

THERMAL AND RADIOLYTIC GAS GENERATION IN HANFORD HIGH-LEVEL WASTE

SA Bryan and LR Pederson
Pacific Northwest National Laboratory
P.O. Box 999; MSIN P7-25
Richland, Washington 99352 USA

CM King
Department of Chemistry, Troy State University
Troy, Alabama 36082 USA

ABSTRACT

Mixed radioactive and chemical wastes stored in tanks across the DOE complex generate hydrogen, ammonia, nitrous oxide, and nitrogen by a complex series of radiolytic and thermolytic reactions. Flammable conditions may result when these gases accumulate in the dome space of the waste tanks. A phenomenological model was developed that successfully predicts gas generation rates for many of Hanford's tanks as a function of waste composition, temperature, and radiation dose rate, based in large part on the results of laboratory studies using actual waste core samples. That model, along with gas monitoring, is used as a guide for selecting dome space ventilation rates that provide an adequate margin of safety.

The basic thermal and radiolytic chemistry has been studied extensively over the last decade using simulated and actual Hanford wastes in an effort to understand and predict gas generation rates from Hanford high-level wastes. Predictive models are based on the basic chemical pathways involved in the thermal and radiolytic gas generation. This paper summarizes 1) chemical and radiolytic pathways to gas generation, 2) models for predicting gas generation, and 3) comparisons of predicted hydrogen generation rates to field-measured values for Hanford wastes.

INTRODUCTION

The Hanford Site has 177 underground storage tanks containing radioactive wastes that are complex mixes of radioactive and chemical products. Some of these wastes are known to generate and retain large quantities of flammable gases consisting of hydrogen, nitrous oxide, nitrogen, and ammonia. Because these gases are flammable and have the potential for rapid release, the gas generation rate for each tank must be determined to establish the flammability hazard (1).

An understanding of gas generation is important to the operation of the waste tanks for several reasons. First, knowledge of the overall rate of generation is needed to verify that any given tank has sufficient ventilation to ensure that flammable gases are maintained at a safe level within the tank dome space. Understanding the mechanisms for production of the various gases is important so that future waste operations do not create conditions that promote the production of

hydrogen, ammonia, and nitrous oxide. Studying the generation of gases also provides important data for the composition of the gas mixture, which in turn is needed to assess the flammability characteristics. Finally, information about generation of gases, including the influence of various chemical constituents, temperature, and dose, would aid in assessing the future behavior of the waste during interim storage, implementation of controls, and final waste treatment.

This paper summarizes the current knowledge of gas generation pathways and discusses models used in predicting gas generation rates from actual Hanford radioactive wastes. A comparison is made between gas generation rates that are measured and those forecast by the predictive models.

PATHWAYS OF GAS GENERATION

In all known studies of gas generation from simulated or actual Hanford waste mixtures by thermal and radiolytic processes, the product gases consist of a mixture of hydrogen, nitrous oxide, nitrogen, and ammonia (1-14). Ammonia is also a major product of thermal and radiolytic decomposition reactions. Nitrous oxide was usually produced in quantities much higher than hydrogen in these studies, as was molecular nitrogen. The hydrogen/ nitrous oxide ratio was found to depend on many factors, including identity and concentration of the organic components, temperature, hydroxide content, and the presence of minor waste components. An overview of the known processes leading to gas production is given in this section.

Hydrogen-Generating Reactions

Hydrogen is produced principally in Hanford wastes via the radiolysis of water, hydrogen atom abstraction reactions of the organic molecules, and base-catalyzed hydride transfer reactions of the organic molecules formed during radiolysis. Synergism between radiolytic and thermal reactions may also exist, where the partial radiolytic decomposition of a particular organic component leads to the formation of more thermal reactive fragments. Thermal reactions leading to the formation of hydrogen are summarized first, while radiolytic hydrogen-generating reactions are summarized in the following section.

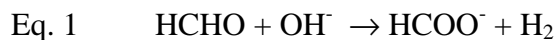
Thermal Generation of Hydrogen

The first study of gas generation in simulated Hanford wastes was performed by Delegard (10). Important conclusions from this work were that 1) gas generation rates were linearly dependent on the concentrations of hydroxide ions within a certain concentration range, nitrite ions, and aluminate ions; 2) if aluminate ions were absent from the simulant, gas generation rates were very small; 3) gas generation rates were independent of the concentration of nitrate ions; and 4) gases were readily generated from decomposition of the complexant HEDTA, but EDTA was unreactive. Both EDTA (ethylenediaminetetraacetate) and HEDTA (hydroxyethylethylenediamminetriacetate) were original waste constituents. Subsequent analyses of Tanks 241-SY-101 (SY-101) and 241-SY-103 (SY-103) wastes have shown that all HEDTA and a large fraction of EDTA have been consumed (15-18).

Based on studies with simulants, the thermal generation rates for hydrogen were sensitive to many factors. In addition to a dependence on aluminate, hydroxide, and nitrite ion concentra-

tions, as well as on the identity and concentration of organic components, Bryan and Pederson (8) have shown that hydrogen generation rates also depend on the presence and concentration of minor components such as transition metals and chloride ions. Activation energies for gas generation have been found to vary considerably depending on the identity of the organic component. Delegard (10) reported an activation energy of 102.5 kJ/mol for total gas generated from a simulated waste containing EDTA and HEDTA. Siemer determined a value of 96 kJ/mol for a similar waste (19). Meisel et al. (12) found activation energies of 84.8 kJ/mol when formaldehyde was the sole organic component of the simulatant and a 40.9 kJ/mol when sodium glyoxylate was present. For formaldehyde in a 2.3 M NaOH solution, Meisel et al. (12) obtained an activation energy of 64.4 kJ/mol, considerably smaller than found for a simulated waste mixture. For a simulatant containing sodium glycolate, Ashby et al. (4) gave the activation energies for hydrogen generation of 125.6 kJ/mole when air was excluded and 113.0 kJ/mole when air was present. For simulatants containing HEDTA, Ashby et al. (4) reported an activation energy of 71.1 kJ/mole for hydrogen generation. Actual waste mixtures contain a variety of chelators, chelator fragments, and solvents, not all of which have been identified (15-18,20). Clearly, any prediction of thermal hydrogen generation rates for a given waste without an extensive knowledge of the composition of that waste may be subject to considerable uncertainty. For this reason, the results of laboratory gas generation studies using actual waste mixtures by Bryan et al. (9,21-24), King (25-27), and Person (13) during the past several years are particularly important, as discussed in the last section of this paper.

The mechanism of hydrogen generation from chelators such as HEDTA and EDTA involves extensive fragmentation of those molecules (4-6). The aluminate and nitrite ions are believed to play an important role in initiating the decomposition reaction through formation of a trihydroxynitritoaluminum complex for Hanford waste mixtures. The coordinated nitrito ligand is expected to be much more electrophilic than the free nitrite ion and more reactive toward HEDTA. Breakdown products of HEDTA include ethylenediaminetriacetate (ED3A), glycine, asymmetric ethylenediaminediacetate (u-EDDA), symmetric ethylenediaminediacetate (s-EDDA), ethylenediaminemonoacetate (EDMA), imidodiacetate (IDA), formaldehyde, formate, acetate, oxalate, and others (6,28). Formaldehyde is believed to be among the most important hydrogen-producing species, a by-product of a number of fragmentation steps (3-6,11). Formaldehyde is known to react in basic solutions to form hydrogen:



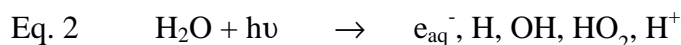
Similar reactions will occur with other organic decomposition products containing the aldehyde functionality, such as glyoxylate. That fragments such as formaldehyde are important sources of hydrogen is consistent with the commonly observed induction period in tests with simulated wastes.

Radiolytic Generation of Hydrogen

There are two principal radiolytic routes to hydrogen production in Hanford wastes (11,12,29): direct radiolysis of water and abstraction of a hydrogen atom from organic compounds. Several comprehensive reviews on water radiolysis have been given (30,31). Radiolytic reactions are altered in concentrated electrolyte solutions, particularly those containing high concentrations of nitrate, nitrite, and hydroxide ions, as discussed in Meisel et al. (11,12,29).

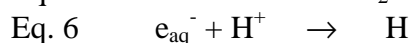
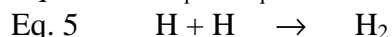
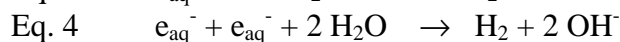
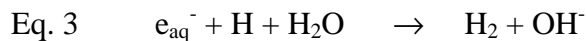
It is well known that gamma ray irradiation of an aqueous solution leads to the formation of energetic electrons (30,31). Gamma ray photons lose part of their energy in collisions with water molecules, transferring this energy to an electron, a process known as Compton scattering. The energy from these electrons is deposited in localized spurs approximately 2 nm in diameter and 50 nm apart along the electron track.

Primary radiolytic decomposition products of water are



While the overall concentration of these radiolytic products in an irradiated solution are generally quite small, localized concentrations within a spur may be quite high—more than 1 mole/liter.

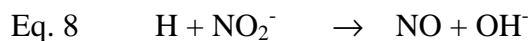
Reactions of primary radiolytic products leads to the formation of hydrogen and other products. Among important reactions that take place are



The nitrate ion is an efficient scavenger of the hydrated electron, e_{aq}^- , resulting in inhibition of hydrogen formation:



Meisel et al. (12) found that nitrate ion concentrations of 0.5 M are effective in suppressing other reactions involving e_{aq}^- . The principal scavenger for the hydrogen atom is the nitrite ion:



This reaction is slower than nitrate ion reactions with the hydrated electron. A nitrite ion concentration of 2 M or higher is needed to be effective.

Meisel et al. (12) determined hydrogen yields for a simulated waste mixture containing sodium hydroxide, sodium nitrate, sodium nitrite, and sodium aluminate. At 30°C, the yield was 0.031 molecules/100 eV, which is very low compared with the value for pure water of 0.45 molecules/100 eV (30,31). Lowered hydrogen yields due to water radiolysis in the simulated waste mixtures are due to nitrate ions scavenging the hydrated electrons and nitrite ions scavenging hydrogen atoms, as discussed above. Very little temperature dependence on radiolytic yields was observed in these concentrated solutions (12).

The rates of hydrogen formation are much enhanced by the presence of organic components. Hydrogen radicals produced via water radiolysis can abstract a hydrogen radical from organic

complexants despite competition from reaction 8, which consumes most of the hydrogen radicals that are formed:



Meisel et al. (12) found that the hydrogen yield increased approximately linearly with the concentration of C-H and N-H bonds present in the simulant without regard to the identities of specific organic solutes. Figure 1 presents the hydrogen generation efficiency (G-value/M) plotted as a function of number of C-H and N-H bonds present per organic molecule used in preparing the simulated waste solutions tested by Meisel. A relation was developed to estimate hydrogen generation rates by radiolytic processes:

$$\text{Eq. 10} \quad G(\text{H}_2) = 0.031 + 0.013 \times \eta_{\text{x-H}} \times [\text{RH}]$$

where $\eta_{\text{x-H}}$ is the number of C-H and N-H bonds in a given organic molecule present in the wastes and $[\text{RH}]$ is the molar concentration of that organic component. This earlier work by Meisel et al. sums the H_2 produced by water radiolysis, H atom abstraction of organic compounds, and the base catalyzed ionic reactions.

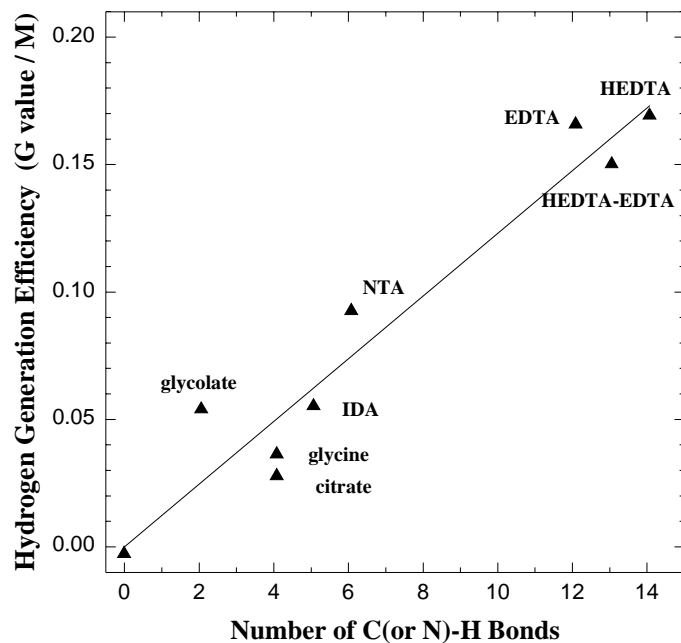
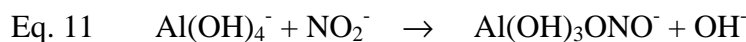


Fig. 1. Molar efficiency of hydrogen generation for chelators using simulated Tank SY-101 waste

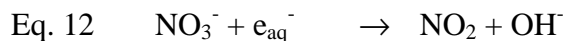
Nitrous Oxide, Nitrogen, and Ammonia-Generating Reactions

Both thermal and radiolytic pathways are known to lead to the formation of nitrous oxide, nitrogen, and ammonia. For nitrous oxide formation, both pathways require the presence of organic compounds, but the majority of the nitrogen in nitrous oxide derives from inorganic sources, not from organic nitrogen according to work using N-15 isotopically labeled compounds (3,4,12). Hydroxylamine is believed to be an important common intermediate in the formation of nitrous oxide, nitrogen, and ammonia, whether by thermal or radiolytic routes.

The reaction of organic waste components with the nitrite ion is an important initiating step in the formation of nitrogen, nitrous oxide, and ammonia. In the absence of radiation, the aluminate ion must be present to catalyze decomposition reactions (4-6,10). Here, a nitrite ion reacts with the aluminate ion to yield a product more electrophilic than free nitrite:



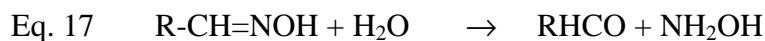
In subsequent reactions, the trihydroxynitrito-aluminum complex acts as an NO^+ donor. Radiolytic reactions produce active nitrogen oxide radicals by the following reactions (12):



Species such as NO_2 can readily react with organic radicals following Meisel et al. (12) and Camaioni et al. (32,33):



Through reaction with a reductant such as NO with an organic radical, oxime ($\text{RCH}=\text{NOH}$) formation is expected. Hydrolysis of oximes yields an aldehyde plus hydroxylamine (4-6,32,33):

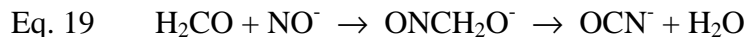


The oxime may also react with a hydroxyl ion to yield ammonia and a carboxylate:

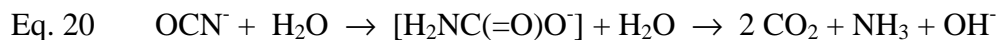


There are several ways to form hydroxylamine from the components in the waste, including hydrolysis of oximes that are formed by radical recombination reactions, as shown in Equations 16 and 17. Another route to hydroxylamine originates in the decomposition reactions of the wastes that produce hyponitrite ion and formaldehyde.

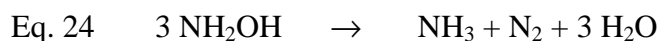
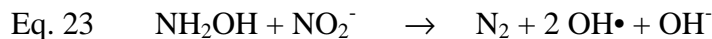
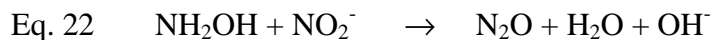
Ammonia can be formed via the decomposition of cyanate anion, OCN^- . The cyanate ion can be formed in wastes via the dehydration of the adduct of nitrosyl anion and formaldehyde:



Cyanate anion decomposes in both acidic and alkaline aqueous solutions to yield ammonia and carbon dioxide (34). March (35) suggests the reaction proceeds through the adduct shown in Equation 20:



Ashby et al. (4) showed that the reaction of formaldehyde and hydroxylamine in alkaline solutions led to formation of the cyanide ion and ammonia, consistent with the above. A variety of reactions involving hydroxylamine have been proposed to account for the formation of nitrogen and nitrous oxide (4-6,11):



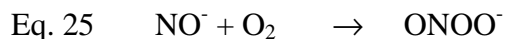
In many previous studies of gas generation from simulated wastes ammonia was detected as a product, but quantitative information was not obtained. Ammonia remains highly soluble in the liquid phase, even in concentrated electrolyte solutions (36,37). Thus, mass spectrometry or other methods of analysis of the gas phase would lead to an underestimate of the quantity of ammonia formed.

Formation and Reaction of Oxygen

Oxygen is not a primary product of water radiolysis but may be formed through secondary reactions such as the decomposition of hydrogen peroxide (31). Meisel et al. (12) determined the radiolytic yield for oxygen to be $G(\text{O}_2) = 0.08 \pm 0.05$ molecules/100 eV for the homogeneous simulated waste SY1-SIM-91C (no organic additives present). No oxygen formation was apparent in simulated waste mixtures when organic solutes were present. In tests in which the sample containing organic solutes was saturated with air prior to irradiation, oxygen was consumed rapidly. The value obtained for the destruction of oxygen in a simulant containing 0.085 M each of EDTA and HEDTA was $G(-\text{O}_2) = 7 \pm 1$ molecules/100 eV. Meisel et al. (12) concluded that radiolytic oxygen formation occurred whether organic solutes were or were not present, but the majority of the oxygen formed reacted with organic radicals, possibly involving intermediates with NO_x radicals. There are no known thermally activated reactions leading to oxygen generation in solutions relevant to Hanford wastes and storage temperatures.

The presence of oxygen as a cover gas has been found to have a marked effect on the distribution of gaseous products formed in thermally activated reactions involving HEDTA (5,6). Yields of hydrogen were enhanced significantly in the presence of an oxygen-containing cover gas, while yields of nitrogen-containing gaseous products (nitrous oxide, nitrogen, and ammonia) were greatly reduced. Ammonia yields were approximately half that produced with an argon cover gas with $\text{NH}_3/\Delta\text{HEDTA}$ (moles NH_3 produced per mole HEDTA consumed) equal to 0.35. The overall yield for nitrogen-containing products in the presence of oxygen was $\Sigma\text{N}/\Delta\text{HEDTA} < 1$, compared with 2.17 with an argon cover gas. Oxygen appears to markedly inhibit the reaction of HEDTA with the nitrite ion.

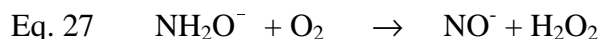
The mechanism responsible for this behavior is not well understood at present, but several observations have been made by Barefield et al. (6). Based on the mechanism they have proposed for the reaction of HEDTA, at least one NO^- should be formed for each HEDTA that reacts. If the further reaction of NO^- resulted in the formation of only NH_3 , N_3 , or N_2O , the ratio of $\Sigma\text{N}/\Delta\text{HEDTA}$ should be greater than 1. A ratio of less than 1 suggests that oxygen reacts with some nitrogen-containing intermediate, leading to reformation of NO_3^- . The species NO^- , expected to be an important intermediate in the absence of oxygen, is known to react with oxygen to yield the peroxy nitrate radical, as shown in Equation 25:



The peroxy nitrate radical will decompose to yield the nitrite ion, as shown in Equation 26:



A significant yield of ammonia suggests that hydroxylamine must continue to be produced as an intermediate. Its disproportionation to yield ammonia must therefore be competitive with autoxidation. Among the products of autoxidation of hydroxylamine are hydrogen peroxide and the nitroxyl radical:



Barefield et al. (6) reported that the ratio $\text{H}_2/\Delta\text{HEDTA}$ rose significantly with time and was always higher than the values obtained with an argon cover gas, as shown in Figure 2. This increased molecular hydrogen yield was suggested to be associated with a buildup of hydrogen peroxide in the solution. Formaldehyde is known to react with hydrogen peroxide in a basic solution to yield hydrogen and the formate ion.

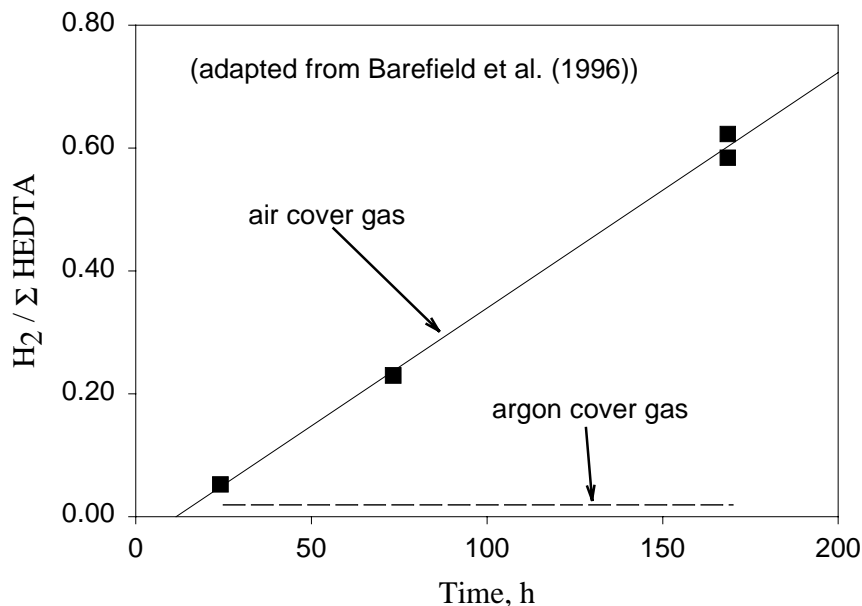


Fig. 2. Hydrogen yield per molecule HEDTA consumed versus time for tests with air cover gas and argon cover gas (6). Hydrogen yields are significantly enhanced by the presence of oxygen and increase with time, possibly due to buildup of hydrogen peroxide. Yields of nitrogen-containing products are suppressed.

As found in earlier studies by Meisel et al. (12), Camaioni et al. (32) found that oxygen was consumed in tests with simulants under radiolytic conditions. With a gamma dose rate of $>10^5$ R/h, oxygen was consumed more rapidly as the temperature increased, but to a non-zero, final steady-state value. In the study of Meisel et al. (12), oxygen concentrations were lowered to below detection limits. High dose rates and the inclusion of relatively unreactive organic solutes by Camaioni et al. (32) may be responsible for some oxygen remaining in the test vessel in that study. The effect of the presence of oxygen on the stoichiometry of gaseous products of organic solute decomposition was much less important under radiolytic conditions (12,32) than under thermal-only conditions (5,6).

Inclusion of oxygen in the cover gas of laboratory tests using actual tank waste led to an increase in the overall rate of gas generation (13). Rate data obtained using a cover gas consisting of 30% oxygen in helium are included in Figure 3. Hydrogen production was significantly increased and oxygen was partially consumed; nitrous oxide and nitrogen yields were not substantially affected. This behavior is generally consistent with observations made by Barefield et al. (6), Camaioni et al. (32,33), and Meisel et al. (12) in studies that used simulated waste.

High hydrogen-to-nitrous oxide ratios found in analyses of the gases present in the headspace of various Hanford waste tanks could indicate the presence of oxygen, as discussed above. Long diffusion times preclude atmospheric oxygen from being an effective source. Oxygen will be

produced radiolytically in low concentrations, as described by Meisel et al. (12). Oxygen is believed to be rapidly consumed in tanks such as SY-101 and SY-103; it may build up in other tanks containing low concentrations of reactive organic solutes or in relatively thermally cool wastes. Low temperatures favor hydrogen generation even without oxygen being present, as shown in Figure 4 (21).

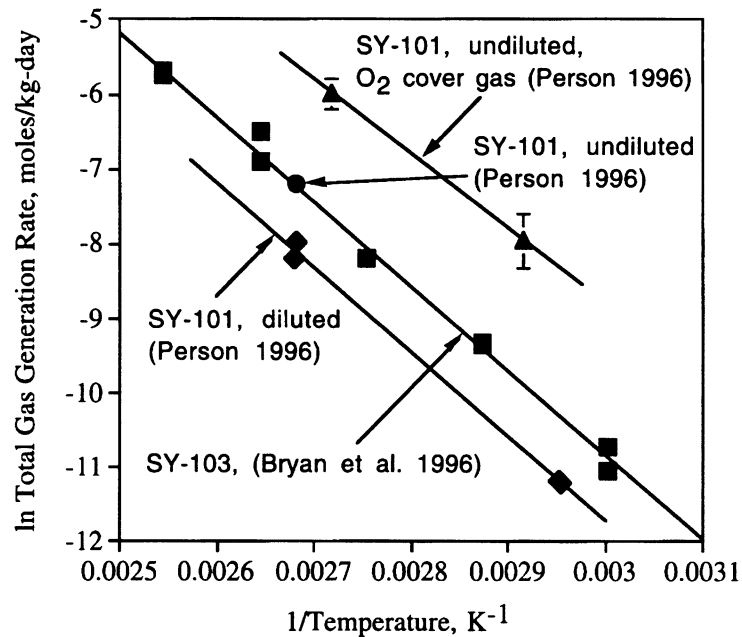


Fig. 3. Comparison of total gas generation from Tank SY-101 core composite (13) and SY-103 convective layer sample (9). Diluted SY-101 signifies a 50% dilution with 2 M NaOH.

MODELS FOR PREDICTING GAS GENERATION RATES FROM HANFORD WASTES

While flammable gas generation rates in several select double shell tanks (SY-101, SY-103, AN-105, and AW-101) have been reasonably well established through laboratory studies and tank behavior observations, there are many other tanks for which such rates are not known but are desired. This section describes the chronological development of the gas generation models used for the prediction of gas generation behavior from Hanford tank wastes. The assumptions and uncertainties associated with each modification of the predictive model are also detailed.

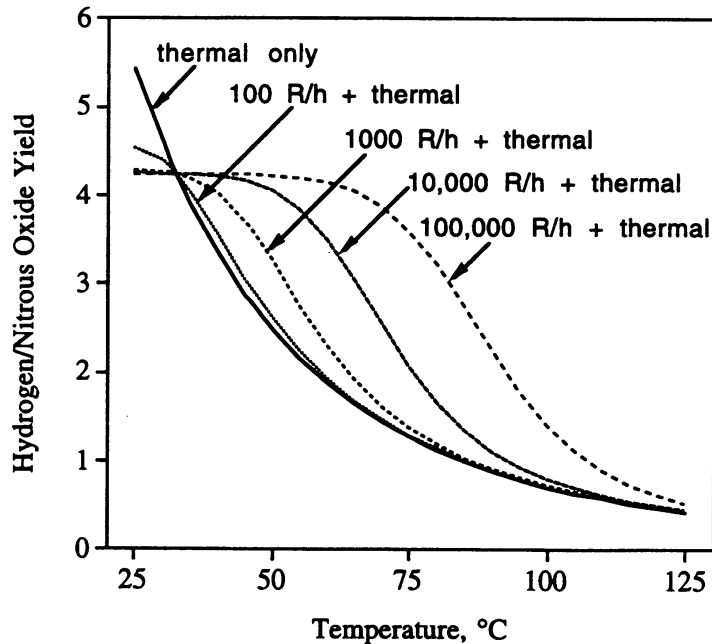


Fig. 4. Hydrogen-to-nitrous-oxide yield ratio from thermally activated and radiolytic reactions (calculated from kinetic parameters determined by Bryan et al. [21] for convective layer samples from Tank SY-103)

Both Hopkins (39, 40) and Graves (41) have given equations to estimate the rate of hydrogen generation from tank wastes as a function of temperature and waste composition. Kinetic gas generation parameters determined in laboratory tests by Bryan et al. (21-24), King (25-27) and Person (13) using actual waste samples were not available when the reports by Hopkins (39,40) and Graves (41) were prepared. Incorporation of recently determined kinetic parameters allows incremental improvements in estimates made by Pederson and Bryan (38) and Hu (42) to be made. Estimates by Pederson and Bryan (38) that incorporate recently determined hydrogen generation rate parameters are provided in the first section below. These models were used by Hu (42) to compare calculated hydrogen release rates with measured hydrogen release rates from Hanford Tank monitoring data; results of this comparison are presented in the subsequent section. A summary and recommendations for improving gas generation models are presented at the end of this section.

Estimates of Hydrogen Generation

Pederson and Bryan (38) proposed an incremental improvement in expressions given by Hopkins (39, 40) and Graves (41) for estimating the rate of hydrogen generation in Hanford wastes using kinetic parameters obtained recently in laboratory tests with actual waste samples. Bryan et al. (38) obtained very good agreement between hydrogen generation rates estimated for Tank SY-103 from laboratory measurements and the actual tank observations reported by Wilkins (14). They determined both the thermal and the radiolytic components of gas generation from Tank SY-103 wastes. Person (13) likewise obtained very important kinetic parameters for gas generation from Tank SY-101 core composite samples. That study emphasized the effect of dilution with sodium hydroxide solution and the effect of oxygen as a cover gas on the rate and

stoichiometry of gas generation. In consideration of the good statistical basis for kinetic parameters reported by Bryan et al. (21) and agreement between laboratory and tank observations, Tank SY-103 was chosen as the baseline for estimating hydrogen generation in other waste tanks.

Thermolytic Rates

The thermal component of hydrogen generation was found by Bryan et al. (21) to obey a simple Arrhenius behavior characterized by an activation energy of 91 ± 9 kJ/mol and a pre-exponential factor of $9 \times 10^8 \pm 1 \times 10^8$ mol/kg waste-day. The activation energy is similar to that chosen by Hopkins (39) of 90 ± 45 kJ/mol for wastes maintained at temperatures greater than that in Tank SY-101 but with a substantial improvement in measurement uncertainty. In the results of Bryan et al. (21), the indicated uncertainty in the activation energy for thermal hydrogen generation reflects a 95% confidence level.

Delegard (10), Ashby et al. (4), Bryan and Pederson (8), and others have found first-order kinetic dependencies of hydrogen generation on hydroxide, aluminate, nitrite, and organic solute concentrations in studies with simulated wastes. Using correction factors in gas generation estimates for each of these waste components is not appropriate, however, because this behavior sometimes holds for only narrow concentration ranges. For example, first-order dependence on the nitrite ion concentration holds for concentrations up to approximately 0.5 M; for higher concentrations, gas generation rates are nearly independent of the nitrite ion concentration (10). A significant number of Hanford waste mixtures contain well over 0.5 M sodium nitrite, so minor differences in nitrite ion concentrations can be ignored. This rule holds for all the modeled tank wastes except those from T-104 and T-110, which are unusually dilute in all salts, including nitrite.

Person (13) studied the effect of diluting Tank SY-101 samples with sodium hydroxide solutions on the thermal rate of gas generation. The concentration of the diluent was chosen such that the sodium hydroxide concentration in the waste sample was insensitive to the extent of dilution. Person found that dilution of core composite samples to 65% of their original concentration of unsaturated components slowed the initial rate of gas generation to 52% of that determined for the undiluted sample. Dilution of the soluble organic fraction alone should lower the gas generation rate to 65% of that determined for the undiluted sample, as noted by Person. If the aluminate concentration and the soluble organic concentration were lowered by this same factor (and both show first-order kinetic dependencies), the rate should decrease to $(0.65)^2 = 42\%$ of the original from the results of studies with simulated wastes. Similarly, first-order dependencies on aluminate, nitrite, and soluble organic concentrations should result in a decrease in the gas generation rate to $(0.65)^3 = 27\%$ of the original value. Dissolution of any nitrite or aluminate present as solids in the original waste would decrease the effect of dilution on thermal gas generation rates. The results of Person (13) are most consistent with the hypothesis that thermal gas generation reactions show first-order kinetic dependence on two components. Delegard (10) found gas generation rates insensitive to the concentration of nitrite ions at the concentration of that component found in Tank SY-101. This leaves soluble organic solutes and aluminate ions as components on which thermal gas generation rates directly depend, consistent with the approach of Hopkins (39,40).

A modified expression to estimate the thermal component of hydrogen generation from a given waste, based on Tank SY-103 behavior, is given in Equation (28):

$$\text{Eq. 28} \quad r_{t,X} = r_{t,SY-103} \frac{[TOC]_X}{[TOC]_{SY-103}} \frac{[Al]_X}{[Al]_{SY-103}} \exp\left(-91 \pm 9 \left(\frac{1}{T_X} - \frac{1}{T_{SY-103}}\right)\right)$$

where

- r_t = the thermolytic hydrogen generation rate per unit waste; X denotes the waste for which the rate is being calculated, SY-103 denotes the rate for Tank SY-103
- [TOC] = % TOC in the waste
- [Al] = % Al in the waste
- T = the absolute temperature (K) of the waste
- 91 ± 9 = activation energy for hydrogen generation from Tank SY-103 waste, kJ/mol/R.

The baseline rate for thermally activated hydrogen generation from Tank SY-103 is 3.5×10^{-7} mol/kg/day at 31.7°C, as given by Bryan et al. (21). Other parameters are (in wt%) TOC = 0.74% (convective/supernate layer) and Al = 2.8% (14). All of the TOC in the convective layer sample from SY-103 derived from soluble organic compounds; insoluble compounds such as oxalate should be excluded. Equation 28 is identical in form to that originally proposed by Hopkins (39,40) but with Tank SY-103 wastes rather than Tank SY-101 wastes used as the baseline.

Using TOC as a scaling parameter to predict gas generation capacity should be viewed with some caution. Baldwin et al. (45) demonstrated that sensitivity factors vary widely for different organic compounds, from 0.1 to 1.0 depending on the method of analysis used (persulfate oxidation or total furnace oxidation). Unfortunately, there is no other measure of the organic solute content widely available for Hanford tank wastes. A method that applies vibrational spectroscopy to evaluate the concentration of specific organic functional groups is under development (43) and shows considerable promise as a means to estimate the enthalpy of reaction of a complex mixture of organic solutes without requiring the precise identification of each organic component.

Radiolytic Rates

For the radiolytic portion of hydrogen generation, both Hopkins (39,40) and Graves (41) based their calculations on the form of a relation given in Equation 10 developed by Meisel et al. (11,12,29). The radiolytic portion of hydrogen generation derives from two principal reactions (12): the direct radiolysis of water and abstraction of a hydrogen atom from organic solutes by a hydrogen radical. Meisel et al. (12) determined a $G(H_2)$ value for a simulated waste in the absence of organics of 0.031 molecules/100 eV. If the nitrate ion concentration is maintained at 0.5 M or higher and the nitrite ion concentration is 2 M or higher, hydrogen yields from direct water radiolysis are not expected to vary substantially from the given value for different waste mixtures. Meisel et al. (12) developed a correlation between hydrogen generation rates by radiolysis and the total C-H and N-H bond density given as Equation 10. Unfortunately, it is difficult to apply that correlation to actual wastes because detailed organic compositional information is available for only a small number of tanks.

Bryan et al. (21) determined a $G(H_2)$ value of 0.14 ± 0.02 molecules/100 eV for the convective layer of SY-103. The organic fraction contains principally chelators and chelator fragments, with a TOC value in the convective layer of 0.74 wt% (18). The hydrogen yield due to radiolytic reactions involving organic solutes can be estimated by subtracting the $G(H_2)$ value for radiolysis of a simulated waste containing no organic solutes (0.031 molecules/ 100 eV) from the total $G(H_2)$ value for the waste (0.14 ± 0.02 molecule) to give 0.11 molecules of hydrogen per 100 eV. Normalizing to the organic carbon content, the radiolytic yield of hydrogen from an organic source is $0.11/0.74 = 0.15 \pm 0.05$ molecules of hydrogen per 100 eV per gram TOC, assuming a 20% relative uncertainty in the TOC concentration. The estimated radiolytic hydrogen yield for a waste, consistent with recent results of Bryan et al. (21) and Equation 10 (12), is thus

$$\text{Eq. 29} \quad G(H_2) = 0.031 + 0.15 [\text{TOC}]$$

The G-value for hydrogen generation for various tank waste materials is shown in Figure 5 as a function of the TOC content within this waste. The calculated line using Equation 29 is also shown within this figure.

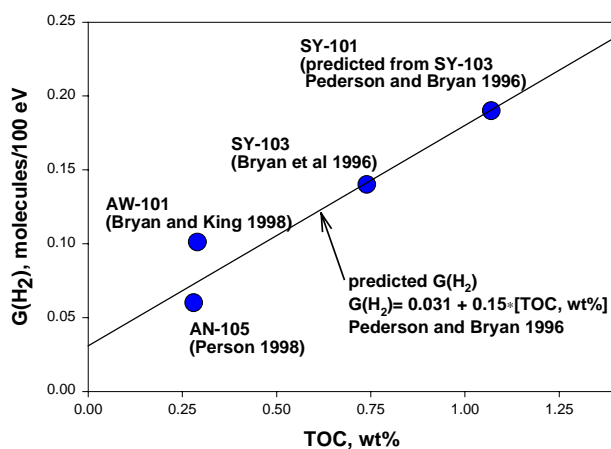


Fig. 5. G-values for hydrogen generation from double-shell tank wastes as a function of TOC content in waste

The term in Equations 10 and 29 associated with radiolytically generating hydrogen in the absence of organics (0.031 molecules/100 eV) is valid under waste conditions where the nitrate and nitrite concentrations are higher than approximately 0.5 M. Several tanks contain sufficiently low nitrate and nitrite concentrations to significantly alter and increase the G-values for hydrogen generation from the baseline value of 0.031 molecules/100eV. An empirical formula (Equation 30) given by Tabata (44) relates the variability of the G-value for hydrogen production in nitrite and nitrate brines. For low nitrite and/or nitrate wastes, the predicted G-value for hydrogen production from water radiolysis (no organics) could exceed the baseline value of 0.031. In these instances, the value 0.031 should be substituted for $G(H_2)_{\text{nitrate,nitrite}}$ from

Eq 30. Of the laboratory studies using tank waste samples for gas generation to date (13,21-27,38) all contain nitrate and nitrite concentrations sufficiently high to eliminate the need for the correction in Equation 30.

$$\text{Eq. 30} \quad G(\text{H}_2)_{\text{nitrate,nitrite}} = 0.45 - 0.31[\text{NO}_2^-]^{1/3} - 0.41[\text{NO}_3^-]^{1/3}$$

where

$[\text{NO}_2^-]$ = molar concentration of nitrite in solution

$[\text{NO}_3^-]$ = molar concentration of nitrate in solution.

Equation 30 predicts about a factor of 2 more radiolytic production of hydrogen predicted by Hopkins (40) or Graves (41) for Tank SY-101 for a specified radiation dose rate. Again, we caution that TOC is a less than ideal parameter. Baldwin et al. (45) demonstrated at least a factor of 10 variation in sensitivity factors for different organic compounds. Some compounds that contribute to TOC have little or no gas generation capacity. But in the absence of a better global characterization of the organic content of a given waste, TOC is used.

COMPARISONS OF PREDICTED HYDROGEN GENERATION RATES AND FIELD-MEASURED VALUES FOR HANFORD WASTES

Hu (42) presented a comparison of the calculated hydrogen release rates at steady state, based on the gas generation models presented above, with field-measured values from Wilkins et al. (14). The gas generation model used by Hu predicts gas generation within a factor of 2 or better for double-shell tank wastes. There is great uncertainty and difference in tank-to-tank waste components, and the models use only a few parameters related to waste composition as inputs to predict gas generation rates. However, in the absence of any other means to predict gas generation rates from Hanford waste tanks for which there are no direct gas measurements, the models represent the best prospect.

The thermal and radiolytic calculations summarized by Hu (42) are based on the thermal and radiolytic models first outlined by Hopkins (40) and Graves (41), as modified by Pederson and Bryan (38). These models employed (among other inputs) the total organic carbon (TOC) concentrations from samples of liquid in the tanks. Thus, the TOC used in gas generation calculations was predominantly soluble TOC.

As well as the thermolytic and radiolytic hydrogen generation rates, the total hydrogen generation estimate by Hu (42) also included a factor for tank wall corrosion that assumes a corrosion rate of 0.1 mil/yr and a stoichiometry of 1 mole of hydrogen generated per mole of iron corrosion. This corrosion rate was chosen to be conservative. Although the established corrosion allowance for these tanks is 1 mil/yr, corrosion rates measured in simulated Hanford wastes under thermal and irradiated conditions show steel corrosion rates on the order of 0.01 mil/yr (19). The low corrosion rates were measured under conditions of high pH (>13) where the mild steel is expected to be passivated (46). Even under the reduced pH conditions of some single-shell tanks (as low as 9.5), the mild steel is expected to remain passive (47). Under conditions of neutral or acidic pH—a condition not expected in Hanford wastes—the mild steel is expected to be strongly corroded, and expected corrosion rates would be much higher than the

allowance of 1 mil/yr (46,48). For Hanford wastes with adequately high pH control, the assumption used by Hu (42) for corrosion rates is conservative.

Using the thermal, radiolytic, and corrosion models outlined above, Hu calculated the steady-state hydrogen gas generation rates for seven Hanford double-shell tanks and compared these values with field measurement data for these tanks (49). The comparisons between model and field data were made for Tanks AN-103, AN-104, AN-105, AW-101, AY-102, SY-101, and SY-103. The results of this comparison are shown in Table I.

Table I. Comparison of model and field data hydrogen generation rates for double-shell tanks (42)

Tank ID	Total H ₂ generation rate using field data (cfm) (49)	Total H ₂ generation rate using model (cfm) (42)	Ratio of H ₂ generation rate between model and field data	H ₂ /N ₂ O ratio from field data ^(a)
241-AN-103	4.28E-3	5.05E-3	0.83	15
241-AN-104	4.35E-3	5.9E-3	0.71	7
241-AN-105	5.06E-3	7.4E-3	0.66	6.9
241-AW-101	5.8E-3	4.3E-3	1.4	33
241-AY-102	1.05E-2	1.78E-2	0.58	-
241-SY-101	2.9E-2	3.65E-2	0.76	1.48
241-SY-103	5.11E-3	5.9E-3	0.83	2.5

(a) Ratios of H₂/N₂O from field data are summarized in Pederson and Bryan (38).

The gas generation rates determined by the model overestimate the amount of hydrogen gas generated for all waste types in Table I except for AW-101. For AW-101, the ratio of the predicted versus the field data was 0.74, which represents an underestimate of 26% by the model. When evaluating the ability of the model to predict measured hydrogen generation rates, the measured H₂/N₂O product ratio (shown in Table I) in the headspaces of these tanks provides some insight into the conservatism of the model. For most tanks, the headspace H₂/N₂O ratio ranges from approximately 1 to 15. For the tanks with a hydrogen-to-nitrous oxide ratio in this range, the model is accurate and slightly overpredicts hydrogen. For AW-101, the H₂/N₂O ratio is approximately 33, much higher than for the other tanks. We believe the inability of the model to predict the hydrogen generation rate for AW-101 is related to the unusually high H₂/N₂O ratio.

Figure 6 shows a comparison of predicted and measured hydrogen generation rates from Table I as a function of the headspace H₂/N₂O ratio. The data are grouped by waste type: the complexant concentrate wastes (SY-101 and SY-103) are in one group, the double-shell slurry feed and double-shell slurry wastes (AN-103, AN-104, AN-105, and AW-101) compose a second group. The trend in the data suggests that the higher the H₂/N₂O ratio, the less the model tends to overpredict the hydrogen generation from the waste. For AW-101 waste (H₂/N₂O ~33), the model underpredicts hydrogen generation.

The reason for the relatively high H₂/N₂O ratio observed in AW-101 relative to other tanks is not known but is of interest. The presence of molecular oxygen has been found to have a marked

effect on the distribution of gaseous products formed in thermally activated reactions involving HEDTA (5,6). Yields of hydrogen were significantly enhanced in the presence of an oxygen-containing cover gas, while yields of nitrogen-containing gaseous products (nitrous oxide, nitrogen, and ammonia) were reduced. Camaioni et al. (32,33) observed similar trends in aging studies dominated by radiolytic reactions. While the mechanism responsible for this behavior is not well understood, it is expected that oxygen reacts with active nitrogen oxide radicals that otherwise would eventually form nitrogen-containing gases (6,12,32,33). Thus, oxygen reactions could be related to the correlation between the H_2/N_2O ratio and the hydrogen generation rate shown in Figure 6.

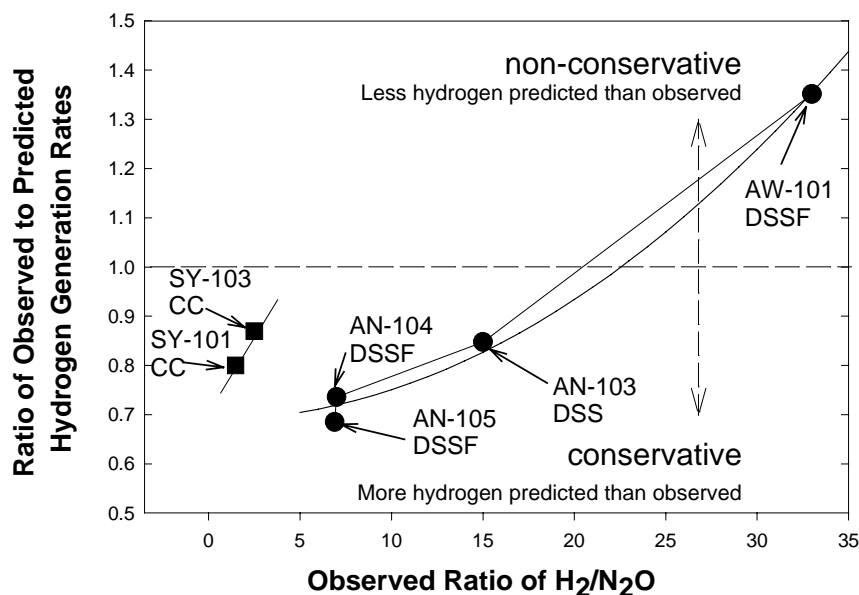


Fig. 6. Comparison of the ratio of observed to predicted hydrogen generation rates to the ratio of hydrogen to nitrous oxide rates for selected double-shell tanks. Waste types are complexant concentrate (CC; SY-101 and SY-103), double-shell slurry feed (DSSF; AN-104, AN-105, AW-101), and double-shell slurry (DSS; AN-103).

Including oxygen in the cover gas of laboratory tests led to an increase in the overall rate of gas generation (13). Hydrogen production was increased significantly, oxygen was consumed, and nitrous oxide and nitrogen yields were essentially unchanged. Studies with simulated wastes conducted by Barefield et al. (6), Camaioni et al. (32,33), and Meisel et al. (12) found that oxygen enhanced hydrogen production but depressed formation of nitrogen-containing gases. Long diffusion times preclude atmospheric oxygen from being an effective source in most waste tanks; however, oxygen is produced radiolytically in low concentrations, as described by Meisel et al. (12). Oxygen will probably be consumed rapidly by reaction with organic solutes in tanks such as SY-101 and SY-103, but it may build up in tanks containing low concentrations of reactive organic solutes or in relatively cool wastes.

SUMMARY AND RECOMMENDATIONS FOR IMPROVING GAS GENERATION MODELS

The total rate of hydrogen generation is the sum of the thermal and radiolytic components. While these expressions provide qualitative guidance about the rates of hydrogen generation in the Hanford tanks, it is evident that they will need to be modified to quantitatively predict hydrogen generation. Factors such as the nature of the organic compounds (for example, sodium glycolate provides hydrogen but sodium oxalate does not) are not considered in the TOC parameter, and the synergisms between the radiolytic and thermal reactions are not considered in the analysis.

Significant differences exist in composition among Hanford waste tanks; thus gas generation behaviors are expected to vary considerably. Most of the technical work has focused on chelator and chelator fragments, which dissolve in the liquid fraction. Other wastes contain solvents that are largely insoluble in the liquid fraction and may decompose by totally different pathways. Laboratory gas generation studies using actual waste mixtures that represent different waste classes will significantly enhance our ability to predict gas generation behavior in Hanford wastes.

LITERATURE CITED

1. Johnson GD, WB Barton, JW Brothers, SA Bryan, PA Gauglitz, RC Hill, LR Pederson, CW Stewart, and LH Stock. 1997. *Flammable Gas Project Topical Report*. PNNL-11500, Pacific Northwest National Laboratory, Richland, Washington.
2. Ashby EC, EK Barefield, CL Liotta, HM Neumann, F Doctorovich, A Konda, K Zhang, J Hurley, D Boatwright, DA Annis, G Pansino, M Dawson, and M Juliao. 1992. *Am. Chem. Soc. Symp. Ser.* 554:249.
3. Ashby EC, R Doctorovich, CL Liotta, HM Neuman, EK Barefield, A Konda, K Zhang, J Hurley, and DD Siemer. 1993. *Concerning the Formation of Hydrogen in Nuclear Waste. Quantitative Generation of Hydrogen via a Cannizzaro Intermediate*. *J. American Chemical Society* 115, 1171.
4. Ashby EC, DA Annis, EK Barefield, D Boatwright, F Doctorovich, CL Liotta, HM Neumann, A Konda, CF Yao, K Zhang, and NG McDuffie. 1994. *Synthetic Waste Chemical Mechanism Studies*. WHC-EP-0823, Westinghouse Hanford Company, Richland, Washington.
5. Barefield EK, D Boatwright, A Deshpande, F Doctorovich, CL Liotta, HM Neumann, and S Seymore. 1995. *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1994 Progress Report*. PNL-10822, Pacific Northwest Laboratory, Richland, Washington.
6. Barefield EK, D Boatwright, A Deshpande, F Doctorovich, CL Liotta, HM Neumann, and S Seymore. 1996. *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY*

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

- 1994 Progress Report*. PNL-11247, Pacific Northwest National Laboratory, Richland, Washington.
7. Bryan SA, LR Pederson, JL Ryan, RD Scheele, and JM Tingey. 1992. *Slurry Growth, Gas Retention, and Flammable Gas Generation by Hanford Radioactive Waste Tanks*. PNL-8169, Pacific Northwest Laboratory, Richland, Washington.
 8. Bryan SA and LR Pederson. 1994. *Composition, Preparation, and Gas Generation Results from Simulated Wastes of Tank 241-SY-101*. PNL-10075. Pacific Northwest Laboratory, Richland, Washington.
 9. Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, Washington.
 10. Delegard C. 1980. *Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101*. RHO-LD-124, Rockwell International, Richland, Washington.
 11. Meisel D, H Diamond, EP Horowitz, CD Jonah, MS Matheson, MC Sauer, Jr., JC Sullivan, F Barnabas, E Cerny, and YD Cheng. 1991. *Radiolytic Generation of Gases from Synthetic Waste: Annual Report 1991*. ANL-91/41, Argonne National Laboratory, Argonne, Illinois.
 12. Meisel D, CD Jonah, S Kapoor, MS Matheson, and MC Sauer. 1993. *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*. ANL-93/43, Argonne National Laboratory, Argonne, Illinois.
 13. Person JC. 1996. *Effects of Oxygen Cover Gas and NaOH Dilution on Gas Generation in Tank 241-SY-101 Waste*. WHC-SD-WM-DTR-043. Westinghouse Hanford Company, Richland, Washington.
 14. Wilkins NE. 1995. *Tank 241-SY-103 Core Sample: Interpretation of Results*. WHC-SD-WM-TI-712, Westinghouse Hanford Company, Richland, Washington.
 15. Campbell JA, S Clauss, KA Grant, FV Hoopes, BD Lerner, RB Lucke, GM Mong, JK Rau, RT Steele, and KL Wahl. 1994. *Flammable Gas Safety Program Analytical Methods Development: FY 1994 Progress Report*. PNL-10127, Pacific Northwest Laboratory, Richland, Washington.
 16. Campbell JA, RW Stromatt, MR Smith, DW Koppenaal, RM Bean, TE Jones, DM Strachan, and H Babad. 1994. *Anal. Chem.*, 66, 1208A-1215A.
 17. Campbell JA, S Clauss, KA Grant, FV Hoopes, BD Lerner, RB Lucke, GM Mong, JK Rau, RT Steele, and KL Wahl. 1995. *Organic Analysis and Analytical Methods Development: FY 1995 Progress Report*. PNL-10776, Pacific Northwest Laboratory, Richland, Washington.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

18. Campbell JA, S Clauss, KA Grant, FV Hoopes, GM Mong, JK Rau, RT Steele, and KL Wahl. 1996. *Flammable Gas Safety Program: Actual Waste Organic Analysis, FY 1996 Progress Report*. PNNL-11307, Pacific Northwest National Laboratory, Richland, Washington.
19. Strachan DM, and LG Morgan. 1991. *Minutes of the Tank Waste Science Panel Meeting July 20, 1991*. PNL-7598, Pacific Northwest Laboratory, Richland, Washington.
20. Gerber MA, LL Burger, DA Nelson, JL Ryan, and RL Zollars. 1992. *Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford*. PNL-8339, Pacific Northwest Laboratory, Richland, Washington.
21. Bryan SA, CM King, LR Pederson, SV Forbes, and RL Sell. 1996. *Gas Generation from Tank 241-SY-103 Waste*. PNNL-10978, Pacific Northwest National Laboratory, Richland, Washington.
22. Bryan SA, CM King, and LR Pederson. 1997. *Thermal and Radiolytic Gas Generation from Tank 241-S-102 Waste*. PNNL-11600, Pacific Northwest National Laboratory, Richland, Washington.
23. Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste*. TWS98.39, Pacific Northwest National Laboratory, Richland, Washington.
24. King CM, LR Pederson, and SA Bryan. 1997. *Thermal and Radiolytic Gas Generation from Tank 241-S-102 Waste*. PNNL-11600, Pacific Northwest National Laboratory, Richland, Washington.
25. King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste*. TWS98.77, Pacific Northwest National Laboratory, Richland, Washington.
26. King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste*. TWS98.78, Pacific Northwest National Laboratory, Richland, Washington.
27. King CM and SA Bryan. 1999. *Thermal and Radiolytic Gas Generation Tests on Material from Tanks 241-U-103, 241-AW-101, 241-S-106, and 241-S-102: Status Report*. PNNL-12181, Pacific Northwest National Laboratory, Richland, Washington.
28. Delegard CH. 1987. *Identities of HEDTA and Glycolate Degradation Products in Simulated Hanford High-Level Waste*. RHO-RE-ST-55-P, Rockwell International, Richland, Washington.
29. Meisel D, H Diamond, EP Horowitz, CD Jonah, MS Matheson, MC Sauer, and JC Sullivan. 1991. *Radiation Chemistry of Synthetic Waste*. ANL-91/40, Argonne National Laboratory, Argonne, Illinois.
30. Spinks JTW and RJ Woods. 1990. *An Introduction to Radiation Chemistry*. John Wiley and Sons, New York, p. 210.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

31. Draganic IV and ZD Draganic. 1971. *The Radiation Chemistry of Water*. Academic Press, New York, pp. 123-162.
32. Camaioni DM, WD Samuels, SA Clauss, BD Lenihan, KL Wahl, JA Campbell, and WJ Shaw. 1995. *FY95 Waste Aging Studies*. PNL-10794, Pacific Northwest Laboratory, Richland, Washington.
33. Camaioni DM, WD Samuels, JC Linehan, SA Clauss, AK Sharma, KL Wahl, and JA Campbell. 1996. *FY95 Waste Aging Studies*. PNL-11312, Pacific Northwest Laboratory, Richland, Washington.
34. Cotton FA and G Wilkinson. 1980. *Advanced Inorganic Chemistry, 4th Ed.* John Wiley and Sons, New York.
35. March J. 1992. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th Edition. John Wiley and Sons, New York.
36. Norton JD and LR Pederson. 1994. *Ammonia in Simulated Hanford Double-Shell Tank Wastes: Solubility and Effects on Surface Tension*. PNL-10173, Pacific Northwest Laboratory, Richland, Washington.
37. Norton JD and LR Pederson. 1995. *Solubilities of Gases in Simulated Tank 241-SY-101 Wastes*. PNL-10785, Pacific Northwest Laboratory, Richland, Washington.
38. Pederson LR and SA Bryan. 1996. *Status and Integration of Studies of Gas Generation in Hanford Wastes*, PNNL-11297, Pacific Northwest National Laboratory, Richland, Washington.
39. Hopkins JD. 1994. *Criteria for Flammable Gas Watch List Tanks*, WHC-EP-0702 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
40. Hopkins JD. 1995. *Methodology for Flammable Gas Evaluations*. WHC-SD-WM-TI-724, Westinghouse Hanford Company, Richland, Washington.
41. Graves RD. 1994. *Topical Report on Flammable Gases in Non-Burping Waste Tanks*. WHC-SD-WM-SARR-015, Westinghouse Hanford Company, Richland, Washington.
42. Hu A. 1997. *Calculations of Hydrogen Release Rate at Steady-State for Double Shell Tanks*. HNF-SD-WM-CN-117 Rev 0, Lockheed Martin Hanford Company, Richland, Washington.
43. Wahl KL, JA Campbell, IE Burgeson, SA Bryan, DM Camaioni, RT Hallen, BD Lerner, and RD Scheele. 1996. *Use of Organic Functional Group Concentrations as a Means of Screening for Energetics*. PNNL-10883, Pacific Northwest National Laboratory, Richland, Washington.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

44. Tabata Y, Y Ito, and S Tagawa. 1991. *Handbook of Radiation Chemistry*. CRC Press, Boca Raton, Florida.
45. Baldwin DL, RW Stromatt, and WI Winters. 1994. *Comparative Study of Total Organic Carbon (TOC) Methods for High-Level Mixed Waste*. PNL-SA-2374, Pacific Northwest Laboratory, Richland, Washington.
46. Pourbaix M. 1974. *Atlas of Electrochemical Equilibria*. National Association of Corrosion Engineers, Houston.
47. Wodrich DD, GS Barney, GL Borsheim, DL Becker, WC Carlos, MJ Klein, RE van der Cook, and JL Ryan. 1992. *Summary of SST Stability*. WHC-EP-0347 (Supplement), Westinghouse Hanford Company, Richland, Washington.
48. Elmore MR. 1995. *Mild Steel Corrosion in Oxalic Acid Solutions: (Simulated Cesium Removal Process Solutions)*. Pacific Northwest Laboratory, Richland, Washington.
49. Wilkins NE, RE Bauer, and DM Ogden. 1997. *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*. Lockheed Martin Hanford Corporation, Richland, Washington.