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Effects of Oxygen Cover Gas and NaOH Dilution on Gas Generation in Tank 241-SY-101 Waste

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Abstract: Laboratory studies are reported of gas generation in heated waste from tank 241-SY-101. The rates of gas generation and the compositions of product gas were measured. Three types of tests are compared. The tests use: undiluted waste, waste diluted by a 54% addition of 2.5 M NaOH, and undiluted waste with a reactive cover gas of 30% O₂ in He. The gas generation rate is reduced by dilution, increased by higher temperatures (which determines activation energies), and increased by reactions of O₂ (these primarily produce H₂). Gases are generated as reduction products during oxidation of organic carbon species by nitrite and O₂.

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EXECUTIVE SUMMARY

This report presents studies of gas generation in heated tank waste. The waste is a whole-tank composite of material from tank 241-SY-101 (referred to as Tank 101-SY). The experiments measured the rates of gas generation and the compositions of product gas. Tests were done using undiluted waste under an inert cover gas (He). Other tests used tank waste diluted by addition of 54% (by volume) of 2.5 M NaOH under He cover gas. Additional tests studied gas generation in undiluted waste under a reactive cover gas of 30% oxygen in He.

The results show that dilution reduces the gas generation rate, higher temperatures increase the rate, and reactions of O_2 increase the rate, especially for H_2 production. The average rates for gas release, in units of millimoles of gas per liter of waste (or diluted waste) per day, are listed.

For undiluted waste at 100 °C, the rate was 0.78 mmole/L/day (Day 25); it was faster at first (1.2 mmole/L/day at Day 10).

For diluted waste at 100 °C, the rate was 0.45 (Days 15 - 34), or 0.46 mmole/L/day (Days 0 to 34).

For diluted waste at 65 °C, the rate was 0.019 (Days 0 - 34), or 0.016 mmole/L/day (Days 15 to 34).

For undiluted waste (with O_2 present) at 70 °C, the rate was 0.2 to 0.5; at 90 to 100 °C it was 2 to 3 mmole/L/day for the later fillings.

The average gas compositions were (for the tests and temperatures):
 Undiluted waste, 100 °C: 22% H_2 , 43% N_2O , 27% N_2 , 2% NH_3 , and 5% CH_4 ;
 Diluted waste, 100 °C: 22% H_2 , 49% N_2O , 22% N_2 , 1% NH_3 , and 5% CH_4 ;
 Diluted waste, 65 °C: 22% H_2 , 48% N_2O , 25% N_2 , 1% NH_3 , and 1% CH_4 ;
 In-Tank values, ~50 °C: 29% H_2 , 24% N_2O , 33% N_2 , 11% NH_3 , and 0.4% CH_4 .

The present gas compositions differ from the in-tank values (Sullivan 1995). The smaller values for ammonia (NH_3) were poorly determined, but they may reflect ammonia losses during storage of waste samples. The higher values for methane reflect the larger activation energy for production. The relatively smaller H_2 and larger N_2O values may result from different activation energies and from a different N_2O/H_2 ratio for radiolysis, as well as from some O_2 reactions in the tank primarily producing H_2 .

Measurements at different temperatures allowed calculation of activation energies. The value for total gas release in diluted waste was 24 ± 5 kcal/mole. Releases of H_2 , N_2O , and N_2 gave similar values: 23, 23, and 22 kcal/mole, respectively. Methane has a higher value (35 kcal/mole). The activation energy for total gas production in undiluted waste (with O_2 present) was 17 ± 2 kcal/mole; it was 11 ± 2 kcal/mole for the removal of O_2 .

The measurements using waste material diluted by addition of 54% of 2.5 M NaOH showed little effect on the activation energy for gas generation, and only minor effects on the gas composition. One minor effect was a decrease in the N_2/N_2O ratio for diluted material, as expected from the reduced viscosity (Ashby 1994). The gas generation rate after dilution is 52 to 58% of the value in undiluted waste. Dilution lowered the solution concentrations of unsaturated species to 0.65 (1/1.54) of their undiluted values. Studies in synthetic waste found the rate to depend on the concentrations of organic species, nitrite, aluminate, and hydroxide (e.g., Ashby 1994). Detailed considerations indicate that dilution with 2.5 M NaOH should lower the rate by a factor of about 0.65² (0.42) from dilution of the organic species and the aluminate. The observed reduction factor (about 0.55) does not significantly disagree with this; however it suggests there are compensating effects of dilution, such as rate constants increasing from the reduced viscosity. Another possibility is that dilution might dissolve organic species that generate a significant amount of gas. This would imply a gas generation rate faster than expected for oxalate, or that additional organic species dissolve. Only oxalate is expected to dissolve (Barney 1994); dilution data suggest a possibility of other organic species dissolving (Person 1996a, Hudson 1995).

Oxygen reactions are discussed in the general context of effects of reduction/oxidation (redox) reactions. Other evidence indicates that the dominant oxidation reaction oxidizes the total organic carbon (TOC) to carbonate (or to a temporary end point by forming insoluble sodium oxalate). The major reduction reactions are removal of O_2 and formation of gaseous products, so that the summed rate of these reduction reactions is an estimate of the rate of oxidation of TOC. The amount of gas produced (and O_2 removed) thus measures TOC oxidation. The gas yield from oxidation of TOC is about 0.6 to 0.8 moles of gas per mole of TOC. This corresponds to an average of 2.5 or 3.5 equivalents to oxidize a mole of TOC to oxalate or carbonate, and 4.3 equiv/mole for the gas mixture produced in the tank (Sullivan 1995). The gas yield depends on whether the final product is carbonate or oxalate, and on the gas composition. This gas yield estimate indicates that Tank 101-SY has enough TOC to release gas for around 80 to 110 years at the current release rate (if O_2 reactions are ignored). The estimated half-life (assuming first-order removal) is around 50 to 80 years. Bringing O_2 into contact with the bulk of the waste volume would dramatically shorten this half-life (to about 2 years, if the entire volume is in contact). However, safety issues must be considered, including the increased rate of gas production for H_2 and NH_3 . The gas yield per O_2 molecule removed was estimated from the present work to be 0.06 to 0.23 for H_2 and 0.03 to 0.09 for NH_3 , but only 0.002 to 0.03 for N_2 , and 0.001 to 0.013 for N_2O .

The gas generation rates in the present experiments primarily result from thermal processes. These rates allow calculation of the rate for thermal processes (with no O_2) at tank temperature as about 0.2 of the observed rate of gas release in the tank. Thermal reactions with O_2 seem to also occur in the tank, but radiolytic processes may be the largest gas source in the tank.

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LIST OF TERMS

ANL	Argonne National Laboratory
EDTA	ethylenediaminetetraacetic acid
ED3A	ethylenediamine triacetic acid
GIT	Georgia Institute of Technology
HEDTA	hydroxyethylethylenediamine triacetic acid
IDA	iminodiacetic acid
NPH	normal paraffin hydrocarbon
NTA	nitrilotriacetic acid
PNNL	Pacific Northwest National Laboratory
psia	lb/in ² , absolute
SCF	standard ft ³
SpG	specific gravity
TOC	total organic carbon
TRU	transuranium
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

This report presents studies of gas generation in heated tank waste. The results are compared with earlier studies (Person 1996b) using waste from the same tank (241-SY-101, referred to as Tank 101-SY) and studies (Bryan 1996) using waste from tank 241-SY-103 (Tank 103-SY). The present tests used a whole-tank composite of material from Tank 101-SY collected during "Window C" (May 1991) and "Window E" (December 1991).

This report consists of the following: Section 2 contains a summary of major results, together with an application that discusses gas generation within the tank. Section 3 describes the experimental apparatus and the waste material used. Section 4 introduces the measurements and the data analysis for the amount of gas produced; Section 5 introduces the results of measurements of the gas composition. Section 6 discusses gas generation in undiluted tank waste with an inert cover gas of helium. Section 7 presents results for gas generation in tank waste diluted by addition of 54% (by volume) of 2.5 M NaOH with helium cover gas; 2.5 M NaOH is the average concentration used in dilution studies discussed in another report (Person 1996a). Section 8 presents results of gas generation in undiluted tank waste in contact with a reactive cover gas of 30% oxygen mixed with helium. Oxygen reactions are reduction reactions, which are discussed in the general context of effects of reduction/oxidation (redox) reactions. A major oxidation reaction is the oxidation of total organic carbon (TOC) to carbonate (CO_3^{2-}) or to oxalate ($\text{C}_2\text{O}_4^{2-}$), and the major reduction reactions are the removal of O_2 and formation of gaseous products, so the rate of the reduction reactions is an estimate of the rate of oxidation of TOC.

Gas generation experiments at different temperatures (typically, 65 and 100 °C) allowed apparent activation energies to be determined. The gas generation results are compared with measurements on undiluted waste with He cover gas in an earlier whole-tank composite (Person 1996b). The gas generation experiments in Section 7 study the changes in gas generation when the waste is diluted. This study compares with new measurements using the undiluted waste (Section 6). The reduction in rate after dilution is compared with expectations based on earlier synthetic waste studies (Delegard 1980, Ashby 1994). Section 8 presents new results for undiluted waste with oxygen in the cover gas. Additional experiments are continuing for the studies in Section 8.

Gas retention in Tank 101-SY waste is enhanced by the presence of solid material in the unstirred tank, which settles in the nonconvective layer. Aluminum (Al) is present in significant quantities in the tank. Aluminum is soluble at high pH in the form of the aluminate ion $[\text{Al}(\text{OH})_4^-]$. The Al solubility depends upon the hydroxide ion (OH^-) concentration: at low hydroxide ion concentrations gibbsite $[\text{Al}(\text{OH})_3]$ precipitates, and at high OH^- sodium aluminate $[\text{NaAlO}_2]$ precipitates (Barney 1976). One suggestion for mitigation postulates using dilution to dissolve a significant amount of solid

material, which is expected to reduce the ability of the waste to retain gas. In addition, dilution of the waste may be desirable (or required) during removal from the tank. Because of the nature of the Al solubility, dilution with NaOH keeps most of the Al in solution (Person 1996a). For these reasons, the effects of dilution by NaOH on gas generation were studied.

The present studies provide information on the effect of dilution on the rate of gas generation, and on the composition of product gas. The effects of using O_2 in the cover gas were studied in order to evaluate the importance of oxygen reactions within the tank. The effects in the laboratory tests were dramatic: O_2 was consumed rapidly and production of H_2 was enhanced. The effects of dilution and of using oxygen were deduced from comparisons with gas generation results for undiluted material under an inert cover gas (He). Comparisons were also made to studies using synthetic waste (e.g., Delegard 1980, Ashby 1994, Barefield 1996) and to studies using waste from Tank 103-SY (Bryan 1996).

2.0 CONCLUSIONS AND RESULTS SUMMARY

This section summarizes the major results and conclusions. The conclusions are based on new experimental results that use a composite (94A) of actual waste material from Tank 101-SY. This composite simulates the whole tank, with material from four segments in the convective layer combined with material from four segments in the nonconvective layer. Before discussing the results of the different studies, Section 2.1 gives an overview of the results and Section 2.2 applies the results to draw conclusions about gas generation within the tank.

The major conclusions are:

- Gas generation measurements at 100 °C and 65 °C in diluted waste show that dilution does not change the activation energy, and that the gas generation rate decreases by a larger factor than the dilution of the organic species concentration (but less than expected for the combined effect of diluting both organic and aluminate).
- The predicted rate of gas generation from thermal processes (in the absence of O_2) within the tank is about 0.2 of the measured rate. Most of the gas is produced by radiolytic processes, but the amount produced by thermal reactions with O_2 may be around 0.2 of the total. The reactions with O_2 primarily produce H_2 .
- Tank 101-SY has enough TOC to release gas for 80 to 110 years at current release rates, if reactions with oxygen are negligible.
- Oxygen reduction reactions significantly increase the rate of reduction reactions, so that the rate of TOC oxidation of TOC can be significantly increased by contact with O_2 .

2.1 Overview of Gas Generation Results

This section presents an overview of the gas generation studies in this report. The present experiments measured gas release at different temperatures for two cover gases for diluted or undiluted waste. Table 2-1 highlights the major results. The gas generation rate was measured for the total amount of gas, and measurements of the gas composition allow calculation of rates for production of the different gaseous species. Table 2-1 shows rates for total gas and for hydrogen (H_2) production. The effects of dilution, temperature, and cover gas are illustrated by comparing the column entries: dilution by addition of 54% (by volume) of 2.5 M NaOH reduced the rates, higher temperatures increase the rates, and reactions with oxygen (O_2)

Table 2-1. Overview of Results of Gas Generation Rate Experiments

Material	Temp °C	Cover Gas	Gas Rate, mmole/L/day		Reduce Rate (Gas, O ₂) mequiv/l/day	Reference
			Total	H ₂		
Diluted	65	He	0.017	0.0036	0.067 (Gas)	Table 7-1
	100		0.45	0.10	1.8 (Gas)	Table 7-2
Undiluted	100		0.78	0.17	3.2 (Gas)	Fig 6-3
	70	O ₂ /He	0.2-0.5	0.1-0.4	0.2 (Gas) 0.8-1.5 (O ₂)	Fig 8-5
	90- 100		1.7-2.9	1.4-2.2	5-8 (Gas) 37-38 (O ₂)	

increase the rates, especially for H₂ production. Quantitative comparisons of these effects are discussed later. The rates are quoted in units to show the amount of gas produced (millimoles) per liter of waste (or liter of diluted waste) per day.

As discussed in Sections 2.6 and 8.4, the gases are formed as reduction products of redox (reduction/oxidation) reactions. Reduction reactions are balanced by oxidation reactions, with oxidation of the total organic carbon (TOC) being a principal source of electrons. Oxygen (if present) is also reduced. The number of equivalents (moles of electrons) transferred per mole of product gas depends on the gaseous species produced (e.g., 2 equiv/mole for H₂). Table 2-1 shows the rate of reduction, computed from the gaseous products produced (average of 4.1 equiv per mole of gas) and from the removal of O₂. These rates are expressed in units of milliequivalents per liter per day. A comparison of the reduction rates shows that O₂ significantly increases the rate of reduction (implying a corresponding increase in the rate of TOC oxidation). The final column references more detailed discussions of the results.

Gas is generated by thermal processes and by radiolysis. The present experiments enhance the rate of thermal processes by using higher temperatures. In addition, radiolytic processes are suppressed because more than half of the ionizing radiation escapes from the small waste volumes used. Thus the gas generation rates measured in the present experiments are primarily the result of thermal processes. Measurements at different temperatures are used to calculate apparent activation energies (E_{act}). These are used to calculate rates for thermal processes at tank temperature. Table 2-2 gives a summary of the activation energies for rates for the generation of the total gas and for H₂. The present value, determined using

Table 2-2. Overview of Measurements of E_{act} for Gas Generation and Oxygen Reduction of Waste from Tanks 103-SY and 101-SY (Comp93A, 94A).

Material	Cover Gas	Process	E_{act} (Total, H ₂) kcal/mole	Reference
Diluted, 94A, 101-SY	He	Gas Generation	24 ± 5 (Total) 23 ± 5 (H ₂)	Sec 2.4, Tab 7-3
Undiluted, 93A, 101-SY	He		22 ± 4 (Total)	Person (1996b)
Undiluted, 103-SY	Ar		22 ± 1 (Total) 22 ± 1 (H ₂)	Bryan (1996)
Undiluted, 94A, 101-SY	He/O ₂	Gas Generation O ₂ Reduction	17 ± 2 (Total Gas) 11 ± 2 (O ₂ Reduct)	Sec 2.5, Fig 8-11

diluted composite 94A, is seen to be in good agreement with the value determined earlier for undiluted material (Person 1996b), using a similar composite (93A). The table includes values measured using the convective layer liquid from Tank 103-SY (Bryan 1996). The good agreement is consistent with the similar waste compositions of the two tanks.

The studies using an inert atmosphere of helium or argon (Ar) find higher activation energies than found for gas generation when O₂ is present; the activation energy for the rate of O₂ reduction is even lower. The activation energies are used to estimate rates of thermal processes at tank temperature.

2.2 Estimation of Gas Generation Rates Within Tank 101-SY

This section applies the results by estimating the contributions of different processes within Tank 101-SY. The main objective in this section is to examine the contributions of the three processes that produce gas: radiolysis, thermal reactions in the absence of oxygen, and thermal reactions in the presence of oxygen. These estimates are crude, but they serve to illustrate the insight that can be gained by understanding the separate processes that generate gas.

Table 2-3 compares the rates of gas generation (total gas and for H₂ only). Estimated rates from in-tank measurements are compared with values expected for the different processes producing gas. The table also shows the ratio of nitrous oxide (N₂O) to H₂. Nitrous oxide supports combustion, and the ratio depends on the organic species present during tests in synthetic waste (e.g.,

Table 2-3. Estimated Rates of Gas Generation for Thermal and Radiolytic Processes Compared for Tanks 101-SY and 103-SY.

Process Tank 101-SY	Temp °C	Rate, mmole/L/day				N2O/H2 Ratio
		Total		H2		
		Best	Range	Best	Range	
Estimates from In-Tank Data: Unmixed (1992 Estimate) and Mixed (Current)						
Unmixed	47-58	0.046	0.037-0.054	0.018	0.014-0.021	0.8
Mixed	47	0.028	0.023-0.034	0.0074	0.006-0.009	0.85
Estimated Values at 47 or 58 °C from Laboratory Data						
Thermal	47	0.005	0.003-0.014	0.0010	0.0004-0.0026	0.6-1.2
Thermal	58	0.015	0.010-0.037	0.0034	0.0016-0.0070	0.8-1.3
Radiol	47	0.005-0.015		0.0014-0.0028		1-20
With O2	47	0.07	0.01-7	0.04	0.005-5	0.01-0.03
Thermal 103-SY	47	0.0068		0.0028	0.0022-0.0036	0.3 ± 0.1
Laboratory Results						
Thermal	65	0.029-0.038		0.011-0.015		0.5-1.1
	100	0.78	0.6-0.8	0.18	0.13-0.20	1.9
With O2	70	0.2-0.5		0.1-0.4		0.02
	90-100	1.7-2.9		1.4-2.2		0.03
Thermal 103-SY	60	0.022-0.038		0.005-0.013		0.3-1.2
	105	1.2-2.4		0.37-0.68		1.2-1.6
Radiol Synth	30, 60			0.0014 For In-Tank Radiation Level		1.3-21

Bryan and Pederson 1994, Ashby 1994). Two estimates of the rates are shown for the in-tank conditions. One set (Ashby 1992) represents older estimates for the unmixed tank. The second set shows the current conditions for the mixed tank. The rates shown are calculated from the total rates of 160 (Ashby 1992), or 100 (Brewster 1995, Stewart 1994) SCF/day (standard ft³/day), using a waste volume of 4.2×10^6 L; the current rate for H₂ generation and the N₂O/H₂ ratio are calculated using gas compositions given by Sullivan (1995).

The temperature values for the unmixed tank show a typical range in temperatures reported. The mixed tank has a more uniform temperature; the new value is somewhat lower than expected from earlier measurements.

It is well known that gas is generated within the tank by both thermal and radiolytic process. Work with synthetic waste at the Georgia Institute of Technology (GIT) established that reactions of several organic species with oxygen preferentially produce H_2 , rather than N_2O (Ashby 1994, Barefield 1996). The present experiments indicate that the total gas production is faster when oxygen is present, with H_2 being a major product. Thus thermal reactions with oxygen may make a significant contribution to gas generation, at least for H_2 production. However, the GIT results suggest a slower total gas production rate in the presence of O_2 when the organic is HEDTA (Barefield 1996).

The gas generation rates quoted for the unmixed tank (Ashby 1992) were not direct measurements, so the rate differences shown may not represent any actual difference in the rate within the tank. However, the lower temperature indicated for the mixed tank would be expected to reduce the contribution of thermal reactions. Furthermore, mixing could alter the fraction of the waste that is in contact with oxygen.

- Gas generation within the tank is faster than predicted for thermal processes in the absence of oxygen. Most gas is produced by radiolytic processes; some is produced by thermal reactions with O_2 (especially the production of H_2).

The second section of Table 2-3 shows estimated values for different processes individually. These estimates are rough values with large uncertainties, especially for the radiolysis. The thermal processes without oxygen are shown for the current tank temperature (47 °C) and for a temperature (58 °C) typical of the maximum temperature that occurred in the nonconvective layer before the mixing pump was installed (e.g., Table B.1 of Bryan 1992). The thermal processes without oxygen contribute about 0.2 of the total gas production in the mixed tank (and probably a smaller fraction of the H_2 production). At the maximum temperature of the unmixed tank, this fraction was perhaps 0.3 (assuming the 1992 estimate rate was correct) or 0.5 (assuming the rate in the unmixed tank was the same as the current rate). The thermal processes (no oxygen present) are seen to have reasonably similar rates for both Tank 101-SY and 103-SY. This is also true for the values shown for these two tanks in the lower portion of Table 2-3, which lists some of the experimental observations used to estimate values at tank temperatures.

The rates of radiolytic gas generation can be calculated from the $G(\text{gas})$ and $G(H_2)$ values. The G values give the number of molecules formed per 100 eV of energy absorbed. The radiolysis rates are calculated by assuming that all energy from the radioactive decay of ^{137}Cs (0.57 MeV gamma plus 0.23 MeV beta) is absorbed within the tank, using the ^{137}Cs value (600 mCi/L) measured for

composite 94A (Person 1996a; Section 4.3.3 of Person 1996c shows an example calculation).

The estimated value for $G(H_2)$ is based on irradiation studies of synthetic waste that revealed a correlation of this value with the number of C-H (or N-H) bonds per molecule times the molar concentration of organic (Meisel 1993). Analyses of the organic species in Tank 101-SY waste (Campbell 1995) allow the number of C-H bonds to be estimated as 1.33 (Table 8-2). Using the molar concentration of 1.4 for the soluble TOC (Person 1996a) in the correlation equation gives 0.055 for $G(H_2)$. As this value is based on studies using synthetic waste, the value is the tank may be different. The actual $G(H_2)$ value might well be twice as large. A preliminary result from a study of Tank 103-SY waste at Pacific Northwest National Laboratory (PNNL) (Bryan 1996) is consistent with $G(H_2) = 0.11$, so this value is used to calculate the faster rate of radiolytic production of H_2 .

The $G(\text{gas})$ value is the sum of $G(H_2)$, $G(N_2O)$, $G(N_2)$, etc., so it is larger than $G(H_2)$. There is a greater uncertainty in $G(\text{gas})$, as a wide range (1.3 to 21) was found for N_2O/H_2 in the synthetic waste studies, depending on the organic species used (Meisel 1993). The range of $G(\text{gas})$ used was 0.2 to 0.6, which includes a preliminary result from PNNL for Tank 103-SY waste. Thus the estimates given in Table 2-3 for the rates of the total gas generation by radiolysis are very approximate. The radiolysis rate estimates all ignore the small differences in G values between measurements at 30 and 60 °C (Meisel 1993).

The sums of the rates estimated for thermal and for radiolytic gas generation are smaller than the observed rates in the tank for both the total gas generation and for H_2 . The low value for the total gas may simply reflect a low estimate for $G(\text{gas})$. The low value for the hydrogen generation rate might also reflect a low estimate for $G(H_2)$. However the sum is much smaller than the generation rate in the tank. This seems to indicate there is some contribution from reactions with oxygen to produce H_2 in the tank. The $G(H_2)$ value of 0.11 would be the best estimate, if this is the value determined for Tank 103-SY. This value leads to an estimated rate for H_2 production of 0.0028 mmole/L/day, so that the sum of the radiolytic and thermal production of H_2 is 0.0038 mmole/L/day. If the difference between this sum and the observed rate is the result of O_2 reactions, the O_2 reactions produce H_2 at a rate of 0.0036 mmole/L/day. This could occur if about 10% of the waste was in contact with O_2 . A rough estimate of the total gas generation rate from O_2 reactions would then be about 0.007 mmole/L/day (0.2 to 0.3 of the total rate in the tank).

Oxygen was formed with a $G(O_2)$ of 0.08 in the irradiation of synthetic waste (Meisel 1993). In addition, diffusion and/or convective mixing will transport oxygen from the tank surface into some fraction of the tank volume. Thus, reactions with oxygen will occur; these may be more important in the production of H_2 .

A further conclusion is that thermal reactions produced a larger fraction of gas in the nonconvective layer of the unmixed tank, at least during the period where the layer was hotter than the remainder of the tank.

Table 2-3 suggests that oxygen reactions may be as important as thermal reactions in the absence of oxygen in total gas production, and that oxygen reactions may produce half of the H_2 . If the operation of the mixer pump increased the fraction of the waste in contact with oxygen, then differences in gas generation would be expected. For example, any increase in the fraction of the waste in contact with oxygen should increase both the total gas generation rate and the H_2 production rate, while decreasing the N_2O/H_2 ratio.

The present tests are dominated by thermal processes. Better estimates of the rate of gas production by radiolytic processes are needed to provide reliable estimates of the gas composition expected within the tank. The present estimates of the contributions of different processes within the tank indicate that reactions with O_2 significantly contribute to the production of H_2 . Thus, the product gas composition in the tank can not be estimated reliably from the present experiments, as the fraction of the waste in contact with oxygen is not known, and the product gas composition was not measured for radiolysis. Thus no comparison can be made with the composition determined by Sullivan (1995). The present results indicate that the product gas composition could be changed by operation of the mixer pump. Increased contact with oxygen would increase the relative contribution of H_2 in the product gas.

In summary, the entries in Table 2-3 indicate the mixed tank to be cooler than the unmixed tank. A cooler tank will have a lower contribution of gas generation from thermal processes. The rate of H_2 production suggests that thermal reactions of O_2 are important in this production. The oxygen reactions could produce a similar amount of the total gas as the thermal reactions in the absence of O_2 . In this case, about 0.5 to 0.6 of the total gas generation would be from radiolysis. Note however that the estimates in Table 2-3 are very rough.

2.3 Estimation of Rate of Oxidation of TOC Within Tank 101-SY

This section estimates the rate of oxidation of total organic carbon (TOC) within the tank. The goal is to estimate the half-life for removal of soluble TOC by conversion of the carbon in the organic species into oxalate and carbonate. Table 2-4 shows estimated rates for the oxidation of the carbon in the organic species, with the final species being either oxalate ($C_2O_4^{2-}$) or carbonate (CO_3^{2-}). These rates are estimated from the measured rates of reduction reactions (those that produce gas and those that remove O_2) and from the average amount of electrons transferred in producing the two final species

Table 2-4. Estimated Rates of TOC Reaction to Oxalate or Carbonate for Thermal Reaction at 47 °C Compared With Radiolysis at Two G-Values for Gas Generation, With and Without the Presence of O₂.

Oxygen	Rate to Oxalate, mmole/L/day			Rate to Carbonate, mmole/L/day		
	Thermal	Radiolysis G(gas)		Thermal	Radiolysis G(gas)	
		0.2	0.6		0.2	0.6
Absent	0.0075	0.0080	0.024	0.0054	0.0056	0.017
Present	1.6	0.008 ¹	0.024 ¹	1.1	0.0056 ¹	0.017 ¹

¹Rough estimate by assuming no effect from the presence of oxygen.

(Section 8.4). The oxalate will eventually be oxidized to carbonate, but the low solubility of oxalate will slow this process. Table 2-4 shows the rates for the individual thermal and radiolytic processes at 47 °C, the tank temperature. The main point of this comparison is that the rate is much faster if oxygen is present, even without assuming any increase in the radiolytic reactions in the presence of oxygen.

Table 2-5 shows the half-lives ($\tau_{1/2}$) that correspond to the rate of oxidation of TOC (assuming the reaction to be first order in the concentration of TOC). The first row shows the rates calculated from the rate of gas production in the tank currently (ignoring the contribution from the reduction of the limited amount of oxygen present). These half-lives are thus overestimates, but the next two lines show that the half-life for TOC oxidation could be decreased if the entire waste volume could be brought into contact with oxygen. The half-lives shown on the bottom two lines correspond to the total rates estimated from the sum of the individual processes listed in Table 2-4.

Note that the half-lives in Table 2-5 (and the rates in Table 2-4) correspond to the total oxidation of TOC, so that these half-lives are longer than for destruction of a particular organic species, such as the aging studies (Camaioni 1995). The estimates in Table 2-5 show that gas will be generated for decades, even allowing for some contribution from oxygen reduction. The gas yield estimate indicates that Tank 101-SY has enough TOC to release gas for around 80 to 110 years at the current release rate, ignoring O₂ reactions. The estimated half-life (assuming first-order removal) is around 55 to 76 years. Bringing O₂ into contact with the bulk of the waste volume would dramatically shorten this half-life (to about 2 years, if the entire volume is in contact). However, safety issues must be considered, including the increased rate of gas production for H₂ and NH₃.

Table 2-5. Estimated Half-Lives for TOC Reaction to Oxalate or Carbonate for Thermal Reaction Plus Radiolysis, Showing Importance of Oxygen.

Rate Source	Oxygen	$\tau_{1/2}$ (Oxalate), year	$\tau_{1/2}$ (Carbonate), year
Actual In-Tank	Limited, O ₂ Reduction Ignored	55	76
Table 2-4	Absent	84 ¹	240 ²
	Present	1.7	2.4

¹G(gas) = 0.6 molecule/100 eV²G(gas) = 0.2 molecule/100 eV

2.4 Gas Generation in Undiluted Waste (He Cover Gas)

The objective of the gas generation experiments is to gather data to help understand the generation of gas within the tank. The experiments measure the pressure buildup in closed containers that are sampled for analysis by mass spectrometry. Section 6 presents results for gas generation 100 °C in undiluted material. The experiments were conducted under an inert cover gas of helium in two reaction vessels (reactors G1 and G2).

The results showed:

- At 100 °C the gas generation rate decreases after the first 10 days. It was 1.1 and 1.3 mmole/L/Day at Day 10 in reactors G1 and G2, respectively; at Day 25 the respective rates were 0.75 and 0.81 mmole/L/Day.
- Gas was generated about 22% faster in Reactor G2; the additional gas was primarily N₂O.
- The average gas composition produced at 100 °C was 22.5% H₂, 42.6% N₂O, 27.2% N₂, 2% NH₃, and 5.0% CH₄.

This gas composition differs from those reported for the tank (Sullivan 1995) at tank temperature. The smaller value for ammonia (NH₃) may be the result of a loss of ammonia during storage of the waste samples. In addition, ammonia is poorly determined in the present experiments. The higher value for methane reflects the larger activation energy for this gas. The relatively lower quantities of H₂ and more N₂O may also result from different activation energies (and from different production rates by radiolysis). However, it probably also reflects a significant contribution of oxygen reactions in the tank increasing the H₂ with little production of N₂O.

2.5 Effects of NaOH Dilution on Gas Generation

Section 7 presents results for gas generation at 65 and 100° C in actual material from Tank 101-SY that has been diluted by addition of 54% (by volume) of 2.5 M NaOH. These data are compared with data from undiluted waste (Section 6).

The results showed:

- At 65 °C gas is generated at an average rate of 0.019 mmole/L/day for the 34-day test period. The rate slows after the first six days, with Days 15 to 34 having an average rate of 0.016 mmole/L/day.
- At 100 °C, the average rate is 0.45 mmole/L/day for days 15 - 34, compared with an average rate for days 0 - 34 of 0.46 mmole/L/day.
- At 100 °C gas is generated at a faster rate than at 65 °C (23 to 29 times faster). The increase in rate corresponds to an activation energy of 24 kcal/mole. Using rates determined over different time periods gives activation energies from 18 to 31 kcal/mole, including activation energies calculated using short time periods and small temperature (5 to 10 °C) intervals.
- Estimates of the activation energies for individual gaseous species found similar values of 21, 22, and 20 kcal/mole for H₂, N₂O, and N₂, respectively. A larger value (36 kcal/mole) was found for methane.
- At 100 °C the rate is about 58% as large as in undiluted waste. The rate reduction is somewhat less than expected from the solution concentration changes for species that determine the gas generation rate.
- The gas composition showed that heating with an inert cover gas released more N₂O than H₂, with similar production in the diluted and undiluted material.
- There was a decrease in both the N₂/N₂O ratio and a small decrease in the NH₃/N₂O ratio in diluted material. Decreased ratios were predicted by considering the effects of viscosity (Ashby 1994).
- Reduced viscosity may increase rate constants for gas generation reactions to partially compensate for the reduced concentrations of reactants.

The gas generation rate in the diluted material is 52 to 58% of the value in undiluted waste. The rate in synthetic waste has been shown to depend upon the concentrations of organic species, nitrite, aluminate, and hydroxide (e.g., Ashby 1994). Dilution with 2.5 M NaOH maintains the hydroxide

concentration approximately constant, and the nitrite concentrations are high enough that the rate is relatively independent of the nitrite (Delegard 1980), and some solid nitrite dissolves during the dilution (Person 1996a). The dilution added 54% (by volume) of 2.5 M NaOH, which lowered the solution concentrations of any unsaturated species to 0.65 (1/1.54) times its undiluted value. The organic species are expected to be completely dissolved, with the exception of oxalate (Barney 1994). The aluminate does not appear to significantly dissolve upon the dilution (Person 1996a). These considerations suggest that the rate should be lowered by a factor of about 0.65^2 (0.42) from dilution of the organic species and the aluminate. The observed reduction to about 0.55 does not definitely disagree with this expectation. It does suggest that there are compensating effects of dilution, such as the rate constants being increased by the reduction of viscosity. Another possibility is that the dilution dissolves organic species that generate a significant amount of gas, which would imply that the oxalate generation rate is larger than expected, or that an additional species dissolves.

2.6 Effects of Oxygen Reactions on Gas Generation

Results are given in Section 8 for measurements of gas generation in undiluted waste under a reactive cover gas (a mixture of 30% oxygen in helium). The oxygen is rapidly removed from the gas volume when the waste is heated at 70 to 100 °C, being removed much faster than gas is generated in the absence of oxygen. The reaction of the waste with oxygen produces H_2 and NH_3 ; it seems to slow the production of N_2O and to not change production of N_2 .

The O_2 removal is approximately a first-order process. The first-order decay rate decreases with time and increases with temperature. The decay rate was especially fast during the first four fills, suggesting that reactive organic species accumulated while the material was previously heated under an inert cover gas.

The results showed:

- Oxygen is rapidly removed, presumably by reaction with organic species, at a rate much faster than gas generation in the absence of oxygen,
- Reactions removing oxygen lead to production of H_2 and NH_3 . The ratio of H_2 produced to O_2 removed is 0.06 to 0.23; the ratio of NH_3 produced to O_2 removed is 0.03 to 0.09.
- Reactions of oxygen with waste seems to slow production of N_2O , with little effect on N_2 production. The ratio of N_2O produced per O_2 removed is 0.001 to 0.013; the ratio of N_2 produced to O_2 removed is 0.002 to 0.027.

- The O_2 removal is approximately first-order with respect to amount of O_2 . The decay rate decreases with time, going from about 0.6 to 0.2 Day⁻¹ at 70 °C. The decay rate is faster (ca. 0.9 Day⁻¹) at temperatures of 90 to 100 °C; it was even faster during the first four fills at 100 °C.
- The faster decay rate at higher temperatures implies an activation energy around 9 to 17 kcal/mole.
- Oxidation of TOC is balanced by reduction reactions. In the absence of O_2 , the reduction products are primarily gases. The amount of gas produced is shown to be a measure of TOC oxidation.
- The gas yield from oxidation of TOC is about 0.6 to 0.9 moles of gas/mole of TOC. It depends on whether the final product is carbonate or oxalate, and on the gas composition. Tank 101-SY has enough TOC to release gas for 80 to 110 years at current release rates.
- Oxygen reduction reactions significantly increase the rate of reduction reactions, which means the oxidation reactions are also faster.
- Oxygen reactions require O_2 within the waste volume, so mixing is important in a large volume.
- The N_2O/H_2 ratio is low (0.02 to 0.05) when O_2 reactions are important.
- Some O_2 reactions now occur within Tank 101-SY, which lowers the N_2O/H_2 ratio.

3.0 EXPERIMENTAL

3.1 Description of Test Procedure

The experiments discussed in this report observe the rate of gas generation and the composition of the product gas in tests that compare results for undiluted and diluted waste, and for an inert cover gas (He) and a reactive cover gas (30% O_2 in He). The tests also varied the temperature. Table 3-1 shows the approximate temperatures and the length of heat time for each run.

The diluted waste was loaded into the reactors at the start of the tests. The dilution did not dissolve all of the solid material (see Person 1996a for the amount of solids after similar dilutions); undissolved solids were included when the waste was loaded into the reactors. This waste was removed and analyzed (Person 1996a) at the end of the tests of diluted material. The reactors were then cleaned and loaded with undiluted waste. This waste was still in the reactors at the end of the tests described here.

Table 3-1. Gas Generation Test Matrix.

Label	Material	Cover Gas	Temperature, °C	Heat Time, Day
OH65	Diluted	He	65	34
OH100			100, 94, 90, 97	73 Total
Org100	Undiluted	He	100	27
Fill 1			100, 94	22
Fill 2		O ₂ /He	100	3
Fill 3			100	7
Fill 4			100	2
Fill 5			70	2
Fill 6			69	5
Fill 7			90	2
Fill 8			69	4
Fill 9			95	2
Fill 10			70	5
Fill 11			100	2

The flushing of the headspace gas for the diluted waste material included cycling the He cover gas pressure between high values (950 to 1020 Torr) and low values (23 to 29 Torr) three times while measuring the gas volume (with an additional expansion cycle at intermediate pressures for each of the three cycles). Gas samples were collected after each run (each row) shown in Table 3-1. After each run, a new filling of cover gas was introduced by using a similar pressure cycling with two or three flushes of cover gas while measuring the gas volume.

Several of the initial fillings of cover gas were analyzed. These are labelled "Ini" or "In" in Table B-1 in Appendix B. These analyses and the analyses of gas samples collected at the end of each run (row) in Table 3-1 were analyzed at PNNL using the Finnigan MAT-271 (WC38625) quantitative gas mass spectrometer.

3.2 Experimental Observations for Gas Generation Studies

Gas generation is studied by measuring the pressure changes when a slurry of actual waste (undiluted, or diluted by addition of 2.5 M NaOH) is maintained at an elevated temperature in a sealed reaction vessel. The observed variables are the gas pressure and temperature versus time, plus analyses of the gas composition. The gas compositions are especially important for the studies with a reactive cover gas. This is because less gas is produced than O_2 is consumed, so that the gas pressure decreases.

3.3 Gas Generation Apparatus

The tests were performed in two reaction vessels (reactors G1 and G2) constructed from 304 stainless steel ultra-high vacuum components with copper gaskets. Figure 3-1 is a diagram showing the vacuum manifold that is attached to two reactors. The manifold and reactors are installed in a hood in the 222-S Laboratory. The reactors are connected through a filter to (1) a gas sample bulb (valves R and S), (2) two additional pressure gauges (valve P), (3) a vacuum pump (valve V), and (4) a port designed to connect a quadrupole mass analyzer (valve GC). The filter keeps the gas samples free from radioactive particles. This filter (Millipore Wafergard F Mini Inline Gas Filter WGFG 01 HSI) removes 99.999999% of particles larger than $0.003 \mu m$. The two pressure gauges are from MKS Instruments, Inc. The pressure transducers are Type 122 with ranges of 1000 Torr or 10 Torr.

The reactors are designed for leak-free operation, in addition, maintaining the gas pressure above atmospheric pressure reduces air leakage. The

Figure 3-1. Manifold with Pressure Transducers (10 Torr and 1000 Torr), Valve S (Sample, with Sample Bulb), Valve B (To Reactors), Valve V (Vacuum Pump), Valve G (Cover Gas), and Valve GC (Unused).

Figure 3-2. Oven with Reactors G1 and G2, Each With Pressure Transducer and Valve A. Valve I Connects to Valve B in Figure 3-1.

apparatus is designed to withstand pressures up to 10 atm. The two reactors (G1 and G2) are located in an oven. As shown in Figure 3-2, they each have a pressure transducer (Sensotec, Inc. Model Super TJE) and an A valve; valve I connects to valve B in Figure 3-1. The temperature of the oven is controlled to maintain the reactors at the desired control temperature (usually 65 or 100 °C), with the controlled temperature usually maintained within about 1 °C.

3.4 Material Used

Two jars of composite were prepared using material from different segments in order to simulate whole-tank composites (i.e., to make a pseudo whole-tank composite). Due to availability limitations, the composites used only four segments from each of the convective and the nonconvective layers, with the assumption that material from any segment within the layer can be used to represent that layer (and that material collected during Window C and Window E are interchangeable). Composite jar (Comp94A) has the composition shown in Table 3-2. The material from Jar Comp94A (referred to as 94A) was used for the experiments described in this report. The weight ratio of convective to nonconvective material was 1.10 in the composite. This is reasonably close to the ratios found for the tank, ratios of 1.15 for Window C (Herting 1992a) or 1.30 for Window E (Herting 1992b).

3.5 Laboratory Notebooks

Entries are recorded in the WHC controlled laboratory notebooks: WHC-N-1016 1, WHC-N-1124, and WHC-N-310. Entries include data sheets and reports of the mass spectrometric analyses.

Table 3-2. Composition of Tank 101-SY Composite (94A)

Segment	Window	Jar	Convective, Nonconvective	Comp94A Mass, g
4	E	1262	Convective	36.0
9	E	1282	Convective	103.0
10	C	506	Convective	21.1
14R	E	1312	Convective	153.0
Convective Layer Total =				313.1
14b	C	524	Nonconvective	44.6
16	E	1270	Nonconvective	44.1
17	E	1269	Nonconvective	53.1
20R	C	546	Nonconvective	143.5
Nonconvective Layer Total =				285.2
Convective/Nonconvective =				1.10

4.0 GAS GENERATION RATE DATA AND EQUATIONS

This section introduces the results on the rate of gas generation. This includes the general equations showing how the data were analyzed, the measurements of temperature and pressure, the corrections for temperature effects, and tables of the volumes used.

4.1 Equations

The gas generation rate is expressed as the amount of gas produced per volume of waste per unit of time, e.g., mmole/L/day. The amount of gas produced is determined from changes in the pressure (after correcting for temperature effects) by assuming ideal gas behavior.

The measured free volume of the vessel (V) and the change in pressure of gas produced (ΔP) are used to calculate the moles of gas produced (Δn) from the ideal gas equation as

$$\Delta n = \Delta P V / (R T_K), \quad (4-1)$$

where R is the gas constant and T_K is the Kelvin temperature. Here ΔP is calculated from the observed change in permanent gas pressure. The rate of gas generation/release in the time period (Δt) is $\Delta n/\Delta t$. This report normally uses the term "rate" to refer to the rate per unit volume (r_g), which is

$$r_g = (\Delta n/\Delta t)/V_w, \quad (4-2)$$

where $\Delta n/\Delta t$ is the rate of gas release (millimoles per day) and V_w is the waste volume (liters). In this report, the waste volume for the diluted waste refers to the volume after dilution with NaOH.

The discussion in Section 8 uses the rate constant (k), which is the rate per unit volume is divided by the concentration(s) of the reactant(s). For the example of a reaction that is first-order with respect to the concentration of component A (written as $[A]$), k and r_g are related by

$$k = r_g/[A]. \quad (4-3)$$

The reader may wish to compare rates in this report with rates given in different units. Table 4-1 gives the conversion factors for some other units. Different factors are given for some conversions to account for the different densities of the diluted and undiluted waste.

Table 4-1. Conversion Factors for Different Rate Units.

To Convert mmole/L/day to:	Multiply By:
mole/kg/day	0.625 (Undiluted Waste) 0.676 (Diluted Waste)
mmole/moleTOC/day	0.71 (Undiluted Waste) 1.10 (Diluted Waste)
mole/L/s	1.157×10^{-8}
mole/g/s	7.23×10^{-9} (Undiluted Waste) 7.82×10^{-9} (Diluted Waste)

Note that the observations of the gas produced are based on changes in pressure. In this report, the expression "gas release" refers to the process that increases the pressure, i.e., to release from solution. It includes pressure changes that result from bubble growth within the slurry, but it does not include gas dissolved in solution. The terms "produced," "released," and "generated" are not distinguished within this report: they all refer to increases in the amount of permanent gas.

Rates (r_{g1} and r_{g2} , Eq. 4-2) at two temperatures (T_1 and T_2) are used to calculate an empirical energy of activation (E_{act})

$$E_{act} = [RT_1T_2/(T_1 - T_2)] \ln (r_{g1}/r_{g2}). \quad (4-4)$$

The energy of activation (E_{act}) may be used to estimate rates (r_{gn}) at other temperatures (T_n)

$$\ln (r_{gn}) = E_{act}(T_n - T_2)/(RT_nT_2) + \ln (r_{g2}). \quad (4-5)$$

4.2 Results of Temperature and Pressure Measurements

Appendix A has figures that show the pressure increases in the reactors as a function of time. The pressure steps (changes greater than 0.2 psia) are the result of deliberate temperature changes of 2 to 3 °C. The temperature data are shown in Figures A-2, A-4, A-6, and A-8. From these figures it is evident that temperature has a large effect on pressure.

4.3 Determination of Moles of Gas

4.3.1 General Considerations

The ideal gas law is used to relate the moles of gas present to the measured values of the pressure, temperature, and the free volume. If the temperature of each run were controlled so well that all pressure measurements were at a single temperature, the conversion to the number of moles of gas would be a simple application of the ideal gas law. When there are temperature changes, the measured pressure is the sum of the pressure of permanent gas (P_g) and the vapor pressure (P_v). The amount of gas (n) is given by the ideal gas equation as

$$n = (P - P_v) V / (R T_k). \quad (4-6)$$

The largest pressure effect from temperature changes is from the change of the vapor pressure of the waste, which has a nonlinear temperature dependence. The data that were collected for the diluted waste at 65 °C used conditions where the range of temperature changes was small (a few degrees), so that this data set can be corrected for temperature effects by using a linear correction with temperature. However, the linear approximation breaks down for the larger temperature changes that were present for the other runs. These data must account for vapor pressure changes (Section 4.3.3). Section 4.3.2 discusses the determination of the amount of gas using a linear correction for temperature effects.

Both methods of temperature correction work well when the temperature range is small. Temperature steps as large as 5 °C cause some discontinuities when the linear temperature correction is used. There is some offset between the two methods, part of which results from inaccurate estimation of the vapor pressure changes during large (80 °C) temperature changes.

4.3.2 Determinations for Diluted Waste at 65 °C

The amount of gas produced (Δn) at nearly constant temperature (65 °C) are determined from changes in the pressure (ΔP) after correcting for temperature effects, using a linear correction with temperature. The raw data for pressure and temperature for these measurements are presented in Appendix A, Figures A-3 and A-4. The first step in determining the amount of gas produced was to correct the observed pressures for temperature variations. The corrections for small drifts of the temperature from the set point are done by adding a correction. The correction is found by multiplication of the temperature change by the pressure variation factor (f_p). This factor is the average of the pressure change per degree of temperature change. These are measured when the temperature was changed by 1 - 3 °C over short time periods (2 to 12 hours), which are the pressure offsets shown in Figure A-3 in

Appendix A. The average of these changes determines the pressure variation factor (f_p)

$$f_p = \langle (P_2 - P_1) / (T_2 - T_1) \rangle_{av}, \quad (4-7)$$

where the numerator is the pressure change and the denominator is the temperature change. Using the f_p factor, the observed pressure (P) is adjusted to 65 °C from the observed temperature in Celsius (T_c) as

$$P_a = P - (T_c - 65) f_p. \quad (4-8)$$

The amount of gas produced (Δn) is then computed from the change in the adjusted pressure (ΔP_a) as

$$\Delta n = \Delta P_a V / (338.15 R). \quad (4-9)$$

4.3.3 Determinations for Other Tests

For the tests (other than the diluted waste at 65 °C), larger temperature changes require using Eq. 4-6. The vapor pressure was estimated by assuming a constant ratio between the vapor pressure of the waste and the vapor pressure of pure water at the same temperature. This ratio is the activity of the water in the waste material. This report assumes that the water activity is constant for the temperature changes considered. This is an approximation that does not include the activity changes that occur with temperature when salts dissolve or precipitate. The magnitude of such effects is illustrated by the example later in this section.

The vapor pressure must be estimated at each temperature. This was done by varying an assumed value of the water activity, the ratio between the vapor pressure of the waste and the vapor pressure of pure water at the same temperature. This activity was estimated by comparing the observed moles of gas for a range of temperatures with values calculated for the permanent gas and the vapor. The activity was varied to minimize the changes in the amount of permanent gas during any temperature change. The result gave reasonable matches for the range of temperatures using a single value of the activity (i.e., one value for both reactors). However, this correction is approximate, as the vapor pressure includes ammonia, as well as water. Furthermore, Norton and Pederson (1995) show that the vapor pressure of water in simulated waste from Tank 101-SY was better fit with an equation using different coefficients than for pure water. This means the water activity is not precisely constant over a wide temperature range. However, the differences in vapor pressure are reasonably small, so that the activities were determined to an uncertainty of about 0.04 (i.e., a pressure uncertainty equal to 4% of the water vapor pressure). The activity was higher for the diluted waste than for the undiluted waste (0.63 compared with 0.50 for undiluted waste with He cover gas and 0.49 for undiluted waste with the O₂/He cover gas).

The fitting process for the ratio to the water activity involves trial calculations using two activities for time periods where there was a large temperature change. The different activities change the amounts of permanent gas, with the best fit found by interpolation. For example, the comparison of the calculated amounts of permanent gas for the undiluted waste experiment between Day 27.9 and Day 28.8 when the reactors were cooled from 100 °C to 22 °C can be used to estimate the water activity as about 0.49 (reactor G1) or 0.47₅ (G2). A similar comparison for the heating at the start of the experiment gives 0.54 (G1) or 0.50 (G2). The average of these four values is 0.50, which was used for the undiluted waste. The effect of small changes in the activity is to shift all values of moles of permanent gas up or down, which does not change the estimated Δn . Changes in the activity during the experiment will change Δn . During heating or cooling, the temperature and pressure measurements are somewhat out of phase, which produces short-term dips and rises in the amount of gas, and is partially responsible for the noise present on the later figures that show the gas buildup.

The water activity may change if the water content of the waste changes. Sampling the gas removes some water vapor during the time periods (25 sec) when the valve is open, especially for samples at 100 °C. The loss of water will make the waste more concentrated, which will decrease the water activity. Also, some water may be distilled from the waste during heating to cooler parts of the reactor. In the present reactors, this condensate should drain back into the waste (heating the cooler region during the condensation). However, the condensate may not remix rapidly. Thus there could be a layer of diluted waste where condensate is mixing. Such a layer would have an increased water activity.

Because the water activity has not been determined very precisely, the results in this report use the assumptions that the activity is constant, and that it is the same in both reactors. As an example of the error this may produce, the changes indicated above for undiluted waste (0.54 to 0.49 for reactor G1 and from 0.50 to 0.475 for G2) would mean that Δn should be increased by 1.3 (G1) or 0.7 (G2) mmole/L. The relative errors are 5% (G1) and 2% (G2); the shift would account for Δn being 0.6 mmole/L smaller for reactor G1 than in G2.

In summary, using trial water activities gives temperature corrections that minimize changes of the amount of permanent gas (except for some minor effects from the temperature and pressure measurements being out of phase). Furthermore, the use of the same water activity for both reactors only introduces a small uncertainty (about 4% of the water vapor pressure).

4.4 Volume Determinations

Tables 4-2 through 4-4 summarize the volume measurements for the original (undiluted) waste (Table 4-2), the diluted waste (4-3), and original waste

with oxygen in the cover gas (4-4). The free volume of the gas within each reactor was measured more than once, giving the values in the tables. Pressure changes during expansions into and from a calibrated volume were used to measure the free volume for the gas. The calibrated volume was measured at PNNL to be 33.5 ± 0.3 mL. The calibration was done by pressure measurements with an accurate pressure gauge during expansions into this volume from the PNNL standard volume (see WMC controlled laboratory notebook WMC-N-313 1, p. 24). Weighing the calibrated volume while filled with water gave a volume within the limits given by PNNL. The calibrated volume was used to calibrate a secondary standard volume that was also used for volume measurements. More digits are given in Tables 4-2 through 4-4 than are justified by the number of significant figures. These extra digits are quoted to retain internal precision; they should be rounded when quoted separately.

The volumes quoted were measured at ambient temperature. Other measurements at elevated temperature indicate that changes in the waste density will cause errors less than 3% over the temperature range used.

The free volumes used in calculations are shown together with the waste volumes. The initial waste volumes in Tables 4-2 and 4-3 were measured from the mass of material added, using the average density measured for the unheated waste. For the undiluted material, there were 4 density determinations, ranging from 1.59 to 1.66 g/mL. The largest value was unusually large compared with the others; it was discarded as being outside the 95% confidence range of the other 3 readings, which average to 1.60 ± 0.01 g/mL. One sample of this composite waste was also measured by the 222-S Laboratory to have a value of 1.56 ± 0.04 g/mL. These values are considered to agree within the measurement accuracy.

The empty reactor volumes were also measured. For reactors G1 and G2, the sum of the waste volume and the initial free volume averaged 2.9% larger than the average empty volume for original waste and 0.2% smaller for the diluted waste. The differences are within the absolute measurement accuracy; however, they could result from the gaskets being compressed to a greater or lesser degree after the waste was loaded. Note that uncertainties in the density measurements also contribute to differences in the total volume determinations.

Most gas samples were collected at 45 °C or less. At these temperatures the vapor pressure is small, so there was little danger of violent boiling incidents ejecting a significant amount of material from a reactor. One boiling event occurred, producing a change of 2.4 mL in free volume in reactor G1 between the initial filling and the value after heating (Table 4-2). This probably occurred during collection of the final gas sample. The uncertainties in the volumes are relatively small. The same waste that was used for the undiluted waste measurements was also used for the measurements using oxygen in the cover gas. The measured volumes tend to show

Table 4-2. Volumes of Reactors, Waste, and Gas for Studies in Undiluted Waste.

Volumes at Ambient Temperature	Reactor G1	Reactor G2
Empty Volume, mL	56.83	56.34
Volume of Waste, mL (SpG=1.599)	31.47	30.71
Value Used, mL	31.47	30.71
Expected Free Volume (From Empty Volume), mL	25.36	25.63
Measured Free Volume, mL		
Initial Filling	26.71	27.57
After 100 °C Heating	29.11	27.60
Value Used, mL	26.71	27.57

Table 4-3. Volumes of Reactors, Diluted Waste, and Gas for Studies in Diluted Waste.

Volumes at Ambient Temperature	Reactor G1	Reactor G2
Empty Volume, mL	56.83	56.34
Volume of Diluted Waste, mL (SpG=1.48)	29.14	29.21
Expected Free Volume (From Empty Volume), mL	27.69	27.13
Measured Free Volume, mL		
Initial Filling	27.30	27.32
After 65 °C Heating	27.08	27.07
Average Value for 65 °C Heating	27.19	27.19
After 100 °C Heating	27.12	27.11
Average Value for 100 °C Heating	27.10	27.09

Table 4-4. Volumes of Waste and Gas for Studies in Undiluted Waste With O₂/He Cover Gas.

Volumes at Ambient Temperature	Reactor G1	Reactor G2
Waste Volume Used, mL	28.55	30.25
Free Volume, mL		
Start	29.11	27.60
After Fill 1	29.34	27.75
After Fill 12	29.22	27.68
Value Used	29.34	27.75

losses of small amounts of material, presumably by water evaporation during sampling and during the volume measurements that flush the reactor while refilling the cover gas.

5.0 PRODUCT GAS COMPOSITION DATA

The product gas composition measured at each sampling event for each reactor is listed in Table 5-1. The "Reactor" column indicates the reactor used (G1 or G2). The upper portion of the table shows results for the diluted material (labeled with "OH") and the original, undiluted material (labeled "Org"). The lower portion of the table gives results for the O_2/He cover gas. These are labeled with a number (F1, F2, etc.) indicating each time the reactor was filled with a new filling of O_2/He cover gas.

Column 1 in Table 5-1 shows the approximate test temperature (in $^{\circ}C$) at which the reactors were heated before the samples were collected. After the sample label, the next two columns in Table 5-1 gives the percentage of air in the sample and the percentage of product gas (as opposed to cover gas) after subtracting the air and renormalizing. The next six columns contain the percentages of the major species in the product gas: H_2 , N_2O , N_2 , NH_3 , CH_4 , and NO_x . The other nitrogen oxides are referred to as NO_x . They consist of the sum of NO and NO_2 measured in the mass analysis, which would also include any N_2O_3 or N_2O_4 that was present.

All of the results from mass-spectral analysis ignore water vapor. The data in Table 5-1 are calculated from the gas compositions of multiple sample bulbs. Table B-1 in the Appendix B shows the analyses of the individual gas sample bulbs, with renormalized values in Tables B-2 (no air or cover gas) and B-3 (no air).

The values in Table 5-1 for the two reactors are averaged to produce Table 5-2, where the first three rows give the average product gas compositions for the diluted material at the two test temperatures, together with the original, undiluted material at $100^{\circ}C$. The next three rows show average data for the product gas composition for three samples collected during a similar heating period for the undiluted tank 101-SY material in composite 93A (Person 1996b). The final rows give average compositions for the 11 fillings of the cover gas containing oxygen.

- The apparatus was free from air leaks. Repeated fillings of the O_2/He cover gas reduced the air contamination of most samples to $<0.02\%$.

The percentage of air in the sample is shown in column 3 of Table 5-1, as determined from the amount of argon (Ar) present in the sample. The composition of dry air has 0.934% Ar (*A Physicist's Desk Reference*, 2nd Ed., p. 199, 1989). Table 5-1 shows that the percentage of air is small in most samples. Table B-1 in Appendix B gives the percentages of the gaseous species in the sample, including the air.

The percentages of air in the samples were low; there were no examples where there was a definite leak in a sample bulb. A few sample bulbs may have

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Table 5-1. Temperatures, Percentages of Air, Product Gas, and Individual Product Gases. Averages for Reactors G1 and G2.

Temp °C	Reactor	Air %	Product %	Percentage Composition in Product Gas					
				H2	N2O	N2	NH3	CH4	NOx
He Cover Gas									
65	G1,OH	0.25	1.97	21.23	51.79	24.67	0.0	0.95	0.00
	G2,OH	0.26	1.97	23.63	45.01	24.86	2.4	1.07	1.48
100	G1,OH	0.20	80.41	19.19	54.80	20.38	0.8	4.48	0.26
	G2,OH	0.43	75.30	25.23	43.71	23.42	1.1	6.14	0.24
100	G1,Org	0.77	81.29	24.52	39.37	27.92	1.9	5.62	0.36
	G2,Org	0.73	81.27	20.46	45.78	26.45	2.3	4.32	0.52
O2/He Cover Gas									
100	G1,F1	0.10	41.99	40.12	27.35	21.47	5.7	4.81	0.37
	G2,F1	0.08	49.37	34.92	35.88	20.59	4.4	3.57	0.46
99	G1,F2	0.21	20.46	57.06	14.12	9.70	14.0	2.69	2.32
	G2,F2	0.18	21.83	49.74	17.80	10.46	17.2	2.83	1.82
99	G1,F3	0.00	21.22	51.16	18.54	17.93	6.8	4.67	0.78
	G2,F3	0.01	19.29	49.50	24.54	17.36	4.4	3.85	1.32
101	G1,F4	0.00	7.61	60.74	3.67	3.71	28.7	2.95	0.23
	G2,F4	0.01	6.62	68.31	4.06	3.24	21.6	2.60	0.19
69	G1,F5	0.01	2.76	60.19	1.04	2.58	33.5	1.96	0.71
	G2,F5	0.01	3.18	47.70	0.98	2.54	45.5	2.50	0.78
69	G1,F6	0.01	4.35	75.87	1.17	1.87	19.6	1.15	0.32
	G2,F6	0.00	4.31	65.43	1.14	1.52	29.9	1.67	0.32
90	G1,F7	0.01	5.60	72.99	1.69	2.59	20.7	1.57	0.46
	G2,F7	0.01	4.48	71.91	1.20	1.81	23.1	1.71	0.30
69	G1,F8	0.01	3.32	79.35	1.17	2.73	15.7	0.98	0.12
	G2,F8	0.01	3.05	68.17	1.17	2.06	26.3	1.42	0.89
95	G1,F9	0.01	7.80	86.26	2.87	4.36	5.2	1.28	0.04
	G2,F9	0.00	6.90	83.04	2.20	3.26	9.9	1.43	0.13
70	G1,F10	0.01	3.58	66.97	1.81	3.00	26.1	1.50	0.64
	G2,F10	0.01	3.93	73.91	1.77	1.69	20.8	1.21	0.66
100	G1,F11	0.01	9.57	74.52	3.10	4.65	15.2	2.27	0.23
	G2,F11	0.01	9.29	73.51	2.52	4.13	17.4	2.31	0.15

Table 5-2. Temperatures and Individual Product Gases Averaged Over Reactors. Compare With 93A Composite At Two Heating Times.

Temp °C	Sample	Average Percentage Composition in Product Gas					
		H2	N2O	N2	NH3	CH4	NOx
Composite 94A, He Cover Gas							
65	Dilute	22.43	48.40	24.76	1.2	1.01	0.74
100	Dilute	22.21	49.25	21.90	0.9	5.31	0.25
100	Undilute	22.49	42.57	27.18	2.1	4.97	0.44
Compare Composite 93A (Two Heating Times) and Composite 94A							
100	93A,15Day	16.81	33.11	17.89	25.8	3.80	2.46
100	93A,41Day	23.49	25.74	21.56	19.2	8.47	0.74
100	94A,27Day	22.49	42.57	27.18	2.1	4.97	0.44
Composite 94A, O2/He Cover Gas							
100	Fill 1	37.52	31.62	21.03	5.1	4.19	0.42
100	Fill 2	53.40	15.96	10.08	15.6	2.76	2.07
100	Fill 3	50.33	21.54	17.64	5.6	4.26	1.05
100	Fill 4	64.53	3.86	3.48	25.1	2.78	0.21
69	Fill 5	53.95	1.01	2.56	39.5	2.23	0.75
69	Fill 6	70.65	1.16	1.69	24.8	1.41	0.32
90	Fill 7	72.45	1.45	2.20	21.9	1.64	0.38
69	Fill 8	73.76	1.17	2.40	21.0	1.20	0.50
95	Fill 9	84.65	2.53	3.81	7.6	1.36	0.08
70	Fill 10	70.44	1.79	2.34	23.4	1.35	0.65
100	Fill 11	74.02	2.81	4.39	16.3	2.29	0.19

leaked 1% air or so. There were only four bulbs with more than 1% air, and two of these were collected at low pressure, where a larger percentage of air may be present in the background pressure in the manifold.

Table 5-1 shows that many samples have very little air, with 44 samples (of 76 total) having less than 0.02%. This percentage of air is an approximate value

that could be as large as 0.08% air, as the analytical report gives the Ar percentage as a limit of <0.001%. The value of 0.02% was chosen to avoid the negative values calculated for N_2 (after correcting for air) for some samples when the air percentage was larger. The 44 samples include all of the last 41 sample bulbs, which indicates the waste material has become completely degassed by the repeated filling of the O_2/He cover gas. In any case, the lack of air indicates that the method of sample collection, using three helium flushes and the vacuum produced by a mechanical pump, adequately reduces air contamination.

Because of the low levels of air present (some of which may have originated in the sampling), no corrections for air leakage were made to the rates of gas production. Some of the air may have been released from the waste material, especially during the first few days of heating. The uncertainty is greatest for the heating at 65 °C, where the amount of gas released is small. There the observed 0.25 to 0.26% of air represents about 11 to 12% of the gas collected other than helium. Thus, the larger rates of gas release during the first days of heating (given below in Table 7-1) may be too high because of the release of air. This is not a problem for the experiments at 100 °C, where the amount of air collected represents less than 1% of the non-helium gas collected.

- The gas compositions showed that heating with an inert cover gas released more N_2O than H_2 , with similar production in the diluted and undiluted material. There was a small decrease in the N_2/N_2O and in the NH_3/N_2O ratio in the diluted material.

The gas compositions for the samples collected after heating were determined by averaging the sample gas percentages (after correcting for air) in each sample weighted by the moles of gas collected in that sample. The averaged analyses are presented in Tables 5-1 and 5-2, as well as in figures that are discussed individually in Sections 6 and 7.

The averaging of the sample bulbs usually involved two bulbs for each reactor for each filling. This averages data for the samples, although the first sample collected usually has a weight around 75%, as it has more gas. The results of the summation give the composition of the filling at the time of sampling. In some cases, sample bulbs were collected over a period of time (up to 3 days, with the first day at 100 °C), so that a small portion of the gas was generated during the collection time. In most cases, the second bulb was collected within an hour (usually within 30 min). However, the percentage of cover gas was always higher in the initial sample bulb than in later ones. This indicates that some of the product gas collected in later sample bulbs was released into the headspace after the initial sample bulb had been collected. The later sample bulbs thus include gas from bubbles within the slurry and gas coming out of solution.

6.0 GAS GENERATION RESULTS IN UNDILUTED WASTE

This section presents the gas generation measurements of the undiluted waste under an inert cover gas of helium. These tests were performed to confirm tests conducted earlier (Person 1996b), and to provide assurance that the waste being tested was substantially the same as that used previously. Whereas the material used in the present studies was a pseudo whole-tank composite of Tank 101-SY (as explained in Section 3.4), the previous tests used a true whole-tank composite (a portion of every segment from the tank). The earlier tests used a composite prepared in 1993. The portion used in that experiment was from Jar 93A of that composite. Because the results using the present composite were expected to agree well with previous results, only a limited set of measurements were made with the new composite, referred to as 94A. These experiments studied gas generation at 100 °C.

6.1 Amount of Gas Released at 100 °C

Figure 6-1 shows the amount of permanent gas, after subtracting the vapor pressure, using the free volume and the sample volume (Table 4-2) to calculate the millimoles of permanent gas per liter of waste. This gas consists of the He cover gas plus the product gas released. The figure shows the amount of gas present in the initial filling at room temperature. The step at the start of heating may have some contribution from the estimated vapor pressure being too low at the start of the experiment (Section 4.3.3). Also, it may include some rapid release of gas from solution. The time axis approximates the heating time. However, a day or two of heating time was ignored during the degassing steps in the procedure. The raw data for pressure and temperature are presented and discussed in the Appendix A in Figures A-1 and A-2. In Figure 6-1, the amount of gas is seen to increase with time. The figure shows the decreases in the amount of gas when the gas samples were collected on Day 27 (sample bulb numbers 14 and 15 for reactor G1) and on Day 27.9 (bulb 16). Figure 6-1 also shows the continued gas release for the time between these samples at 100°C. At Day 29.9 sample bulbs were collected at room temperature (bulbs 17 and 18 for G1), which reduced the amount of gas to 3.8 (for reactor G1) or 2.8 mmole/L (for G2). This final value was 12.4% of the value before sampling for reactor G1 and 7.4% for G2. Thus, nearly all of the gas was sampled.

The amount of gas per liter of waste agrees modestly well in the two reactors, as reactor G2 released 22% more gas. The difference is similar to differences in gas released in other studies of tank waste (e.g., Person 1996b). It is interesting to note that the faster gas release includes more N_2O . This phenomenon is discussed in the next section.

Figure 6-1. Amount of Permanent Gas in Reactors G1 and G2 (Undiluted Waste).

6.2 Composition of Product Gas Released at 100 °C

The gas analysis shows that the faster gas release in reactor G2 contains more N_2O . Figure 6-2 plots the amount of each gas released in the two reactors. The figure shows the mmole/liter of waste for each of the product gases as two bar charts. The amount of each gas species is computed by multiplication of the total amount of gas times the mole fraction of each product gas.

Note that Table 5-1 indicates that the percentage of product gas is essentially the same in both reactors. It is not understood why the apparently greater gas production in reactor G1 did not dilute the He cover gas more than in reactor G2.

The differences in gas production are within the measurement uncertainty, and the differences are typical of the reproducibility of other measurements using actual tank waste, as noted above. Thus, the short answer is that the experiments are reproducible to within about 22%. However, it is instructive to consider why the production is somewhat different, which is done in the remainder of this section.

Figure 6-2. Amount of Product Gas Released in Reactors G1 and G2 (Undiluted Waste) at 100°C.

Figure 6-2 plots the amount of gas released in a fixed length of time (ca. 28 days), so that the heights of the bars are proportional to the gas release rate (assumed equal to the gas production rate). This figure shows the major difference is the rate of production of N_2O , but there is also increased production of N_2 . The different product gas composition is somewhat surprising, as the easiest explanation of the different amount of gas released is a difference in temperature between the two reactors, but a small temperature difference would not be expected to make so large a difference in the product gas composition.

Temperature differences can account for the difference in the amount of gas released. The measured temperatures averaged 0.8 °C higher in the faster reactor. This would correspond to an increase in rate of 8%, if the activation energy is 23 kcal/mole, one value determined for the 93A composite (Person 1996a). The actual difference in temperatures may be larger than the difference of the measured temperatures, as the temperature is measured close to the flange, rather than inside the waste. Thus, the temperature of the waste may differ from the values plotted in Figure A-2 by 2 °C, a difference large enough to account for a 20% difference in the rate of gas generation.

A similar difference in the amount of gas released is also present for the diluted waste (Section 7). In that case, reactor G1 is faster, so the

difference is not specific to the different reactors. Furthermore the gas analysis shows that the faster release contains more N_2O in both cases, with the difference in gas release primarily accounted for by the difference in the amount of N_2O (a smaller amount of N_2 also released). If the different amount of gas were the result of a small temperature difference, the product gas composition would be expected to be nearly the same. For example, even if the activation energy for production of N_2O were as much as 15 kcal/mole higher than for H_2 (i.e., even larger than the 6 kcal/mole difference reported for Tank 103-SY waste by Bryan 1996), a 2 °C temperature difference would give about 11% more N_2O than H_2 , rather than the large difference shown. Therefore, the enhanced N_2O production suggests some other mechanism is important.

Some of the difference in the release of N_2O is likely to be gas coming out of solution, but the difference of 5 mmole/L more N_2O probably is larger than can be explained by the solubility (unless the solution was supersaturated, or the waste was not equilibrated with the N_2O pressure). Both reactors were repeatedly (6 times or more) flushed with He during volume measurements prior to the heating. It would be surprising for the difference to be so large, even though the solubility has not been measured in this waste.

The solubility of N_2O in a diluted simulated waste for tank 101-SY (SY1-SIM-93B, with no solids present) was measured to be 0.0212 mole of gas per kg of water (in the simulant) per atmosphere of N_2O at 29.8 °C (Norton and Pederson 1995). This corresponds to 16.7 mmole per liter of the simulant. However, the solubility will be less in the waste, because the ionic strength is higher. Norton and Pederson (1995) give two limits estimated for the solubility in actual waste from Tank 101-SY. The lower estimate is 0.583 at 20 °C (0.438 at 30 °C), decreasing to 0.232 mmole/kg water/atm at 60°C. The higher estimate is 8.66 at 30 °C, decreasing to 1.16 mmole/kg water/atm at 60°C. Taking 36.6 as the Wt% H_2O (Herting 1992b) and 1.60 as the specific gravity (SpG) converts the two estimates of N_2O solubility at 30 °C to 0.249 and 4.92 mmole/L/atm. Thus, the larger solubility value for N_2O could explain the difference, if the N_2O partial pressure were about 1 atm. This seems higher than the pressures during storage, or during the current experiments. During storage, the total pressure of gas within the slurry should be around 1 atm, and only part of this gas is N_2O .

If gas is in solution after equilibration at a higher pressure of N_2O , how long will it take to equilibrate with the lower pressure? Reactor G2 has a faster rate of gas release for 20 days or more (see Figure 6-3 below), which is a long time for gas to come out of solution (see the gas diffusion estimate in Section 8.5). However, the largest differences in rate occur during the first 4 days or so, a time scale more compatible with gas coming out of solution. The integrated difference in rate during the first 4 days is about 2 mmole/L. Thus gas coming out of solution seems to be a more reasonable explanation of the initial release of about 2 mmole/L, than for the 5 mmole/L difference. Even the smaller value implies a large solubility of N_2O and a reasonably large internal pressure of N_2O .

Another mechanism that may produce different rates is if the solution concentrations differ, as a result of variable losses of water. The estimated water activity (discussed in Section 4.3.3) has a lower value for reactor G2. This suggests that reactor G2 has increased solution concentrations, as the vapor pressure decreases in more concentrated solutions. For example, see the vapor pressures in simulated 101-SY wastes of different concentrations (Norton and Pederson 1995). In addition, the discussion in Section 4.3.3 indicates a difference in vapor pressure may account for 0.6 mmole/L more gas in reactor G2. However, small increases in concentration would be expected to only make small changes in the product gas distribution, which argues against this mechanism being the major one.

A fourth possibility is that the difference in the N_2O release may result from sampling differences during loading of waste into the reactors. Some differences may occur, even though the slurry was mixed before loading. A significant difference in the amount of some reactive species could explain a difference in the N_2O (and N_2) production until this species is consumed. The difficulty with this explanation is that the concentrations of soluble species should not be significantly different in a stirred slurry, and an insoluble species would be unlikely to react quickly.

However, there could have been different amounts of solid material containing gas bubbles. The N_2O may have been in bubbles trapped within solids, the "spongy" material noted in the microscopic examination of material from tank 101-SY (Herting 1992a). For example, the waste could contain, say 10% gas (by volume, at room temperature), which would correspond to about 4 mmole/L. Thus, these bubbles would have to be primarily N_2O for this to explain the difference. However, the gas could have a large percentage of N_2O , as the bubbles may have been generated over past few years. The formation at low (room) temperature would favor generation by radiolysis, and studies in simulated Tank 101-SY waste find larger G values for N_2O production than for H_2 production for several organic species (Meisel 1993).

In conclusion, some of the extra N_2O may have come from bubbles encased in solid material, some from dissolved N_2O , some from the different temperatures, some from differences in solution concentrations, and some from other slurry sampling differences, but the details are unknown. In any case, the difference is only 22%.

6.3 Rate at 100 °C

The rate of gas release at any time is the slope of the curve at that time on plots such as Figure 6-1. The curvature shown in Figure 6-1 means that the rate is time dependent. Figure 6-3 shows the rate calculated from the change in the amount of gas produced (Δn) over an approximately 4-day period, plotted at the center of the period. Points were not used in the rate calculation when the temperature changed by >1 °C between the point i and the $i-2$ point, a

criterion that screens out most of the data where the reactor is not at temperature equilibrium. The data shown were smoothed by taking a 5-point moving average, plotted at the middle point. The time interval between points was usually 4 hours, but some intervals were 1 hour.

The rates at the end of the period shown in Figure 6-3 are 0.75 (G1) and 0.81 (G2) mmole/L/Day. These values can be compared with results for the 93A composite, which were 0.68 (Days 20 to 70 of Test 2) or 0.56 (Days 19 to 124 of Test 4) mmole/L/Day (Person 1996b). The somewhat larger values in the new, 94A composite could be the result of differences between the reactive species present in the two composites, or it could mean that the rate is still decreasing as the 94A composite is heated. Because the rate was essentially constant during tests that lasted longer using composite 93A, the decrease in rate shown in Figure 6-3 probably does not result from a decrease in concentration of the major organic species. The decreased rate likely results from a decrease in a small concentration of reactive species and/or from N_2O coming out of "spongy" material (with some coming out of solution), as discussed in Section 6.2.

Figure 6-3. Rate of Gas Release in Reactors G1 and G2 (Undiluted Waste).

7.0 GAS GENERATION IN DILUTED WASTE

This section presents the measurements of gas generation in diluted waste under an inert cover gas of helium. These measurements were performed before those in Section 6. The results are compared with data for the original waste, and with earlier data for a different whole-tank composite, composite 93A (Person 1996b).

7.1 Rate at 65 °C

Figure 7-1 shows the result of using the free volume and the waste volume in Table 4-3 to convert the adjusted pressure data taken at 65 °C into the amount of gas released, which is plotted as millimoles of gas released per liter of diluted waste. In this case, the ordinate zero is somewhat arbitrary. The method used to set the zero was to use a linear fit of the early data, with the fitted intercept giving the zero. The time period used for the fitting was Days 1 through 5.

Figure 7-1. Gas Generated Per Liter of Diluted Waste at 65 °C in Reactors G1 and G2.

The rate of gas release were determined from several linear fits. Table 7-1 summarizes the fitting results. The rates are seen to decrease with time during the first several days. After Day 15, the rates are more constant, with values of 0.0178 ± 0.0002 (reactor G1) and 0.0169 ± 0.0002 mmole/L/day (G2) for Days 15 through 34.3. These values are lower than the initial values. The fits for Days 0.5 to 7 give rates of 0.0440 ± 0.0011 (G1) and 0.0418 ± 0.0010 mmole/L/day (G2), with the fits for the full period (Days 0 to 34.3) giving rates of 0.0209 ± 0.0002 (G1) and 0.0199 ± 0.0002 (G2). The slightly more rapid release in reactor G1 is the result of the slightly higher temperatures in this reactor, as the values corrected to 65 °C agree within 0.0001 mmole/L/day. Reactor G1 does have a greater percentage of N₂O in the product gas. However, this release does not seem to increase the rate, in contrast to the behavior at 100 °C (Section 7.2).

The lower portion of the table shows the longer-term fits, with the fit after Day 15 probably the most representative of gas release at 65 °C. The average rates have been corrected to 65 °C, using Eq. (4-5) and the activation energy of 23.9 kcal/mole, as given in Section 7.3.

Table 7-1. Rate of Gas Release from Diluted Waste at 65°C in Reactors G1 and G2.

Start Day	End Day	Average T, °C		Gas Release Rate, mmole/L/Day		R ²	
		G1	G2	G1	G2	G1	G2
0.5	7	65.02	64.59	0.0440 ± 0.0011	0.0418 ± 0.0010	0.98	0.98
7	15	65.44	65.03	0.0259 ± 0.0008	0.0219 ± 0.0007	0.92	0.97
15	24	65.81	65.33	0.0190 ± 0.0005	0.0183 ± 0.0006	0.97	0.94
24	34.3	66.27	65.79	0.0174 ± 0.0007	0.0172 ± 0.0004	0.89	0.96
0	34.3	65.71	65.26	0.0209 ± 0.0002	0.0199 ± 0.0002	0.97	0.96
0	34.3	Average (Corrected to 65 °C) = 0.0194 ± 0.0001					
15	34.3	66.09	65.62	0.0178 ± 0.0002	0.0169 ± 0.0002	0.97	0.98
15	34.3	Average (Corrected to 65 °C) = 0.0159 ± 0.0001					

7.2 Rate at 100 °C

Figure 7-2 shows gas production in the two reactors at 100°C. In this case the ordinate zero was determined from the initial gas pressure and the estimated value of the vapor pressure. The sampling of the gas is shown, which removed 96.6% of the gas from reactor G1 and 95.9% from G2. The apparent decrease in rate after Day 42 is primarily the result of the lower temperatures at later times.

Table 7-2 shows the results of several linear fits, whose slopes measure rates of gas release. The fits are for time periods where the temperature was reasonably constant, with the period from Day 1.3 to Day 33.6 divided into four, shorter periods. The lower portion of the table gives the rates fit for the longer periods of Days 0 to 33.6 and Days 15 to 33.6; the rate of gas release was nearly constant during the latter period. The rates of gas release are rather well determined from a statistical point of view (except for the shortest time period at Day 35), as shown by the small uncertainties in the rates (the estimated standard deviations given in Table 7-2) and by R^2 values that are reasonably close to unity.

The final row of the shorter-term fits in Table 7-2 shows the rate of gas release when the reactors were heated at low pressure for Days 69.3 to 72.8. This occurred after the reactors were at ambient temperature and reduced pressure for a week following gas sampling. These rates are reasonably consistent with earlier fits. However, there may be some additional release of gas generated earlier, as the rates are somewhat higher than the fit for Day 15 - 33.6 (11% for reactor G2, 18% for G1), when corrected for the lower temperature by using the activation energy given in Section 7.3. This activation energy was also used to correct the rates to 100 °C for the longer-term fits shown in the lower portion of Table 7-2.

Figure 7-3 shows the gas release rates determined from the slopes of linear fits (the data in Table 7-2). Note that the rate decreases during the first 10 days or so, with the decrease greater for the waste in reactor G1. The later values show relatively little variation, except for the three values at Days 35, 45, and 55. These periods have lower temperatures (around 95, 95, and 90 °C). Thus these rates are expected to be lower. There is some scatter in the magnitude of these rate changes, compared with values expected from the E_{act} value, as discussed in Section 7.3.

The percentage of product gas (compared to product gas plus He) is measured to be 80.4% for reactor G1 and 75.3% for G2 (Table 5-1). This is in excellent agreement with the percentages calculated using the starting and ending amounts of permanent gas (Figure 7-2), which are 80.9% for G1 and 75.9% for G2.

Figure 7-2. Amount of Permanent Gas in Reactors G1 and G2 (Diluted Waste).

It is interesting that the rate is larger in reactor G1 than in reactor G2 at 100 °C, even though the rates in the two reactors are nearly the same at 65 °C (essentially identical when corrected for the higher temperature in reactor G1). Figure 7-4 shows the rate of production of the different product gases. The production of NO_x is not shown, as it is small (0.12 mmole/L or less). The bars show the production of H_2 , N_2O , N_2 , NH_3 , and CH_4 (from left to right). The increased production is seen to be primarily N_2O , as the differences (production in reactor G1 minus that in G2, in mmole/L) are 0.2 H_2 , 6.1 N_2O , and 0.9 N_2 .

Possible causes of these differences are discussed in Section 6.2. Note that the faster reactor for the filling of undiluted material is the slower reactor for the filling of undiluted material. This indicates that the difference is not caused by something associated with a specific reactor (e.g., pressure transducer). As for the undiluted material, some of the difference may result from N_2O coming out of solution at the higher temperature. Another contribution to the difference could be the increased solubility of the precipitates at the higher temperature causing "spongy" crystals to dissolve, releasing trapped bubbles that could be high in N_2O . In addition, the waste in reactor G1 may have a greater concentration of some species that reacts at a faster rate at the elevated temperature, producing a greater fraction of N_2O .

Table 7-2. Rate of Gas Release from Diluted Waste at Higher Temperatures in Reactors G1 and G2.

Start Day	End Day	Average T, °C		Release Rate, mmole/L/Day		R ²	
		G1	G2	G1	G2	G1	G2
1.3	7	101.00	101.34	0.723 ± 0.013	0.479 ± 0.005	0.982	0.995
7	15	99.59	100.05	0.501 ± 0.004	0.400 ± 0.003	0.996	0.996
15	24	99.66	99.99	0.480 ± 0.004	0.395 ± 0.003	0.996	0.997
24	33.6	99.62	99.98	0.488 ± 0.006	0.389 ± 0.003	0.986	0.994
34.1	35.7	94.83	95.28	0.284 ± 0.022	0.212 ± 0.015	0.932	0.941
36.2	41.8	99.44	99.78	0.483 ± 0.013	0.367 ± 0.007	0.974	0.986
42.4	48.8	94.35	94.83	0.331 ± 0.009	0.255 ± 0.007	0.967	0.966
49.3	60.8	90.36	91.02	0.204 ± 0.001	0.139 ± 0.001	0.995	0.989
69.3	72.8	97.14	97.76	0.463 ± 0.009 Low-Pressure	0.362 ± 0.014 Low-Pressure	0.991	0.969
0	33.6	99.79	100.11	0.514 ± 0.002	0.406 ± 0.001	0.994	0.999
0	33.6	Average (Corrected to 100°C) = 0.460 ± 0.076					
15	33.6	99.64	99.99	0.488 ± 0.002	0.394 ± 0.001	0.998	0.999
15	33.6	Average (Corrected to 100°C) = 0.450 ± 0.077					

7.3 Empirical Activation Energy

The rates at the two temperatures (T_1 and T_2) can be used to calculate the empirical energy of activation (E_{act}) from the Arrhenius equation (Eq. 4-4). Figure 7-5 shows a plot of $\ln(r_g)$ versus the reciprocal of the Kelvin Temperature. Two lines are plotted, whose negative slopes give values for E_{act}/R . The lines shown are fits for the two reactors, using the average rates for days 15 to 34 at the two temperatures. The values for E_{act} are 24.8 (reactor G1) and 23.0 (G2) kcal/mole, which average to 23.9 kcal/mole (99.8 kJ/mole). The figure includes rates at the start of the new temperature settings, plotted with "+" and "x" symbols. These show that the rates decrease at later times in the group of points for 65 °C ($1/T = 0.00296$); the

Figure 7-3. Rate of Gas Release in Reactors G1 and G2 (Diluted Waste) at Temperatures of 90 to 101°C.

Figure 7-4. Amount of Product Gases Released in Reactors G1 and G2 (Diluted Waste) at Temperatures of 90 to 101°C.

Figure 7-5. Arrhenius Plot For Activation Energy in Reactors G1 and G2, Showing Initial Rates at Temperature.

first rate determination at 100 °C is also a little larger. The changes in rate cause the E_{act} determination to depend on which rates are used. If the changes with time were primarily the result of decay of a reactant, then the appropriate time periods would be the initial periods at each temperature. However, the initial periods may not be typical of longer term behavior. Also, the initial rate at 100 °C was determined for material that had been previously heated at 65 °C. Thus, the lines shown on Figure 7-5, using the rates determined at later times when the rates are nearly constant, are believed to be the most representative. Lines could also be drawn between the first (largest rate) point at 65 °C and the initial point at 100 °C. These give E_{act} values of 19.5 (G1) and 16.7 (G2) kcal/mole, averaging to 18.1 kcal/mole (75.7 kJ/mole).

The different values for E_{act} from different time periods illustrate the uncertainty in the E_{act} value. The values from the fits of the entire period from Day 0 to about 34 gives 23.6 (G1) and 21.7 kcal/mole (G2), for an average of 22.7 kcal/mole. The decrease in rate at the three lower temperatures (90 to 95 °C) in Table 7-2 can also be used to estimate E_{act} values. As shown in Figure 7-5, four of these six points ($1/T$ values from 0.00271 to 0.00275) are reasonable fits to the lines shown, so that these points match the E_{act} values in the two reactors. The scatter of these points reflects the small temperature steps (around 5 °C) and the times being fairly short. When these

small temperature steps (Table 7-2) are used to estimate E_{act} values by comparing the rates before and after the steps, the results give the four values of 31, 31, 20, and 32 (average = 29 ± 6) kcal/mole for reactor G1, and 35, 33, 20, and 42 (average = 33 ± 9) kcal/mole for reactor G2. When the rates at the lower temperatures are compared with the average rate for Days 15-34, the results give activation energies of 31, 20, and 25 kcal/mole for reactor G1 (average = 25 ± 4) kcal/mole). For reactor G2, these values are 36, 23, and 31 (average = 30 ± 5) kcal/mole. Thus the average values are approximately within their uncertainty range with the value from the rates at 65 and 100 °C (23.9 kcal/mole). The large scatter for the determinations from the three small steps suggests that longer time periods may be required to reduce the effects of aberrations in the rate that occur after the temperature is changed (an effect similar to the larger rates found during the first several days at 100 °C).

The gas compositions at the two temperatures (Table 5-1) can be used with the rate of gas release to give rough estimates of the activation energies for the different gaseous species. This is an approximate determination, because the different temperatures were used during the 61 days of heating at higher temperatures. The rates of production of the individual gaseous species are shown in Table 7-3, as calculated using total production rates for Days 0 to 34. These rates were used to estimate the E_{act} values shown in the lower rows of the table. The average values for H_2 , N_2O , N_2 , and CH_4 are 23, 23, 21, and 34 kcal/mole (94, 95, 91, and 145 kJ/mole), respectively. These values are essentially the same as the value for the sum of all species for this time period (22.6 kcal/mole, 94.6 kJ/mole), except for the higher value for methane.

Table 7-3. Rate of Gas Release (Days 0 to 34) and Activation Energies for Gaseous Species from Diluted Waste in Reactors G1 and G2.

Reactor	Temp	H2	N2O	N2	NH3	CH4	Total
Rate of Release (mmole/L/day)							
G1	65.71	0.0044	0.0108	0.0052		0.0002	0.0209
G1	99.79	0.099	0.282	0.105	0.004	0.023	0.514
G2	65.26	0.0047	0.0090	0.0049	0.0005	0.0002	0.0199
G2	100.11	0.102	0.177	0.095	0.004	0.025	0.406
E_{act} (kcal/mole)							
G1		23	24	22		35	23.5
G2		22	22	21	16	34	21.7
Ave		23	23	22		35	22.6

Workers at PNNL (Bryan 1996) have measured E_{act} for liquid material from the convective layer of Tank 241-SY-103 (Tank 103-SY), which has similar waste to Tank 101-SY. They found similar values for E_{act} values fitted to rates simultaneously measured for the initial heating at five temperatures from 60 to 120 °C. Their value for total gas production was 94 ± 6 kJ/mole. They found larger differences between the E_{act} values for H_2 (90 ± 9), N_2O (116 ± 9), and N_2 (80 ± 8 kJ/mole). Their uncertainties are 95% confidence intervals. The present uncertainties are even larger, so the values for the two tanks agree within the uncertainty intervals. As discussed in Sections 7.4 and 7.5, there are dilution effects on the relative amounts of N_2 , so that it would be better to compare results for undiluted Tank 101-SY liquid with the Tank 103-SY results.

It is interesting that the present values are close to the value of 24.5 kcal/mole reported by Delegard (1980) for synthetic waste containing EDTA (0.17 M) and HEDTA (0.35 M), even though HEDTA (which is responsible for producing most of the gas in that mixture) represents only a small fraction of the organic species currently in Tank 101-SY waste (Campbell 1995). The present value is somewhat higher than the value of 20.3 kcal/mole reported (Meisel 1993) for E_{act} for H_2 production by reactions of formaldehyde in simulated waste solutions; it is larger than their value of 9.8 kcal/mole for glyoxylate reactions. It is also comparable to values of 17 kcal/mole for H_2 production by reaction of HEDTA, and 30 kcal/mole by reaction of glycolate (which has 26 kcal/mole for N_2O production) in dilute simulated waste (Ashby 1994).

In conclusion, the best value for E_{act} is believed to be the value calculated for the constant rates reached after the initial heating. This value is 24 kcal/mole (96 kJ/mole). The initial rates at each temperature give an average value of 18 kcal/mole, and the range of average values for different time periods and smaller temperature steps goes from 18 to 31 kcal/mole. The selected value is similar to the values of 23 and 19 - 22 kcal/mole found earlier for these two temperatures for undiluted waste in the 93A whole-tank composite (Person 1996b), as well as the value of 22 kcal/mole found when temperatures up to 124 °C were included (Person 1996b). The present values are in good agreement with the value reported for total gas production (94 kJ/mole) in Tank 103-SY (Bryan 1996). Estimates of E_{act} for H_2 , N_2O , and N_2 indicate that all three values are all reasonably close to the value for total gas production, with a higher value (35 kcal/mole) for methane.

7.4 Gas Composition

Figure 7-6 shows a graphical comparison of the product gas compositions measured for the diluted material at 65 and 100 °C, compared with the distribution for undiluted material at 100 °C. As noted in Section 7.3, similar temperature effects were found for most of the gaseous species. Also, there is a general agreement between the data for diluted material and the

undiluted material at 100 °C. The figure shows the differences in N_2O production between the two reactors. It also shows that CH_4 is a more important product gas at 100 than at 65 °C (reflecting the larger value of E_{act} shown in Table 7-3), a result which has also been found for the undiluted waste in composite 93A (Person 1996b). There is more nitrogen relative to N_2O in the undiluted waste, which is discussed further in Section 7.5.

The results for ammonia are tentative, as ammonia is not measured quantitatively in the present apparatus. However, Table 5-2 indicates that the present 94A composite produces less ammonia than the 93A composite did. This may be the result of not using material from all core segments in forming the 94A composite; it is likely that the waste material loses ammonia as time progresses, so that there may have been less ammonia present when the 94A composite was formed. Ammonia is removed by surface absorption on the walls of stainless steel reactors, so it is likely that a larger percentage of the ammonia has been removed from the small amount of gas collected at 65 °C. However, the smaller amount of ammonia observed for the diluted material may result from changes in physico-chemical properties, e.g., the reduced viscosity may reduce reactions within the solvent cage, as discussed in Section 7.5. Also, the relatively large percentage of NO_x shown for the small amounts of gas produced at 65 °C are suspect. The experimental determination of NO_x is not much more quantitative than the ammonia. In any case, NO_x is not an important product.

7.5 Comparison of Gas Generation in Diluted and Undiluted Waste

The present gas generation rates can be compared to the values measured for the undiluted waste (Section 6), and with our earlier measurements using a similar composite of undiluted material from Tank 101-SY. The second comparison is somewhat indirect as the earlier composite (93A) used material from a different composite and an older (larger) reactor. The earlier (93A) composite was a whole-tank composite, as there was material from all segments available when that composite was made. Furthermore, the waste is a complex mixture of many solid and liquid species, so that the simple analysis given in this section is incomplete.

Earlier workers have found that gas generation in synthetic Tank 101-SY waste had approximately linear dependencies on the solution concentrations of (1) the active organic species, (2) the aluminate ion, and (3) the nitrite ion; the rate also depended on the hydroxide ion concentration (Ashby 1994, Bryan and Pederson 1994, and Delegard 1980). The diluted waste has not dissolved all solids (Person 1996a), so some species remain saturated. These species will have quite similar solution concentrations in the undiluted and the diluted waste. Most of the solid species after dilution have little effect on the rate of gas generation, e.g., carbonate and oxalate salts. However, the

Figure 7-6. Product Gas Composition in Diluted Waste at 65 and 100 °C, and in Undiluted Waste at 100 °C. (Diluted waste labeled OH; original labeled Org.)

species that were saturated in the undiluted waste will have their solution concentrations decrease by a smaller amount than for species that are unsaturated.

Nitrite is saturated, with the average of four samples finding 13% (by weight) present as solids (Person 1996a). A small amount of aluminate may be present in the solids of the undiluted material, as 14% of Al (by weight) as solids was reported (Herting, 1994, quoted in Person 1996a), although Al is not expected to be saturated according to earlier solubility studies (Reynolds and Herting 1984, Barney 1976). Furthermore, analyses of composites 94A estimated that none was present in one sample and 10 Wgt% in another; an average of NaAlO₂ in four samples was estimated as -1 ± 12 Wgt% (Person 1996a). In any case, dilution studies indicate that neither nitrite nor aluminate has enough solid material to accommodate dissolving an additional 54% (by volume) to maintain a constant concentration after the dilution (Person 1996a). Thus the 54% dilution will reduce the solution concentrations of both nitrite and Al. The concentration of hydroxide ion is approximately the same before and after dilution, as its concentration in undiluted waste is close to that of the 2.5 M NaOH diluent. The similarity can be seen from the following. Analyses of filtrates of composite 94A found that the undiluted material had OH⁻ = 1.96 M, with the 54% dilutions having 1.94 (for 2 M NaOH diluent) and 2.36 M

(for 3 M NaOH) (Person 1996a). These diluted values lead to an estimate of 2.15 M after 54% dilution with 2.5 M NaOH, which indicates an increase of only 0.2 M from the undiluted value of composite 94A. Furthermore, the diluted estimate indicates a decrease of about 0.1 M from the earlier analysis of composite 93A, where $\text{OH}^- = 2.26 \text{ M}$ (Person 1996b).

The organic species are expected to be diluted, with the notable exception of oxalate. Oxalate has been found to have a low rate of gas generation in the synthetic waste (Ashby 1994, Bryan and Pederson 1994, and Person 1993). The combination of the very low solubility and rather low rate of gas generation is expected to make the contribution from oxalate negligible in Tank 101-SY. The dilution is 54% by volume, meaning that 35 parts of NaOH were added to 65 parts of waste. Thus the dilution will reduce the concentration of an unsaturated species to a value around 0.65 of the value in undiluted waste. Thus, if the rate constants for the rate-limiting reaction(s) remain the same, the simulated waste studies predict that dilution should lower the rate by a factor of about 0.65 simply from the dilution of the concentration of organic species. If the nitrite and the aluminate were also diluted by the same factor, then the rate would be expected to decrease to $0.65^3 (= 0.27)$ of the undiluted value. As noted above, the concentrations of both species will not decrease this much, as solids are present for the nitrite (and possibly the aluminate). Furthermore, Delegard (1980) found the rate to have a complicated dependence on nitrite ion concentration at higher concentrations, with only a minor increase for concentrations greater than 0.5 M. As the diluted concentration is greater than 0.5 M, only a small change is expected in the rate as a result of the dilution of nitrite ion. Thus the studies with synthetic waste predict that the dilution will lower the rate by a factor around $0.65^2 (= 0.42)$ of the undiluted value (that is, full dilution of the TOC and nearly full dilution of the aluminate, with only a small effect from the nitrite). The prediction depends on exactly how much aluminate is initially in the solids, the exact dependence on nitrite ion, and the change in hydroxide ion activity.

If rate constants for the rate-limiting reactions are limited by viscosity effects, then dilution would increase these rate constants, as dilution will decrease the viscosity. In this case, the decrease in gas generation rate (which is the product of the reaction rate constant times the product of the reactant concentrations) from the decrease in the reactant concentrations would be partially compensated by an increase in the reaction rate constant. Also, viscosity effects have been postulated to promote reactions between the glycolate decomposition products of NO^- and H_2CO within a solvent cage. These reactions produce products other than N_2O , including N_2 and NH_3 (Ashby 1994, Barefield 1995, Barefield 1996). Thus, dilution would be expected to produce lower ratios of $\text{N}_2/\text{N}_2\text{O}$ and $\text{NH}_3/\text{N}_2\text{O}$, if other factors are not changed significantly.

The present results at 65 °C can be compared with tests using the earlier composite (93A) (Person 1996b). When comparing all 34 days of data, the diluted and the undiluted waste generated 0.0194 and 0.0370 mmole/l/day,

respectively. Thus, dilution reduced the rate to 52% of the undiluted value. Comparing the slower rates found after the first 15 days in the present tests with the average rate found after Day 12 for one of the earlier tests shows rates of 0.0159 and 0.0286 mmole/L/day for the diluted and the undiluted waste, respectively. This comparison has dilution reducing the rate to 56% of the original.

The test at 100 °C may be compared directly with tests with undiluted waste using the same composite, as well as with measurements with the 93A composite. One difficulty in this comparison is the observation (Section 6) that the rate decreases for a longer period of time in the undiluted waste. Thus the rate observed for the undiluted waste may still be decreasing, so that it is high in comparison to the average for Days 15 to 34 for the undiluted waste. Comparing 0.78 (for the undiluted waste in composite 94A) with 0.45 mmole/L/Day in the diluted waste indicates that dilution reduced the rate to 58% of the undiluted value.

The comparisons at both temperatures indicate that the addition of NaOH has reduced the gas generation rate by a more than the amount expected for the reduction of the solution concentration for one reagent, but smaller than the expected reduction from the combined effects on three rate-determining reagents.

As noted in Section 7.3, the activation energy in approximately the same in diluted as in undiluted waste. This is expected result when the dilution does not change the nature of the rate-limiting reaction(s).

Some decrease is observed in the N_2/N_2O ratio upon dilution (0.65 ± 0.09 for undiluted, 0.44 ± 0.12 for diluted), although it is not definitely outside the experimental scatter. There is also a smaller NH_3/N_2O ratio (0.05 for undiluted, 0.02 for diluted). Both decreases may result from the reduced viscosity after dilution. The decreased viscosity is expected to decrease the reaction of the decomposition products of glycolate (the reactive species are NO^- and H_2CO) within a solvent cage. As discussed by the GIT group (Ashby 1994, Barefield 1995), the product is the formohydroxamate ion, which decomposes to formate ion and hydroxylamine (NH_2OH). The disproportionation of NH_2OH then leads to production of N_2 and NH_3 . Thus the somewhat smaller N_2/N_2O ratio and the smaller NH_3/N_2O ratio are both consistent with effects expected from the reduced viscosity after dilution.

In summary, dilution lowers the rate of gas generation by an amount consistent with (but smaller than) the expectations from studies in simulated waste. The decreased rate is 0.52 to 0.58 of the undiluted rate, which is smaller than the 0.65 that results from the decrease in the concentration of soluble organic species, but larger than would be expected if the rate were also first-order with respect to both nitrite and aluminate (and there were no rate effects from decreased viscosity). Furthermore, dilution has little effect on the activation energy. The product gas composition for the diluted material shows lower N_2/N_2O and NH_3/N_2O ratios, which is consistent with expectations

that the decreased viscosity allows more of the reaction products of glycolate decomposition to escape from the solvent cage.

8.0 GAS GENERATION IN UNDILUTED WASTE WITH O₂/HE COVER GAS

Earlier workers (e.g., Meisel 1993, Ashby 1994) have found that synthetic waste reacts with oxygen (O₂). Results presented in this section show that tank waste also reacts with oxygen. Because of these reactions, the oxygen concentration will be small within the tank. However, the surface of the tank has waste exposed to O₂. Operation of the mixing pump may expose a larger fraction of the waste to oxygen. The results presented here show that the presence of oxygen increases the rate of gas production. Furthermore, hydrogen is a larger fraction of the gas generated in the presence of oxygen. Consequently, understanding gas generation within the tank requires understanding the effects of oxygen.

This section presents measurements of gas generation in undiluted waste under a reactive cover gas consisting of a mixture of 30% (approximately) oxygen in helium. Additional experiments are still in progress. The experiments all used the same filling of waste material, material that had been heated previously under inert cover gas for the test reported in Section 6. In the results presented here, oxygen is seen to react quickly, with enhanced production of H₂ and ammonia. Results are presented on the kinetics of the reaction, and on the product gas distribution.

The results are given for reaction at temperatures from 69 to 101° C. The oxygen removal is much faster than gas is generated in the absence of oxygen. The heating of the waste material under He cover gas prior to these tests may have increased the concentration of species that react rapidly with oxygen, as the rate of oxygen removal decreased during repeated fills of O₂/He cover gas. Even after 11 fills, the O₂ removal rate remained faster than normal gas generation.

8.1 Evidence of O₂ Removal

- Oxygen is rapidly removed, probably by reaction with organic species, at a rate much faster than gas generation in the absence of oxygen.

When the first filling of the oxygen/helium cover gas (about 30% O₂) was heated, the oxygen reacted so rapidly that it was essentially gone by the time the temperature had stabilized at 100 °C. As seen in Figure A-7 in Appendix A, the first three fillings only have small decreases in the pressure at the start of heating. This is because the decrease in oxygen pressure is masked by the increase in vapor pressure when the waste is heated. Figure 8-1 shows the rapid decrease in the amount of permanent gas at the start of each of the first four fillings (Days 0, 22, 27, and 34).

The permanent gas is determined by subtracting the vapor pressure, which was calculated by using a fitted water activity of 0.49 (Section 4.3.3). This value of the activity gives a reasonable match when the reactors are heated

to, or cooled from operating temperature, as can be seen on Figures 8-1 and 8-2. The cooling begins at the downward spikes shown at Days 21 (shortly after sampling), 25, 33, 36, 41, 47, 49, 56, and 61. The downward spikes are the result of the recorded temperature and the pressure being somewhat out of phase (Section 4.3.3). Fills 1 through 4 were heated to 100 °C (95 °C for Fill 1 after Day 13, where the rate of increase slows). The steepness of the negative slopes shows that the pressure decreases much faster from the oxygen removal than it increases by gas generation after the oxygen is gone. The observed rate of gas release after the removal of oxygen is approximately the same as it was when the material was heated under He cover gas (Section 6). Thus, Figure 8-1 shows the dramatic difference in the rate of oxygen removal compared with the rate of gas generation. Furthermore, some of the removal of oxygen is compensated by production of product gas, so the oxygen removal is actually faster than the decrease of permanent gas indicates.

Figure 8-2 shows the amount of permanent gas for Fills 3 through 11; this repeats the final 10 days shown on Figure 8-1 to show an example of the slope for gas generation at 100 °C. Fills 5, 6, 8, and 10 (beginning at Days 38, 42, 51, and 57) are seen to have slower removal rates, which is expected because these fills were at lower temperatures (around 70 °C). The lower portion of Figure 8-2 shows the temperature (right-hand scale), which varies from the heated temperature to the cooler temperatures used for sampling and refilling the cover gas (23 °C for Fills 1 to 3, and 45 °C for the later fills). Fills 7, 9, and 11 (beginning at Days 48, 54, and 61) were heated to 89, 95, and 100 °C, respectively. The rate of removal slows during the period shown, as the negative slope for Fill 11 is slower than for Fill 4, even though the temperatures are both near 100 °C. The amount of gas per volume of waste is seen to always be lower in reactor G2. This is primarily because the waste volume is 6% larger for reactor G2 (Table 4-4), as the initial filling pressure was lower only for Filling 1. Figure A-7 (Appendix A) shows that the pressures in the two reactors are often very nearly the same.

The gas analyses show that oxygen was completely removed (0.03% or less remaining), except for Fills 5, 7, 8, and 10, which were stopped after 66 to 97% removal (also, Fill 6 had 0.07% remaining in reactor G1). The amount removed is much greater than the expected solubility of O₂ in waste, as Norton and Pederson (1995) reported an oxygen solubility at 29.8 °C of 0.10 mmole/L for the dilute simulated waste (SY1-SIM-93B), where the solubility is greater than in the present waste. The observation of H₂ production is also evidence for reaction. When the waste is analyzed, it will establish what chemical changes are produced by the reacting oxygen; oxidation of organic species is expected to be the major reaction.

Figure 8-1. Amount of Gas (O_2/He + Product) for Fills 1 to 4 at $100^\circ C$ in Reactors G1 (Upper Curve) and G2 (Lower).

Figure 8-2. Amount of Gas in Reactors G1 (Upper Curve) and G2 (Lower) and Temperature for Fills 3 - 11 of O_2/He Cover Gas.

8.2 Kinetics of Oxygen Removal at 69 to 101 °C

- Oxygen removal is approximately first-order with respect to the amount of O_2 . The decay rate decreases with time, from about 0.6 to 0.2 Day^{-1} at 70°C . The decay rate is faster (ca. 1 Day^{-1}) at temperatures of 90 to 100°C , and even faster during the first four fills at 100°C .

8.2.1 Rates of Various Processes

The removal of O_2 is dramatic in the present apparatus, where the gas volume is approximately equal to the waste volume. Studies with simulated waste did not observe such a dramatic decrease (Delegard 1980, Ashby 1994, Barefield 1996). However, the first two studies used reactors with gas volumes much larger than the waste volume. For example, Ashby (1994) used reactors with a gas volume of 64 mL with 5 mL of simulant. Also, the present reactors have the entire gas volume heated, whereas the first two studies used a condenser. The condenser tends to isolate gas in the cold part of the reactor (above the condenser) from the heated gas in contact with the material. These differences may explain why those studies find oxygen remaining after 40 days of heating at 120°C . Unexplained differences remain with the later study in synthetic waste (Barefield 1996). The actual tank waste may have more reactive species present. These presumably would be organic species, as the simulant studies indicate that the oxygen reacts with organic species, rather than with nitrite (Ashby 1994).

The rate of the observed decrease in the amount of gas depends on the kinetics of the reaction of oxygen with organic species within the waste, but the relationship is indirect. Several processes occur prior to the reaction with organic species. First, oxygen has to diffuse within the gas to the surface of the waste. The time for this is short, as it is fast enough to allow the rapid decay observed for Fills 1 to 4. Oxygen will dissolve in the waste liquids until the solubility limit is reached. As discussed above, much more oxygen is removed than would occur if the only loss were gas going into solution. Thus the oxygen must be reacting within the waste. Before this happens, oxygen must diffuse (or mix) within the waste volume to reach reactive species (or the waste must mix to bring fresh reactants to the surface). If diffusion (mixing) within the waste is the rate-limiting step, the rate of decay will approach this limiting rate, which is discussed in Section 8.5. Diffusion or mixing by convection currents may be fast enough to keep up with decay rates on the order of 1 Day^{-1} . However, oxygen may not need to diffuse very far, as it could be removed within a thin layer at the surface. A typical gas filling has around 15 mmole of O_2 per liter of waste compared with about 100 times as much TOC (1.4 mole/L). Thus, the oxygen could be removed in a small volume, depending on the reaction efficiency.

8.2.2 First-Order Decay Rate

It is reasonable to assume that the oxygen concentration in the waste will be proportional to the oxygen gas pressure, and that the rate of decrease in oxygen concentration will be proportional to the rate of reaction within the waste. The term to describe the kinetics of a reaction between one reactant, present at a small concentration, and other reactants with large concentrations is pseudo first-order kinetics. For example, consider the decay of O_2 in a bimolecular reaction with a reactant R, where the reaction follows the 2nd-order kinetic equation with the time dependence of the O_2 concentration (shown as $[O_2]$) given by

$$-d[O_2]/dt = k_2 [O_2] [R]. \quad (8-1)$$

When $[R]$ is much larger than $[O_2]$, the value of $[R]$ can be taken as constant. Then the kinetics follows the 1st-order rate law

$$-d[O_2]/dt = k_1 [O_2], \quad (8-2)$$

$$-d\ln[O_2]/dt = k_1, \text{ with}$$

$$k_1 = k_2 [R], \quad (8-3)$$

where k_1 is the pseudo 1st-order decay constant.

The observation of $[O_2]$ is indirect (except for the point for the gas analysis at the end of each filling), as any gas generated compensates for some of the loss of oxygen. The observation of falling pressures shows that the yield is less than one for the number of gas molecules produced per oxygen molecule removed. In this report, no correction has been applied to correct the decay rates for the gas produced. This causes the apparent value of k_1 to increase as the $[O_2]$ decreases. This error is not serious when $[O_2]$ is much greater than the concentration of product gas, and when the yield of product gas is small.

Figure 8-3 shows the 1st-order decay rate k_1 , determined from the slope of linear fits of logarithmic plots of $[O_2]$ (actually, this is the upper limit to $[O_2]$, as it includes any gas produced as if it were O_2). The decay rates are shown for Fills 5, 6, 8, and 10 at 70 °C, and the later fills at higher temperatures, Fills 7 (90 °C), 9 (95 °C), and 11 (100 °C). Figure 8-3 shows that the decay rate decreases with time, with the decay rate in the 70-°C fills decreasing from 0.6 to 0.2 Day⁻¹. At higher temperatures, the values of k_1 increase as the $[O_2]$ decreases with time during each filling. This suggests that the yield of product gas increases as the temperature increases, so that ignoring the product gas produces a larger error at the higher temperatures. It is interesting that the decay rate seems to be faster in reactor G2, the reactor that generated gas faster under He cover gas.

Figure 8-3. Oxygen Removal Decay Rate Constant, Fills 5 - 11 in Reactors G1 and G2 (Uncorrected for Gas Produced). Fills 5, 6, 8, and 10 at Lower Temperature (70°C).

8.2.3 Activation Energy for Oxygen Decay Rate

- The differing decay rates at different temperatures imply an activation energy around 9 to 17 kcal/mole.

The decay rates at pairs of temperatures were used to calculate the empirical energy of activation, E_{act} , from the Arrhenius equation (4-4). The use of pairs of values attempts to reduce the effects of the rate changing with time. These pairs give activation energies from 9 to 17 kcal/mole, with an average value of 13 kcal/mole. These are rough values from decay rates that are uncorrected for gas production, but they indicate a weaker dependence on temperature than for gas generation under inert cover gas, where the activation energy is 22 to 23 kcal/mole (Person 1996b). The activation energy values are consistent with the value of 11 ± 2 kcal/mole that is estimated below (Figure 8-11) for the rate of oxygen reduction in waste.

The decay rates at higher temperatures are faster than at 70 °C. The rate is, around 0.8-0.9 at 90 °C (Fill 7), 0.8-1.0 at 95 °C (Fill 9), and 0.7-1.0 Day⁻¹

at 100 °C (Fill 11). In this sequence, the decrease in decay rate with time is approximately compensated by the higher temperatures of the later fills.

8.2.4 Rates for Reaction With Organic Species

The observed decay rates give some measure of k_2 [R] (Eq. 8-3). Assume that the reaction with the waste is the rate-limiting step and that it occurs throughout the bulk of the waste volume, which allows an upper limit for the rate constant k_2 to be calculated from $k_1/[R]$ in Eq. (8-3). (However, this is not a true upper limit if oxygen reacts with species other than R.) Using 1.4 mole/L for the soluble TOC concentration (Person 1996a) gives k_2 values of 0.4 (Fill 5) to 0.14 L/moleTOC/Day (Fill 10) at 70 °C, and the Fill 11 decay rates give 0.5 to 0.7 L/moleTOC/Day at 100 °C. Considering that most of the reactive organic species have more than one carbon atom, the rate per mole of reactive species will be even faster. Thus the value of k_2 should use a weighted average of the rate per carbon times the number of carbon atoms in each species. Taking 2 to 6 as reasonable limits for the weighted-average of carbon atoms gives k_2 estimates as 1 to 4 L/mole/Day for Fill 11 at 100 °C, and 0.8 to 2.4 (Fill 5) decreasing to 0.3 to 0.8 L/mole/Day (Fill 10) at 70 °C.

8.2.5 Rate of O₂ Removal Compared With Gas Generation Rate

The rate of oxygen removal is computed by multiplication of k_1 by the oxygen gas concentration $[O_2]$. This value obviously changes with time; a typical initial value for $[O_2]$ is about 15 mmole/L. As an example, the rate for Fill 11 (k_1 values of 0.7 to 1.0 Day⁻¹, Figure 8-3) gives a removal rate at 100 °C of 11 to 15 mmole/L/Day. This removal rate is 14 to 20 times faster than gas generation under inert cover gas at the same temperature (Section 6). Recall that the Fill 11 removal rate was slower than rates for earlier fills at 100 °C. The initial O₂ removal rate is for a mixture with 30% O₂, so that the rate would be 0.63 times as large in air (with 19% O₂). Thus the decay rate measured for Fill 11, scaled to 19% O₂, would be 9 to 13 times as fast as gas generation in the absence of oxygen.

8.3 Composition of Gas Produced Using O₂/He Cover Gas

The gas analyses give information on both the product gas and the amount of oxygen remaining. The percentage of O₂ that reacted is found by dividing the Vol% of O₂ in the sample by the Vol% in the samples taken before any significant amount of O₂ had reacted. These percentages of reacted O₂ are shown in Table 8-1. This table shows the weighted sums of the compositions found in the two sample bulbs (from Table B-3 of Appendix B, where the percentages for each gaseous species are normalized for no air and no oxygen). In Table B-3, the sum of Vol% of O₂ plus Vol% of He is greater than 100% in

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Table 8-1. Percentage of Oxygen Reacted, Ratios of Product Species Per O₂ Removed, N₂O/H₂, and N₂/N₂O for 11 Fills in Reactors G1 and G2.

Fill	-O2%	Ratio of Product Species to Oxygen Removed								
		Gas	H2	N2O	N2	NH3	CH4	NOx	N2O/H2	N2/N2O
Reactor G1										
1	99.99	2.517	0.998	0.6754	0.5498	0.155	0.1294	0.0094	0.677	0.81
2	100.00	0.890	0.497	0.1230	0.0845	0.140	0.0245	0.0204	0.247	0.69
3	100.00	0.910	0.463	0.1676	0.1631	0.067	0.0428	0.0069	0.362	0.97
4	100.00	0.272	0.155	0.0095	0.0101	0.088	0.0085	0.0006	0.061	1.07
5	72.45	0.125	0.059	0.0011	0.0026	0.058	0.0033	0.0005	0.018	2.40
6	99.93	0.146	0.096	0.0015	0.0024	0.043	0.0024	0.0005	0.016	1.60
7	93.67	0.203	0.137	0.0032	0.0062	0.052	0.0038	0.0009	0.024	1.93
8	67.63	0.161	0.102	0.0016	0.0037	0.051	0.0029	0.0004	0.015	2.38
9	99.97	0.273	0.208	0.0079	0.0179	0.034	0.0046	0.0002	0.038	2.27
10	66.93	0.178	0.101	0.0027	0.0061	0.064	0.0037	0.0010	0.026	2.28
11	99.74	0.342	0.228	0.0126	0.0265	0.066	0.0086	0.0006	0.055	2.10
Reactor G2										
1	100.00	3.529	1.237	1.2473	0.7331	0.161	0.1340	0.0160	1.008	0.59
2	100.00	0.967	0.468	0.1678	0.0989	0.187	0.0282	0.0162	0.358	0.59
3	99.99	0.808	0.384	0.2021	0.1370	0.044	0.0309	0.0102	0.526	0.68
4	100.00	0.234	0.145	0.0086	0.0073	0.066	0.0067	0.0005	0.060	0.84
5	74.97	0.140	0.055	0.0012	0.0029	0.076	0.0042	0.0008	0.021	2.52
6	100.00	0.145	0.081	0.0014	0.0020	0.057	0.0030	0.0005	0.018	1.37
7	97.21	0.155	0.102	0.0017	0.0027	0.044	0.0030	0.0005	0.017	1.58
8	66.61	0.150	0.086	0.0016	0.0025	0.055	0.0030	0.0011	0.018	1.60
9	100.00	0.239	0.176	0.0057	0.0110	0.041	0.0043	0.0003	0.032	1.93
10	74.23	0.177	0.111	0.0028	0.0031	0.056	0.0032	0.0009	0.025	1.10
11	99.97	0.330	0.221	0.0107	0.0216	0.069	0.0083	0.0005	0.048	2.02

Figure 8-4. Percentage of Initial Oxygen Removed for 11 Fills in Reactors G1 and G2. Fills 5, 6, 8, and 10 at Lower Temperature (70°C).

the initial fillings; the percentages of He plus the product gases add to 100% when no oxygen is present. The Vol% of O_2 present divided by the Vol% of O_2 in the initial filling gives the fraction of oxygen remaining. Figure 8-4 plots the percentage of oxygen reacted. This shows that the amount reacted was essentially 100% for most fills.

Figure 8-1 shows that there was a significant pressure increase after the initial drop in pressure for Fillings 1 - 3, which means that much of the product gas formed in the absence of oxygen. Table 5-1 also shows this, as the product gas composition is similar to products produced when no O_2 was present. Thus, much of the product gas in Fillings 1 - 3 was formed independent of oxygen, probably by the same processes that produce gas in the absence of oxygen. This production mechanism is probably present in the later fillings in varying degrees. One way to understand gas production is to separate the production via oxygen reactions from production independent of oxygen. The product gases from oxygen reactions have compositions that depend on the relative reaction rates to produce different species. The reaction rates depend on temperature and on the reactive organic species concentrations, in addition to the oxygen concentration (which decreases with time).

Figure 8-5. Estimated Rate of Species Production for Oxygen Fills 1 - 11 in Reactor G1.

Another parameter of interest is the gas yield, the ratio of the amount of product gas to the amount of oxygen reacted. The yield depends on the conditions for the heating of the different fillings. For the fillings that continued long after the oxygen was depleted, the gases produced independent of oxygen are relatively more important. Table 8-1 summarizes information on the ratio of various species produced per O₂ removed, with the column labelled "Gas" representing the sum of all the product gases.

- Oxygen reactions lead to production of H₂ and NH₃. The ratio of H₂ produced to O₂ removed is 0.06 to 0.23; the ratio of NH₃ produced to O₂ removed is 0.03 to 0.09.

The temperature and the length of heating varied for the different fillings, so that variable amounts of gas were produced. Figure 8-5 shows rough estimates for the rate of gas production of the different gaseous species for the different fillings in Reactor G1. The rates are calculated from adding the gas produced while the O₂ is reacting to the gas produced after oxygen removal. The amount of product gas present at the minimum (of the amount of gas) was calculated as the difference between the amount of gas present minus the amount of He (added with O₂ at the start of the fill). The lower temperatures for Fills 5, 6, 8, and 10 cause lower rates of gas production.

The rates for the first four fills represent the average rate for the sum of the oxygen reactions and the oxygen-independent reactions.

The relative rates for the different species in Figure 8-5 are seen to change from Fill 1, where the oxygen independent process contributes most of the gas, to Fills 5 to 11, where oxygen was present during most of the gas production period. The changes in the production rate for N_2 approximately reflect changes in the overall gas generation rate expected for gas generated at the rate shown at the end of Figure 6-3 with an activation energy around 23 kcal/mole. This suggests that the production of gas via the oxygen independent process occurs at about the same rate for N_2 , at a somewhat reduced rate for N_2O , at a somewhat enhanced rate for methane, and at significantly enhanced rates for H_2 and NH_3 . The results for NH_3 may be distorted, as there was a relatively small amount of product gas collected so that any NH_3 coming out of solution during the second gas sampling at reduced pressure will enhance the apparent rate of production. However, the continued collection of ammonia for many gas fillings indicates that the production of NH_3 was enhanced. As the production of N_2 in the absence of O_2 is thought to proceed through an intermediate that produces N_2O (Ashby 1994), the apparently constant production rate for N_2 may mean that the oxygen independent process produces less, which is approximately compensated by a small production of N_2 via an oxygen dependant process.

Figure 8-6 shows the yields of H_2 and NH_3 per O_2 removed (i.e., the ratio of moles of product gas produced per mole of oxygen removed for the product gases of H_2 and NH_3). The plot uses a log axis, as there was substantial gas production during Fills 1-3 that occurred after the removal of oxygen. As shown in Figure 8-4, the smallest percentages of O_2 removed were for Fills 5, 8, and 10, so that these have greater relative contributions from oxygen-dependent processes. Figure 8-2 shows that Fill 5 contained a somewhat smaller amount of gas in the initial filling than did the later fills. Thus, a smaller amount of oxygen reacted in Fill 5 than in other fills in the range of 5 to 11. Therefore, the minimum at Fill 5 for the yield of H_2 produced per O_2 removed appears to result from the other fills having a relatively larger contribution from H_2 produced in the absence of O_2 . In the case of ammonia, the minimum yield per O_2 consumed is at Fill 9, but ammonia is not measured very quantitatively. The yield of ammonia per O_2 removed shows the least variation of any product gas, indicating that ammonia is produced by processes that consume oxygen, as well as by oxygen-independent processes.

- Reaction of oxygen with waste seems to slow production of N_2O , with little effect on N_2 production. The ratio of N_2O produced per O_2 removed is 0.001 to 0.013; the ratio of N_2 produced per O_2 removed is 0.002 to 0.027.

Figure 8-6 shows the smaller variation in the H_2 and NH_3 ratios in comparison with the larger variation at different fills for the yield ratios of N_2O and N_2 , which are shown in Figure 8-7. Thus, the first fills had a substantial

Figure 8-6. Ratio of Product Gas to O_2 Removed in Reactors G1 and G2 for H_2 and NH_3 Product Gases at Different O_2/He Fills.

Figure 8-7. Ratio of Product Gas to O_2 Removed in Reactors G1 and G2 for N_2O and N_2 Product Gases at Different O_2/He Fills.

Figure 8-8. Ratio of CH_4 Produced to O_2 Removed in Reactors G1 and G2.

amount of gas produced independent of oxygen, but the gas produced for Fills 5 - 11 shows a greater influence of oxygen. Figure 8-7 shows that there is a large variation in the amount of N_2O produced per O_2 removed: approximately 3 orders of magnitude. Thus N_2O production is relatively uncorrelated with O_2 removal. The conclusion is that H_2 and NH_3 are produced by processes related to oxygen removal, as well as by processes independent of O_2 , while N_2O and N_2 are produced almost exclusively by processes independent of O_2 . However, a small amount of N_2 seems to be produced by oxygen-dependent processes, as the $\text{N}_2/\text{N}_2\text{O}$ ratio increases for fills where little gas is produced by the oxygen-independent processes (however, this ratio is not well determined for the small amounts found for the fills at 70°C). Figure 8-8 shows that methane is also produced by oxygen reactions, but at a lower yield per oxygen removed than for hydrogen or ammonia.

Figure 8-9 shows the ratio of the total number of gas molecules produced per O_2 molecule removed for Fills 4 through 11. The measurements are plotted as symbols for comparison with lines depicting what would be expected if the product gas were produced at a rate of 0.6 mmole/L/Day at 100°C , with slower rates at lower temperatures predicted using an activation energy of 23 kcal/mole (Person 1996b). This rate is close to the rate that gas was produced in He cover gas (Section 6), and to the rate of gas production after

Figure 8-9. Gas Produced Per O_2 Removed in Reactors G1 and G2. Lines Show That Normal Gas Generation Rate Is Too Small.

the oxygen reacted in Fill 1. The lower values shown by the lines demonstrate that gas is produced more rapidly when oxygen is present (as did Section 8.2.5). Some (all) of the gas may be reaction products of reactions that remove oxygen. For this gas, the amount of product is proportional to the amount of oxygen reacted. There does not seem to be a constant value at all fills for the yield of gas produced per O_2 removed, but the information in Tables 8-1 and 5-5 could be used to derive detailed information on the products produced at different temperatures and times.

The studies at 120 °C using simulated waste at Georgia Institute of Technology (Ashby 1994) found that different organic species give different ratios of $H_2/(-O_2)$ and $N_2O/(-O_2)$. Thus the present observations may be useful in evaluating the importance of oxygen reactions with different organic species. For example, the GIT studies find relatively small values of the $H_2/(-O_2)$ ratio for formate (ratios of 0.1 to 0.2) and citrate (0.17). The ratio for both of these species compares reasonably well with the $H_2/(-O_2)$ ratios in Table 8-1 for Fills 4 to 11 (ratios of 0.06 to 0.23). Furthermore, formate and citrate both have low values for the $N_2O/(-O_2)$ ratio, <0.01 and <0.006, respectively. These compare well with the $N_2O/(-O_2)$ ratios in Table 8-1 for Fills 4 to 11 (ratios of 0.001 to 0.013). This is in contrast with glycolate, for which the GIT studies find a ratio of 1.06 for $H_2/(-O_2)$ and 0.38 for $N_2O/(-O_2)$, although the yields may change with temperature. The ratios found

at GIT for EDTA of 0.4 for $H_2/(-O_2)$ and <0.006 for $N_2O/(-O_2)$ are consistent with some reaction with EDTA occurring, although the present results have a somewhat lower value for $H_2/(-O_2)$.

The increase in $H_2/(-O_2)$ ratio at Fills 8 and 10 from the minimum at Fill 5 may indicate changes in the relative concentrations of the different reactive species. For example, Table 8-1 suggests that Fill 5 has a greater relative concentration of organic species that react to give a low $H_2/(-O_2)$ ratio than do Fills 8 or 10. These same species may react more rapidly with oxygen to give the faster decay rate for Fill 5 (Figure 8-3).

The studies at GIT (Ashby 1994, Barefield 1995, Barefield 1996) find that the presence of oxygen suppresses the formation of N_2O . This may also be true for the present work, but the reduction is less apparent. The GIT studies indicate that the rate of gas generation is slower when oxygen is present, while the present results find the rate enhanced. This may reflect the actual waste having different organic species present.

Destruction of EDTA via reaction with oxygen could be very important in removing Sr/TRU from solution, as simulant studies (Ashby 1994) found destruction of EDTA in the presence of oxygen (and not under inert cover gas), and EDTA is a complexant present at a fairly high concentration in Tank 101-SY waste (Table 8-2, below). The resistance of EDTA to reaction in the absence of oxygen could explain the long heating time required to reduce the solution concentration of Sr in Tank 101-SY waste with He cover gas (Person 1996b).

8.4 Rate of Reduction Within Waste

- Oxidation of TOC is balanced by reduction reactions. In the absence of O_2 , the reduction products are primarily gases. The amount of gas produced measures TOC oxidation. The gas yield is 0.6 to 0.9 moles of gas/mole of TOC, depending on whether the final product is carbonate or oxalate.

The gaseous species provide insight into oxidation/reduction reactions within the waste, as the product gases are primarily reduced species. The oxidized species are nonvolatile products, or are readily absorbed into the alkaline waste (e.g., CO_2). With the possible exception of a minor amount of NO_2 , the gaseous products are all the products of reduction reactions (the NO_x observed may not even contain NO_2). The reaction of O_2 is an additional redox reaction, where the disappearance of O_2 measures the rate of the reduction reaction. Each electron transferred in the formation of a reduced product came from formation of an oxidized product. Thus, gas monitoring provides a measure of the minimum amount of oxidation that has occurred. The progress of redox reactions are measured in equivalents, one mole of electrons. The electrons transferred per mole of gas can be calculated using the following reactions:

These reactions are reasonable representations of reduction reactions in the alkaline waste; they use results of studies using synthetic waste that indicate that the nitrite ion is the source of the bulk of the N_2O , and that N_2 and most NH_3 come from the same precursor (Ashby 1994). This same study found that a fraction of the NH_3 contained N atoms from the organic species. The number of equivalents per mole of CH_4 depends on which organic species is used; the average species identified in the analyses (see Table 8-2 below) transfers 4.6 equivalents to produce CH_4 . Reactions (8-4) to (8-9) give the

Figure 8-10.

Estimated Rate of Formation of Gaseous Reduction Products from Oxidation of Organic Species Via NO_2^- Reactions Alone and With Added O_2 , Compared With Reduction of O_2 .

number of equivalents transferred in the production of gas independent of oxygen. These same number of equivalents are used for reactions in the presence of oxygen, which is reasonable except that some of the additional NH_3 production may come from organic species.

- Oxygen reduction reactions are significantly faster, which means the oxidation reactions are faster when oxygen is present.

A minimum rate of production of reduced species can be calculated by summing the production rates for the individual gas species times the number of electrons transferred shown in Eq. (8-4) to (8-9). The result is shown in Figure 8-10. The left bar for each filling shows the reduced product production rate for the nitrite reactions alone, with the number of milliequivalents per liter per day calculated at the temperature of the filling, using the product distribution found in Section 6 for a rate of 0.75 mmole/L/Day at 100 °C, and $E_{\text{act}} = 23$ kcal/mole. The second bar shows the reduction rate estimated from the observed products and the estimated gas generation rates in Reactor G1 (Figure 8-4). Comparing these two bars shows that the presence of oxygen has significantly enhanced the reduction rate for Fills 5 to 11, where O_2 was present for most of the test. This shows that the rate of reduction for production of gases has increased, so that increased production of H_2 (a 2-electron transfer) has more than compensated for the decreased rate of reduction in producing N_2O (a 4-electron transfer). Furthermore, the third bar in the comparison in Figure 8-10 shows rate of reduction of O_2 in the waste [Eq. (8-10) shows that this is 4 times the estimated removal rate of O_2]. The large reduction rates shown for Fills 1 to 4 have large uncertainties; comparison of these rates with Fill 11 gives a rough indication of the initial enhancement of the rates of O_2 removal reactions.

The comparison of the three modes of reduction in Figure 8-10 shows that oxygen has greatly enhanced the rate of reduction, which means that the rate of oxidation has increased dramatically. Furthermore, the estimated rate of O_2 reduction was calculated from the decrease in the O_2 pressure between the start and the minimum pressure reached during the fill. This is corresponds to the reduction rate for some average O_2 concentration (i.e., around 15% of the cover gas). The O_2 reduction rate would be faster if oxygen were not being depleted during the measurement.

From the estimated reduction rates shown in bars 2 and 3 in Figure 8-10, activation energies can be estimated for the gas production when O_2 is present and for the O_2 reduction. An Arrhenius plot for this purpose is shown in Figure 8-11. The lines shown are fits to the results for Fills 6 - 11, as earlier points show enhanced rates of O_2 removal. The activation energies are 11 ± 2 kcal/mole for O_2 reduction and 17 ± 2 kcal/mole for gas production (these uncertainties are the estimated standard deviations for the fits; the total uncertainties are larger.). The oxygen reduction activation energy is in agreement with the estimates given in Section 8.2.3; gas production has a

Figure 8-11. Fits of Estimated E_{act} for Rate of Formation of Gaseous Reduction Products from Oxidation of Organic Species Via NO_2^- and O_2 Reactions, Compared With Reduction of O_2 .

lower activation energy than the value of 23 kcal/mole (Person 1996b, and Section 7.3) found for reactions in the absence of oxygen.

The equation for the line fit shown in Figure 8-11 for oxygen reduction can be used to estimate the rate at tank temperature (47 °C). This rate is 4 mequiv/L/Day (for the average O_2 concentration). Furthermore, the number of equivalents required to oxidize the organic species can be estimated, so that the length of time for this process at 47 °C can be estimated. The number of electrons transferred during oxidation of organic species depends on the species and the reaction products. For example, when the carbon in EDTA goes to carbonate 34 electrons are transferred

If oxalate is formed, the low solubility in tank waste will make further oxidation slow (Barney 1994, Person 1996a). Thus, another limit for the number of equivalents transferred assumes that oxalate is the final product, where the transfer is 24 electrons

This illustrates that there is one less equivalent transferred per carbon atom when the final product is oxalate, compared with carbonate. Thus the transfer is 2.4 or 3.4 equivalents per mole of TOC, depending on whether the final products are oxalate or carbonate. This assumes that the nitrogen in the EDTA all becomes NH_3 . Producing N in other oxidation states will result in different electron transfers, e.g., producing N_2O changes the electron transfer by 0.8 equivalents per mole of TOC (to 3.2 or 4.2). The extreme oxidation state of N is production of nitrate, where the transfer is 4.0 or 5.0 equivalents per mole of TOC. That is, the extreme difference between producing ammonia and nitrate is 8 equivalents per mole of N atoms. Isotopic substitution shows that heating synthetic waste forms products where organic N is found in NH_3 and not in N_2O (Ashby 1994). This report assumes that the N atoms present in organic species form ammonia.

Different organic species have carbon in different oxidation states. For example, citrate oxidation to carbonate transfers 3 equivalents per mole of TOC

Glycolate oxidation to carbonate transfers 3 equiv/moleTOC

IDA oxidation to carbonate transfers 3 equiv/moleTOC

Acetate oxidation to carbonate transfers 4 equiv/moleTOC

Formate oxidation to carbonate transfers 2 equiv/moleTOC

The average oxidation state of the soluble TOC with the tank material can be estimated from the analytical results at PNNL (Campbell 1995, Campbell 1994 explains that the NIDA entry actually measures IDA), which give quantitative analyses of the organic species for the convective and the nonconvective layers. These results are then weighted by the weight ratio used to form our composite (1.1, as shown in Section 3.4). Table 8-2 shows the calculation. The entry for normal paraffin hydrocarbon (NPH) in the analysis (Campbell 1995) presumably represents material introduced during the core sample collection from the tank, so that it should be less important within the tank. The material used for the current tests presumably this amount of NPH.

The concentration of oxalate in Table 8-2 was reduced from the amount reported (Campbell 1995), in order to approximate the TOC that is in solution. The

Table 8-2. Calculation of Average Soluble TOC Anion and Number of Equivalents to Oxidize C to Oxalate or Carbonate (Concentrations from Campbell 1995).

Species	Concn mole/L	#C	#H	#O	#N	Charg	C ₂ O ₄ ²⁻ Equiv	CO ₃ ²⁻ Equiv
EDTA	0.0206	10	12	8	2	-4	24	34
ED3A	0.0048	8	11	6	2	-3	20	28
NTA	0.0061	6	6	6	1	-3	12	18
Citrate	0.0069	6	5	7	0	-3	12	18
IDA	0.0311	4	5	4	1	-2	8	12
Succinate	0.0020	4	4	4	0	-2	10	14
Oxalate	0.0040	2	0	4	0	-2	0	2
Glycolate	0.0167	2	3	3	0	-1	4	6
Acetate	0.170	2	3	2	0	-1	6	8
Formate	0.137	1	1	2	0	-1	1	2
NPH	0.0060	13	28	0	0	0	67	80
Sum	0.4055	TOC = 0.97 mole/L						
Ave		2.59	3.45	2.69	0.22	-1.32	6.51	9.10
Ave/TOC		1.00	1.33	1.04	0.08	-0.51	2.51	3.51

average molecular composition is calculated as the number of atoms of each element weighted by the concentration and averaged. The result is a representation of the average soluble organic species detected, which has a formula of

Normalizing this by the amount of TOC gives the formula as $CH_{1.33}O_{1.04}N_{0.084}^{0.51-}$, which transfers 3.51 equivalents to go to carbonate

or 2.51 equivalents to go to oxalate

The soluble species listed in Table 8-2 have a total TOC of 1.05 mole/L. This is only about 75% of the soluble TOC found in our analyses (Person 1996a,b). Much of this discrepancy may relate to systematic differences in determinations of the amount of TOC in Tank 101-SY waste at WHC, compared with PNNL. This is discussed by Herting (1992a), where the average ratio for 21 samples was 0.77. In any case, the average number of oxidation equivalents per TOC for the waste in the 94A composite should be around 3.5, when carbonate is the final product, as at least 75% (and probably more) of the TOC was speciated, and the number of equivalents per TOC does not vary by a large factor for other complexant fragments that might be present within the waste.

The oxidation equivalents from the TOC must be matched by reduction equivalents. The amount of gas produced by 2.5 to 3.5 reduction equivalents depends on the composition of the product gas. For the mix found during the test with helium cover gas (Section 6), the number of reduction equivalents per mole of gas is 4.1. Thus, oxidation of TOC to oxalate or carbonate should produce about 0.6 to 0.9 moles of gas per mole of TOC, if no other reduction reactions are important. The observation that our long-term heating test of tank material produced a gas yield around 0.8 ± 0.4 moles of gas per mole of TOC (Person 1996b) indicates that other redox reactions are minor (or that they cancel). Therefore, measuring the amount of gas produced in the absence of oxygen measures the reduction equivalents, which measures progress in oxidation of organic species.

- Tank 101-SY has enough TOC to release gas for 80 to 110 years at current release rates, if reactions with oxygen are negligible.

The gas yield and the amount of TOC can be used to estimate the amount of gas that would be generated by Tank 101-SY by the oxidation of TOC, if there are no oxygen reactions. For the gas mixture produced within the tank (Sullivan 1995), the number of reduction equivalents per mole of gas is 4.3, so that the gas yield in the tank is 0.6 to 0.8 moles of gas per mole of TOC. Tank 101-SY has about 1.4 mole/L of soluble TOC (Person 1996a), so the gas yield corresponds to production of 0.84 to 1.1 mole/L of gas. At the present rate of gas generation (0.028 mmole/L/day, Table 2-3) the time for this gas to evolve would be

$$\begin{aligned} \text{Time} &= (0.84 \text{ to } 1.1 \text{ mole/L}) / (0.000028 \text{ mole/L/day}) \\ &= 30000 \text{ to } 39000 \text{ day.} \end{aligned}$$

This is 80 to 110 years, but the actual time would be longer, as the rate decreases as the TOC reacts. The corresponding half-life estimates for the 1st-order decay are 60 to 80 years. The reaction with oxygen will decrease the time required; Section 2.2 gives an estimate of the oxygen reactions in the tank.

Reactions with O_2 increase the relative concentration of H_2 , which lowers the reduction equivalents per mole of gas. However, the increase in the relative

concentration of NH_4 offsets some of this loss. For example, the average composition after Fill 8 has 3.0 equivalents/mole of gas. For this composition, oxidation of TOC to oxalate or carbonate via production of gases should produce about 1.2 to 1.5 moles of gas per mole of TOC. In addition, Figure 8-10 shows that most of the reduction equivalents come from the reduction of oxygen. This reduction reaction provides 4 equivalents/mole of O_2 , which will oxidize 1.14 moles of TOC to carbonate, or 1.59 moles of TOC to oxalate.

A reduction rate of 4 mequivalents/L/Day at 47 °C (tank temperature) was estimated for reduction of oxygen, at an average concentration around 8 mmole of O_2 in the headspace per liter of waste. The concentration of O_2 within the waste was not determined. This reduction rate can be used in a rough estimate of the time that would be required to oxidize the TOC, assuming that the waste in the tank could be mixed well enough to achieve the same oxygen concentration as was achieved within our small waste samples. The rate of reaction of 4 mequivalents/L/Day means that the time to oxidize waste with 1.4 moleTOC/L and 2.5 to 3.5 equivalents/moleTOC is

$$\begin{aligned}\text{Time} &= (1.4)(2.5 \text{ to } 3.5 \text{ equivalents/L}) / 0.004 \text{ equivalents/L/Day} \\ &= 900 \text{ to } 1200 \text{ Day (2.4 to 3.4 yr)}.\end{aligned}$$

The actual time would be longer, as the oxidation rate for the TOC will decrease as the TOC is depleted. The half-life for the 1st-order reaction would be 600 to 850 Day (1.7 to 2.4 yr).

8.5 Oxygen Diffusion Within Waste

- Oxygen reactions require O_2 within the waste volume, so that mixing is important in a large volume.

Appendix C shows that diffusion alone is approximately fast enough to allow reaction throughout the small volume of the present reactors at 70 °C. The decay at 100 °C is probably too fast for diffusion alone. However, waste mixing by convection currents could occur at a rate comparable to the 1 Day^{-1} decay rates.

The decreases in the decay rate at 70 °C in Figure 8-3 do not indicate rate enhancement from mixing during the cooling and heating between fills (i.e., there does not seem to be any decay rate increase from an influx of reactive species into a small volume near the surface). This lack of enhanced mixing between fills suggests that the entire volume is already mixed by convection currents (or by diffusion being fast enough). The observation that the rate of gas release decreases for time periods of 15 days or so (Sections 6 and 7) is approximately consistent with the estimates of gas diffusion rates in Appendix C, as the depth of waste in the reactors is about 3 cm.

Tank 101-SY has a slower diffusion time. However, the waste in the convective layer mixes (via convection) in less time than the time period for diffusion in a

stagnant layer (ca. 60 day). Mixing by convection is expected to be faster than diffusional mixing (McGrail 1993, McGrail 1994). Thus the fraction of waste in contact with oxygen is larger than the very small region accessible by diffusion (i.e., the region within a few cm of the surface, <0.5% of the volume). As discussed next, the N_2O/H_2 ratio of 0.85 within the tank may be evidence for some contribution of H_2 from oxygen reactions.

8.6 Some Implications of O_2 Reactions Within the Tank

This section discusses some of the implications of oxygen reactions within the tank. As discussed in Section 2.2, the rate of gas production in the tank (especially the production of H_2) seems faster than expected from radiolysis and thermal reactions in the absence of oxygen, which may be evidence for oxygen reactions within the tank being significant. The rapid decay rate and the small activation energy imply that oxygen reactions should occur reasonably rapidly in the actual tank. The decay rate of 0.2 Day^{-1} at 70°C and the activation energy of 11 kcal/mole can be used in Eq. 4-5 to estimate a decay rate of 0.063 Day^{-1} for the actual tank at 47°C . This corresponds to a half-life of 11 days, which is long compared with the ventilation time. Thus, there will only be a very small depletion of O_2 in the ventilation air.

During the earlier period when air sparging was used as a mitigation technique, there would have been enhanced reaction with oxygen, to the extent that the air sparging was successful in introducing air into the tank beneath the surface. The operation of the mixing pump could enhance O_2 reactions, as mixing might bring more waste material in close contact with air. The increased oxygen reactions would decrease the N_2O/H_2 ratio, as reactions in the presence of oxygen greatly enhance the production of H_2 relative to N_2O . An increase is also expected in the NH_3/N_2O ratio. The magnitude of these effects depends upon the fraction of waste in contact with oxygen. However, the relatively large rate of gas generation in the presence of oxygen will cause a greater effect than would be expected from the ratio of the volume with oxygen to the volume without.

- Some O_2 reaction may now occur within Tank 101-SY to give the observed N_2O/H_2 ratios around 0.85.

The large difference between the N_2O/H_2 ratio for gas produced by oxygen reactions and gas produced in the absence of oxygen suggests that any significant enhancement factor in the mixing of the tank could be estimated from changes in the N_2O/H_2 ratio (here "mixing" refers to circulating waste from the interior to the region close to the surface). That is, the N_2O/H_2 ratio observed for gas released from the tank has values around 0.85 (Sullivan 1995). This is lower than the ratios found in our laboratory studies at 100°C (Person 1996b and Section 6, although the ratios of 1.6 or greater shown in Table 5-2 probably are high because the initial gas releases tend to be rich in N_2O). The ratio has not been determined very well in the small amount of gas collected at 65°C (Person 1996b). Furthermore, the N_2O/H_2 ratio for the radiolytic production of gas is unknown, and

this produces a larger fraction of the gas in the tank (Section 2.2). The gas generated by radiolysis probably has a N_2O/H_2 ratio greater than one, as the ratio $G(N_2O)/G(H_2)$ is greater than one for gas produced by radiolysis for each of the several organic species in simulated waste mixtures reported in Tables B3-1 and B3-3 in one study (Meisel 1993). However, the observed N_2O/H_2 ratio for the tank could be reduced because oxygen reactions produce some of the H_2 in the tank. For example, if the N_2O/H_2 ratio for gas produced at tank temperature without oxygen were 1.06, then the observed ratio of 0.85 would imply that 20% of the H_2 was produced via reaction with oxygen (where the ratio may be 0.02 or so, as shown in Table B-1). If mixing doubled the contact of the waste with oxygen in this example, then the observed N_2O/H_2 ratio would go from 0.854 to 0.716. Section 2.2 estimates that half of the H_2 in the tank could be produced by O_2 reactions.

Oxygen is produced during the radiolysis of tank waste. Because of the slow diffusion, O_2 reacts within a short distance of where it is formed in the tank. The products of this reaction will be primarily H_2 and NH_3 . The $G(O_2)$ value measured at Argonne National Laboratory (ANL) in simulated tank waste without organic species was 0.08 (Meisel 1993). However, when organic species were present, these workers found oxygen was consumed, with $G(-O_2)$ of 7. Thus, the oxygen that is produced by radiolysis in the tank will react. Table B-1 indicates that O_2 reaction will yield about 0.1 H_2 molecules per molecule of O_2 . This would produce an extra contribution to $G(H_2)$ of about $0.08 \times 0.1 = 0.008$, which is small compared with the $G(H_2)$ from the organic species (Meisel 1993).

As pointed out in Section 8.4, introducing oxygen within the waste should speed the destruction of TOC. The enhanced production of flammable product gases (H_2 and NH_3) when oxygen is present is a consideration when evaluating this option. Other considerations include the rate of gas production and the method of bringing O_2 in contact with waste within the tank.

Additional implications are discussed in Section 2.2, where the rates of various processes are compared with the gas generation rate within the tank. This comparison suggests that thermal reactions with oxygen may produce about half of the H_2 formed in the tank.

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APPENDIX A: UNCORRECTED PRESSURE AND TEMPERATURE DATA

Raw data for pressure and temperature are presented in Figures A-1 through A-8. In Figures A-1, A-3, and A-5, note the trend of increasing pressure with time heated. Also note the effect of temperature on the uncorrected pressure. The changes in pressure for Figure A-2 observed during temperature changes were averaged to calculate a factor for the pressure change with temperature given in Eq. 4-7. This factor was used in Eq. 4-8 to calculate the pressure corrected to the temperature set point, giving the temperature-corrected values shown in Figure 7-1. The temperature was controlled within about 1 °C of the set point, with the exception of larger variations during the first days of heating (refer to Figures A-2, A-4, A-6, and A-8).

Figure A-1. Pressure in Reactors G1 and G2, Undiluted Waste.

Figure A-2. Temperature of Heated Reactors G1 and G2 (Undiluted Waste).

Figure A-3. Pressure in Reactors G1 and G2, Diluted Waste at 65 °C.

Figure A-4. Temperature (Celsius) of Reactors G1 and G2, Diluted Waste.

Figure A-5. Pressure in Reactors G1 and G2 at Higher Temperature, Diluted Waste.

Figure A-6. Temperature (Celsius) of Reactors G1 and G2, Diluted Waste.

Figure A-7. Pressure in Reactors G1 (Upper Curve) and G2 (Lower) for 101-SY Material With O_2/He Cover Gas.

Figure A-8. Temperature in Reactors G1 and G2 (O_2/He Cover Gas).
A-5

APPENDIX B: MASS SPECTROMETRIC DATA

Table B-1 gives the results for analyses of the individual gas sample bulbs. The data in Table B-1 are the compositions of the gas sample bulbs (in Mole%). The amount of cover gas (and of air) are subtracted to generate Table B-2, the composition of the product gas after renormalization. Table B-3 gives the composition of the gas, after subtracting any air present and renormalizing. The results are arranged to show results in approximate chronological order (the sampling date is shown as Column 1 in Table B-3, with the year not listed for dates in 1995). The sample bulb order has the bulbs collected from Reactor G1 listed before the bulbs collected from Reactor G2 for that sampling. Table B-1 has columns giving a short label of the sample; the sample bulb number (the order in the table); and the percentage composition in the gas sample bulb (Vol% or Mole%) for argon (Ar), helium (He), hydrogen (H_2), methane (CH_4), nitrogen (N_2), oxygen (O_2), nitrous oxide (N_2O), other nitrogen oxides (NO_x), ammonia (NH_3 , estimates only), and ethane (C_2H_6 , which would include any contribution from other C_2 species).

Table B-2 has columns that give: the relative amount of gas in bulb (used as weighting factor to compute average gas composition); the sample label; the approximate temperature ($^{\circ}C$) of the reactor when the sample bulb was filled; the sample bulb number; the percentage of air estimated to be in the sample; the estimated percentage of the sample that is product gas (i.e., gas other than cover gas); the percentage composition of the product gas (Vol%, or Mole%) for hydrogen (H_2), nitrous oxide (N_2O), nitrogen (N_2), ammonia (NH_3 , estimates only), methane (CH_4), and other nitrogen oxides (NO_x); and the N_2O/H_2 ratio. Small amounts of other hydrocarbons (C_xH_y , where x is 3 or 4) were sometimes reported. Carbon monoxide (CO) and carbon dioxide (CO_2) were almost always less than detection limits. No other gases were reported.

Table B-3 has columns giving the date the sample was collected (month and day only for 1995); the sample labels; the sample bulb number; the percentage composition of the gas in the sample bulb after subtracting any air and renormalizing (for the bulbs from the O_2/He cover gas experiments for bulb numbers 24 to 76, the renormalization ignores the O_2 to give relative concentrations (Vol%, or Mole%) for helium (He), hydrogen (H_2), nitrous oxide (N_2O), nitrogen (N_2), ammonia (NH_3 , estimates only), methane (CH_4), other nitrogen oxides (NO_x), and oxygen (O_2). The final column gives the N_2/N_2O ratio.

Key to Sample Labels

G1	- G1 and G2 refer to Reactors G1 and G2.
OH	- OH designates for material diluted with NaOH.
Ini	- Ini (or In) for initial filling (before heating).
65C	- 65C designates sample collected after heating at 65 °C.
100C	- 65C designates sample collected after heating at 100 °C.
ManGas	- He sample from manifold (test for valve leak during heating).
G1,He	- Undiluted material, He cover gas, heated at 100 °C.
G1,He,24hr	- Collected 24 hr after first sample (Bulb 14).
G1,O2,F1In	- O ₂ /He cover gas, Fill 1, initial filling of Reactor G1.
G1,O2,F1	- O ₂ /He cover gas, sample at end of Fill 1.
G,O2,F5Ini	- O ₂ /He cover gas, Fill 5, initial filling of both reactors.

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Table B-1. Percentage Composition in Gas Sample Bulbs

Sample	#	Ar	He	H2	CH4	N2	O2	N2O	NOx	NH3	C2H6
G1,OH,ini	1	0.002	99.76	0.04	<.01	0.13	0.02	0.03	<.01	<.01	<.01
G1,OH,65C	2	0.005	97.70	0.41	0.02	0.76	0.01	1.05	<.05	<.01	<.01
G1,OH,65C	3	0.002	97.80	0.42	0.02	0.72	0.00	1.00	<.05	<.01	0.01
G2,OH,ini	4	0.002	99.75	0.05	<.01	0.11	0.01	0.03	<.01	<.01	<.01
G2,OH,65C	5	0.005	97.70	0.46	0.02	0.77	0.01	0.91	<.05	0.1	0.01
G2,OH,65C	6	0.002	97.90	0.46	0.02	0.72	0.01	0.86	<.05	<.01	0.01
G2,OH,65C	7	0.004	97.20	0.47	0.03	0.78	0.01	0.93	0.34	0.2	0.01
G1,OH,100C	8	0.003	19.10	15.00	3.60	16.50	0.00	44.10	0.26	1.3	0.09
G1,OH,100C	9	0.002	19.90	15.70	3.60	16.60	<.001	43.90	0.17	0.1	0.08
G2,OH,100C	10	0.005	24.10	18.50	4.60	18.00	0.01	32.80	0.10	1.6	0.10
G2,OH,100C	11	0.004	24.90	19.20	4.60	18.00	0.00	32.90	0.19	0.2	0.10
G2,OH,100C	12	0.009	24.80	19.00	4.60	17.80	0.02	32.20	0.36	1.1	0.10
ManGas	13	<.001	99.88	0.02	<.001	0.08	<.001	0.03	<.01	<.01	<.01
G1,He	14	0.004	29.10	16.50	2.13	18.80	0.02	32.30	0.38	0.7	0.08
G1,He	15	0.009	24.30	16.60	4.02	21.50	0.07	30.80	0.26	2.4	0.12
G1,He,24hr	16	0.009	10.80	23.50	5.83	26.30	0.08	32.10	0.25	1.0	0.17
G1,He,70hr	17	0.010	9.40	23.60	6.90	27.30	0.08	30.70	0.22	1.7	0.19
G1,He,70hr	18	0.027	6.20	24.80	7.10	26.70	0.15	29.20	0.23	5.4	0.22
G2,He	19	0.003	26.00	13.50	1.45	19.30	0.02	39.00	0.53	0.1	0.08
G2,He	20	0.011	25.10	13.40	1.70	19.80	0.15	38.40	0.31	1.0	0.09
G2,He,24hr	21	0.008	15.00	18.30	4.54	23.00	0.07	35.50	0.61	2.8	0.14
G2,He,70hr	22	0.007	10.70	20.70	6.30	25.70	0.04	34.50	0.28	1.7	0.17
G2,He,70hr	23	0.022	4.50	21.50	7.10	24.20	0.15	27.70	0.21	14.5	0.19
G1,O2,F1In	24	0.015	70.10	0.01	<.001	1.33	28.50	0.03	<.01	<.01	<.01
G1,O2,F1	25	0.002	64.10	15.00	1.07	6.44	0.02	11.00	0.14	2.2	0.03
G1,O2,F1	26	<.001	59.30	16.90	1.91	9.05	0.00	11.20	0.14	1.5	0.04
G1,O2,F1	27	0.003	42.30	18.50	4.93	15.30	0.00	11.80	0.24	6.8	0.08
G2,O2,F1In	28	0.007	71.80	0.02	0.00	0.59	27.50	0.02	<.01	<.01	<.01
G2,O2,F1	29	<.001	53.40	15.20	1.03	8.71	<.001	18.00	0.21	3.4	0.04
G2,O2,F1	30	0.001	52.70	16.70	1.41	9.80	<.001	17.80	0.24	1.3	0.05
G2,O2,F1	31	0.002	36.90	23.20	5.25	15.20	0.00	14.80	0.17	4.3	0.08
G1,O2,F2	32	0.002	80.90	11.60	0.47	2.17	0.01	2.87	0.46	1.4	0.02
G1,O2,F2	33	0.003	73.70	10.60	0.88	2.01	0.01	2.62	0.49	9.6	0.02
G2,O2,F2	34	0.002	80.10	10.80	0.50	2.39	0.00	3.85	0.46	1.9	0.02
G2,O2,F2	35	0.003	71.80	9.77	1.04	2.45	0.01	3.56	0.08	11.2	0.03
G1,O2,F3	36	<.001	79.80	10.80	0.91	3.67	<.001	3.92	0.19	0.7	0.02
G1,O2,F3	37	<.001	75.40	10.70	1.29	4.25	<.001	3.85	0.06	4.5	0.02
G2,O2,F3	38	<.001	82.10	9.10	0.61	3.09	0.00	4.82	0.29	0.1	0.02
G2,O2,F3	39	<.001	75.90	9.40	1.20	3.93	<.001	4.84	0.08	4.6	0.02
G1,O2,F4	40	<.001	93.60	4.35	0.17	0.24	<.001	0.26	0.02	1.4	<.01
G1,O2,F4	41	<.001	88.30	4.33	0.47	0.44	0.00	0.29	0.03	6.1	<.01
G2,O2,F4	42	<.001	94.70	4.11	0.12	0.19	0.00	0.24	0.01	0.6	<.01
G2,O2,F4	43	<.001	89.00	4.03	0.43	0.28	0.00	0.25	0.03	6.0	0.01

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Table E-1. Percentage Composition in Gas Sample Bulbs (Cont.)

Sample	#	Ar	He	H2	CH4	N2	O2	N2O	NOx	NH3	C2H6
G,02,F5Ini	44	<.001	69.00	<.001	<.001	0.01	30.90	<.001	0.01	0.0	<.01
G1,02,F5	45	<.001	89.80	1.30	0.03	0.06	8.40	0.02	0.01	0.4	<.01
G1,02,F5	46	<.001	86.10	1.25	0.24	0.07	7.90	0.03	0.03	4.4	<.01
G2,02,F5	47	<.001	90.20	1.24	0.05	0.07	7.62	0.03	0.02	0.8	<.01
G2,02,F5	48	<.001	86.50	1.21	0.25	0.07	7.09	0.03	0.04	4.8	<.01
G1,02,F6	49	<.001	96.68	2.89	0.02	0.07	0.03	0.04	0.01	0.3	<.01
G1,02,F6	50	<.001	92.03	2.77	0.26	0.08	0.00	0.05	0.03	4.8	<.01
G2,02,F6	51	<.001	96.78	2.44	0.04	0.06	<.001	0.04	0.01	0.6	<.01
G2,02,F6	52	<.001	91.83	2.34	0.28	0.08	0.00	0.05	0.03	5.4	<.01
G1,02,F7	53	<.001	93.94	3.30	0.05	0.09	1.91	0.08	0.02	0.6	<.01
G1,02,F7	54	<.001	87.70	5.37	0.28	0.48	1.71	0.14	0.04	4.3	<.01
G2,02,F7	55	<.001	95.56	2.86	0.05	0.07	0.85	0.05	0.01	0.6	<.01
G2,02,F7	56	<.001	91.50	3.34	0.23	0.13	0.77	0.06	0.03	3.9	<.01
G,02,F8Ini	57	<.001	68.70	<.001	<.001	0.01	31.30	<.005	<.01	0.0	<.01
G1,02,F8	58	<.001	88.00	1.87	0.01	0.07	10.00	0.03	<.01	0.1	<.01
G1,02,F8	59	<.001	83.10	2.81	0.25	0.13	9.10	0.05	0.04	4.5	<.01
G2,02,F8	60	<.001	87.70	1.50	0.02	0.05	10.30	0.03	0.02	0.4	<.01
G2,02,F8	61	<.001	83.40	2.64	0.22	0.08	9.50	0.06	0.03	4.0	<.01
G,02,F9Ini	62	<.001	69.00	<.001	<.001	0.01	31.00	<.01	<.01	0.0	<.01
G1,02,F9	63	<.001	95.42	4.25	0.05	0.13	0.01	0.13	<.01	<.01	<.01
G1,02,F9	64	<.001	81.20	11.70	0.43	1.85	0.00	0.55	0.03	4.3	0.01
G2,02,F9	65	<.001	96.26	3.31	0.05	0.09	<0.001	0.08	0.01	0.2	<.01
G2,02,F9	66	<.001	81.70	11.40	0.41	1.15	0.00	0.47	0.02	4.8	0.01
G,02,F10In	67	<.001	68.90	<.001	<.001	0.00	31.00	<.01	<.01	<.01	<.01
G1,02,F10	68	<.001	87.80	1.57	0.02	0.06	10.10	0.04	0.02	0.4	<.01
G1,02,F10	69	<.001	82.20	3.56	0.25	0.33	9.20	0.09	0.03	4.3	<.01
G2,02,F10	70	<.001	90.00	1.71	0.02	0.04	7.90	0.04	0.02	0.3	<.01
G2,02,F10	71	<.001	82.60	5.20	0.27	0.18	6.90	0.14	0.03	4.7	<.01
G,02,F11In	72	<.001	69.00	<.001	<.001	<.001	31.00	<.01	<.01	<.01	<.01
G1,02,F11	73	<.001	95.17	3.78	0.10	0.13	0.08	0.13	0.01	0.6	<.01
G1,02,F11	74	<.001	75.70	14.30	0.67	2.60	0.07	1.03	0.04	5.6	0.01
G2,02,F11	75	<.001	95.43	3.48	0.10	0.13	0.01	0.10	0.01	0.7	<.01
G2,02,F11	76	<.001	73.70	15.90	0.71	2.30	0.01	1.03	0.04	6.3	0.01

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Table B-2. Relative Amount, Sample Temperature (°C), Percentages of Air and Product Gas; Percentage Composition of Product Gas; N₂O/H₂ Ratio.

Amt	Sample	#	T	Air%	Prod%	Percentage Composition Product Gas						
						H2	N2O	N2	NH3	CH4	NOx	N2O/H2
1.00	G1,OH,Ini	1	23	0.17	0.07	51.01	48.99	-0.0	0.0	0.00	0.00	0.96
0.32	G1,OH,65C	2	65	0.42	1.85	22.26	56.88	18.9	0.0	0.87	0.00	2.55
0.68	G1,OH,65C	3	23	0.17	2.02	20.76	49.44	27.3	0.0	0.99	0.00	2.38
1.00	G2,OH,Ini	4	23	0.13	0.08	63.64	36.36	0.0	0.0	0.00	0.00	0.57
0.28	G2,OH,65C	5	65	0.42	1.87	24.60	48.76	19.1	4.8	1.07	0.00	1.98
0.61	G2,OH,65C	6	23	0.17	1.93	24.03	44.64	28.7	0.0	1.04	0.00	1.86
0.11	G2,OH,65C	7	23	0.35	2.49	18.80	37.28	18.2	9.7	1.21	13.69	1.98
0.43	G1,OH,100C	8	100	0.25	80.85	18.61	54.70	20.2	1.6	4.47	0.32	2.94
0.57	G1,OH,100C	9	23	0.17	80.08	19.62	54.87	20.5	0.1	4.50	0.21	2.80
0.37	G2,OH,100C	10	100	0.42	75.76	24.57	43.55	23.4	2.1	6.11	0.13	1.77
0.49	G2,OH,100C	11	23	0.34	75.04	25.65	43.95	23.6	0.2	6.15	0.25	1.71
0.14	G2,OH,100C	12	23	0.76	75.01	25.52	43.26	22.9	1.5	6.18	0.48	1.69
1.00	ManGas	13	23	0.00	0.12	13.43	23.40	63.2	0.0	0.00	0.00	1.74
0.26	G1,He	14	100	0.35	70.80	23.38	45.77	26.2	1.0	3.02	0.54	1.96
0.26	G1,He	15	100	0.81	75.53	22.13	41.06	27.7	3.2	5.36	0.35	1.86
0.22	G1,He,24hr	16	100	0.82	89.12	26.55	36.27	28.9	1.1	6.59	0.28	1.37
0.22	G1,He,70hr	17	23	0.91	90.54	26.23	34.12	29.4	1.9	7.67	0.24	1.30
0.03	G1,He,70hr	18	23	2.40	93.65	27.11	31.92	26.8	5.9	7.76	0.25	1.18
0.25	G2,He	19	100	0.27	73.92	18.32	52.92	25.9	0.1	1.97	0.72	2.89
0.25	G2,He	20	100	1.06	74.62	18.16	52.03	25.6	1.3	2.30	0.42	2.87
0.19	G2,He,24hr	21	100	0.74	84.90	21.70	42.10	26.5	3.3	5.38	0.72	1.94
0.26	G2,He,70hr	22	23	0.62	89.25	23.31	38.85	28.3	1.9	7.09	0.32	1.67
0.05	G2,He,70hr	23	23	1.98	95.41	22.97	29.59	23.9	15.5	7.58	0.22	1.29
1.00	G1,O2,F1Ini	24	23	1.58	0.14	9.83	18.48	71.7	0.0	0.00	0.00	1.88
0.30	G1,O2,F1	25	94	0.17	35.79	41.98	30.78	17.6	6.2	2.99	0.39	0.73
0.54	G1,O2,F1	26	23	0.01	40.73	41.48	27.49	22.2	3.7	4.69	0.34	0.66
0.16	G1,O2,F1	27	23	0.28	57.57	32.23	20.56	26.2	11.8	8.59	0.42	0.64
1.00	G2,O2,F1Ini	28	23	0.74	0.06	27.18	41.03	25.0	0.0	6.84	0.00	1.51
0.24	G2,O2,F1	29	94	0.00	46.60	32.62	38.63	18.7	7.3	2.21	0.45	1.18
0.61	G2,O2,F1	30	23	0.09	47.26	35.37	37.69	20.6	2.8	2.99	0.51	1.07
0.14	G2,O2,F1	31	23	0.15	63.02	36.90	23.54	23.9	6.8	8.35	0.27	0.64
0.78	G1,O2,F2	32	23	0.20	18.86	61.68	15.26	10.5	7.4	2.50	2.45	0.25
0.22	G1,O2,F2	33	23	0.26	26.08	40.77	10.08	6.8	36.9	3.38	1.88	0.25
0.75	G2,O2,F2	34	23	0.15	19.81	54.59	19.46	11.3	9.6	2.53	2.33	0.36
0.25	G2,O2,F2	35	23	0.28	27.97	35.05	12.77	7.8	40.2	3.73	0.29	0.36
0.77	G1,O2,F3	36	23	0.00	20.20	53.46	19.40	18.1	3.5	4.50	0.94	0.36
0.23	G1,O2,F3	37	23	0.00	24.65	43.38	15.61	17.2	18.2	5.23	0.24	0.36
0.78	G2,O2,F3	38	23	0.01	17.97	50.61	26.81	17.2	0.3	3.39	1.61	0.53
0.22	G2,O2,F3	39	23	0.00	24.07	39.06	20.11	16.3	19.1	4.99	0.33	0.51
0.77	G1,O2,F4	40	45	0.00	6.43	67.63	4.01	3.7	21.8	2.64	0.23	0.06
0.23	G1,O2,F4	41	45	0.01	11.65	37.18	2.49	3.7	52.4	4.02	0.22	0.07
0.76	G2,O2,F4	42	45	0.01	5.26	78.14	4.62	3.5	11.4	2.21	0.17	0.06
0.24	G2,O2,F4	43	45	0.01	11.02	36.58	2.24	2.5	54.5	3.87	0.25	0.06

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Table B-2. Relative Amount, Sample Temperature (°C), Percentages of Air and Product Gas; Percentage Composition of Product Gas; N₂O/H₂ Ratio (Cont.).

Amt	Sample	#	T	Air%	Prod%	Percentage Composition				Product Gas		
						H2	N2O	N2	NH3	CH4	NOx	N2O/H2
1.00	G,02,F5Ini	44	45	0.01	0.03	0.00	0.00	3.3	74.4	0.00	22.31	NA
0.78	G1,02,F5	45	45	0.01	1.82	71.59	1.21	3.0	22.0	1.38	0.77	0.02
0.22	G1,02,F5	46	45	0.01	6.01	20.80	0.47	1.1	73.2	3.96	0.52	0.02
0.77	G2,02,F5	47	45	0.01	2.19	56.52	1.14	3.0	36.5	2.05	0.82	0.02
0.23	G2,02,F5	48	45	0.01	6.40	18.90	0.45	1.0	75.0	3.97	0.66	0.02
0.78	G1,02,F6	49	45	0.01	3.29	87.79	1.34	2.1	7.9	0.55	0.30	0.02
0.22	G1,02,F6	50	45	0.01	7.98	34.69	0.60	1.0	60.1	3.24	0.38	0.02
0.78	G2,02,F6	51	45	0.00	3.22	75.90	1.31	1.7	19.6	1.18	0.31	0.02
0.22	G2,02,F6	52	45	0.01	8.16	28.67	0.55	0.9	66.2	3.37	0.37	0.02
0.77	G1,02,F7	53	45	0.01	4.15	79.48	1.81	2.0	14.9	1.25	0.48	0.02
0.23	G1,02,F7	54	45	0.01	10.60	50.64	1.30	4.5	40.6	2.67	0.38	0.03
0.78	G2,02,F7	55	45	0.01	3.58	79.85	1.31	1.9	15.4	1.34	0.28	0.02
0.22	G2,02,F7	56	45	0.01	7.69	43.46	0.79	1.6	50.7	3.02	0.39	0.02
1.00	G,02,F8Ini	57	45	0.01	0.01	NA	NA	NA	NA	NA	NA	NA
0.78	G1,02,F8	58	45	0.01	2.04	91.85	1.33	3.0	3.4	0.34	0.00	0.01
0.22	G1,02,F8	59	45	0.01	7.78	36.14	0.63	1.7	57.9	3.16	0.51	0.02
0.78	G2,02,F8	60	45	0.01	1.96	76.53	1.28	2.3	17.9	0.97	1.02	0.02
0.22	G2,02,F8	61	45	0.01	7.02	37.64	0.78	1.0	57.0	3.08	0.43	0.02
1.00	G,02,F9Ini	62	45	0.01	0.01	NA	NA	NA	NA	NA	NA	NA
0.77	G1,02,F9	63	45	0.01	4.55	93.39	2.86	2.8	0.0	0.99	0.00	0.03
0.23	G1,02,F9	64	45	0.01	18.85	62.03	2.92	9.8	22.8	2.28	0.16	0.05
0.78	G2,02,F9	65	45	0.00	3.73	88.79	2.09	2.4	5.4	1.21	0.13	0.02
0.22	G2,02,F9	66	45	0.01	18.26	62.46	2.58	6.3	26.3	2.25	0.11	0.04
1.00	G,02,F10Ini	67	45	0.01	-0.00	NA	NA	NA	NA	NA	NA	NA
0.77	G1,02,F10	68	45	0.01	2.11	74.45	2.04	2.7	19.0	1.09	0.71	0.03
0.23	G1,02,F10	69	45	0.01	8.56	41.61	1.03	3.8	50.3	2.88	0.39	0.02
0.78	G2,02,F10	70	45	0.01	2.12	80.66	1.89	1.7	14.2	0.85	0.75	0.02
0.22	G2,02,F10	71	45	0.01	10.52	49.43	1.35	1.7	44.7	2.52	0.32	0.03
1.00	G,02,F11Ini	72	45	0.01	-0.00	NA	NA	NA	NA	NA	NA	NA
0.75	G1,02,F11	73	45	0.01	4.75	79.63	2.72	2.7	12.6	2.11	0.25	0.03
0.25	G1,02,F11	74	45	0.01	24.24	58.99	4.25	10.7	23.1	2.76	0.15	0.07
0.78	G2,02,F11	75	45	0.01	4.51	77.16	2.13	2.8	15.5	2.20	0.16	0.03
0.22	G2,02,F11	76	45	0.01	26.29	60.50	3.92	8.7	24.0	2.70	0.14	0.06

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Table B-3. Date Sampled, Percentage Composition in Gas Sample (No Air), and N₂/N₂O Ratio.

Sampled	Sample	#	Percentage Composition in Gas Sample (No Air)								
			He	H ₂	N ₂ O	N ₂	NH ₃	CH ₄	NO _x	O ₂	N ₂ /N ₂ O
12-1-94	G1,OH,Ini	1	99.93	0.04	0.03	-0.00	0.0	0.00	0.00	0.00	-0.00
1-4	G1,OH,65C	2	98.15	0.41	1.05	0.35	0.0	0.02	0.00	0.00	0.33
1-5	G1,OH,65C	3	97.98	0.42	1.00	0.55	0.0	0.02	0.00	0.00	0.55
12-1-94	G2,OH,Ini	4	99.92	0.05	0.03	0.00	0.0	0.00	0.00	0.00	0.00
1-4	G2,OH,65C	5	98.13	0.46	0.91	0.36	0.1	0.02	0.00	0.00	0.39
1-5	G2,OH,65C	6	98.07	0.46	0.86	0.55	0.0	0.02	0.00	0.00	0.64
1-5	G2,OH,65C	7	97.51	0.47	0.93	0.45	0.2	0.03	0.34	0.00	0.49
3-8	G1,OH,100C	8	19.15	15.04	44.22	16.30	1.3	3.61	0.26	0.00	0.37
3-9	G1,OH,100C	9	19.92	15.71	43.94	16.45	0.1	3.60	0.17	0.00	0.37
3-8	G2,OH,100C	10	24.24	18.61	33.00	17.69	1.6	4.63	0.10	0.00	0.54
3-9	G2,OH,100C	11	24.96	19.25	32.98	17.72	0.2	4.61	0.19	0.00	0.54
3-9	G2,OH,100C	12	24.99	19.15	32.45	17.19	1.1	4.64	0.36	0.00	0.53
6-27	ManGas	13	99.88	0.02	0.03	0.07	0.0	0.00	0.00	0.00	2.70
6-27	G1,He	14	29.20	16.55	32.41	18.53	0.7	2.14	0.38	0.00	0.57
6-27	G1,He	15	24.47	16.72	31.01	20.90	2.4	4.05	0.26	0.00	0.67
6-28	G1,He,24hr	16	10.88	23.66	32.32	25.74	1.0	5.87	0.25	0.00	0.80
6-30	G1,He,70hr	17	9.46	23.75	30.89	26.64	1.7	6.94	0.22	0.00	0.86
6-30	G1,He,70hr	18	6.35	25.39	29.89	25.06	5.5	7.27	0.24	0.00	0.84
6-27	G2,He	19	26.08	13.54	39.12	19.11	0.1	1.45	0.53	0.00	0.49
6-27	G2,He	20	25.38	13.55	38.83	19.11	1.0	1.72	0.31	0.00	0.49
6-28	G2,He,24hr	21	15.10	18.42	35.74	22.49	2.8	4.57	0.61	0.00	0.63
6-30	G2,He,70hr	22	10.75	20.80	34.67	25.25	1.7	6.33	0.28	0.00	0.73
6-30	G2,He,70hr	23	4.59	21.91	28.23	22.82	14.8	7.24	0.21	0.00	0.81
7-6	G1,O2,F1Ini	24	99.81	0.02	0.04	0.14	0.0	0.00	0.00	40.10	3.88
7-27	G1,O2,F1	25	64.21	15.02	11.02	6.29	2.2	1.07	0.14	0.00	0.57
7-28	G1,O2,F1	26	59.27	16.89	11.19	9.04	1.5	1.91	0.14	0.00	0.81
7-28	G1,O2,F1	27	42.43	18.56	11.84	15.07	6.8	4.94	0.24	0.00	1.27
7-6	G2,O2,F1Ini	28	99.92	0.02	0.03	0.02	0.0	0.01	0.00	38.05	0.61
7-27	G2,O2,F1	29	53.40	15.20	18.00	8.71	3.4	1.03	0.21	0.00	0.48
7-28	G2,O2,F1	30	52.74	16.71	17.81	9.72	1.3	1.41	0.24	0.00	0.55
7-28	G2,O2,F1	31	36.98	23.25	14.83	15.09	4.3	5.26	0.17	0.00	1.02
8-1	G1,O2,F2	32	81.14	11.63	2.88	1.99	1.4	0.47	0.46	0.00	0.69
8-1	G1,O2,F2	33	73.92	10.63	2.63	1.77	9.6	0.88	0.49	0.00	0.67
8-1	G2,O2,F2	34	80.19	10.81	3.85	2.24	1.9	0.50	0.46	0.00	0.58
8-1	G2,O2,F2	35	72.03	9.80	3.57	2.19	11.2	1.04	0.08	0.00	0.61
8-9	G1,O2,F3	36	79.80	10.80	3.92	3.67	0.7	0.91	0.19	0.00	0.94
8-9	G1,O2,F3	37	75.35	10.69	3.85	4.24	4.5	1.29	0.06	0.00	1.10
8-9	G2,O2,F3	38	82.03	9.09	4.82	3.08	0.1	0.61	0.29	0.00	0.64
8-9	G2,O2,F3	39	75.93	9.40	4.84	3.93	4.6	1.20	0.08	0.00	0.81
8-14	G1,O2,F4	40	93.57	4.35	0.26	0.24	1.4	0.17	0.01	0.00	0.93
8-14	G1,O2,F4	41	88.35	4.33	0.29	0.43	6.1	0.47	0.03	0.00	1.49
8-14	G2,O2,F4	42	94.74	4.11	0.24	0.18	0.6	0.12	0.01	0.00	0.75
8-14	G2,O2,F4	43	88.98	4.03	0.25	0.28	6.0	0.43	0.03	0.00	1.13

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Table B-3. Date Sampled, Percentage Composition in Gas Sample (No Air), and N₂/N₂O Ratio (Cont.).

Sampled	Sample	#	Percentage Composition in Gas Sample (No Air)								N ₂ /N ₂ O
			He	H ₂	N ₂ O	N ₂	NH ₃	CH ₄	NO _x	O ₂	
8-14	G,02,F5Ini	44	99.96	0.00	0.00	0.00	0.0	0.00	0.01	44.76	NA
8-16	G1,02,F5	45	98.02	1.42	0.02	0.06	0.4	0.03	0.02	9.17	2.50
8-16	G1,02,F5	46	93.47	1.36	0.03	0.07	4.8	0.26	0.03	8.58	2.28
8-16	G2,02,F5	47	97.63	1.34	0.03	0.07	0.9	0.05	0.02	8.25	2.64
8-16	G2,02,F5	48	93.11	1.30	0.03	0.07	5.2	0.27	0.05	7.63	2.31
8-22	G1,02,F6	49	96.71	2.89	0.04	0.07	0.3	0.02	0.01	0.03	1.59
8-22	G1,02,F6	50	92.02	2.77	0.05	0.08	4.8	0.26	0.03	0.00	1.62
8-22	G2,02,F6	51	96.78	2.44	0.04	0.05	0.6	0.04	0.01	0.00	1.31
8-22	G2,02,F6	52	91.84	2.34	0.05	0.07	5.4	0.28	0.03	0.00	1.60
8-25	G1,02,F7	53	95.77	3.36	0.08	0.09	0.6	0.05	0.02	1.95	1.13
8-25	G1,02,F7	54	89.21	5.46	0.14	0.48	4.4	0.29	0.04	1.74	3.43
8-25	G2,02,F7	55	96.39	2.88	0.05	0.07	0.6	0.05	0.01	0.86	1.42
8-25	G2,02,F7	56	92.25	3.37	0.06	0.12	3.9	0.23	0.03	0.78	2.00
8-25	G,02,F8Ini	57	99.98	0.00	0.00	0.00	0.0	0.00	0.00	45.55	NA
8-29	G1,02,F8	58	97.74	2.08	0.03	0.07	0.1	0.01	0.00	11.11	2.29
8-29	G1,02,F8	59	91.44	3.09	0.05	0.14	5.0	0.27	0.04	10.01	2.65
8-29	G2,02,F8	60	97.81	1.67	0.03	0.05	0.4	0.02	0.02	11.49	1.84
8-29	G2,02,F8	61	92.24	2.92	0.06	0.08	4.4	0.24	0.03	10.51	1.31
8-29	G,02,F9Ini	62	99.98	0.00	0.00	0.01	0.0	0.00	0.00	44.92	NA
8-31	G1,02,F9	63	95.45	4.25	0.13	0.13	0.0	0.05	0.00	0.01	0.97
8-31	G1,02,F9	64	81.15	11.69	0.55	1.84	4.3	0.43	0.03	0.00	3.36
8-31	G2,02,F9	65	96.27	3.31	0.08	0.09	0.2	0.05	0.01	0.00	1.15
8-31	G2,02,F9	66	81.74	11.41	0.47	1.15	4.8	0.41	0.02	0.00	2.43
8-31	G,02,F10Ini	67	100.00	0.00	0.00	-0.00	0.0	0.00	0.00	44.99	NA
9-5	G1,02,F10	68	97.65	1.75	0.05	0.06	0.4	0.03	0.02	11.23	1.35
9-5	G1,02,F10	69	90.57	3.92	0.10	0.36	4.7	0.27	0.04	10.14	3.74
9-5	G2,02,F10	70	97.70	1.86	0.04	0.04	0.3	0.02	0.02	8.57	0.90
9-5	G2,02,F10	71	88.70	5.58	0.15	0.19	5.0	0.28	0.04	7.41	1.25
9-5	G,02,F11Ini	72	100.01	0.00	0.00	-0.01	0.0	0.00	0.00	44.93	NA
9-7	G1,02,F11	73	95.25	3.78	0.13	0.13	0.6	0.10	0.01	0.07	-0.98
9-7	G1,02,F11	74	75.74	14.31	1.03	2.60	5.6	0.67	0.04	0.07	2.52
9-7	G2,02,F11	75	95.49	3.48	0.10	0.13	0.7	0.10	0.01	0.01	1.33
9-7	G2,02,F11	76	73.71	15.90	1.03	2.30	6.3	0.71	0.04	0.01	2.23

APPENDIX C: OXYGEN DIFFUSION WITHIN WASTE

The thickness of the surface layer in contact with oxygen in stagnant waste (no mixing of any kind) can be calculated from the diffusion distance. That is, the reacting oxygen will be almost completely reacted by the time it has been in the waste for 6 half-lives $[(1/2)^6 = 0.016]$. (The half-life is the appropriate time measure for the pseudo 1st-order decay of oxygen, see Section 8.2.2). When there is no mixing, only a surface layer has O_2 within it. The mean square distance x travelled in time t by a gas molecule diffusing in a liquid is given by

$$x = (2 D t)^{0.5} \quad (C-1)$$

where D is the diffusion coefficient. The value of D for O_2 in water at 25 °C is $2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ (Perry, *Chemical Engineer's Handbook*, p. 14-26, 1963). Furthermore, the Stokes-Einstein equation shows that D is proportional to the temperature and inversely proportional to the viscosity of the liquid, which is 0.8937 cP (1 centiPoise = 1 mPas) for water at 25 °C (Perry, *ibid*, p. 3-201). For Tank 101-SY, the viscosity of the convective liquid is around 30 cP at the tank temperature of 50 °C (Herting 1992a), so that the expected value of D is $0.8 \times 10^{-6} \text{ cm}^2/\text{s}$. For this value of D , the mean distance travelled in 6 half-lives can be calculated by using the estimated half-life at 50 °C of around 10 days.

$$x = (2 \times 0.8 \times 10^{-6} \times 6 \times 10 \times 24 \times 3600)^{0.5}$$

$$x = 3 \text{ cm}$$

The corresponding mean distance for a period of 1 day is about 0.4 cm.

The present experiment has a larger diffusion distance because of the lower viscosity at the higher temperatures in the tests. At 65 °C the reported viscosity of the waste is about 7 cP; it decreases to about 5 cP at 80 °C (Herting 1992a). A viscosity of 6 cP at 70 °C increases D to $4 \times 10^{-6} \text{ cm}^2/\text{s}$, which increases the mean distance to 0.8 cm for 1 day. During one half-life of the oxygen at 70 °C (1.2 to 3.5 day), the mean diffusion distance would be 0.9 to 1.6 cm. During one half-life an oxygen molecule can diffuse within a waste volume of about 9 to 15 mL (30 to 50% of the total waste volume in the reactor). Thus, diffusion alone is approximately fast enough to allow reaction throughout the waste volume at 70 °C. The decay at 100 °C is probably too fast for diffusion alone. However, waste mixing by convection currents may occur at a rate comparable to the 1 Day⁻¹ decay rates.

The lower temperature in Tank 101-SY increases the value of D , so that the tank has a slower diffusion time. The slower decay of oxygen in contact with waste at tank temperature (47 °C; even lower at the surface) means that the surface layer in contact with oxygen by diffusional mixing will be somewhat thicker layer than the 3 cm value calculated above for the decay at 70 °C. However, waste in the convective layer should mix (via convection) in less time than the time period for diffusion in a stagnant layer (ca. 60 day). Thus the fraction of waste in contact

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with oxygen is likely to be larger than the very small region within a few cm of the surface (<0.5% of the volume).

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