in some of the gas release events, but it is at that value for only a short time. The total amount of gas released in these episodic events ranges from 85 to 311 m³ (3,000 to 11,000 ft³). Similarly, the observed changes in the surface level of the waste range from about 0.13 to 0.25 m (5 to 10 in.). During a gas release event, the hotter waste from the bottom portion of the tank moves to the top; this movement has been postulated to be due to a density instability that results from the entrainment of the gas.

A major effort was initiated to understand the mechanisms that are involved in the production of the various gases. Studies are being conducted on synthetic waste mixtures to determine the radiolytic mechanisms for the production of

hydrogen and nitrous oxide. These studies have shown that the H₂ and N₂O are produced in the synthetic wastes that contain various organic compounds, but the production rates do not match those inferred from the analysis of the gas release events. Laboratory studies are also being conducted to evaluate the production of gases by the thermochemical degradation of the various chelating agents. Tests are being done to determine the amount and composition of gases produced as a function of time at various temperatures. Possible Cannizzaro-type reaction mechanisms may be involved in the formation of hydrogen.

In the remainder of fiscal year 1992, laboratory studies on the gas-generation mechanisms will continue, and studies will also be conducted to gain insight on the processes responsible for gas retention and release.

REFERENCES

1. BABAD, H., G. D. JOHNSON, D. A. REYNOLDS, and D. D. STEPNEWSKI, *Evaluation of Tanks That Contain Flammable Gases*, WHC-SA-1216-FP, Westinghouse Hanford Company, Richland, Washington (1991).
2. JOHNSON, G. D., H. BABAD, D. A. REYNOLDS, J. A. LEHEL, L. R. PEDERSON, D. STRACHAN, D. MEISEL, and G. ASHBY, *An Evaluation of the Generation and Release of Flammable Gases in Tank 241-SY-101*, A Period Report October 1990 - September 1991, WHC-EP-0517, Westinghouse Hanford Company, Richland, Washington (November 1991).
3. BARKER, J. J., *Evaluation of October 24, 1990 Tank 241-SY-101 Gas Release Event*, WHC-SD-WM-PE-041, Westinghouse Hanford Company, Richland, Washington (1991).
4. STRACHAN, D. M., Tank Waste Science Panel, 1991, *Chemical and Physical Processes in Tank 241-SY-101: A Preliminary Report*, PNL-7595, Pacific Northwest Laboratory, Richland, Washington (1991).
5. MEISEL, D., *Radiolytic and Radiolytically Induced Generation of Gases in Simulated Mixed Waste Solutions*, D. Meisel, H. Diamond, C. D. Jonah, M. C. Sauer, Jr., J. C. Sullivan, F. Barnabas, E. Cerny and Y. Di Cheng, Argonne National Laboratory, Presented at Waste Management '92, Tucson, Arizona (March 4, 1992).