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COMPOSITION, PREPARATION, AND GAS
GENERATION RESULTS FROM SIMULATED
WASTES OF TANK 241-SY-101

S. A. Bryan
L. R. Pederson

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Pacific Northwest Laboratory
Richland, Washington 99352

MASTER *ud*

SUMMARY

This document reviews the preparation and composition of simulants that have been developed to mimic the wastes temporarily stored in Tank 241-SY-101 at Hanford. The kinetics and stoichiometry of gases that are generated using these simulants are also compared, considering the roles of hydroxide, chloride, and transition metal ions; the identities of organic constituents; and the effects of dilution, radiation, and temperature. Work described in this report was conducted for the Flammable Gas Safety Program at Pacific Northwest Laboratory,^(a) whose purpose is to develop information that is necessary to mitigate potential safety hazards associated with waste tanks at the Hanford Site. The goal of this research and of related efforts at the Georgia Institute of Technology (GIT), Argonne National Laboratory (ANL), and Westinghouse Hanford Company (WHC) is to determine the thermal and thermal/radiolytic mechanisms by which flammable and other gases are produced in Hanford wastes, emphasizing those stored in Tank 241-SY-101.

A variety of Tank 241-SY-101 simulants have been developed to date. The use of simulants in laboratory testing activities provides a number of advantages, including elimination of radiological risks to researchers, lower costs associated with experimentation, and the ability to systematically alter simulant compositions to study the chemical mechanisms of reactions responsible for gas generation. The earliest simulants contained the principal inorganic components of the actual waste and generally a single complexant such as N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA) or ethylenediaminetriacetic acid (EDTA). Both homogeneous and heterogeneous compositional forms were developed. Aggressive core sampling and analysis activities conducted during Windows C and E provided information that was used to design new simulants that more accurately reflected major and minor inorganic components. Future simulant design will be buoyed by recent success in identifying the majority of organic constituents of the wastes.

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The stoichiometry of gas products and the kinetics of their formation were found to be sensitive to the concentrations of both major and minor components. Transition metals, including copper, nickel, chromium, and iron, enhanced formation of nitrous oxide relative to nitrogen but did not substantially change hydrogen yields in thermally driven reactions. A maximum in the rate of nitrous oxide formation as a function of chloride ion concentration in simulated wastes was observed for chloride ion concentrations of 0.5 M, which is the approximate concentration of chloride in actual wastes. High hydroxide ion concentrations favored hydrogen and nitrogen production and depressed nitrous oxide yields.

Gas generation from a homogeneous simulant (SY1-SIM-93B) and a heterogeneous simulant (SY1-SIM-91A), both of which contain only the major inorganic components of the actual waste and identical concentrations of HEDTA, were compared under thermal conditions. Rates of gas generation from the homogeneous simulant were more than a factor of ten smaller than those obtained from the heterogeneous simulant. Differences in rates are not explainable by differences in the concentrations of the key reactants hydroxide, aluminate, and nitrite; results suggest that the presence of excess solids in the heterogeneous simulant may enhance the rate of gas generation.

Dilution of simulated waste slurries containing HEDTA with two molar sodium hydroxide solutions gave no statistically significant change in the gas generation behavior under thermal conditions. Here, gases produced by the original sample plus the diluent are considered.

Under combined radiolytic and thermal conditions, hydrogen generation rates from the simulant plus sodium hydroxide solution diluent remained constant as the extent of dilution was increased, within experimental error. In contrast, rates of nitrous oxide production increased approximately proportionally with the dilution fraction. Studies performed at ANL have shown that hydrogen is produced both by the direct radiolysis of water and by the abstraction of hydrogen atoms from organic compounds by radiolytically generated hydrogen radicals. While dilution would decrease the concentration of HEDTA available for hydrogen production, more water is available for radiolysis in the diluted simulants. Studies at ANL have also shown that nitrous oxide derives principally from the reduction of nitrite ions. Organic compounds serve as the reducing agent in the production of nitrous oxide; nitrous oxide production has been shown to be

sensitive to the organic compounds that are present. However, nitrous oxide yields are weakly dependent upon the concentration of a specific organic compound added to the waste simulant.

Ammonia is produced in gas generation tests but also enters into further reactions that affect yields of nitrous oxide and nitrogen. It has been shown in earlier studies that nitrous oxide and nitrogen derive principally from the nitrite ion, with certain organic compounds serving as reducing agents. Nitrogen originally present as an amine was also shown to be converted to nitrous oxide and molecular nitrogen in studies performed at ANL and GIT. The present results show that when ammonia is present, molecular nitrogen and nitrous oxide can be produced under both thermal and combined thermal and radiolytic conditions, even when the simulant contains neither nitrite ions nor organic nitrogen.

Simulants containing formate or oxalate produced very small but measurable quantities of flammable gases. Both formate and oxalate have been identified as degradation products of the chelators and are present in actual wastes. However, it was not unambiguously determined whether this gas generation was due to small impurity concentrations or actual formate and oxalate decomposition to carbonate.

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1.0 INTRODUCTION

This document reviews the compositions and preparation of simulants that have been developed to mimic the wastes temporarily stored in Tank 241-SY-101. The production kinetics and stoichiometry of gases that are generated using these simulants are also compared, considering the roles of hydroxide ions, chloride ions, and transition metal ions; the identities of organic constituents; dilution effects; radiation; and temperature. Work described in this report was conducted for the Flammable Gas Safety Program at Pacific Northwest Laboratory (PNL), whose purpose is to develop information that is necessary to mitigate potential safety hazards associated with waste tanks at the Hanford Site. The goal of this research and of related efforts at the Georgia Institute of Technology, Argonne National Laboratory, and Westinghouse Hanford Company is to determine the thermal and thermal/radiolytic mechanisms by which flammable and other gases are produced in Hanford wastes, emphasizing those stored in Tank 241-SY-101.

1.1 SIMULANT FORMULATIONS

There is a clear and obvious need for waste simulants to use in laboratory testing programs. Among the advantages of using simulants rather than actual waste samples are the elimination of radiological exposure risks to researchers and a substantial reduction in costs associated with experimentation. Actual waste core samples are not only expensive to obtain and to eventually dispose but are heterogeneous and in limited supply. Few laboratories are equipped to handle highly radioactive samples; shipping such samples to other laboratories offsite is complex and expensive.

However, through systematic alteration in the composition of the waste simulants, one can probe the mechanisms for gas generation and, perhaps, gas retention phenomena. In addition, using simulants allows analytical procedures to be developed that can then be applied to the study of actual waste samples. It is essential that the simulants be carefully designed so that their use can provide information that is relevant to the behavior of actual wastes. Measurements of simulants should be considered a complement to, rather than a replacement for, measurements of actual waste samples.

A system was developed to name simulant compositions, as suggested by the Tank Waste Science Panel (Pederson and Strachan 1992). The names of the waste simulants reflect the waste tank to which they correspond, indicate that the formulation is indeed a simulant, and indicate the year and the order within that year that the formulation was created. For example, the designation of waste simulant SY1-SIM-91A indicates that the formulation relates to Tank 241-SY-101, is a simulant, and was the first (A) such composition created in 1991.

This report addresses the following Tank 241-SY-101 simulants that have been formulated to date: SY1-SIM-91A, SY1-SIM-91B, SY1-SIM-91C, SY1-SIM-92A, SY1-SIM-93A, SY1-SIM-93B, SY1-SIM-94A, and SY1-SIM-94B. Simulant compositions were developed primarily from information gained from two core sampling activities: Window C (Herting et al. 1992a) and Window E (Herting et al. 1992b). Overall waste compositions determined from these sampling and analysis activities are briefly summarized in Section 2. The earliest simulants that were developed contain the principal inorganic components plus one or two organic compounds; later simulant compositions generally increased in complexity and included minor and trace components as well.

- Waste simulant SY1-SIM-91A is based on early work by Delegard (1980) for the mechanistic study of slurry growth within Tank 241-SY-101, modified somewhat by Herting et al. (1992a) (see Appendix A). This formulation contained the major inorganic components found in Tank 241-SY-101.
- The homogeneous waste simulant SY1-SIM-91B is closely related to -91A. Developed by Herting (see Appendix A), all of the concentrations in the homogeneous simulant are 0.7 times those in the slurry except sodium hydroxide, which was boosted to maintain sodium aluminate in solution.
- The homogeneous waste simulant SY1-SIM-91C was developed at Argonne National Laboratory (ANL) for the study of radiolytic and radiolytically induced generation of gases from synthetic wastes (Meisel et al. 1991b). A homogeneous waste was required to simplify chemical kinetics studies and to ensure the complete removal of gaseous products from solution after each experiment.
- Based on Window C waste core analyses (Herting et al. 1992a), the heterogeneous waste simulant SY1-SIM-92A was developed at PNL (Bryan et al. 1992). This formulation contains the major inorganic components as well as several transition metals and various other minor components of Tank 241-SY-101 waste.

- Waste simulant SY1-SIM-93A was developed by Westinghouse Hanford Company (WHC) for the Tank Waste Remediation System (TWRS) program as a benchmark simulant so laboratories within that program could baseline performance tests to the same formulation (Hohl 1993). Based on Window E waste core analyses (Herting et al. 1992b), this simulant includes the major and minor inorganic components as well as trace levels of (stable) metals such as cesium and strontium to match the concentration of the radioisotopes of these ions in Tank 241-SY-101.
- A homogeneous waste simulant SY1-SIM-93B was developed to be used as a test simulant for round-robin type testing among research groups (Bryan et al. 1993). This simulant contains only the major inorganic components found in Tank 241-SY-101 but at lower concentrations than in the actual waste. A homogeneous waste was needed to ensure that each site had identical simulants; eliminating the solid phase greatly simplified this task.
- Trace noble and transition metals were added to the base SY1-SIM-93A simulant composition for use in waste aging studies by Samuels (see Appendix B). The first such simulant, SY1-SIM-94A, is no longer being used, but was replaced by a modified composition described by Samuels (Appendix C) and designated SY1-SIM-94B.

1.2 GAS GENERATION KINETICS

Among the purposes of studies being conducted on a laboratory scale using simulated Tank 241-SY-101 wastes is developing an understanding of the chemical mechanisms leading to flammable gas formation in that tank (Reynolds et al. 1991; Tank Advisory Panel 1991). The wastes stored in this tank are known to generate gases, primarily nitrous oxide, hydrogen, nitrogen, and ammonia (Ashby et al. 1992; Babad et al. 1991, 1992). Prior to the placement of a mixer pump in the tank, gases were periodically released from the wastes and, on a few occasions for short time periods, exceeded the lower flammability limit in the dome space of the tank (Babad et al. 1991, 1992).

Rates of gas generation and the stoichiometry of the products have been shown in laboratory studies to be sensitive to the composition of the simulant. Nitrite, hydroxide, and aluminate ion concentrations, as well as the identity and concentration of organic constituents, have been shown to influence gas generation kinetics significantly, whereas nitrate and carbonate had little effect on gas generation (Delegard 1980; Jansky and Meissner in Tank Advisory Panel 1991; Ashby et al. 1992, 1993, 1994; Meisel et al. 1991a, 1992, 1993; Bryan et al. 1992, 1993). Elimination of oxygen significantly slowed gas generation rates.

These results have been summarized previously in other reports (Strachan and Morgan 1991a, 1991b; Strachan 1991, 1992a, 1992b; Schulz and Strachan 1992; Strachan and Schulz 1993).

In early work, it became apparent that not all organic waste constituents supported flammable gas generation. Delegard (1980) observed thermally induced gas generation from HEDTA decomposition but not from EDTA. The difference between these two chelating agents is that one of the carboxylate groups of EDTA is replaced by an alcohol group. Similarly, Jansky and Meissner (in Tank Advisory Panel 1991) reported significant hydrogen generation when HEDTA and/or glycolic acid (hydroxyacetic acid) were present, but no gases were generated in their absence.

Considerable progress has been made in determining the mechanisms of degradation reactions under both radiolytic and thermal conditions. Nearly complete descriptions of the decomposition of HEDTA have been developed (Ashby et al. 1993, 1994). Formaldehyde, which can be formed through degradation of various complexants, has been identified as an important intermediate in the formation of hydrogen via a Cannizzaro-type reaction (Ashby et al. 1993, 1994; Meisel et al. 1993). Direct radiolysis of water has been shown to yield hydrogen, but an additional amount was shown to be produced when hydrogen radicals abstracted a hydrogen atom from organic molecules (Meisel et al. 1991a, 1991b, 1992, 1993). The generation of nitrous oxide was found to require the presence of organics serving as reducing agents, but the nitrogen atoms in nitrous oxide derived from nitrite ions. Formation of this product is believed to proceed through a trihydroxynitritoaluminum(III) complex, which can attack the N position or the -OH position of an organic complexant. Nitrogen can be formed via the decomposition of nitrous oxide, especially in the presence of radiation (Bryan and Pederson, in Strachan and Schulz 1993) and from reactions involving hydroxylamine (Ashby et al. 1993, 1994). Another important decomposition product is ammonia. Meisel et al. (1993) report that all of the nitrogen in ammonia derives from organic sources, while Ashby et al. (1993, 1994) have reported that 90% derives from inorganic nitrogen. In high-temperature organic destruction tests (200°C and higher), Bryan et al. (1993) showed that the majority of ammonia derived from organic nitrogen.

Pre-irradiation of simulated waste mixtures was shown to substantially enhance the rate of hydrogen generation by thermal processes (Meisel et al. 1993). Original chelators, including EDTA and HEDTA but not citrate, could be completely destroyed by pre-irradiation. Those chelators that are known to produce formaldehyde gave the greatest enhancement in hydrogen generation rates due to pre-irradiation.

One justification for using simulants is that they can be used in experiments that closely mimic conditions in the actual waste tank. From aggressive tank monitoring activities over a period of years, estimates are available of the quantity of gases that are produced and their stoichiometry. The best estimates for the composition of released gases from Tank 241-SY-101 are hydrogen, 28.8%; nitrous oxide, 24.5%; methane, 0.35%; water, 2.4% (LANL 1994). The ammonia content has been revised upward from earlier estimates of approximately 4% (Babad et al. 1991, 1992; Strachan and Schulz 1993). From waste levels measured prior to emplacement of a mixer pump, Strachan (1991; Pederson and Strachan 1993) calculated a growth in the height of the waste of 2.8 mm (0.11 in.)/d, thought to be the result of gas retention in the nonconvective layer, where the average hydrostatic pressure is approximately 2 atmospheres. From this, a daily production of approximately 50 moles of hydrogen—and similar quantities of nitrogen and nitrous oxide—was estimated in the tank.

In many of the earlier studies involving simulated wastes under thermal and combined thermal and radiolytic conditions, the yield of nitrous oxide to hydrogen was considerably different from actual tank observations. These differences have been discussed in detail by Ashby et al. (1992). Rather than a ratio of approximately 1:1, simulated wastes containing complexants such as EDTA and HEDTA typically yielded nitrous oxide:hydrogen ratios of 5:1 to 20:1. The fraction of hydrogen that could be produced was much higher when the organic fraction consisted of glyoxylate, formaldehyde, or components that could lead to these intermediates (Ashby et al. 1993, 1994; Meisel et al. 1993).

Activation energies and pre-exponential factors have been determined for flammable gas generation and organic destruction in a number of studies, with reasonably good agreement. The first such measurement reported by Delegard (1980) was 24.5 kcal/mole for gas generation for a simulated waste containing EDTA and HEDTA. Similar results were found by Siemers (in Strachan et al. 1991).

The activation energy for EDTA destruction [reduction of total organic carbon (TOC)] in hydrothermal tests has been given by Schmidt et al. (1993) to be 22.1 kcal/mole for a simulant diluted 3:1 with water. Later measurements led to an activation energy of 24.7 kcal/mole (Orth et al. 1993). The activation energy for hydrogen generation from formaldehyde was given by Meisel et al. (1993) in the simulant SY1-SIM-91C as 20.3 kcal/mole, whereas a value of 9.8 kcal/mole was obtained when glyoxylate was present in the same simulant.

Some very important gas generation measurements have been performed by Person (1993) using actual Tank 241-SY-101 waste samples. Initial measurements yielded activation energies in the range of 14.4-16.0 kcal/mole, while more recent measurements are in the range of 19-25 kcal/mole. For tests conducted at approximate tank temperature, hydrogen was the predominant product, whereas at 100°C, hydrogen, nitrous oxide, and nitrogen were produced approximately equally. Ammonia was a principal product in these tests, accounting for 13-17 percent of the product at 100°C. At 65°C, gases were generated at 0.037 mmole/liter/day, roughly equivalent to the rate estimated for Tank 241-SY-101. An interesting finding in this work was that hydrogen represented a greater fraction of gases produced at 65° than at 100°C.

Section 2 briefly reviews information on the composition of Tank 241-SY-101. In Section 3, the compositions and methods of preparing Tank 241-SY-101 simulants are described. The gas generation kinetics and stoichiometry that were determined using different simulant compositions are presented in Section 4. Section 5 contains a discussion of the conclusions reached as a result of this research, and supporting information can be found in the appendixes at the end of the report.

2.0 COMPOSITION OF TANK 241-SY-101 CONTENTS

The most complete information about the contents of Tank 241-SY-101 was obtained from the analyses of cores taken during Window C in May 1991 (Herting et al. 1992a) and during Window E in December 1991 (Herting et al. 1992b). Extensive measurements were made to determine both the physical and chemical properties of the waste. These sampling activities clearly demonstrated that the wastes were stratified into a floating crust, a convecting liquid layer, and a bottom sludge layer. While physical properties, including density, viscosity, and yield strength, varied significantly from the top to the bottom of the wastes, chemical compositions did not show such wide variations. Overall waste compositions determined from Window C and Window E cores are given in Table 2.1. Note that the organic content of the waste was indicated only by the TOC value in the initial reports on Tank 241-SY-101 waste compositions; specific organic components were not identified at that time.

Recently, Campbell et al. (1994) have identified the majority of the organic constituents of the waste in Tank 241-SY-101 using a combination of derivatization followed by gas chromatography/mass spectrometry and liquid chromatography. Among the major organic components of the waste that have been identified are the sodium salts of ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citric acid, succinic acid, ethylenediaminetriacetic acid (ED3A), oxalic acid, glycolic acid, formic acid, and acetic acid. Although N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was contained in the wastes originally, apparently none of this chelator remains in the core samples (Campbell et al. 1994). The quantity of each of these components varied considerably with the depth in the wastes from which the core samples were obtained.

TABLE 2.1.1. Waste Compositions from Tank 241-SY-101

<u>Component</u>	Tank 241-SY-101 ^(a)		Tank 241-SY-101 ^(b)	
	<u>wt%</u>		<u>wt%</u>	
TOC	1.58		1.53	
Na	20.5		20.7	
Al	3.5		3.2	
Cr	0.37		0.41	
Fe	0.03		0.03	
Ni	0.01		0.02	
Ca	0.02		0.02	
K	0.37		0.03	
Cl ⁻	1.5		0.79	
PO ₄ ⁻³	1.1		0.64	
NO ₄ ⁻	11.5		10.5	
NO ₂ ⁻	10.0		11.7	
NO ₃ ⁻²	1.6		3.15	
CO ₃ ⁻²	0.1		0.03	
F ⁻	3.1		2.47	
OH ⁻	0.19		0.4	
SO ₄ ⁻²	38.0		35.5	
H ₂ O	100.9		91.1	
TOTAL				

(a) Calculated from Herting et al. (1992a) and Reynolds (1992).
(b) Calculated from Herting et al. (1992b).

3.0 SIMULANT COMPOSITIONS

In this section, compositions and preparation methods of various simulants used to mimic the actual wastes in Tank 241-SY-101 are reviewed. Simulants that have been developed include those having only the major inorganic components, both as a homogeneous solution and as a heterogeneous slurry, and those containing minor and trace components as well. Organic components of the simulants are generally not specified. Initially, this was done out of necessity, because the identity of the organic fraction was known. Adding single or small numbers of organic components to the specified inorganic components facilitates mechanistic studies of decomposition pathways.

3.1 SY1-SIM-91A SIMULANT

Tank waste simulant SY1-SIM-91A was initially used in laboratory studies to evaluate crust growth phenomena (Delegard 1980). This simulant also has been used extensively in studies of the rate of flammable gas generation. The simulant contains all the major inorganic chemicals contained in Tank 241-SY-101, which are sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, and sodium carbonate. Organic components are generally represented by a single compound. Table 3.1 lists the components and concentrations of the slurry SY1-SIM-91A.

The composition of simulant SY1-SIM-91A, as defined by Herting (see Appendix A) is given in Table 3.1, expressed in moles per liter and weight percent. A detailed preparation of SY1-SIM-91A is included in Appendix A. The simulant is prepared by starting with a dilute feedstock solution, followed by evaporation of excess water under reduced pressure.

3.2 SY1-SIM-91B SIMULANT

Tank waste simulant SY1-SIM-91B is very closely related to SY1-SIM-91A (see Appendix A and Table 3.2). All the concentrations in this homogeneous simulant are 0.7 times that of SY1-SIM-91A in order to prepare a homogeneous solution. The exception is the NaOH concentration, which was boosted to 2.00 M to help prevent precipitation of aluminum hydroxide. Appendix A contains a detailed preparation procedure for this simulant.

TABLE 3.1. Concentrations of Components Used in SY1-SIM-91A Simulated Waste

<u>Component</u>	<u>M (mol/L)</u>	<u>Wt%</u>
NaOH	2.3	5.9
NaAl(OH) ₄	2.2	16.3
NaNO ₃	3.7	20.3
NaNO ₂	3.2	14.3
Na ₂ CO ₃	0.6	4.1
Organic ^(a)	0.3	7.4
H ₂ O		<u>31.7</u>
Total		100.0

(a) Added as Na₃HEDTA.

TABLE 3.2. SY1-SIM-91B Composition

<u>Component</u>	<u>M (mol/L)</u>	<u>Wt%</u>
NaOH	2.0	6.4
NaAl(OH) ₄	1.54	14.2
NaNO ₃	2.59	17.7
NaNO ₂	2.24	12.4
Na ₂ CO ₃	0.42	3.6
Organic ^(a)	0.21	6.4
H ₂ O		<u>39.4</u>
Total		100.0

(a) Added as HEDTA.

3.3 SY1-SIM-91C SIMULANT

Gas generation work performed at ANL primarily used homogeneous simulated waste solutions (Meisel et al. 1991a, 1993). The focus of this work was evaluating radiolytic yield (G) values and mechanisms for generating gases within Tank 241-SY-101 waste. Homogeneous solutions were required to avoid the complications of solids interfering with gas release from solution for quantitative measurements of gases generated from radiolytic and radiolytically induced generation of gases.

Table 3.3 contains the components and concentrations of the primary solution used in these studies. Organics were added at various levels as required. Differences between this simulant and SY1-SIM-91B are few: sodium aluminate concentration is approximately half that in SY1-SIM-91B, and no sodium carbonate is present in the SY1-SIM-91C simulant.

A typical formulation of SY1-SIM-91C involved the sequential addition of each ingredient listed in Table 3.3 at room temperature. Care was taken to add the sodium aluminate after the addition of sodium hydroxide to prevent the precipitation of aluminum hydroxide. Otherwise, no special attempt was made to control the order in which components were added.

3.4 SY1-SIM-92A SIMULANT

The simulant SY1-SIM-92A represents the first attempt to match, as closely as possible, the inorganic components and concentrations present in the actual waste in Tank 241-SY-101 (Strachan 1993). Based on Window C core sampling and analysis (Herting et al. 1992a), the simulant contains all the major inorganic components plus many of the minor constituents at chemically significant levels.

While the inorganic components were reasonably well understood, such was not true for the organic components when this simulant was developed. The simulant was typically prepared with one organic component at a concentration approximating the total organic carbon (TOC) content of actual wastes, an example of which is given in Table 3.4.

TABLE 3.3. Concentrations of Components Used in SY1-SIM-91C Simulated Waste

<u>Components</u>	<u>Concentration, M</u>	<u>Wt%</u>
NaOH	2.3	8.6
NaAlO ₂	0.86	9.2
NaNO ₃	2.8	22.2
NaNO ₂	2.2	14.2
H ₂ O		<u>45.8</u>
Total		100.0

TABLE 3.4. Concentrations of Components Used in SY1-SIM-92A Simulated Waste

<u>Component</u>	<u>M (mole/L)</u>	<u>Wt%</u>
Na ₃ HEDTA	0.205	4.99
NaCl	0.526	1.97
Na ₃ PO ₄ • 12 H ₂ O	0.179	4.36
NaNO ₂	3.95	17.45
NaNO ₃	2.2	11.97
Na ₂ CO ₃	0.4	2.71
NaF	0.1	0.27
Na ₂ SO ₄	0.032	0.29
CaCl ₂	0.0083	0.06
KCl	0.146	0.7
Cr(NO ₃) ₃ • 9 H ₂ O	0.1051	2.69
Cu(NO ₃) ₂ • 2.5 H ₂ O	0.0002	0.0
Fe(NO ₃) ₃ • 9 H ₂ O	0.0074	0.19
Ni(NO ₃) ₂ • 6 H ₂ O	0.0021	0.04
NaOH	2.45	6.28
NaAlO ₂ • 0.21 NaOH • 1.33 H ₂ O	2.05	15.1
H ₂ O		<u>30.93</u>
TOTAL		100.0

Table 3.4 lists the concentrations of the components within waste simulant SY1-SIM-92A. Appendix B contains a copy of a spreadsheet that was used in the preparation of the Tank 241-SY-101 simulated waste SY1-SIM-92A. The wt% of the major elements and ions found in actual Tank 241-SY-101 analyses is matched by the addition of compounds listed in the spreadsheet.

A typical preparation of simulated waste was made by adding each ingredient from the spreadsheet in the order given. First, the required amount of water (except what is needed to dissolve the transition metal salts) was added to the mixing container. Transition metal salts were dissolved in a minimal amount of water before adding them to the formulation. The ingredients were vigorously and continuously mixed by mechanical stirring. Batches were stirred at room temperature for several days prior to use.

Because of a potential problem with glass corrosion, using glass containers and all-glass surfaces in making the simulated waste was avoided. The use of polypropylene carboys in the preparation allowed for the convenient preparation

of large-scale batches (up to 15 L). Batches prepared on a smaller scale (typically 1 L or less) are usually prepared using polymethylpentene (PMP) containers.

3.5 SY1-SIM-93A SIMULANT

Waste simulant SY1-SIM-93A was developed by Westinghouse Hanford Company for the Tank Waste Remediation System (TWRS) program as a benchmark simulant for laboratories within that program to baseline performance tests to the same formulation (Hohl 1993). Table 3.5 contains the concentrations of each component in this simulated waste. This simulant includes the major and minor inorganic components as well as trace levels of (stable) metals such as cesium and strontium to match the concentration of the radioisotopes of these ions in Tank 241-SY-101; its formulation is based on the analysis of core samples taken during Window E in December 1991 (Herting et al. 1992b).

Programs involved with development of organic destruction methodologies required a basis simulant that was consistent for all test sites. A waste type simulating Tank 241-SY-101 was agreed upon as one basis of waste composition representative of complex concentrate tank waste.

3.6 SY1-SIM-93B SIMULANT

A homogeneous waste simulant SY1-SIM-93B was developed to be used as a test simulant for round-robin type testing among research groups (Bryan et al. in Strachan and Schulz 1993). This simulant contains only the major inorganic components found in Tank 241-SY-101 but at lower concentrations than in the actual waste. A homogeneous waste was needed to ensure each site had identical simulants that could be simply prepared and reproduced; eliminating the solid phase greatly simplified this task. The concentrations of the components in SY1-SIM-93B are listed in Table 3.6. The $\text{Al}(\text{NO}_3)_3$ was added after adding NaOH to prevent the precipitation of aluminum hydroxide.

TABLE 3.5. Concentrations of Components Used in SY1-SIM-93A Simulated Waste

<u>Component</u>	<u>M (mole/L)</u>	<u>Wt%</u>
Na ₄ EDTA (Na ₄ C ₁₀ H ₁₆ O ₈ N ₂)	0.205	5.02
Na ₃ PO ₄ • 12 H ₂ O	0.1078	2.64
NaNO ₂	3.6517	16.23
NaNO ₃	2.4563	13.45
Na ₂ CO ₃	0.8399	5.73
Na ₂ SO ₄	0.0666	0.61
NaCl	0.3555	1.34
NaF	0.0253	0.07
Ca(NO ₃) ₂ • 4 H ₂ O	0.0092	0.14
KNO ₃	0.1334	0.87
ZnCl ₂	0.0005	0.0
CsNO ₃	0.00017	0.0
Sr(NO ₃) ₂	0.00001	0.0
Cr(NO ₃) ₃ • 9 H ₂ O	0.1262	3.25
Fe(NO ₃) ₃ • H ₂ O	0.008	0.21
Ni(NO ₃) ₂ • 6 H ₂ O	0.0041	0.08
NaOH	2.35	6.06
NaAlO ₂ • 0.21 NaOH • 1.33 H ₂ O	1.9098	14.15
H ₂ O		<u>30.15</u>
TOTAL		100.00

TABLE 3.6. Concentrations of Components Used in SY1-SIM-93B Simulated Waste

<u>Component</u>	<u>M (mole/L)</u>	<u>Wt%</u>
Na ₃ HEDTA	0.21	6.04
Al(NO ₃) ₃ • 9 H ₂ O	0.43	12.49
NaNO ₂	2.0	10.69
NaNO ₃	0.4	2.63
Na ₂ CO ₃	0.2	1.64
NaOH	3.4	10.53
H ₂ O		<u>55.98</u>
TOTAL		100.00

This simulant differs from earlier simulants mostly in the replacement of sodium aluminate with aluminum nitrate ($\text{Al}(\text{NO}_3)_3$). The relative ease of dissolution and ability to procure a certified grade of the aluminum nitrate make this source of aluminum advantageous compared with sodium aluminate. Large quantities of sodium aluminate could only be purchased as technical grade and needed to be analyzed prior to use.

The concentrations of the solution species in this simulant are comparable to the homogeneous simulant SY1-SIM-91B but are more dilute in all the components. The apparent higher concentration of sodium hydroxide in SY1-SIM-93B is actually taken up in the reaction with the aluminum. The total sodium hydroxide concentration was boosted to 3.4 M to allow for the conversion of $\text{Al}(\text{NO}_3)_3$ to $\text{NaAl}(\text{OH})_4$. The final hydroxide concentration is still around 2 M. This simulant contains carbonate, and the concentrations of nitrate and nitrite are close to Window C and E analyses.

3.7 SY1-SIM-94A AND SY1-SIM-94B SIMULANTS

Trace noble and transition metals were added to the base SY1-SIM-93A simulant composition for use in waste aging studies by Samuels (see Appendix B). The first such simulant, SY1-SIM-94A, is no longer being used; it was replaced by a modified composition described by Samuels and designated SY1-SIM-94B (see Appendix C). The concentration of each component within this simulant is listed in Table 3.7.

TABLE 3.7. Concentrations of Components Used in SY1-SIM-94B Simulated Waste

Component	M (mole/L)	Wt%
Na ₄ EDTA	0.1	2.24
Hexadecanoic acid	0.1	1.43
Na ₃ Citrate • H ₂ O	0.092	1.59
Tributyl phosphate	0.1	1.57
Dibutyl phosphate	0.1	1.24
Hexone	0.1	1.0
NPH	0.1	1.0
Na ₃ PO ₄ • 12 H ₂ O	0.1078	2.41
NaNO ₂	3.6517	14.83
NaNO ₃	2.4563	12.29
Na ₂ CO ₃	0.8399	5.24
Na ₂ SO ₄	0.0666	0.56
NaCl	0.3555	1.22
NaF	0.0253	0.06
Ce(NO ₃) ₃ • 6 H ₂ O	0.0031	0.08
Ca(NO ₃) ₂ • 4 H ₂ O	0.0092	0.13
KNO ₃	0.1334	0.79
ZnCl ₂	0.0005	0.0
CsNO ₃	0.0002	0.0
Sr(NO ₃) ₂	0	0.0
NaOH	2.35	5.53
Cr(NO ₃) ₃ • 9 H ₂ O	0.1262	2.97
Fe(NO ₃) ₃ • 9 H ₂ O	0.008	0.19
Ni(NO ₃) ₂ • 6 H ₂ O	0.0041	0.07
RuCl ₄ • 5 H ₂ O	0.0001	0.0
Rh(NO ₃) ₃ • H ₂ O	0.0001	0.0
Mn(NO ₃) ₂	0.01	0.11
Pb(NO ₃) ₂	0.01	0.19
Zr Citrate	0.008	0.13
Pd(NO ₃) ₂	0.0001	0.0
NaAlO ₂ • 0.21 NaOH • 1.33 H ₂ O	1.9098	12.93
H ₂ O		30.58
TOTAL		100.4

4.0 GAS GENERATION STOICHIOMETRY AND KINETICS FROM SIMULANTS

The purpose of this section is to compare the kinetics of gas generation and the stoichiometry of the products obtained in laboratory tests using simulated Tank 241-SY-101 wastes. Results obtained using simulants are also compared with the behavior of actual wastes from that tank. In this report, an emphasis is placed on the role of minor waste components.

This section is organized as follows:

- Section 4.1 describes the experimental procedures that were used in these tests.
- Gas generation behaviors using the simulants containing HEDTA as the only organic constituent are compared in Section 4.2; an important finding is that relative nitrous oxide and nitrogen yields were strongly affected by the presence of various transition metals in the simulant, while hydrogen yields were fairly insensitive to such compositional differences.
- Gas generation results from a recently developed homogeneous simulant, SY1-SIM-93B, are described in Section 4.3. This particular simulant composition was primarily designed for use in "round-robin" testing by various laboratories involved in gas generation studies in support of Hanford tank safety issue resolution.
- Section 4.4 contains a discussion of how hydroxide addition to simulants affects gas generation yields. Delegard (1980) was the first to show that slurry growth (and gas generation) kinetics were first order with respect to hydroxide up to 1.5 M. Waste dilution with water or sodium hydroxide solutions are the options being considered as part of pretreatment (Schmidt et al. 1993; Orth et al. 1993) and as a means to mitigate cyclic gas buildup and release (Johnson 1991).
- Changes in gas generation kinetics resulting from dilution with 2 M NaOH solutions are described in Section 4.5. Chloride was reported to be present in Tank 241-SY-101 core samples analyzed from both Window C (1.5 weight percent) (Herting et al. 1992a) and Window E (0.8 weight percent) (Herting et al. 1992b).
- Section 4.6 presents information on how gas generation kinetics are affected by changing chloride ion concentrations.
- The results of gas generation tests using the simulant SY1-SIM-91A containing varying concentrations of the transition metals Cr, Cu, Fe, and Ni are described in Section 4.7. Previously, Ashby et al. (1993, 1994) observed that small additions of Cu(II) significantly enhanced initial rates of hydrogen generation from simulated wastes. Meisel et al. (1993) reported a strong lowering of radiolytic yields of nitrous oxide by the presence of Cr(III).

- In Section 4.8, gas generation from simulants containing formate and oxalate as the only organic components of the waste is presented. Both of these products are expected to be formed by the decomposition of complexants (Delegard 1987; Babad et al. 1993; Campbell et al. 1994; Schmidt et al. 1993; Orth et al. 1993), but the extent of gas generation from either is expected to be small (Ashby et al. 1993, 1994; Meisel et al. 1993; Bryan and Pederson in Strachan and Schulz 1993).
- The role of ammonia in gas generation tests with SY1-SIM-93B containing citrate or HEDTA is discussed in some detail in Section 4.9.

4.1 EXPERIMENTAL METHODS FOR GAS MEASUREMENTS AND SAMPLE IRRADIATION

Sample irradiation experiments were performed within the Gamma Irradiation Facility operated by PNL located in the 3730 Building in the 300 Area. The facility contains 37 stainless steel irradiation tubes positioned in a 7-foot diameter by 13-foot-8-inch-deep stainless steel tank (Figure 4.1). Two arrays of ^{60}Co with a combined inventory of 32 kCi are located near the bottom of the tank. For radiation shielding purposes, the tank is completely filled with water; and a concrete wall, 3-1/2 feet in height, surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length from 16 to 18 feet and in diameter from 1.8 to 6 inches. The irradiation flux of the tubes range from 2×10^6 R/hr to 2×10^2 R/hr. The uniform flux region varies from ~6 inches for the tubes closest to the sources to greater than 12 inches for the tubes farthest from the sources. All flux measurements of the tubes are traceable to the National Bureau of Standards.

Materials, capsules, and test systems are lowered into the irradiation tubes to the desired flux manually or by using the half-ton crane. They are left in the tubes for a specific length of time to attain the required exposure. There are no activation products associated with the gamma irradiation, so the materials can be transported to other facilities for examination after removal from the tubes. The gamma pit test facility is shown in Figure 4.1. A test vessel is being prepared for insertion into an access tube within the gamma pit. The test reaction vessel is shown being held in the foreground. The technician in the background is positioned to lower the test vessel into an open gamma irradiation access tube.

FIGURE 4.1. Preparing and Loading Reaction Vessel into Gamma Facility

The temperatures of the reaction vessels were thermostatically controlled using heat tapes. Thermocouples used to measure reaction vessel temperatures were monitored using a data logger. Pressures in each reaction vessel were measured using a pressure transducer connected to the gas manifold line of each reaction vessel. Small-diameter stainless steel tubing connected the reaction vessel to the gas manifold system.

Total moles of gases produced were calculated based on the measured pressure, temperature, and known volume of the gas phase of the reaction vessel. Analyses to determine the mole percent (mol%) of the molecular components within the gas phase of each reaction vessel were performed using the Mass Spectrometry Facility operated by PNL and located in the 325 Building in the 300 Area. The amounts of specific gases generated were calculated from the total moles of gas generated and the mole fraction data.

No attempt was made to extract product gases that were either dissolved in the simulated waste mixtures or present as gas bubbles. For all product gases except ammonia, this approach should result in negligible errors. Solubilities of gases such as hydrogen, nitrogen, and nitrous oxide are known to be quite low in concentrated brines compared with behavior in pure water (Schumpe 1993). Any gas bubbles will contribute to the total pressure in the test vessel much as if the bubbles were brought to the slurry surface and eliminated. Ammonia values are likely to be significantly underestimated, however, because that gas retains significant solubility in the concentrated simulant mixtures.

Analyses of gas generation from repeated experiments provided estimates of the errors for determining hydrogen, nitrogen, and nitrous oxide generated from simulated wastes. A conservative estimate for the relative error is 20% for replicate gas samples from 30-mL reaction vessels. The relative error for replicate gas samples using large capacity reaction vessels (1 L) is approximately 5%.

There are several contributors to measurement error. Uncertainties in temperature are believed to be the most important, especially for the small reaction vessels, which were embedded in an aluminum block. Temperatures were not measured for each individual vessel but only at one location in the common block. For an activation energy of 25 kcal/mole, approximately that reported for

gas generation and related reactions (Delegard 1980; Schmidt et al. 1993; Orth et al. 1992; Meisel et al. 1993; Ashby et al. 1993; Person 1993), a one-degree difference in temperature from 90°C would yield a 10% change in rate, a two-degree difference would yield a 20% change in rate, and a five-degree difference would yield a 60% change. A one- to two-degree temperature gradient for the set of six small vessels is quite likely and would account for essentially the entire data scatter. The large reaction vessels were independently temperature controlled and monitored throughout the tests to within $\pm 0.5^\circ\text{C}$, leading to a 5% error due to changes in reaction rates and assuming a 25 kcal/mole activation energy. Other direct contributors to measurement uncertainties are mass spectrometry analyses and pressure measurements. The precision in mass spectrometry measurements was approximately 2%, while the precision in pressure measurements is approximately 1%. The absolute reaction vessel volume was known to better than 1%, while the quantity of simulant introduced into the reaction vessels was known to better than 0.1%. The calculated root-mean-square error from all of the contributors to measurement uncertainty for the small vessels is similar to the estimated temperature contribution, or 20%. For the large vessels, temperature uncertainties also could account for a 5% scatter.

The gas manifold system used to connect multiple reaction vessels is shown in Figure 4.2. This figure shows two gamma facility staff members taking a gas sample for later analysis by mass spectroscopy using an evacuated bulb sampler. The data logger used for automated temperature and pressure measurements of the reaction vessels is shown to the right of the gas manifold system.

4.2 COMPARISON OF GAS GENERATION BEHAVIOR FOR SIMULATED WASTES CONTAINING HEDTA

The kinetics and stoichiometry of gaseous degradation products resulting from thermal and radiolytic processes were compared for several different waste simulant formulations that contained HEDTA as the sole organic constituent. Simulant compositions that were used in these tests were SY1-SIM-91A (a slurry composed of only the major inorganic components), SY1-SIM-92A (a slurry similar to -91A but containing transition metal and chloride ions), and SY1-SIM-93B (a homogeneous solution containing only the major inorganic components).

FIGURE 4.2. Manifold System Used for Gas Pressure Measurement and Sampling During Gas Generation Experiments

Minor waste components have previously been observed to alter gas generation kinetics from simulants. Ashby et al. (1993, 1994) observed that small additions of Cu(II) ions to a homogeneous simulant significantly enhanced the initial rate of hydrogen generation. Meisel et al. (1993) found that Cr(III) ions depressed the radiolytic rate of nitrous oxide formation in both simulants and slurries, whereas no effect could be found for Pt(IV), Cl⁻ or F⁻. Although Pd(IV) did not alter gas generation kinetics, it did tend to retain hydrogen. The presence of undissolved solids somewhat depressed the radiolytic yields of hydrogen and nitrous oxide, presumably because radiation absorption by the solids is less efficient than aqueous solutions (Meisel et al. 1993). However, the thermal yields of nitrous oxide were not affected by the presence of Cr(III).

The rate of gas generation and the identities of the decomposition products under thermal-only conditions were similar for SY1-SIM-91A and SY1-SIM-92A, but the stoichiometries of the products were quite different. A comparison of thermally generated gaseous products for these two simulants is given in Table 4.1 and Figure 4.3 as a function of HEDTA concentration. Values given reflect moles of gases produced per day averaged over four weeks of reaction at 90°C. The

TABLE 4.1. Comparison of Thermal Gaseous Products from Different Formulations of SY1-SIM-91A and SY1-SIM-92A (25-g samples, 90°C for 115 hr)

<u>SY1-SIM-92A Simulant</u>			
<u>[HEDTA]</u>	<u>mol/kg/day</u>		
	<u>H₂</u>	<u>N₂O</u>	<u>N₂</u>
0	5.13E-05	2.02E-06	6.74E-06
0.35	6.32E-05	1.02E-03	5.84E-04
0.7	1.33E-04	2.30E-03	9.35E-04
<u>SY1-SIM-91A Simulant</u>			
<u>[HEDTA]</u>	<u>mol/kg/day</u>		
	<u>H₂</u>	<u>N₂O</u>	<u>N₂</u>
0	0	0	0
0.15	3.51E-05	1.56E-04	3.61E-04
0.3	1.88E-05	2.89E-04	6.54E-04

FIGURE 4.3. Comparison of Thermal Gaseous Products from Different Formulations of SY1-SIM-91A and SY1-SIM-92A

simulant SY1-SIM-92A produced gases in the order $N_2O > N_2 > H_2$; SY1-SIM-91A generated in the order $N_2 > N_2O > H_2$. Hydrogen yields were low in both simulants.

Thermal results support the conclusions of mechanistic studies that nitrogen and nitrous oxide are formed by similar pathways. In experiments using ^{15}N -labeled nitrate and nitrite ions. Ashby showed that the source of nitrogen in both nitrous oxide and nitrogen derives from the nitrite ion. Organic compounds were present to serve as reducing agents, however (Ashby et al. 1993; Meisel et al. 1993). Bryan and Pederson (in Strachan and Schulz 1993) confirmed that nitrous oxide could be decomposed in the gas phase to produce nitrogen and oxygen. Intended to simulate reactions that could occur within gas bubbles trapped in the wastes, such reactions were accelerated when gamma-irradiated.

Under combined radiolytic and thermal conditions, the quantity of gases that was produced was greater than under thermal-only conditions, as has been widely observed. With HEDTA present, the ratio of generated product gases was in the (decreasing) order $N_2O > H_2 > N_2$ for both simulants heated to 90°C in a

gamma field of 6×10^5 R/h, as shown in Figure 4.4 and Table 4.2. Hydrogen was the predominant gaseous product in a test where HEDTA was absent. Hydrogen is known to be produced both by the direct radiolysis of water and via the abstraction of hydrogen atoms from organic molecules by radiolytically generated hydrogen radicals (Meisel et al. 1993). Direct radiolysis of water accounts for the observation that hydrogen was formed in simulants containing no HEDTA. Hydrogen abstraction reactions by a hydrogen radical accounts for increased molecular hydrogen yields with increases in the concentration of HEDTA.

Trends in the quantity of nitrous oxide produced under combined radiolytic and thermal conditions as a function of the concentration of HEDTA differ from those observed for other gaseous products, but are consistent with results reported previously. As discussed above, nitrous oxide is known to derive from the nitrite ion, with certain organic compounds serving as the necessary reducing

FIGURE 4.4. Comparison of Radiolytic Gaseous Products from Different Formulations of SY1-SIM-91A AND SY1-SIM-92A

TABLE 4.2. Comparison of Radiolytic Gaseous Products from Different Formulations of SY1-SIM-91A and SY1-SIM-92A (115 hr, 25-g samples, 6×10^5 R/hr, 90°C)

<u>SY1-SIM-92A Simulant</u>			
<u>[HEDTA]</u>	mol/kg/day		
	<u>H₂</u>	<u>N₂O</u>	<u>N₂</u>
0	2.71E-04	4.45E-06	1.33E-05
0.35	1.28E-03	5.20E-03	5.20E-04
0.7	2.38E-03	4.47E-03	7.22E-04

<u>SY1-SIM-91A Simulant</u>			
<u>[HEDTA]</u>	mol/kg/day		
	<u>H₂</u>	<u>N₂O</u>	<u>N₂</u>
0.3	1.21E-03	3.61E-03	9.16E-04

agent (Ashby et al. 1993; Meisel et al. 1993). Meisel found nitrous oxide formation rates to be weakly dependent on the concentration of HEDTA above some minimum concentration (smaller than approximately 0.05 molar). For HEDTA concentrations higher than that minimum amount, yields of nitrous oxide actually decreased simulant with increased HEDTA concentrations. While only two HEDTA concentrations for the -92A simulant formulation are included in Figure 4.4, corresponding nitrous oxide yields are consistent with trends reported by Meisel et al. (1993). The chemical mechanism responsible for this behavior is not well understood, nor has the minimum concentration of HEDTA or other organic compounds needed to produce a maximum yield of nitrous oxide been identified.

Present results show higher nitrous oxide yields for simulants containing the transition metal ions (including chromium) and other minor components under thermal conditions, and relatively few differences between nitrous oxide yields from the two simulants under combined thermal and radiolytic conditions. These observations are contrary to those of Meisel et al. (1993), who found no effect of transition metals on gas yields under thermal conditions and a suppression of nitrous oxide yields via radiolytic reactions in the presence of Cr(III). An

explanation for these differences is not apparent; however, the present results were obtained from reactions occurring over periods up to four weeks, whereas results of Meisel et al. (1993) corresponded to reaction times of less than two days. In the present, longer-term experiments, the extent of degradation of HEDTA to products such as NTA, glycolate, glyoxylate, formaldehyde, hydroxylamine, formate, oxalate, ethanolaminemonoacetate (EAMA), ethylenediamine-triacetate (ED3A), and ethylenediaminediacetate (EDDA) is expected to be more extensive.

4.3 GAS GENERATION FROM HOMOGENEOUS SIMULATED WASTE

Gas generation experiments using the homogeneous simulated waste SY1-SIM-93B have been performed with an initial goal of providing a standard database for comparing results obtained at different laboratories. A homogeneous waste simulant containing the major inorganic waste constituents is advantageous from an experimental standpoint. Solution concentrations of chemical additives are much more easily determined in homogeneous solutions than in heterogeneous mixtures, enabling a more direct correlation between the chemical additive and its effect on gas generation.

Gas generation results using the homogeneous simulant SY1-SIM-93B can be compared most directly with those obtained using the heterogeneous (slurry) simulant SY1-SIM-91A because their compositions are quite similar (see Section 3). The experimental conditions were as follows: the reaction temperature was 90°C; 1-L- and 30-mL-capacity stainless steel reaction vessels were used; and the reaction times were two weeks (or longer). Approximately 600 grams of reagent were used in the 1-L vessels, and approximately 20 grams of material were used in the 30-mL vessels.

Comparisons of the results of generation of the gases H_2 , N_2 , and N_2O for SY1-SIM-91A and the homogeneous simulated waste are presented in Figures 4.5-4.7 and Table 4.3. The gas results are normalized to moles of gas produced per kilogram of simulated waste to facilitate comparison. Total gas generation from the homogeneous waste simulant SY1-SIM-93B was clearly much less than that from the heterogeneous waste simulant SY1-SIM-91A.

FIGURE 4.5. Comparison of Hydrogen Gas Generation in SY1-SIM-91A, a Heterogenous Simulant, and in SY1-SIM--93B, a Homogeneous Simulated Waste

FIGURE 4.6. Comparison of Nitrogen Gas Generation in the Simulated Wastes SY1-SIM-91A and SY1-SIM-93B

FIGURE 4.7. Comparison of Nitrous Oxide Gas Generation from SY1-SIM-91A and SY1-SIM-93B

That the heterogeneous simulant should produce greater quantities of gases than the homogeneous simulant may not appear surprising. Thermal rates of gas generation have been shown to be first order with respect to hydroxide, nitrite, aluminate, and organic components (Delegard 1980; Jansky and Meissner in Babad et al. 1991; Ashby et al. 1993, 1994; Bryan et al. 1992). A higher concentration of critical components is expected to be in solution at 90°C in the heterogeneous simulant than in the homogeneous simulant (Barney 1976; Reynolds and Herting 1984). However, these differences in concentrations probably would not account for the observed order of magnitude difference in gas generation rates between heterogeneous and homogeneous simulants. Enhanced gas generation rates in slurries may also be the result of catalysis by solid surfaces.

In contrast to the thermal results reported above, Meisel et al. (1993) found that heterogeneous simulants produced smaller yields of gases via radiolysis than similar homogeneous simulants did. Tests at 30°C showed the greatest differences; those conducted at 60°C were nearly identical. In this

TABLE 4.3. Comparison of Gas Generation from SY1-SIM-91A, a Heterogeneous Simulated Waste, and SY1-SIM-93B, a Homogeneous Simulant

SY1-SIM-91A Simulated Waste (large reaction vessel, 650-g sample)			
Reaction Time, h	Gas Produced (mol/Kg)		
	<u>N₂</u>	<u>H₂</u>	<u>N₂O</u>
409	0.00856	0.000447	0.0073
690	0.01487	0.000766	0.01286
977	0.0194	0.001127	0.01911
1262	0.02463	0.00147	0.024599
	Gas Produced (mol/kg/day)		
	4.91E-04	2.72E-05	4.54E-04
	Standard Deviation (mol/kg/day)		
	2.33E-05	8.30E-07	1.90E-05
SY1-SIM-93B Simulated Waste (large reaction vessel; 520-g sample)			
Reaction Time, h	Gas Produced (mol/kg)		
	<u>N₂</u>	<u>H₂</u>	<u>N₂O</u>
0	0	0	0
317	3.77E-04	2.50E-05	7.80E-04
317	6.38E-04	1.50E-05	5.84E-04
701	1.22E-03	6.03E-05	3.03E-03
701	1.60E-03	4.90E-05	4.16E-03
954	2.23E-03	9.90E-05	5.82E-03
	Gas Produced (mol/kg/day)		
	4.59E-05	1.85E-06	1.31E-04
	Standard Deviation (mol/kg/day)		
	1.13E-05	5.00E-07	2.37E-05
SY1-SIM-93B Simulated Waste (small reaction vessel, 15-g sample)			
Reaction Time, h	Gas Produced (mol/kg)		
	<u>N₂</u>	<u>H₂</u>	<u>N₂O</u>
355	9.5E-4	9.1E-5	8.6E-4
355	9.7E-4	5.6E-5	8.1E-4
355	2.9E-3	9.0E-5	1.2E-3
355	1.2E-3	7.0E-5	2.4E-3
355	1.5E-3	7.21E-5	2.0E-3
	Gas Produced (mol/kg/day)		
	1.02E-04	5.14E-06	9.72E-05
	Standard Deviation (mol/kg/day)		
	5.51E-05	9.98E-07	4.68E-05

case, it was concluded that the differences arose because the excess solids absorbed gamma radiation less efficiently than the aqueous solution. At higher temperatures the fraction of solids was reduced, so differences were smaller. Of course, apparent gas generation yields using heterogeneous simulants may be lowered because some of the product may be trapped as bubbles on particle surfaces and be difficult to detect (Bryan, Pederson, and Scheele 1992). Trapped gases could constitute a larger fraction of the total at the lowest temperatures.

For the homogeneous simulant in Figures 4.5 through 4.7, there is an apparent dependence of gas generation on the size of reaction vessel (30 mL or 1 L). Several factors could contribute to this: The smaller vessels result in a much larger surface area-to-volume ratio. It is possible that the stainless steel surface may be able to catalyze gas generation reactions, but this effect has not been directly examined. In mild steel corrosion studies with simulated wastes by Bryan and Pederson (in Strachan and Schulz 1993), however, the steel produced a small quantity of additional hydrogen, while nitrogen and nitrous oxide yields were unchanged. In addition, the slight additional amount of hydrogen was apparent only at the beginning of the tests; long-term gas generation rates were not affected. Stainless steel surfaces, especially when oxidized, are usually enriched in chromium (Flinn and Trojan 1990). The results given in Section 4.2 showed that higher gas generation rates were obtained using simulants containing chromium and other transition metals than when using simulants without those minor components. However, Meisel et al. (1993) did not observe the same trends, finding instead that chromium (III) actually suppressed the radiolytic generation of nitrous oxide. Thus the possible role of steel surfaces on gas generation kinetics is difficult to assess at this time but is probably negligible.

Other reasons for the observed differences in rates in large and small reaction vessels are possible artifacts in temperature measurements and possible differences in precision between the two approaches. In the large (1-L) reaction vessels, we can measure both the solution temperature and the gas phase temperature directly and independently using thermocouples. However, the temperature of the contents of the small vessels is measured indirectly using a thermocouple in the heated metal block in which the vessels are housed. Thus a determinate temperature measurement error may be present, with the vessel

temperatures lower than that of the heater block. Much better statistics are possible with the large reaction vessels, given that the quantity of simulant used in each test is approximately 20 times larger than is possible with the small vessels. For more direct reaction temperature measurement, smaller steel surface area-to-volume ratio, and improved precision in measuring the extent of gas generation, the 1-L vessels are preferred. Gas generation results obtained using the large reaction vessels should be the standard for comparing laboratory testing methods.

4.4 FUNCTIONAL DEPENDENCE OF GAS GENERATION ON AMOUNT OF HYDROXIDE ADDED TO SIMULATED WASTE FORMULATION

The functional dependence of the kinetics and stoichiometry of gas generation from simulated wastes on hydroxide ion concentrations was examined. The waste matrix chosen was SY1-SIM-91A; hydroxide ion concentrations in the simulant were varied from approximately 0.5 M to 6.5 M in 1.2 M increments. Several different organic compounds were added singly to the simulant, including HEDTA (0.3 M), EDTA (0.3 M), and citrate (0.5 M).

Delegard (1980) showed that reactions leading to slurry growth in a very similar simulant were first order with respect to the hydroxide ion concentration for concentrations less than 1.5 M. More recently, Ashby et al. (1993) reported that hydrogen generation from formaldehyde in sodium hydroxide solutions was first order with respect to the hydroxide ion concentration from 4 to 16 M. Of course, the hydroxide ion concentration will have a big effect on the solubility of aluminum. If the total hydroxide content drops below 1 to 2 M, aluminum will precipitate as the hydroxide. Sodium aluminate is the predominant form of aluminum at higher base contents and slowly decreases in solubility with increased base content (Barney 1976; Reynolds and Herting 1984). An important reactive intermediate that has been proposed is the nitritotrihydroxyaluminum (III) complex (Delegard 1980; Ashby et al. 1993), whose concentration is expected to depend on the nitrite, aluminate, and thus hydroxide ion concentrations. Thus simple reaction orders will probably not be apparent in concentrated simulants over a wide range of hydroxide ion concentrations in this particular matrix.

Rates of gas production from simulants containing HEDTA were strongly affected by changes in the hydroxide ion concentration, but the dependence was

not particularly straightforward. The reaction with 0.5 M NaOH produced the least amount of gas, while the reaction containing 6.5 M NaOH generated the greatest amount of gas. Test results are given in Figure 4.8 and Table 4.4. Tests with 4.1 M hydroxide produced more gas than the reaction containing 5.3 M hydroxide. Also, a long induction period was observed for the reaction with 6.5 M hydroxide; after that, the rate of total gas generation was much enhanced.

The moles of N_2 , N_2O , and H_2 produced from this thermolysis experiment are presented in Figure 4.9 as a function of the hydroxide content. The yield of nitrogen, the predominant product for all base concentrations, steadily increased with the base content. Hydrogen, although produced in much smaller quantities, behaved in a similar manner. Nitrous oxide production differed, exhibiting a maximum at approximately 4 M hydroxide ion content. For the highest hydroxide concentrations, the average gas production rate over the entire length of the test did not well reflect the actual gas generation rate at approximately 100 hours. One must compare gas production rates corresponding to similar reaction times unless it can be shown that the rates do not vary with time.

FIGURE 4.8. Gas Production from Thermolysis of Simulated Waste Containing 0.3 M HEDTA and Varying Concentrations of Hydroxide at 90°C

TABLE 4.4. N_2 , N_2O , and H_2 Produced (mol/kg/day) from SY1-SIM-91A Simulated Waste Containing 0.3 M HEDTA and Various Concentrations of Hydroxide (20-g sample; 96 hr at 90°C)

[NaOH], M	Gas Produced (mol/kg/day)			
	N_2	H_2	N_2O	N_2O/H_2 mol ratio
0.46	4.20E-04	1.78E-05	1.29E-05	0.728
1.66	7.09E-04	2.00E-05	8.48E-05	4.23
2.89	9.10E-04	2.76E-05	5.06E-05	1.84
4.06	1.45E-03	8.63E-05	1.07E-03	12.47
5.26	1.44E-03	1.70E-04	6.68E-04	3.92
6.46	2.55E-03	4.04E-04	5.59E-04	1.38

FIGURE 4.9. Moles of N_2 , N_2O , and H_2 Produced by Simulated Waste with 0.3 M HEDTA and Various Concentrations of Hydroxide (96 hr at 90°C)

Corrosion of the steel reaction vessel could have contributed in a minor way to the increase in gas generation rates with increased hydroxide content, as shown in Figure 4.9. Divine et al. (1985) have evaluated the corrosion behavior of A-537 steel in a simulated double-shell slurry and in other solutions and demonstrated that increased hydroxide content enhances the corrosion rate. Steel corrosion should produce hydrogen, however, not nitrous oxide or nitrogen. Nitrite and nitrate reduction are of minor importance in contributing to the direct cathodic corrosion reaction; such reactions are extremely slow in strong caustics (Divine et al. 1985).

Delegard (1980) reported that slurry growth rates increased with the hydroxide content for hydroxide ion contents up to 1.5 M and decreased with hydroxide ion content above that value. A small maximum in the rate of nitrous oxide production at 1.7 M and an inflection in the rate of nitrogen production are apparent in Figure 4.9, but no variation in the rate of hydrogen production is seen at that same base content. Delegard's tests did not extend to the high base contents shown in Figure 4.9.

The mole ratio of N_2O to H_2 obtained in these simulant formulations containing HEDTA and varying hydroxide ion content is of interest. As given in Figure 4.10 and Table 4.4, the N_2O/H_2 ratio reached a maximum of approximately 12 with a concentration of 4 M NaOH and values of 2 and 4, respectively, when the hydroxide ion concentration was 3 M or 5 M. Of course, the molar quantities of N_2O and H_2 are approximately equal during a release event from Tank 241-SY-101. The present finding is significant because it indicates the fuel/oxidant ratio of the product gases can be greatly altered by a relatively small shift in base balance in the waste. This information may be important in terms of changing the base concentration while using waste mitigation strategies, including dilution.

Similar experiments were performed where EDTA was added to the simulant SY1-SIM-91A in the place of HEDTA, and the sodium hydroxide concentration was varied. Results of these tests are presented in Figure 4.11 and Table 4.5. The production of nitrous oxide, nitrogen, and hydrogen generally increased with rising hydroxide concentration, although not in a particularly linear manner and in smaller total quantities than were found for HEDTA.

FIGURE 4.10. Molar Ratio of N_2O to H_2 Produced from Waste Formulations with 0.3 M HEDTA² as a Function of Varying Amounts of NaOH

FIGURE 4.11. Moles of N_2 , N_2O , and H_2 Produced by Simulated Waste Containing 0.3 M EDTA at Various Concentrations of NaOH (120 hr at 90°)

TABLE 4.5. Production of N_2 , N_2O , and H_2 from SY1-SIM-91A with 0.3 M EDTA at Various Concentrations of NaOH (20-g samples at 90°C for 120 hr)

[NaOH], M	Gas Production, mol/kg/day			N_2O/H_2 mol ratio
	N_2	H_2	N_2O	
0.46	5.12E-05	3.60E-06	1.61E-06	0.45
1.66	1.41E-04	2.35E-06	5.88E-06	2.50
4.06	1.10E-04	1.15E-05	1.12E-04	9.73
5.26	1.40E-04	1.20E-05	8.68E-05	7.21
6.46	3.48E-04	5.50E-05	2.39E-04	4.35

For the simulant SY1-SIM-91A containing 0.3 M EDTA, relative amounts of thermally produced N_2O and H_2 were significantly affected by the hydroxide ion concentration, similar to behavior previously described for simulants containing HEDTA. A maximum in N_2O/H_2 mole ratios was observed at approximately 4 M NaOH, as is shown in Table 4.5 and Figure 4.12.

A third set of tests was performed in which sodium citrate was the sole organic constituent of the simulant and the base content varied as before. Results of these tests are given in Table 4.6 and Figure 4.13. Again, for simulants containing HEDTA or EDTA, gas yields varied considerably with the sodium hydroxide concentration. The amount of H_2 and N_2O produced was much less than has been observed for similar formulations containing HEDTA and EDTA, however, even though the TOC values were identical. A relatively large quantity of nitrogen was produced for low base contents. When citrate decomposes, intermediate degradation products that yield hydrogen at high rates (such as formaldehyde and glycolate) are not produced (Ashby et al. 1993, 1994; Meisel et al. 1993). However, pre-irradiation of solutions containing citrate has been found to enhance the later thermal yield of nitrous oxide (Meisel et al. 1993).

As found for simulants containing HEDTA or EDTA, the N_2O/H_2 molar ratio obtained for simulants containing citrate showed a strong hydroxide ion dependence. As shown in Table 4.6 and Figure 4.14, a maximum in this ratio was observed for a sodium hydroxide concentration of 5 M NaOH. Citrate contains no

FIGURE 4.12. Mole Ratio of N₂O to H₂ Produced from Waste Formulations Containing 0.3 M EDTA as Function of Varying Amounts of NaOH

TABLE 4.6. Gas Production as a Function of NaOH Concentration in SY1-SIM-91A Simulated Waste Containing 0.5 M Citrate (reaction time 120 hr; reaction temperature 90°C; 20-g samples)

[NaOH], M	Gas Produced (mol/kg/day)			N ₂ O/H ₂ mol ratio
	N ₂	H ₂	N ₂ O	
0.46	4.41E-04	1.89E-05	DL ^(a)	~0
1.66	6.96E-04	4.39E-06	DL ^(a)	~0
2.89	1.18E-04	6.80E-06	DL ^(a)	~0
4.06	5.11E-05	3.84E-05	1.87E-05	0.487
5.26	5.74E-05	2.18E-05	2.39E-05	1.096
6.46	6.83E-05	2.67E-05	4.75E-06	0.1779

(a) DL = less than detection limit.

FIGURE 4.13. Gas Production as a Function of NaOH Concentration in Simulated Waste Containing Citrate at 0.5 M

organic nitrogen, which might be offered as an explanation for relatively low nitrous oxide yields. However, it is fairly well established that the nitrogen atoms found in molecular nitrogen and nitrous oxide derive from the nitrite ion, whereas the organic carbon components serve as reducing agents (Meisel et al. 1991a, 1993; Ashby et al. 1993, 1994).

4.5 GAS PRODUCTION AS A FUNCTION OF SIMULATED WASTE DILUTION

One strategy that has been considered to interrupt the gas retention/release cycle prior to emplacement of the mixer pump is dilution of the waste in Tank 241-SY-101 (Johnson 1991; Ashby et al. 1992). The rationale is to force the solids to dissolve and therefore release the gases built up within the tank. Gases generated would then be continually released without being held in place by the solids (Bryan, Pederson, and Scheele 1992). Waste dilution by a factor

FIGURE 4.14. Molar Ratio of N_2O to H_2 Produced from Waste Formulations with 0.5 M Citrate as a Function of Varying Amounts of NaOH

of three is a probable pretreatment step if hydrothermal processing is to be used to destroy organic waste constituents (Schmidt et al. 1993; Orth et al. 1993). It is thus useful to consider changes in gas generation and stoichiometry that occur as a function of waste dilution.

To determine the effect of dilution on gas generation, experiments were performed using SY1-SIM-91A simulated waste containing 0.3 M HEDTA in the undiluted sample. Each reaction vessel contained the same total sample volume (15 mL) including the diluent. In these experiments, a 5 vol% dilution refers to 95 parts of undiluted sample plus five parts sodium hydroxide solution. The amount of product gas reported has been normalized to reflect the product per 15 mL of undiluted simulated waste.

The quantity of gas products as a function of volume percent dilution using 2 M NaOH is given in Figures 4.15 and 4.16, corresponding to thermal/radiolytic

FIGURE 4.15. Moles of Gases Produced as Function of Dilution Using 2 M NaOH (SY1-SIM-91A with 0.3 M HEDTA for 100 hr at 90°C)

and thermal-only conditions, respectively. In Figure 4.15, the lines represent least squares fits. N_2O is the most prominent radiolytic product, followed by N_2 and then by H_2 , as described previously. The enhancement in the rate of N_2O production with dilution of the waste appears to occur over the entire range of dilution (0 to 30 vol%). The following explanation is offered for these trends. The simulant SY1-SIM-91A is saturated with respect to sodium nitrite.

Dissolution of excess sodium nitrite solids when the sample is diluted results in little actual change in the sodium nitrite concentration in the liquid. The organic component, however, initially was completely dissolved, and its concentration fell with dilution. Nitrous oxide is known to derive from the nitrite ion but requires HEDTA or certain other organic compounds as reducing agents (Meisel et al. 1991a, 1992, 1993). Nitrous oxide formation is weakly dependent on the concentration of HEDTA above minimum concentrations (Meisel et al. 1993). Thus normalization by the dilution fraction leads to an apparent

FIGURE 4.16. Moles of Various Gases Produced as a Function of Dilution Using 2 M NaOH (SY1-SIM-91A with 0.3 M HEDTA, 100 hr, 90°C)

enhancement in the nitrous oxide yield with increased dilution. Hydrogen production, on the other hand, involves not only water radiolysis but abstraction of a proton from the organic molecule. Dilution would lower the concentration of HEDTA that could participate in abstraction reactions to produce molecular hydrogen. This is at least partially offset by the introduction of additional water by dilution, which can produce molecular hydrogen by direct radiolysis.

As shown in Figure 4.16 and Table 4.7, the thermal production of gases was in the order $N_2 \geq N_2O > H_2$ over the entire range of dilution, identical to trends described in Section 4.2. Also, the thermal production was much less than the radiolytic production. The thermal production of N_2 and N_2O decreased slightly from 0 to 30 vol% dilution, but the data were sufficiently scattered to preclude any recognition of a trend. The thermal H_2 production did not show any significant change with dilution.

TABLE 4.7. Gas Production from SY1-SIM-91A Containing 0.3 M HEDTA as a Function of Dilution Using 2 M NaOH (100 hr, 90°C, 20-g samples)

Vol% Dilution	Gamma, 5×10^5 R/h and Thermal, 90°C Gas Produced (mol/kg/day)			Vol% Dilution	Thermal Only, 90°C Gas Produced, mol/kg/day		
	N ₂	H ₂	N ₂ O		N ₂	H ₂	N ₂ O
0	8.56E-04	1.13E-03	3.37E-03	0	6.54E-04	1.88E-05	2.89E-04
0	8.78E-04	1.22E-03	5.64E-03	5	6.53E-04	2.61E-05	7.45E-04
5	7.82E-04	1.21E-03	5.19E-03	10	9.28E-04	2.84E-05	6.23E-04
10	1.11E-03	1.16E-03	5.59E-03	15	6.08E-04	2.20E-05	5.68E-04
15	7.32E-04	1.08E-03	5.79E-03	20	3.83E-04	1.23E-05	1.30E-04
20	6.63E-04	9.21E-04	5.29E-03	25	3.82E-04	1.42E-05	4.81E-04
25	7.47E-04	9.71E-04	6.24E-03	30	4.72E-04	9.87E-06	9.13E-05
30	8.71E-04	9.27E-04	6.20E-03	30	3.20E-04	1.42E-05	1.75E-04
30	7.15E-04	1.04E-03	6.85E-03				

Mole ratios of N₂O/H₂ from the radiolytic production of gases from SY1-SIM-91A are shown in Figure 4.17 and Table 4.8 as a function of volume percent dilution using 2 M NaOH. The data reveal an increasing N₂O/H₂ ratio from approximately 4 to almost 7 over the range 0 to 30 vol% dilution. As described above, these changes in gas product ratio may be explained qualitatively in consideration of the different dependencies of formation on simulant components. Molecular hydrogen is produced both via the abstraction of an organic hydrogen by a hydrogen radical that was formed from water radiolysis and by the direct radiolysis of water. As such, hydrogen production will depend on the concentration of HEDTA present in the simulant. Nitrous oxide is not sensitive to the concentration of HEDTA, as long as sufficient material is present to serve as a reducing agent (Meisel et al. 1993). A key intermediate step in nitrous oxide formation has been proposed to be hydroxylamine (Ashby et al. 1993, 1994; Meisel et al. 1993). No statistically significant trends were found in molar ratios versus dilution for thermal reactions.

FIGURE 4.17. N_2O/H_2 Product Ratio for Radiolytic Production of Gases from SY1-SIM-91A as Function of Dilution (2 M NaOH, 90°C, 100 hr)

TABLE 4.8. N_2O/H_2 Product Ratio for Radiolytic Production of Gases from SY1-SIM-91A as Function of Dilution (2 M NaOH, 90°C, 100 hr)

<u>Vol%</u> <u>Dilution</u>	<u>Gamma 5×10^5 R/hr</u> <u>and Thermal</u>	<u>Thermal</u> <u>Only</u>
0	3.0	15.4
0	4.6	
5	4.3	28.5
10	4.8	22.0
15	5.3	25.8
20	5.7	10.5
25	6.4	33.9
30	6.6	12.4
30	6.7	9.3

4.6 CHLORIDE CONCENTRATION EFFECTS ON GAS PRODUCTION

A series of tests was performed to assess the effect of changing chloride concentrations on gas generation in simulated wastes. Chloride was identified in both Window C (Herting et al. 1992a) and Window E (Herting et al. 1992b) core sampling and analysis activities. In this set of experiments, NaCl was added in increasing amounts to a series of vessels containing SY1-SIM-92A simulant. The NaCl concentration was varied from 0 to 2.0 M to bound the known concentration of chloride (~0.5 M) in Tank 241-SY-101. The slurry was heated to 60°C overnight after adding the NaCl to allow for equilibrium of this salt in the formulation. The formulation was then placed in the reaction vessel for gas generation and the temperature raised to 90°C. The reactions were carried out for four weeks at 90°C. Gas samples were taken each week to establish whether gas ratios changed with time. The gas compositions were determined by mass spectral analysis.

The amount of gases generated (H_2 , N_2 , and N_2O) as a function of time for the various formulations containing differing amounts of NaCl are plotted in Figure 4.18. Induction periods of approximately 100 hours were observed for both H_2 and N_2O , whereas no induction period was apparent for N_2 . Trends in nitrogen production are considered unusual when compared with the results for nitrous oxide and hydrogen. Air leaks might be suspected but are unlikely to be causing these observations, because oxygen was not detected in subsequent gas analyses. At least some of the delay in detecting nitrous oxide may be due to its being dissolved in the liquid. These data are also summarized in Table 4.9.

The total moles of N_2O , N_2 , and H_2 gases produced over the 420-hour period for these formulations are shown in Figure 4.19 as a function of NaCl concentration. This figure indicates that the production of N_2O and N_2 is influenced a great deal by the change in the chloride concentration. The production of N_2O shows a maximum at approximately 0.5 M chloride concentration in this simulated waste. This concentration is significant, because it is approximately the concentration of chloride found in Tank 241-SY-101 (Herting et al. 1992a; Herting et al. 1992b). The production of N_2O dropped off dramatically from increasing or decreasing the chloride concentration from this value. The effect of chloride addition on the H_2 production was not as pronounced as for the other gases.

FIGURE 4.18. N_2O , H_2 , and N_2 Gases Produced at 90°C as a Function of Reaction Time in Simulated Waste SY1-SIM-92A for Various Added NaCl Concentrations

TABLE 4.9. Production of N_2 , H_2 , and N_2O as Function of Time (SY1-SIM-92A with Varied NaCl Concentrations and 0.3 M HEDTA (90°C; 24-g sample wt))

$[Cl^-]M$	Accumulated Production of N_2 (mol/kg)				Average mol/kg/day
	96 hr	209 hr	327 hr	420 hr	
0.00	1.54E-03	2.61E-03	2.97E-03	6.94E-03	1.65E-05
0.10	1.56E-03	2.54E-03	2.91E-03	3.20E-03	7.62E-06
0.25	1.81E-03	3.14E-03	3.87E-03	4.43E-03	1.05E-05
0.50	1.67E-03	3.03E-03	4.43E-03	5.32E-03	1.27E-05
1.00	1.98E-03	3.04E-03	4.11E-03	5.32E-03	1.27E-05
2.00	2.14E-03	2.87E-03	3.53E-03	3.83E-03	9.12E-06

$[Cl^-]M$	Accumulated Production of H_2 (mol/kg)				Average mol/kg/day
	96 hr	209 hr	327 hr	420 hr	
0.00	4.72E-05	4.23E-04	6.85E-04	9.57E-04	2.28E-06
0.10	3.99E-05	3.57E-04	6.17E-04	8.17E-04	1.95E-06
0.25	4.72E-05	3.93E-04	6.51E-04	8.38E-04	2.00E-06
0.50	2.50E-05	4.85E-04	8.72E-04	1.11E-03	2.64E-06
1.00	2.48E-05	4.38E-04	7.70E-04	1.04E-03	2.48E-06
2.00	3.46E-05	1.95E-04	4.47E-04	6.55E-04	1.56E-06

$[Cl^-]M$	Accumulated Production of N_2O (mol/kg)				Average mol/kg/day
	96 hr	209 hr	327 hr	420 hr	
0.00	6.26E-06	6.26E-04	1.67E-03	3.19E-03	7.60E-06
0.10	6.64E-06	5.11E-04	1.55E-03	2.42E-03	5.76E-06
0.25	6.30E-06	4.81E-04	1.45E-03	2.24E-03	5.33E-06
0.50	5.02E-06	1.57E-03	6.21E-03	1.01E-02	2.40E-05
1.00	2.48E-06	8.30E-04	4.10E-03	7.57E-03	1.80E-05
2.00	2.88E-06	7.11E-05	7.45E-04	1.41E-03	3.36E-06

These findings of a strong dependence of gas generation behavior on the chloride ion concentration are somewhat surprising considering that Meisel et al. (1993) found no effect of chloride on either radiolytic or thermal reactions. However, the experiments performed by Meisel were of comparatively short duration (typically less than 100 hours). No effect of chloride ions on gas generation kinetics were observed in these experiments until after at least 100 hours had passed.

FIGURE 4.19. Gases Produced After 420 Hr Reaction Time as a Function of Added NaCl (NaCl concentration in the base SY1-SIM-92A composition is 0.5 M)

4.7 TRANSITION METAL CONCENTRATION EFFECTS ON GAS PRODUCTION

The effect of transition metals on gas generation was evaluated in a series of tests using SY1-SIM-91A simulated waste as the base formulation. Transition metals were added in increasing amounts to a series of reaction vessels containing 15 mL of SY1-SIM-91A. The transition metals used in this study, all known to be present in chemically significant levels in Tank 241-SY-101, are Cr, Cu, Fe, and Ni as nitrate salts. Table 4.10 presents the concentrations of transition metals found in Tank 241-SY-101 that were used in this experiment. The relative concentration of these metals was varied from 0 to 3 times that found in the tank. Transition metals were added as a concentrated solution to each formulation slurry. The slurry was heated to 60°C overnight after adding

TABLE 4.10. Concentrations of Transition Metals Used in Simulated Waste

<u>Component</u>	<u>Concentration, M</u>
Cr(NO ₃) ₃	0.105
Cu(NO ₃) ₂	0.00021
Fe(NO ₃) ₃	0.0074
Ni(NO ₃) ₂	0.0021

the metals to allow for equilibration into the formulation. The formulation was then placed in the reaction vessel for gas generation and the temperature raised to 90°C. Reactions were carried out for five days at 90°C. Gas compositions and quantities were measured by mass spectrometry.

The first incremental addition of transition metals to the simulant mixture produced the greatest change in gas generation behavior, as shown in Figure 4.20 and Table 4.11. Subsequent transition metal additions resulted in little further effect. Thermal nitrogen and nitrous oxide yields were most affected by the addition of transition metals. Hydrogen production was much less altered by production was much less altered by this addition. There was no simple concentration dependence of gas generation rates at this temperature for these relatively short-term (five-day) tests. These results contrast with the findings of Meisel et al. (1993), who reported only a depression in the radiolytic production of nitrous oxide by Cr(III) and no effect on thermal processes in short-term tests. Ashby et al. (1993) found that a small addition of Cu(II) enhanced the initial kinetics of overall gas generation.

Figure 4.21 details N₂O/H₂ and N₂O/N₂ molar ratios of the gaseous products. The N₂O/H₂ ratio shows a general decrease with increasing transition metal concentration in the simulated waste formulation, but with a small maximum at a relative concentration ratio of transition metals added to the simulated waste of about 1. A value of 1 corresponds to the concentrations given in Table 4.10. The N₂O/N₂ mole ratio also changed considerably as a function of the transition metal concentration. Nitrous oxide was favored by low transition metal concentrations, while nitrogen formation was favored by high concentrations of these metals. These results are consistent with the discussion in Section 4.2.

FIGURE 4.20. Gas Produced as Function of Concentration of Transition Metals Added to SY1-SIM-91A (relative concentrations based on actual tank waste analyses; 90°C for 5 days)

TABLE 4.11. Gas Produced as a Function of Concentration of Transition Metals Added to Simulated Waste SY1-SIM-91A (90°C; 100 hr; 20-g sample)

Relative Trace Metal	Gas Production (mol/kg/day)			N ₂ O/H ₂ mol ratio	N ₂ O/N ₂ mol ratio
	N ₂	H ₂	N ₂ O		
0.0X	6.54E-04	1.88E-05	2.89E-04	15.4	0.44
0.2X	7.28E-05	2.56E-05	1.11E-04	4.3	1.5
0.5X	1.52E-04	4.01E-06	1.61E-05	4	0.11
1.0X	7.34E-05	3.11E-06	2.80E-05	9	0.38
2.0X	5.74E-05	4.27E-06	1.59E-05	3.7	0.28
3.0X	4.80E-05	4.30E-06	8.60E-06	2	0.18

FIGURE 4.21. Mole Ratio of N_2O/H_2 and N_2O/N_2 Products from Thermal Reaction of SY1-SIM-91A with Varying Relative Amounts of Added Transition Metals (90°C, 100 hr)

4.8 GAS GENERATION FROM SIMULANTS CONTAINING FORMATE AND OXALATE

The kinetics and stoichiometry of gas generation have been assessed for simulants containing formate and oxalate. Both organic compounds have been identified in actual waste cores (Campbell et al. 1994) and as breakdown products of chelators (Ashby et al. 1993, 1994; Delegard 1987). Formate and oxalate are nearly fully oxidized and would not be expected to support significant gas generation reactions. However, oxidation to carbonate is expected to yield hydrogen from the reduction of water/hydroxide (Schmidt et al. 1993; Bryan et al. in Schulz and Strachan 1992). High reaction temperatures are probably necessary.

4.8.1 Gas Production from SY1-SIM-92A with Formate Added

Sodium formate (2.1 M) was added to the simulated waste SY1-SIM-92A. This waste formulation was placed in a series of six stainless steel reaction vessels,

each containing different total concentrations of hydroxide (0.43 M to 6.5 M OH^-). These vessels were then heated to 90°C for three weeks. Gas samples were taken for analysis periodically during the heating process to follow the progress of the reaction. Small but measurable quantities of nitrous oxide, nitrogen, and hydrogen were found, as shown in Figure 4.22 and Table 4.12. A small maximum in the nitrous oxide and nitrogen yields was observed for hydroxide ion concentrations of approximately 4 M. Hydrogen production rates increased with increased base content.

Variations in the gas product ratios were also apparent, as shown in Figure 4.23. Nitrous oxide yields were much higher than those of hydrogen except at high base contents. Relative nitrogen and nitrous oxide yields varied by nearly a factor of 10.

FIGURE 4.22. Gas Production from Simulated Waste SY1-SIM-92A as Function of Hydroxide Concentration (simulant contains 2.1 M formate) (90°C, 325 hr)

TABLE 4.12. Gas Production from SY1-SIM-92A Simulated Waste Containing 1.5 wt% (TOC) Formate (reaction time 325 hr; temperature 90°C; 25-g sample)

[OH ⁻] wt%	Gas Production (mol/kg/day)			H ₂ /N ₂ O mol ratio	N ₂ /N ₂ O mol ratio
	N ₂	H ₂	N ₂ O		
0.43	5.57E-05	7.93E-06	6.79E-05	0.11645	0.82084
1.63	4.12E-05	1.33E-06	9.19E-06	0.14483	4.4937
2.83	1.75E-04	1.61E-05	8.67E-05	0.18533	2.0143
4.03	1.44E-04	2.10E-05	2.88E-04	0.072956	0.49872
5.25	1.56E-04	4.91E-05	8.52E-05	0.57601	1.8357
6.43	9.70E-05	1.18E-04	3.89E-05	3.0248	2.498

FIGURE 4.23. Mole Ratio of Gaseous Products from SY1-SIM-92A as a Function of Added Hydroxide (2.1 M formate, 90°C, 345 hr)

4.8.2 Gas Production from SY1-SIM-92A with Oxalate Added

Tests identical to those described in Section 4.8.1 were performed, but sodium oxalate (1.5 wt% TOC) was used in place of sodium formate. Simulant formulation was placed in a series of six stainless steel reaction vessels, each containing different total concentrations of hydroxide (0.4 M to 6.4 M OH⁻). These vessels were then heated to 90°C for three weeks. Gas samples were taken for analysis periodically during the heating process to follow the progress of the reaction.

After one week of reaction at 90°C, the production of H₂, N₂O, and N₂ was not statistically significant when compared to the detection limit. Depending on the hydroxide concentration, small but non-zero quantities of both hydrogen and nitrous oxide were obtained from oxalate-containing waste simulants following three weeks reaction at 90°C. Hydrogen, nitrogen, and nitrous oxide yields after 345 hours of reaction are given in Figure 4.24 and Table 4.13.

These results must be viewed with care, because they could be skewed by the presence of small concentrations of contaminants and the small quantities of gases produced. A better approach would be to measure the rate of disappearance of both oxalate and formate.

TABLE 4.13. Gas Production from SY1-SIM-92A Simulated Waste Containing 1.5 wt% (TOC) Oxalate (reaction time 345 hr; temperature 90°C; 25-g sample)

[OH] wt%	Gas Production, mol/kg/day				
	N ₂	H ₂	N ₂ O	N ₂ /N ₂ O mol ratio	H ₂ /N ₂ O mol ratio
0.47	5.03E-05	4.12E-06	8.28E-07	60.7	4.98
1.72	4.06E-05	7.79E-07	5.85E-07	69.4	1.33
2.9	1.18E-04	4.82E-06	7.17E-07	164.6	6.72
4	6.75E-05	1.05E-05	4.49E-05	1.50	0.234
5.06	7.20E-05	8.97E-06	5.65E-05	1.27	0.159
6.05	4.56E-05	6.21E-06	4.45E-07	102.5	14.0

FIGURE 4.24. Gas Produced from SY1-SIM-92A Containing 1.05 M Oxalate as a Function of Hydroxide Concentration (90°C, 345 hr)

4.9 THE ROLE OF AMMONIA IN GAS GENERATION TESTS WITH SY1-SIM-93B CONTAINING CITRATE OR HEDTA

Ammonia is known to be produced in Tank 241-SY-101 along with nitrous oxide, hydrogen, nitrogen, methane, and other products (Person 1993; Ashby et al. 1993; Meisel et al. 1993; Strachan and Schulz 1993). But none of the simulants that have been developed to date contain this component. The relatively high vapor pressure of ammonia in basic solutions would cause the continual loss of this component unless the simulants were kept tightly sealed. Ammonia may contribute to the kinetics and stoichiometry of further gas generation reactions, however. The tests described below were performed as a preliminary assessment of the role of ammonia in these reactions.

The base formulation for this series of tests was the homogeneous waste simulant SY1-SIM-93B. Sodium citrate (0.28 M, 1.58 weight percent total organic carbon) or trisodium HEDTA (0.21 M, 1.58 weight percent TOC) were added. In one

set of tests, 0.5 M ammonium sulphate was added to the base formulation, which will convert to aqueous ammonia in that simulant. In another set, 0.5 M ammonium sulphate was added, but the sodium nitrite was removed. Because citrate contains no nitrogen, and the nitrate ion is well known to be inactive (Delegard 1980, for example), ammonia would provide the only source of nitrogen in any nitrous oxide or molecular nitrogen that could be produced. Tests were performed under thermal only (90°C) and thermal with gamma radiation (90°C, 5×10^5 R/hr dose rate). Reaction times extended to almost 600 hours. Gases were analyzed using mass spectroscopy.

4.9.1 Thermal Gas Generation Tests with Citrate

The base homogeneous SY1-SIM-93B simulant composition containing sodium citrate yielded nitrogen, ammonia, nitrous oxide, hydrogen, and trace amounts of methane (and perhaps ethane). These results are given in Figure 4.25a. Because there was no initial organic nitrogen, all of the nitrogen present in molecular nitrogen, ammonia, and nitrous oxide must have derived from the nitrite ion, consistent with the findings of Ashby et al. (1993, 1994). All of the data for these tests containing citrate are also given in Table 4.14.

In tests with citrate, ammonia, and nitrite ions present, as shown in Figure 4.25b, ammonia gas was the predominant species (as expected). Yields of both nitrogen and nitrous oxide were enhanced by the presence of ammonia. It is possible that ammonia, as well as sodium citrate, acts as a reductant towards the nitrite ion to yield these products. This conclusion is further supported by the results shown in Figure 4.25c, where nitrite ions have been removed from the simulant. Although the yield of nitrous oxide was much reduced by the removal of nitrite ions, a substantial amount of molecular nitrogen was produced; the only sources of this are ammonia and nitrate. These tests indicate that ammonia is not a "dead-end" product but continues to participate in gas generation reactions.

4.9.2 Radiolytic Gas Generation Tests with Citrate Present

Under radiolytic conditions for the base formulation (SY1-SIM-93B simulant, citrate and nitrite present, no ammonia), nitrous oxide was the predominant product, followed by hydrogen and nitrous oxide in approximately equal quantities

FIGURE 4.25. Thermal Gas Generation at 90°C from SY1-SIM-93B Homogeneous Waste Simulant with a) Citrate, b) Citrate and Ammonium Sulfate, c) Citrate and Ammonium Sulfate Without Nitrite

TABLE 4.14. Gas Generation Results from Radiolytic and Thermal Reactions Using SY1-SIM-93B Simulant with Citrate (90°C, 20-g sample)

Reaction Conditions: 90°C thermal only						
SY1-SIM-93B; citrate; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	1.11E-05	7.07E-04	2.14E-05	0.00E+00	2.50E-06	3.90E-06
579	1.99E-05	1.08E-03	3.47E-05	3.66E-04	2.50E-06	3.90E-06
mol/kg/day	8.25E-07	4.48E-05	1.44E-06	1.52E-05	1.04E-07	1.62E-07
SY1-SIM-93B; citrate with (NH₄)₂SO₄ added; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	1.79E-05	1.06E-03	1.69E-04	4.76E-03	0.00E+00	2.61E-05
579	4.68E-05	1.71E-03	5.75E-04	1.06E-02	5.32E-06	4.78E-05
mol/kg/day	1.94E-06	7.09E-05	2.38E-05	4.39E-04	2.21E-07	1.98E-06
SY1-SIM-93B; citrate with (NH₄)₂SO₄ added, without nitrite; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	6.69E-06	6.46E-04	1.89E-05	3.77E-03	0.00E+00	1.11E-05
579	1.38E-05	9.34E-04	4.47E-05	8.20E-03	0.00E+00	1.92E-05
mol/kg/day	5.72E-07	3.87E-05	1.85E-06	3.40E-04	0.00E+00	7.96E-07
Reaction Conditions: 5x10⁶R/h gamma; 90°C thermal						
SY1-SIM-93B; citrate; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	4.43E-03	4.54E-03	1.58E-02	1.51E-03	1.87E-05	7.24E-06
579	9.40E-03	9.12E-03	2.53E-02	2.25E-03	8.32E-05	7.24E-06
mol/kg/day	3.90E-04	3.78E-04	1.05E-03	9.33E-05	3.45E-06	3.00E-07
SY1-SIM-93B; citrate with (NH₄)₂SO₄ added; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	6.76E-03	1.19E-02	3.24E-03	3.78E-03	5.62E-05	1.15E-05
579	1.11E-02	2.54E-02	5.65E-03	7.30E-03	1.45E-04	1.64E-05
mol/kg/day	4.60E-04	1.05E-03	2.34E-04	3.03E-04	6.01E-06	6.80E-07
SY1-SIM-93B; citrate with (NH₄)₂SO₄ added, without nitrite; mol/Kg						
<u>Time</u>	<u>H₂</u>	<u>N₂</u>	<u>N₂O</u>	<u>NH₃</u>	<u>CH₄</u>	<u>C₂H₆</u>
0	0	0	0	0	0	0
289	1.21E-02	5.52E-03	4.46E-03	7.31E-03	2.25E-04	4.71E-05
579	2.30E-02	1.60E-02	9.98E-03	1.01E-02	5.97E-04	1.23E-04
mol/kg/day	9.53E-04	6.63E-04	4.14E-04	4.19E-04	2.47E-05	5.10E-06

ammonia, and methane. These results are shown in Figure 4.26a. The total quantity of gases produced was higher by approximately a factor of ten under radiolytic conditions than with nonradiolytic conditions. Hydrogen production was the most enhanced, due to water radiolysis and proton abstraction from the organic (Meisel et al. 1991a; Meisel et al. 1993).

The yield of nitrogen was enhanced and that of nitrous oxide suppressed by the addition of ammonia to the simulant, whereas hydrogen yields were unaffected. These results are shown in Figure 4.26b. One quite probable explanation is that ammonia can reduce nitrous oxide to nitrogen in the gas phase, but this has not been proven. In tests where nitrite ions were absent, as shown in Figure 4.26c, the most obvious change was a large increase in hydrogen yields. This is expected, because nitrite ions are known to be efficient scavengers of the hydrated electron; further reactions of the hydrated electron lead to hydrogen formation (Meisel et al. 1991a). Even though there was no organic nitrogen present and no nitrite present, nitrogen and nitrous oxide were both formed. Nitrite can be formed radiolytically from nitrate solutions (Meisel et al. 1991a); however, both ammonia and nitrate ion could have served as the nitrogen source under these conditions.

4.9.3 Thermal Gas Generation Tests with HEDTA Added

Nitrous oxide and nitrogen produced in tests with HEDTA present were higher than those observed in similar tests with citrate present. These results are given in Figure 4.27a. Test results corresponding to thermal and radiolytic conditions with HEDTA are summarized in Table 4.15. HEDTA and citrate differ in two basic ways; HEDTA contains an organic nitrogen source but citrate does not, and citrate is a more oxidized compound than HEDTA (HEDTA has a higher chemical oxygen demand per mole carbon than citrate).

Because it has been shown that organic nitrogen is not required for the production of nitrogen containing gases in this waste simulant, the enhancement of these nitrogen containing gases due to the use of HEDTA in place of citrate may be explained in either or both of the following ways: 1) HEDTA is thermodynamically a better reductant than citrate toward nitrite for the production of nitrogen, nitrous oxide, and ammonia; 2) the nitrogen in the additional quantity of product comes directly from an organic nitrogen source.

FIGURE 4.26. Thermal and Radiolytic Gas Generation from Simulant SY1-SIM-93B with Added a) Citrate, b) Citrate and Ammonium Sulfate, c) Citrate and Ammonium Sulfate Without Nitrite

TABLE 4.15. Gas Generation Results from Radiolytic and Thermal Reactions Using SY1-SIM-93B Simulant with HEDTA (90°C, 20-g sample)

Reaction Conditions: 90°C thermal only						
SY1-SIM-93B; HEDTA						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	6.16E-05	1.35E-03	3.76E-03	0.00E+0	0.00E+0	0.00E+0
550	1.56E-04	2.88E-03	8.23E-03	9.21E-05	0.00E+0	0.00E+0
SY1-SIM-93B; HEDTA with (NH ₄) ₂ SO ₄ added						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	1.32E-05	8.80E-04	1.36E-03	2.42E-03	0.00E+0	6.98E-06
550	3.67E-05	1.76E-03	3.14E-03	7.59E-03	2.17E-06	1.78E-05
SY1-SIM-93B; HEDTA with (NH ₄) ₂ SO ₄ added, without nitrite						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	1.21E-05	9.40E-04	1.16E-04	1.56E-03	0.00E+0	7.95E-06
550	3.40E-05	1.50E-03	2.22E-04	5.74E-03	2.84E-06	2.19E-05
Reaction Conditions: 5x10 ⁵ R/h gamma; 90°C thermal						
SY1-SIM-93B; HEDTA						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	1.77E-02	6.51E-03	2.40E-02	0.00E+0	7.90E-05	0.00E+00
550	3.32E-02	2.03E-02	5.98E-02	6.54E-04	2.51E-04	2.37E-05
SY1-SIM-93B; HEDTA with (NH ₄) ₂ SO ₄ added						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	7.75E-03	1.03E-02	3.41E-02	9.26E-03	7.70E-05	1.30E-05
550	1.59E-02	3.11E-02	6.96E-02	1.56E-02	2.07E-04	2.89E-05
SY1-SIM-93B; HEDTA with (NH ₄) ₂ SO ₄ added, without nitrite						
Time	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	C ₂ H ₆
0	0	0	0	0	0	0
260	2.63E-02	3.43E-03	2.71E-03	1.21E-03	2.50E-04	5.07E-05
550	4.31E-02	1.74E-02	2.17E-02	1.32E-02	5.43E-04	8.38E-05

FIGURE 4.27. Thermal Gas Generation from SY1-SIM-93B Homogeneous Waste Simulant with Added a) HEDTA, b) HEDTA and Ammonium Sulfate, c) HEDTA and Ammonium Sulfate Without Nitrite

Both organic and inorganic sources of nitrogen have been reported for nitrogen, nitrous oxide, and ammonia, but without complete agreement concerning the relative importance (Ashby et al. 1993, 1994; Meisel et al. 1993; Bryan et al. in Strachan and Schulz 1993).

In tests conducted with ammonia added (see Figure 4.27b), nitrous oxide and nitrogen were the predominant products. Nitrous oxide yields were higher in these tests with HEDTA than in similar tests containing citrate. Removal of nitrite ions lowered, but did not eliminate, gas generation (see Figure 27c), similar to the behavior of citrate-containing simulants. Although less easily shown in these tests because HEDTA contains organic nitrogen, ammonia appears to be the source of nitrogen in molecular nitrogen and nitrous oxide product.

4.9.4 Radiolytic Gas Generation Tests with HEDTA Present

Similar product distributions were found under radiolytic conditions with HEDTA present as found for companion tests with citrate present. The overall quantities of gases produced were higher in the case of HEDTA, as expected (see Figure 4.28a). For the base simulant composition (no ammonia added, nitrite present), nitrous oxide was the predominant product, followed by hydrogen, nitrogen, and ammonia. Hydrogen production was higher for HEDTA, a result of a greater concentration of organic hydrogen that can participate in abstraction reactions with hydrogen radicals formed via radiolysis.

The addition of ammonia led to slight increases in the amounts of nitrous oxide and nitrogen, and to a decrease in the amount of hydrogen that was formed, as is shown in Figure 4.28b. Much more nitrous oxide was formed than in similar tests containing citrate in the place of HEDTA. Ammonia may have contributed nitrogen atoms to the formation of molecular nitrogen and nitrous oxide, as could be more clearly shown in similar tests with citrate present. The higher reactivity of HEDTA and the presence of organic nitrogen in that component obscures trends that were visible in the citrate tests. As shown in Figure 4.28c, removal of nitrite ions again resulted in increased hydrogen production because hydrated electron scavenging reactions by nitrite ions were no longer taking place. Gas generation reactions continued in the absence of nitrite ions, a critically important component, indicating that ammonia can play a key role.

FIGURE 4.28. Thermal and Radiolytic Gas Generation from SY1-SIM-93 Waste Simulant with Added a) HEDTA, b) HEDTA and Ammonium Sulfate, c) HEDTA and Ammonium Sulfate Without Nitrite

5.0 CONCLUSIONS AND FUTURE DIRECTIONS

In summary, the compositions and methods of preparation of formulations that have been developed to simulate the actual wastes contained in Tank 241-SY-101 were reviewed. The kinetics and stoichiometry of gases that are generated from these simulants have been summarized with an emphasis on the variations in behavior that occur with changes in minor waste components such as transition metals, chloride, and hydroxide.

Sufficient similarity exists among a number of the simulants that not all are needed in future testing. The following simulant compositions are believed to be the most useful:

- Simulant SY1-SIM-91A, a slurry, contains the major inorganic waste components sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate, and sodium carbonate.
- The homogeneous simulant SY1-SIM-93B contains the same components. Aluminum nitrate, which is much more easily dissolved, was used in place of sodium aluminate in this simulant. Reagent-grade sodium aluminate contains approximately 30 wt% sodium hydroxide and insoluble aluminum oxide.
- The simulant SY1-SIM-92A contains the major inorganic components present in the above simulants plus transition metals, chloride, fluoride, sulphate, phosphate, and other minor components.
- A new simulant, SY1-SIM-94B, includes all the components of SY1-SIM-92A plus additional transition metals, rare earths, and other trace constituents. While organic components were specified in this recipe, others can be added or substituted as needed.

Other simulant recipes are duplicative and need not be considered further. Simulant usage provides definite advantages, including lower costs and radiological risks to researchers as well as an ability to modify compositions to facilitate mechanistic studies. Simulant studies should be considered complementary to measurements with actual wastes, however, not a replacement for all such studies, because it is virtually impossible to exactly reproduce the compositions in the actual waste tank.

The kinetics and stoichiometry of gases generated in studies with simulated wastes were shown to be sensitive to major and minor waste components. Nitrous oxide-to-hydrogen ratios, for example, were significantly affected by hydroxide,

chloride, and transition metal concentrations. The presence of solids appears to accelerate the rate of thermally driven gas generation reactions, especially rates based on liquid volume.

No significant effect on the gas generation behavior of simulated waste slurries was found to result when the slurries were diluted with sodium hydroxide solutions. Under radiolytic/thermal conditions, hydrogen production rates remained approximately constant when expressed in terms of moles of gas produced per day per kg of the original, undiluted sample (the mass of the diluent is neglected). Nitrous oxide production rates increased when expressed in the same manner. This behavior is expected because a rate-determining step in one route to the production of hydrogen involves the abstraction of a hydrogen atom from an organic molecule and thus depends directly on the concentration of the organic in the simulant. Molecular hydrogen may also be produced by the direct radiolysis of water. The rate-determining step for nitrous oxide does not directly involve organic constituents but requires a minimum concentration of certain organics to serve as reducing agents (Meisel et al. 1992).

Ammonia is not only produced in gas generation tests but appears to be chemically active in this system, altering nitrous oxide and nitrogen product distributions. In tests with simulants containing no organic nitrogen and no nitrite ions but with ammonia present, it was shown that nitrogen and nitrous oxide could still be produced under both thermal and radiolytic conditions. Under radiolytic conditions, conversion of nitrate ions to nitrite will occur, which can contribute to nitrogen and nitrous oxide formation.

The activation energies for gas generation, organic destruction, and slurry growth that have been determined in a number of studies are surprisingly consistent. From the earliest work by Delegard (1980) to recent organic destruction studies at high temperatures and gas generation studies with actual waste core samples as well as with individual compounds such as formaldehyde, activation energies in the range of 20 to 25 kcal/mole have been found.

The following areas require further attention. Activation energies and pre-exponential factors should be established for known organic waste constituents and product ratios determined. Detailed degradation pathways are needed for the principal organic waste constituents and their degradation

products need to be identified. The GIT is developing time profiles for formation and disappearance of products in the thermal decomposition of HEDTA. They will also complete a kinetic and product description for reactions of glycolate and N-hydroxyethyl-N-ethylglycine. Some of the fragments, especially formaldehyde and glycolate, that are produced by degradation of larger chelators are believed to be responsible for the majority of continued gas generation. Mechanisms for ammonia formation and reactions of ammonia should be determined. It was concluded in studies conducted at ANL that the primary source of ammonia is organic nitrogen, whereas studies at GIT showed that inorganic nitrogen is the primary source. Studies reported here show that ammonia participate in reactions to produce nitrogen and nitrous oxide as well. Further reactions of ammonia in both the gas phase (as may occur in trapped gas bubbles) and the liquid phase should be examined.

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APPENDIX A

FINAL WORD SIMULATED WASTE RECIPE

Westinghouse
Hanford Company

P.O. Box 1970 Richland, WA 99352

May 1, 1991

DISTRIBUTION (see distribution list attached)

Ladies and Gentlemen:

FINAL WORD ON SIMULATED WASTE RECIPE

Three recipes are proposed here for synthetic Tank 101-SY waste. The first, labeled "Homog. Sol'n" in the table below, is to be used for experiments requiring the use of a homogeneous solution. The second, labeled "Feed", is to be used for preparing the third, which is labeled "Slurry". These recipes are slightly different than those we discussed at the April 23-24 meetings in Richland. The carbonate has been reduced in order to make the solutions easier to prepare. The hydroxide in the homogeneous solution has been increased in order to ensure that the aluminate will stay in solution and to increase the gas generation rate. The FINAL WORD on the proposed solution compositions is as follows:

<u>COMPONENT</u>	<u>Homog. Sol'n</u>	<u>Feed</u>	<u>SLURRY</u>
NaOH	2.00	1.61	2.3
NaAl(OH) ₄	1.54	1.54	2.2
NaNO ₃	2.59	2.59	3.7
NaNO ₂	2.24	2.24	3.2
Na ₂ CO ₃	0.42	0.42	0.6
Organic	0.21	0.21	0.3

All numbers in the table represent moles per liter of solution at room temperature or moles per liter of slurry at room temperature. All of the concentrations in the homogeneous solution are 0.7 times the slurry concentration except for NaOH, which has been increased from 1.61 to 2.00 to help prevent precipitation of Al(OH)₃. Due to the instability of some organics in this solution matrix, all solutions should be made up shortly before use. I will not attempt to dictate a shelf life, but we know that HEDTA undergoes substantial degradation in one year at room temperature.

Solution Preparation

As long as a homogeneous solution is the end result, the method of getting there shouldn't (and doesn't) make any difference. However, we have found some procedural "tricks" to making the solutions easier to prepare.

- 1) If you're making up one liter of solution in a two liter beaker, start with about 500 mL of water. A round Teflon stirbar works much better than the standard cigar-shaped stirbar for stirring thick slurries.
- 2) Heat the water to about 90°C and add the sodium aluminate. Stir and heat until the solution is almost clear. (It will never get completely clear because of the metal hydroxide impurities in the aluminate. If you wait too long for the aluminate to dissolve, you may start to precipitate aluminum hydroxide, and the solution will begin to cloud up again.)
- 3) Turn off the heat, and then SLOWLY add the NaOH pellets. (If the NaOH is added all at once, the solution will self heat to boiling, and will probably spatter solution out of the beaker.)
- 4) Add the sodium carbonate and stir until dissolved. You may need to cool the solution somewhat to get all the carbonate into solution. (The solubility of sodium carbonate in this matrix as a function of temperature has not been fully studied. Increased temperature may speed up the dissolution, but decrease the equilibrium solubility of sodium carbonate.) Getting all the sodium carbonate into solution has proved to be a real problem, even at the reduced levels. If you don't get it all into solution at this point, or if it comes back out later as you add other salts, don't panic. See step 8.
- 5) Turn the heat back on, and add remaining ingredients in any order, stirring to dissolve the solids after each addition, and keeping the solution hot.
- 6) Always add the organic as the fully deprotonated sodium salt, if at all possible. The sodium salts are much more readily soluble than the free acids, and you don't have to make a hydroxide correction to account for the neutralization of the acid. With EDTA and HEDTA, solubility will not be a problem. For others, such as oxalate, it may not be possible to reach the standard concentration for the homogeneous solution. You might want to add the organic earlier than last in the order of addition in order to check for complete dissolution.
- 7) Add water at any point during the solids additions that it seems appropriate, but try to end up with close to 900 mL total volume. Filter the solution while it is hot (around 50°C) through a medium glass frit filter funnel. Of course, filtering a hot caustic solution through a glass frit may not be the ideal course of action, but it's the only

reasonable way we've found to do it. Standard filter papers are dissolved or otherwise made useless by hot caustic except for some of the teflon types (which require pre-wetting with an organic solvent), and a paper called "Solvinert", which is no longer manufactured. Filtration is about a factor of ten faster with the hot solution than a cool one.

- 8) If there is a significant amount of solids in the filter, transfer the solids to a 150 mL beaker and add water until the total volume is a little under 100 mL. Stir briefly, then transfer the slurry back to the filter.
- 9) Cool the solution to room temperature, then transfer to a volumetric flask and dilute to one liter. Keep in mind that solution volumes are not nearly additive when mixing water with these concentrated high-salt solutions. That means that when you add water to the mark on the volumetric flask, add the stopper and mix, the final volume in the flask will be substantially below the mark, so you need to add water again to the mark. That's just one of the many small difficulties you encounter in dealing with concentrated solutions. You also need to keep this volume non-additivity in mind when making dilutions for analysis. Always dilute to a final volume. Never mix one volume of concentrated solution (x) with another volume of water (y) and assume the final volume is x+y.
- 9) Because the sodium aluminate may vary from batch to batch in Al and hydroxide composition, it would be a good idea to analyze the final solution to see how close it is to the desired make-up.

Slurry Preparation

Prepare the "Feed" solution, which is 0.7 times the concentrations shown under the heading "Slurry" in the table. All of the numbers are the same as shown under the heading "Homog. Sol'n" except for hydroxide, which is 1.61 M instead of 2.00 M.

Set up a vacuum still that you can control to a constant pressure of 60 torr. Evaporate 100 mL of the feed solution at a constant 60 torr until the volume of slurry remaining is 70 mL. You should find that the solution nucleates not long before the end of the volume reduction, but the solution "thickens up" rapidly after nucleation. This "thickening up" of the slurry is much more pronounced when organics are present than when they aren't.

It's up to you to determine when the volume of slurry remaining is 70 mL. In our system, we measure the volume of condensate collected, and stop when it reaches 30 mL. We know at that point there's 1-2 mL of condensate held up in the condenser, which about accounts for the volume additivity issue mentioned earlier: 70 mL slurry + 32 mL H₂O = 100 mL starting solution.

Distribution

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May 2, 1991

Pipets

One final word of caution to those trying to make quantitative measurements on concentrated solutions involving the use of pipets: standard TD (to deliver) pipets are not reliable for concentrated solutions. Because of the high density and viscosity, the solutions do not drain from the glass in the same way that water does, so the amount of solution that remains in the drained pipet is not the correct amount. Air displacement type automatic pipets with

the plastic disposable tips, such as Eppendorf or Oxford pipets, give very reproducible, but incorrect results. They're fine if you calibrate them, but don't expect a 2 mL pipet to deliver 2.0 mL. The pipets that give the best results are the TC (to contain) glass pipets, but they're also the most difficult to use. I usually go with the Eppendorfs, and calibrate them myself with concentrated solutions of well documented density. By the way, the calibration varies with temperature of the solution. I have also been known to do dilutions by weight instead of by volume, especially when final results are needed in units "per gram of sample" instead of molarity. Also, if you have accurately determined the density of the solution, then it is much easier to do dilutions by weight, converting to volume by calculation.

That's it for solution composition and preparation. I'm waiting to hear from others on use of a standard "synthetic air". Please call me at (509) 373-2532 if you have any corrections or additions to this memo.

Very truly yours,

D. L. Herting, Principal Scientist
Process Chemistry Laboratories

tth

APPENDIX B

CALCULATIONS FOR SY1-SIM-92A FORMULATION

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	SY1-SIM-92A	Prepared by SA Bryan												
2						Check	Actual	total						
3	COMPONENT	F. Wt. (g/mol)	M (mole/L)	VOLUME(L)	grams	When Added	Added	Weight%		wt% TOC	wt% org O	wt% org N	wt% org H	wt% Na
4														
5	Na4EDTA	380.18	0	1	0.00			0.00		0	0	0	0	0
6	Na3HEDTA	380.24	0	1	0.00			0.00		0	0	0	0	0
7	Na3C6H5O7*2H2O (citrate)	294.1	0.34	1	99.99			6.31		1.54574059	2.40448536	0	0.1073431	1.48133473
8	NaCl	58.44	0.526	1	30.74			1.94		0	0	0	0	0.76390399
9	Na2PO4 * 12 H2O	380.13	0.179	1	68.04			4.30		0	0	0	0	0.77987917
10	NaAlO2 * 0.21NaOH * 1.33 H2O	115	2.05	1	235.75			14.89		0	4.14218066	0	0	3.60240274
11	NaNO2	69	3.95	1	272.55			17.21		0	0	0	0	5.73654136
12	NaNO3	84.99	2.2	1	186.98			11.81		0	0	0	0	3.19503569
13	Na2CO3	105.99	0.4	1	42.40			2.68		0	0	0	0	1.16183116
14	NaF	41.99	0.1	1	4.20			0.27		0	0	0	0	0.14522289
15	NaOH	40	2.45	1	98.00			6.19		0	0	0	0	3.55810793
16	Cr(NO3)3 * 9 H2O	400.15	0.1051	1	42.06			2.66		0	0	0	0	0
17	Cu(NO3)2 * 2.5 H2O	232.59	0.00021	1	0.05			0.00		0	0	0	0	0
18	Fe(NO3)3 * 9 H2O	404	0.0074	1	2.99			0.19		0	0	0	0	0
19	Ni(NO3)2 * 6 H2O	290.81	0.0021	1	0.61			0.04		0	0	0	0	0
20	Na2SO4	142.04	0.032	1	4.55			0.29		0	0	0	0	0.09294649
21	CaCl2	110.99	0.0083	1	0.92			0.06		0	0	0	0	0
22	KCl	74.56	0.146	1	10.89			0.69		0	0	0	0	0
23	H2O	18		1	483.00			30.50		0	0	0	0	0
24	TOTAL			1	1583.71			100.00		1.54574059	6.54666602	0	0.1073431	20.5172122
25														
26	Total density =	1583.706877	g / 1,000 mL =		1.58		Tank 101-SY analysis ->			1.58				20.5

B.1

	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD
1																
2																
3	wt% Al	wt% Cl	wt% PO4	wt% NO2	wt% NO3	wt% CO3	wt% F	wt% OH	wt% Cr	wt% Cu	wt% Fe	wt% Ni	wt% SO4	wt% Ca	wt% K	wt% H2O
4																
5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.77287
8	0	1.1790692	0	0	0	0	0	0	0	0	0	0	0	0	0	2.441361
9	0	0	1.07374668	0	0	0	0	0	0	0	0	0	0	0	0	3.098869
10	3.49496493	0	0	0	0	0	0	0.46211203	0	0	0	0	0	0	0	0
11	0	0	0	11.4730827	0	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	8.61270491	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	1.51543195	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0.1199717	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	2.62990586	0	0	0	0	0	0	0	1.075085
16	0	0	0	0	1.23435721	0	0	0	0.34509	0	0	0	0	0	0	0.000597
17	0	0	0	0	0.00164424	0	0	0	0	0.00084	0	0	0	0	0	0.075696
18	0	0	0	0	0.08691002	0	0	0	0	0	0.02607	0	0	0	0	0.014321
19	0	0	0	0	0.01644244	0	0	0	0	0	0	0.007784	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0	0	0.193975	0	0	0
21	0	0.03721017	0	0	0	0	0	0	0	0	0	0	0	0.0210054	0	0
22	0	0.32727016	0	0	0	0	0	0	0	0	0	0	0	0	0.36045812	0
23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30.49807
24	3.49496493	1.54354953	1.07374668	11.4730827	9.95205882	1.51543195	0.1199717	3.09201789	0.34509	0.00084	0.02607	0.007784	0.193975	0.0210054	0.36045812	37.97687
25																
26	3.5	1.5	1.1	11.5	10	1.6	0.1	3.1	0.368		0.028	0.008	0.19	0.021	0.37	38

	AE
	Total wt%
	0
	0
	6.311774
	1.942973
	4.294987
J	14.80053
I	17.20962
2	11.80774
J	2.677263
I	0.265201
5	6.188014
5	2.654532
7	0.003083
3	0.188679
J	0.038547
J	0.286922
I	0.058216
2	0.687728
J	30.49807
I	99.91388
5	
5	

APPENDIX C

CALCULATIONS FOR SY1-SIM-94A AND SY1-SIM-94B FORMULATION

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	SY1-SIM-94A	Prepared by WD Samuels (modified from T Hohl formulation)													
2						total									
3	COMPONENT	F. Wt. (g/mol)	M (mole/L)	VOLUME(L)	grams	Weight%		wt% TOC	wt% O	wt% org N	wt% org H	wt% Na	wt% Al	wt% Cl	wt% PO4
4															
5	Na4EDTA	380.18	0.10	2	76.04	2.24	0.7085907	0.7558301	0.1653378	0.0708591	0.5432529	0	0	0	0
6	Hexadecanoic acid	242.5	0.10	2	48.50	1.43	1.1337452	0.0944788	0	0.2007674	0.1358132	0	0	0	0
7	CITRIC ACID	294.1	0.10	2	58.82	1.74	0.4251544	0.7558301	0	0.0177148	0.3151876	0	0	0	0
8	TRIBUTYL PHOSPHATE	266.3	0.10	2	53.26	1.57	0.8503089	0.3779151	0	0.1653378	0	0	0	0	0
9	DIBUTYL PHOSPHATE	210	0.10	2	42.00	1.24	0.5668726	0.3779151	0	0.1121935	0	0	0	0	0
10	HEXONE	100.2	0.10	2	20.04	1.01	0.4251544	0.0944788	0	0.0708591	0	0	0	0	0
11	NPH	170.3	0.10	2	34.06	1.01	0.8503089	0	0	0.1417181	0	0	0	0	0
12	Na3PO4 * 12 H2O	380.13	0.1078	2	81.96	2.42	0	0	0	0	0.43922	0	0	0.6047231	0
13	NaNO2	69	3.6517	2	503.93	14.88	0	0	0	0	4.9594915	0	0	0	0
14	NaNO3	84.99	2.4563	2	417.52	12.33	0	0	0	0	3.3359802	0	0	0	0
15	Na2CO3	105.99	0.8399	2	178.04	5.26	0	0	0	0	2.2813906	0	0	0	0
16	Na2SO4	142.04	0.0666	2	18.92	0.56	0	0	0	0	0.1809032	0	0	0	0
17	NaCl	58.44	0.3555	2	41.55	1.23	0	0	0	0	0.482816	0	0.745216	0	0
18	NaF	41.99	0.0253	2	2.12	0.06	0	0	0	0	0.0343607	0	0	0	0
19	Ce(NO3)3*6H2O	434.23	0.0031	2	2.69	0.08	0	0.0263596	0	0	0	0	0	0	0
20	Ca(NO3)2 * 4H2O	236.15	0.0092	2	4.35	0.13	0	0	0	0	0	0	0	0	0
21	KNO3	101.1	1.1334	2	26.97	0.80	0	0	0	0	0	0	0	0	0
22	ZnCl2	136.29	0.0005	2	0.14	0.00	0	0	0	0	0	0	0.0020962	0	0
23	CsNO3	194.91	0.00017	2	0.07	0.00	0	0	0	0	0	0	0	0	0
24	Sr(NO3)2	211.63	0.000011	2	0.00	0.00	0	0	0	0	0	0	0	0	0
25	NaOH	40	2.35	2	188.00	5.55	0	0	0	0	3.1916108	0	0	0	0
26	Cr(NO3)3 * 9 H2O	400.15	0.1262	2	101.00	2.98	0	0	0	0	0	0	0	0	0
27	Fe(NO3)3 * 9 H2O	404	0.008	2	6.46	0.19	0	0	0	0	0	0	0	0	0
28	Ni(NO3)2 * 6 H2O	290.81	0.0041	2	2.38	0.07	0	0	0	0	0	0	0	0	0
29	RuCl4*5 H2O	333.7	9.8E-08	2	0.00	0.00	0	0	0	0	0	0	4.109E-07	0	0
30	Rh(NO3)3 * H2O	288.9	9.7E-08	2	0.00	0.00	0	8.248E-07	2.406E-07	0	0	0	0	0	0
31	PdCl2	177.4	9.4E-09	2	0.00	0.00	0	0	0	0	0	0	0	0	0
32	NaAlO2 * 0.21NaOH * 1.33 H2O	115	1.9098	2	439.25	12.97	0	3.6087109	0	0	3.1384508	3.0448498	0	0	0
33	H2O	18		2	1038.92	30.67	0	0	0	0	0	0	0	0	0
34	TOTAL			2	3387.00	100.41	4.9601352	6.0915192	0.1653381	0.7794498	19.038478	3.0448498	0.7473127	0.6047231	0
35															
36		3387.004474 g			1.69			1.58			20.5	3.5	1.5	1.1	
37								1.53			20.7	3.2	0.79	0.64	
38								1.53	5.46	0.36	0.15	20.27	3.22	0.79	0.64

SIM94B

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
SY1-SIM-94B	Prepared by WD Samuels (modified from T Hohl formulation) 2/12/94														
COMPONENT	F. Wt. (g/mol)	M (mole/L)	OLUME(L)	grams	Weight%	wt% TOC	wt% O	wt% org N	wt% org H	wt% Na	wt% Al	wt% Cl	wt% PO4	wt% NO2	
Na4EDTA	380.18	0.1000	2	76.04	2.24	0.706	0.753565	0.164842	0.070647	0.541625	0	0	0	0	
HEXADECANOIC ACID	242.5	0.1000	2	48.50	1.43	1.130	0.094196	0	0.200166	0.135406	0	0	0	0	
CITRIC ACID(3Na*H2O)	294.1	0.0920	2	54.11	1.59	0.390	0.69328	0	0.016249	0.289104	0	0	0	0	
TRIBUTYL PHOSPHATE	266.3	0.1000	2	53.26	1.57	0.848	0.376783	0	0.164842	0	0	0	0	0	
DIBUTYL PHOSPHATE	210	0.1000	2	42.00	1.24	0.565	0.376783	0	0.111857	0	0	0	0	0	
HEXONE	100.2	0.1000	2	20.04	1.00	0.424	0.094196	0	0.070647	0	0	0	0	0	
NPII	170.3	0.1000	2	34.06	1.00	0.848	0	0	0.141293	0	0	0	0	0	
Na3PO4 * 12 H2O	380.13	0.1078	2	81.96	2.41	0	0	0	0	0.437904	0	0	0.602911	0	
NaNO2	69	3.6517	2	503.93	14.83	0	0	0	0	4.94463	0	0	0	9.88926	
NaNO3	84.99	2.4563	2	417.52	12.29	0	0	0	0	3.325984	0	0	0	0	
Na2CO3	106.29	0.8399	2	178.04	5.24	0	0	0	0	2.274554	0	0	0	0	
Na2SO4	142.04	0.0666	2	18.92	0.56	0	0	0	0	0.180361	0	0	0	0	
NaCl	58.44	0.3555	2	41.55	1.22	0	0	0	0	0.481369	0	0.742983	0	0	
NaF	41.99	0.0253	2	2.12	0.06	0	0	0	0	0.034258	0	0	0	0	
Ce(NO3)3*6H2O	434.23	0.0031	2	2.69	0.08	0	0.026281	0	0	0	0	0	0	0	
Ca(NO3)2 * 4H2O	236.15	0.0092	2	4.35	0.13	0	0	0	0	0	0	0	0	0	
KNO3	101.1	0.1334	2	26.97	0.79	0	0	0	0	0	0	0	0	0	
ZnCl2	136.29	0.0005	2	0.14	0.00	0	0	0	0	0	0	0.00209	0	0	
CsNO3	194.91	0.0002	2	0.07	0.00	0	0	0	0	0	0	0	0	0	
Sr(NO3)2	211.63	0.0000	2	0.00	0.00	0	0	0	0	0	0	0	0	0	
NaOH	40	2.3500	2	188.00	5.53	0	0	0	0	3.182047	0	0	0	0	
Cr(NO3)3 * 9 H2O	400.15	0.1262	2	101.00	2.97	0	0	0	0	0	0	0	0	0	
Fe(NO3)3 * 9 H2O	404	0.0080	2	6.46	0.19	0	0	0	0	0	0	0	0	0	
Ni(NO3)2 * 6 H2O	290.81	0.0041	2	2.38	0.07	0	0	0	0	0	0	0	0	0	
RuCl4*5 H2O	333.7	0.0001	2	0.07	0.00	0	0	0	0	0	0	0.000418	0	0	
Rh(NO3)3 * H2O	288.9	0.0001	2	0.06	0.00	0	0.000848	0.000247	0	0	0	0	0	0	
Mn(NO3)2	178.95	0.0100	2	3.58	0.11	0	0.084776	0.024726	0	0	0	0	0	0	
Pt(NO3)2	331.2	0.0100	2	6.62	0.19	0	0.084776	0.024726	0	0	0	0	0	0	
Zr(CITRATE)	282	0.0080	2	4.51	0.13	0.034	0.067821	0.019781	0	0	0	0	0	0	
Pd(NO3)2	230.72	0.0001	2	0.05	0.00	0	0	0	0	0	0	0	0	0	
NaAlO2 * 0.21NaOH * 1.33 H2O	115	1.9098	2	439.25	12.93	0	3.597897	0	0	3.129046	3.035726	0	0	0	
H2O	18		2	1038.92	30.58	0	0	0	0	0	0	0	0	0	
TOTAL			2	3397.18	100.41	4.945	6.2512	0.234323	0.775701	18.95629	3.035726	0.745491	0.602911	9.88926	
TOTAL WEIGHT	3397.18441	g	DENSITY =	1.70											

SIM94B

Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF
wt% NO3	wt% CO3	wt% F	wt% OH	wt% Cr	wt% Cu	wt% Fe	wt% Ni	wt% SO	wt% Ca	wt% K	wt% Zn	wt% Cs	wt% Sr	wt% H2	Total wt
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.23715
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.56012
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.19498	1.58359
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.38939
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.05381
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.58872
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.98905
0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.37083	2.41164
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	14.8339
8.965695	0	0	0	0	0	0	0	0	0	0	0	0	0	0	12.2917
0	2.96681	0	0	0	0	0	0	0	0	0	0	0	0	0	5.24136
0	0	0	0	0	0	0	0	0.37641	0	0	0	0	0	0	0.55677
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.22435
0	0	0.0283	0	0	0	0	0	0	0	0	0	0	0	0	0.06256
0.022631	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.04891
0.100742	0	0	0	0	0	0	0	0	0.021708	0	0	0	0	0.039	0.16145
0.486921	0	0	0	0	0	0	0	0	0	0.307074	0	0	0	0	0.794
0	0	0	0	0	0	0	0	0	0	0	0.001925	0	0	0	0.00401
0.000621	0	0	0	0	0	0	0	0	0	0	0	0.00133	0	0	0.00195
8.03E-05	0	0	0	0	0	0	0	0	0	0	0	0	5.67E-05	0	0.00014
0	0	0	2.35194768	0	0	0	0	0	0	0	0	0	0	0	5.53399
1.381921	0	0	0	0.3863	0	0	0	0	0	0	0	0	0	1.20361	2.97187
0.087602	0	0	0	0	0	0.0263	0	0	0	0	0	0	0	0.0763	0.19018
0.029931	0	0	0	0	0	0	0.01417	0	0	0	0	0	0	0.02607	0.07017
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00064	0.00105
0.001095	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00032	0.00251
0.073002	0	0	0	0	0	0	0	0	0	0	0	0	0	0.03179	0.2143
0.073002	0	0	0	0	0	0	0	0	0	0	0	0	0	0.03179	0.2143
0.058401	0	0	0	0	0	0	0	0	0	0	0	0	0	0.02543	0.20535
0.00073	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00073
0	0	0	0.4013904	0	0	0	0	0	0	0	0	0	0	2.69168	12.8557
0	0	0	0	0	0	0	0	0	0	0	0	0	0	30.5818	30.5818
11.28237	2.96681	0.0283	2.75333808	0.3863	0	0.0263	0.01417	0.37641	0.021708	0.307074	0.001925	0.00133	5.67E-05	36.2742	99.88

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