1 of 2

Distribution Category: UC-601

ANL-93/43

ARGONNE NATIONAL LABORATORY

9700 South Cass Avenue

Argonne, IL 60439

RADIOLYTIC AND RADIOLYTICALLY INDUCED GENERATION OF
GASES FROM SYNTHETIC WASTES

FINAL REPORT

D. Meisel, C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr.

Chemistry Division

October 1993

MASTER

Work performed for Westinghouse Hanford Company in accordance with PO M652408.

28

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY.....	2
A. INTRODUCTION.....	4
B. RADIOLYTIC YIELDS OF GASES.....	4
1. Introduction.....	4
2. Experimental.....	5
a. Radiation Sources and Dosimetry	5
b. Gas Measurements	5
c. Solutions and Slurry Preparation	5
3. Results and Discussion.....	7
a. H ₂ Yields from Homogeneous Solutions.....	7
b. N ₂ O Yields from Homogeneous Solutions.....	9
c. Origin of Nitrogen in Radiolytic N ₂ O.....	9
d. H ₂ and N ₂ O Yields from Slurries	16
e. Yields of Other Gases	16
f. Effects of Carbonate, Sulfide, Formate, and Oxalate on Radiolytic Yields.....	20
g. Comparison with Modeling Calculations	21
4. Conclusions.....	23
C. RADIOLYTIC DEGRADATION OF ORGANICS AND THERMAL GENERATION.....	24
1. Introduction.....	24
2. Experimental.....	25
3. Results and Discussion.....	25
a. Effect of Degradation on H ₂ Thermal Generation	25
b. Effect of Degradation on Thermal Generation of N ₂ O	27
c. Effect of Degradation Products on Thermal Generation Rates	37
d. Role of Hydroxylamine.....	37
4. Conclusions.....	37
D. THE FORMALDEHYDE REACTION	39
1. Introduction.....	39
2. Experimental.....	39
a. Procedures.....	39
b. Effect of Formaldehyde Polymers.....	40

3.	Results and Discussion.....	40
a.	Formaldehyde in Simulated Waste Solutions	40
b.	Formaldehyde in Aqueous Solutions.....	44
c.	Computer Modeling	58
d.	Effect of O ₂ on the Thermal Generation of H ₂	61
e.	Source of the Hydrogen Atoms	61
f.	Effect of "Minor" Components on H ₂ Generation from Formaldehyde	65
4.	Conclusions.....	65
E.	EFFECT OF MINOR COMPONENTS	65
1.	Introduction.....	65
2.	Experimental.....	67
3.	Results and Discussion.....	68
a	Effect of "Minor" Components on Radiolytic Yields.....	68
b.	Effect of "Minor" Components on Thermal Generation Rates	73
4.	Conclusions.....	74
F.	GAS RETENTION.....	74
1.	Introduction.....	74
2.	Experimental.....	74
3.	Results and Discussion.....	81
4.	Conclusions.....	83
G.	MECHANISMS OF GAS GENERATION	84
1.	Radiolytic Mechanisms.....	84
2.	Thermal Mechanisms	86
3.	Integrated View.....	86
	REFERENCES.....	91

LIST OF FIGURES

<u>No.</u>		<u>Page</u>
B3-1.	The yield, $G(H_2)$, from slurry SY1-SIM-91A (composition given in Table B3-4) containing 0.3 M EDTA at 30 °C as a function of total dose delivered to the slurry. Dose rates are shown in the figure.	11
B3-2.	The yield, $G(H_2)$, as a function of dose rate for slurry SY1-SIM-91A containing 0.3 M EDTA at 30 °C.	11
B3-3.	Radiolytic yield of H_2 from slurry SY1-SIM-91A containing 0.3 M HEDTA at 30 °C measured at two dose rates.	12
B3-4.	Radiolytic yield of H_2 from slurry SY1-SIM-91A containing 0.065 M each of HEDTA and EDTA, and 0.1 M citrate, measured at two dose rates, at 30 °C. This mixture is the control slurry for the preirradiated slurries.	12
B3-5.	Radiolytic yield of H_2 at 30 °C from slurry SY1-SIM-91A containing 0.3 M IDA measured at two dose rates.....	13
B3-6.	$G(H_2)$ at various doses for slurry SY1-SIM-91A containing 0.3 M EDTA from irradiations at 3.1 krad/min. The values of the least-squares fit parameters are given in the same units shown in the axes labels.....	13
B3-7.	Radiolytic yield of H_2 at 60 °C from standard slurry containing 0.3 M IDA.	14
B3-8.	Radiolytic yield of H_2 at 60 °C from slurry SY1-SIM-91A containing 0.3 M HEDTA.....	14
B3-9.	The yield of N_2O , $G(N_2O)$, at 30 °C vs. dose and for a range of dose rates for slurry SY1-SIM-91A containing 0.3 M EDTA. "Feed solution" (triangles) is the solution used in the preparation of the slurry prior to the 30%-v water distillation (labeled SY1-SIM-91B).....	17
B3-10.	The yield of N_2O at 60 °C vs. dose at a dose rate of 3.5 krad/min for slurry SY1-SIM-91A containing 0.3 M HEDTA.	18
B3-11.	$G(N_2O)$ at 60 °C vs. dose at a dose rate of 3.5 krad/min for slurry SY1-SIM-91A containing 0.3 M EDTA.	18
B3-12.	Yields of ammonia from solution SY1-SIM-91C containing the organic additives shown as a function of dose.	22
C3-1.	Thermal generation of H_2 at 60 °C from preirradiated (dose of 35 Mrad) solution SY1-SIM-91C (solution P) originally containing 0.065 M EDTA. Shown are the rates measured 5 and 46 days after termination of the preirradiation.	28

LIST OF FIGURES (Cont'd.)

<u>No.</u>		<u>Page</u>
C3-2.	The dependence of the (initial) rate of thermal generation of H ₂ and N ₂ O at 60 °C on total dose of preirradiation for solution SY1-SIM-91C containing 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate (POI). Experimental details are given in Table C3-2. The dashed line is the estimated rate for 101-SY.....	30
C3-3.	Thermal generation of H ₂ at 60 °C following 16 Mrad preirradiation of SY1-SIM-91C containing (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate.	32
C3-4.	Thermal generation of H ₂ at 60 °C following 24 Mrad preirradiation of solution SY1-SIM-91C containing (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate.	33
C3-5.	Thermal generation of H ₂ at 60 °C from preirradiated slurry SY1-SIM-91A with (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate.....	34
C3-6.	Thermal generation of H ₂ at 60 °C from preirradiated slurry SY1-SIM-91A with 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate (SOI). The slurry was dissolved prior to degassing and running the reaction. The dissolution dilutes all concentrations to ~55% of their original value; [H ₂] is back-calculated to correct for this dilution.	35
C3-7.	Thermal generation of H ₂ at 60 °C from control slurry SY1-SIM-91A with (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate. Dissolved and "not dissolved", aged and fresh slurries were used as shown in the legend. The dissolution dilutes all concentrations to ~ 55% of their original value; [H ₂] is back-calculated to correct for this dilution.....	36
C3-8.	The ratio of initial rates of N ₂ O and H ₂ generation from solution SY1-SIM-91C containing 0.065 M each of EDTA and HEDTA, and 0.1 M citrate (sodium salts), as a function of preirradiation dose.	38
C3-9.	Rate and yield of N ₂ O generation at 60 °C from SY1-SIM-91C (solution P) containing 0.01 M NH ₂ OH.....	41
D2-1.	Test for leakage of H ₂ in/out of the modified Erlenmeyer vessels during the time of a thermal decomposition experiment. 50 µl of H ₂ was injected into 10 ml of 2.3 M NaOH at 60 °C and the amount of H ₂ in the gas phase determined at various times.....	42
D2-2.	The rate of generation of H ₂ from 1.67 mM trioxane in 2.3 M NaOH at 60 °C.....	43
D3-1.	Thermal generation of H ₂ from solution SY1-SIM-91C containing 0.065 M formaldehyde at 23, 45, and 60 °C.	45
D3-2.	Determination of the activation energy for the reaction assumed to be as shown in the title.....	46

LIST OF FIGURES (Cont'd.)

<u>No.</u>		<u>Page</u>
D3-3.	Activation energy for the H ₂ generation reaction from glyoxylate in SY1-SIM-91C. The reaction is assumed to be as shown in the title.....	47
D3-4.	Rate of H ₂ generation at 60 °C from 2.3 M NaOH (no NO _x or aluminate) solution at various HCHO concentrations.....	48
D3-5.	Rate of H ₂ generation at 60 °C from 5 mM HCHO (no NO _x or aluminate) solution at various NaOH concentrations	49
D3-6.	Rate of H ₂ generation from 0.065 M HCHO and 2.3 M NaOH (no NO _x or aluminate) solution at three temperatures.....	50
D3-7.	Arrhenius plot for the rate constant of the H ₂ generation reaction in aqueous solution containing 2.3 M NaOH and 0.065 M HCHO	51
D3-8.	Generation of H ₂ from 5 mM HCHO in aqueous solutions at three NaOH concentrations, at 60 °C.....	53
D3-9.	Generation of H ₂ from aqueous solutions of 0.065 M HCHO and 2.3 M NaOH, at 60 °C.....	54
D3-10.	Generation of H ₂ from aqueous solutions of 0.5 mM HCHO and 2.3 M NaOH, at 60 °C.....	55
D3-11.	The dependence of the initial rate of H ₂ generation in aqueous solution on [HCHO] (circles; at 2.3 M NaOH) and on [NaOH] (squares; at 5 mM HCHO)	56
D3-12.	Log of the initial rate of H ₂ generation from formaldehyde in aqueous solution at 60 °C as a function of log([OH ⁻]). The slope, n, represents the order of the reaction in [OH ⁻].	57
D3-13.	Computation of the generation of H ₂ from solution P (SY1-SIM-91C) containing various concentrations of HCHO and OH ⁻ at 60 °C. Curves are calculated using the parameters given in Table D3-3 as Fit 1. Points are experimental data	60
D3-14.	Effect of oxygen concentration on the rate of generation of H ₂ from 0.065 M HCHO in solution SY1-SIM-91C	62
D3-15.	Effect of oxygen concentration on the rate of generation of H ₂ from 0.065 M HCHO in 2.3 M NaOH	63
D3-16.	The effect of the "minor" components (shown in title to the figure) on the rate of H ₂ generation from solution SY1-SIM-91C containing formaldehyde at the concentrations indicated at 60 °C.....	66

LIST OF FIGURES (Cont'd.)

<u>No.</u>		<u>Page</u>
E3-1.	The rate of thermal generation of H_2 from preirradiated (16 Mrad) solutions SY1-SIM-91C containing organics (designated POI) and "minor" components at 60 °C. Solid circles: all minor components except Pd(IV). Open squares: all minor components including Pd	75
E3-2.	The rate of thermal generation of N_2O from preirradiated (35.8 Mrad) solutions SY1-SIM-91C containing organics and minor components at 60 °C. Solid triangles: all minor components. Open circles: all minor components except Cr(III)	76
E3-3.	The rate of thermal generation of N_2O from control SY1-SIM-91C containing organics and all minor components, but not preirradiated, at 60 °C.....	77
E3-4.	The rate of thermal generation of N_2O from solution SY1-SIM-91C containing 0.01 M NH_2OH and 5 mM $Cr(NO_3)_3$ at 60 °C. The rate is an order of magnitude smaller than in the absence of Cr(III).....	78
F2-1.	Pressurization cell and extraction vessel inside the housing. The internal cell was also used for gas bubbling	80
F2-2.	Extraction vessel of retained gas and related connections	82

LIST OF TABLES

<u>No.</u>	<u>Page</u>
B2-1. Composition of standard solutions and slurries	6
B3-1. Yields, $G(H_2)$, and efficiencies, R_X , at 30 and 60 °C	8
B3-2. Rate constants, k_1 , and activation energies, E_a , for the hydrogen abstraction reaction: $H + RH \rightarrow H_2 + R$	8
B3-3. $G(N_2O)$ from irradiation of solution SY1-SIM-91C containing various additives at 30 and 60 °C	10
B3-4. Radiolytic yields of H_2 for slurries compared with homogeneous solutions.....	15
B3-5. Radiolytic yields of N_2O for slurries compared with homogeneous solutions.....	15
B3-6. $G(N_2)$ from solution SY1-SIM-91C under various experimental conditions.	19
B3-7. Effect of formate and oxalate on $G(H_2)$ in SY1-SIM-91C.	21
C3-1. Rates of thermal generation of H_2 and N_2O at 60 °C from slurries and homogeneous solutions. Numbers in parenthesis are days elapsed from end of preirradiation to measurement of the thermal reaction.	29
C3-2. Rates of thermal generation of H_2 and N_2O at 60 °C from solution SY1-SIM-91C containing 0.065 M of EDTA, HEDTA and 0.1 M citrate following various doses of preirradiation.....	31
D3-1. H_2 production vs. $[NaOH]$ and $[HCHO]$ in aqueous solution.....	52
D3-2. H_2 production vs. $[NaOH]$ and $[HCHO]$ in aqueous solution at 60 °C	52
D3-3. Parameters obtained from the model calculations.....	59
D3-4. Isotopic composition of the dihydrogen generated from formaldehyde or glyoxylate in basic solutions of various isotopic compositions.....	64
E2-1. Composition of homogeneous solution and slurry used to measure the effect of "minor" components	67
E3-1. The effect of minor components on $G(H_2)$ in solution SY1-SIM-91C containing 0.065 M HEDTA, 0.065M EDTA, and 0.1 M citrate.....	69
E3-2. The effect of Pd(IV) in SY1-SIM-91C solution containing 0.065 H MEDTA, 0.065 M EDTA, and 0.1 M citrate on H_2 yields.....	70

LIST OF TABLES (Cont'd.)

<u>No.</u>	<u>Page</u>
E3-3. Radiolytic H ₂ yields at 30 °C from solution SY1-SIM-91C in the presence of minor components but in the absence of organics.....	71
E3-4. Radiolytic H ₂ yields obtained for slurry SY1-SIM-92A at 30 °C.....	71
E3-5. The effect of minor components on G(N ₂ O) at 30 °C in SY1-SIM-91C solution containing 0.065 M HEDTA, 0.065M EDTA and 0.1 M citrate.....	72
E3-6. Radiolytic yield of N ₂ O obtained for slurry SY1-SIM-92A at 30 °C	72
F3-1. Behavior of N ₂ O and H ₂ in irradiated slurries	83

RADIOLYTIC AND RADIOLYTICALLY INDUCED GENERATION OF GASES FROM SYNTHETIC WASTES

FINAL REPORT

D. Meisel, C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr.

ABSTRACT

In an effort to better understand the chemical processes that lead to the generation and periodic release of gases from waste tanks, such as tank 101-SY, we have studied the radiolytic and thermal generation of H_2 , N_2O , N_2 , O_2 , and NH_3 in nonradioactive waste simulant solutions and slurries. The radiolytic sources for H_2 are e_{aq}^- and its predecessors and H atoms. Direct radiolysis of the water generates some H_2 ($G(H_2) = 0.03$ molecules per 100 eV) and an additional amount comes from the hydrogen abstraction reaction $H + RH \rightarrow H_2 + R\cdot$; the added yield correlates well with the rate constants measured for hydrogen abstraction. Nitrate scavenges e_{aq}^- and its predecessors whereas nitrite is the major H-atom scavenger. Computer modeling shows that if $[NO_3^-]$ is above 0.5 M, and $[NO_2^-]$ is above 2M, the addition of other scavengers will have little effect on the yield of H_2 .

The generation of N_2O requires the presence of organic molecules; the nitrogen atoms in N_2O , however, both come from inorganic sources (NO_2^- , NO_3^-). The dependence of the yield of N_2O on the dose rate suggests that N_2O is produced by a first-order reaction of a radiolytic intermediate competing with a second-order reaction of the same intermediate; as the temperature increases the first-order reaction speeds up and becomes dominant. In the presence of organic molecules, O_2 is efficiently destroyed ($G(O_2) = -7$). Small yields of ammonia were measured and the yields increase linearly with dose indicating that the ammonia is produced from radiolysis of an intermediate. The nitrogen in NH_3 comes from organic chelators, such as EDTA.

The yields of gases in solution depend only weakly on temperature, up to 60 °C. The yield of H_2 in slurries at 30 °C is significantly lower than in solution. However, as the temperature increases more of the solids are soluble and the yields approach those in solution.

The rate of thermal generation of gases increases upon preirradiation, reaches a maximum (at approximately 20 Mrad), and then declines. Therefore, the known radiolytic degradation products of chelators, NTA, IDA, glycolate, glyoxylate, formaldehyde, formate, oxalate, and hydroxylamine were examined for their roles in the thermal generation of H_2 and N_2O at 60 °C. Among these degradation products, only glyoxylate and formaldehyde generate H_2 at significant rates. Hydroxylamine generates N_2O and N_2 at significant rates with standard waste simulants.

The rate of the hydrogen evolution reaction from formaldehyde has been measured under various experimental conditions and at various temperatures relevant to the conditions in the waste tanks. Rate constants and activation energies for formaldehyde and glyoxylate have been determined. The fraction of HCHO producing H_2 increases with decreasing $[HCHO]$, increasing $[OH^-]$, and increasing temperature. From D-labeling experiments we conclude that for most of the H_2 , both atoms come from formaldehyde. In clear distinction, for glyoxylate, only one H atom comes from glyoxylate and the other from H_2O .

The minor components showed no catalytic effects on the generation rates of the gases. In solution or slurry only radiolytically produced Pd intermediate, possibly metallic Pd, strongly retains H_2 , but does not reduce the rate of its generation. Radiolytic yields of N_2O are strongly reduced by Cr(III), but not by other minor components. In irradiated slurry, loose and tight gas were found. The loose gas could be removed by bubbling from the slurry, but the tight gas could be released only by dissolution of the slurry.

SUMMARY

Radioactive wastes are stored in million-gallon tanks at the Hanford site. The wastes in some of these tanks (e.g., tank 101-SY) are known to generate gases, primarily H_2 and N_2O , that are periodically released, generating potentially flammable mixtures during the release. Our goal in this research has been to examine the mechanisms of radiolytic and radiolytically induced thermal generation of gases in solutions and slurries simulating these wastes. Because the radioactive isotopes in the tanks are predominantly β and γ emitters, a ^{60}Co γ source accurately simulates their radiolytic effects.

Reactions of the initial products of aqueous radiolysis (primarily e_{aq}^- and its precursor and H atoms) in high localized concentrations lead to H_2 generation from water. High concentrations of NO_3^- suppress this gas by rapidly reacting with e_{aq}^- and its predecessors. When organics are present, H_2 is also produced by the hydrogen abstraction reaction $H + RH \xrightarrow{k_1} H_2 + R\cdot$. Nitrite suppresses this reaction by reacting with H atoms. Measured rate constants, k_1 , correlate well with the efficiency of various organics in producing H_2 . Computer modeling shows that when $[NO_3^-]$ exceeds approximately 1 M, and $[NO_2^-]$ exceeds 2M no added chemical scavenger will significantly diminish the yield of H_2 over the suppression already achieved by NO_3^- and NO_2^- . The yield of hydrogen at 30 °C was found to be independent of dose rate and dose in waste simulant solutions with or without organics.

The radiolytic formation of N_2O in waste simulant solutions is more complex. No N_2O is produced unless organics are present, but both nitrogen atoms in N_2O come from inorganic sources (NO_2^- , NO_3^-). At 30 °C, $G(N_2O)$ increased three- to fourfold as the dose rate decreased when EDTA or HEDTA (but not IDA) are the organics present. In these cases, there is post-irradiation generation of N_2O that, when included, substantially decreases the observed effect of dose rate on the yield. At 60 °C with EDTA or IDA there is no dose rate effect and no post-irradiation formation of N_2O . This suggests that the N_2O is produced by a first-order reaction of a radiolytic intermediate, competing with a second-order reaction of the same intermediate.

G values for other gases were also measured. A small yield of oxygen, $G(O_2) = 0.08$, was observed in the standard simulant in the absence of organics. However, oxygen is efficiently destroyed, $G(O_2) = -7$, when organic molecules are added. Nitrogen is also generated and organics are required for its production, but N_2O is not a major source of N_2 . Ammonia is produced by the radiolysis of a degradation product of the original chelators; the yield of NH_3 increases linearly with dose, and the nitrogen atom in NH_3 comes from the organic chelator.

Several additives were tested for their effects on $G(H_2)$. Carbonate and Na_2S had only minor effects. Oxalate or formate (known degradation products) have negligible effect on $G(H_2)$ and generated no N_2O upon radiolysis. The yield of hydrogen in the standard slurry hardly depends on dose or dose rate. The yield of H_2 in the solution simulants is only weakly dependent on temperature. It depends more strongly on temperature in the slurry simulants, probably because of the increased solubility of some of the organic salts upon increasing the temperature. $G(N_2O)$ is lower in the slurry than in the solution simulant. We believe that radiation absorbed in the solids is not effective in the generation of gases.

The rate of thermal generation of H_2 following preirradiation increased to a maximum and then declined. Thus, an H_2 -producing intermediate is generated radiolytically and is eventually destroyed by radiolysis. The original chelators EDTA and HEDTA (but not citrate) are largely destroyed at the doses of preirradiation where the thermal rates maximize. Known degradation products of the chelators (NTA, glycolate, glyoxylate, formaldehyde, hydroxylamine, formate, and oxalate) were examined for their roles in the thermal generation of H_2 and N_2O at 60 °C. With oxalate or formate, no H_2 or N_2O was detected. With NTA, IDA, or glycolate the generation rate of H_2 was very slow, whereas with glyoxylate the rate was two orders of magnitude faster and for

formaldehyde it was about three orders of magnitude faster. Therefore, the rate of generation of H_2 from these two intermediates was quantitatively studied.

The effect of formaldehyde and NaOH concentrations on the rate of H_2 generation was studied at 23, 45, and 60 °C. The reaction is first order in formaldehyde and approaches second order in $[OH^-]$ as $[HCHO]$ decreases. The fraction of HCHO that is converted to H_2 increases with decreasing $[HCHO]$, increasing $[OH^-]$, or increasing temperature. Activation energies have been determined. Nitrate, nitrite, and aluminate have little effect on the H_2 generation rate. Deuterium labeling showed that a major portion of H_2 has both atoms from formaldehyde. For glyoxylate, which has only one reactive H atom, one H comes from water. This suggests that the HCHO reaction to give H_2 is unimolecular. Hydroxylamine, a possible degradation product, generates both N_2O and N_2 in the standard simulant at 60 °C. The ratio between the two depends on experimental conditions.

A large number of minor components were tested in solution, and no catalytic effect was found for either the radiolytic or thermal generation rates. Irradiated solutions of Pd(IV), however, retained H_2 . This is due to reduction of the Pd ions by organic radicals, probably to metallic Pd. The reduced Pd(IV) retains H_2 , but does not inhibit its generation. Radiolytic N_2O yields are strongly reduced by Cr(III) in solution or slurry simulants. It also reduced the rate of thermal generation of N_2O from NH_2OH at 60 °C by an order of magnitude. This supports the postulate that hydroxylamine is an intermediate in the mechanism of N_2O generation.

Pressurization, bubbling, and irradiation were tested as methods for introducing H_2 and N_2O into a slurry. All three gave different behaviors for gas retention. Tight and loose gases were found in the irradiated slurry; the loose was easily extracted; the tight only by dissolution of the slurry. The retention is nonspecific, independent of the identity of the gas. The amount retained strongly depends on the history of the slurry.

Finally, a few mechanistic conclusions: NO_2 is the major oxidizing radical in these systems, and its reaction products probably include glyoxylate and formaldehyde as thermal precursors for H_2 , and hydroxylamine for N_2O . The thermal generation of H_2 decreases as irradiation eventually decreases degradation to formaldehyde. From the data, and assuming the H_2 generation rate is 50 mole/day in Tank 101-SY, ~30% comes from radiolytic and the rest from thermal reactions. However, the intermediates that are efficient in the generation of these gases are also generated radiolytically. We estimate that only 10% of the degradation of organics must produce HCHO to account for the H_2 yield in 101-SY.

A. INTRODUCTION

Some of the mixed radioactive wastes in temporary storage tanks at the Hanford site are known to generate mixtures of gases (primarily H_2 and N_2O , but also N_2 , NH_3 , and small quantities of other gases). Of particular concern is tank 241-SY-101, where potentially flammable mixtures of H_2 and N_2O are released periodically. During the last two years, we attempted to determine the role of radiation in the production of H_2 and the other gases in the waste tanks. With sufficient information, one could then propose strategies to substantially decrease the buildup of hazardous gas mixtures. This report summarizes the results and conclusions of this effort. Interim reports have been issued,^{1,2} including a literature report,³ and these will be frequently referred to here.

The yields of the radiolytic generation of gases in homogeneous aqueous solutions, similar in composition to the waste in tank 101-SY were first studied; the yields in a heterogeneous simulant were then determined and compared to the yields of the homogeneous solutions. These are summarized in Section B. It was then discovered that the rate of thermal generation of gases from the simulants is much faster after exposure to irradiation than in its absence. Therefore, the effect of preirradiation on the rate of thermal generation was investigated (Section C). It became clear that the most efficient product to generate hydrogen in the irradiated waste simulants is formaldehyde and its analogs; quantitative determination of the rate of its reaction to thermally generate H_2 followed (Section D). The presence of a large number of compounds in the waste, at relatively low concentrations (thus labeled "minor components"), raised the concern of a possible catalytic effect; none was found, and the results of these studies are given in Section E. Whereas prevention of gas generation will completely alleviate any possible flammability concerns, prevention of the retention of gas in the tank will stabilize the situation and remove most such concerns as well. The phenomenon of gas retention was addressed (Section F); the interaction between gas bubbles and solid particles seems to depend strongly on the particles and the mode of generation of the gas. Extracting conclusions from our studies and applying them to the actual conditions in the tanks is hampered by a lack of information on the chemical composition of the organic compounds in the tank. Nonetheless, we attempt to draw such conclusions in Section G.

B. RADIOLYTIC YIELDS OF GASES

1. Introduction

Over several decades liquid and solid radioactive wastes have accumulated at the Hanford, Washington site. Liquid waste is stored in large tanks containing up to a million gallons. In addition to radioactive isotopes (largely β - or γ -emitting fission products), the solutions contain high concentrations of $NaOH$, $NaNO_3$, $NaNO_2$, $NaAlO_2$, and medium concentrations of dissolved organic complexants (EDTA, HEDTA, NTA, etc.); the fate and present status of the latter are not known. In this section, we focus on the direct role of radiolysis in the generation of gases that are evolved in simulated waste solutions. A literature search³ revealed that much of the detailed information collected on radiolytic processes that generate the gases is inadequate to describe the chemistry in the highly basic and complex solutions and slurries similar to those in 101-SY. Our research has closely defined the mechanism for radiolytic H_2 production. This includes: (1) a portion of the yield that comes directly from water radiolysis; (2) an additional yield, proportional to the rate of $H + RH \rightarrow H_2 + R\cdot$ (where RH is a hydrogen-containing organic compound), accounts for the effect of organic compounds.

Significant knowledge about N_2O formation has been gained, but the mechanism that can describe its generation remains on a qualitative level. We have shown that: (1) organic compounds are necessary for N_2O formation (and the destruction of O_2); (2) the nitrogen in the radiolytically

generated N_2O comes from NO_2^- and/or NO_2^- but not from the organic components, and (3) hydroxylamine is a likely intermediate.

2. Experimental

Details of the experimental techniques used for the studies reported here have been given in a previous report.¹ Below is a brief description of these techniques and some details of additional procedures that were not given in earlier reports.

a. Radiation Sources and Dosimetry

A ^{60}Co source was used to irradiate the samples in syringes (or in stainless steel beakers for preirradiation; see Section C). Dosimetry was done by measuring the production of Fe^{+3} spectrophotometrically in Fricke dosimeter solutions containing 1 mM NaCl. Details were given previously.^{1,4}

b. Gas Measurements

The yields of all gases, except ammonia, were determined by gas chromatography. Emphasis was placed on H_2 , N_2O , N_2 , and O_2 in the irradiated solutions. For the homogeneous solutions, irradiations were carried out in syringes; the gases generated, then, were all below their solubility at 1 atm partial pressure of the gas in the solution. The Van Slyke manometric apparatus was used to extract the gases from these solutions. An Infotronics Model 15C-3 gas chromatograph equipped with a dual column flow system, a thermal conductivity detector, and a recorder-integrator ("ChromJet Integrator," Spectra Physics, Inc.) was used for these measurements. The separating columns were homemade 1/4-inch-diameter, several feet long copper tubing filled with the appropriate separating material (13X molecular sieve for most experiments). Argon was used as a carrier gas for most experiments and the flow rate was adjusted to about 60 cc/min. For H_2 and N_2O , the column temperature was maintained at 23 or 158 °C, respectively. Air (21% oxygen and 78% nitrogen), pure hydrogen, and pure N_2O samples were used to calibrate the apparatus for its response to the corresponding gases. Further details of the Van Slyke apparatus and the gas chromatograph are given in previous reports.^{1,5}

Yields of ammonia were determined by back titration of a standard HCl solution with a standard sodium carbonate solution after bubbling the ammonia through the HCl solution.⁶ Details of the procedure are given in Section B3e below. Mass spectrometry was used primarily to determine the isotopic composition of gases. A differentially pumped 30 cm radius 90° sector magnetic deflection mass spectrometer from Vg-Micromass (MM3001) of 7500 maximum resolving power and 10 kV maximum accelerating voltage was used for these studies. The sensitivity for N_2 is 2.0×10^{-4} ampere/mbar at 8 kV and for H_2 and its isotopes it is smaller by a factor of two.

c. Solutions and Slurry Preparation

Unless otherwise specified, all chemicals were obtained from Aldrich and used as received. For long-time thermal reactions, NaAlO_2 (from ICN) was baked at ~ 900 °C for 6 hrs to remove traces of organic impurities. Concentrations of aluminum in stock solutions of the processed aluminate samples were determined by ICP. The standard waste solution, designated SY1-SIM-91C (at times labeled solution P), was used for most of the studies of homogeneous simulants. Its composition is given in Table B2-1. Other additives, such as organics, transition metals, halide ions, and noble metals were added as needed for the experiment after the SY1-SIM-91C preparation.

The standard slurry, designated SY1-SIM-91A, was prepared following the recipe provided by Herting of WHC. A feed solution (designated SY1-SIM-91B) was prepared to give the following final concentrations: 1.61 M NaOH, 1.54 M NaAlO₂, 2.59 M NaNO₃, 2.24 M NaNO₂, 0.42 M Na₂CO₃, and 0.21 M EDTA. To obtain this composition, NaAlO₂ was added to 250-300 ml of preheated water at 90 °C. The solution was further heated until it became clear. Pellets of NaOH were then added slowly to the solution (if necessary, the solution was heated until clear again). The solution was cooled and Na₂CO₃ was added. Then NaNO₃ and NaNO₂ were added with vigorous stirring, the solution was heated, and 100 ml solution of the sodium salt of EDTA in water was added with stirring until all solids were dissolved. The solution was filtered while hot (≈ 50 °C), through a fritted glass funnel. This solution is labeled SY1-SIM-91B or sometimes just "feed solution". The feed solution was distilled using a "Rotovap" apparatus (at reduced pressure) with the distillation bath temperature maintained at 65-70 °C. The weight loss (measured by measuring the distillate volume) was 32 g water per 100 ml of feed solution. The compositions of the various standard slurries and solutions are given in Table B2-1. Slurry SY1-SIM-92A is discussed in Section E.

Table B2-1. Composition of standard solutions and slurries

	SY1-SIM-91A (standard slurry)	SY1-SIM-91B (feed solution)	SY1-SIM-91C (solution P)	SY1-SIM-92A (Bryan slurry)
NaOH	2.3 M	1.61 M	2.3 M	2.45 M
NaNO ₃	3.7 M	2.59 M	2.8 M	2.2 M
NaNO ₂	3.2 M	2.24 M	2.2 M	3.95 M
NaAlO ₂	2.2 M	1.54 M	0.86 M	2.05 M
Na ₂ CO ₃	0.6 M	0.42 M		0.4 M
Other Components	0.3 M EDTA	0.21 M EDTA		0.526 M NaCl 0.179 M Na ₃ PO ₄ 0.146 M KCl 0.14 M HEDTA 0.14 M EDTA 0.105 M Cr(NO ₃) ₃ 0.1 M NaF 0.032 M Na ₂ SO ₄ 8.3×10 ⁻³ M CaCl ₂ 7.4×10 ⁻³ M Fe(NO ₃) ₃ 2.1×10 ⁻³ M Ni(NO ₃) ₂ 2.1×10 ⁻⁴ M Cu(NO ₃) ₂

3. Results and Discussion

a. H₂ Yields From Homogeneous Solutions

The G(H₂) at 30 °C from SY1-SIM-91C was determined to be independent of dose (30-1000 krad) and dose rate (0.15-20 krad/min). Likewise, over the same dose range, no effect of dose or dose rate was observed on G(H₂) at 30 °C when solution SY1-SIM-91C contained organic solutes (see Figures 2-7 of reference 1).

G(H₂) at 30 °C increases linearly with concentration of the organic in SY1-SIM-91C (Figures 8-12, reference 1), as is expected from the mechanism for H₂ production that includes the hydrogen abstraction reaction:

and as predicted by model calculations (Figure 33 in reference 1). From measurements of G(H₂) with and without organic solutes, the efficiencies, R_x, of several organics, x = RH, were determined at 30 and 60 °C. These R_x values, when multiplied by the molar concentration of the organic, give the increase in G(H₂) by the organic compound above the yield in the same solution without the organic. A summary of the G(H₂) results and the R_x values at 30 and 60 °C is given in Table B3-1. The R_x values at 30 °C are based on results from a series of concentrations of organic additive; the R_x values at 60 °C are based on results with only one concentration of organic additive and are therefore likely to be less accurate. Thus, to a good approximation, G(H₂) can be calculated from eq. B-2.

$$G(H_2) = G(H_2)_{[RH]=0} + R_x \times [RH] \quad (B-2)$$

For compounds not measured, and therefore not listed in Table B3-1, some prediction could be made on their effect on the yield of H₂. A correlation between the R_x values and the number of C-H and N-H bonds, η_{x-H}, in the organic has been noted (Figure 14 of reference 1). The R_x values at 30 °C are given by:

$$R_x = 0.013 \times \eta_{x-H}, \quad (B-3)$$

and thus the yield of hydrogen, for a compound of a known formula but whose effect on G(H₂) has not been measured, can be described by eq. B-4.

$$G(H_2) = 0.031 + 0.013 \times \eta_{x-H} \times [RH]. \quad (B-4)$$

This correlation is not exact, but it does provide some predictive capability for a broad range of organic additives. It should be emphasized that this equation is only of empirical value; it will be followed only for a background solution of the same composition as SY1-SIM-91C. Such an approximate correlation is to be expected from the mechanism of abstraction of H from the organic solute by radiolytically produced H atoms to yield H₂.

Table B3-1 indicates that the efficiency, R_x, of H₂ production by the organic solutes is larger at 60 °C than at 30 °C for all solutes except citrate. In the framework of the mechanism for radiolytic hydrogen production (hydrogen abstraction by H atoms from the organic solute), this result indicates that the rate of hydrogen abstraction reaction increases more upon increasing temperature than increase in the rate of the other reactions with H atoms (most dominating is the reaction with nitrite) that do not produce H₂. This is reflected in the rate constants that we have determined for reaction of hydrogen atoms with organics. The method for these determinations is described in reference 1, and the rate constants for reaction B-1 under conditions similar to those in solution SY1-SIM-91C are summarized in Table B3-2.

Further verification of the impact of reaction B-1 on the yield of H₂ comes from the correlation between k₁ and R_x. If the presence of the organics in SY1-SIM-91C causes an increase in the H₂ yield because of the hydrogen abstraction reaction, the values of the rate constants, k₁, at 30 and

60 °C should correlate with the empirical parameter. A good correlation is indeed observed (Figure 25 of reference¹). Taken together with the known reactions of all other primary radicals from the radiolysis of water, this correlation is a strong indication that the mechanism proposed to explain the effect of organic additives on $G(H_2)$ is correct.

Table B3-1. Yields, $G(H_2)$, and efficiencies, R_x , at 30 and 60 °C.^a

Organic Additive	[X] M	$G(H_2)$ 60 °C	$G(H_2)$ 30 °C	Ratio $\frac{G_{60°C}}{G_{30°C}}$	$R_x(30)$ 30 °C	$R_x(60)$ 60 °C	Ratio, $\frac{R_{x,60°C}}{R_{x,30°C}}$
none	0	0.033	0.031	1.06			
EDTA	0.085	0.053	0.045	1.18	0.167	0.20	1.20
HEDTA	0.085	0.054	0.045	1.20	0.170	0.25	1.45
NTA	0.17	0.054	0.047	1.15	0.094	0.124	1.31
IDA	0.17	0.045	0.041	1.10	0.056	0.071	1.26
citrate	0.17	0.037	0.036	1.03	0.029	0.024	0.81
glycine	0.3	0.045	0.042	1.07	0.038	0.040	1.05
glycolate	0.3	0.055	0.048	1.15	0.055	0.073	1.33
POC	b	0.063	0.045	1.40			
POI	c	0.080	0.047	1.70			

^a Samples irradiated to approximately 140 krad in 30-min irradiations.

^b SY1-SIM-91C with 0.065 M EDTA, 0.065 M HEDTA (sodium salts), and 0.1 M sodium citrate aged at 30 °C for the same period of time as solution POI.^c

^c Same as b, but received 31.5 Mrad at 0.51 krad/min preirradiation; it was then degassed and used as starting material for further irradiation.

Table B3-2. Rate constants, k_1 , and activation energies, E_a , for the hydrogen abstraction reaction:
 $H + RH \rightarrow H_2 + R$

RH	$10^{-9} \times k_1$ at 30 °C $M^{-1} s^{-1}$	$10^{-9} \times k_1$ at 60 °C $M^{-1} s^{-1}$	E_a kcal M^{-1}	$10^{-9} \times k_1$ at 25 °C and pH 1 (literature value)
EDTA	1.2	2.7	5.4	0.065
HEDTA	1.4	1.6	0.9	
NTA	0.6	1.3	5.2	0.0075
IDA	0.55	0.85	2.9	0.00040
glycolate		0.14		
citrate	≈0.007	≈0.02	7.1	0.00043
OH ⁻ a	0.033	0.13	9.2	

^a The reaction rate constants in columns 2 and 3 were measured relative to the known literature values of the rate constants for the reaction $H + OH^- \rightarrow e^-_{aq}$ at the two temperatures.⁸

b. N₂O Yields From Homogeneous Solutions

In SY1-SIM-91C, no N₂O is generated from irradiated samples unless an organic solute is present. A summary of measured G(N₂O) from various solutions at 30 and 60 °C is given in Table B3-3.

The generation of N₂O in SY1-SIM-91C containing organic solutes seems to follow a more complex mechanism than that for H₂ generation. For irradiations at 30 °C, pronounced effects of dose rate (intensity of radiation source) on G(N₂O) were observed when EDTA and HEDTA were the organic additives. The G values increase by a factor of three or four as the intensity decreases from 17 to 0.2 krad/min; however, for IDA there was little change in G(N₂O) with changes in intensity of irradiation. These G values were measured within ~30 min of the end of the irradiation; N₂O production was observed to continue for about 20 hrs after the irradiation, increasing the G value by a factor of about two at 4.2 krad/min (Figure 26 of reference 1). Increasing the dose rate increased this factor. Indeed, if the postirradiation yield of N₂O is included in the G value, the effect of dose rate is substantially diminished. This postirradiation effect and the intensity effect indicate the complexity of the mechanism(s) for producing N₂O.

At 60 °C, no dose rate effect was observed in the two cases where it was examined (EDTA and IDA as additives), and there was no postirradiation production of N₂O. The existence of a dose rate effect at the lower temperature indicates that the reaction that produces N₂O is a first-order (or pseudo first-order) reaction of a radiolytically produced intermediate (e.g., a radical or a short-lived molecule) that competes with a second- (or higher) order reaction of the same intermediate. The vanishing dose rate effect at the higher temperature indicates, in general, that the N₂O-producing reactions, which are slow at 30 °C, are markedly accelerated at 60 °C relative to the competing pathways available to the precursors of N₂O; that is, the second order pathway no longer competes. The postirradiation effect is due to a slower set of thermal reactions than those responsible for the dose rate effect; the irradiation times for which intensity effects were observed are 10-30 minutes, whereas the post irradiation effect occurs on a 100 times slower time scale. This time scale at 30 °C suggests that the key intermediate produced during the radiolysis is a molecule that subsequently reacts to yield N₂O. The lack of postirradiation production of N₂O at 60 °C also means that the slow thermal reactions producing N₂O are markedly accelerated at 60 °C and occur during irradiation times at the higher temperature.

There is little variation of G(N₂O) with total dose, but there is a tendency for G(N₂O) to decline at higher concentrations of the organic additives. Table 7 of reference 1 summarizes the results on G(N₂O) at different concentrations of the organic solutes and at different doses and dose rates. Reproducibility of the G(N₂O) determinations is ±20%, which is markedly poorer than that for the H₂ determinations.

c. Origin of Nitrogen in Radiolytic N₂O

Experiments with ¹⁵N-labeled glycine have been performed to determine what part of the N in N₂O, if any, comes from the organic solutes. Glycine was utilized as a representative N-containing organic additive and is a known radiolytic degradation product of the chelators originally placed in the tank. ¹⁵N-labeled glycine was chosen for this experiment as it is readily available commercially at a reasonable cost. It has been shown that N₂O is produced in solution SY1-SIM-91C containing glycine and its yield was determined (Section 2b-iv in reference 1). We find that less than 2.6% of the N in the radiolytically generated N₂O comes from the glycine; that is, it is overwhelmingly from inorganic sources (NO₂⁻ or NO₃⁻). Nonetheless, the organic component is essential for the production of N₂O. The conclusion from the isotopic labeling experiments is in agreement with the observation that N₂O is produced in irradiated SY1-SIM-91C containing glycolate; as glycolate contains no nitrogen, it is clear that the organic moiety need not contain nitrogen to result in N₂O production.

Table B3-3. $G(N_2O)$ from irradiation of solution SY1-SIM-91C containing various additives at 30 and 60 °C.^a

Additive	[RH] M	$G(N_2O)$ at 60 °C	$G(N_2O)$ at 30 °C	Ratio $\frac{G_{60\text{ °C}}}{G_{30\text{ °C}}}$
none	0	0	0	--
EDTA	0.085	1.10	0.60	1.8
HEDTA	0.085	0.77	0.50	1.43
NTA	0.17	0.48	0.56	0.86
IDA	0.17	0.94	0.76	1.24
citrate	0.17	0.064	0.045	1.42
glycine	0.3	0.47	0.15	3.1
glycolate	0.3	0.86	0.42	2.0
POC	b	0.87	0.49	1.8
POI	c	1.06	0.48	2.2

^aAll samples irradiated to 125 krad in 30-min irradiations.

^bSolution SY1-SIM-91C with 0.065 M EDTA, 0.065 M HEDTA (sodium salts), and 0.1 M sodium citrate aged at 30 °C for the same period of time as solution POI.^c

^cSame as b, but preirradiated to 31.5 Mrad at 0.51 krad/min; it was then degassed and used as starting material for further irradiation.

Figure B3-1. The yield, $G(H_2)$, from slurry SY1-SIM-91A (composition given in Table B3-4) containing 0.3 M EDTA at 30 °C as a function of total dose delivered to the slurry. Dose rates are shown in the figure.

Figure B3-2. The yield, $G(H_2)$, as a function of dose rate for slurry SY1-SIM-91A containing 0.3 M EDTA at 30 °C.

Figure B3-3. Radiolytic yield of H₂ from slurry SY1-SIM-91A containing 0.3 M HEDTA at 30 °C measured at two dose rates.

Figure B3-4. Radiolytic yield of H₂ from slurry SY1-SIM-91A containing 0.065 M each of HEDTA and EDTA, and 0.1 M citrate, measured at two dose rates, at 30 °C. This mixture is the control slurry for the preirradiated slurries.

Figure B3-5. Radiolytic yield of H₂ at 30 °C from slurry SY1-SIM-91A containing 0.3 M IDA measured at two dose rates.

Figure B3-6. G(H₂) at various doses for slurry SY1-SIM-91A containing 0.3 M EDTA from irradiations at 3.1 krad/min. The values of the least-squares fit parameters are given in the same units shown in the axes labels.

Figure B3-7. Radiolytic yield of H₂ at 60 °C from standard slurry containing 0.3 M IDA.

Figure B3-8. Radiolytic yield of H₂ at 60 °C from slurry SY1-SIM-91A containing 0.3 M HEDTA.

Table B3-4. Radiolytic yields of H₂ for slurries compared with homogeneous solutions

slurries ^a				solutions ^b		
temp	composition	dose rate krad/min.	G(H ₂)	composition	dose rate krad/min.	G(H ₂)
30 °C	0.3M EDTA	3.5	0.044±0.003	0.3 M EDTA	4.4	0.081±0.005
30 °C	0.3 M EDTA	15	0.040±0.004			
30 °C	0.3 M HEDTA	3.5	0.052±0.003	0.3 M HEDTA	4.4	0.084
30 °C	0.3 M HEDTA	15	0.049±0.003			
30 °C	0.3 M IDA	3.5	0.034±0.002	0.3 M IDA	4.4	0.049
30 °C	0.3 M IDA	15	0.027±0.005	0.3 M IDA	17	0.048
30 °C				0.3 M citrate	4.4	0.040
30 °C	SOC ^c	3.5	0.040±0.005	POC ^c	4.4	0.045
30 °C	SOC ^c	15	0.039±0.001			
60 °C				0.3M citrate	4.7	0.040
60 °C	0.3 M EDTA	3.1	0.080±0.006	0.3 M EDTA	4.7	0.093
60 °C	0.3 M IDA	3.1	0.064±0.008	0.3M IDA	4.7	0.054
60 °C	0.3 M HEDTA	3.1	0.080±0.006	0.3M HEDTA	4.7	0.108
60 °C				POC ^c	4.4	0.063

^aSlurry SY1-SIM-91A contains 2.3 M NaOH, 2.2 M NaAlO₂, 3.7 M NaNO₃, 3.2 M NaNO₂, and 0.6 M Na₂CO₃.

^bSolution SY1-SIM-91C contains 2.3 M NaOH, 0.86 M NaAlO₂, 2.8 M NaNO₃, and 2.2 M NaNO₂. (Results obtained from ANL- 91/41.)

^cSOC and POC indicate 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate in the SY1-SIM-91A slurry or SY1-SIM-91C solution, respectively.

Table B3-5. Radiolytic yields of N₂O for slurries compared with homogeneous solutions.

slurries ^a				solution P ^b		
temp	composition	dose rate krad/min.	G(N ₂ O)	composition	dose rate krad/min.	G(N ₂ O)
30 °C	0.3 M EDTA	3.5	0.37±0.08	0.17 M EDTA	4.4	0.5±0.1
30 °C	0.3 M EDTA	16	0.26±0.06	0.085 M EDTA	17	0.4±0.1
60 °C	0.3 M EDTA	3.5	0.26±0.08	0.17 M EDTA	4.4	0.83±0.09
60 °C	0.3 M IDA	3.5	0.41±0.14	0.17 M IDA	4.4	0.69±0.04
60 °C	0.3 M HEDTA	3.5	0.40±0.08			

^aSlurry SY1-SIM-91A

^bSolution SY1-SIM-91C: 2.3 M NaOH, 0.86 M NaAlO₂, 2.8 M NaNO₃, and 2.2 M NaNO₂.

d. H_2 and N_2O Yields From Slurries

Yields of H_2 in Slurries. Figures B3-1 through B3-5 show the effect of total dose and dose rate at 30 °C on $G(H_2)$ for the slurry SY1-SIM-91A containing either EDTA, HEDTA, EDTA + HEDTA + citrate, or IDA. Similarly, Figure B3-6 shows the effect of dose on $G(H_2)$ at 60 °C for the slurry containing EDTA. The dependence of $G(H_2)$ on dose (e.g., Figure B3-1) or dose rate (e.g., Figure B3-2), if any, is very weak and within experimental error. In Table B3-4 we quote average values. Figures B3-7 and B3-8 show the effect of dose (at 3.1 krad/min) on $G(H_2)$ in slurry SY1-SIM-91A at 60 °C containing 0.3M IDA and 0.3M HEDTA, respectively. $G(H_2)$ is independent of dose within experimental error at this temperature as well. A comparison of H_2 radiolytic yields from the slurries and solutions at 30 and 60 °C is given in Table B3-4. At 30 °C, the radiolytic yield for a slurry is clearly smaller than for the corresponding solution. However, at 60 °C the yields from the slurries and the homogeneous solutions are comparable. The effect of temperature is attributed primarily to changes of solubilities, that is, less solid material is present at the higher temperature and radiation that is deposited in a solid is less efficient than that deposited in the solution.

Yields of N_2O for Slurries. G values at 30 and 60 °C for the generation of N_2O for slurry SY1-SIM-91A containing 0.3 M of either EDTA, HEDTA, or IDA were measured at a dose rate of 3.5 krad/min and total doses of 200 to 700 krad. The results are given in Table B3-5. Results at 30 °C for EDTA are shown in Figure B3-9. Results for HEDTA and EDTA at 60 °C are shown in Figures B3-10 and B3-11, respectively. The scatter in the results is appreciable, as we commonly find in determinations of N_2O yields for both slurries and homogeneous solutions. There seems to be some dependence of $G(N_2O)$ on dose but the uncertainty in this dependence is large. No such dependence on dose has been observed in any of the systems studied previously. None is expected theoretically. The figures, therefore, display the least-squares fit to the dose dependence, whereas in Table B3-5 we give the average values of $G(N_2O)$ with the corresponding standard deviations. It is unlikely that an observed "dose effect" is actually due to an increase in thermal decomposition rate with increasing dose (equivalent to time). For a $G(N_2O) = 0.35$ at a dose rate of 3.5 krad/min, the rate of radiolytic generation of N_2O is $1.9 \times 10^{-6} \text{ M min}^{-1}$. This is (coincidentally) similar to the fastest thermal generation rate observed for slurries that were preirradiated for very long periods of time. It is highly unlikely that the low doses utilized for $G(N_2O)$ measurements (compare 0.8 Mrad with ~ 40 Mrad employed for preirradiation of slurries) will generate enough of the thermally reactive intermediate (see Section C) to contribute significantly to the radiolytic rate. In general, dependence of the yield on total dose indicates that a radiolytic intermediate product is required for generation of the gas rather than the original components. The intercept in the figures reflects the yield before changes in the composition have occurred by radiolysis.

e. Yields of Other Gases

In addition to H_2 and N_2O , only O_2 and N_2 were detected by gas chromatography in the irradiated samples. NH_3 was determined by a titration technique described in the experimental section.

Oxygen. We have already reported $G(O_2) = 0.08 \pm 0.03$ for the homogeneous solution SY1-SIM-91C (no organic additives) at 30 °C in the intensity range studied (0.2 to 20 krad/min).¹ When an organic solute is present in SY1-SIM-91C, O_2 is not generated radiolytically. In fact, analysis of the gases remaining in irradiated SY1-SIM-91C containing 0.085 M each of EDTA and HEDTA, which was saturated with air prior to irradiation, showed that O_2 is consumed upon irradiation. The value obtained for the destruction of O_2 is $G(-O_2) = 7 \pm 1$. The mechanism for

the generation of O_2 in highly concentrated nitrate solutions is well established to involve direct absorption of a fraction of the radiation energy by the solute rather than the solvent. This fraction is not expected to change significantly by the addition of the organic components at the concentrations discussed here. Therefore, we believe that generation of dioxygen in the solutions containing the organic solutes proceeds at the same rate as in their absence. The observation that no oxygen is found and, in fact, is destroyed when organic chelators are added must mean, therefore, that an organic intermediate that is produced by the radiolysis destroys O_2 . Because the yield of O_2 destruction is so high, this also means that the majority of the radiolytically produced intermediates react with the organic components. Because most of the radicals in the waste simulant are NO_x radicals, they must participate in the chain that leads to the destruction of O_2 . We show below, in Section C, that most of the NO_x radicals lead to the destruction of organic material. Therefore, the sequence of reactions has to go from the NO_x radicals to organic radicals and eventually to O_2 .

Figure B3-9. The yield of N_2O , $G(N_2O)$, at 30 °C vs. dose and for a range of dose rates for slurry SY1-SIM-91A containing 0.3 M EDTA. "Feed solution" (triangles) is the solution used in the preparation of the slurry prior to the 30%-v water distillation (labeled SY1-SIM-91B).

Figure B3-10. The yield of N₂O at 60 °C vs. dose at a dose rate of 3.5 krad/min for slurry SY1-SIM-91A containing 0.3 M HEDTA.

Figure B3-11. G(N₂O) at 60 °C vs. dose at a dose rate of 3.5 krad/min for slurry SY1-SIM-91A containing 0.3 M EDTA.

Nitrogen. $G(N_2)$ was measured from Ar or N_2O saturated SY1-SIM-91C solutions containing 0.065M EDTA, 0.065 M HEDTA, and 0.1 M citrate. The experiments in N_2O saturated solutions were done to estimate the contribution of N_2O to the generation of N_2 in the waste simulant. The effect of organic additives to solution SY1-SIM-91C on $G(N_2)$ was also determined. The experimental procedure was slightly modified as follows: SY1-SIM-91C solutions in syringes at 60 °C were saturated with N_2O . The solutions were then cooled to 30 °C prior to irradiation. This procedure prevents N_2O gas bubbles from forming during radiolysis. A similar procedure (but Ar instead of N_2O) was used for $G(N_2)$ determination from Ar saturated solutions. $G(N_2)$ was determined using the same Van Slyke-gas chromatograph technique as in our routine procedure.

Table B3-6 summarizes the results obtained for measurements of $G(N_2)$. More weight is given to points at higher doses because blank corrections for atmospheric N_2 leakage are about 25% of the total N_2 at the lowest dose used. Within experimental accuracy, no effect of dose on $G(N_2)$ could be determined for solutions containing no organic additives or for the mixture of 0.065M EDTA, 0.065 M HEDTA, and 0.1 M citrate. However, high doses were required in order to measure these yields. Our results in Section C indicate that substantial degradation of the organic chelators occurs when such doses are delivered. Thus, by definition, there will be a dose effect on the yield of N_2 if degradation is a prerequisite. It can be seen in Table B3-6 that the addition of the organic chelators significantly increases the yield of nitrogen. On the other hand, N_2O has little, if any, effect on the yield. The latter observation indicates that radiolytic destruction of N_2O to generate N_2 is not a significant process and cannot account for the relatively high ratios of N_2O/H_2 observed in the laboratory. The yield of N_2 is smaller than that of H_2 , even in the presence of the organic additives. With a $G(N_2) = 0.014$ one calculates a rate of $3.5 \times 10^{-10} \text{ M min}^{-1}$ under the conditions of 101-SY (dose rate of $0.025 \text{ krad min}^{-1}$).

Nitrogen was also measured for irradiations at 60 °C; $G(N_2) = 0.07$ was measured in SY1-SIM-91C containing 0.3 M glycine, and $G(N_2) = 0.13$ for a preirradiated sample of SY1-SIM-91C containing three organics (designated "POI" in Tables B3-1 and B3-3). These results seem to indicate that the radiolytic degradation products are more efficient in N_2 generation, just as they are more efficient in H_2 and N_2O generation.

Table B3-6. $G(N_2)$ from solution SY1-SIM-91C under various experimental conditions.

additive	saturated (saturation at 60 °C)	$G(N_2)$ (Yields at 30 °C)
none	N_2O	0.0018 ± 0.0005
0.065M EDTA, 0.065 M HEDTA, and 0.1 M citrate	Ar	0.014 ± 0.002
0.065M EDTA, 0.065 M HEDTA, and 0.1 M citrate	N_2O	0.012 ± 0.002

Ammonia. $G(NH_3)$ was measured for argon-saturated SY1-SIM-91C solutions containing 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate irradiated at a dose rate of 10.7 krad/min. Gas chromatography was found unsatisfactory for these measurements because of interference from water vapor and the irregular shape of the peaks (using either "HayeSepTM Q" or "HayeSepTM P" columns), which in turn led to poor reproducibility. Therefore, yields of ammonia were measured by bubbling the irradiated samples with argon at 51-52 °C for 4 hours, in order to drive the ammonia out of the solution. The ammonia was passed first through two traps of

glass wool to prevent any aerosol containing NaOH from reaching the acid standard solution. The NH_3 flowed into an HCl solution of known molarity, and the HCl remaining, after absorption of the ammonia, was back titrated with standard Na_2CO_3 . An identical unirradiated solution, which underwent an identical procedure, was used as a blank for these determinations. The concentration of NH_3 was calculated from the amount of HCl consumed and the G value was calculated from the concentration of ammonia and the dose.

Figure B3-12 shows the results for $G(\text{NH}_3)$ from the solutions mentioned above at three different doses. It can be seen from this figure that $G(\text{NH}_3)$ increases linearly with dose. No particular significance is attached to the linear dependence on dose (clearly, the yield will start to decrease at sufficiently high doses). However, the increase in yield with increasing dose indicates that the ammonia is produced from a degradation product whose concentration increases with dose. To obtain some information on the source of NH_3 in the above solutions (organic or inorganic), the experiment was repeated using SY1-SIM-91C solution containing 0.1 M citrate and 0.13 M glycolate. The solutions were again irradiated at a dose rate of 10.7 krad/min up to a maximum of 26.7 Mrad. No ammonia was detected. Based on results obtained by back titrating HCl after reaction with genuine ammonia solutions, we estimate the upper limit of $G(\text{NH}_3)$ at the highest dose studied to be $G(\text{NH}_3) \leq 6 \times 10^{-3}$. These results seem to indicate that the nitrogen in the radiolytically produced ammonia comes from the organic nitrogen in EDTA and HEDTA. From information in the literature, the mechanism for radiolytic generation of ammonia is probably similar to the mechanism of the radiolytic generation of glyoxylate or formaldehyde. Oxidation, probably by NO_2 radicals, of EDTA, for example, at the N-C bond will initially yield glyoxylate on one side and $\text{HN} < \text{R}$ on the other. Repetitive oxidations will eventually yield the ammonia. Such a mechanism would predict an S-shaped dependence of $G(\text{NH}_3)$ on dose; the range of doses delivered in the experiments shown in Figure B3-12 were apparently insufficient to obtain the expected curvature.

f. Effects of Carbonate, Sulfide, Formate, and Oxalate on Radiolytic Yields

The effects of Na_2CO_3 and Na_2S on the yield of H_2 from SY1-SIM-91C were determined. The former is present in 101-SY and in the SY1-SIM-91B standard waste solution but is absent in SY1-SIM-91C; the latter was of interest as a source for radical scavengers. To check the effect of carbonate, 0.4 M Na_2CO_3 was added to SY1-SIM-91C containing 0.17 M EDTA. This solution was irradiated at 30 and 60 °C at 4.2 krad/min to a dose of 150 krad. The values of $G(\text{H}_2)$ obtained are 0.047 at 30 °C and 0.059 at 60 °C. These are somewhat lower than the values for identical solutions without the added carbonate (0.059 at 30 °C and 0.066 at 60 °C). The apparent small inhibition effect is unexpected because Na_2CO_3 does not react with hydrogen atoms. Carbonate may, however, affect solubility of the organic component and thereby reduce the yield.

Sulfur has been considered (Seimer, private communication, 1991) as a possible additive to inhibit H_2 formation. In basic solutions H_2S will autooxidize to polysulfide and will have a similar effect; the relative ratio of S to S^{2-} in the solutions used has not been determined. We measured H_2 yields in solutions of 0.17 M EDTA in SY1-SIM-91C containing 0.01 and 0.1 M Na_2S , irradiated at 4.2 krad/min to a dose of 130 krad. The results show that 0.1 M Na_2S increases the yield of H_2 by about 20% at both 30 and 60 °C. A possible explanation is the hydrogen abstraction reaction:

The effects of formate and oxalate on the yields of H_2 and N_2O in solution SY1-SIM-91C were determined. Both of these additives are known radiolytic degradation products of the chelators originally present in tank SY-101. $G(\text{H}_2)$ was measured for SY1-SIM-91C containing either ≈ 0.001 M oxalate (the solubility limit of oxalate in this solution) or 0.13 M formate. The results are shown in Table B3-7. The effect of either one of these on $G(\text{H}_2)$ is negligible. From informa-

tion in the literature, no effect is expected. The yields for the oxalate and formate containing solutions are similar to those from SY1-SIM-91C solutions containing citrate.

Measurements on N_2O yields from solutions of the same compositions indicate that N_2O is not radiolytically generated in the presence of formate or oxalate. Organic components are required for radiolytic generation of N_2O , but in this regard, oxalate and formate resemble "inorganic" ions. As we have concluded previously,¹ organic radicals are responsible for the radiolytic generation of N_2O . In the case of formate and oxalate, no organic radicals that can form N_2O are produced.

Table B3-7. Effect of formate and oxalate on $G(H_2)$ in SY1-SIM-91C.^a

solution	$G(H_2)$
SY1-SIM-91C	3.1×10^{-2b}
SY1-SIM-91C + 0.13 M formate	3.4×10^{-2}
SY1-SIM-91C + 0.001 M oxalate	3.2×10^{-2}

^a Irradiations at 30 °C at a dose rate of 3.3 krad/min to a total dose of 130 krad. SY1-SIM-91C contains 2.3 M NaOH, 0.86 M $NaAlO_2$, 2.8 M $NaNO_3$, 2.2 M $NaNO_2$.

^b From reference 1.

g. Comparison with Modeling Calculations

Because the precise composition of the waste solutions is presently unknown, it is difficult to define a simulant for experimental studies that will perfectly match the waste solutions in the tanks. Furthermore, tanks other than SY-101 may have varying compositions and correspondingly different rates of excess gas generation. It is obvious that a model that could predict the rate of gas generation and its dependence on composition would be very beneficial in many practical applications. In this subsection we try to apply known computer modeling procedures of radiation chemical processes and test their predictive capabilities for the waste solutions. Because the energy is deposited nonhomogeneously, and because there are a large number of interrelated reactions taking place, it is not simple to predict how different chemical species will alter the rate of generation of hydrogen. To address this complexity, we utilize a computer program to:

- 1) compare the predictions with the experimental results and possibly adjust the parameters of the model to obtain better agreement with experiments; and
- 2) predict the consequence of changes in various parameters, in particular changes in concentration of various species.

The calculations were not intended to simulate quantitatively the experimental data obtained in the laboratory. Even more, they were not intended to simulate conditions in tank SY-101. Instead, they were to provide guidance to the experimental program and to define the importance of different mechanisms. Nonetheless, the calculations did reproduce the experimental trends and predict hydrogen yields to within a factor of two of the experimental observations.

The specific questions that the theoretical effort is addressing are:

- (1) What are the mechanisms of hydrogen production from radiolytic reactions? How do the concentrations of the various components in the system (primarily nitrate, nitrite and organics) affect the yield of H_2 ? What chemistry affects the production mechanisms?
- (2) How much hydrogen peroxide will be formed from radiolytic processes?
- (3) What possible mechanisms exist for the production of N_2O ?

The results are summarized below; detailed data are given in reference 1.

Figure B3-12. Yields of ammonia from solution SY1-SIM-91C containing the organic additives shown as a function of dose.

Hydrogen-Production Mechanisms and Yields. There are two dominant radiolytic H_2 -forming pathways that occur in the waste storage tanks: a) the formation of hydrogen from the direct excitation of water, and b) the abstraction of a hydrogen atom from an organic molecule in the solution by a hydrogen atom formed in the radiolysis of water. The high concentrations of scavengers for electrons (e^-_{aq} and its precursors), H atoms and OH radicals eliminate all other possible major pathways - the various reactions among radicals formed in the radiolysis of water.

A key result of these calculations is the observation that the yield of H_2 will depend directly on $k_1 \times [RH]$, the product of the concentration and the rate constant of the organic molecules toward the H atoms. The results of these calculations were given in Figure 33 of reference 1. Furthermore, these calculations show that the $G(H_2)$ calculated at high concentrations of organics is within a factor of two of the experimental results. Thus, both theory and experiment show that to predict the H_2 production rate by radiolysis, the concentration and identity of the organic compounds must be known. It is not sufficient to know the initial concentrations, for, as is well established, radiolysis will change both the concentration and identity of the initial species over time.

The dependencies of $G(H_2)$ on $[NO_3^-]$ and $[NO_2^-]$ were also computed (Figure 31 of reference 1). Whereas the yield of H_2 is virtually independent of the NO_3^- concentration over the range of 0.5-3.0 M, it varies by nearly a factor of two over the same concentration range for NO_2^- . Thus it is of importance to know the concentration of nitrite in the tank and maintain it at high levels.

Yields of Hydrogen Peroxide Formation. It has been suggested that hydrogen peroxide, a known product of the radiolysis of aqueous solutions, is a precursor to hydrogen. Upper limits to the hydrogen peroxide yields have been estimated (Figure 34 of reference 1). The results are an upper limit because we have assumed that all of the oxidizing radicals produced by the ionizing radiation are OH radicals. Because of the high salt concentration, considerable direct ionization of nitrite and nitrate would occur. The products of these events are unlikely to be OH radicals. Furthermore, the yield of hydrogen peroxide will be inversely proportional to the concentration of organic molecules. Experimentally, we observe that H_2 yield is directly proportional to the concentration of organics, suggesting that the peroxide pathway to H_2 generation is unlikely to be the dominant one. Under the high concentrations of base and in the presence of metal ions, the non-productive (for H_2 generation) destruction of hydrogen peroxide is expected to be fast. In summary, it is unlikely that the peroxide pathway is important in radiolytic production of hydrogen.

N_2O Production Mechanisms. Because several stable, but reactive, intermediates are formed in the radiolysis of the waste simulants, the chemistry of the NO_x system is highly complex. Most of the reactions of the various NO_x radicals are not sufficiently fast to compete effectively with the initial reactions that occur in the spurs. Therefore, the modeling was done using homogeneous kinetics rather than nonhomogeneous kinetics as was done for the hydrogen formation. The mechanism that was used to describe the chemistry is described in detail in reference 1. No reactions of the organics with NO_x radicals were included in the mechanism, because no quantitative data on these reactions are available in the literature. No N_2O was formed in the calculations under such conditions. These results are consistent with the experimental data; in the absence of organics, no N_2O was obtained experimentally.

4. Conclusions

In this section we have described the determination of the radiolytic yields of H_2 , N_2O , N_2 , O_2 , and NH_3 in various waste simulants, homogeneous solutions, and slurries. Hydrogen is generated from direct radiolysis of water, but its yield is further increased by the presence of organic compounds (RH) due to the reaction of hydrogen atoms with the organic (reaction B-1); the

increased efficiency correlates well with the rate constants for that reaction. The efficiency of producing H_2 is roughly proportional to the total number of C-H and N-H bonds in RH, and is generally higher at 60 °C than at 30 °C. The yield of hydrogen decreases on increasing the fraction of solids in the slurry.

No N_2O is generated by radiolysis unless organics are present. Yet, the nitrogen in N_2O comes exclusively from inorganic components of the waste simulant. The pathways for N_2O generation are quite complex and a mechanism that is consistent with the observations reported in this section is proposed in Scheme IV of Section G. Oxygen is produced by well understood processes known to occur during the radiolysis of concentrated nitrate solutions; it is efficiently consumed, however, in the presence of organics. Nitrogen gas is generated from N-containing organics and not from N_2O . Ammonia yields increase with dose and come from degradation products of N-containing chelators. Neither oxalate nor formate contribute to the yield of H_2 , and neither enables N_2O production.

The calculations subtask of this program reproduced the trends observed experimentally and verified the primary mechanisms for hydrogen production in the waste simulants. The yield of hydrogen could be semiquantitatively determined to within a factor of two of the experimentally determined yield of H_2 and its dependence on organic reactivity and concentration is well reproduced. No N_2O production in the absence of organic compounds is predicted by the calculations, in agreement with the experimental measurement. The calculations show that the concentrations of NO_3^- and NO_2^- will not appreciably change over long periods (decades) of storage and they suggest that no chemical scavenger will significantly diminish the yield of H_2 at the high nitrate and nitrite concentrations that exist in tank 101-SY.

C. RADIOLYTIC DEGRADATION OF ORGANICS AND THERMAL GENERATION

1. Introduction

The following significant observations were made by Campbell of PNL.⁹ In a preirradiated (31.5 Mrad) SY1-SIM-91C solution (see Table B2-1 for composition) containing 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate, the concentration of EDTA and HEDTA after the irradiation is less than $\approx 1\%$ that of an unirradiated identical control solution. In contradistinction, the concentration of citrate was only slightly reduced by the preirradiation. Hence, EDTA, HEDTA and, to a much smaller extent, citrate, will be degraded under the irradiation field in the storage tanks. A yield of $G(-RH) \geq 2.6$ molecules per 100 eV has been estimated for the destruction of these chelators from Campbell's analytical result. Thus, the concentration of EDTA or HEDTA will drop from 0.1 M to half its original concentration within less than 1.5 years under the field of radiation in tank 101-SY (assumed to be 25 rad/min). From this observation one may conclude that the focus on the original chelators may be unjustified; very little of these will survive several years of storage in the waste tank. Indeed, to the best of our knowledge, less than 10% of the TOC can be identified as EDTA and HEDTA in 101-SY core samples. The question, therefore, arises as to the effect of the degradation products (and the reduction in concentration of the original components) on the rate of generation of the gases, thermal or radiolytic.

The effect of preirradiation on the radiolytic yields has already been given in the previous section (e.g., entries designated POI in Tables B3-1 and B3-3). The effect of various degradation products on G values has also been discussed in Section B. In the following, we describe studies of the rates for *thermal* generation of gases from preirradiated SY1-SIM-91C solutions containing either HEDTA, EDTA, or citrate and their mixture. The degradation of the above mentioned chelators will undoubtedly depend on the dose delivered to the solution. Therefore, we studied in detail the effect of the preirradiation dose on the thermal generation rate.

Campbell also found NTA and glycolate in the analysis of the preirradiated SY1-SIM-91C solution mentioned above, and in analyses of core samples from tank SY-101. Both are known radiolytic degradation products of the chelators. Glyoxylate and formaldehyde are also known radiolytic products, further down the degradation chain (scheme III in reference 3); they were also considered as possible intermediates, along with NTA and glycolate, for the thermal generation of H_2 . The possible role of hydroxylamine, formate, and oxalate in the thermal generation of H_2 and N_2O was also examined.

2. Experimental

Preirradiations were performed in covered (but not gas tight) stainless steel beakers. It was observed that during irradiation the temperature of the solutions increased from 24 °C to 38 °C for all doses utilized, except for the dose of 10.2 Mrad where the temperature increased only to 32 °C. An aqueous solution of $NaClO_4$ (density identical to SY1-SIM-91C to ensure absorption of the same amount of radiation) was also irradiated under identical conditions. A similar increase in temperature was observed for this solution as well. Therefore, the increase in temperature during irradiation is attributed to the absorption of radiation energy by the solution and not to any possible exothermic chemical reaction.

After the preirradiation, 10 ml aliquots of the solution were put into Erlenmeyer flasks and deaerated by bubbling argon, at room temperature, using a needle-septum arrangement. These vessels were then put into a water bath at 60 °C. At various time intervals, just before sampling for gas analysis, 0.5 ml of argon-saturated water was injected into the vessel through the septum. This was done in order to ensure no air leakage into the vessels when the samples were withdrawn from the vessels, that is, to create slight over-pressure in the vessel. The small dilution introduced by this injection was factored into the calculation. The solution was then stirred for 5 min., and 4 ml of the gas phase above the sample were withdrawn and injected into the gas chromatograph for analysis. The amounts of gas calculated from these measurements were converted to concentrations (i.e., moles of gas generated per liter of solution) and plotted against the time since the initiation of the thermal reaction. The rates for thermal generation were obtained from the slopes of such plots at the early stages of the reaction and refer, therefore, to initial rates. For measuring the thermal generation rates in solution SY1-SIM-91C containing NTA or glycolate (not preirradiated), the reaction was performed in syringes placed in the 60 °C bath. For glyoxylate and formaldehyde, experiments were done using the Erlenmeyers as described above for preirradiated solutions. However, the required glyoxylate or formaldehyde solution was injected after deaeration to initiate the thermal reaction. These experiments are described in Section D.

The preparation of slurries is reported in Section B2c. After preirradiation, slurries were transferred to the Erlenmeyers and were deaerated by bubbling with argon at ambient temperature. The slurries were then placed in the water bath held at 60 °C to study the thermal production of the gases. For analysis at various time intervals, the slurries were dissolved by injecting an appropriate amount of water (usually 4 ml water per 10 ml of slurry), and then proceeding as described above for the homogeneous solutions. The dissolution of the slurry prior to analysis was necessary to minimize significant retention of the gases by particles in the slurry.

3. Results and Discussion

a. Effect of Degradation on H_2 Thermal Generation

The rate of thermal generation of H_2 as a function of preirradiation dose was measured for several different solutions. An example is shown in Figure C3-1. The results from the preirradi-

ated homogeneous solutions of SY1-SIM-91C containing either EDTA, HEDTA, or citrate are tabulated in Table C3-1. It can be seen from the table that the rates of thermal H_2 generation depend markedly on the identity of the organic molecules present in the solution. The solution that originally contained citrate shows the slowest rate of H_2 generation among those studied. The rate of generation in this solution is similar to the one in non-preirradiated solutions. This agrees well with the observation of Campbell that citrate is degraded only to a minor degree by the preirradiation.

Figure C3-1 also shows the effect of "aging" on the thermal generation of H_2 for a solution of SY1-SIM-91C containing 0.065 M EDTA. It can be seen that the H_2 generation rate decreased by about 50% upon aging the preirradiated solution at ambient temperature for 46 days. Therefore, the preirradiated solution probably generated H_2 at a slow rate while standing at room temperature before the measurement at 60 °C. From the decrease in the rate of thermal generation upon aging, we also infer that the intermediate that efficiently produces H_2 is consumed upon this aging at room temperature. For this reason, the time elapsed between termination of preirradiation and the measurement of the generation rate is also shown (in parentheses) in Table C3-1. From Table C3-1 one notes a similar aging effect for HEDTA and for EDTA. However, for the SY1-SIM-91C/citrate solution, little effect of this time interval was observed, consistent with our earlier conclusions that citrate is not an important precursor of the reactive intermediate. Thus, we may conclude that the major source of the intermediate is EDTA, and the order of efficiency of its production is EDTA > HEDTA >> citrate.

To determine the effect of dose and dose rate on the rates of thermal generation of H_2 , SY1-SIM-91C containing all three organics was preirradiated for various doses and dose rates. To minimize the thermal deterioration of the intermediate produced by the irradiation on standing at room temperature, all measurements were performed on the sample the same day that the preirradiation was terminated. The results are tabulated in Table C3-2, where it can be seen that the rates for thermal generation of H_2 are independent of dose rate. Table C3-2 also contains the rates for thermal generation of H_2 when the solutions were aged for two weeks after the preirradiation.

Figure C3-2 shows the variation of the rate for thermal generation of H_2 with the total dose of preirradiation. The rate passes through a maximum and then declines. As is mentioned above, following irradiation to 31.5 Mrad, almost all of the EDTA and HEDTA is destroyed. Therefore, it is not surprising that the radiation degrades products of the original starting compounds at these high doses. The decrease in the rate of H_2 generation indicates that the reactive intermediate (or a secondary precursor) is destroyed to produce a product that is less effective in the generation of H_2 . Two pathways to this destruction may exist: radiolytic destruction or thermal destruction. That is, some thermal reaction may occur for higher doses (at the same dose rate) because of the longer periods of irradiation (see Table C3-2). Therefore, the decrease in H_2 generation rate could be due to the increase in dose and/or the longer time elapsed. On the other hand, the time of irradiation for the samples receiving 37 Mrad (dose rate = 9.47 krad/min) and 58.5 Mrad (dose rate = 14.9 krad/min) was identical. The decrease in the rate in that case must be due to greater dose, that is, to radiolytic destruction.

Figure C3-2 shows that the rates for thermal generation of H_2 for preirradiation doses in the range of 10-24 Mrad do not vary significantly. The thermal generation of H_2 was determined in this dose range for extended periods of time. Figures C3-3 and C3-4 show these results. The plateau value for H_2 is similar for the two doses used (as are the generation rates). One can calculate from the values shown in these results that only a small fraction of the total original concentration of HEDTA and EDTA (0.13 M combined) can be converted to H_2 . This may result from competitive pathways in the radiolytic degradation of the chelators or from competitive, non-hydrogen producing, pathways for the disappearance of the reactive intermediate.

The rates of thermal generation of H_2 in preirradiated slurries are also given in Table C3-1. An example of the thermal generation of H_2 is shown in Figure C3-5. As can be seen in this figure, even at zero time of thermal reaction there is an observable amount of H_2 in the preirradiated slurry. This is because the gas produced during the preirradiation is tightly held by the slurry, and cannot completely be removed by bubbling argon through the slurry. As described in the experimental section, the slurries were dissolved after the thermal reaction period, but before the gas extraction. Dissolution of the particulate matter releases any adsorbed H_2 . Hence, the intercept in Figure C3-5 reflects this adsorbed gas. Several experiments were done in unsuccessful attempts to remove the adsorbed H_2 (bubbling at ambient temperature, bubbling at 60 °C, bubbling overnight, bubbling with water-saturated argon to avoid extensive loss of water, all with vigorous stirring). None was particularly efficient. It was noticed that extensive argon bubbling for several hours leads to appreciable thickening of the slurry because of water loss. On the other hand, bubbling with water saturated argon leads to water uptake by the slurry (thinning). An attempt was made to estimate the amount of gas accumulated on the particles during preirradiation. This was done by measuring the amount of gas that could be released prior to bubbling Ar through the slurry. The results indicate that the bubbling procedure removes only about half of the H_2 generated during the irradiation.

The large scatter in the experimental results (see Figure C3-5) obtained in studies of the thermal generation of H_2 from the preirradiated slurries is attributed to sample-to-sample variations in the amount of H_2 retained by the slurry after the bubbling procedure. This problem was eliminated if the preirradiated slurry was dissolved prior to the thermal generation studies, thus releasing the adsorbed gas. Because of the difficulties involved in the removal of the gases generated by the long-term preirradiations of slurries, several experiments were conducted where the preirradiated slurry was dissolved prior to the bubbling and before thermal generation rates were measured. The dissolution leads to dilution of all the slurry components to 55% of their original concentration. However, in calculating the concentration of gases, correction was made to account for this dilution. Such a correction arbitrarily assumes that the reaction is first order in the significant reactants. Results from these experiments are given in Figure C3-6. As can be seen in this figure, and as was expected, the bubbling procedure now removes all residual gases that were generated by the preirradiation.

Results from dissolved and "undissolved" slurries are shown in Figure C3-7 and also in Table C3-1. It is clear that the rate of generation is much slower in the dissolved slurries than in those that were not dissolved. However, it should be recognized that the significant dilution of nearly a factor of two in the concentrations of all components will also cause a reduction in rate. Therefore, it cannot be concluded that the effect is necessarily a catalytic effect of the solids in the slurry. To conclude this section, it is clear that radiolytic degradation products are significantly more efficient in the thermal generation of H_2 than the original chelators, whether the gases are generated from a homogeneous solution or from a slurry.

b. Effect of Degradation on Thermal Generation of N_2O

The rate of thermal generation of N_2O was measured for solution SY1-SIM-91C containing either EDTA, HEDTA, or citrate. Unlike H_2 , the rate of N_2O generation is markedly enhanced in the citrate solution following the preirradiation. Therefore, we conclude that some degradation does occur in the citrate-containing solution and the rate of N_2O generation is much more sensitive to the presence of the degradation product than is the rate of H_2 generation. The rate of thermal generation of N_2O from preirradiated solution SY1-SIM-91C containing 0.1 M citrate levels off at times of about 25 hrs. The total amount of N_2O produced at this time is ca. 7×10^{-5} M, that is, <0.1% of the initial concentration of citrate.

Figure C3-1. Thermal generation of H₂ at 60 °C from preirradiated (dose of 35 Mrad) solution SY1-SIM-91C (solution P) originally containing 0.065 M EDTA. Shown are the rates measured 5 and 46 days after termination of the preirradiation.

Table C3-1. Rates of thermal generation of H_2 and N_2O at 60 °C from slurries and homogeneous solutions. Numbers in parenthesis are days elapsed from end of preirradiation to measurement of the thermal reaction.

sample description (XYZ) ^a	$H_2 \times 10^9$ (M min ⁻¹) ^b	$N_2O \times 10^9$ (M min ⁻¹) ^b
PCI	0.78 (68), 0.58 (42)	80 (22)
PCC	3.0	
SY1-SIM-91C + 0.085 M HEDTA (not preirradiated but aged)	0.7	≤ 10
POC	1.2	20
SY1-SIM-91C + 0.17 M IDA (not preirradiated)	1.3	≤ 10
SOC (in dissolved slurry)	1.9	not measured
PHI	2.8 (63), 3.9 (41)	440 (21)
PHC (fresh)	4.9	
POI	8.3 (≈100)	510 (≈100)
SOC (in slurry, not dissolved)	12	≤9
SOI (in dissolved slurry)	13 (10)	1700 (7)
PEI	39 (5), 18 (46)	72 (20)
PEC	5.9	
SOI (reaction in slurry)	78 (10)	≈800 (2)
estimated for 101-SY	8.7	8.7

^aWhen **X=P**: solution SY1-SIM-91C.

When **X=S**: slurry SY1-SIM-91A.

When **Y=O**: organics added: 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate.

When **Y=E, H, or C**: 0.065 M EDTA, 0.065 M HEDTA, or 0.1 M citrate (sodium salts), respectively.

When **Z=I**: irradiated to 31 - 45 Mrad preirradiation over about 45 days.

When **Z=C**: control system, i.e., no preirradiation.

^bRates for slurries and dissolved slurries are per volume of slurry prior to dissolution.

Figure C3-2. The dependence of the (initial) rate of thermal generation of H_2 and N_2O at $60^\circ C$ on total dose of preirradiation for solution SY1-SIM-91C containing 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate (POI). Experimental details are given in Table C3-2. The dashed line is the estimated rate for 101-SY.

Table C3-2. Rates of thermal generation of H₂ and N₂O at 60 °C from solution SY1-SIM-91C containing 0.065 M of EDTA, HEDTA and 0.1 M citrate following various doses of preirradiation.

dose Mrad	irrad. time, hours	tank equiv. years ^d	H ₂ × 10 ⁸ M min ⁻¹		N ₂ O × 10 ⁶ M min ⁻¹	
			immediately after irradiation ^e	two weeks after irradiation	immediately after irradiation	two weeks after irradiation
0			0.12		0.02	
1.79 ^a	2.0	0.14	3.58			
10.2 ^b	18.0	0.78	7.65	1.66	1.65	0.46
16.1 ^a	18.0	1.22	7.77	1.52	1.52	0.39
21.3 ^a	23.8	1.62	6.22	2.35	1.37	0.39
24.4 ^b	42.9	1.86	7.20	2.68	2.01	0.58
37.4 ^b	65.8	2.85	5.70	2.37	2.08	0.79
50.8 ^b	89.5	3.87	3.26		1.15 (?)	
58.5 ^a	65.8	4.45	3.74		1.78	
68.1 ^c	89.5	5.18			1.78	

^aDose rate = 14.91 krad/min.

^bDose rate = 9.47 krad/min.

^cDose rate = 12.64 krad/min.

^dAssuming 25 rad min⁻¹ in the tank

^eSamples were analyzed same day of termination of irradiation.

Figure C3-3. Thermal generation of H_2 at 60 °C following 16 Mrad preirradiation of SY1-SIM-91C containing (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate.

Figure C3-4. Thermal generation of H_2 at $60^\circ C$ following 24 Mrad preirradiation of solution SY1-SIM-91C containing (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate.

Figure C3-5. Thermal generation of H₂ at 60 °C from preirradiated slurry SY1-SIM-91A with (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate.

Figure C3-6. Thermal generation of H₂ at 60 °C from preirradiated slurry SY1-SIM-91A with 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate (SOI). The slurry was dissolved prior to degassing and running the reaction. The dissolution dilutes all concentrations to ~55% of their original value; [H₂] is back-calculated to correct for this dilution.

Figure C3-7. Thermal generation of H₂ at 60 °C from control slurry SY1-SIM-91A with (sodium salts) 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M sodium citrate. Dissolved and "not dissolved", aged and fresh slurries were used as shown in the legend. The dissolution dilutes all concentrations to ~ 55% of their original value; [H₂] is back-calculated to correct for this dilution.

The effects of dose and dose rate on the rate of thermal generation of N_2O were also studied. Results are summarized in Table C3-2. The effect of aging of the preirradiated solution on the rates of thermal generation is also included in this table. The variation of thermal rates with dose is shown in Figure C3-2. The rates of thermal generation of N_2O do not change in the range of 10-68 Mrad as much as they change for H_2 generation.

Thermal generation of N_2O was also studied in preirradiated slurries. As was observed for H_2 , N_2O produced in the preirradiation was also tightly held by the slurry. The results are given in Table C3-1. Figure C3-8 shows the ratio of the rates of N_2O and H_2 formation for experiments performed immediately after irradiation and two weeks later. This ratio hardly changes across the range of preirradiation doses examined.

c. Effect of Degradation Products on Thermal Generation Rates

In an attempt to identify the radiolytic degradation products that are responsible for the enhanced rate of thermal generation, we studied the rate of thermal generation of H_2 and N_2O in the presence of several known radiolytic degradation products. Solutions of SY1-SIM-91C containing 0.065 M NTA or 0.065 M glycolate were tested for thermal generation of H_2 at 60 °C. No H_2 was detected from these solutions under our experimental conditions. We estimate an upper limit for the rate of H_2 generation from NTA and glycolate solutions to be $0.54 \times 10^{-9} \text{ M min}^{-1}$ and $0.87 \times 10^{-9} \text{ M min}^{-1}$ respectively. Solution SY1-SIM-91C containing 0.1 M IDA generates H_2 at a rate of $1.3 \times 10^{-9} \text{ M min}^{-1}$. Clearly these rates are too slow to account for the observations of enhanced rates in the preirradiated solutions. For comparison, the rate of thermal generation of H_2 at 60 °C from a similar solution containing glyoxylate was $1.37 \times 10^{-7} \text{ M min}^{-1}$. The latter will be discussed in Section D.

Solutions of SY1-SIM-91C containing either 0.01 M formate or $\approx 0.001 \text{ M}$ oxalate (we are not certain that oxalate was completely dissolved at this concentration) were tested for thermal generation of H_2 and N_2O at 60 °C. No H_2 or N_2O was detected. We estimate upper limits for the rates of H_2 and N_2O generation from 0.01M formate solution to be $\leq 1.4 \times 10^{-10} \text{ M min}^{-1}$ and $\leq 1.2 \times 10^{-9} \text{ M min}^{-1}$, respectively. For oxalate in SY1-SIM-91C solution we estimate upper limits for the rates of H_2 and N_2O generation to be $\leq 1.4 \times 10^{-10} \text{ M min}^{-1}$ and $\leq 1.7 \times 10^{-9} \text{ M min}^{-1}$, respectively.

d. Role of Hydroxylamine

Hydroxylamine is a possible degradation product of the waste simulants. It is also known to thermally generate N_2O , although under much milder pH conditions than those in the waste solutions. Therefore, we measured the yields and rates of N_2 and N_2O formation from 0.01 M NH_2OH solution at 60 °C in SY1-SIM-91C. The results are shown in Figure C3-9. One obtains a total yield of N_2O of 14% of the initial NH_2OH concentration (assuming the two nitrogens in N_2O come from hydroxylamine) under the conditions given in Figure C3-9. Similar results were obtained for N_2 formation and the yield of N_2 was 60% of the initial NH_2OH . Products other than nitrous oxide and nitrogen are also possible in the decomposition of hydroxylamine and the ratio between them strongly depends on experimental conditions.

4. Conclusions

The presence of organics in preirradiated solutions of SY1-SIM-91C is necessary for the thermal production of H_2 and N_2O . The original chelators EDTA and HEDTA (but not citrate) are largely destroyed at the radiation doses where the thermal rate maximizes (about 15-20 Mrad for H_2 and about 25-40 Mrad for N_2O or equivalent to 1.5 and 2 years in 101-SY where the dose rate

Figure C3-8. The ratio of initial rates of N_2O and H_2 generation from solution SY1-SIM-91C containing 0.065 M each of EDTA and of HEDTA, and 0.1 M citrate (sodium salts), as a function of preirradiation dose.

is believed to be 25 rad/min). The half-life for EDTA and HEDTA would be less than 1.5 years in Tank 101-SY from the analytical results of PNL. It seems that radiolytic degradation of the organics produces intermediates responsible for efficient thermal generation of H_2 and N_2O .

Experimental evidence suggests that these intermediates are HCHO and glyoxylate for H_2 and NH_2OH for N_2O (and N_2). The ratio between N_2O and N_2 that is obtained from this precursor is known to be strongly dependent on experimental details. NTA, IDA, glycolate, formate, and oxalate are not effective thermal generators of H_2 . Formate and oxalate are not thermal generators of N_2O . Citrate in a preirradiated solution does produce an intermediate that enhances the thermal generation of N_2O but not of H_2 . Tangential, but important to the issue of gas retention in 101-SY, we notice in preirradiated slurries that a large fraction of the gases produced during the pre-irradiation is tightly held by the slurry particulate after irradiation (see also Section F).

D. THE FORMALDEHYDE REACTION

1. Introduction

Formaldehyde is a well-documented radiolytic degradation product of the original chelators that were placed in the waste tanks. It has been shown that formaldehyde in basic aqueous solutions will generate dihydrogen.^{10,11} Efforts at Georgia Tech have established that formaldehyde and similar aldehydes may quantitatively be converted to hydrogen at extremely high concentrations of hydroxide.^{12,13} In this section we provide quantitative descriptions of the reactions of formaldehyde and glyoxylate and attempt to shed further light on the mechanism of their hydrogen-generating reaction. We provide effective rate constants and activation energies for the H_2 production reaction of these two substrates. We further verify that the mechanism for this reaction utilizes one water proton in the case of glyoxylate, as proposed earlier,^{12,13} but not in the case of formaldehyde.

2. Experimental

a. Procedures

Because of the volatility of formaldehyde, the experimental procedure for the measurement of products of its thermal decomposition was modified from that described in the previous section. Solution SY1-SIM-91C was first bubbled with argon at room temperature in Erlenmeyer vessels. The sample was then put into a thermostated water bath held at the desired temperature. Formaldehyde or glyoxylate was then injected from another syringe into the Erlenmeyer vessel. Gas samples were withdrawn for chromatographic analysis at various time intervals following the injection. For measurements of the rate from formaldehyde, the time of initiation of the reaction is somewhat uncertain because the rate of H_2 generation is fast on the time scale required for manipulation of the samples for analysis.

To examine the possibility of leakage of gases to/from the vessels during long thermal reaction times, several control experiments were performed. 50 μ l of H_2 was injected into 10 ml of an argon-saturated solution of 2.3 M NaOH. The solution was kept at 60 °C and the concentration of H_2 , N_2 , and O_2 (from possible air leaks) was measured as a function of time. Equilibrium between the solution and the gas phase was maintained by stirring, and the concentration of the gases in the liquid phase was calculated from the ratio of volumes of the two phases, as was the procedure in all our experiments with these vessels. The results for H_2 are shown in Figure D2-1. We conclude that the loss of H_2 by leakage in our experiments at the longest times used is not more than $\approx 10\%$. The maximum leakage of air into the vessel resulted in a concentration of O_2 in the liquid of less than 2% of the concentration that would result from 1 atm of air in equilibrium with

solution SY1-SIM-91C. From determinations of the effect of O_2 on the rate of thermal production of H_2 (*vide infra*), the effect of O_2 leakage on H_2 production rates is negligible even at the longest time shown in Figure D2-1.

b. Effect of Formaldehyde Polymers

To examine the possibility that polymers of HCHO that may be present in the original source of HCHO and generate H_2 , the following tests were conducted.

Paraformaldehyde. The source of formaldehyde was a 37% solution of formaldehyde in water containing 15% methanol. We find that paraformaldehyde is insoluble in these mixtures and therefore cannot be present in the original source of HCHO. This observation means only that paraformaldehyde is not the source of H_2 in the experiments reported below. It does not reflect on the ability of paraformaldehyde to generate H_2 .

Trioxane, a cyclic trimer of HCHO. This polymer is soluble in water and, therefore, may be present in the original source HCHO. Thus, we have determined the rate for thermal generation of H_2 at 60 °C from 1.67 mM trioxane solution in 2.3 M NaOH. The results are shown in Figure D2-2. Because each molecule of trioxane consists of three molecules of HCHO, the rate of H_2 generation from trioxane was compared with that from 5 mM HCHO in 2.3 M NaOH. The rate of H_2 generation from 1.67 mM trioxane is more than two orders of magnitude smaller than the rate for 5 mM HCHO in 2.3 M NaOH. We conclude trioxane cannot be the reactant in the experiments described below. This result may indicate either that the rate of depolymerization of trioxane is the rate-limiting step in this experiment or that if trioxane reacts directly, its rate of reaction is much slower than that of formaldehyde. Because the trimer does not contain the reactive hydrogen atoms of formaldehyde, the latter is an unlikely proposition.

Because the formaldehyde is in a solution containing 10-15% methanol by weight, a 15% weight methanol (no formaldehyde) in solution SY1-SIM-91C was tested to determine whether any thermal production of H_2 results from the methanol. Under our experimental conditions, no H_2 could be produced from this solution.

3. Results and Discussion

a. Formaldehyde in Simulated Waste Solutions

The initial rate of H_2 generation in solution SY1-SIM-91C containing 0.065 M formaldehyde was determined at 23, 45, and 60 °C. Figure D3-1 shows the rate of H_2 production from these formaldehyde-containing solutions at the three temperatures mentioned above. The rate for formaldehyde far exceeds the rates of H_2 production from the other organics tested in solution SY1-SIM-91C (Section C). The initial rate (this is the experimentally measured parameter, that is, the slopes of the lines in Figure D3-1) can be expressed by eq. D-1:

$$\left[\frac{d(H_2)}{dt}\right]_{\text{initial}} = k_{\text{obs}} \times [\text{OH}^-]^n \times [\text{HCHO}]^m, \quad (\text{D-1})$$

where n and m are the order of reaction in the corresponding reactant. As will be shown below, the initial rate depends on $[\text{OH}^-]$ to a power greater than 1, but at constant $[\text{OH}^-]$ and $[\text{HCHO}]$, an effective activation energy for the reaction can be derived from eq. D-1. The rate constant, k_{obs} , is determined from eq. D-1 and the rates shown in Figure D3-1, and using $[\text{HCHO}] = 0.065 \text{ M}$ and $[\text{OH}^-] = 2.3 \text{ M}$. Because of the higher order in $[\text{OH}^-]$, this treatment will yield an activation energy that is slightly dependent on $[\text{OH}^-]$. Figure D3-2 shows an Arrhenius plot, $\ln(k_{\text{obs}})$ vs. $1/T$, from

Figure C3-9. Rate and yield of N₂O generation at 60 °C from SY1-SIM-91C (solution P) containing 0.01 M NH₂OH.

Figure D2-1. Test for leakage of H_2 in/out of the modified Erlenmeyer vessels during the time of a thermal decomposition experiment. 50 μ l of H_2 was injected into 10 ml of 2.3 M NaOH at 60 °C and the amount of H_2 in the gas phase determined at various times.

Figure D2-2. The rate of generation of H_2 from 1.67 mM trioxane in 2.3 M NaOH at $60^\circ C$.

which one obtains an activation energy of 20.3 kcal per mole for this reaction. A similar treatment for the glyoxylate system (Figure D3-3) yields 9.8 kcal per mole.

Solution SY1-SIM-91C containing 0.065 M HCHO was also tested for thermal generation of N_2O at 60 °C. No N_2O was detected from this solution under our experimental conditions. We estimate an upper limit for the rate of N_2O generation from this formaldehyde containing solution to be $<1 \times 10^{-8} \text{ M min}^{-1}$ and thus (assuming first order in formaldehyde), $k_{\text{obs}} < 7.6 \times 10^{-8} \text{ M}^{-1} \text{ min}^{-1}$. The rate of N_2O generation from this solution is at least two orders of magnitude smaller than the rate of H_2 generation.

b. Formaldehyde in Aqueous Solutions

To determine the effect of the high concentration of NaNO_3 , NaNO_2 , and NaAlO_2 present in solution SY1-SIM-91C on the rates of H_2 generation from formaldehyde, the rates were measured in alkaline solutions containing HCHO only. Figures D3-4 and D3-5 show the effect of $[\text{HCHO}]$ and $[\text{NaOH}]$ on the rates of thermal generation of H_2 at 60 °C. The rate increases upon increasing the concentration of either reactant. Comparing these results with those reported for HCHO in solution SY1-SIM-91C, one sees that the effect of NaNO_3 , NaNO_2 , and NaAlO_2 is rather small. We conclude that the catalytic effect of aluminate, reported previously,¹⁴ operates on the thermal decomposition of the precursor (e.g., EDTA, etc.) and not on the hydrogen generation reaction.

Figure D3-6 shows the effect of temperature on the rates of thermal generation of H_2 in the HCHO-containing solution (2.3 M NaOH, no NO_x or aluminate). Assuming that the rates determined from the slopes of the lines of Figure D3-6 are defined by eq. D-1 with $n = m = 1$, effective rate constants were calculated as described above, and used for an Arrhenius plot given in Figure D3-7. The activation energy determined from this plot is $15.5 \text{ kcal mole}^{-1}$, which is somewhat smaller than the activation energy obtained for the same reaction in solution SY1-SIM-91C. The latter solution, of course, better reflects the conditions in tank SY-101. Importantly, we also observe that the conversion ratio of formaldehyde to H_2 increases with increasing temperature (in both cases, with or without NaNO_3 , NaNO_2 , and NaAlO_2).

The initial rates (i.e., initial slopes) of H_2 formation obtained at various concentrations of NaOH and HCHO are compiled in Table D3-1. The amount of H_2 generated vs. time at various concentrations of NaOH and HCHO is shown in Figures D3-8 through D3-10. Also shown in Table D3-1 are the observed rate constants, k_{obs} , calculated from eq. D-1 assuming $n = m = 1$. If the latter assumption holds, then a constant k_{obs} should be obtained. Figure D3-11 shows the dependence of initial rate of H_2 generation on $[\text{HCHO}]$ and $[\text{NaOH}]$. For $[\text{HCHO}]$ a linear dependence is observed and thus the assumption of $m=1$ in Eq. D-1 is justifiable. However, it is clear from Figure D3-11 that the rate is higher than first order in $[\text{NaOH}]$. A plot of $\log_{10}$ (initial rate) as a function of the $\log_{10}[\text{OH}^-]$ at two concentrations of HCHO is shown in Figure D3-12. The slopes of the lines are the order of the reaction in $[\text{OH}^-]$ (i.e., n in eq. D-1). On decreasing $[\text{HCHO}]$ from 5 mM to 0.5 mM, the order in $[\text{NaOH}]$ increases from 1.53 to 1.85. It seems that the order of the reaction asymptotically approaches two as the interference from the Cannizzaro reaction is minimized.

The conversion ratios of HCHO to H_2 , at long times after initiation of the thermal reaction, were measured and summarized in Table D3-2. This conversion ratio increases on decreasing HCHO concentration and on increasing $[\text{OH}^-]$. Similar observation was reported earlier by Ashby and coworkers¹² at much higher base concentrations.

Figure D3-1. Thermal generation of H₂ from solution SY1-SIM-91C containing 0.065 M formaldehyde at 23, 45, and 60 °C.

Figure D3-2. Determination of the activation energy for the reaction assumed to be as shown in the title.

Figure D3-3. Activation energy for the H_2 generation reaction from glyoxylate in SY1-SIM-91C. The reaction is assumed to be as shown in the title.

Figure D3-4. Rate of H₂ generation at 60 °C from 2.3 M NaOH (no NO_x or aluminate) solution at various HCHO concentrations.

Figure D3-5. Rate of H₂ generation at 60 °C from 5 mM HCHO (no NO_x or aluminate) solution at various NaOH concentrations.

Figure D3-6. Rate of H_2 generation from 0.065 M HCHO and 2.3 M NaOH (no NO_x or aluminate) solution at three temperatures.

Figure D3-7. Arrhenius plot for the rate constant of the H_2 generation reaction in aqueous solution containing 2.3 M NaOH and 0.065 M HCHO.

Table D3-1. H₂ production vs. [NaOH] and [HCHO] in aqueous solution.

[NaOH] M	[HCHO] M	temperature °C	initial rate $\times 10^8$ (M min. ⁻¹)	k _{obs} $\times 10^8$ (M ⁻¹ s ⁻¹)
1.0	5×10^{-3}	60	2.00	6.7
2.3	5×10^{-3}	60	6.50	9.00
4.0	5×10^{-3}	60	17.0	13.93
2.3	5×10^{-4}	60	0.77	10.00
4.0	5×10^{-4}	60	2.21	18.4
2.3	0.0325	60	24.7	5.51
2.3	0.065	60	55.2	6.15
2.3	0.13	60	91.0	5.01
2.3	0.065	21	2.5	0.28
2.3	0.065	45	14.0	1.56

Table D3-2. H₂ production vs. [NaOH] and [HCHO] in aqueous solution at 60 °C

time of measurement, Hours	[HCHO], M	[NaOH], M	conversion ratio [H ₂] _t / [HCHO] ₀
46.6	0.065	2.3	1.91×10^{-3}
52.6	0.005	1.0	3.2×10^{-3}
52.6	0.005	2.3	11.6×10^{-3}
52.6	0.005	4.0	26.7×10^{-3}
52.6	0.0005	2.3	34.9×10^{-3}
92.8	0.0005	2.3	48.5×10^{-3}

Figure D3-8. Generation of H₂ from 5 mM HCHO in aqueous solutions at three NaOH concentrations, at 60 °C.

Figure D3-9. Generation of H_2 from aqueous solutions of 0.065 M HCHO and 2.3 M NaOH, at 60 °C.

Figure D3-10. Generation of H₂ from aqueous solutions of 0.5 mM HCHO and 2.3 M NaOH, at 60 °C.

Figure D3-11. The dependence of the initial rate of H_2 generation in aqueous solution on $[HCHO]$ (circles; at 2.3 M NaOH) and on $[NaOH]$ (squares; at 5 mM HCHO).

Figure D3-12. Log of the initial rate of H_2 generation from formaldehyde in aqueous solution at 60°C as a function of $\log([\text{OH}^-])$. The slope, n , represents the order of the reaction in $[\text{OH}^-]$.

c. Computer Modeling

The experimental results at 60 °C for formaldehyde in solution SY1-SIM-91C were fit to a model that includes literature values for the rate constants of the Cannizzaro reactions and the equilibrium constants for the species derived from formaldehyde in basic solution. The reactions in the model (and their rate constants), except for the reactions postulated to lead to H₂, are taken or calculated from the work of Martin and material referred to therein.¹⁵ Martin's work was performed at 40 °C, whereas our experiments were conducted at 60 °C. The analysis below should, therefore, be considered with some reservation.

Let F designate formaldehyde (CH₂O); it is well established that formaldehyde hydrolyzes entirely in water to form the hydrate, methylene glycol (designated FH₂O). The hydrate is in equilibrium with the two base forms FOH⁻ and FO²⁻, which result from successive removal of protons from FH₂O. The equilibria among these species are described by eqs. D-2 and D-3 (equilibrium constants K₀ and K₁). As will be seen, K₀ and K₁ are not actually used in the modeling, but they are described here because of their relationship to K₂ and K₃. Values of K₀ as a function of temperature are also given by Martin¹⁶ and his work indicates that K₁ is at least 10³ times smaller than K₀.

Equilibria D-2 and D-3 can be transformed to D-4 and D-5, which were used in the calculations.

With $K_2 = K_2'/[\text{H}_2\text{O}]$ and $K_3 = K_3'/[\text{H}_2\text{O}]$, and using the dissociation constant of water (and its known temperature dependence), $K_d = [\text{H}^+] \times [\text{OH}^-]$, K₂ and K₃ are given by $K_2 = K_0/K_d$ and $K_3 = K_1/K_d$. Martin derives a value of $K_2 = 3.3 \text{ M}^{-1}$ at 40 °C.¹⁵ Using this value of K₂ and retaining the factor of $K_0 = 10^3 \times K_1$, one obtains $K_3 = 3.3 \times 10^{-3} \text{ M}^{-1}$. These values of K₂ and K₃ were used in the computations. From the measured values of K₀ and K_d at 40 and 60 °C, one can calculate that K₂ increases 33% in going from 40 to 60 °C. No information is available on the temperature dependence of K₁.

The rate constants, k₁ and k₂, of the Cannizzaro reactions D-6 and D-7 at 40 °C, have been measured¹⁵ and were used in the modeling calculations.

The following H₂-producing reactions were included in the model:

The rates of the forward and reverse reactions for equilibria D-4 and D-5 (K_2 and K_3) are needed for the calculations, but are unavailable in the literature. These were, therefore, assumed to be sufficiently fast, compared to the observed reaction rates, that is, the equilibria were fast achieved and always maintained during the H_2 generation reaction. Values of k_{forward} of $10 \text{ M}^{-1} \text{ min}^{-1}$ (and the corresponding k_{back} to give the correct equilibrium constant) were used in both cases. Increasing these values by an order of magnitude did not have any effect on the results of the calculation. No attempt was made to evaluate the effect of changes in K_2 and K_3 on the fit; the literature values were assumed to be correct. The fitting was done by integration of the set of differential equations representing the reaction mechanism given above (reactions D-6 to D-10) using a "Gear-type" ordinary differential equation solver,¹⁷ in conjunction with a non-linear least squares fitting routine.

The experimental data for formaldehyde in solution SY1-SIM-91C, but with varying $[\text{NaOH}]$, are shown by the points in Figure D3-13, and the lines are the results of the least-squares fit to the five data sets shown using the model described above. The parameters obtained from three attempts to fit the data are given in Table D3-3. The quality of the three fits is essentially equal, and only the results of "Fit 1" parameters (Table D3-3) are shown in the figure. In "Fit 1", all four parameters were allowed to vary. In the other two fits, the indicated parameters were fixed to the literature values. Note that only a lower limit is available for k_2 in the literature. The column labeled "Fit 3" provides parameters that are closest to those in the literature. The value for k_3 was set to zero in all fits because when it was allowed to float the standard deviations in k_3 through k_5 were larger than the values themselves. A good fit could not be obtained by fixing k_1 and k_2 to the literature values.

A fit using the same mechanism, except that reactions D-8 through D-10 do not contain OH^- as a reactant (e.g., reaction with water instead of OH^-), was attempted but an acceptable fit could not be obtained. This is consistent with the observation from Figure D3-12 that the rate of H_2 production is higher than first order in $[\text{OH}^-]$. The major uncertainty in this treatment is the use of literature values determined at 40°C for experiments performed at 60°C .

Table D3-3. Parameters obtained from the model calculations^a.

parameter	fit 1	fit 2	fit 3
k_1	1.05 ± 0.67	3.13 ± 0.72	3.0×10^{-3} (fixed)
k_2	273 ± 14	24.3 (fixed)	398 ± 87
k_4	$(0.93 \pm 0.32) \times 10^{-5}$	$(0.137 \pm 0.017) \times 10^{-4}$	$(0.72 \pm 0.27) \times 10^{-5}$
k_5	$(0.51 \pm 0.30) \times 10^{-3}$	$(0.65 \pm 0.08) \times 10^{-7}$	$(0.76 \pm 31) \times 10^{-3}$
σ_0^2 ^b	0.090	0.090	0.090

^aRate constants are given in units of $\text{M}^{-1} \text{ min}^{-1}$. Fixed values are also literature values.

^bStandard deviations from the least-squares fit; defined as: sum of the squares of the deviations divided by the number of points minus the number of free parameters.

Figure D3-13. Computation of the generation of H₂ from solution P (SY1-SIM-91C) containing various concentrations of HCHO and OH⁻ at 60 °C. Curves are calculated using the parameters given in Table D3-3 as Fit 1. Points are experimental data.

A more quantitative treatment of these data requires the use of activity coefficients for the ionic species. Whereas the activity coefficients of the common ions (e.g., sodium, hydroxide, nitrate, etc.) are well documented, those of many of the reactive species, in particular FOH^- and FO_2^{2-} , are not available. It is not expected that the changes in activity coefficients will be large when the formaldehyde reactions are carried out in the waste simulant, SY1-SIM-91C. The high concentrations of the other ions mean that changing OH^- concentration will not significantly change the ionic strength of the solution and thus the activity coefficients will not change significantly. Furthermore, the activity coefficients do not change sharply as a function of ionic strength at high ionic strengths. On the other hand, when the formaldehyde reactions were carried out in water as a function of OH^- concentration, the ionic strength and the activity coefficients do change due to the changes in OH^- concentration. This may explain the inability of the model to satisfactorily fit the formaldehyde reactions when carried out in water whereas a satisfactory fit is obtained for the reactions done in the high ionic strength of solution SY1-SIM-91C.

d. Effect of O_2 on the Thermal Generation of H_2

The effect of O_2 on the rate of the thermal generation of H_2 from formaldehyde either in solution SY1-SIM-91C or in aqueous alkaline solution at 60 °C was also studied. Results are shown in Figures D3-14 and D3-15. As can be seen in these figures, the rate of thermal generation of H_2 increases with the increase in concentration of O_2 in the solution. We can only speculate that the effect of oxygen in this case is via conversion of some O_2 to H_2O_2 (e.g., via reduction by formaldehyde), which in turn reacts with formaldehyde to generate H_2 ; this reaction has been studied by Ashby et al.¹² Because we believe that the contents of 101-SY are essentially deaerated, the relevant results are those from the Ar-saturated solutions, and we did not pursue this effect any further.

e. Source of the Hydrogen Atoms

Table D3-4 gives the results of experiments designed to determine the isotopic composition of the dihydrogen produced by the thermal decomposition of basic solutions of deuterated DCDO in H_2O or HCHO in D_2O at 23 °C. Clearly, under the experimental conditions of Table D3-4, a large fraction of the dihydrogen comes exclusively from the formaldehyde moieties. The presence of a significant percentage of HD, however, indicates that processes utilizing hydrogen atoms from water molecules also occur. Well-documented exchange processes, involving dihydrogen and water or hydroxide, were ruled out as contributing to the generation of HD because saturating 2.3 M $\text{NaOH}/\text{H}_2\text{O}$ with D_2 in a syringe (with no head space) generated very little HD or H_2 (last line, Table D3-4) on the time scale of these experiments. NMR experiments have shown little or no exchange between C-H in formaldehyde or formate and $\text{D}_2\text{O}/\text{NaOD}$. It is not clear, at this time, whether the two hydrogen atoms come from a single formaldehyde molecule or from two of them. The results from Section D3c above indicate that the former is more probable.

Table D3-4 also shows the results of similar experiments conducted with glyoxylate in $\text{NaOD}/\text{D}_2\text{O}$ solution. Most of the dihydrogen, in this case, is HD, which clearly indicates that one of the hydrogen atoms comes from water and the other from the glyoxylate (which has only one H atom per molecule). Two different mechanisms for H_2 production seem to operate for these aldehydes. Because the major difference between formaldehyde and glyoxylate is the number of hydrogen atoms on the carbonyl carbon, the difference in the mechanisms may reflect the ability of formaldehyde to produce dihydrogen from a single molecule. The rate of this "unimolecular" reaction in formaldehyde is apparently faster than the one that requires water participation (which is the only possible mechanism in glyoxylate).

Figure D3-14. Effect of oxygen concentration on the rate of generation of H₂ from 0.065 M HCHO in solution SY1-SIM-91C.

Figure D3-15. Effect of oxygen concentration on the rate of generation of H₂ from 0.065 M HCHO in 2.3 M NaOH.

Table D3-4. Isotopic composition of the dihydrogen generated from formaldehyde or glyoxylate in basic solutions of various isotopic compositions^a.

Sample Composition	% H ₂ , HD, or D ₂			Comments
	H ₂	HD	D ₂	
0.13 M CD ₂ O in 2.3 M NaOH/H ₂ O	15	28	57	
"	6	19	75	
"	10	11	79	
"	16	20	64	
Average (Std. Dev.)	12 (4.6)	19 (7.0)	69 (10.0)	isotopic composition at another CD ₂ O concentration
0.065 M CD ₂ O in 2.3 M NaOH/H ₂ O	6.8	26	67	isotopic composition at another CD ₂ O concentration
0.0325 M CD ₂ O in 2.3 M NaOH/H ₂ O	5.2	10.3	84.5	
"	4.7	11.0	84.4	
Average (Std. Dev.)	4.9 (0.4)	10.7 (0.5)	84.4 (0.2)	isotopic composition at another CD ₂ O concentration
0.13 M CH ₂ O in 2.3 M NaOD/D ₂ O	64	34	2	
"	67	32	1	
Average (Std. Dev.)	65.5 (2.1)	33.0 (1.4)	1.5 (0.7)	reverse labeling
0.0325 M CH ₂ O in 2.3 M NaOD/D ₂ O	42	57	0.3	
"	39	61	0.6	
Average (Std. Dev.)	40.5 (2.7)	59.0 (2.4)	0.5 (0.2)	reverse labeling another CH ₂ O concentration
0.13 M Glyoxylate in 2.3 M NaOD/D ₂ O	3.8	94	2.2	
"	9.1	89	1.3	
Average (Std. Dev.)	6.5 (3.7)	91.8 (3.1)	1.8 (0.6)	exclusively H ₂ O/RCHO mechanism
2.3 M NaOH/H ₂ O saturated with D ₂	0.25	0.84	98.9	test for D ₂ /OH ⁻ exchange

^a Gases extracted 30 min. after injection of CH₂O or CD₂O or glyoxylate into the basic solution at room temperature (23.1 ± 0.2 °C).

f. Effect of "Minor" Components on H₂ Generation From Formaldehyde

Figure D3-16 shows the rates of thermal generation of H₂ from SY1-SIM-91C solutions containing formaldehyde and 5.0 mM Cr(NO₃)₃, 1.0 mM K₂PtCl₆, 1.0 mM K₂PdCl₆, 0.25 M NaCl, 0.05 M NaF. The effects of these minor components on the radiolytic generation of H₂ is discussed in detail in Section E. The rates are quite comparable to the rates obtained above for SY1-SIM-91C solution containing formaldehyde only and no unusual behavior was encountered in the extraction procedure. This supports the conclusion reached in Section E that the "retention" of H₂ observed in irradiated solutions results from the radiolytic reduction of the Pd(IV) ions.

4. Conclusions

Formaldehyde is a well-documented degradation product of the original chelators that were placed in the tank. Formaldehyde does not affect the thermal generation of N₂O, but it does thermally generate H₂ in the waste simulants and in concentrated NaOH solutions. Rate laws for the direct generation of H₂ from formaldehyde were derived along with their corresponding rate constants and their temperature dependencies (i.e., activation energies) were determined. Isotopic composition studies show that a major source of both H atoms in the hydrogen molecule is the formaldehyde (i.e., little from the water). The observation that the reaction is first order in formaldehyde suggests that a single formaldehyde molecule is involved in the generation of one H₂ molecule. In clear distinction to the formaldehyde reaction, one H atom comes from water and the other from glyoxylate, in the case of glyoxalate.

Oxygen enhances H₂ generation from formaldehyde, but Tank 101-SY is presumed to be essentially deaerated. The minor components (Cr(III), Pt(IV), Pd(IV), Cl⁻, and F⁻) do not affect the thermal generation of H₂ from formaldehyde in the standard solution, neither do the high concentrations of nitrate, nitrite, and aluminate. Since paraformaldehyde is absent from the systems under study, and trioxane is very slow in H₂ generation, these two formaldehyde polymers are not important in that reaction.

E. EFFECT OF MINOR COMPONENTS

1. Introduction

Studies at PNL¹⁸ indicate that components of the waste that were considered relatively inert may have a significant effect on the composition of the gases generated. These components include transition metal ions, in particular Cr(III), Fe(III), Pd(IV), and Pt(IV), as well as halide ions (Cl⁻, F⁻). In this section we explore the effect of these "minor" components on the radiolytic yields of H₂ and N₂O. Our studies so far have established that radiolytic degradation products are very efficient in the thermal generation of H₂ and N₂O. These thermal processes, induced by radiolytic degradation products, may be significantly affected by the presence of small quantities of the minor components as these thermal processes occur on time scales that are longer than those considered in the pure radiolytic mechanisms. It is possible, therefore, that the presence of the above-mentioned minor components in the nuclear waste may change the course of degradation processes (e.g., via complexation with the chelators). We have, therefore, studied the effects of the minor components on the thermal rate of H₂ and N₂O generation as well.

We find no catalytic enhancement of either the radiolytic or thermal generation rates. Perhaps surprisingly, we observe that H₂ is retained in the solution or slurry by a degradation product of Pd ions (probably metallic Pd). Cr(III) ions reduce the radiolytic yield of N₂O but not the rate of thermal generation of N₂O.

Figure D3-16. The effect of the "minor" components (shown in title to the figure) on the rate of H₂ generation from solution SY1-SIM-91C containing formaldehyde at the concentrations indicated at 60 °C.

2. Experimental

Commercial NaOH, NaNO₃, NaNO₂, EDTA, HEDTA, sodium citrate, Cr(NO₃)₃, K₂PtCl₆, K₂PdCl₆, NaCl, and NaF were obtained from Aldrich and used as received. Aluminate, NaAlO₂ (from ICN), was baked at ca. 900 °C for 6 hours, dissolved in water, and filtered to remove small amounts of remaining particulate matter.

Solution SY1-SIM-91C containing 0.065 M EDTA, 0.065 M HEDTA and 0.1 M citrate was prepared and the following minor components added: 5.0×10^{-3} M Cr(NO₃)₃, 1.0×10^{-3} M K₂PtCl₆, 1.0×10^{-3} M K₂PdCl₆, 0.25 M NaCl and 0.05M NaF. This solution appears homogeneous with no visible evidence of a precipitate. Fe(III) salts could not be dissolved in the solution and were, therefore, not used. For determination of the radiolytic yields, homogeneous solutions were deaerated by argon bubbling in syringes before irradiation. Slurries were irradiated in Erlenmeyer vessels after deaeration by argon bubbling. For convenience, the composition of the homogeneous solution with the minor components and the SY1-SIM-92A slurry is given in Table E2-1.

The preparation of 1 liter of the slurry SY1-SIM-92A followed a procedure provided by S. Bryan of PNL.¹⁸ The following three solutions were prepared:

(i) Into 48.30 g water in a volumetric flask, 42.10 g Cr(NO₃)₃·9H₂O, 0.049 g Cu(NO₃)₂·3H₂O, 2.99 g Fe(NO₃)₃·9H₂O, 0.61 g Ni(NO₃)₂·6H₂O, 0.486 g K₂PtCl₆, and 0.397 g K₂PdCl were added.

(ii) Into 48.30 g water, in another volumetric flask, 4.55 g Na₂SO₄, 0.92 g CaCl₂, and 10.89 g KCl were added.

(iii) Into 386 g water in a 2 liter stainless steel beaker the following were added with constant vigorous stirring (listed in order of addition): 52.2 g EDTA, 53.2 g HEDTA, 30.7 g NaCl, 68.1 g Na₃PO₄·12H₂O, 272.6 g NaNO₂, 187.0 g NaNO₃, 42.4 g Na₂CO₃, and 4.20 g NaF.

Table E2-1. Composition of homogeneous solution and slurry used to measure the effect of "minor" components.

homogeneous solution			Bryan's standard slurry SY1-SIM-92A					
no.	component	conc. M	no.	component	conc. M	no.	component	conc. M
1	NaNO ₂	2.2	1	NaNO ₂	3.95	13	Na ₂ SO ₄	0.032
2	NaOH	2.3	2	NaOH	2.45	14	CaCl ₂	8.3×10^{-3}
3	NaNO ₃	2.8	3	NaNO ₃	2.2	15	Fe(NO ₃) ₃	7.4×10^{-3}
4	NaAlO ₂	0.86	4	NaAlO ₂	2.05	16	Ni(NO ₃) ₂	2.1×10^{-3}
5	NaCl	0.25	5	NaCl	0.526	17	Cu(NO ₃) ₂	2.1×10^{-4}
6	NaF	0.05	6	Na ₂ CO ₃	0.4			
7	EDTA	0.065	7	Na ₃ PO ₄	0.179			
8	HEDTA	0.065	8	KCl	0.146			
9	citrate	0.1	9	EDTA	0.14			
10	Cr(NO ₃) ₃	5.0×10^{-3}	10	HEDTA	0.14			
11	K ₂ PtCl ₆	1.0×10^{-3}	11	Cr(NO ₃) ₃	0.105			
12	K ₂ PdCl ₆	1.0×10^{-3}	12	NaF	0.1			

The contents of solution (i), then the contents of solution (ii), and finally 83.04 g NaOH, 184.2 g NaAlO₂ (containing 0.18 g NaOH and 0.03 g H₂O) were added to solution (iii). The resultant solution was covered with a watch glass, wrapped with aluminum foil, and stirred at 60-70 °C overnight. The final molarities of the various components based on the density of the slurry, 1.56 g/cm³, as provided by Bryan, are given in Table E2-1. However, we consistently find the density to be slightly higher, 1.60 g/cm³, and use this value to calculate the absorbed dose. For thermal generation experiments using preirradiated samples, the preirradiations were performed in covered (but not gas-tight) stainless steel beakers. Gases were analyzed using the usual Van Slyke-gas chromatographic technique.

3. Results and Discussion

a. Effect of "Minor" Components on Radiolytic Yields

Homogeneous Solutions. $G(H_2)$ was determined for argon-saturated SY1-SIM-91C solutions containing the components given in Table E2-1. The solutions were irradiated at a dose rate of 3.3 krad/min to a total dose of 130 krad. Results are given in Table E3-1. In all the irradiated solutions shown in Table E3-1, except those containing Pd, 98% of the H₂ was extracted in the first extraction using the Van Slyke technique. In the presence of Pd, the amount of gas obtained on the first extraction was drastically reduced (to approximately 2% of the amount obtained in the other solutions). On successive extractions, H₂ was continually extracted. The amount of time that the solution spends under vacuum (during the extraction) seems to affect the amount extracted; in other words, equilibration of the gas between the solution and the gas phase is very slow. Therefore, the value of $G(H_2)$ for solutions that contained Pd could not be determined. The detailed results given in Table E3-1 show that it is indeed the Pd that is responsible for this unusual behavior. Several conceivable possibilities were checked to determine the reasons for this "retention" of H₂ (we emphasize, though, that no particulate could be observed in any of these solutions):

1. The possibility of a postradiolytic chemical reaction was checked as follows: An irradiated sample of SY1-SIM-91C containing the organics and minor components was left overnight to determine whether a slow, postradiolytic, chemical reaction was producing H₂. This long aging did not change the results, that is, little H₂ was obtained on the first extraction and more was obtained on successive extractions. Therefore, we conclude that a postirradiation chemical reaction is not responsible for the retention.

2. The possibility that the original palladate (or a product of a chemical reaction prior to the irradiation) is responsible for the retention was checked as follows: A SY1-SIM-91C solution containing all the organics and minor components was 10% saturated with H₂. The solution was not irradiated. Hydrogen could then be completely recovered (98%) after an hour of equilibration. Therefore, this possibility was ruled out.

3. The possibility that the original palladate (or a product of a chemical reaction prior to the irradiation) in combination with some other irradiation product is responsible for the "retention" was checked as follows: SY1-SIM-91C solution with the organics and the minor components, except K₂PdCl₆, was irradiated. After irradiation, K₂PdCl₆ was added to the solution and the solution analyzed for H₂. The usual behavior (98% of the H₂ recovered on the first extraction) was observed. Thus, neither the original palladate ions, nor a product of a chemical reaction of it, is responsible for the above-described observations; to obtain the observed effect, Pd(IV) must be present during radiolysis. The last line in Table E3-1 also shows that none of the other components, or their irradiation products, is necessary in order to obtain that effect.

4. The possibility that the effect could be eliminated by dilution (e.g., due to dissolution of colloidal, invisible to the naked eye, particles) was also investigated. Five ml of water was added to 10 ml of irradiated SY1-SIM-91C solution containing the organics and all minor components.

The same retention was observed and addition of water did not change the results. Thus, 50% dilution with water did not alter the situation.

5. To examine whether irradiated Pd(IV) retains H₂, a known amount of H₂ was added to solution SY1-SIM-91C containing the organics and Pd(IV) after its irradiation. As can be seen in Table E3-2, when H₂ is injected after the irradiation, it is retained in the solution.

6. Two samples of SY1-SIM-91C solution containing organics were irradiated and the amount of H₂ generated in one was determined. After irradiation, 1 mM of K₂PdCl₆ was added to the other sample and it was further irradiated. It was observed that most of the H₂ generated in the solution before the addition of Pd(IV), as well as most of the H₂ generated in the second irradiation, was now "retained" in the solution. Results and experimental details are summarized in Table E3-2. This result can be rationalized on the basis that the solution of the irradiated Pd(IV) retains H₂ that was generated radiolytically before Pd(IV) addition, rather than inhibiting the generation of H₂.

Table E3-1. The effect of minor components on G(H₂) in solution SY1-SIM-91C containing 0.065 M HEDTA, 0.065M EDTA, and 0.1 M citrate^a.

Solution	G(H ₂)	Comments
SY1-SIM-91C + organics ^b (= POC)	0.053	blank; similar results to Section B
POC ^b + Cl ^c + F ^c	0.058	no effect of Cl or F
POC ^b + Cl ^c + F ^c + Cr ^c	0.051	no effect of Cr
POC ^b + Cl ^c + F ^c + Cr ^c + Pt ^c	0.055	no effect of Pt
POC ^b + Cl ^c + F ^c + Cr ^c + Pt ^c + Pd ^{c,d} (Pd(IV) added after irradiation)	0.058	original Pd(IV) is not responsible
POC ^b + Cl ^c + F ^c + Cr ^c + Pt ^c + Pd ^c (Pd(IV) added before irradiation)	could not measure; see text ^e	irrad. product of Pd(IV) is responsible
POC ^b + Pd ^c (Pd(IV) added before irradiation)	could not measure see text ^e	no other minor component is necessary

^a Irradiations were done at a dose rate of 3.3 krad/min to a total dose of 130 krad.

^b SY1-SIM-91C contains 2.3 M NaOH, 0.86 M NaAlO₂, 2.8 M NaNO₃, and 2.2 M NaNO₂, and the organics are 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate. Sometimes designated POC.

^c [Cr] = 5.0×10^{-3} M Cr(NO₃)₃; [Pt] = 1.0×10^{-3} M K₂PtCl₆; [Pd] = 1.0×10^{-3} M K₂PdCl₆; [Cl] = 0.25 M NaCl; [F] = 0.05 M NaF.

^d Pd was added to POC containing Cr, Cl, F, and Pt after the irradiation.

^e The amount of H₂ extracted at the first attempt is approximately equivalent to G(H₂)=0.001 but the equivalent of at least G(H₂)=0.007 can be extracted in further consecutive extractions.

Table E3-2. The effect of Pd(IV) in SY1-SIM-91C solution containing 0.065 M HEDTA, 0.065 M EDTA, and 0.1 M citrate on H₂ yields.

#	solution	[H ₂], M	comments
1	SY1-SIM-91C + organics ^a (no Pd; =POC), + 65 krad ^b	4.2×10^{-6} (98% H ₂ extracted in first extraction)	similar to G(H ₂) determined earlier for POC; blank for #2
2	POC + 65 krad then POC+Pd(IV) added and irradiated to 65 krad ^c	2×10^{-7} successive extractions continue to give H ₂	<5% of H ₂ that was generated in first irradiation. compare with #1
3	to POC (no irradiation, no Pd) H ₂ saturated POC was added ^d	1.17×10^{-5} (98% H ₂ extracted in first extraction)	provides a measure for added H ₂ ; compare with row 6
4	to POC + 65 krad (no Pd), H ₂ saturated POC was added ^d	1.39×10^{-5} (98% H ₂ extracted in first extraction)	added H ₂ plus radio- lytically generated H ₂ ; compare with #6
5	POC+Pd(IV) + 65 krad ^e	4×10^{-7} successive extractions continue to give H ₂	<10% of H ₂ generated in irradiation. was extracted; compare with #1
6	POC+Pd(IV) + 65 krad, H ₂ saturated POC was added ^e	6×10^{-7} successive extractions continue to give H ₂	<5% of H ₂ that was added was extracted; compare with #4

^a SY1-SIM-91C contains 2.3 M NaOH, 0.86 M NaAlO₂, 2.8 M NaNO₃, 2.2 M NaNO₂, and the organics are 0.065 M EDTA, 0.065 M HEDTA and 0.1 M citrate. Labeled POC.

^b Irradiated at a dose rate of 3.3 Krad/min. to total dose of 65 Krad.

^c 8 ml of POC was irradiated to a dose of 65 krad. Then 2 ml. of 5 mM K₂PdCl₆ in POC solution was added (to give 10 ml of 1 mM Pd(IV) in POC) and was further irradiated an additional 65 krad.

^d To 9 ml. of solution POC (irradiated to 65 krad when indicated), 1 ml of H₂ saturated POC solution was added. No Pd.

^e To 9 ml. solution POC containing 1 mM Pd(IV) irradiated to 65 krad, 1 ml of solution POC (saturated with Ar for row 5, or H₂ for row 6) solution was added.

It is clear from these observations that the presence of Pd(IV) *during* the irradiation affects the measurable yield of H₂; when it is added after the irradiation, there is no effect on the yield of H₂. The exact mechanism for the effect of Pd is not known. Several unusual lower oxidation states of Pd are known to exist following irradiation (e.g., Pd(III), Pd(I), or Pd₂²⁺, as well as metallic palladium colloids). The retention of H₂ in irradiated solutions, originally containing Pd(IV), may be due to lower oxidation states of Pd (probably the metallic state), which are formed during irradiation. Most probable reducing species are the organic radicals produced by degradation of the organic compounds present in the solution. To verify this hypothesis, the radiolytic yields of H₂ were determined for SY1-SIM-91C solutions containing either all minor components, or Pd only, but in the absence of any organic component in both cases. In all cases, shown in Table E3-3, 98% of the H₂ was extracted in the Van Slyke apparatus in the first extraction. It seems that the organics are necessary to induce the retention of H₂. From the results reported earlier, one may conclude that the organic radicals reduce Pd(IV), perhaps to the metallic oxidation state.

Table E3-3. Radiolytic H₂ yields at 30 °C from solution SY1-SIM-91C in the presence of minor components but in the absence of organics^a.

solution:	SY1-SIM-91C	SY1-SIM-91C + all minor components	SY1-SIM-91C + 1.0 mM K ₂ PdCl ₆
G(H ₂)	0.030	0.035	0.033

^a Minor components are: 5.0×10^{-3} M Cr(NO₃)₃, 1.0×10^{-3} M K₂PtCl₆, 1.0×10^{-3} M K₂PdCl₆, 0.25 M NaCl, and 0.05 M NaF. Dose rate = 3.31 krad/min and dose = 130 krad.

Slurries. The radiolytic yields of H₂ were determined in the SY1-SIM-92A slurry prepared as described above. The slurry was irradiated at 3.31 krad/min to a dose of 545 krad. The radiolytic yields of H₂ are affected by Pd(IV) in the same way as was observed for the homogeneous SY1-SIM-91C solutions. The results are summarized in Table E3-4.

Nitrous oxide yields, G(N₂O), were measured for the argon-saturated standard homogeneous solution given in Table E2-1 following irradiation at 3.3 krad/min to a total dose of 130 krad. The results are summarized in Table E3-5. It can be seen in this table that G(N₂O) is strongly reduced by the presence of Cr(III). The radiolytic yields of N₂O were also determined for SY1-SIM-92A slurry. The slurry was irradiated at 3.31 krad/min to a dose of 545 krad. The radiolytic N₂O yields are substantially reduced by Cr(III) (or its radiolytic products), as it was for the homogeneous solution SY1-SIM-91C. G(N₂O) results from this slurry, and several blanks, are summarized in Table E3-6.

In summary, no qualitative difference between the homogeneous solutions and the slurries was observed with respect to the effect of the minor components, either on G(H₂) or G(N₂O). It should be clearly recognized that the two metal ions have very different effects. Although Pd does not seem to inhibit the generation of H₂ (only its release from the simulant is inhibited), Cr seems to genuinely reduce the yield of N₂O. Chromium seems to intercept the sequence of reactions that leads to N₂O but Pd does not intercept the generation of H₂.

Table E3-4. Radiolytic H₂ yields obtained for slurry SY1-SIM-92A at 30 °C^a

slurry	G(H ₂)	comments
SY1-SIM-92A (no Pd(IV))	0.067	
SY1-SIM-92A (with Pd(IV))	(0.007) ^c	Pd retains G(H ₂) (90% retained)
SY1-SIM-91A + 0.3 M EDTA ^b	0.04	similar to SY1-SIM-92A (first row above)

^a Dose rate = 3.31 krad/min and dose = 545 Krad.

^b 2.3 M NaOH, 2.2 M NaAlO₂, 3.7 M NaNO₃, 3.2 M NaNO₂, 0.6 M Na₂CO₃, and 0.3 M EDTA.

^c Could not be determined, as in footnote e of Table E3-1

Table E3-5. The effect of minor components on $G(N_2O)$ at 30 °C in SY1-SIM-91C solution containing 0.065 M HEDTA, 0.065M EDTA, and 0.1 M citrate^a.

solution	$G(N_2O)$	comments
SY1-SIM-91C +organics ^b = POC	0.55	blank; similar results in section B.
POC ^b + Cl^- ^c + F^- ^c	0.52	No effect of Cl or
POC ^b + Cl^- ^c + F^- ^c + Cr(III) ^c	0.29	Cr reduces $G(N_2O)$
POC ^b + Cl^- ^c + F^- ^c + Cr(III) ^c + Pt(IV) ^c	0.26	Pt has little effect.
POC ^b + Cl^- ^c + F^- ^c + Cr(III) ^c + Pt(IV) ^c + Pd(IV) ^c	0.22	Pd has little effect.
POC ^b + Pd(IV) ^c	0.66	Pd has little effect.

^a Irradiations were done at a dose rate of 3.3 krad/min to a total dose of 130 krad.

^b SY1-SIM-91C contains 2.3 M NaOH, 0.86 M NaAlO₂, 2.8 M NaNO₃, and 2.2 M NaNO₂, and the organics are 0.065 M EDTA, 0.065 M HEDTA, and 0.1 M citrate. This composition is labeled POC.

^c Cr = 5.0×10^{-3} M Cr(NO₃)₃; Pt(IV) = 0.001 M PtCl₆; Pd(IV) = 0.001 M K₂PdCl₆; Cl^- = 0.25 M NaCl; F^- = 0.05 M NaF.

Table E3-6. Radiolytic yield of N_2O obtained for slurry SY1-SIM-92A at 30 °C^a

slurry	$G(N_2O)$	comments
SY1-SIM-92A (no transition or noble metals)	0.421	
SY1-SIM-92A (no Cr(III))	0.377	none of the "minor components" affects the yield
SY1-SIM-92A	0.133	Cr reduces $G(N_2O)$
SY1-SIM-91A + 0.3 M EDTA ^b	0.37	similar to SY1-SIM-92A (rows 1 and 2 above)

^a Dose rate = 3.31 krad/min; dose = 545 krad.

^b 2.3 M NaOH, 2.2 M NaAlO₂, 3.7 M NaNO₃, 3.2 M NaNO₂, 0.6 M Na₂CO₃ and 0.3 M EDTA.

b. Effect of "Minor" Components on Thermal Generation Rates

The rate of thermal generation of H_2 from preirradiated solutions SY1-SIM-91C containing 0.065 M EDTA, 0.065 M HEDTA, 0.1 M citrate and the minor components given in Table E2-1, was measured. The solution was preirradiated to 16 Mrad, a dose that gave the maximum rate for thermal generation of gases as described in Section C (see Figure C3-2).

Figure E3-1 shows the thermal production of H_2 from samples of this preirradiated solution (note that the samples were degassed after the preirradiation and used as starting material for the thermal studies). It can be seen that the presence Pd(IV) in the original solution leads to the same retention of H_2 as discussed above. Hydrogen is retained, as in the case of the radiolytic studies, that is, successive extractions of gas result in further release of hydrogen. This effect was not observed when Pd(IV) was absent from the preirradiated solution (solid circles in Figure E3-1). The rate of thermal generation of H_2 for the solutions containing organics and minor components, except Pd(IV), is roughly the same as was observed earlier for SY1-SIM-91C solution containing the organics only (Section C of this report). A blank experiment, where the rate of the thermal generation of H_2 was determined for identical, but not preirradiated, SY1-SIM-91C solutions containing the organics and all the minor components (including Pd) was also performed. No H_2 was detected under these experimental conditions. We estimate an upper limit for the rate of H_2 production from this solution to be $< 2.1 \times 10^{-10} \text{ M min}^{-1}$.

Rates of thermal generation of N_2O from preirradiated SY1-SIM-91C solutions of the composition shown in Table E2-1 were measured. As for H_2 , the solutions were preirradiated to a dose that gave the maximum rate for thermal generation of gases. Figure E3-2 shows the thermal production of N_2O from preirradiated (35.8 Mrad) solution of SY1-SIM-91C containing the components listed above. As can be seen in Figure E3-2, the presence of Cr(III) does not affect thermal generation of N_2O . A control experiment was also performed in which the rates of the thermal generation of N_2O were determined for identical but unirradiated solutions. Thermal generation of N_2O from this control solution is shown in Figure E3-3. On comparing Figures E3-2 and E3-3 it seems that the preirradiation enhances the rate of N_2O generation by approximately a factor of five, regardless of the presence of the minor components (including Cr(III)).

In both Figures E3-2 and E3-3 one observes an induction period. This is an indication that the N_2O is a secondary product resulting from degradation of a predecessor degradation product. For the solutions that were not preirradiated, this degradation product must be thermally generated. It can also be seen that an induction period is shorter for the preirradiated solutions than for the control solutions, by approximately the same factor that the rate is enhanced.

The radiolytic yields of N_2O for homogeneous solutions, as well as for slurries, decrease when Cr(III) is present, as is shown above. Hydroxylamine has been proposed as an intermediate in the mechanism of N_2O generation. We, therefore, studied the effect of Cr(III) on the rate of thermal generation of N_2O from solution SY1-SIM-91C containing 5 mM Cr(III) and 0.01 M NH_2OH at 60 °C (no organics nor other minor component). The rate of N_2O generation from a similar solution that did not contain Cr(III) is described in Section C3d. Figure E3-4 shows the generation of N_2O from the solution containing Cr(III). The rate is an order of magnitude slower than that obtained for the same solution without Cr(III) ($8.8 \times 10^{-6} \text{ M min}^{-1}$, as can be calculated from Figure C3-9). This observation is compatible with the mechanism that invokes NH_2OH as an intermediate. In distinction to the effect of chromium ions on the radiolytic yields, no effect was observed on the thermal generation rate. A possible explanation for this difference would invoke different mechanisms for N_2O generation radiolytically and thermally.

4. Conclusions

Among the minor components, Pd(IV), after irradiation in the presence of organics, strongly retains hydrogen, but does not inhibit its formation. The other minor components (Cr(III), Pt(IV), Cl⁻, and F⁻) have little effect on either H₂ yields or its retention. The retention is attributed to a reduced form of Pd, probably metallic Pd produced by a reaction of organic radicals with the original ion. The effect of Pd(IV) is similar in both homogeneous solutions and slurries.

In the radiolysis of solution or slurry simulants, the yield of N₂O is strongly reduced by Cr(III), but is not affected by the other minor components. The thermal rates of N₂O generation from these simulated waste solutions are not affected by Cr(III). However, in SY1-SIM-91C with hydroxylamine (a degradation product intermediate), the thermal rate of N₂O generation is reduced by an order of magnitude upon the addition of Cr(III).

F. GAS RETENTION

1. Introduction

The problems of gas generation and retention couple to create the potentially flammable conditions in tank 101-SY. The rate of hydrogen generation is low and would not present a serious problem if the gases were released continuously. However, much of each gas is retained within the tank and then released periodically. During such an episodic release of gas, the concentration of hydrogen in the oxidizing atmosphere of nitrous oxide is within the flammability limits. To shed some light on the mechanisms of retention, we measured the retention of H₂ and N₂O in a few simulant slurries.

2. Experimental

The slurry used for these experiments was the standard SY1-SIM-91A slurry to which 0.3 M EDTA was added. The first problem addressed was the method of supersaturating the slurry in a manner consistent with the conditions in 101-SY. Three approaches were undertaken - bubbling the sample, pressurizing the sample, and irradiation. Irradiation would simulate the generation and retention of gas in tank 101-SY best; the former two were explored because they would have been easier to perform and would have been quicker. However, the behavior of the gas retention in the irradiated samples was different from either of the other two techniques and it became evident that the results depend strongly on the method utilized for supersaturation. Therefore, only the results from the irradiation experiments will be discussed in detail.

Methods of Supersaturation. To measure the amount of gases retained by a slurry, provisions were made to introduce the gas into the slurry in a manner similar to gas formation in the tank and to measure it with minimum manipulation. Three methods of addition of the gas to the slurry were tested: 1) bubbling, 2) pressurization, and 3) radiolytic generation of the gases. For all three methods, identical vessels were utilized in the measurements. However, the pressure cell described below was utilized only for method 2. Each method gave different results, indicating strong dependence of the total gas retained on the slurry pretreatment, age of the slurry, and time that the gases were in contact with the slurry particles. Method 3 is believed to best simulate gas generation in the tank.

Method 1: The gas was bubbled in the glass vessel described in Figure F2-1. Extraction of the gas using the Van Slyke gas apparatus was discussed previously.¹

Method 2: To simulate the gas formed in the nonconvective layer of the tank, the slurry was put in a glass vessel inside a pressurization cell housing (Figure F2-1) under gas pressure and allowed to equilibrate. After a preset time, the excess gas was released slowly, and the glass vessel was removed from the pressurization cell and connected to the Van Slyke apparatus for gas extraction (Figure F2-2).

Figure E3-1. The rate of thermal generation of H₂ from preirradiated (16 Mrad) solutions SY1-SIM-91C containing organics (designated POI) and "minor" components at 60 °C. Solid circles: all minor components except Pd(IV). Open squares: all minor components including Pd.

Figure E3-2. The rate of thermal generation of N_2O from preirradiated (35.8 Mrad) solutions SY1-SIM-91C containing organics and minor components at 60 °C. Solid triangles: all minor components. Open circles: all minor components except Cr(III).

Figure E3-3. The rate of thermal generation of N₂O from control SY1-SIM-91C containing organics and all minor components, but not preirradiated, at 60 °C.

Figure E3-4. The rate of thermal generation of N_2O from solution SY1-SIM-91C containing 0.01 M NH_2OH and 5 mM $\text{Cr}(\text{NO}_3)_3$ at 60°C . The rate is an order of magnitude smaller than in the absence of Cr(III).

Method 3: Long-term irradiation generated gases in amounts far exceeding the saturation levels of the various gases. The irradiation was carried out in 100 ml stainless steel beakers (each containing 50 ml of slurry) covered with glass dishes. The cover protects the samples from external contamination but is not gas-tight. At the end of the irradiation the samples were transferred into the same gas extraction vessel (Figure F2-2) with minimum manipulation. In all of the irradiated samples foamy crust, of variable consistency and thickness, was formed on top of the samples. This crust had to be broken before transferring the samples to the extraction vessel. During this manipulation, gas was released and a strong ammonia odor was noticed. The irradiation is essentially the same as the preirradiation described in Section C of this report.

The pressurization system is shown in Figure F2-1. The pressurization vessel is a plastic housing (5" diameter, 18" long); no pressure differential develops between the inside and outside of the internal glass cylinder containing the slurry and thus no special high-pressure arrangements need to be made for the slurry-containing cell. Copper tubing is connected from both cap openings at the top of the housing to a common line. This common line is attached to a compressed gas cylinder with a regulator that can maintain the desired pressure. This same common line also serves as the gas outlet when the valve to the gas tank is closed and a bleed-off needle valve (labeled A in Figure F2-1) is opened. The pressure on both sides of the slurry-containing extraction cylinder, attached to the central opening, is therefore the same at all stages of the pressurization cycle. The line to the central connection is also provided with a shut-off valve (labeled B) to prevent any back-flow of air upon removing the extraction cylinder from the pressurization system.

The extraction apparatus is an adaptation of a Van Slyke apparatus and is shown in Figure F2-2. Because of the consistency of the slurry, we wished to minimize its manipulation, and especially to avoid passing it through small orifices, such as in stopcocks. The apparatus also required easy access to various parts for cleaning purposes. It, therefore, requires separable and interchangeable parts. There are four parts to it, as shown in Figure F2-2.

The mercury manifold is secured at an angle, and is connected to a mercury-filled leveling bulb at one end. It has a vertical ground glass joint in the center, and can be connected to a vacuum pump at the other end. Each end can be closed off from the center by a stopcock. The graduated container has a ground glass joint at the bottom portion that fits into the mercury manifold, allowing mercury to be raised into the cylinder through the center stem and stopcock. The cylinder top also has a ground glass joint. The cap segment has a ground glass joint for connection to the top of the container, a short glass tube that can be connected to a vacuum pump (the exhaust port), and a three-way stopcock. The glass loop has a short vertical tube (with a spherical joint for attachment to the upper segment) which intersects the horizontal loop in a T-junction. Both arms of the loop lead to a four-way stopcock that enables the loop to be connected to a gas chromatograph. The cylinder and cap segments together form the extraction vessel.

For pressurization experiments, 10 ml of the slurry under investigation is placed into the extraction cylinder, a magnetic stirring bar is added, and the cap segment of the extraction vessel is clamped into position, with the three-way stopcock open to the cylinder. This complete extraction vessel is secured to the central connection at the top of the pressurization housing, and lowered into the vessel. The vessel is tightly capped and gas from a cylinder is introduced through both the central and side gas connections, both into the surrounding and extraction vessel. The pressure is raised to the desired level. The stirring motor is turned on for the desired period of time. The pressure is maintained for an additional time after stirring is stopped. The gas tank is then shut off, and the pressure gradually released from the vessel through the bleed-off valve (A, in Figure F2-1) over a period of approximately an hour. As soon as gas ceases to flow through the bleed-off valve, the line connection to the gas tank is closed with a valve (B, in Figure F2-1) to prevent any air from entering the extraction vessel. The pressurization vessel is opened, the extraction vessel lifted out, and the three-way stopcock closed to seal in the gas atmosphere. Only then is the extraction vessel detached from the central gas connection.

Figure F2-1. Pressurization cell and extraction vessel inside the housing. The internal cell was also used for gas bubbling.

The extraction vessel is clamped onto the mercury manifold, and air in the manifold and the portions of the extraction cylinder below its bottom stopcock is pumped out. Mercury is then allowed into the evacuated segment, the stopcock is opened, and the mercury is raised into the cylinder using the mercury-leveling bulb. This pushes the slurry to the upper end of the bore of the three-way stopcock; excess gas in the head space is released, and the stopcock is closed. The loop is then connected and clamped at the ball joint, opened to the exhaust port by the three-way stopcock, and evacuated by the vacuum pump. The three-way stopcock then connects the loop to the cylinder, and the slurry is lowered back to the bottom of the cylinder using the mercury manifold. The slurry becomes very frothy as it is subjected to vacuum. The magnetic stirrer is turned on and the slurry is mixed for 20 minutes. The slurry is then raised all the way to the T-junction of the loop to compress all the released gas into the loop, which is opened to the gas chromatograph for quantitative analysis. After a number of repetitive extractions, the slurry is dissolved with 10 ml of deaerated water while the slurry is maintained under vacuum; final extraction then follows.

To saturate the slurry by bubbling, a 10 ml slurry sample was bubbled for 45 minutes, at atmospheric pressure, in the same vessel. The slurry was then allowed to equilibrate for the desired time under 1 atm of the gas and then analyzed as above. It was noticed that the mechanical treatment by the bubbling changes the consistency of the slurry. Similarly, the irradiation and the pressurization each yields slurries of different thickness, "stickiness", and viscosity.

3. Results and Discussion

The gases generated by irradiation were of two types - loosely bound gas (loose) and tightly bound gas. The "loose" gas can be easily extracted from the sample using a Van Slyke apparatus, whereas the tightly bound gas could not be extracted from the slurry (except by dissolution of the solids). These two retention modes describe the gas that is formed by irradiation. Both hydrogen and nitrous oxide were found as part of the loose and tight fractions. In addition, nitrogen was found as part of the tightly bound gas. Nitrogen could also have been present in the loose gas fraction; however because the irradiation was done in an open atmosphere, it was not possible to discriminate against the atmospheric nitrogen that would also be present.

The amount of gas retained in the sample and released as loose gas depended on the dose rate and the amount of dose (see Table F3-1). A description of the slurry after irradiation can also be found in this table. These are given in an attempt to correlate the apparent gas retention and the visual form of the slurry. The retention appears to arise from the physical characteristics of the irradiated sample (probably surface tension characteristics). For example, for short, high-dose-rate irradiations, a persistent foam is formed; whereas for longer irradiations, an easily broken foam is formed. Because the samples were stirred before measurement, the samples with the easily broken foam showed much lower gas retention. It is known that small quantities of organic molecules can strongly affect foam stability. Changes in the composition of the organic molecules probably cause the differences that were seen between similar irradiations (the loose hydrogen in the 16 Mrad, 23 day irradiation and the 16 Mrad, 21 day irradiation). Supporting the hypothesis that it is the physical entrapment rather than specific chemical interactions is the similarity in the ratio of H_2 to N_2O between the 23-day and 63-day irradiations despite the nearly factor-of-five difference in the total amount of gas.

The tightly bound gas could only be released on dissolution of the solid phase of the slurry. The gas may be formed inside the irradiated solids and there is no facile pathway for gas exchange into the liquid. We cannot estimate the rate at which the transfer occurs to the liquid. However, if one compares the data for a 23-day and a 63-day irradiations, one finds that the ratio of the amount of tightly bound H_2 in the 63-day to the 23-day is 2.25 whereas the ratio of the dose is 3.13. For N_2O , the comparable ratio is 1.25. These results suggest that N_2O can escape more quickly into the liquid. If one assumes that the release of gas from the particles is proportional to the amount of

gas trapped within the particle, one can estimate the $1/e$ time for release of H_2 from the solid to be approximately 90 days; similarly for N_2O the release time is approximately 15 days. However, if the trapped gas reacts within the particle, the release times would be even longer.

Figure F2-2. Extraction vessel of retained gas and related connections.

The only role of such tightly bound gas in 101-SY would be to supply an additional mechanism for the release of gas into the tank mixture. Because stirring and evacuation were incapable of releasing this gas, it cannot be contributing to a venting event. After the system has reached steady state, the gas trapped in the solid will be released as fast as it is formed. Because the G values for gases, measured elsewhere in this report, were determined for all fractions, not just loose ones, these values will be appropriate for a system that has reached steady state - the situation that will have occurred in SY-101.

4. Conclusions

Measurements of gas retention suggest that the retention mechanism is primarily physical entrapment rather than strong chemical attachments. They also suggest that this retention will be independent of the chemical composition of the gas, at least for H_2 and N_2O . The gas generated within a particle in the slurry will be released slowly. Because the generation rate measurements described in this report followed the total gas, and not just loose gas, these rates and yields will appropriately describe a system that is near steady state, presumably the situation in 101-SY. The dose and dose rate in the tank will affect gas retention properties because they affect the rate of gas generation.

Table F3-1. Behavior of N_2O and H_2 in irradiated slurries.

N_2O			
irradiation	initial $N_2O \times 10^4, M$	tightly bound $N_2O \times 10^4, M$	sample description
44 hr, 16 Mrad	34	2.51	not well consolidated
23 day, 16 Mrad	35	1.9	steamed bun like
63 day, 50 Mrad	8	2.37	very firm and not bubbly
H_2			
=====	Initial $H_2 \times 10^4, M$	Tightly bound $H_2 \times 10^4, M$	=====
21 day, 16 Mrad	1.5	0.19	crudy
same	1.14	0.18	after one day
same	1.37	0.21	after two days sonicated
same	1.03	0.16	sonicated
42 hr, 16 Mrad	6.04	(0.61?)	creamy
22 hr, 16 Mrad	10.7	0.27	meringue-like
23 day, 16 Mrad	4.84	0.24	steamed bun-like and foamy
63 day, 50 Mrad	1.08	0.54	measured after several days; steamed bun-like and foamy

G. MECHANISMS OF GAS GENERATION

1. Radiolytic Mechanisms

Hydrogen Generation: It is well established that γ photons from a ^{60}Co source yield fast electrons and thus accurately simulate the radiation in Tank 101-SY, where the major radiation source are electrons from ^{137}Cs . The chemical consequences of these electrons have been summarized in our earlier report.³ Scheme I shows that the energy from these energetic electrons is deposited in localized volumes, where 20-30 eV is deposited in each event in "spurs" of about 20 Å in diameter and ~ 5000 Å away from one another along the electron track. The initial dissociation products of the water molecules are e_{aq}^- , H, OH, and H^+ . In concentrated solutions such as that in the tank, most of the e_{aq}^- and H react with solutes, especially NO_3^- and NO_2^- . The low, experimentally measured value of $G(\text{H}_2) = 0.03$ in our simulant (SY1-SIM-91C) in the absence of organic molecules is indeed quite small. In the absence of nitrite and nitrate this yield would have increased by more than an order of magnitude. The principal reactions involved in H_2 formation at this early stage are:

The high efficiency of nitrate in inhibiting hydrogen formation results from its fast reaction with hydrated electrons (reaction G-5), and, to an even larger extent, with the precursor to e_{aq}^- . This is reflected in the results of modeling calculations (Section B3g), which show that above ~0.5 M nitrate, the reduction in $G(\text{H}_2)$ will be small.

The main scavenger for hydrogen atoms is nitrite. However, the rate constant for reaction G-6 is much slower than the one for reaction G-5. For that reason it is important to maintain the concentration of nitrite concentration at the >2 M level (as compared with >0.5 M for nitrate).

Another source of the H_2 produced in the radiolysis of SY1-SIM-91C in the presence of chelators is the abstraction of an H atom from an organic molecule (reaction G-7). The dependence

of $G(\text{H}_2)$ on the concentration of the various organic molecules and the correlation between the efficiency of enhancing $G(\text{H}_2)$ by the organic and the rate constant for reaction G-7 (i.e., $[\Delta G(\text{H}_2)]/[\text{RH}]$ vs. k_7) substantiate this conclusion. Of course, the majority of H atoms react with nitrite rather than with RH at the concentrations available in SY1-SIM-91C. Nonetheless, the competition between reactions G-6 and G-7 contributes to the yield of H_2 .

Scheme I: Early events in the radiolysis of water.

Radiolytic Degradation of Chelators and Thermal Generation of H_2 . Literature data show that OH radicals react primarily with $-\text{CH}_2-$ in the chelators. In the highly concentrated nitrite and nitrate solutions the major oxidizing radical will be the NO_2 radical. The high yield of degradation of the original chelators necessitates that this is the radical responsible for the degradation of these organic molecules. Assuming that the strongly oxidizing NO_2 radicals follow a similar scheme of reactions to that of OH (or O^-) radicals, then the products will include glyoxalate and formaldehyde, according to Scheme II. These will generate hydrogen more efficiently than any of the degradation products along the pathway from the original chelator to the aldehydes, as discussed in Section D. From the rate constants determined in that Section, it is clear that the rate-determining step in the sequence will be the radiolytic degradation of the chelators and not the formation of H_2 from the aldehyde. To our knowledge, thermal degradation of the chelators is much too slow to account for the thermal generation of H_2 . With these considerations we may construct Scheme III, which attempts to provide quantitative accounting for the gas generation of H_2 in tank 101-SY.

2 of 2

Scheme II also shows a probable pathway to the generation of ammonia that is consistent with our experimental observations. The circular arrow in that scheme indicates repetition of the same pathway to replace all the organic moieties on N by hydrogen atoms. Because the quantities of ammonia generated in 101-SY are unknown to us, it is difficult to estimate whether this mechanism for ammonia formation could operate in the tank. Because the source of NH_3 is entirely organic in this scheme, one could estimate the amount of organic that will be degraded in the tank from such a mechanism.

N₂O Generation. We have shown that organics must be present for the radiolytic formation of N_2O , although both nitrogen atoms in N_2O come from inorganic sources (nitrate and nitrite). Our modeling results also show that in the absence of organics no N_2O will be radiolytically generated. Hydroxylamine is a likely intermediate in the generation of N_2 and N_2O . We indeed observe that the same inhibitor (Cr(III)) that reduces the rate of the hydroxylamine reaction will also reduce the yield of N_2O . Hydroxylamine can be produced radiolytically via the documented mechanism shown in Scheme IV. The mechanism in this scheme fulfills the requirement for participation of an organic; the source of nitrogen is entirely inorganic and it will show slight dose-rate dependence because of the participation of two radicals (NO and R). Bonner et al.¹⁹ find that NO reacts with NH_2OH to give equal amounts of N_2 and N_2O at room temperature above pH 13, and this reaction may provide another mechanism to N_2O formation.

2. Thermal Mechanisms

Among the radiolytic intermediates that we have identified, only formaldehyde and glyoxalate could generate hydrogen fast enough in SY1-SIM-91C at 60 °C to account for the amounts of gases released in 101-SY. As was shown in Section D, the reactions of formaldehyde in basic solutions to give hydrogen in competition with the Cannizzaro reaction can be quantitatively modeled. As the irradiation persists, the rate of thermal generation of H_2 will decrease as the rate of degradation of the organics to give formaldehyde is reduced.

Formaldehyde is not involved in the thermal generation of N_2O ; hydroxylamine, however, is a likely intermediate. Our experiments have shown that thermal generation of N_2O and N_2 from hydroxylamine does not require organics. Therefore, it is the generation of the hydroxylamine that necessitates the intervention of organic radicals as shown in the top of Scheme IV. With the addition of minor components to SY1-SIM-91C containing chelators, we find that radiolytically reduced Pd(IV) retains hydrogen, whereas Cr(III) in its original oxidation state (i.e., with or without irradiation) reduces the rate of N_2O formation.

3. Integrated View

The original solution SY1-SIM-91C containing the chelators EDTA, HEDTA and citrate does not generate hydrogen appreciably prior to irradiation. On irradiation, a small amount of H_2 ($G(\text{H}_2) = 0.03$) is generated by the direct radiolysis of water. Little can be done to eliminate this source of hydrogen short of extraction of the irradiation source (mostly ^{137}Cs). This small hydrogen yield corresponds to a rate of generation of approximately 4.4 mole of hydrogen per day in a 4×10^6 liter tank that absorbs 25 rad min^{-1} of irradiation. This yield could be more than doubled when the hydrogen abstraction reaction is taken into account. The latter can be eliminated by complete destruction of the organic contents in the waste. Assuming that the rate of generation of H_2 in 101-SY is 50 mole day^{-1} , the direct radiolytic pathways will account then for up to 30% of the total generation rate; the remainder has to come from thermal reactions. The right hand side of Scheme III provides this accounting.

The rate of thermal H_2 formation is appreciably augmented by radiolytic degradation of the original chelators. Such degradation can proceed through NTA, IDA, glycine (and other chelating

intermediates) to glyoxylate and in parallel to produce formaldehyde (Scheme II). Because the yield for degradation of the original chelators is $G(-RH) \geq 2.9$, the rate of generation of any degradation product, and specifically formaldehyde, cannot exceed this rate. As shown in Scheme III, this yield corresponds to 415 mole per day per 4×10^6 liter of waste. From the rate constants determined in Section D, if all of the degradation leads to formaldehyde, the rate of H_2 generation will exceed that observed in 101-SY by an order of magnitude. Therefore, if only 10% of degradation leads to formaldehyde (a very reasonable estimate), a full accounting of the sources for hydrogen in 101-SY is obtained.

Of the minor components, only Cr(III) and the radiolytic product of Pd(IV) seem to affect the rate of generation of N_2O and H_2 , respectively. The Cr(III) reduces the rate of N_2O production radiolytically and thermally from hydroxylamine. Reduced Pd(IV), perhaps Pd particles, strongly retain H_2 . In 101-SY, considering the long period of irradiation and small amount of Pd, retention by Pd has long reached saturation, and this bound hydrogen is insignificant. The important observation, however, is the lack of any significant catalytic effect by any of the minor components.

Scheme II. Radiolytic Degradation of Chelators

Scheme III. Pathways and Rates in the Generation of Hydrogen.

REFERENCES

- (1) Meisel, D.; Diamond, H.; Horwitz, E. P.; Jonah, C. D.; Matheson, M. S.; Sauer, Jr., M. C.; Sullivan, J. C.; Barnabas, F.; Cerny, E.; Cheng, Y. D. "Radiolytic Generation of Gases from Synthetic Waste," ANL report -91/41, 1991.
- (2) Meisel, D.; Diamond, H.; Jonah, C. D.; Sauer, Jr., M. C.; Sullivan, J. C.; Barnabas, F.; Cerny, E.; Cheng, Y. D., "Radiolytic and Radiolytically Induced Generation of Gases in Simulated Mixed Waste Solutions", In "Waste Management 92", ; R. G. Post and M. E. Wacks, Ed.; Am. Nuc. Soc. & IAEA: 1992; Vol. 1; p. 859.
- (3) Meisel, D.; Diamond, H.; Horwitz, E. P.; Jonah, C. D.; Matheson, M. S.; Sauer, Jr., M. C.; Sullivan, J. C., "Radiation Chemistry of Synthetic Waste," ANL report -91/40, 1991.
- (4) Spinks, J. W.; Woods, R. J., "An Introduction to Radiation Chemistry" J. Wiley & Sons: New York, 1976.
- (5) Hart, E. J.; Thomas, J. K., "Application of the Van Slyke Manometric Apparatus to Radiation Chemistry," ANL report 7856, 1971.
- (6) Vogel, A. I. "Quantitative Inorganic Analysis", 3rd Edition, Longmans, 1961; p. 254.
- (7) Herting, D. L., Letter of May 1, 1991.
- (8) Han, P.; Bartels, D. M., "Reevaluation of Arrhenius parameters for $H + OH^- \rightarrow e^-_{aq} + H_2O$ and the enthalpy and entropy of hydrated electrons." J. Phys. Chem., 1990, 94, 7294.
- (9) Campbell, J. A., Appendix K in "Minutes of the Tank Waste Science Panel Meeting March 25-27, 1992" Compiled by W. W. Schultz and D. M Strachan," PNL report PNL-8278/AD-940, 1992.
- (10) Loew, *Ber.*, 1887, 20, 144.
- (11) Siemer, D. D., INEL Letter DDS-27-90 of December 7, 1990.
- (12) Ashby, E. C., Appendix H in "Minutes of the Tank Waste Science Panel Meeting March 25-27, 1992" Compiled by W. W. Schultz and D. M Strachan," 1992.
- (13) Ashby, E. C.; Doctorovich, F.; Liotta, C. L.; Neumann, H. M.; Barefield, E. K.; Konda, A.; Zhang, K.; Hurley, J.; Siemer, D. D., "Concerning the Formation of Hydrogen in Nuclear Waste. Quantitative Generation of Hydrogen via a Cannizzaro Intermediate." J. Am. Chem. Soc., 1993, 115, 1171.
- (14) Delegard, C., "Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101," Rockwell Hanford Operations, 1980.
- (15) Martin, R. J. L., Australian J. Chem., 1954, 7, 335.
- (16) Martin, R. J. L., Aust. J. Chem., 1954, 7, 400.
- (17) A. C. Hindmarsh, "Instruction for LSODE. Installation of ODEPACK", LLNL Report M-4162, May 1983.
- (18) Bryan, S. A.; Pederson, L. R.; Scheele, R. D.; Adami, S. R. In "Proceedings 4th Annual International Conference on High Level Radioactive Waste Management;" Am. Nuclear Soc.: Las Vegas, Nevada, 1993; Vol. 2, p. 1348.
- (19) Bonner, F. T.; Dzelzkalns, L. S.; Bonucci, J. A., "Properties of Nitroxyl as Intermediate in the Nitric Oxide - Hydroxylamine Reaction in Trioxodinitrate Decomposition." Inorg. Chem., 1978, 9, 2487.

Distribution for ANL 93/43Internal:

F. A. Cafasso
E. P. Horwitz
C. D. Jonah
S. Kapoor
M. S. Matheson

D. Meisel (36)
M. C. Sauer, Jr.
L. M. Stock
TIS Files

External:

DOE-OSTI for distribution per (UC-601) (12)
ANL-E Library (2)
ANL-W Library
Manager, Chicago Operations Office, DOE
G. D. Johnson, Westinghouse Hanford Company (40)

**DATE
FILMED**

2 / 10 / 94

END