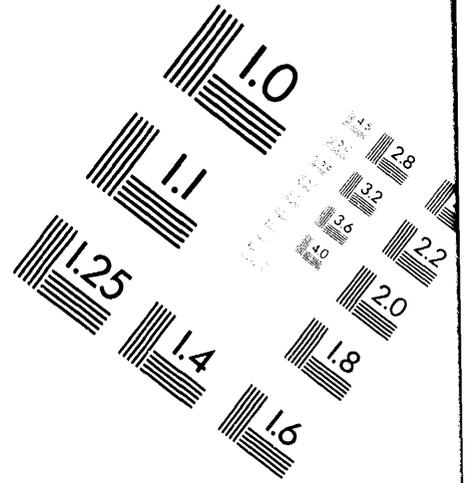
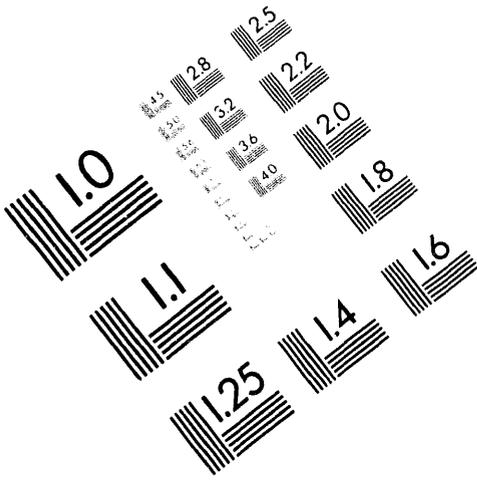




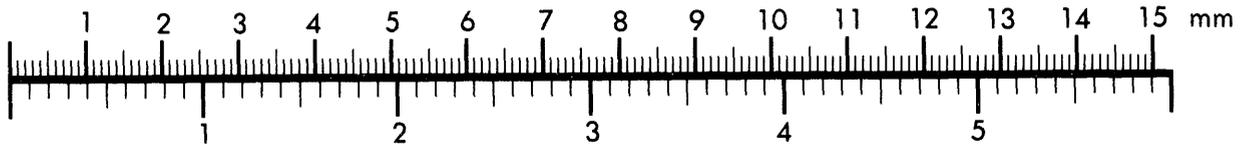
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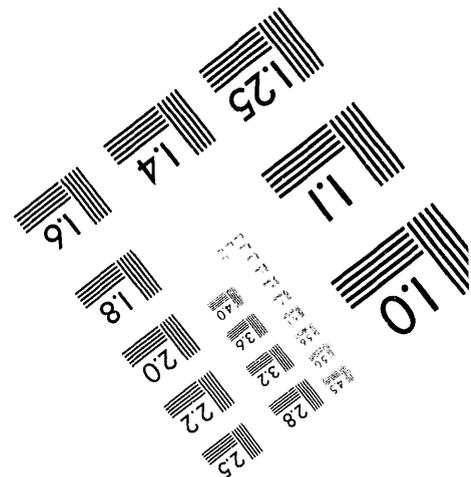
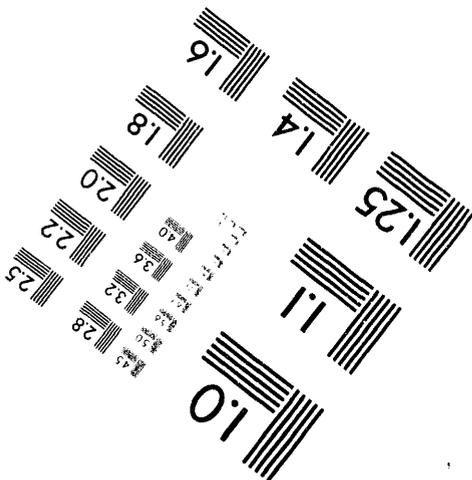
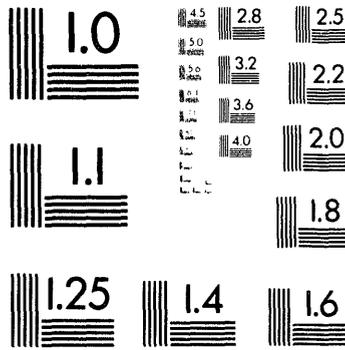
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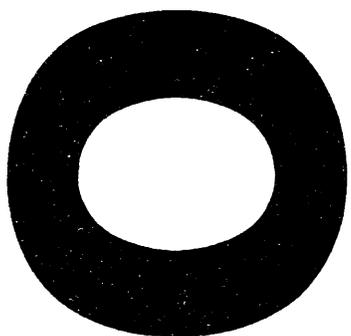
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**Status and Integration of the  
Gas Generation Studies  
Performed for the Hydrogen  
Safety Program—FY 1993  
Annual Report**

D. M. Strachan

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April 1994

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

Pacific Northwest Laboratory  
Operated for the U.S. Department of Energy  
by Battelle Memorial Institute



PNL-9459

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Pacific Northwest Laboratory  
Richland, Washington 99352

**MASTER**

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## Introduction

This document represents the second in a series of documents (Pederson and Strachan 1993) in which information is summarized and integrated on the chemical mechanisms for gas generation from simulated wastes that mimic the nuclear waste in Tank 241-SY-101 (hereinafter Tank 101-SY).

Over the past year the reliability of the instrumentation that has been installed on Tank 101-SY has been increased dramatically. Gases composed of  $H_2$ ,  $N_2O$ ,  $N_2$ , and  $NH_3$  are continuously released at low levels and also periodically released from the waste stored in this tank such that the lower flammability limit of 4%  $H_2$  is sometimes exceeded. To better understand the reasons for this phenomenon and with the goal of mitigating the potential safety problem associated with the flammability, instrumentation has been installed on the tank and studies have been carried out to understand the mechanism by which these gases are generated. It is worthwhile to annually summarize this information in a single document, to integrate the information, and to highlight the remaining open questions surrounding the mechanism of gas generation. This is the goal of this document.

Information on simulated wastes under thermal and radiation conditions has been collected from work performed at Argonne National Laboratory, Georgia Institute of Technology, and Pacific Northwest Laboratory;<sup>(a)</sup> this report attempts to correlate the simulated data with that of actual tank waste. This document is lengthier than the former report because so much more information was available this year.

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## A Summary of Information

### Tank 101-SY

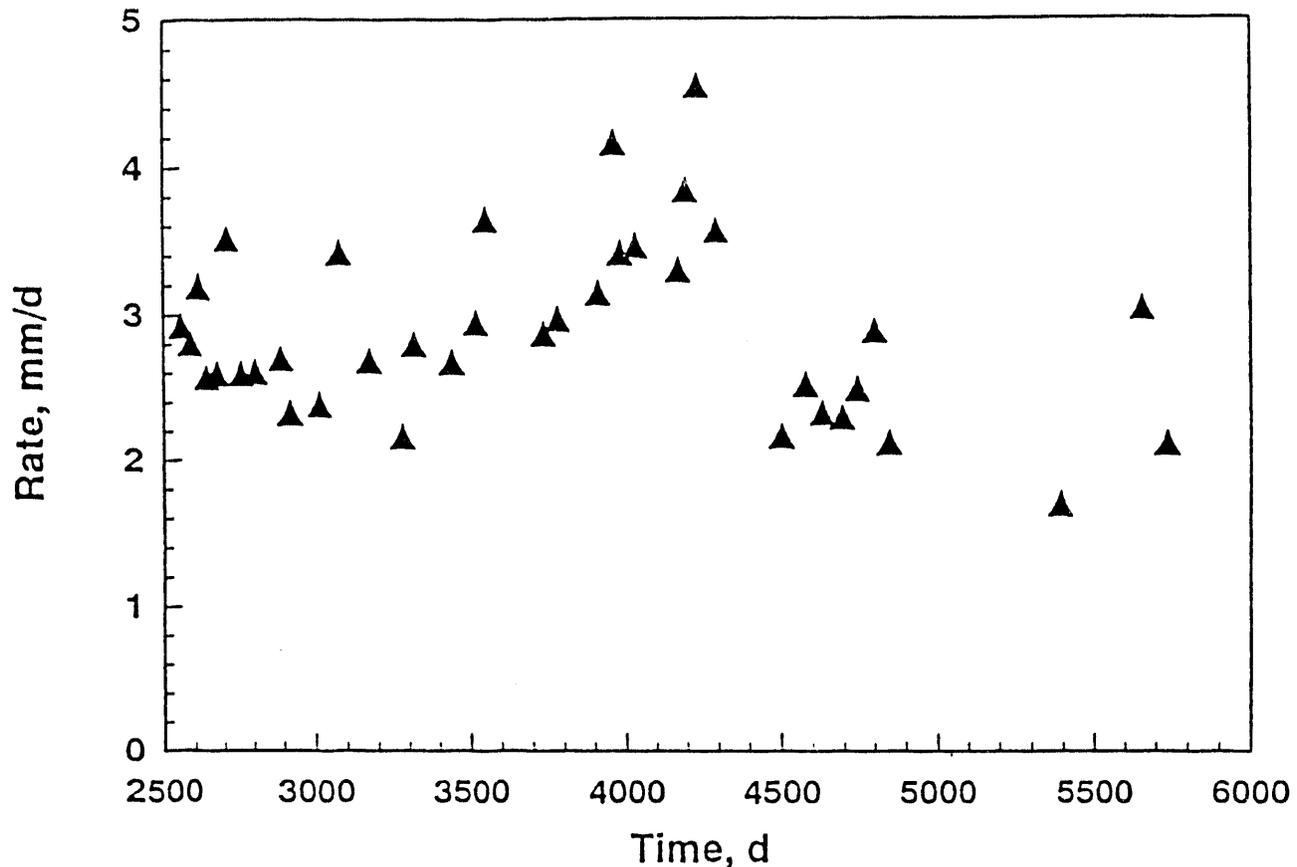
As indicated above, the amount and reliability of instrumentation installed on this tank have improved dramatically over the past year. Newly installed instruments include gas chromatographs for the measurement of  $H_2$ , a mass spectrometer for the measurement of  $H_2$ ,  $N_2O$ , and other gases, and a Fourier transform infrared (FTIR) spectrometer for the measurement of  $N_2O$  and  $NH_3$ . Samples of the ventilation gas continue to be taken on a frequent, but not regular, basis. High resolution mass spectral data are collected on these samples. The information derived from these instruments will be discussed here, although a complete discussion of the instrumentation and the quality of output is beyond the scope of this work.

Data from Tank 101-SY that are discussed are the waste level measurements and the rate of gas generation derived therefrom, as well as the composition of gases given off by the wastes, the reaction mechanisms that can be implied, and the relationship to the observations in the laboratory.

### Gas Generation Rates Deduced from Surface Level Measurements

Examination of surface level data led Strachan (1991) to propose that the rate of gas generation could be derived from these data and used to give some insight on the mechanism of generation. Surface level measurements have been made in this tank since waste was first placed in the tank in 1977. Arguments were made that the rate of gas generation could be limited by diffusion of some species in the waste (Pederson and Strachan 1993). At that time, the rates of gas generation were determined using only a small part of the available surface level data. All of these data have now been analyzed and are reported below.

Using the method reported by Strachan (1991; Pederson and Strachan 1993), the rates of gas generation since 1984 have been determined and are shown as a level rise rate in Figure 1. Many of the data collected before 1984 are not suitable for analysis because the frequency of the release was high and the frequency of data collection was low. Consequently, the number of data points between gas release events were too small for reliable rates to be calculated. The results shown in Figure 1 indicate that during air lancing, or that period around 4000 d, the apparent rate of gas generation increased. Surface level data are expected to reflect the quantity of gases generated in the non-convecting (bottom) sludge layer of the wastes, whereas gases produced in the convecting liquid layer should be vented continuously (Strachan 1991). The cause for the increase in the surface level is not clear; there are at least two possibilities for this increase. 1) Introduction of air through the lances increased the  $O_2$  concentration in the waste. It is known from studies with simulated waste (Ashby et al. 1994a; Ashby in Schulz and Strachan 1992) that gas generation increases when the experiments are performed under an air atmosphere as opposed to an argon or helium atmosphere. 2) An alternative explanation for the increase in level during air lancing is that some of the air was trapped by solids and created a foam that was detected as an increase in surface level. Work carried out at Pacific



**Figure 1.** Gas Generation Rates in Tank 101-SY (Day 0 = April 23, 1977; Day 2500 = February 26, 1984; Day 6000 = September 26, 1993)

Northwest Laboratory has shown that the solids in simulated waste can hold gas bubbles (see Bryan and Pederson in Strachan 1992a,b; Meisel et al. 1993). The increased rate interpretation is favored because of the rapid decrease in rate since air lancing was stopped in 1989 (about 4500 d). One would expect loosely trapped gases to be readily removed during one or two gas release events.

Antoniak (1993) has recently retrieved and analyzed the temperature data from 1977 through the present. These data indicate that the mean temperature of the waste was about 52°C until hot waste (about 80°C) from the evaporator was added to the tank in late 1980 and again in 1981. In late 1981, the mean temperature of the waste was about 60°C. Over the years, the mean temperature decreased to the present value of about 50°C. About four months into 1982, the temperature profiles began to look much like they do today, i.e., a lower hotter layer and an upper cooler layer, which are now interpreted as the nonconvective and convective layers, respectively. Using this temperature profile information, Antoniak (1993) determined the time variation of the nonconvective layer thickness.

Using the information on the depth, and hence the volume, of the nonconvective layer, the rates of gas generation shown in Figure 1 can be corrected for the variations in the volume of the layer in which the gas is stored and which gives rise to the observed level changes. The normalized rates in units of  $m/(d \cdot m^3)$  are shown in Figure 2, where the "m" in the numerator is the measured level change (meters) in the tank and the " $m^3$ " in the denominator is the volume of the nonconvective layer (cubic meters). It is interesting to note that the rate from about 2500 d to about 4000 d is constant even though the temperatures were decreasing and, one might expect, the concentration of the reactant was decreasing. This supports the earlier conclusion that the gas generation rate is relatively insensitive to temperature (Pederson and Strachan, 1993). It should be noted that there is some ambiguity here because Antoniuk does not report the mean temperatures in the tank. The mean temperatures have to be estimated from his color plots.

From the data shown in Figure 2, the "increase" in gas generation rate (rate of level rise) in the non-convecting layer during air lancing can be clearly seen. However, since air lancing was terminated, the rate of generation has been steadily decreasing. The caveat that is needed on this conclusion, however, is that this interpretation relies heavily on Antoniuk's (1993) ability to estimate the depth of the nonconvective layer. There is a large amount of uncertainty in his analyses for the early years from 1981 to about 1989. The degree of uncertainty decreases somewhat for recent data because of the more plentiful and reliable data currently available.

## Gas Composition

The analyses of the gases exiting the waste and the tank are being done with increasing confidence and are providing a number of surprises. Since late 1992, reliable data for  $N_2O$  and  $NH_3$  have been obtained using an FTIR with gases being obtained from the head space of the tank through a heated line. The concentration for the  $N_2O$  exactly tracks the concentration for the  $H_2$ . However, the data seem to indicate a  $N_2O/H_2$  ratio that is different than normally observed during a gas release event. At "steady state," the ratio is greater than one, usually about 1.2. When there is a release, even a small release, which increases the  $H_2$  from 10 to 20 ppm up to 40 ppm or more, the ratio decreases to less than one; a value also seen during large releases and reported much earlier (Strachan 1991). This observation is consistent with the laboratory data reported by Bryan and Pederson (Strachan and Schulz 1993) in which the  $N_2O$  was observed to decompose under radiolysis conditions to  $N_2$  and  $O_2$ . Thus, gases released during a release event appear to be relatively old gases ( $\sim 100$  d) that may be coming from the nonconvecting layer of the waste, where it is currently felt the gases are retained in the waste.

Less clear is the observed  $NH_3$  behavior and concentration. One of the surprises is the relatively high concentration of  $NH_3$ . During steady state release  $NH_3$  is the major, non-air, gas component. The concentration of  $NH_3$  is typically in the range of 60 ppm to 100 ppm. At times the swings in the concentration appear to be connected to the swings in the  $N_2O$  and  $H_2$  concentrations in most instances but at other times appears to be independent. When there is a release of  $N_2O$  and  $H_2$ , there is an increase in the  $NH_3$ . However, the increase may be large or small relative to the other two gases. At other times, the  $NH_3$  is released without a concomitant release of the other two gases. Two possible reasons for this may be that the  $NH_3$  gas is being generated at a different place than the other two gases

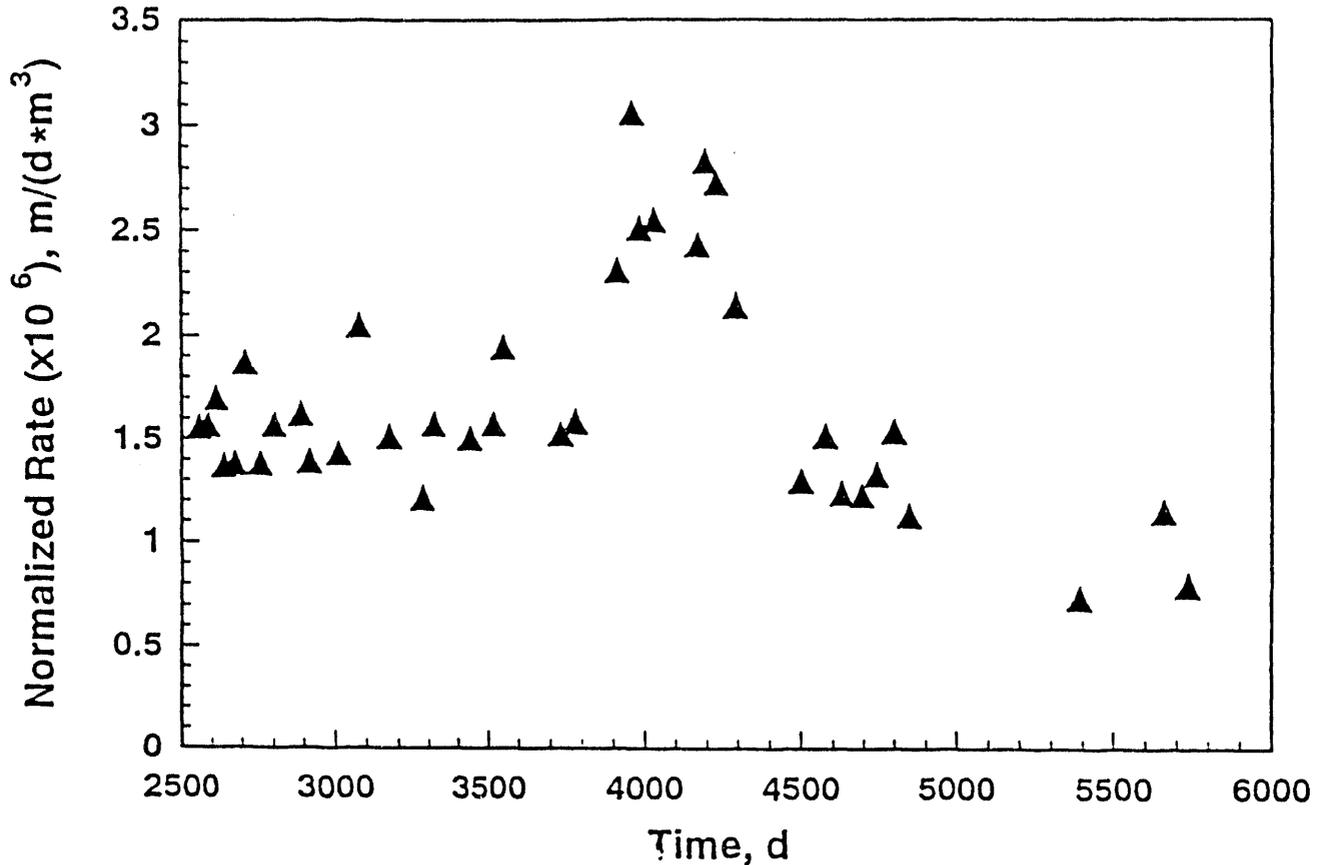


Figure 2. Normalized Gas Generation Rate in Tank 101-SY (Day 0 = April 23, 1977; Day 2500 = February 26, 1984; Day 6000 = September 26, 1993)

or because the  $\text{NH}_3$  has such a high solubility relative to the other gases. Studies are underway to determine, if possible, which explanation is correct. The safety implications of the latter mechanism is that a relatively large release of  $\text{NH}_3$  could occur during mixing of the waste.

Steady state concentrations (i.e., not during gas release events) for  $\text{H}_2$  are from about 10 ppm to 25 ppm with peak values up to 100 ppm. Taking the value of 25 ppm as a mean steady state  $\text{H}_2$  concentration and the mean ventilation flow rate of  $0.27 \text{ m}^3/\text{s}$  (580 cfm), the steady state release of  $\text{H}_2$  is 26 mol/d, in good agreement with Ashby et al. (1992), or 52 mol  $\text{H}_2/\text{d}$  if the  $\text{H}_2$  production in the non-convecting layer just equals the production in the convecting layer (i.e., the gas released continuously). Based strictly on gas release events, Ashby et al. (1992) estimated the amount of  $\text{H}_2$  being retained in the nonconvecting layer to be 33 mol/d. Assuming that estimate to be correct, the total production of  $\text{H}_2$  is 59 mol/d. In addition, the quantities of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NH}_3$  are 32 mol/d, 32 mol/d, and 70 mol/d, respectively, based on estimated steady state concentrations of 30 ppm for  $\text{N}_2\text{O}$  and 65 ppm for  $\text{NH}_3$ . Nitrogen is assumed to be at equal concentration in the gases emitted from the waste as  $\text{N}_2\text{O}$ .

Babad et al. (1991) estimated the composition of the gas emanating from the waste during a gas release event. Their estimates for H<sub>2</sub>O and NH<sub>3</sub> were based on equilibrium calculations and are probably still valid. Keeping the ratio of the gases the same as observed in the tank head space, an estimate for the remaining gas composition can be made. Under these assumptions, the gases emanating from the non-convecting layer during a release event of the waste have the composition shown in Table 1.

**Table 1.** Estimated Composition of Gases in Tank 101-SY Waste  
(based on the assumptions outlined in the text)

<u>Component</u>	<u>Volume, %</u>
H <sub>2</sub>	27
N <sub>2</sub> O	30
N <sub>2</sub>	30
H <sub>2</sub> O	4
NH <sub>3</sub>	4
	95

### **Correlation Between the Gas Generation Rate and the Rate of Level Growth**

Previously, the composition of the gas released at steady state were calculated based on the rate of level growth, the pressure at depth in the waste, and the composition of the gas during a gas release event (Strachan and Morgan 1991a). Now that the steady state composition of the gas can be measured, the growth of the waste can be estimated using some of the same assumptions. Using the above listed rates of generation and assuming that the steady state concentration of gases comes from the convective layer, two rates of level increases can be calculated depending on the volume of the non-convecting layer, which in recent months has increased from 5.1 m (200 in.) to 6.4 m (250 in.) [total waste depth = 10.2 m (400 in.)]. Both cases will be considered and, in both cases, the rate of gas generation in the nonconvecting layer will be assumed to be equal to the rate in the convecting layer. Since the NH<sub>3</sub> is quite soluble in the aqueous phase (Pederson and Bryan in Strachan and Schulz 1993), the NH<sub>3</sub> gas that is generated does not contribute appreciably to the volume of the gas bubbles, especially at depth in the tank.

<u>Case 1:</u>	From the steady state gas composition:	26 mol H <sub>2</sub> /d 32 mol N <sub>2</sub> O/d <u>32 mol N<sub>2</sub>/d</u> 90 mol gas/d
	Volume of the convecting layer (5.1 m depth):	2.1•10 <sup>6</sup> L
	Volume of the nonconvecting layer:	2.1•10 <sup>6</sup> L
	Gas generation in the nonconvecting layer:	90 mol gas/d
	Volume of gas at 0.2 MPa (2 atm):	2.8 mm/d (0.11 in/d)
<u>Case 2:</u>	Volume of the convecting layer (3.8 m depth):	1.6•10 <sup>6</sup> L
	Volume of the nonconvecting layer (6.4 m depth):	2.5•10 <sup>6</sup> L
	Gas generation in the nonconvecting layer:	142 mol gas/d
	Volume of gas at 0.2 MPa (2 atm):	4.6 mm/d (0.18 in/d)

The observed level rise of about 3mm/d is consistent with Case 1 but not Case 2. This would indicate, especially since the rate of rise is observed to be constant over the period between gas release events, that the appropriate depth of the nonconvecting layer in which gases are retained is about 5 m. One can argue over the possible difference between the rate in the homogeneous solution and the slurry. If, however, the rates are substantially different, then, as the nonconvecting layer grows, it should be possible to observe a difference in the rate of growth of the waste in the tank. Rather than wander too far from the main purpose of this document, the answer to the rate of growth dilemma will be left as an open question to be resolved at a later date.

## Research at Georgia Institute of Technology

Research on the mechanism of the generation of gases from simulated waste solutions has been carried out at Georgia Institute of Technology for the past two years. The main goal of the program has been to investigate the mechanisms by which organic compounds believed to be present in the waste in Tank 101-SY decompose to generate H<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, and N<sub>2</sub>.

Reactions have been carried out using a homogeneous solution at 120°C. A homogeneous solution was used to avoid the changes in kinetics that can occur when solids are present during the reactions. The solution has a relatively simple composition compared to the composition of the actual waste; only the major constituents of the waste are included in the simulated waste. A temperature higher than the temperature of the waste (ca 50°C) was used to promote the reaction rate and allow meaningful results to be obtained in a reasonable period of time. Ashby (TAP 1992) indicated that there may be no change in the mechanism between the two temperatures. Additional tests at other temperatures are being conducted to gain insight on the kinetics of gas generation. Reactions have been carried out for periods approaching 2000 h. Gases generated during these experiments were contained in a glass system that is maintained at nearly constant pressure by use of a mercury

manometer. This gas storage portion of the apparatus was held at room temperature. Pressure and temperature corrections were made before the data were used in other calculations or reported.

### Generation of Hydrogen

Early in the research effort, it was observed that aldehydes with no hydrogen in the alpha position, i.e., hydrogens on the carbon atom next to the aldehyde carbon, could participate in a Cannizzaro-type reaction to yield the salt of the corresponding acid and  $H_2$ . This was first determined to be the case for formaldehyde ( $H_2CO$ ) (see Siemer in Strachan and Morgan 1991b) and later confirmed by Ashby and coworkers (see Ashby in Strachan and Morgan 1991a). This portion of the mechanism appears still to be valid. Two aldehydes appear to be active in yielding  $H_2$  -  $H_2CO$  and  $OCHCOO^-$  (glyoxylate).

According to the proposed mechanism, the reaction proceeds through the Cannizzaro intermediate, which, instead of reacting with another aldehyde, reacts with water to produce  $H_2$ . The conclusion by Ashby et al. (1994a) is supported by several experiments carried out in strong base and experiments using deuterium-labeled formaldehyde ( $D_2CO$ ). This reaction appears to be first order.

Experiments carried out in strong base show that the yield of  $H_2$  decreases with decreasing base strength. The yield of  $H_2$  was measured at  $60^\circ C$  and until no more  $H_2$  was generated. The yield of  $H_2$  decreased in direct response to the decrease in base strength from 16 M to 4 M; these data were suggested as supportive of first order kinetics. Meisel et al. (1993) (see later in this report) suggests that the reaction of  $H_2CO$  to yield  $H_2$  may be a higher order than one in  $OH^-$ .

To better determine the order of the reaction, experiments were carried out using deuterioformaldehyde ( $D_2CO$ ). If the rate-limiting reaction involves the breaking of a C-H (C-D) bond, then the rate of reaction should be slower for the deuterio form. The reaction was attempted in  $D_2O/OD^-$  as well, but interpretation of the data was complicated when significant exchange between the gas state and the aqueous phase was observed (see Ashby et al. in Strachan and Schulz 1993). If the reaction involved one H on the  $H_2CO$  and one on  $D_2O$ , then the product would be HD. However, significant amounts of exchange between  $H_2$  or HD and the  $D_2O$  aqueous phase at high base concentrations forced Ashby et al. (1994b) to abandon this approach.

### Generation of Nitrogen-bearing Gaseous Species

As noted in earlier reports (Strachan and Morgan 1991b) nitrogen-bearing species have been observed in the waste from Tank 101-SY in which each of five oxidation states of nitrogen exist. The species  $NO_3^-$ ,  $NO_2^-$ ,  $N_2O$ ,  $N_2$ , and  $NH_3$  have been reported in the waste. Hydroxylamine ( $NH_2OH$ ) has been found in simulated waste studies but was not analyzed as it was not found in actual wastes. Of interest in the work performed at Georgia Institute of Technology is the generation of the gaseous species. In earlier work at Georgia Institute of Technology (see Ashby in Strachan and Schulz 1993 and earlier references), Ashby et al. (1994a) determined that the source of the  $N_2O$  and  $N_2$  was the  $NO_2^-$  in the simulated waste. This was unambiguously determined using  $^{15}N$  labeling of the  $NO_2^-$  and  $NO_3^-$  and confirmed by Meisel et al. (see Meisel in Schulz and Strachan 1992) also using  $^{15}N$  labeling.

Nitrous oxide is proposed as a product of the reaction between the proposed trihydroxynitrate aluminum (III) complex  $[\text{Al}(\text{OH})_3(\text{NO}_2)^-]$  and N-bearing organics. The  $\text{Al}(\text{OH})_3(\text{NO}_2)^-$  complex can attack at the N position or the -OH position of the organic complexant. Attack at the N position yields a nitroso group (-N=O) that reacts with both water and  $\text{OH}^-$  to form organic fragments and  $\text{NO}^-$ . Nitrogen appears to result from the decomposition of the  $\text{N}_2\text{O}$ , especially in the presence of radiation (see Bryan and Pederson in Strachan and Schulz 1993) and from the interaction between  $\text{NO}^-$  and hydroxylamine ( $\text{H}_2\text{NOH}$ ). The latter reaction is proposed by Ashby et al. (1994b) and the  $\text{H}_2\text{NOH}$  results from the reaction between  $\text{NO}^-$  and  $\text{H}_2\text{CO}$ . Hydroxylamine may also be formed by radiolysis, as discussed in the section "Research at Argonne National Laboratory."

While this explanation of the gas generation mechanism appears to be sound, parts of the mechanism are not directly observable. For instance, aluminum nuclear magnetic resonance (NMR) was used in an attempt to find the  $\text{Al}(\text{OH})_3(\text{NO}_2)^-$  species (see Ashby in Strachan 1992a). No evidence of it was found, and it was concluded that the steady state concentration of this species was below detection limits. Similarly, reaction to form  $\text{N}_2\text{O}$  from  $\text{NO}^-$  were inferred from studies done by others (Bonner and Hughes 1988), but in aqueous systems with lower ionic strength and lower base content than the simulated wastes used in the studies at the Georgia Institute of Technology.

The source of  $\text{NH}_3$  has also been studied at the Georgia Institute of Technology. From the  $^{15}\text{N}$ -labeling studies, it has been concluded that the source of the  $\text{NH}_3$  is predominantly (90%) the  $\text{NO}_2^-$ , but the organic material is needed for the reaction to proceed. From the use of  $^{15}\text{N}$ - and  $^{13}\text{C}$ -labeled organic compounds, it can be surmised that the attack by  $\text{Al}(\text{OH})_3(\text{NO}_2)^-$  on HEDTA at the amine nitrogen occurs with a much slower rate than the attack at the -OH. The proposed inorganic reaction sequence, through which the majority of the  $\text{NH}_3$  (90%) evolves, involves the following steps.



The reason for suggesting this mechanism is because both  $\text{H}_2\text{NOH}$  and  $\text{CN}^-$  have been detected in the experiments carried out at Georgia Institute of Technology. Cyanide has also been found at the level of hundreds of parts-per-million in samples from the waste in Tank 101-SY (Herting et al. 1992a). If this mechanism is correct, then the presence of  $\text{CN}^-$  in the waste might not be as alarming as once thought when the other possible source for  $\text{CN}^-$  was ferrocyanide from the single-shell tanks.

### Generation of Organic Fragments

Another major contribution to the studies of the reactions that could be taking place in the waste contained in Tank 101-SY comes from the mechanistic studies by which the organic molecules react. Initially, it was thought that organic compounds entered the waste streams at various processing plants in the form of water soluble complexants. From a knowledge of the process flowsheets, the complexants ethylenediaminetetraacetic acid (EDTA), 2-hydroxyethylethylenediaminetriacetic acid (HEDTA),

nitrilotriacetic acid (NTA), and glycolic acid were identified. Since the organics must be decomposing in the alkaline waste in Tank 101-SY, identification of the organic fragmentation products would assist the chemist performing the organic analyses on the actual waste. A knowledge of the reaction mechanism might also identify an avenue to mitigation or remediation of the hydrogen safety issue with the waste in Tank 101-SY.

The mechanistic scheme for the thermal decomposition of HEDTA based on the results from the work carried out at Georgia Institute of Technology is shown in summary form in Figure 3. A large part of this mechanism is based on the results of NMR work with  $^{13}\text{C}$ -labeled HEDTA and glycolate (not shown in Figure 3). Data from the reaction of  $^{13}\text{C}$ -labeled HEDTA in simulated waste are shown in Table 2 for approximate reaction times (Ashby et al. 1994a).

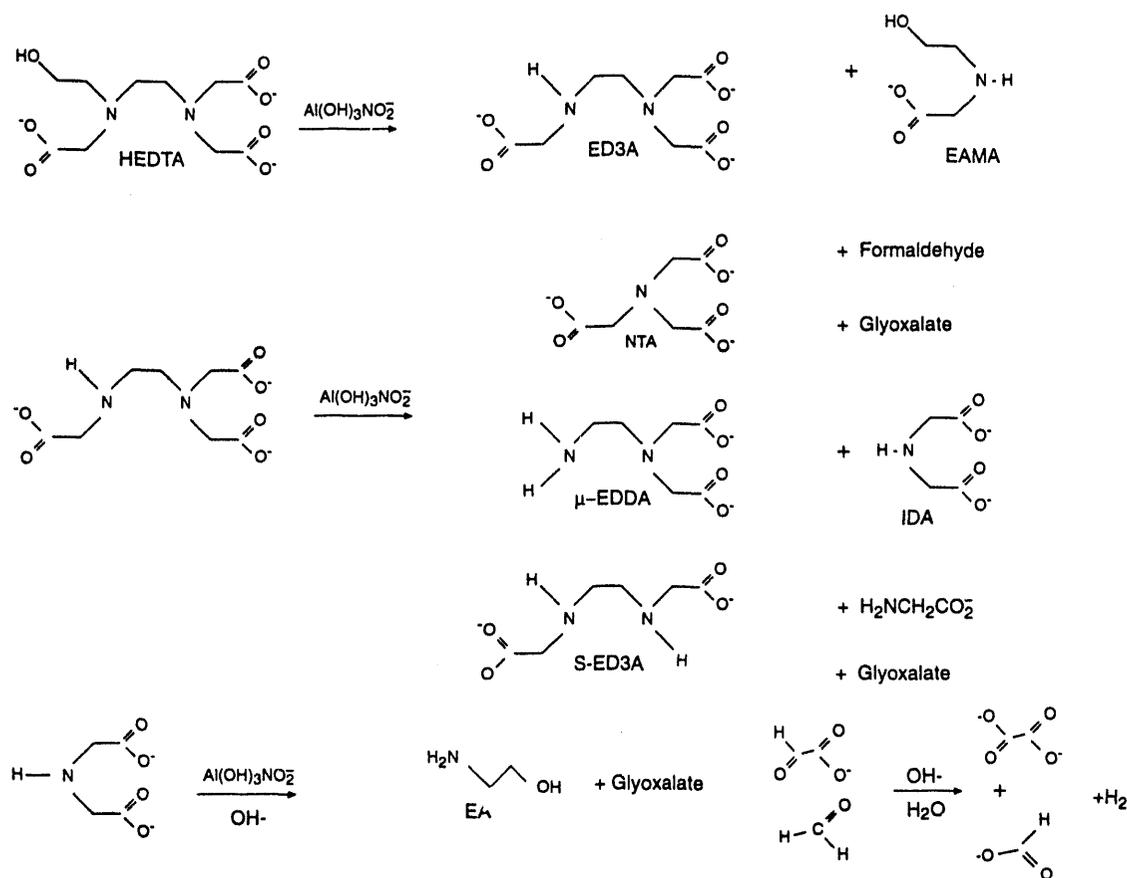


Figure 3. Mechanistic Scheme for Thermal Decomposition of HEDTA

**Table 2.** Results from the Experiments with  $^{13}\text{C}$ -labeled HEDTA  
( $T = 120^\circ\text{C}$ ) (Ashby et al. 1994a)

Approximate Reaction Time, h	Reaction Products From	
	HEDTA-A <sup>(a)</sup>	HEDTA-B <sup>(a)</sup>
0-50	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$	ND <sup>(b)</sup>
0-100	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$	ND
100-150	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA
150-200	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA(trace)	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA
200-400	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA, $\text{C}_2\text{O}_4^{2-}$	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA
400-600	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA, $\text{C}_2\text{O}_4^{2-}$	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA
600-800	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA, $\text{C}_2\text{O}_4^{2-}$	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA, IDA, $^{13}\text{C}$ - glycine, ED3A lactam
800-1000	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA, $\text{C}_2\text{O}_4^{2-}$ , EA, $^{13}\text{C}$ -glycine	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA, IDA, $^{13}\text{C}$ - glycine, ED3A lactam
1000-1400		$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA, IDA, $^{13}\text{C}$ - glycine, ED3A lactam
1400-1800	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , EAMA, $\text{C}_2\text{O}_4^{2-}$ , EA, $^{13}\text{C}$ -glycine, $^{12}\text{C}$ -glycine	$\text{HCO}_2^-$ , $\text{CO}_3^{2-}$ , $\text{C}_2\text{O}_4^{2-}$ , ED3A &/or u-EDDA, s-EDDA, IDA, $^{13}\text{C}$ - glycine, ED3A lactam

(a) HEDTA-A has the hydroxyethyl group with  $^{13}\text{C}$  labeled C; HEDTA-B has the carboxymethyl groups with  $^{13}\text{C}$  labeled C.

(b) ND = no reaction detected.

From this reaction scheme, it appears that initially HEDTA is attacked at the hydroxyethyl group yielding formaldehyde, which then reacts to yield formate, and  $\text{CO}_2$ , which reacts to yield  $\text{CO}_3^{2-}$  (Table 2, 0-150 h, HEDTA-A). The intermediate that forms after the attack at the -OH generates a species with a short half-life such that the steady state concentration is not detectable. The reaction yields  $\text{CO}_3^{2-}$ . The end result of these reactions is the formation of ED3A, which is consistent with the

reaction sequence for HEDTA-B (Table 2, 100-150 h). The next product from HEDTA-A is EAMA (Table 2, 150-200 h). This product suggests that there has been an attack at the nitrogen to which the hydroxyethyl group is attached and before the hydroxyethyl group is attacked, i.e., a competing reaction to the attack at the -OH group. Reaction at the amine group must be kinetically less favorable than reaction at the hydroxyethyl group. The intermediate aldehyde that forms, as the other fragment of the reaction at the nitrogen, must react rapidly to form NTA. Either NTA reacts rapidly, or could not be identified in the NMR spectra, because it is not listed as a product in Table 2 and no reaction is given by Ashby et al. (1994b). The next product to appear from HEDTA-A is  $C_2O_4^{2-}$  (Table 2, 200 h), the presence of which suggests that the alcohol is oxidized to a carboxyl group and the hydroxyethyl-nitrogen bond is broken along with oxidation of that end of the carbon fragment to a carboxyl group. This sequence is difficult to understand and suggests that other compounds exist, but their presence is not readily apparent in the NMR spectrum. Lastly, while EA (Table 2, 800 h, HEDTA-A) product is understandable, the presence of glycine again indicates oxidation of the alcohol to a carboxyl group occurs.

Ethanolaminediacetate (EADA) is also a possible product in these schemes, but was not included in the  $^{13}C$  NMR database. Products such as EAMA should also be found in the suite of compounds from HEDTA-B and NTA possibly should have been found in the reaction products from HEDTA-A. The reason that there are more possible interpretations is the complex nature of the resulting NMR spectra. It might be better to chromatographically separate the various organic constituents before analysis so that both chromatographic and NMR results could be used to unambiguously identify the products of the reactions.

Samples of the  $^{13}C$ -labeled HEDTA were sent to Argonne National Laboratory to be irradiated and returned to Georgia Institute of Technology to be analyzed using NMR. The results of the NMR analysis (Ashby et al. 1994a) indicate that almost all of the HEDTA was destroyed in about 17 h at  $60^\circ C$  in a gamma field at a total dose of about 0.4 MGy (20 Mrad). As a result of the irradiation, IDA was found as one of the major contributors to the resulting NMR spectrum. A new compound found in the spectrum was HEEDMA. The conclusion from this experiment is that the presence of radiation enhances the rate of decomposition of the parent compound and allows for different reaction pathways than those observed during straight thermal decomposition reactions.

## Research at Argonne National Laboratory

Research at Argonne National Laboratory has been aimed at understanding the chemistry that takes place in these complex solutions in the presence of a radiation field (Meisel et al. 1993). Work has been carried out on the yield of gases and the dependence of that yield on the intensity of the radiation field, the effect of radiation on subsequent thermal reactions that take place in solution, the effect of the presence of solids in the solutions being studied, conditions of gas retention, and the dependence of gas retention on radiation dose.

## Radiolytic Generation of Gases

This topic is of great interest because it was initially thought to be the major contributor to the gases being generated in Tank 101-SY. However, the rates at which  $H_2$  and  $N_2O$  are generated in the experiments at Argonne National Laboratory are much different than the apparent gas generation rates from the waste in Tank 101-SY. The rate at which  $N_2O$  is generated relative to the rate at which  $H_2$  is generated is about 10:1 for the studies carried out at Argonne National Laboratory and the other laboratories, but range from about 0.8 to 2 for the gases coming from Tank 101-SY (Meisel et al. 1993). While the absolute rate of  $H_2$  generation from radiolytic processes is estimated to be about 5 mol/d out of an estimated 25 mol/d (see above), the  $N_2O$  is estimated to be 415 mol/d, while the observed generation rate in the tank is about 30 mol/d. These estimates from the work at Argonne National Laboratory are for the temperature and the radiation field typical of the waste [4.2 mGy/s (25 Rad/d)].

One of the possible explanations for the lower observed  $N_2O/H_2$  in the gases coming from Tank 101-SY is that the  $N_2O$  decomposes to  $N_2$  and  $O_2$  (see Bryan and Pederson in Strachan and Schulz 1993). Results from experiments at Argonne National Laboratory suggest that the radiolytic decomposition of  $N_2O$  cannot be the reason for the lower ratios (Meisel et al. 1993). In experiments with  $N_2O$  and Ar and with and without organics present, the yield of  $N_2$  was found to depend on the presence of the organics and, in fact, the source of  $N_2$  was the reaction of the organic in the simulated waste solutions. It is noted, however, that the radiolysis experiments were short-term, high-flux tests.

The yield of  $NH_3$  was similarly found to depend on the concentration of a species that increased with increasing dose. In the case of  $NH_3$ , however, Meisel's data suggested that  $H_2NOH$  was the species involved in the production of  $NH_3$ , a species that is part of the thermal reaction mechanism suggested, as well, by Ashby et al. (1994a).

It was concluded by Meisel et al. (1993) that no chemical could be added to the tank to stop the generation of  $H_2$  completely. This conclusion was based in the observation that the most efficient scavengers of the precursors to  $H_2$  were  $NO_2$  and  $NO_3$ . The concentrations of these two species were high and unlikely to decrease significantly during continued storage of the waste. Thus, the radiolytic generation of  $H_2$  at about 5 mol/d is the minimum to which one could expect to reduce the  $H_2$  generation rate by somehow stopping the thermal generation. This reduction would, however, represent a 10-fold decrease in the  $H_2$  production.

## Radiolytic Destruction of Organics

Preirradiation was shown by Meisel et al. (1993) to substantially enhance the rate of thermal generation of gases. A maximum in  $NO_3$  effect was observed to occur at approximately 20 Mrad. Preirradiated samples had been heated to 60°C for about 200 minutes (Meisel et al. 1993). Irradiated and preirradiated/thermally-treated samples yielded similar results in that less than 1% of the HEDTA and EDTA remained after treatment. Citrate, however, remained largely unaffected. Meisel et al. (1993) conclude that HEDTA and EDTA should not remain in the tank environment for more than

about 5 years. The dose used in the experiments was 0.315 MGy (31.5 Mrad); the estimated dose rate in the tank is 4.2 mGy/s (25 rad/min). Counter to this prediction is the observation that the EDTA is still a significant fraction of the remaining total organic carbon (> 10%) (Campbell et al. 1994).

Meisel et al. (1993) observed that it must be the intermediate compounds produced via radiolytic degradation of the chelators that are responsible for the efficient thermal generation of hydrogen and nitrous oxide. Glyoxalate and formaldehyde were identified as fragments that will produce hydrogen efficiently, while hydroxylamine was identified as a source of nitrous oxide and nitrogen. Experimental results showed that NTA, IDA, glycolate, formate, and oxalate did not yield appreciable amounts of hydrogen by thermal reactions, while oxalate and formate did not yield nitrous oxide or nitrogen. Preirradiated citrate was found to produce enhanced nitrous oxide yields by thermal reactions but not hydrogen.

### Mechanism of Reaction for Formaldehyde

As a check on the results from the group at Georgia Institute of Technology, Meisel et al. (1993) performed experiments with formaldehyde ( $\text{CH}_2\text{O}$ ) in both simulated waste and NaOH solutions. Polymers of  $\text{CH}_2\text{O}$  were found not to contribute to the gas generation from solutions containing  $\text{CH}_2\text{O}$  in the concentrations used in the experiments reported by Meisel et al. (1993). Results from these experiments suggested that the reaction is first order with respect to  $\text{CH}_2\text{O}$  but second order with respect to  $\text{OH}^-$ . These results are in apparent disagreement with the kinetic analysis carried out at Georgia Institute of Technology where the reaction was reported to be first order with respect to  $[\text{OH}^-]$  (Ashby et al. 1994a). Experiments reported by Meisel et al. (1993) were carried out at three temperatures and these data yielded an estimate of the activation energy of 84.9 kJ/mol (20.3 kcal/mol), which is slightly dependent on the concentration of  $\text{OH}^-$ . The rate of  $\text{H}_2$  generation in simulated waste was found to be about 12 times faster than in NaOH, and, in both cases, only  $\text{H}_2$  gas was observed.

As a result of their work and previous investigations at Georgia Institute of Technology, Meisel et al. (1993) determined that the conversion of  $\text{CH}_2\text{O}$  to form  $\text{H}_2$  decreases with increasing concentration of  $\text{CH}_2\text{O}$ . The reason is the increasing influence of the competing second-order Cannizzaro reaction to produce formate ( $\text{HCOO}^-$ ) and methanol ( $\text{CH}_3\text{OH}$ ). The existence of the competing reaction was included in a computer analysis by Meisel et al. (1993). Under conditions expected to predominate in Tank 101-SY, the Cannizzaro reaction should yield conventional products, however.

The kinetic mechanism was further studied by Meisel et al. (1993) using  $\text{D}_2\text{O}$  and deuterium substituted  $\text{CH}_2\text{O}$  in experiments at 23°C. The exchange between  $\text{H}_2$  and an  $\text{OD}^-/\text{D}_2\text{O}$  solution was minimized by using very short reaction times versus the long reaction times used at Georgia Institute of Technology (see Ashby in Schulz and Strachan 1992 and the discussion in a previous section). Results clearly indicate that both H atoms come from  $\text{CH}_2\text{O}$ , either a single  $\text{CH}_2\text{O}$  or two molecules of  $\text{CH}_2\text{O}$ , and the yield of hydrogen does not appear to be a function of the  $[\text{CH}_2\text{O}]$  (Meisel et al. 1993). Results with  $\text{OCHCOO}^-$  show that one H comes from  $\text{OCHCOO}^-$  and one from  $\text{H}_2\text{O}$ .

## Effect of Minor Components

The effect of minor dissolved solution species was briefly studied by Meisel et al. (1993). This scouting study indicated that the presence of  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{K}_2\text{PtCl}_6$ ,  $\text{K}_2\text{PdCl}_6$ ,  $\text{Cl}^-$ , and  $\text{F}^-$  do not appreciably change the kinetics of  $\text{H}_2$  and  $\text{Cr}(\text{III})$  causes a reduction of the  $\text{N}_2\text{O}$  generation; Cr was found in significant quantities in samples from Tank 101-SY (Herting et al. 1992a,b). This is significant because a reduction in the rate of  $\text{N}_2\text{O}$  production would bring the ratio of the gas generation rates closer to those found in the gases being generated from the waste in Tank 101-SY. The ratio of  $\text{N}_2\text{O}/\text{H}_2$  with  $\text{Cr}(\text{III})$  present in the test solution was about 4:1. If one takes into account that some of the  $\text{N}_2\text{O}$  in the actual waste might have decomposed to  $\text{N}_2$  and  $\text{O}_2$ , this ratio is encouragingly close to the ratio found in the gases from Tank 101-SY.

The other observations of note from Meisel et al. (1993) experiments with minor components were the effect of dissolved/particulate Pd and  $\text{H}_2\text{NOH}$ . A higher amount of gas appeared to be retained in the solution when Pd was present. Hydroxylamine also greatly reduced the  $\text{N}_2\text{O}$  generation. Those results also agree with the observations and the proposed nitrogen kinetic mechanism proposed by Ashby et al. (1994b). In the proposed mechanism, reactions involving  $\text{H}_2\text{NOH}$  produce  $\text{NH}_3$  and/or  $\text{N}_2$ .

## Gas Retention and Solids

For the most part these reaction studies at Argonne National Laboratory and Georgia Institute of Technology have been carried out using homogeneous solutions. However, during FY 1993, experiments were carried out using slurries (Meisel et al. 1993). The conclusion from this work is that some of the gas appears to be trapped within the solid particles. Meisel et al. (1993) arrive at this conclusion because the solid particles needed to be totally dissolved before all of the gas could be released. The exact mechanism is not known.

## Mechanism of Radiolytic Gas Generation

The mechanism by which gases are formed from the radiolysis of the solutions was investigated by Meisel et al. (1993) and was based on a thorough review of the literature (Meisel et al. 1991a,b). From that review, it was concluded that the primary reaction involving the organics that yields  $\text{H}_2$  is the hydrogen abstraction reaction:



In highly concentrated solutions containing  $\text{NO}_2$  and  $\text{NO}_3^-$ , the  $\text{NO}_2$  radical is formed. This radical reacts with the organic material in a similar fashion to OH radical, which attacks primarily the  $-\text{CH}_2-$  bonds. The end result is the generation of organic fragments, perhaps similar to those that are generated during thermal decomposition of the organic material. Meisel et al. (1993) conclude that the rate limiting step in the process is the radiolytic degradation of the organic material to form aldehydes

and not the reaction of the aldehyde to form  $H_2$ . This conclusion appears to be consistent with the low activation energy suggested by the data from the actual waste (Pederson and Strachan 1993) and the high activation energy measured for the formaldehyde reaction (Meisel et al. 1993).

Meisel et al. (1993) also developed a scheme by which the production of  $NH_3$  could be measured. In their experiments, the only source of  $NH_3$  identified was the organic amine nitrogens. This runs counter to the studies at Georgia Institute of Technology in which  $^{15}N$ -labeled compounds were used, and it was determined that 90% of the  $NH_3$  came from the  $NO_2$  and 10% from the organic material.

Based on the experiments performed at Argonne National Laboratory, the low intensity of radiation in the waste contained in Tank 101-SY is predicted to yield about 5 mol  $H_2$ /d and about 415 mol  $N_2O$ /d. These generation rates are too low for  $H_2$  and much too high for  $N_2O$  relative to the quantities being generated in the tank. It is concluded that the thermal reactions are the primary sources of  $H_2$ . However, the reactions carried out at Georgia Institute of Technology were purely thermal whereas radiation was used at Argonne National Laboratory. As noted above, most of the HEDTA that was present in the samples sent from Georgia Institute of Technology to Argonne National Laboratory had reacted. Thus, the difference in the results might lie in the different experimental conditions.

## Research at Pacific Northwest Laboratory

Research at the Pacific Northwest Laboratory this year consisted of work with simulated wastes of complex composition, gas generation during corrosion, reactions of  $N_2O$ , and vapor pressures of  $NH_3$  above simulated waste.

### Experiments with Simulated Waste

At a coordinating meeting in 1992 it was decided that, to better understand the results from the various laboratories, a simulated waste of known composition and properties and without solids was needed for a "round robin" test. After some discussion, the waste composition shown in Table 3 (see Pederson and Bryan in Strachan and Schulz 1993) was developed and used in a limited number of tests at the Pacific Northwest Laboratory.

Use of reagent grade  $Al(NO_3)_3 \cdot 9H_2O$  makes this solution much easier to make than previous formulations. Note that the NaOH has been increased to compensate for the tetrahydroxyaluminum (III) complex that forms and the corresponding release of  $NO_3^-$ . This solution is homogeneous, although solids can form during testing depending on the conditions.

Thermal gas generation rates have been measured using this solution and found to be much less than the rates measured using slurries, i. e., SY1-SIM-91A, at 90°C. Initially, the gas generation rates appear to be about a factor of 10 lower than the rates measured using a slurry. However, the result depends on the size of the reaction vessel suggesting that the vessel surface has some effect on the generation rate. Based on six tests (see Pederson and Bryan in Strachan and Schulz 1993), the gas

**Table 3. Homogeneous Simulated Waste Composition**

<u>Component</u>	<u>Concentration, M</u>
NaOH	3.4
Al(NO <sub>3</sub> ) <sub>3</sub> • 9H <sub>2</sub> O	0.43
Na <sub>2</sub> CO <sub>3</sub>	0.2
NaNO <sub>2</sub>	2.0
NaNO <sub>3</sub>	0.4
Na <sub>4</sub> EDTA	0.21

composition is predominantly composed of N<sub>2</sub> (36%) followed by N<sub>2</sub>O (27%) and H<sub>2</sub> (20%). The ratio of N<sub>2</sub>O/H<sub>2</sub> = 1.35 is closer to the ratios observed in the gases coming from the waste in Tank 101-SY (0.8 to 2). However, that ratio was found to be sensitive to the concentration of a variety of major and minor waste components, including hydroxide, chloride, and transition metals. These results are consistent with similar results reported by Ashby et al. (1994a).

### Corrosion Tests

Results from steel corrosion tests started last fiscal year were reported at the Tank Waste Science Panel meeting in January 1993 (Strachan and Schulz 1993). In these tests, A516 steel coupons were submersed in simulated wastes at 90°C with and without gamma radiation present. This steel was widely used in the construction of double-shell waste tanks at the Hanford Site. Steel corrosion contributed only a very small quantity of hydrogen; the amount of hydrogen produced was stoichiometrically equivalent to the weight loss of the corrosion coupons. No other gas products could be attributed to steel corrosion. Corrosion rates extrapolated to a year were 0.02 to 0.03 mils per year, well below the design limit of 1 mil per year. No correlation between corrosion rate and gamma radiation dose rate could be discerned.

### Conversion of N<sub>2</sub>O to Other Forms

The perplexing and inconsistent values for the N<sub>2</sub>O/H<sub>2</sub> and the knowledge that N<sub>2</sub>O degrades in a radiation field to other gases, led Pederson and Bryan to perform experiments to determine the rate of degradation for simulated waste (Strachan and Schulz 1993). Their experiments were performed both in and out of a gamma radiation field of 1.4 Gy/s (5•10<sup>5</sup> R/h) for 2 weeks at 90°C (dose equivalent to 13 y exposure in Tank 101-SY). The solutions over which N<sub>2</sub>O gas was placed and allowed to equilibrate were H<sub>2</sub>O, SY1-SIM-92A without organic, and SY1-SIM-92A with 0.21 M citrate and no NO<sub>2</sub> or NO<sub>3</sub>. Results from these experiments reveal that N<sub>2</sub>O does decompose to N<sub>2</sub> and O<sub>2</sub> both over simulated waste without radiation and over all three solutions with radiation. However, at the radiation conditions in the tank, 1.4 Gy/s versus 4.2 mGy/s in the waste, the rate of decomposition would be

about 0.1 %/d absolute, e.g., 35%  $N_2O$  would be reduced to 34% in 10 d and to 25% in 100 d. The concentration of  $N_2$  would change accordingly. These data are consistent with the results of Meisel et al. (1993) because the duration of his experiments was on the order of one day.

One gas that was reported by Pederson and Bryan (in Strachan and Schulz 1993) was methane ( $CH_4$ ). Methane was found in the experiment performed with SY1-SIM-92A in a 1.4 Gy/s gamma radiation field. In this test, they measured 4.5%  $CH_4$  that was produced during the 14 d experiment at 90°C. Methane has been observed recently in the gases exiting from the tank.

### Vapor Pressure of Ammonia

In recent months, ammonia in the gases emanating from Tank 101-SY has become an important issue. Since installation of the Fourier transform infrared (FTIR) spectrometer with which to analyze the gases,  $NH_3$  has been observed as the major component in the gases emanating from the tank. The steady state concentrations in the ventilation gases have been about 80 ppm or more and, during a gas release event, more than 1 vol%. Pederson and Bryan (in Strachan and Schulz 1993) have measured the vapor pressures of  $NH_3$  above simulated waste solutions for different concentrations of ammonia in solution. Ammonia, as  $NH_4OH$  or  $NH_3,aq$ , is extremely soluble in aqueous solutions, even solutions with high dissolved solids and/or high concentrations of  $OH^-$ . By adding known but small concentrations of  $NH_4Cl$  to the simulated waste solutions, Pederson and Bryan were able to measure the vapor pressure above the solutions using an  $NH_3$  specific ion electrode. They concluded that the vapor pressure of  $NH_3$  above simulated waste solutions was about twice what would be measured if the solution was water or dilute solutions of salts for the same solution concentration of  $NH_4OH$  and  $OH^-$ . This result is not unexpected, since it is well known that the activity of water is diminished in solutions of high ionic strength, which would shift the aqueous ammonia/ammonia vapor equilibria to the ammonia vapor side.

## Discussion

If the analysis of the gas generation rate is correct (Figure 2), the gas generation rate is decreasing with time. The rate is falling at about 50% in 5.5 y. Thus, if the analysis is correct and nothing is done to the waste in the tank, the rate will have decreased to 0.1 of the present rate in about 18 y. This analysis depends on the accuracy of the determination of the volume of the nonconvecting layer by Antoniak (1993). A possible reason for the decreasing normalized rate is that the volume of the nonconvecting layer is increasing. Thus, the rate may decrease to some limiting value because the volume of the nonconvecting layer equals the volume occupied by the existing waste.

Results for the mechanism of gas generation have advanced the understanding of the processes that may be taking place in the waste, but have also left many questions. There are indications that there may be more EDTA in the waste than reported earlier (see Campbell et al. in Strachan and Schulz 1993). Also, NNIDA remains a strong possibility for the major organic constituent in the waste and is in agreement with some of the results obtained in the laboratory and at odds with others. Overall, however, the picture is improving, and continued perseverance by all involved will yield a satisfying product.

At Georgia Institute of Technology, research indicates that EDTA does not react at test temperatures up to 120°C. However, in the presence of radiation EDTA is rapidly decomposed (Meisel et al. 1993). The initial product of this radiolysis is identified as NTA. The other logical decomposition product should have been predicted to be IDA. Since many of the steps in the reaction mechanism proposed by Ashby et al. (1994a) involve the formation of nitroso compounds, NNIDA should also be a strong possibility as an intermediate compound. Thus, the presence of both EDTA and NNIDA in waste samples is strong evidence that the rate of decomposition of EDTA is limited by radiolysis with NNIDA as a major product of that reaction. Other products such as NTA and ED3A may also be identified and would be consistent with this interpretation. Radiolysis may also be the rate limiting step in the decomposition of NNIDA, but the decomposition may also be limited by some thermal reaction.

Ashby et al. (1994a) report the half life of NNIDA as 250 h. These experiments were performed at 90°C, and the waste is currently at approximately 50°C. If the activation energy for the decomposition of NNIDA is about 100 kJ/mol, then the half life at 50°C is 740 d. There are about  $7.5 \cdot 10^6$  mol C in the tank. Assuming 30% of this carbon is NNIDA, then there exists  $5.5 \cdot 10^5$  mol NNIDA. At a half life of 740 d, about 0.06% is destroyed per day at 50°C. This can be compared to data from the waste in Tank 101-SY by assuming that 80% of the  $H_2$  comes from  $OCHCOO^-$  and 20% from  $H_2CO$  (Ashby et al. in Strachan and Schulz 1993). This assumption leads to the result that 90 mol C/d is affected, i.e., yields  $H_2$ . If all of this  $H_2$  resulted because NNIDA decomposed, then 22.5 mol NNIDA/d ( $4 \cdot 10^{-3}\%$ /d) should be compared with the laboratory result of 0.06%/d. Although the "observed" rate is about 10 times lower than the laboratory result, the comparison is encouraging.

A similar calculation can be performed, but using the  $NH_3$  data discussed earlier. About 140 mol  $NH_3$ /d is generated in the waste, assuming that there are equal amounts stored in the waste as released from the waste. If the EDTA is about 10% of the TOC, then there are about  $7 \times 10^4$  mol

EDTA. Further assuming that 1 mol EDTA reacts to yield 1 mol  $\text{NH}_3$ , then 0.2%/d EDTA decomposes if all the  $\text{NH}_3$  comes from the organic nitrogen (Meisel et al. 1993) and 0.02% if only 10% comes from the organic nitrogen (Ashby et al. 1994b). The latter appears, from an order-of-magnitude point of view, to be in closer agreement with the calculations shown in the previous paragraph for  $\text{H}_2$ .

With respect to the proposed mechanism, the logic for the decomposition of HEDTA and glycolate appear basically sound, but here again gaps and unanswered questions remain. The use of  $^{13}\text{C}$ -labeled compounds clearly enhances the understanding of the reaction mechanism, but the NMR spectrum is very complex, and critical compounds can be easily overlooked or not detected. It is suggested that chemical separations be performed before obtaining the NMR spectrum or high resolution mass spectrum. The presence of  $\text{C}_2\text{O}_4^{2-}$  as an early reaction product suggests that the alcohol group in HEDTA is oxidized to an acid followed rapidly by cleaving of the N-C bond and oxidation to an acid at the other end. This seems to be an unlikely event. Similarly, the presence of glycine and EA in the suite of reaction products suggests that the -OH group is oxidized.

Several steps in the proposed mechanism for the decomposition of the organic compounds and the nitrogen chemistry require two molecules of the same species to react as one of the critical steps in the reaction sequence. This seems to be an unlikely event especially when the molecule is relatively unstable with respect to other forms, as in the case of  $\text{NO}^-$ , or both molecules are of equal charge and contain high charge density, as in the case of  $\text{NO}^-$  and  $\text{H}_2\text{CO}_2^-$ . These parts of the mechanism need to be carefully examined.

The results of the work carried out at Argonne National Laboratory also suggest further work is needed on the decomposition of EDTA, especially since significant quantities of EDTA have been identified in the organic material in the waste from Tank 101-SY. It appears from the analysis of the data performed here that NNIDA may be the rate limiting species from a thermal reaction perspective and that EDTA is initially reacted through a radiolysis-based reaction. Results from the studies at Georgia Institute of Technology indicate that EDTA does not react by strictly thermal reactions. At no point in any of the analyses of the reaction products has NNIDA been found. It is becoming clear that this chemical is one of the predominant species in the waste. If this reactant is truly not found in the solutions from the thermal or the radiolysis studies, then these studies need to be assessed to determine if they are correctly structured. However, the lack of evidence for NNIDA may lie in analytical error or some other logical explanation that must be forthcoming.

As indicated above, the current concentrations of  $\text{NH}_3$  in the gases coming from Tank 101-SY are a source of concern. Here the mechanism of formation is crucial because of the safety implications. Only a few of the experiments reported to date from both Georgia Institute of Technology and Argonne National Laboratory give information on the formation of  $\text{NH}_3$ . Of particular interest is the rate of  $\text{NH}_3$  formation under air and argon. If the rate of formation of  $\text{NH}_3$  is substantially enhanced when  $\text{O}_2$  is present, then the possibility exists that the  $\text{NH}_3$  is mostly formed in the "foam" layer that comprises the upper portions of the waste. However, if the  $\text{NH}_3$  is formed generally throughout the waste, then mixing of the waste could potentially release large amounts of  $\text{NH}_3$ . If large releases of  $\text{NH}_3$  were to take place, worker safety would be a concern.

Gas generation has been discussed in this report. Although this is an important part of the puzzle that is Tank 101-SY, the mechanism by which gases are retained in the waste has not been well studied. Bryan and Pederson (Strachan 1992b) suggested that surface tension and the hydrophobic nature of the surface of the solids was partially responsible for gas retention. Antoniak (1993) reported results from experiments with simulated wastes. He concluded that the scale of the experiment was important in obtaining meaningful results with simulated wastes. The general conclusion appears to be that in situ measurements and the taking of samples at temperature and pressure appear necessary to obtain data useful to the modeling of gas retention. Without these data, there is no benchmark for the physical models of gas retention and release.

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