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Laboratory Testing of Ozone Oxidation of Hanford Site Waste from Tank 241-SY-101

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EXECUTIVE SUMMARY

Ozone was investigated as a reagent to oxidize and destroy organic species present in simulated and genuine waste from Hanford Site Tank 241-SY-101. High-shear mixing apparatus were tested to perform the gas-to-solution mass transfer necessary to achieve efficient use of the ozone reagent. Oxidations of nitrite (to form nitrate) and organic species were observed. The organics oxidized to form carbonate and oxalate as well as nitrate and nitrogen gas from nitrogen associated with the organic. Oxidations of metal species also were observed directly or inferred by solubilities. Chemical precipitations of metal ions, including strontium and americium, were observed as the organic species were destroyed by ozone. The chemical reaction stoichiometries were consistent with the reduction of one oxygen atom per ozone molecule. Chemical analyses showed that acetate, oxalate, and formate comprised about 40% of the genuine waste's total organic carbon.

The reported investigations were conducted for the Initial Pretreatment Module Technology Project and summarize work completed by June 1993 under the Westinghouse Hanford Company fiscal year 1993 Work Breakdown Structure 1.1.2.8.2.2.20 milestone entitled, "Compare Synthetic and Actual Waste Performance: Ozone."

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LIST OF TERMS

cm	centimeter
COD	chemical oxygen demand
CSTR	continuous stirred-tank reactor
DSC	differential scanning calorimetric or calorimeter
EDTA	ethylenediaminetetraacetate
g	gram
HEDTA	N-(hydroxyethyl)-ethylenediaminetriacetate
IDA	iminodiacetate
L	liter
M	moles per liter
mL	milliliter
NTA	nitrilotriacetate
ppm	parts per million
rpm	revolutions per minute
RTW	radioactive tanked waste
Tank 101-SY	Tank 241-SY-101
TOC	total organic carbon
WHC	Westinghouse Hanford Company
wt%	weight percent

**LABORATORY TESTING OF OZONE OXIDATION OF HANFORD SITE
WASTE FROM TANK 241-SY-101**

1.0 ABSTRACT

Ozone was investigated as a reagent to oxidize and destroy organic species present in simulated and genuine waste from Hanford Site Tank 241-SY-101 (Tank 101-SY). Two high-shear mixing apparatus were tested to perform the gas-to-solution mass transfer necessary to achieve efficient use of the ozone reagent. Oxidations of nitrite (to form nitrate) and organic species were observed. The organics oxidized to form carbonate and oxalate as well as nitrate and nitrogen gas from nitrogen associated with the organic. Oxidations of metal species also were observed directly or inferred by solubilities. The chemical reaction stoichiometries were consistent with reduction of one oxygen atom per ozone molecule. Acetate, oxalate, and formate were found to comprise about 40% of the genuine waste's total organic carbon (TOC) concentration. Ozonation was found to be chemically feasible for destroying organic species (except oxalate) present in the wastes in Tank 101-SY. The simulated waste formulation used in these studies credibly modelled the ozonation behavior of the genuine waste.

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2.0 INTRODUCTION

Organic constituents present in Hanford Site radioactive tanked waste (RTW) have been implicated in safety concerns at the Hanford Site because of their chemical and radiolytic instability. The safety problems are rooted in two types of reactions that can occur in the RTW. The first reaction type is the low-temperature degradation of organic species to produce flammable gases including hydrogen and nitrous oxide. Such reactions are occurring in Tank 101-SY and are at least partially responsible for the episodic gas releases observed. The second reaction type is the rapid high-temperature reaction of reduced organic species with strong oxidants, e.g., nitrate and nitrite, present in the RTW. Such reactions are not observed in the RTW at storage temperatures but are observed in laboratory tests at elevated temperatures. The reactions are highly exothermic and thus are potentially self-accelerating.

Destruction of the organics present in Hanford Site RTW would eliminate the safety problems of both organic reaction types. Controlled oxidation of the organics with ozone gas is one candidate technology being considered to destroy organics.

The approach of using ozone to degrade organic species present in Hanford Site RTW has precedent. Several laboratory studies conducted at the Hanford Site around 1980 investigated the use of ozonolysis to destroy organic complexants present in the RTW. The objective of the earlier studies was to facilitate extraction of radionuclides (particularly strontium-90) from the RTW. It was found that RTW having appreciable organic concentrations were resistant to strontium decontamination approaches involving precipitation or sorption.

Ozonation as an approach to destroy organics in Hanford Site RTW was re-examined by Colby (1993). In those scoping studies, a prototype high-shear reactor was used to achieve the intimate gas-liquid contact required to introduce the ozone gas efficiently to the (simulated) RTW stream.

The present studies were conducted to investigate further performance and operation of high-shear reactors for ozonation, and to study the resulting behavior of chemical components in both simulated and genuine Tank 101-SY RTW. Radionuclide behavior during ozonation of genuine Tank 101-SY material was also investigated.

This document completes the Westinghouse Hanford Company (WHC) fiscal year 1993 Work Breakdown Structure 1.1.2.8.2.2.20 milestone entitled, "Compare Synthetic and Actual Waste Performance: Ozone."

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3.0 OZONATION CHEMISTRY

The chemistry of ozone and reactions involving ozone have been studied extensively in qualitative and preparative organic chemistry, in the chemical processing industry and at the Hanford Site. The technical literature relevant to the application of ozonation to Hanford Site RTW materials are surveyed here.

3.1 GENERAL ASPECTS

Ozone (O_3) is an allotrope of oxygen present in trace quantities in the lower atmosphere. The "ozone layer" in the upper atmosphere (peak concentration at about 26 km-elevation) is formed by the reaction of oxygen atoms, (which are present because of ultraviolet photodissociation of diatomic oxygen) with diatomic oxygen. Ozone is a toxic gas with a threshold limit value of 0.1 parts per million (ppm) in air (ACGIH 1991). However, ozone's pungent odor, likened to the smell of newly mown hay, is detectable by the nose at 0.01 ppm.

The odor of ozone also is characteristic of thunderstorms. Not surprisingly then, ozone typically is produced in the laboratory or in industry by corona (electrical) discharge in pure diatomic oxygen gas or in air (which contains about 20% oxygen) (Kirk-Othmer 1981). Concentrations up to 4 weight percent (wt%) in air or 8 to 10 wt% in pure oxygen may be achieved by this method provided the gases are dry (dewpoint less than $-40^\circ C$). Water vapor catalyzes the decomposition of ozone to oxygen. Higher ozone concentrations may be produced by capturing the ozone at cryogenic temperatures in Freon 13¹ and releasing ozone from the Freon by warming. Ozone dissolved in Freon 13 is available commercially (Braker and Mossman 1980).

Ozone is a powerful oxidizing agent with a potential ($E^0_A = 2.075$ volts; $E^0_B = 1.247$ volts) second only to fluorine among common chemical reagents (Bratsch 1989). The reaction of ozone across carbon-carbon double bonds to form molozonides

and further hydrolysis with oxidative/reductive workup to scission the carbon-carbon double bond to form alcohols, aldehydes, ketones, or organic acid moieties is a well-known qualitative approach to identify the presence and location of the double bond (Hudlický 1990).

¹Freon 13 is a trademark of E. I. du Pont de Nemours & Company, Wilmington, Delaware.

Because of ozone's preference for attack at the double bond, this reagent also is used to decolorize organic dyes or other colored organic materials having conjugated double bond chromophores. For example, tannins and lignins from pulp and paper operations can be decolorized (bleached) by ozone (Kirk-Othmer 1981 and Bailey 1982). Environmental concerns related to the possible formation of dioxins by chlorine bleaching in pulp and paper processing may lead to ozone supplanting chlorine in this application. Other industrial applications and equipment for ozonation of waters (e.g., disinfection, odor removal, and clarification) are described in general articles and reviews (Lin and Yeh 1993, Kirk-Othmer 1981, Horváth et al. 1985, and Bailey 1982).

In the reaction of ozone with carbon-carbon double bonds, all three oxygen atoms from ozone are taken up by the organic reactants. Ordinarily, however, only one oxygen atom from ozone reacts with organic or inorganic species. The residual molecular oxygen then is released as a gaseous product.

3.2 OZONATION REACTIONS RELEVANT TO HANFORD SITE RTW

Because of the power of ozone, ozonation reactions often are indiscriminate and oxidize all reduced species. Both inorganic and organic reduced species are present in RTW and potentially are available for ozonation. Thermodynamically, ozone is capable of oxidizing metals to their highest oxidation states (Horváth et al. 1985). Reactions relevant to the ozonation of inorganic components of RTW, described in Table 1, also represent the stoichiometry resulting in liberation of one mole of oxygen per mole of ozone.

Table 1. Ozonation of RTW-Relevant Inorganic Species.

Reaction	Reference
$\text{NH}_3 + 4 \text{O}_3 \rightarrow \text{NO}_3^- + 4 \text{O}_2 + \text{H}_2\text{O} + \text{H}^+$	Singer and Zilli (1974)
$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$	Kirk-Othmer (1981)
$2 \text{Fe}^{2+} + \text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + \text{O}_2 + 2 \text{OH}^-$	Kirk-Othmer (1981)

The products arising from ozonation of organic species present in RTW are difficult to predict because:

- Original organics are numerous and, to a large extent, unknown
- Ozone is a vigorous and powerful oxidizing agent that can fully decompose organic species, via various pathways and intermediate compounds, to carbon dioxide and water (Horváth et al. 1985).

The organic species identified in analyses of genuine Tank 101-SY RTW (Herting et al. 1992) are either the original chelating agents used in the Hanford Site processes or degradation products evidently derived from these

chelating agents. The identified species are all salts of organic acids (i.e., carboxylates, containing the -CO_2^- functional group) and most are amines with a carboxylate group in the β position (i.e., aminocarboxylates containing the $\text{-N(R)-CH}_2\text{CO}_2^-$ functional group). The identified species, however, represent only 10 to 20% of the TOC found in the Tank 101-SY samples.

Herting et al. (1992) speculated that acetate and oxalate might also be present in Tank 101-SY RTW. In the present study, as discussed in a later section of this report, formate, as well as acetate and oxalate, were found in samples of Tank 101-SY RTW. Acetate, oxalate, and formate are all carboxylates. Analyses showed acetate and formate represented about 15% each of the TOC; oxalate accounted for about 8% of the TOC present. With these data for acetate, formate, and oxalate, about 50 to 70% of the organic carbon present in Tank 101-SY RTW is speciated. Table 2 lists the organic species identified in Tank 101-SY RTW and their concentrations.

Ozonation reactions of carboxylates, aminocarboxylates, and amines have been studied and are reported in the technical literature. Ozonation of oxalate was found to be optimum in 60 °C water at pH 8 to 10 and could be driven to complete conversion to carbonate (Aloy et al. 1989). The amount of ozone required was reported as 1 to 2 grams (g) per gram of oxalate (about 2 to 4 moles of ozone per mole of oxalate). The optimum pH and temperature conditions were confirmed by other researchers (Grachok et al. 1987) who found pH 9 to 11 and 50 °C temperatures to be best (in the range pH 1.7 to 11; temperature at 25 and 50 °C) for oxalate destruction.

More detailed oxalate ozonation studies, reported by Galutkina et al. (1977), qualitatively support most of the findings of Aloy et al. (1989) and Grachok et al. (1987). Galutkina et al. (1977) studied the effects of alkali-to-oxalate mole ratio and temperature on oxalate ozonation using a simple bubbler plate to introduce the ozone gas. Alkali:oxalate mole ratios from 0 to 10 (corresponding to 0.2 moles per liter [M] sodium hydroxide) and temperatures from 20 to 70 °C were studied. The effect of temperature was small with higher temperatures slightly favoring more complete reaction. Oxidation of oxalate was also favored by increasing alkali:oxalate ratio to 6; above 6, no additional increase in oxalate oxidation was found. At an alkali:oxalate mole ratio of zero, little oxidation occurred. Oxalate decomposition was found to decrease (but not to zero rate) as the reaction proceeded and carbonate reaction product increased.

The theoretical reaction stoichiometry for the ozonation of oxalate is given by

The stoichiometry shows one mole of ozone is required to oxidize one mole of oxalate to carbonate. Results from Galutkina et al. (1977) showed, however, that even after adding over 60 moles of ozone per mole of oxalate, only about 27% of the oxalate had oxidized. These results indicated that even under

Table 2. Organic Species Identified in Genuine 101-SY RTW.
(Herting et al. 1992; formate, acetate
and oxalate analyses determined
in this study.)

Species	Formula (name)	Concentration ($\mu\text{gC/g}$ sample)
NIDA	$\text{ON-N-(CH}_2\text{CO}_2)_2^{2-}$ (N-nitrosoiminodiacetate)	168 - 2,210
NTA	$\text{N-(CH}_2\text{CO}_2)_3^{3-}$ (nitrilotriacetate)	54 - 337
CA	$^-\text{O}_2\text{CCH}_2\text{-COH(CO}_2^-)\text{-CH}_2\text{CO}_2^-$ (citrate)	10 - 84
ED3A	$^{-2}(\text{O}_2\text{CCH}_2)_2\text{-N-CH}_2\text{CH}_2\text{-NH-CH}_2\text{CO}_2^-$ (ethylenediaminetriacetate)	20 - 260
EDTA	$^{-2}(\text{O}_2\text{CCH}_2)_2\text{-N-CH}_2\text{CH}_2\text{-N-(CH}_2\text{CO}_2)_2^{2-}$ (ethylenediaminetetraacetate)	51 - 480
HEDTA	$^{-2}(\text{O}_2\text{CCH}_2)_2\text{-N-CH}_2\text{CH}_2\text{-N-(CH}_2\text{CH}_2\text{OH)CH}_2\text{CO}_2^-$ [N-(2-hydroxyethyl)ethylenediaminetriacetate]	10 - 20
Formate	HCO_2^-	1,700 - 1,790
Acetate	CH_3CO_2^-	1,640 - 1,840
Oxalate	$^-\text{O}_2\text{CCO}_2^-$	850 - 950

optimum conditions (closely matching expected RTW ozonation conditions), oxalate is relatively stable to ozonation. The results further suggest that oxalate degradation by ozone may be retarded by carbonate and thus indicate that the hydroxyl radical (which is scavenged by carbonate, Hoigné and Bader 1976) is the active oxidizer in the case of oxalate.

Galutkina et al. (1977) also studied the ozonation of acetate under conditions similar to those used for oxalate. As was found for oxalate, the oxidation of acetate increased as the ratio of alkali:acetate increased to 6; above 6, no further increase in acetate oxidation was found. Temperature increase from 20 to 70 °C increased the rate of reaction by about 50%. The theoretical reaction stoichiometry is given by

Because the oxidation state of organic carbon in acetate is lower than that of oxalate, four moles of ozone are required by stoichiometry to effect complete oxidation of one mole of acetate to carbonate. With their relatively inefficient bubbler plate apparatus, Galutkina et al. (1977) found essentially complete oxidation when about 12 moles of ozone had been added. These results indicate that acetate should be amenable to complete oxidation by ozone at RTW ozonation conditions.

Formate represents about 15% of the organic carbon found in Tank 101-SY. However, no studies were found in the technical literature on the ozonation of formate.

The chemistry of ozone oxidation of organic species is surveyed in a two-volume review (Bailey 1982). Though many of the ozonation reactions discussed by Bailey are used in organic synthesis and thus are conducted under conditions that lead only to partial oxidation of the reactant species, the review describes pathways by which amines degrade by ozonation.

The first product of ozonation of an amine is the corresponding amine oxide. For amines having primary alkyl groups attached to the amine nitrogen (which include all the aminocarboxylates listed in Table 2), formation of the alcohol at the α -carbon follows. The reaction sequence (not chemically balanced) is:

Elmghari-Tabib et al. (1982) describe a reaction sequence that carries the above sequence a few steps further:

The studies of Elmghari-Tabib et al. (1982), conducted at pH 7 to 9 using triethylamine, indicated about 2% of the amine nitrogen oxidized to nitrate. The reaction stoichiometry for complete oxidation of triethylamine to carbonate and nitrate calls for 22 moles of ozone per mole of amine

The tests described by Elmghari-Tabib et al. (1982), however, were run only until 2.68 moles of ozone were added per mole of triethylamine. Therefore, insufficient ozone was used to drive the oxidation reactions to completion and the products reported likely were intermediates.

Studies of the ozonolysis of ethylenediaminetetraacetate (EDTA) and related chelating agents have been reported. Aloy et al. (1989) studied the

ozonation of EDTA and demonstrated that essentially complete destruction of EDTA could be obtained with carbonate and nitrate the final products. Reactions were run at pH 8 to 10 and at about 60 °C.

Morooka et al. (1986) studied the ozonation of EDTA, nitrilotriacetate (NTA), and iminodiacetate (IDA) and their metal complexes. They showed that about 2 moles of ozone were required to destroy one ligand coordination site, that metal ion complexing protected the chelates from ozonation, and that the initial reaction involved ozone attack at the amine nitrogen with cleavage of the N-C bonds. Morooka et al. (1986) observed IDA, NTA, and glycine as initial products of oxidation of EDTA. They also observed a 50-fold increase in degradation rate of EDTA as pH was raised from 2 to 8.

In summary, the studies of ozonation of organics found in the technical literature showed:

- Ozone attack on amines initially results in the breaking of the N-C bonds and the formation of the corresponding carboxylic acid(s).
- With sufficient ozone (and at pH 8 to 10), EDTA can be degraded to carbonate and nitrate.
- Acetate will react but oxalate is fairly resistant to ozone in alkaline solutions.

Finally, it is important to note that ozone itself probably is not the active oxidizing agent in alkaline solutions. Ozone interacts strongly with alkaline solution and rapidly forms a number of intermediate species that are themselves active oxidizing agents. Tomiyasu et al. (1985) identified a series of reactions occurring in the introduction of ozone to alkaline solution. The reactions most important in Hanford Site RTW are:

The reactions are rapidly equilibrating in alkaline and carbonate-bearing solutions, such as RTW, with the result that the ozonide anion, not ozone, likely is the active oxidizing species in solution. The hydroxyl radical, a potent oxidizing agent often cited as the active oxidizing agent during aqueous ozonation reactions (Hoigné and Bader 1976), is scavenged by carbonate and therefore probably does not exist in significant concentrations in alkaline carbonate-bearing RTW solutions.

3.3 PREVIOUS HANFORD SITE STUDIES OF OZONATION

Ozonation has been investigated as a general means of destroying complexing agents present in Hanford Site RTW. Subsequent more detailed investigations into the ozonation reactions were undertaken to understand the chemistry of the reaction and to optimize conditions for complexant destruction. Recent development of a prototype ozonation reactor that improved the mass transfer required to introduce ozone gas efficiently to solution has been reported.

3.3.1 Radionuclide Removal Studies

Ozonation of alkaline Hanford Site RTW solution has been studied as a means to destroy organic components responsible for inhibiting the precipitation and sorption of strontium (specifically, strontium-90) during radionuclide removal investigations (Schulz 1980; Strachan and Schulz 1980). In those studies, no investigations were made of the reaction stoichiometry, kinetics, or mechanism. However, explicit research into the chemistry of the ozonation of Hanford Site RTW was undertaken and reported shortly thereafter (Lutton et al. 1980; Winters 1981).

3.3.2 Studies by Lutton et al. (1980)

Studies by Lutton et al. (1980) using simulated RTW containing EDTA demonstrated that ozone oxidized nitrite (present in molar concentrations in RTW) to nitrate. Increased temperature (from 25 to 60 °C) was found to favor oxidation of the EDTA. Lutton et al. (1980) observed the precipitation of gibbsite and sodium oxalate during tests with simulated RTW. In tests conducted with genuine RTW, the sodium hydroxide concentration was increased to 1 M (from its initial value of 0.2 M) to prevent the precipitation of gibbsite. Sodium oxalate precipitate, however, still was observed.

Ozonation of diluted genuine RTW caused reduction of solution concentrations of calcium, nickel, phosphate, barium, chromium, manganese and iron. Nitrite solution concentration also decreased a factor of 100 but since nitrate concentrations were not measured, the expected corresponding increase in nitrate concentration, from oxidation of the nitrite, was not verified. The solution concentrations of the radionuclides, promethium-147, strontium-90, europium-155, cobalt-60, americium-241 and total plutonium decreased by ozonation. The decreases in metal and radionuclide solution concentrations were attributed to the destruction of the organic complexing agents keeping those materials in solution. The concentration of cesium-137 was not affected by ozonation.

During ozonation, organic carbon concentrations decreased 80 to 90% (equivalent to about 0.1 M carbon). Interestingly, however, a corresponding increase in carbonate concentration did not occur. Instead, carbon dioxide, as well as some nitrogen, reported to the offgas. About 50 to 70 moles of ozone were added per mole of organic carbon.

3.3.3 Studies by Winters (1981)

Winters (1981) evaluated the effect of pH (1 to >14) on the destruction of EDTA by ozone in a simulated RTW. The simulated RTW also contained tartrate. Reaction progress was monitored by the decrease in the concentration of EDTA; no determination of the corresponding destruction of organic carbon was made.

Winters (1981) observed three differing regimes of reaction behavior as a function of pH. At high pH levels (10 to >14), two different rates of EDTA destruction were observed. In the initial period (up to about 3 hours), rapid initial EDTA destruction was observed. The initial rapid rate then gave way to an even more rapid rate in the second period. At intermediate pHs (4.5 to 10), again two different rates of EDTA destruction were observed with rates again being higher in the second period. However, both rates were markedly lower than the corresponding rates observed at high pH. In the low pH regime, constant and low EDTA destruction rates were observed.

The step change in EDTA destruction rate observed at pH above 4.5 was attributed to the rapid initial ozone oxidation of nitrite to nitrate. Once nitrite was fully oxidized, more ozone became available for EDTA oxidation and increased EDTA destruction rates were observed. This explanation was corroborated by the observation that at low pH, where nitrite is unstable to disproportionation and thus is not available to consume ozone, no step change in reaction rate occurred. In all cases, EDTA destruction followed first order kinetics, i.e., the destruction rate was proportional to the concentration of EDTA. These data indicated that the kinetics of ozone destruction of EDTA were greatest at high pH.

Winters (1981) measured the moles of ozone consumed per mole of EDTA reacted. The most favorable stoichiometries (i.e., lowest ozone consumption) were found at high and low pH. Correcting for the effect of nitrite oxidation, about 10 moles of ozone were required per mole of EDTA destroyed. Ozone concentrations in the offgas also were sensitive to pH. At high pH, ozone in the offgas was 10 to 20% of the input concentration. At low pH, ozone concentration was >95% of the input concentration. Therefore, high pH was preferred based on ozone uptake and use.

Overall, low ozone use was observed in the studies conducted by Winters (1981). The low use possibly was due to inefficient introduction of ozone by the simple bubbler/mixer apparatus and the intrinsically slow (ozone) gas → solution mass transfer kinetics.

3.3.4 Studies by Colby (1993)

Colby (1993) performed a series of studies of ozonation reactions using diluted simulated Hanford Site RTW and a lab-scale continuous stirred-tank reactor (CSTR). The CSTR provided high-shear mixing that achieved the intimate gas-liquid contact required to introduce the ozone gas efficiently to the simulated RTW stream.

With this apparatus, 90 to 100% ozone use was attained during oxidation of simulated Tank 101-SY RTW containing EDTA. The assessment of ozone use was

based on chemical oxygen demand (COD) of the product solution, and the provision of one atom of oxygen oxidant per molecule of ozone (with the residual oxygen exiting as offgas). About 70% of the COD was due to nitrite and the balance to organic carbon, and a slight amount of oxidizable metal ions in the simulant.

Further tests with simulants were conducted using acetate, citrate, and oxalate as the source organics. For acetate and citrate, 50% of the organic carbon was destroyed rapidly by ozone before the reaction slowed to negligible rates. Only slight organic carbon concentration decrease was found during ozonation of oxalate. The finding that oxalate was stable to ozonation substantiated the earlier findings of Galutkina et al. (1977).

Scoping tests (using EDTA) showed solids removal from the feed, lower ozone concentration, and addition of manganese dioxide as a possible catalyst had no effect on the reaction. Addition of hydrogen peroxide before ozonation, in an attempt to oxidize nitrite, likewise did not improve the rate or extent of organic destruction by ozone. Increasing temperature from 30 to 75 °C and hydroxide concentration from 0.1 to 2 M decreased organic carbon destruction slightly.

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4.0 EXPERIMENTAL MATERIALS AND METHODS

Ozonation testing of genuine Hanford Site RTW from Tank 101-SY and simulated RTW, prepared based on the Tank 101-SY composition, was conducted using an enclosed, high-shear mixer apparatus design similar to that used by Colby (1993). Limited testing of a simpler open high-shear mixer also was conducted using simulant RTW. Experimentation generally followed test plans prepared in anticipation of this work (Delegard 1993; Appendix A). The apparatus, materials, procedures and analyses used during the experimentation are described in the following sections.

4.1 APPARATUS

An enclosed reactor design was tested. The design used a solution/slurry recirculation loop. An open high-shear reactor design was also tested, which maintained the test solution in an open reaction vessel. Associated test equipment included ozone generators and measurement devices, pumps, and control valves. The enclosed and open reactor test apparatus are described in the following sections.

4.1.1 Enclosed Reactor Design

Most experiments using simulated RTW were conducted with the enclosed high-shear mixer reactor design used by Colby (1993). Tests with simulants were conducted in ordinary laboratory hoods. Because of the high radiation dose rates emanating from genuine Tank 101-SY RTW (mostly caused by cesium-137), tests with this material were conducted in a shielded radioactive hot cell. The apparatus used in tests with genuine RTW was similar to the apparatus used for the simulant tests but had additional backflow prevention hardware (a check valve and an emergency trap) to ensure the containment of the radioactive RTW within the hot cell. The layout of the high-shear mixer and associated apparatus, including the backflow prevention hardware used for tests with genuine Tank 101-SY RTW, is shown in Figure 1.

As shown in Figure 1, two streams were metered into the reactor: a liquid stream, containing the diluted waste solution, and the ozone gas stream. The ozone-generating apparatus was located just outside the laboratory hood (for the tests using simulants) or hot cell (for the tests with genuine Tank 101-SY RTW), while the liquid handling portion of the apparatus was located within the hood or hot cell.

The gas stream was produced by an electrolytic ozone gas generator fed by a controlled flow of oxygen gas from a standard pressurized gas bottle. The gas flow was monitored by calibrated ball-in-tube gas flowmeters while the pressure was monitored using pressure gauges installed on the ozone

Figure 1. Layout of Ozonation Apparatus.

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generators. In most experiments, gas flow was set at 1,000 milliliters (mL)/min (at room temperature and pressure). Two different models of ozone gas generator were used in these experiments: the Union Carbide Model SG4060¹ and the PCI Model GS-1.²

The ozone outputs of the two ozone generators were found to vary as functions of gas backpressure and applied power. The ozone concentration outputs of each generator were determined as functions of pressure and power and the performance characteristics were recorded. Separate tests showed ozone concentrations were not diminished or affected by transit through the dry apparatus (i.e., in the absence of test solution), indicating ozone decomposition in the apparatus was negligible.

During the ozonation experiments, the ozone-bearing oxygen gas exiting the ozone generator was conducted to the laboratory hood or hot cell, as appropriate. For tests conducted with genuine Tank 101-SY RTW, the gas passed through a 1-liter (L)-capacity glass flask, which acted as a backflow emergency trap, and a one-way check valve. The gas then was conducted to a "T" fitting located at the base of the reactor. The tubing and fittings used in the gas lines were of polyethylene and stainless steel construction. Rubber, brass, and copper materials are attacked by ozone (Braker and Mossman 1980) and were avoided in the gas system.

The liquid stream was comprised of diluted simulated or genuine RTW which was pumped to the reactor in a recirculation loop from a 1-L glass reservoir. For most experiments, 680 to 800 mL of diluted genuine or simulated Tank 101-SY RTW were used in testing. Flexible Viton³ tubing was used to conduct the solution from the reservoir to and through a peristaltic pump. The pump was calibrated and the rate generally was set to 1,000 mL/min., i.e., the gas and liquid flow rates were identical. The solution was delivered by tubing from the pump to the "T" fitting at the base of the reactor to encounter the incoming ozone/oxygen gas flow.

The metered waste liquid and ozone gas streams were drawn into the reactor by the pressure of their respective flows and the centrifugal pumping action of the high-shear reactor chamber. The gas/solution blend exited the reactor to pass through an inline mixer (a 15-centimeter [cm] length of internally vaned stainless steel tubing). The gas/solution mix then passed to the liquid reservoir where gas/liquid disengagement occurred. The offgas was vented to the exhaust system of the hood or hot cell.

Samples of solution were collected periodically from the liquid reservoir at the sample point shown in Figure 1. Offgas samples also were collected during tests with simulated RTW; no offgas samples were taken during the tests with genuine RTW.

¹Union Carbide Model SG4060 is a trademark of Union Carbide Corporation, Danbury, Connecticut.

²PCI Model GS-1 is a trademark of PCI, Inc., West Caldwell, New Jersey.

³Viton is a trademark of E. I. du Pont de Nemours & Company, Wilmington, Delaware.

Figure 2 is a cutaway drawing of the high-shear enclosed reactor used in these tests. The reactor is the In-line Mixer/Homogenizer.¹ The reactor features a closely fitting square hole screen and propeller where the high gas/solution shear and agitation were accomplished. Solution plus gas were drawn up into the propeller region of the reactor, pushed through the screen, and exited the top of the reactor chamber. To maximize the shearing action and residence time in the mixer, the normal exit port was blocked and a new exit port located 2.54 cm (1 in.) above the normal exit port.

The propeller was driven through a Teflon²-sleeved plain bearing by a 1/3-horsepower (250-watt) electric motor turning at about 5,000 revolutions per minute (rpm). The high speed on the shaft required (water) cooling of the bearing. Except for Viton seals, the Teflon bearing, and a nonwetted graphite bushing, the mixer was constructed entirely of stainless steel.

4.1.2 Open Reactor Design

The open reactor design was tested in an effort to improve the rate of ozone gas introduction to the test slurry while endeavoring to maintain high gas → solution mass transfer. Testing of the open design was limited to simulated Tank 101-SY RTW. The experimental apparatus is shown in Figure 3.

The test slurry was held in a 2-L graduated cylinder cut off at the 1,400-mL mark. The ozone generation, metering, and measurement systems were identical to those described in the previous section. The ozone was introduced below solution level by a length of polyethylene tubing fitted at the end with a sintered stainless steel bubbler.

High-shear agitation was accomplished by a Model LDD Laboratory Duplex Disintegrator Dissolver.³ This mixer has two mixing heads operating coaxially. The mixer was driven by a 1/3-horsepower (250-watt) electric motor turning at about 5,000 rpm. To maximize the rate of ozone introduction to the solution, both the Union Carbide and the PCI ozone generators were used in tandem. Gas flow rate was about 6.6 L/min. into 440 mL of dilute, simulated Tank 101-SY RTW. The specific volumetric gas flow rate of the open reactor thus was about 15 times higher (15 solution volumes/min.) than the specific gas flow rate of the enclosed reactor (generally 1 solution volume/min.).

4.2 MATERIALS

Materials used during the tests included oxygen gas and RTW solutions. Pressurized, bottled oxygen gas (99.5% oxygen) was fed to the ozone generators

¹In-line Mixer/Homogenizer is a trademark of Silversons Machine Incorporated, East Longmeadow, Massachusetts.

²Teflon is a trademark of E. I. du Pont de Nemours & Company, Wilmington, Delaware.

³Model LDD Laboratory Duplex Disintegrator Dissolver is a trademark of Silversons Machine Incorporated, East Longmeadow, Massachusetts.

Figure 2. Cutaway of Enclosed Ozone Reactor.

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Figure 3. Open Ozone Reactor.

to produce the 5 to 8 wt% ozone used in the experiments with simulated Tank 101-SY RTW. High-purity (99.99% oxygen), pressurized bottled oxygen gas was used for the tests with genuine Tank 101-SY RTW. Both genuine and simulated Tank 101-SY RTW were used as feed. To model the dilution caused by the water sluicing of RTW from the tanks, all experiments were conducted using volumetric dilutions of one part (simulant or genuine) RTW to three parts water.

4.2.1 Genuine Tank 101-SY RTW

The chemical, radionuclide, and physical compositions of RTW present in Tank 101-SY have been determined via analyses of samples collected from Tank 101-SY following the Window C (May 1991) and Window E (December 1991) gas release events. The analytical results from these samplings were presented in two reports (Herting 1992 and Herting et al. 1992) and showed little difference in the overall composition of the RTW in Tank 101-SY. Using aliquots of the samples retrieved for these waste characterization analyses, representative composite samples of genuine Tank 101-SY RTW were prepared and placed in four jars (Appendix B).

Two ozonation tests on genuine Tank 101-SY RTW were conducted using the composite material. One test, conducted on April 16, 1993, used material from jar 93B; the second test, conducted on April 18, 1993, used material from composite jar 93C.

4.2.2 Simulated Tank 101-SY RTW

The overall bulk composition of the RTW present in Tank 101-SY is given in Table 5-4 of Herting (1992). Based on this composition, a recipe for simulated Tank 101-SY RTW was prepared (Delegard 1993) and is given in Appendix C. The recipe has been adapted for use as a standard simulant formulation for Tank 101-SY studies (Hohl 1993). For most of the present tests, the sodium salts of N-(hydroxyethyl)-ethylenediaminetriacetate (HEDTA) and EDTA, in a 2:1 mole ratio, were selected as the source of the organic carbon and added to attain the concentration of organic carbon found in genuine Tank 101-SY RTW.

Because no data were found in the technical literature relevant to the response of formate to ozonation and because formate represents a significant fraction of the organic carbon present in genuine Tank 101-SY RTW, a Tank 101-SY simulant containing formate, based on the recipe given in Appendix C, was prepared for ozonation testing. For this simulant, sodium formate, rather than HEDTA and EDTA, was used as the source of the organic carbon.

A third simulant waste was prepared based on the Tank 101-SY recipe given in Appendix C. This simulant was prepared to determine if the nitrogen present in the source organics (HEDTA and EDTA) was oxidized to nitrate by ozonation. To do this, the nitrate and nitrite salts listed in the recipe cited in Appendix C (nitrate salts of sodium, chromium, calcium, iron, potassium and nickel, and sodium nitrite) were avoided in the simulant

preparation. Eliminating the metal nitrate and nitrite salts allowed possible formation of nitrate from organic amine nitrogen to be observed without interference.

4.3 EXPERIMENTAL PROCEDURES

The enclosed reactor apparatus was a dynamic system in which flow rates and gas pressures had to be carefully controlled and balanced. Experimental runs generally lasted 12 to 16 hours. The following sequence of steps was performed to initiate, conduct, and shut down an ozonation experiment in an assembled and calibrated apparatus.

1. Add the diluted simulant or genuine Tank 101-SY material to the liquid reservoir.
2. Open oxygen valves and set oxygen flow to the desired rate.
3. Switch on the peristaltic pump at the predetermined rate to begin the solution flow.
4. Switch on the motor to drive the propeller in the reactor.
5. Adjust the gas flow rate to compensate for the backpressure imposed by the solution flow.
6. Sample the initial solution/slurry (about 10 mL).
7. Switch on the ozone generator and slowly bring the generator power to the level required to achieve the desired ozone concentration at the existing gas pressure and flow. Begin timing from this point.
8. Collect solution samples (~10 mL) periodically as required (usually at 1- or 2-hour intervals).
9. Perform the following steps, in order, to shut down the apparatus: switch off the ozonator, switch off the peristaltic pump, switch off the motor to the reactor, and close the gas flow.

Operation of the open reactor design used the following sequence of steps.

1. Add diluted simulated Tank 101-SY RTW to the graduated cylinder mixing vessel.
2. Set the oxygen gas flow rate to the desired level.
3. Switch on the high shear mixer.
4. Sample the initial solution/slurry (about 10 mL).
5. Switch on both ozone generators and slowly bring the power to the levels required to achieve the desired ozone concentration at the existing gas pressure and flow. Begin timing from this point.

6. Collect solution samples (~10 mL) periodically as required.
7. Perform the following steps, in order, to shut down the apparatus: switch off the ozonators' power, switch off the mixer, and close the gas flow.

4.4 ANALYSES

Sampling for chemical analyses and other quantitative and qualitative determinations were conducted during the course of these experiments. The measurements included gas and liquid flow rates, temperatures, chemical and radionuclide concentrations, crystallographic (X-ray diffraction) analyses, and differential scanning calorimetric (DSC) analyses.

Gas flow rates were determined using standard, ball-in-tube variable area flowmeters. The peristaltic pumps' liquid flow delivery rates were calibrated using volumetric glassware and a stopwatch. Solution temperatures were followed during the ozonation test runs by thermocouples installed in the liquid reservoirs.

Sample solution/slurry pHs were determined using buffer-calibrated glass pH probes and meters. Solution pH was monitored continuously in the tests with genuine Tank 101-SY RTW. The calibrated pH probe was installed in a solution well in the liquid reservoir. Solution pH also was measured on individual samples collected during tests with simulant Tank 101-SY RTW. It was recognized, however, that solution pH is difficult to measure accurately for these high ionic strength and high pH solutions. Therefore the pH measurements were only used to monitor trends during ozonation.

Ozone concentrations in the ozonated oxygen gas produced by the Union Carbide and PCI ozone generators were determined using a PCI Model HC-12¹ ozone monitor. The ozone monitor used the characteristic ultraviolet light absorbance of ozone in a fixed path-length cell to determine ozone concentration via Beer's Law. The ultraviolet absorbance of the feed oxygen gas was used as a reference (zero) point.

Offgas samples were collected for analysis occasionally during tests with Tank 101-SY RTW simulant. Some samples were collected in flowthrough, stainless steel gas sampling vessels. Gas samples collected in this way were analyzed for gas component concentration by mass spectrometry by the Pacific Northwest Laboratory. Analysis of the feed oxygen gas used in the tests with simulants was also performed by mass spectrometry. Qualitative and semiquantitative identification of offgas ozone was determined on occasion by use of Dräger² tubes.

¹PCI Model HC-12 is a trademark of PCI, Inc., West Caldwell, New Jersey.

²Dräger is a trademark of National Dräger Inc., Pittsburgh, Pennsylvania.

COD analyses for selected Tank 101-SY RTW simulant samples were performed offsite by S-Cubed (a laboratory in the Division of Maxwell Industries, Limited, La Jolla, California). The COD is a measure of oxygen-oxidizable material available in the sample.

Most chemical and radionuclide concentration analyses were determined by the Analytical Operations of 222-S Laboratory at WHC. Metal concentration analyses (e.g., aluminum, sodium, chromium, iron, strontium, calcium, nickel, silicon, manganese, silver) were determined via inductively coupled plasma spectrometry. Inorganic anion analyses (e.g., fluoride, chloride, phosphate, sulfate, nitrate, and nitrite) were provided by an ion chromatographic technique. The organic anions of acetate, formate, and oxalate were quantified by a separate ion chromatographic technique.

Hydroxide concentrations were determined by standard acid titration. Carbonate (inorganic carbon) was determined by collecting carbon dioxide expelled and subsequently collected from acidified sample aliquots and by coulometric titration of the resulting carbonic acid. Organic carbon concentrations were determined by collection of carbon dioxide from pyrolyzed sample aliquots and a similar coulometric titration. A spectrophotometric technique was used for chromium (VI) (i.e., chromate) determinations.

Radionuclide concentration analyses were conducted for genuine Tank 101-SY RTW samples. Gamma energy analysis was used to determine cesium-137 concentration (no other radionuclides were detected in the gamma energy analysis scans). Strontium-90 was determined by a solvent extraction technique. Separate solvent extraction techniques were used to determine concentrations of americium-241 and plutonium-239, -240. Uranium was quantified chemically by time-resolved laser fluorescence.

DSC analyses were performed on the feed and product from a simulant ozonation experiment, and on the feeds and products of the experiments of the two tests run using genuine Tank 101-SY RTW. DSC is a method to determine the thermal response of a material to heating. Materials normally require outside heat to increase in temperature. When materials undergo a phase change (such as melting or evaporation), an additional amount of outside heat must be provided; these are called endothermic events. However, chemical reactions may result in heat being produced, i.e., exothermic events. The DSC analyses were used to identify the presence, temperature of initiation, and extent of endothermic and exothermic events in selected samples.

Finally, crystalline solids formed during ozonation runs were identified by X-ray diffractometry.

5.0 RESULTS AND DISCUSSION

Two types of ozonation experiments were conducted in these studies: tests with simulant Tank 101-SY RTW and tests with genuine Tank 101-SY RTW. In the experiments with simulants, both the enclosed and open high-shear reactor types were tested. All experiments with genuine Tank 101-SY RTW were conducted using the enclosed reactor design. Test descriptions, observations, and results were logged in controlled laboratory notebooks.

5.1 SCOPING TESTS WITH SIMULATED TANK 101-SY RTW

The initial ozonation tests under this project used the enclosed reactor design with simulated Tank 101-SY RTW. Only a single experimental run was conducted using the open high-shear reactor design. The initial tests with the enclosed reactor design helped establish operating conditions, determine equipment performance, and gain familiarity with the equipment before tests using genuine Tank 101-SY RTW.

Most tests used the simulant having the HEDTA and EDTA as the organic carbon source material; chemical behavior was determined by analyses of samples taken as ozonation proceeded. Tests also were conducted to determine the stability of formate to ozonation using the simulant having formate as the source organic.

5.1.1 Ozonation of Formate

Ozonation of a simulated Tank 101-SY RTW containing formate as the source of organic carbon was conducted. About 80% of the organic carbon was destroyed readily by ozonation, as shown in Figure 4. The COD analysis of the feed material and comparison with the organic carbon destruction observed showed roughly 85% use of the input ozone. Discussions of additional tests using HEDTA and EDTA as feed organics in later sections of this report explore further the behavior of formate during ozonation.

5.1.2 Effect of Gas:Liquid Ratio

The effect of gas:liquid ratio on the efficiency of ozone use was determined for the enclosed reactor by comparing the performances of two experimental ozonation runs of Tank 101-SY RTW simulant having HEDTA and EDTA as the sources of organic carbon. For both of the runs, gas flow rate was maintained at 1 L/min. In one experiment, the solution flow rate matched the gas flow rate at 1 L/min. In the second experiment, solution flow rate was half the gas flow rate at 0.5 L/min. Ozone concentration was 5.6 wt% for the 1:1 gas:liquid ratio and 7.2 wt% for the 2:1 gas:liquid ratio.

The results of the experiments are presented in Figure 5. Based on the COD of the feed materials and analyses of the residual organic carbon, ozone use was about 85% with the 1:1 ratio. The efficiency dropped significantly (to about 60%) when the gas:liquid volumetric flow ratio was raised to 2:1. These results indicate that the enclosed reactor design was near operational

Figure 4. Ozonation of Formate in Simulated Tank 101-SY RTW.
(The line labelled "Theoretical" shows expected performance based on 100% ozone use and the COD of the feed material.)

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Figure 5. Effect of Gas:Liquid Ratio on the Efficiency of Ozone Usage in the Enclosed Reactor Design. (The lines labelled "Theoretical" show expected performance based on 100% ozone usage and the COD of the feed material.)

**Effect of Gas:Liquid Flow Ratio
on TOC Destruction**

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capacity for gas/liquid mixing with the 1:1 ratio. Except for the single test with the 2:1 ratio, all experimentation using the enclosed reactor design was performed with the 1:1 volumetric ratio.

5.1.3 Ozonation Using the Open Reactor Design

An open reactor design was tested as a means to supply ozone more efficiently and rapidly to the simulated, diluted Tank 101-SY RTW test slurry and thus increase the volumetric reaction rate. As shown in Figure 6, the ozone use efficiency of the open reactor design was comparable with the enclosed reactor design in the ozonation of simulated Tank 101-SY RTW.

The open reactor design supplied the ozone to the solution at 15 times the volumetric rate of the enclosed reactor system. Gas-solution contact times in the enclosed reactor design were about 12 seconds, while contact time for the open reactor was about 0.8 seconds. These data, in conjunction with the results from the gas:liquid ratio tests reported in the previous section, indicate that for the configurations tested, the reaction kinetics were limited by equipment design (gas $\rightarrow$ solution mass transfer) and not by ozone oxidation chemistry. Comparison of the performance of reactor designs (open reactor and enclosed reactor with 1:1 and 2:1 gas:slurry ratios) showed the open design provided the most rapid and efficient introduction of ozone reactant to the simulant RTW.

5.2 CHEMICAL AND THERMAL BEHAVIOR OF SIMULANT TANK 101-SY RTW DURING OZONATION

Further modifications and improvements to the enclosed reactor apparatus and experimental technique were performed in the course of the present work. The design improvements followed the scoping studies conducted by Colby (1993). Based on these modifications, a set of operating parameters and conditions were selected to conduct detailed chemical and thermal investigations of the ozonation of both simulated and genuine Tank 101-SY RTW.

Tests were run initially using simulated Tank 101-SY RTW. By use of simulated Tank 101-SY RTW, experimental techniques could be refined for implementation on tests with genuine Tank 101-SY RTW. Furthermore, by comparison of the test results from the ozonation of simulated and genuine Tank 101-SY RTW, the suitability of the simulant to model credibly the behavior of genuine Tank 101-SY RTW (e.g., for application in nonradioactive scaleup or pilot testing) could be determined.

The selected operating parameters relevant to the baseline ozonation tests for the simulated and genuine Tank 101-SY RTW are summarized in Table 3. The chemical and thermal behaviors of simulated Tank 101-SY RTW during ozonation at the reference conditions described in Table 3 are presented in the following sections. The progress of the chemical reactions was followed by periodic sampling and chemical and thermal analyses of the samples. Measurements of pH and temperature also were performed. The analytical data derived from the sampling and measurements are presented in Appendix D.

Figure 6. Comparison of Ozone Usage in Enclosed and Open Reactor Designs.

Table 3. Reference Conditions for Ozonation Tests of Simulant and Genuine 101-SY RTW in the Enclosed High-Shear Reactor.

Variable	Condition
Ozone generator	PCI Model GS-1 ^a
Ozone concentration	~7.4 weight percent
Gas flow rate	1,000 mL/min. (~0.149 g O ₃ /min. at ~1.6 atmospheres)
Slurry flow rate	1,000 mL/min.
Initial temperature	Ambient room (23 to 25 °C)
Waste:diluent-water volume ratio	1:3
Solution mixture volume	705 mL (simulant) 780 mL (genuine)
Test duration	~16 hours

^aPCI Model GS-1 is a trademark of PCI, Inc., West Caldwell, New Jersey.

5.2.1 Product of Ozonation of Amine Nitrogen

Experiments were performed to determine the product of oxidation of the nitrogen present in HEDTA and EDTA. The organic nitrogens are present in the -3 oxidation state (i.e., as amines) and thus might be susceptible to oxidation by ozone. Nitrogen gas and nitrate were considered to be the most probable products of oxidation of the amine nitrogen with oxides of nitrogen and nitrous oxide also possible gaseous products. Dissolved nitrite, hydrazine, hydroxylamine, and ammonia would be readily oxidized by ozone and not be likely products.

Analyses of solution samples from ozonation of simulated Tank 101-SY RTW prepared using no nitrate or nitrite were done to determine if nitrate formed from oxidation of the amine nitrogen. Mass spectrometric analyses of offgas samples from ozonation of simulated Tank 101-SY RTW were used to determine if nitrogen, oxides of nitrogen, or nitrous oxide were produced during ozonation.

5.2.1.1 Results of Solution Analyses. Ozonation of a Tank 101-SY RTW simulant containing no nitrate or nitrite was conducted. The simulant used HEDTA and EDTA as the source of organic carbon. Thus, the only source of nitrogen in the system was the amine nitrogen in the HEDTA/EDTA.

Ozonation of the diluted simulant yielded measurable concentrations of nitrate in solution. The quantity of nitrate observed was 0.18 moles per mole of organic carbon lost to oxidation. Given the 1:5 nitrogen:carbon mole ratio in HEDTA and EDTA, this concentration of nitrate corresponded to 90% oxidation of amine nitrogen to nitrate. Because the only source of nitrogen in the

waste simulant was the HEDTA and EDTA, nitrate appears to be the primary product of ozonation of the organic nitrogen.

5.2.1.2 Results of Offgas Analyses. Mass spectrometric analyses of offgases taken at various times during the ozonation of the Tank 101-SY RTW simulant containing HEDTA/EDTA showed the expected high concentration of oxygen because of oxygen being the feed gas to the ozonator. As shown in Table 4, trace quantities of hydrogen, carbon monoxide, nitrogen, and, at later stages of the reaction, carbon dioxide also were found in the offgas (high resolution mass spectrometry could distinguish the peaks for nitrogen and carbon monoxide occurring at mass 28). Significantly, nitrous oxide, oxides of nitrogen (such as NO_2 or NO), ammonia, and volatile organic compounds (e.g., methane) were not detected in any offgas sample.

Table 4. Offgas Analyses from Ozonation of Tank 101-SY RTW Simulant.

Percent oxidized	$[\text{OH}^-]$, M	$[\text{CO}]$, mole%	$[\text{CO}_2]$, mole%	$[\text{H}_2]$, mole%	$[\text{N}_2]$, mole%
0, (Initial feed gas)	0.61	<0.01	0.340	<0.001	<0.01
6.7	0.57	0.020	<0.001	0.008	<0.01
33.6	0.35	0.030	<0.001	0.011	0.020
52.4	0.20	0.034	<0.001	0.007	0.017
66.2	0.08	<0.01	0.009	0.004	0.020
78.4	0.11	<0.01	0.155	0.001	0.058
86.4	0.09	<0.01	0.314	<0.001	0.033

NOTE: Balance of gas is oxygen. Less than 0.001 mole% nitrous oxide and oxides of nitrogen were found in the offgas. Ammonia was estimated to be <0.001 mole% in all samples. Organic species (methane, ethane, other hydrocarbons) were <0.001 mole% for all samples.

The quantity of carbon lost from solution as carbon monoxide amounted to about 1% of the initial organic carbon. The carbon monoxide was detected in the period of the ozonation when the organic oxidation rate was greatest.

The gas analyses showed carbon dioxide escaping the solution at later stages of the reaction where hydroxide concentrations were lower (diminished by the prior absorption of the carbon dioxide oxidation product from organic carbon). The expected carbon dioxide scrubbing efficiencies of the alkaline simulant RTW therefore were reduced at later stages of the reaction.

As much as 0.011% hydrogen concentration was observed in the offgas. This concentration of hydrogen in the offgas is low and well below the flammability limit in oxygen. The presence of hydrogen in the offgas, however, may suggest the presence of hydrogen radicals in the ozonation

reactions. As was the case for carbon monoxide, hydrogen concentrations were highest at initial stages of the test when oxidation rates were highest.

Nitrogen comprised up to 0.058% concentration in the offgas. The integrated quantity of nitrogen evolved from solution as nitrogen gas amounts to about 12% of the nitrogen present as amine in the original organic species, HEDTA and EDTA. Thus, strong evidence exists that limited oxidation of amine to form nitrogen gas occurred. The production of nitrogen gas from ozone-influenced reactions with nitrate or nitrite are unlikely because ozone is a strong oxidant and nitrate or nitrite must be chemically reduced to form nitrogen. However, given the observed formation of hydrogen (a chemically reduced species) during ozonation, the production of nitrogen gas from nitrate or nitrite cannot be absolutely dismissed.

The technical literature were ambiguous regarding the oxidation product from ozonation of amine nitrogen. Lutton et al. (1980) found nitrogen in the offgas from their ozonation tests on genuine RTW. However, the nitrogen may have been air contamination, given the observation of significant argon concentrations in the relevant offgas samples. Aloy et al. (1989) found nitrate in the pH 8 to 10 ozonation of EDTA. The present studies indicate nitrate to be the principal product (~90%) from ozone oxidation of amine nitrogen and nitrogen gas to be the minor product (~10%).

5.2.2 Nitrite Oxidation During Ozonation

The Hanford Site RTW contains significant nitrite ion concentrations caused by radiolysis of nitrate and by intentional nitrite additions to inhibit corrosion of the mild steel tank liner. In earlier studies of ozonation of genuine and simulated Hanford Site RTW (e.g., Lutton et al. 1980; Winters 1981), nitrite was found to be oxidized readily by ozone to form nitrate.

The ready oxidation of nitrite by ozone was confirmed in the present studies. As shown in Figure 7, nitrite concentration decreased monotonically to near zero in 6 to 8 hours. The reaction occurred stoichiometrically with 1 mole of nitrate forming per mole of nitrite lost:

5.2.3 Organic Oxidation During Ozonation

The oxidation of organic carbon (initially present as HEDTA and EDTA) in simulated Tank 101-SY RTW during ozonation was followed by chemical analyses of the TOC and total inorganic carbon (i.e., carbonate) concentrations. As shown in Figure 8, the decrease of organic carbon concentration matched, stoichiometrically, a corresponding 1:1 mole increase in inorganic carbon concentration. The destruction rate of TOC was low initially but increased to

Figure 7. Oxidation of Nitrite to Nitrate by Ozone.

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Figure 8. Oxidation of Organic Carbon by Ozone to Form Inorganic Carbon.

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its maximum rate between 6 and 8 hours' ozonation. Therefore, the maximum rate of TOC destruction occurred when nitrite had been fully oxidized to nitrate. The organic oxidation rate then slowed and was essentially zero at 12 hours.

An ion chromatographic technique to identify and quantify small organic acid anions (i.e., acetate, formate, and oxalate) was implemented during the course of these studies. With this technique, the in-growth and subsequent decomposition of acetate and formate during the ozonation of the source HEDTA and EDTA could be followed (Figure 9).

Acetate and formate in-growth was rapid during the first 4 hours of reaction when organic carbon conversion to inorganic carbon was relatively slow. Because the longest carbon chain in HEDTA and EDTA is two carbons long, the acetate and formate in-growth indicates that ozone initially attacked by cleaving one- and two-carbon segments from the source organics (probably at the N-C bonds) and not by oxidation of the source organics' terminal carbons. Formate appeared to be more readily oxidized than acetate but both were essentially destroyed by ozonation.

While acetate and formate were found to be metastable intermediates during ozonation, oxalate was found to grow in, but then be relatively stable to further degradation even during continued ozonation. Oxalate concentration increased slowly during ozonation and increased most rapidly as acetate concentration decreased. This implied that oxalate formed from acetate precursor. The observation of oxalate as a refractory residue from ozonation confirms the similar observations of Galutkina et al. (1977) and Colby (1993).

The organic carbon concentration remaining at the end of the experimental run was about 0.63 g/L of carbon. Of this, 0.44 g/L could be attributed to oxalate and about 0.05 g/L could be ascribed to acetate. The residual oxalate (and, to a lesser extent, acetate) thus represented about 10% of the feed organic carbon concentration; i.e., about 90% of the organic carbon was fully oxidized to carbonate by ozonation.

The finding that the organic residue remaining from ozonation was oxalate is significant. In tests with simulated Tank 101-SY waste having oxalate as the source of organic carbon, oxalate has been shown to be relatively unreactive (compared with HEDTA and glycolate) and thus not participate in gas generation reactions.

5.2.4 The Effect of Organic Oxidation on Hydroxide Concentration

Hydroxide concentration decreased continuously in the initial 6 to 8 hours of reaction and remained unchanged from about 10 to 14 hours (Figure 10). The step increase of hydroxide concentration occurring after 14 hours was due to the intentional addition of sodium hydroxide. Sodium hydroxide was added at the final hour of the test to determine if aluminum hydroxide solids precipitated during the run could be redissolved.

Figure 9. Ingrowth of the Organic Acid Anions (Acetate, Formate, and Oxalate) and Decomposition of Acetate and Formate.

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Figure 10. Hydroxide Concentration Decrease During Oxidation.
(Step increase in concentration after 14 hours because of intentional addition of sodium hydroxide.)

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The observed consumption of hydroxide ion during the ozone oxidation of organic carbon (EDTA, $C_{10}H_{12}N_2O_8^{4-}$, is used as an example in this case) results from the following three reactions:

- Formation of oxide (hydroxide) oxygen from the reduction of one oxygen atom per ozone molecule

- Consumption of hydroxide by the oxidation of organic carbon and nitrogen in the EDTA

- Acid-base neutralization of carbon dioxide (anhydrous carbonic acid) by hydroxide

Combining and chemically balancing the above three reactions yields the net reaction:

In the experiments, however, about 10% of the original organic carbon remained as oxalate after ozonation, while about 10% of the amine nitrogen evolved as nitrogen gas (the rest oxidized to nitrate). The experiments also used both HEDTA ($C_{10}H_{15}N_2O_7^{3-}$) and EDTA, in a 2:1 mole ratio, as the source of the organics.

The observations noted in ozonation of the organics in simulated Tank 101-SY RTW may be summarized by the following balanced reaction (large coefficients were required to yield integral values):

5.2.5 Aluminum Concentration Changes During Ozonation

While hydroxide concentration decreased monotonically during the first 6 hours of ozonation, the concentration of soluble aluminum (present in the solution as the aluminate ion) remained unchanged (Figure 11). However, between 6 and 8 hours, when the hydroxide concentration decreased only

Figure 11. Decrease of Aluminum Solution Concentration During Ozonation. (The step increase in aluminum concentration following 14 hours is due to intentional addition of sodium hydroxide.)

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slightly, the aluminum concentration decreased rapidly. Aluminum concentration then decreased more slowly and was essentially unchanged between 12 and 14 hours. After addition of sodium hydroxide (at 14 hours), the aluminum concentration increased sharply.

At the time aluminum concentration was observed to fall rapidly, precipitation of the aluminum hydroxide mineral bayerite occurred. Bayerite was determined by X-ray diffraction analysis of the solids collected from the reservoir. The following chemical reaction summarizes the observed precipitation reaction:

The aluminum hydroxide mineral usually found precipitating from solutions of sodium hydroxide and sodium aluminate is gibbsite (Wefers and Misra 1987). The observation of bayerite in the present studies is understood in light of the findings of Fricke and Wullhorst (1932) who showed neutralization of aluminate solutions by carbon dioxide gas will precipitate bayerite. Because carbon dioxide neutralization of aluminate solution is essentially what occurred during the ozonation reactions, bayerite precipitation could be expected. In contrast with the present findings, Lutton et al. (1980) reported gibbsite precipitation following ozonation of genuine RTW.

The quantity of sodium hydroxide added after 14 hours of ozonation was sufficient to raise the hydroxide concentration by 0.50 M. The increase in hydroxide concentration noted after the addition was about 0.12 M (about 2 g/L of hydroxide; see Figure 10). The increase in aluminum solution concentration after the sodium hydroxide addition was about 0.28 M (about 7.5 g/L of aluminum; see Figure 11). Thus, of the 0.50 M hydroxide added, 0.40 (= 0.12+0.28) M was accounted for in the increases in hydroxide and aluminate solution concentrations.

The precipitation of aluminum hydroxide and its redissolution by addition of hydroxide showed that aluminate acted as a source of hydroxide in the ozone oxidations of organic carbon. In the absence of aluminate, the hydroxide concentration present in the simulated Tank 101-SY RTW would have been insufficient to scrub the carbon dioxide product from the offgas as efficiently as was noted. Furthermore, the solution pH would have decreased to neutral levels because of the introduction of carbon dioxide and its production of carbonic acid ($\text{pK}_a = 6.4$). The resulting decrease in pH may have reduced reaction rates, as noted earlier by Winters (1981). The hydroxide material balance is discussed in a later section of this report (Section 5.2.9).

5.2.6 Solution pH and Temperature During Ozonation

The solution pH found during the course of ozonation (Figure 12) reflected the hydroxide and aluminum concentration decreases and the buffering of the formed carbonate. The temperature changes also noted in Figure 12 indicated that the reactions caused by ozonation were exothermic (i.e., produced heat). No experimental effort was made to insulate the apparatus nor

Figure 12. Temperature and pH of Solution During Ozonation.

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to determine the heat output for the ozonation reactions. Such measurements would have been difficult in any event because of the large and continuous flow of gas through the solution, causing significant heat loss via evaporation of water and convection.

Though the thermal output was not determined, the temperature changes shown in Figure 12 indicate periods of heat flow. In the first hour, a 5-°C temperature increase occurred. This increase most likely was due to mechanical heating by the peristaltic pump and enclosed reactor mixer. Between 4 and 8 hours, a further 3-°C temperature increase occurred. This increase probably was related to the acid-base neutralization of carbon dioxide by hydroxide to form carbonate because carbonate production was most rapid during this period.

Between 8 and 10 hours, the solution cooled about 4 °C and remained unchanged to 14 hours. The temperature decrease probably reflected the absence of additional reaction heat. Note that the temperature from 8 to 10 hours was about 1 1/2 °C lower than that observed from 1 to 4 hours. The generally higher temperatures in the initial few hours suggest that the ozonation reactions to form nitrate and/or break down the source organic molecules also were exothermic.

Finally, the step 1 1/2-°C temperature increase observed after the introduction of sodium hydroxide at 14 hours was due to the heat of dissolution and reaction of the sodium hydroxide with aluminum hydroxide.

5.2.7 Oxidative Dissolution of Chromium (III) Hydroxide

Chromium represented about 0.4 wt% of Tank 101-SY RTW as reported by Herting et al. (1992). Of this, <1% was present in the hexavalent oxidation state [i.e., as Cr(VI)], implying >99% was present in the (III) state. Chromium (III) is slightly soluble in alkaline solution forming chromium (III) hydroxide precipitate and $\text{Cr}(\text{OH})_4^-$ dissolved species (Rai et al. 1987). The simulant Tank 101-SY RTW was prepared using chromium (III), and the dark green chromium (III) hydroxide precipitate was observed.

During ozonation of the diluted simulant Tank 101-SY RTW, chromium concentrations in solution were observed to increase from <0.05 g/L [i.e., most of the chromium was still present as $\text{Cr}(\text{OH})_3$ (pt)] to about 1.5 g/L (i.e., almost completely dissolved). As shown in Figure 13, the chromium dissolved by being oxidized to chromium (VI). Chromium (VI) is present in alkaline solution as the chromate ion (CrO_4^{2-}).

The dissolution began after about 6 hours of ozonation and continued to the end of the test at 15 hours. In this process, the solution color changed from a pale green caused by suspended $\text{Cr}(\text{OH})_3$ solids, to a brilliant yellow caused by the chromate ion (CrO_4^{2-}). At the same time, the slurry solids changed from dark green [$\text{Cr}(\text{OH})_3$] to near white [$\alpha\text{-Al}(\text{OH})_3$].

Figure 13. Ozone Oxidation of Slightly Soluble Chromium (III) Hydroxide to Form Soluble Chromate.

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The ozone oxidation of $\text{Cr}(\text{OH})_3$ to form chromate is represented by the following balanced reaction:

The oxidation of $\text{Cr}(\text{OH})_3$ was found to be not as rapid as the oxidations of nitrite and the source organics. Oxidation of chromium only began after about 6 hours of ozonation, i.e., after most of the nitrite and organics (except oxalate) were completely oxidized. From that point, in spite of excess ozone, the chromium required almost 9 hours to be fully oxidized. If the ozonation reaction had been efficient and rapid, chromium oxidation should have required only about 15 minutes [ozone was supplied at ~0.37 equivalents per hour vs. ~0.09 equivalents required to oxidize the chromium (III) present completely to chromate].

5.2.8 Precipitation of Calcium and Nickel

Calcium and nickel represent about 0.023 and 0.015 wt%, respectively, of the simulated Tank 101-SY RTW. Both metal ions (present as Ca^{2+} and Ni^{2+}) were soluble initially in the diluted, simulated Tank 101-SY RTW. Following 8 hours of ozonation, however, the solution concentrations of both metal ions were below detection limits (Figure 14).

The drop in solution concentration of calcium and nickel is due to the destruction of the complexing agents. The complexants thus acted in their role as sequestering agents, keeping metal ions in solution that ordinarily would have precipitated. With the destruction of the HEDTA and EDTA, these metal ions became supersaturated with respect to their hydroxides, carbonates, phosphates, or perhaps oxalates and precipitated from solution.

5.2.9 Hydroxide Material Balance

The overall reaction of ozone with simulated Tank 101-SY RTW can be summarized, as shown below, by a balanced chemical reaction with nitrate and nitrogen gas as the oxidation products of amine nitrogen. The reactants being oxidized [nitrite, HEDTA, EDTA, and chromium (III) hydroxide] are given in the proportions used in the simulant Tank 101-SY RTW. The sources of alkali given in the balanced reaction include both hydroxide and aluminate ions in proportion to the amount of hydroxide and soluble aluminum removed from solution during ozonation. The following reaction also shows both oxalate and carbonate as the carbonaceous products of oxidation of HEDTA and EDTA.

According to the above reaction stoichiometry, the hypothetical mole ratio of alkali consumed to source organic carbon is 1.88 [564 moles of alkali

Figure 14. Solution Concentrations of Calcium and Nickel During Ozonation.

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as hydroxide ion plus aluminate ion per 300 moles of organic carbon]. Two alkali:organic carbon mole ratios were measured chemically at the conclusion of the ozonation test. One measurement was just before addition of sodium hydroxide 14 hours into the run; the second measurement was after the sodium hydroxide addition. The alkali:organic ratio found before the addition of the sodium hydroxide was 1.78; after the sodium hydroxide addition, the ratio was 1.97. These ratios, which average to 1.88, are consistent with the 1.88 ratio predicted from the balanced reaction.

5.2.10 Ozone Chemical Equivalence Material Balance

Ozone use and stoichiometry were determined by comparing the chemical equivalents of ozone supplied to the reactor with the sum of the chemical equivalents of nitrite, organic carbon, and chromium (III) being oxidized. That comparison is presented in Figure 15. The ozone reaction assumed operant in the present studies involved the reduction of one atom of oxygen per mole of ozone, i.e.,

Most oxidation reactions by ozone proceed by this stoichiometry. As shown in Figure 15, the observed reaction stoichiometry is consistent with the reduction of one oxygen atom per ozone molecule. Figure 15 also shows the abrupt decrease in ozone use efficiency at about three equivalents of ozone supplied (corresponding to about 8 hours of ozonation) when only chromium (III) and oxalate remained to be oxidized.

5.2.11 Thermal Analyses

DSC analyses were run on samples of simulated Tank 101-SY RTW both before and after ozonation. The analytical results showed that the broad exothermic event presumably associated with the decomposition of the organic carbon in the temperature range 200 to 450 °C was eliminated by ozonation. Organic carbon represented about 2.3 wt% of the dry weight of the simulant before ozonation, and about 0.23 wt% of the simulant after ozonation. The exotherm produced 77 calories/g of diluted Tank 101-SY RTW simulant; the ozonated simulant produced no exotherm. The DSC results are presented in detail in Appendix E.

5.3 CHEMICAL, RADIONUCLIDE, AND THERMAL BEHAVIOR OF GENUINE TANK 101-SY RTW DURING OZONATION

Ozonation tests were conducted using the blended composite of genuine Tank 101-SY RTW at the operational parameters described in Table 3. Two separate tests were run under experimentally identical conditions and yielded similar analytical results. Though results for both tests were similar, generally only results of the second test are discussed in the following sections of this report.

Figure 15. Ozone Usage in the Oxidation of Nitrite to Form Nitrate;
Organic Carbon (Initially Present as HEDTA and EDTA) to Form
Carbonate, Oxalate, Nitrogen, and Nitrate; and
Chromium (III) to Form Chromate.

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Where appropriate, the behaviors of chemical elements and species are discussed and compared with the behaviors of chemically similar radionuclides. The solution concentrations of the radionuclides, as well as a number of trace elements not present in the simulant Tank 101-SY RTW, yielded additional insight into the chemistry of ozonation. The sampling and measurement data taken from the two ozonation tests on genuine Tank 101-SY RTW are presented in Appendix F.

5.3.1 Nitrite Oxidation During Ozonation

The one-to-one (mole) reaction of nitrite to form nitrate observed in the simulant Tank 101-SY RTW was observed in the case of the genuine Tank 101-SY RTW. The experimental data for nitrite and nitrate concentrations given in Figure 16 show that 6 to 8 hours of ozonation were required to complete the oxidation of nitrite. This also was the case for the test with simulants.

5.3.2 Organic Oxidation During Ozonation

The identities and concentrations of organic species found in genuine Tank 101-SY RTW are given in Table 2. In comparison with the organic carbon surrogates (HEDTA and EDTA) used in the simulant Tank 101-SY RTW material, the organic species present in the genuine Tank 101-SY RTW material were more oxidized (i.e., the organic carbon had higher oxidation state). Thus, the genuine RTW material should have been required less ozone than the simulant to attain complete oxidation of a given amount of organic carbon.

As was true for the tests with simulant Tank 101-SY RTW, the decrease of organic carbon concentration observed in ozonation was matched by a corresponding 1:1 stoichiometric mole increase in inorganic carbon (carbonate) concentration (Figure 17).

The maximum rate of organic destruction again was observed between 6 and 8 hours when nitrite oxidation was essentially complete. The rate then slowed with low rates observed after about 12 hours.

Significant concentrations of acetate, formate, and oxalate in the genuine Tank 101-SY RTW were determined by ion chromatographic techniques. As was the case for the test with simulant Tank 101-SY RTW, acetate and formate were found to increase in concentration, then decrease and thus be intermediates in the destruction of the more complex organic species. Oxalate again seemed to increase most during periods (6 to 10 hours) when acetate concentrations decreased and again was found to be refractory to further oxidation. The behaviors of these minor organic acid anions are shown in Figure 18.

The organic carbon remaining at the end of the ozonation run was 0.87 g/L with about 0.53 g/L caused by the residual oxalate. Whereas about 90% of the organic carbon was destroyed during ozonation of the simulant Tank 101-SY RTW, only about 80% of the original organic carbon was destroyed by ozonation of the genuine Tank 101-SY RTW. The lower fraction of organic carbon destroyed may be attributed to the relatively higher concentrations of refractory organics (i.e., oxalate) in the genuine RTW. For the replicate ozonation test

Figure 16. Oxidation of Nitrite to Nitrate
in Genuine Tank 101-SY RTW.

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Figure 17. Oxidation of Organic Carbon By Ozone to Form Inorganic Carbon in Genuine Tank 101-SY RTW.

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Figure 18. Presence and In-growth of the Organic Acid Anions (Acetate, Formate, and Oxalate) and the Decomposition of Acetate and Formate in Genuine Tank 101-SY RTW.

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of genuine Tank 101-SY RTW, residual organic carbon was 0.90 g/L of which 0.44 g/L were oxalate. Again, about 80% of the source organic carbon was destroyed.

The difference between TOC and the oxalate concentrations in the ozonated residue suggests the presence of another refractory organic species (i.e., similar to oxalate in its resistance to ozonation). However, the identity of the possible refractory organic was neither determined nor its presence confirmed by another technique.

5.3.3 Hydroxide Concentration Changes During Ozonation

As was the case for the tests with simulant, hydroxide concentration decreased during the initial 6 to 8 hours of ozonation of genuine Tank 101-SY RTW. The hydroxide concentration then decreased less rapidly and was essentially steady between 12 and 16 hours. The hydroxide concentration behavior with time is shown in Figure 19.

5.3.4 Aluminum and Silicon Concentration Changes During Ozonation

Aluminum concentrations were found to decrease during the period of 4 to 12 hours of reaction time (Figure 20). Before and after this period, aluminum concentrations were relatively static. This behavior was similar to that observed with the simulant test, wherein aluminum concentration decreased between 6 and 12 hours.

Although the decrease in aluminum concentration for the test with the genuine Tank 101-SY RTW material was not as marked as that found for simulant material, the data indicated that dissolved aluminum (as aluminate) again acted as a source of hydroxide for the ozonation reactions. In addition, white solids, presumably because of bayerite, appeared in the residue following ozonation.

Also plotted in Figure 20 is the concentration of silicon. Although the silicon was present at only about 1% of the aluminum concentration, its parallel concentration decrease with that of aluminum suggests that silicon coprecipitated with aluminum.

5.3.5 Solution pH and Temperature During Ozonation

The solution pH and temperature changes during ozonation of the genuine Tank 101-SY RTW matched the behavior observed for the simulant. As before, pH decreased during the first 12 hours of ozonation, reflecting the consumption of hydroxide ion. The temperature and pH plots are presented in Figure 21.

Temperature increased during the first hour of reaction, presumably because of mechanical heating from the peristaltic and mixing pumps. As was the case for the test with simulated RTW, temperature increase again was noted

Figure 19. Hydroxide Concentration Decrease During Ozonation of Genuine Tank 101-SY RTW.

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Figure 20. Decrease of Aluminum Solution Concentration During Ozonation of Genuine Tank 101-SY RTW. (The silicon solution concentration decrease, also shown, follows the aluminum concentration decrease [but at about 100-fold lower concentrations].)

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Figure 21. Temperature and pH of Solution During Ozonation of Genuine Tank 101-SY RTW.

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about 8 hours into the run (when organic carbon concentration decrease and inorganic carbon increase were greatest) because of the acid-base neutralization of carbon dioxide to form carbonate.

The temperature then decreased and remained constant at a level about 2 °C lower than it was before the increase at 8 hours. The higher temperature in the first half of the ozonation run again suggests that the ozonation reactions to form nitrate and/or break down the source organics were exothermic.

5.3.6 Oxidative Dissolution of Chromium (III) Hydroxide and Plutonium

The oxidative dissolution of chromium (III) hydroxide observed in the ozonation of simulant Tank 101-SY RTW occurred also in the ozonation of the genuine material. Again, the dissolution of chromium to form the soluble yellow chromate ion could be readily observed as could the disappearance of the dark green chromium (III) hydroxide solids. The solution concentrations of total chromium and chromium (VI) (i.e., chromate), plotted in Figure 22, were identical throughout the ozonation. Also presented in Figure 22 are the observed concentrations of soluble plutonium.

As was the case for the simulant material, chromium concentrations did not increase significantly until the nitrite and most of the organic carbon was oxidized. Again, chromium oxidation was not as rapid as the supply rate of ozone.

Plutonium likely existed in the alkaline Tank 101-SY RTW as the plutonium (IV) hydrous oxide. Ozonation of plutonium-bearing suspensions has been shown to produce anionic species in the (VII) oxidation state (Peretrukhin and Spitsyn 1982). Production of the (VII) state is doubtful in this case because higher hydroxide concentrations are required. Oxidation to the (V) or (VI) state of plutonium, however, is plausible and would explain the dissolution of plutonium by ozonation because plutonium in these oxidation states in alkaline solution also exist as soluble anionic hydroxide-complexed species (Delegard 1987; Tananaev 1989). Plutonium is more soluble in the (V) and (VI) oxidation states than it is in the (III or IV) state.

5.3.7 Precipitation of Calcium, Nickel, and Strontium

Calcium, nickel, and strontium are present in low concentrations in the genuine Tank 101-SY RTW and are all divalent metal ions (i.e., of the form M^{2+}). Despite high concentrations of hydroxide, all of these metals were found to be soluble in the initial diluted Tank 101-SY solution because they were readily complexed by the chelating agents (e.g., EDTA) present. Calcium and nickel were shown to be soluble in the simulant Tank 101-SY material in the presence of the complexants HEDTA and EDTA. Similarly, enhancement of strontium solubility by the chelating agents HEDTA and EDTA in alkaline simulated Hanford Site RTW has been demonstrated (Delegard and Gallagher 1983). With ozonation and the destruction of the chelating agents, however, all three precipitated from solution as shown in Figures 23 and 24.

Figure 22. Ozone Oxidation of Slightly Soluble Chromium (III) Hydroxide to Form Chromate and the Parallel Dissolution of Plutonium in Genuine Tank 101-SY RTW.

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Figure 23. Solution Concentrations of Calcium and Nickel
During Ozonation of Genuine Tank 101-SY RTW.

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Figure 24. Solution Concentrations of Strontium and Strontium-90 During Ozonation of Genuine Tank 101-SY RTW.

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The behaviors of calcium and nickel matched the behaviors noted for these elements in the test with the simulant material. Calcium and nickel concentrations fell below detection limit levels after 8 to 10 hours of ozonation (see Figure 23). As shown in Figure 24, both total chemical strontium as well as radioactive strontium-90 concentrations decreased monotonically with ozonation and were below detection limits (i.e., >99% precipitated) after 8 hours.

5.3.8 Precipitation of Americium

Americium presumably was present in the (III) oxidation state in the genuine Tank 101-SY RTW and, like strontium, has been shown to have markedly higher solubility in simulated RTW containing complexants (Delegard and Gallagher 1983). Like strontium, americium was observed to precipitate with ozonation (Figure 25). As was found for strontium, calcium, and nickel, americium concentrations decreased to less than the detection limit after 8 hours of ozonation.

Americium has higher oxidation states [i.e., (V) and (VI)], which are more soluble in alkaline solution than the (III) or (IV) states. The higher oxidation states have been obtained electrochemically and with strong oxidants (Peretrukhin and Spitsyn 1982). However, the potentials for oxidation of americium to the (V) and (VI) states are significantly higher than the corresponding transitions of plutonium. Americium, if it were oxidized at all, apparently did not proceed beyond the relatively insoluble (IV) state during ozonation.

5.3.9 Solubility Behavior of Iron, Manganese, and Silver and the Oxidative Potential of the Ozonated Solution

A number of elements present in low concentrations in genuine Tank 101-SY RTW were not included in the simulant Tank 101-SY RTW prepared for this study. Several of these trace components have more than one oxidation state in solution (i.e., they are redox [reduction-oxidation] active). Furthermore, of the two or more oxidation states, one of the oxidation states is more soluble. The redox conditions extant in the solutions during ozonation therefore can be inferred by the solubility behaviors of the redox-active elements.

The ozone-driven oxidative dissolutions of chromium and plutonium, discussed in Section 5.3.6, give some indication of the oxidation potential of ozone. The concentrations of the redox-active elements iron, manganese, and silver as a function of ozonation time, shown in Figure 26, yield further information on the oxidative potential reached.

Color changes caused by the appearance or disappearance of chromophores associated with a particular oxidized or reduced species also indicate redox transitions qualitatively. The appearance of chromate's yellow color in solution is one such indication. During approximately the last 2 hours of ozonation, the genuine Tank 101-SY RTW solution color changed from the

Figure 25. Solution Concentrations of Americium During Ozonation of Genuine Tank 101-SY RTW.

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Figure 26. Concentrations of Iron, Manganese, and Silver
During Ozonation of Genuine Tank 101-SY RTW.

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brilliant yellow, indicative of chromate, to a root beer or topaz color. In a matter of hours after cessation of contact with ozone, however, the solution color reverted to yellow and the topaz color disappeared.

Figure 26 shows that the concentration of silver dropped sharply at 8 hours of ozonation. The drop could indicate the transition from relatively soluble argentous ion (Ag^+) to the less-soluble argentic ion (Ag^{2+}) precipitating as its oxide. Manganese was observed to increase in concentration over the last 2 hours of ozonation. This increase corresponded to the appearance of the topaz color in solution and suggested the possible presence of the green manganate ion (MnO_4^{2-}) from oxidation of relatively insoluble hydrated manganese dioxide [$\text{MnO}_2 \cdot x\text{H}_2\text{O}$ (pt)].

Finally, iron concentrations were found to trend slowly downward with time of ozonation but have no rapid or pronounced increase or decrease. Iron was present in the (III) oxidation state and primarily as a suspension of ferric hydroxide [$\text{Fe}(\text{OH})_3$ (pt)]. The absence of any increase in iron solution concentration indicated that the ozone was not sufficiently powerful to oxidize the iron to the soluble ferrate ion (FeO_4^{2-}). Instead, it appeared that iron may have precipitated slightly with time, perhaps carried by the bayerite precipitate.

The solubility and redox observations may be assessed to determine the oxidation potential of the ozonated solution, especially at the end of the ozonation runs when nitrite and organic carbon oxidations were essentially complete. The oxidation potentials of the redox-active elements are summarized in Table 5.

The dissolution/precipitation behaviors of chromium, manganese, iron, silver, plutonium, and americium and the redox potential data of Table 5 show that the effective potential of the final ozonated solution was between about 0.57 and 0.71 volts. The disappearance of the topaz color (presumed to be caused by manganate) also indicates that species with higher solution potentials may be unstable to reduction (e.g., by hydroxide) with time.

Generally, as seen in the oxidation reactions given in Table 5, higher hydroxide concentrations favor oxidation. This implies that ozonation at higher hydroxide concentrations may yield further or improved (oxidative) dissolution of oxides/hydroxides of iron, manganese, americium, or plutonium.

5.3.10 Cesium Behavior

Cesium concentrations, reflected in cesium-137 measurements made by gamma energy analyses, were not affected by ozonation. Because cesium is present in solution as a monovalent cation (Cs^+), like Na^+ , it should not be complexed by organic complexants nor oxidized. Hence, as observed, ozonation should not have affected its concentration.

Table 5. Oxidation Potentials of Redox-Active Elements in 1 M Hydroxide (Bratsch 1989; Peretrukhin and Spitsyn 1982).

Element	Oxidation half reaction	Potential (volts)
Chromium	$\text{Cr(OH)}_3 \text{ (pt)} + 5 \text{ OH}^- \rightarrow \text{CrO}_4^{2-} + 4 \text{ H}_2\text{O} + 3 \text{ e}^-$	-0.12
Manganese	$\text{MnO}_2 \text{ (pt)} + 4 \text{ OH}^- \rightarrow \text{MnO}_4^{2-} + 2 \text{ H}_2\text{O} + 2 \text{ e}^-$	0.51
Iron	$\text{Fe(OH)}_3 \text{ (pt)} + 5 \text{ OH}^- \rightarrow \text{FeO}_4^{2-} + 4 \text{ H}_2\text{O} + 3 \text{ e}^-$	0.71
Silver	$\text{Ag}_2\text{O (c)} + 2 \text{ OH}^- \rightarrow \text{Ag}_2\text{O}_2 \text{ (c)} + \text{H}_2\text{O} + 2 \text{ e}^-$	0.57
Plutonium	$\text{PuO}_2 \cdot x\text{H}_2\text{O (s)} + 4 \text{ OH}^- \rightarrow \text{PuO}_2(\text{OH})_4^{3-} + x \text{ H}_2\text{O} + \text{e}^-$	-0.72
Plutonium	$\text{PuO}_2(\text{OH})_4^{3-} \rightarrow \text{PuO}_2(\text{OH})_4^{2-} + \text{e}^-$	0.24
Plutonium	$\text{PuO}_2(\text{OH})_4^{2-} + 2 \text{ OH}^- \rightarrow \text{PuO}_4(\text{OH})_2^{3-} + 2 \text{ H}_2\text{O} + \text{e}^-$	0.85
Americium	$\text{Am(OH)}_3 \text{ (s)} + \text{OH}^- \rightarrow \text{AmO}_2 \text{ (s)} + 2 \text{ H}_2\text{O} + \text{e}^-$	0.27
Americium	$\text{AmO}_2 \text{ (s)} + 4 \text{ OH}^- \rightarrow \text{AmO}_2(\text{OH})_4^{3-} + \text{e}^-$	0.40
Americium	$\text{AmO}_2(\text{OH})_4^{3-} \rightarrow \text{AmO}_2(\text{OH})_4^{2-} + \text{e}^-$	0.68
Oxygen	$4 \text{ OH}^- \rightarrow \text{O}_2 \text{ (g)} + 2 \text{ H}_2\text{O} + 4 \text{ e}^-$	0.401

5.3.11 Hydroxide and Ozone Material Balance in the Ozonation of Genuine Tank 101-SY RTW

In the ozonation of the simulant Tank 101-SY RTW, alkali consumed during the reaction was measured to be about 1.88 moles per mole of organic carbon. Alkali included both hydroxide and aluminate lost from solution. In the ozonation of genuine Tank 101-SY RTW, alkali consumption also was measured. In the two ozonation runs conducted, consumptions were measured at 2.02 and 1.98 moles of alkali per mole of organic carbon oxidized.

Derivation of a balanced chemical reaction for the ozonation of genuine Tank 101-SY RTW was not possible because not all of the organic species present were identified and quantified. Hence, the theoretical amount of hydroxide and ozone required to complete the oxidation could not be determined. However, the similarity of the runs using the simulant and genuine Tank 101-SY RTW materials suggests that ozone consumptions were comparable.

A qualitative indicator of the progress of ozonation may be found in the onset of the yellow chromate color. In batch tests with both simulant and genuine Tank 101-SY RTW, the beginning of the increase of the chromate color coincided with the near-complete oxidation of the organic.

5.3.12 Thermal Analyses of Genuine Tank 101-SY RTW

DSC of the diluted, genuine Tank 101-SY RTW before and after ozonation was conducted. While 5.40 and 5.33 calorie/g exotherms, respectively, were found for the two test run materials before ozonation, no exothermic events were recorded for the ozonated materials.

The effective elimination of the potential to exotherm by treatment with ozone matched the observations recorded for the tests with simulant Tank 101-SY RTW material. Note also that the magnitude of the exotherm of the genuine RTW material was over ten-fold less than the exotherm observed for the simulant (which used HEDTA and EDTA as the source organics). These results, shown in Table 6, suggest that organic degradation, occurring through prior operations and during storage in Tank 101-SY, significantly decreased the chemical energy of the waste when compared with the source chemicals of HEDTA and EDTA.

Table 6. Results of Thermal Analyses of
Simulant and Genuine Tank 101-SY RTW.

Waste type	Before/after ozone	Weight percent TOC (dry basis)	Exotherm (cal/g dilution)
Simulated 101-SY	Before	2.3	78
Simulated 101-SY	After	0.23	0
Genuine 101-SY, Jar 93B	Before	1.64	5.40
Genuine 101-SY, Jar 93B	After	0.34	0
Genuine 101-SY, Jar 93C	Before	1.52	5.33
Genuine 101-SY, Jar 93C	After	0.33	0

cal/g = calories per gram
101-SY = Tank 241-SY-101
TOC = total organic carbon.

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6.0 SUMMARY AND CONCLUSIONS

Ozone was investigated as a reagent to destroy organic species present in Hanford Site waste solutions and slurries. The waste materials investigated were both simulant and genuine formulations derived from the contents of Tank 101-SY. High-shear mixing using benchscale apparatus was used to introduce the ozone gas rapidly and efficiently to the waste materials. In performing the tests with genuine Tank 101-SY RTW materials, acetate, oxalate, and formate were identified and their concentrations found to comprise about 40% of the original TOC concentration. With both the enclosed and the open high-shear reactor designs studied, near 100% stoichiometric use of ozone could be attained. The observed chemical reactions were consistent with reduction of one oxygen atom per ozone molecule.

Three oxidation reactions dominated the use of ozone:

- Nitrite to form nitrate
- Source (original) organics to form carbonate, oxalate, nitrate, and small quantities of nitrogen
- Chromium (III) to form chromate.

About 90% destruction of organic carbon was achieved to form inorganic carbon (i.e., carbonate). A refractory organic residue (oxalate) also was produced in tests with simulant waste. With genuine waste, about 80% reduction of organic carbon concentration was achieved. The oxidations of nitrite and the organics occurred as rapidly as the ozone was supplied. The oxidations of residual oxalate and chromium hydroxide were slower than the rate of supply of ozone.

In the oxidations of the organic species and chromium hydroxide, quantities of hydroxide ion were consumed. The consumption of hydroxide was reflected in the observed precipitation of aluminum hydroxide as the mineral bayerite. The bayerite could be rapidly redissolved by introduction of additional hydroxide. Hydroxide consumption was approximately 2 moles per mole of organic carbon oxidized.

The behaviors of elements and radionuclides present in trace concentrations in the genuine Tank 101-SY RTW waste indicated other reactions occurred during ozonation. For example, calcium, nickel, strontium, and americium precipitated from solution as the organic complexing agents were oxidized. Chromium, plutonium, and manganese, on the other hand, were dissolved by ozone oxidation.

Thermal analyses of the simulated and genuine waste materials before ozonation showed exothermic reactions of components occurring at temperatures between 200 and 450 °C. The exothermic phenomena were eliminated entirely following exhaustive treatment of these materials with ozone.

Safety problems related to organic carbon in Tank 101-SY potentially may be addressed by ozone treatment of the waste as supported by the following observations:

- Demonstrated conversion of organic carbon to oxalate and carbonate residue
- Known stability of oxalate to gas-generating reactions under tank conditions
- Elimination of exothermic events in ozonated waste.

The chemical similarity of behaviors of the simulant and genuine Tank 101-SY RTW to ozonation shows that the simulant formulation may be used in engineering tests (e.g., pilot plant testing) as a credible nonradioactive surrogate for genuine RTW.

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8.0 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of G. T. McDonald and D. W. Edmonson for the design of the ozonation apparatus and the conscientious and skilled conduct of the experiments reported in this study. Thermal analyses of simulated waste were performed by D. B. Bechtold. The authors also thank S. A. Colby for initiating this project and for his valuable technical advice.

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WHC-EP-0701

APPENDIX A

ENGINEERING LABORATORY TEST PLAN

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**Westinghouse
Hanford Company****Internal
Memo**

From: Pretreatment Applications
Phone: 6-1677
Date: December 1, 1992
Subject: TEST PLAN FOR LAB SCREENING TESTS-OZONE SYNTHETIC WASTE

AMS-92-001

To: J. N. Appel S4-58
cc: D. R. Bratzel L5-31
S. A. Colby L5-31
R. G. Cowan L5-31
C. H. Delegard T6-50
M. J. Klem S4-58
AMS-File/LB

1.0 INTRODUCTION

This test plan contains instructions for the continued examination of organic destruction with ozone on simulated Hanford tank waste, i.e. 101-SY, begun in FY 1992. Tank safety has become a major concern at the Hanford site over the past several years and many tanks, such as the one mentioned, contain large volumes of organics (EDTA and/or HEDTA) from past operations. The organic material is currently in the process of decomposing and releasing hydrogen as a result of this process. Further investigation of the organic destruction with ozone will benefit the Hanford site by resolving tank safety issues, improve partitioning technologies, and destroy organic complexes that are currently hard to analyze for and characterize.

2.0 OBJECTIVE

Tests will be conducted to measure the oxidation of the organic compounds contained in the simulated waste, as set forth in FY 1992 baseline tests. Testing will verify the data obtained in FY 1992.

3.0 SCOPE

- Verification of reported baseline data with EDTA. The task will be integrated with the 222S labs simulated cold run.
- Verify that ozone will not decompose formate by using baseline procedures on 101-SY simulant. Test ozonation of waste Tank 107-AN under baseline conditions.
- Test effect of varying operating parameters.
- Investigate Scale up.

J. N. Appel
Page 2
December 1, 1992

AMS-92-001

4.0 TEST APPROACH

The parameters to be verified in the efficiency tests of the ozonation reactor using 101-SY simulant prepared in FY 1992.

- Operating temperature of 30°C
- Free hydroxide of 0.1M
- Simulant recycle rate of 0.8 l/min
- Ozone to Oxygen ratio of 1:1
- Ozone addition at 8.0 wt percent

Verify that sodium formate (as the organic) will not decompose during the ozonation of the simulated tank waste under the above baseline conditions. Determine ozone effectiveness on 107-AN under baseline conditions. Total organic carbon will be used to determine the overall organic destruction of all simulated waste solution. Determine the hydrogen generation before and after ozonation of the waste from the integrated testing with 222S lab.

Reduce the liquid feed operating parameter one-half to the ozonator while maintaining the gas flow rate determined in FY 1992. The reduced simulant flow rate will indicate if the gas rate is greater than what is required to cause organic decomposition. Test results will dictate if the gas flow rate at the original liquid rate can be reduced to obtain similar organic destruction.

FUTURE SCALE UP

Investigate ozonation scale up with outside vendors over the next several months with specification generated from lab scale data. Investigate the possible use of pulp bleaching technology for application in Hanford waste ozonation. Investigate the use of ozone producers ability to demonstrate scale up with specifications generated from lab scale data.

DELIVERABLE

A report will be issued by the end of FY 1993 that will describe the repeatability of ozonation of Hanford waste.

- Repeatability of the ozonation work in FY 1992
- Ozone effect on sodium formate
- Ozonation of Complex Concentrate (CC) Tank Waste 107-AN
- Effect of parameter changes.
- Scale up activities and any results from outside contracts used for scale up

J. N. Appel
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December 1, 1992

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SCHEDULE

FY93	
O N D J F M A M J J A S	
A. Duplicate Base Line Test.	A--○
B. Effect of ozone on formate.	B--○
C. Ozone destruction of 107-AN waste tank simulant.	C---○
D. Investigate Scale up.	D-----○
E. Report Results.	E-----○

A. M. Stubbs
Pretreatment Applications

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WHC-EP-0701

APPENDIX B

PREPARATION OF COMPOSITE GENUINE TANK 101-SY RTW

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**Westinghouse
Hanford Company****Internal
Memo**

From: Process Chemistry Laboratory
Phone: 3-2532 T6-50
Date: February 2, 1993
Subject: LARGE COMPOSITE OF TANK 101-SY SAMPLES

12110-PCL93-011

To: J. R. Jewett T6-50

cc: C. H. Delegard T6-50
G. D. Johnson R2-78
N. G. McDuffie R2-78
J. C. Person T6-50
D. A. Reynolds R2-11
DLH File/LB

- References: 1) Internal Memo, J. R. Jewett to G. D. Johnson, "Proposed Large Composite of 101-SY Samples", dated January 14, 1993.
- 2) "Laboratory Characterization of Samples Taken in December 1991 (Window E) from Hanford Waste Tank 241-SY-101," WHC-SD-WM-DTR-026, Rev. 0, D. L. Herting, et al., August 20, 1992.

The consolidation of several archived samples from tank 101-SY, proposed in Reference 1, has been accomplished. Twenty-five archived samples have been consolidated into four virtually identical composite jars labeled "101-SY Tank Comp 93A" (or 93B, 93C, 93D).

Four jars were used rather than a single jar due to limitations of handling such a large container with manipulators. In order to ensure that the four jars were as much alike as possible, every one of the twenty-five consolidated samples were divided equally among the four composite jars. All of the weights of the individual additions to the composite jars are recorded in laboratory notebook WHC-N-577, pages 87-94.

The composites were constructed so that the relative weights of convective layer sample and nonconvective layer sample would represent the relative weights of the two layers in the tank. That weight ratio (convective layer:nonconvective layer) is 1.26 or 1.27 for all four of the composite jars. Therefore, the composition of each of the composite jars should be very close to the overall tank composition given in Table 5-4 (page 5-17) of Reference 2.

Due to water losses, several instances of less-than-expected amount of sample in the archived sample jars, and the expected inability to recover 100% of the sample contained in the jars, the overall amount of composited sample is less than planned (Reference 1,. Actual weights of the four composite samples range from 570 grams to 583 grams, with a total of 2.3 kg, compared to the planned total of 2.9 kg.

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J. R. Jewett
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February 2, 1993

12110-PCL93-011

Please call me at 373-2532 if you have any questions about the large composite samples or the process used to composite them, or if you need more information about the specific samples used to create the composites.

D. L. Herting, Principal Chemist
Process Chemistry Laboratories

tth

WHC-EP-0701

APPENDIX C

PREPARATION OF SIMULATED TANK 101-SY RTW

WHC-EP-0701

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Recipe for Tank 101-SY Simulant Waste. (2 sheets)

Component	Weight%	Conc. (g/L)	Conc. (M)	Cation/ anion balance	Balance			Compound	Formula weight	Compound weight (g)
					Nitrate	Chloride	Sodium			
Na	20.7	341.55	14.8565	14.8565	--	--	--	--	--	--
Al	3.2	116.16	1.9695	-1.9695	--	--	1.9695	NaAlO ₂ *	118.00	232.40
Cr (total)	0.41	6.765	0.1301	0.3903	0.3903	--	--	Cr(NO ₃) ₃ •9H ₂ O	400.20	52.07
Cr (VI)	0.002	0.033	0.0006	-0.0013	--	--	--	--	--	--
Ca	0.023	0.3795	0.0095	0.0189	0.0189	--	--	Ca(NO ₃) ₂ •4H ₂ O	236.15	2.24
Fe	0.028	0.462	0.0083	0.0248	0.0248	--	--	Fe(NO ₃) ₃ •9H ₂ O	404.00	3.34
K	0.326	5.379	0.1376	0.1376	0.1376	--	--	KNO ₃	101.10	13.91
Ni	0.015	0.2475	0.0042	0.0084	0.0084	--	--	Ni(NO ₃) ₂ •6H ₂ O	290.82	1.23
Zn	0.002	0.033	0.0005	0.0010	--	0.0010	--	ZnCl ₂	136.30	0.07
NO ₃	11.7	193.05	3.1135	-3.1135	2.5334	--	2.5334	NaNO ₃	84.99	215.31
NO ₂	10.5	173.25	3.7658	-3.7658	--	--	3.7658	NaNO ₂	69.00	259.84
OH	2.47	40.755	2.3964	-2.8398	--	--	2.8398	NaOH	40.00	113.59
TIC	0.63	51.975	0.8661	-1.7322	--	--	1.7322	Na ₂ CO ₃ •H ₂ O	124.00	107.40
PO ₄	0.64	10.56	0.1112	-0.3336	--	--	0.3336	Na ₃ PO ₄ •12H ₂ O	380.10	42.26
SO ₄	0.4	6.6	0.0687	-0.1374	--	--	0.1374	Na ₂ SO ₄	142.00	9.76
Cl	0.79	13.035	0.3677	-0.3677	--	0.3667	0.3667	NaCl	58.44	21.43
F	0.03	0.495	0.0261	-0.0261	--	--	0.0261	NaF	41.99	1.09
TOC	1.53	75.735	2.1018	--	--	--	--	--	--	--
HEDTA	--	--	0.1401	-0.4204	--	--	0.4204	Na ₃ HEDTA•2H ₂ O	380.24	53.28
EDTA	--	--	0.0701	-0.2802	--	--	0.2802	Na ₄ EDTA•2H ₂ O	416.20	29.16

Recipe for Tank 101-SY Simulant Waste. (2 sheets)

Component	Weight%	Conc. (g/L)	Conc. (M)	Cation/ anion balance	Balance			Compound	Formula weight	Compound weight (g)
					Nitrate	Chloride	Sodium			
NH ₃	0.19	3.135	0.1841	--	--	--	--	--	--	--
H ₂ O	35.5	585.75	32.5142	--	--	--	--	--	--	--
Summation	--	1,625.349	--	0.4501	3.1135	0.3677	14.4051	--	--	1,158.38

*NaAlO₂ stated on label; compound is NaAl(OH)₄.

NOTES: Density is 1.65 g/L. Total chemical conc. (g/L) is 1,625.349 implying 98.5 weight percent mass balance.

- 1) TIC/TOC weight % reported as C; calculations based on CO₃²⁻ for TIC. TOC conc. (g/L) uses factor of 3 to convert from carbon to organic ion weights. TOC is made up using a 2:1 mole ratio of HEDTA:EDTA.
- 2) Cr(VI) is small compared to total Cr and is not added.
- 3) NH₃ added to alkaline solution would immediately volatilize; no NH₃ added; rely on self-generation of NH₃.
- 4) Cation:anion imbalance may imply either too much Na⁺, too little NO₃⁻/NO₂⁻ or no accounting for small organic acid salts (e.g., oxalate, formate). In this recipe, Na⁺ added at lower than analyzed value (smaller relative difference).
- 5) Nonsodium metals added as nitrate salts (except ZnCl₂). Anions added as sodium salts.
- 6) To neutralize acidic hydrolyzable metal salts of Cr, Cu, Fe, Ni, and Zn; 0.4434M "extra" NaOH added. This hydrolyzing OH⁻ not determined or reported in OH⁻ analysis.

RECIPE: For 1-Liter; weights of components are as given in table above, rightmost column.

- 1) Tare weigh a 2-L stainless steel beaker with large Teflon[®]-covered stirbar.
- 2) Add approximately 250 mL H₂O to the beaker and begin stirring and heating.
- 3) Add NaAlO₂ and stir with heating until dissolved. Turn off heat and add NaOH slowly with stirring.
- 4) In a separate beaker, add 150 mL H₂O and the Cr, Ca, Fe, K, Ni, and Zn salts. Stir and dissolve.
- 5) With rapid stirring, add the dissolved metal salts to the NaAlO₂/NaOH solution.
- 6) Add the remaining salts, organics last. Use heat and stirring.
- 7) Add H₂O, as required, to aid the dissolution described in step 6). Water addition to about 2000 g total chemical weight (i.e., about 950 mL H₂O) required.

Boil down to 1,650 g total added weight above tare.

Based on 101-SY window "E" Bulk Composition (from WHC-SD-WM-DTR-026, Rev. 0, Table 5-4).

APPENDIX D

DATA FOR TESTS WITH SIMULATED TANK 101-SY RTW

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WHC-EP-0701

Ozonolysis of Simulated 101-SY (180 mL sim to 540 mL H₂O) on 18-19 March 1993.

Notebook WHC-N-656 1, page 33.

Sample #	Time (h)	TOC (g/L)	TIC (g/L)	TC (g/L)	Cr(VI) (g/L)	Tot.Cr(g/L)	Al(g/L)	Ca(g/L)	Fe(g/L)	Ni(g/L)	Na(g/L)
Makeup											
C-70,R349	0	6.237	2.640	8.877	0.00596	0.0289	12.2	0.0952	0.00152	0.0268	82.2
C-71,R349	1	6.028	3.150	9.178	0.0178	0.0425	12.5	0.0968	0.00128	0.0277	84.8
C-72,R349	2	5.720	3.424	9.144	0.0164	0.0407	12.1	0.0954	0.00118	0.0268	81.5
C-73,R349	3	5.362	3.758	9.120	0.0153	0.0400	12.3	0.0883	0.000775	0.0273	83
C-74,R349	4	4.970	4.134	9.104	0.0206	0.0398	12.1	0.0552	0.000718	0.0267	82.3
C-75,R349	6	4.200	5.160	9.360	0.0375	0.0467	12	<0.00018	<0.0004	0.0273	82.6
C-76,R349	8	1.410	7.600	9.010	0.237	0.2430	5.36	<0.00018	<0.0004	0.00201	83.5
C-77,R349	10	0.885	9.020	9.905	0.962	0.993	3.68	<0.00018	<0.0004	<0.00035	84
C-78,R349	12	0.891	8.510	9.401	1.27	1.29	3.06	<0.00018	<0.0004		83.9
C-79,R350	14	0.858	8.620	9.478	1.32	1.39	3.08	<0.00018	<0.0004	<0.00035	84.6
C-80,R350	14.35	0.715	9.370	10.085	1.44	1.49	10.3	<0.00018	<0.0004	0.000677	94.2
C-81,R350	15	0.632	9.680	10.312	1.56	1.52	10.6	<0.00018	0.001	0.000677	94.8

Sample #	Time (h)	HCO ₂ (g/L)	C ₂ H ₃ O ₂ (g/L)	C ₂ H ₃ O ₂ (g/L)	C ₂ O ₄ (g/L)	C ₂ O ₄ (g/L)	Cl (g/L)	NO ₂ (g/L)	NO ₃ (g/L)	OH (g/L)	PO ₄ (g/L)	SO ₄ (g/L)	F(g/L)
Makeup													
C-70,R349	0	0.149	0.040	0.067	0.027	0.248	0.0676	3.46	42.7	45.4	10.80	2.44	1.75 <0.0101
C-71,R349	1	0.785	0.209	0.553	0.225	0.176	0.0480	3.41	35.7	54.3	9.59	2.42	1.71 <0.0101
C-72,R349	2	1.490	0.397	1.100	0.447	0.285	0.0777	3.70	32.4	70.7	8.49	2.14	1.78 <0.0101
C-73,R349	3	3.460	0.923	1.670	0.679	0.46	0.1255	3.54	24.3	75.8	7.58	2.17	1.82 <0.0101
C-74,R349	4	2.850	0.760	1.930	0.785	0.642	0.1751	3.57	17	85.8	6.29	2.3	1.86 <0.0101
C-75,R349	6	3.19	0.851	2.010	0.818	1.11	0.3027	3.35	3.35	102	3.24	2.32	1.88 3.41
C-76,R349	8	0.170	0.045	0.204	0.083	2.27	0.6191	3.59	<.101	108	2.24	2.13	1.73 <0.0101
C-77,R349	10	0.02	0.005	0.597	0.243	2.1	0.5727	3.47	0.263	102	1.65	2.11	1.66 <0.0101
C-78,R349	12	0.02	0.005	0.56	0.228	2.19	0.5973	3.57	0.284	107	1.85	2.19	2.4 <0.0101
C-79,R350	14	0.02	0.005	0.138	0.056	2.16	0.5891	3.64	0.26	107	1.30	2.08	1.77 <0.0101
C-80,R350	14.35	0.02	0.005	0.02	0.008	1.6	0.4364	3.94	0.29	3.31	2.11	2.15	<0.0101
C-81,R350	15	0.02	0.005	0.18	0.073	1.6	0.4364	3.36	0.292	100	3.60	2.33	1.73 <0.0101

Ozone produced calculated as follows:

- Nominal ozone output is 8.0 weight percent.
- Actual ozone is about 7.4 weight percent due to thumbwheel bias in ozone monitor.
- Average pressure during operation is 8.2 psig.
- Total gas flow rate is 974 mL/minute = 58.46 L/h.
- 7.4 weight percent = $(7.4/48)/[(92.6/32) + (7.4/48)] = 0.050581$ mole fraction.
- $PV=nRT$; $n=PV/RT=0.050581*(22.9/14.7)\text{atm}*(58.5\text{L/h})/[(0.08205\text{L-atm/mol-deg})*(300\text{K})]$
 $n=0.18715$ mol; $eq=0.18715*(2\text{eq/mole})=0.3743$.

Oxidized species calculated as follows:

- Cr(III)->Cr(VI): $(^{\circ}\text{X}^{\circ}\text{gCr(VI)})/(\text{L})*(\text{mole}/51.996\text{g})*0.705\text{L}*(3\text{eq}/\text{mole})$
- N(III)->N(V): $(^{\circ}\text{Y}^{\circ}\text{gNO}_2\text{oxd.})/(\text{L})*(\text{mole}/46\text{g})*0.705\text{L}*(2\text{eq}/\text{mole})$
- C(-0.267)->C(3.6): C(-0.267) represents oxidation state of 2:1 mole ratio of HEDTA:EDTA.
C(3.6) represents oxidation state of 10 mole percent oxalate/90 mole percent carbonate product.
 $(^{\circ}\text{Z}^{\circ}\text{gTOCprod.})/(\text{L})*(\text{mole}/12\text{g})*0.705\text{L}*(3.867\text{eq}/\text{mole})$
- N(-3)->N(0): $(^{\circ}\text{Z}^{\circ}\text{gTOCprod.})/(\text{L})*(\text{mole}/12\text{g})*0.705\text{L}*(2\text{moleN}/5\text{moleC})*(3\text{eq}/\text{moleN})$
- Summing 3 and 4 above, $(^{\circ}\text{Z}^{\circ}\text{gTOCprod.})/(\text{L})*(\text{mole}/12\text{g})*0.705\text{L}*(5.067\text{eq}/\text{mole})$
- If N(-3)->N(5): $(^{\circ}\text{Z}^{\circ}\text{gTOCprod.})/(\text{L})*(\text{mole}/12\text{g})*0.705\text{L}*(2\text{moleN}/5\text{moleC})*8\text{eq}/\text{moleN}$ or 7.067 instead of 5.067 eq/mole.
- If N(-3)->N(0) [at 10%] + N(5) [at 90%]: $(^{\circ}\text{Z}^{\circ}\text{gTOCprod.})/(\text{L})*(\text{mole}/12\text{g})*0.705\text{L}*(2\text{moleN}/5\text{moleC})*(7.5\text{eq}/\text{moleN})$ or 6.867 eq/mole.

WHC-EP-0701

Ozonation of Syn. 101-SY, 5 October 1993, Gas and Solution Analyses

Time (h)	Sample#	Interval(h)	ET(h)	Concentration in the offgas (mole percent)					
				Ar	CO2	CO	H2	N2	O2
0.0	C-230,J1171	0-0.3	0.3	0.140	0.340	<0.01	<0.001	<0.01	99.53
0.6	C-231,J1172	0.3-1.5	1.2	0.140	<0.001	0.020	0.008	<0.01	99.84
2.4	C-232,J1173	1.5-3.0	1.5	0.141	<0.001	0.030	0.011	0.020	99.80
3.6	C-233,J1174	3.0-3.9	0.9	0.141	<0.001	0.034	0.007	0.017	99.80
4.2	C-234,J1175	3.9-4.5	0.6	0.140	0.009	<0.01	0.004	0.020	99.83
4.8	C-235,J1176	4.5-5.4	0.9	0.138	0.155	<0.01	0.001	0.058	99.65
6.0	C-236,J1177	5.4-6.0	0.6	0.136	0.314	<0.01	<0.001	0.033	99.52

Time (h)	Interval(h)	ET(h)	Quantity in the Offgas (moles)					O2
			Ar	CO2	CO	H2	N2	
0.0	0-0.3	0.3	0.0011	0.00255	0.00000	0.000000	0.00000	0.75
0.6	0.3-1.5	1.2	0.0042	0.00000	0.00060	0.000240	0.00000	3.00
2.4	1.5-3.0	1.5	0.0053	0.00000	0.00113	0.000413	0.00075	3.74
3.6	3.0-3.9	0.9	0.0032	0.00000	0.00077	0.000158	0.00038	2.25
4.2	3.9-4.5	0.6	0.0021	0.00014	0.00000	0.000060	0.00030	1.50
4.8	4.5-5.4	0.9	0.0031	0.00349	0.00000	0.000023	0.00131	2.24
6.0	5.4-6.0	0.6	0.0020	0.00471	0.00000	0.000000	0.00050	1.49
		Sum	0.0210	0.01088	0.00249	0.000893	0.00323	14.96
		Amt.Avail.		0.252	0.252		0.0252	15

Time (h)	Sample#	Concentration in solution (g/L)						Eq.Ox./L	% Oxid.	Eq.Ox.
		OH	TOC	TIC	NO3	NO2	Cr(VI)			
0.0	C-230,J1171	10.3	6.61	2.73	34.2	38.6	0.00646	0.000	0.0	0.000
0.6	C-231,J1172	9.72	6.36	2.92	46.6	33.5	0.0108	0.365	6.7	0.172
2.4	C-232,J1173	5.99	5.38	4.03	70.9	12.6	0.0282	1.836	33.6	0.863
3.6	C-233,J1174	3.41	4.46	4.94	76.1	1.19	0.0422	2.859	52.4	1.344
4.2	C-234,J1175	1.39	3.23	6.26	83.0	<0.201	0.0286	3.614	66.2	1.698
4.8	C-235,J1176	1.91	2.08	7.45	87.1	<0.201	0.222	4.283	78.4	2.013
6.0	C-236,J1177	1.46	1.37	7.38	86.4	<0.201	0.754	4.720	86.4	2.218
							TotalEq.Av	5.460		

Ozonation of 101-SY Simulant Having No Nitrate/Nitrite, 30 September 1993

Time (h)	Sample#	NO3	NO2	OH	TOC	TIC	Mole Ratio C ox./NO3
		(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	(ug/mL)	
0	C-220/J1163	<101	<101	2870	1500	728	
0.6	C-221/J1164	821	<101	<1250	550	1700	6.0
2.4	C-222/J1165	1200	<101	<125	240	2000	5.4
3.5	C-223/J1166	1250	<101	<125	210	2070	5.3
4.75	C-224/J1167	1260	<101	<1250	190	2110	5.4
6.1	C-225/J1168	1250	<101	<125	150	2140	5.6
						Avg.M.Rat.	5.54

APPENDIX E

THERMAL ANALYSES OF SIMULATED TANK 101-SY RTW

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**Westinghouse
Hanford Company****Internal
Memo**

From: Process Chemistry Laboratory
Phone: 3-2162 T6-09
Date: April 14, 1993
Subject: DSC ANALYSIS OF SYNTHETIC OZONATION SAMPLES

12110-PCL93-034

To: A. M. Stubbs L5-31

cc: C. H. Delegard T6-09
B. F. Hey T6-09
J. R. Jewett T6-09
J. P. Sloughier T6-07
DBB File/LB

This memo reports differential scanning calorimetry (DSC) results for two samples of simulated tank waste, one before ozonation and one after. The samples are identified in Attachment 1.

Each sample was shaken vigorously to mix the sediment with the liquid before withdrawing a portion for analysis. The samples were analyzed in open, stainless steel containers under air cover gas from 38 to 500 °C, at a scan rate of 10 °C/minute. The work was recorded in laboratory notebook WHC-N-522.

The DSC thermograms are in Attachment 2. The appearance of the "ozone start" DSC is similar to that of synthetic DSC standards or synthetic 101-SY solutions, having a large water evaporation endotherm, followed by a lesser hydrate water-oxidizer melt endotherm, and finally a broad exotherm between 200 and 450 °C. The "ozone finish" DSC contains no discernible exotherm in this temperature region, only a small endotherm not far from the melting point of sodium nitrate or the decomposition temperature of aluminum hydroxide. Apparently the ozonation process that the latter sample was treated with successfully destroyed its capacity to exotherm.

If you have any questions on this matter feel free to call.

D. B. Bechtold, Principal Scientist
Process Chemistry Laboratories

tth

Attachments (2)

DSC of Ozonation Samples		
Sample Label	DSC File I.D.	Appearance/Result
Ozone Start	SSTDSC6:OZST.D4 SSTDSC6:DOZST.D4 (duplicate)	Mostly watery liquid with some dark brown sediment. Average Exotherm -78.3 cal/gm Range 9.3 cal/gm
Ozone Finish	SSTDSC6:OZFN.D4 SSTDSC6:DOZFN.D4 (duplicate)	Mostly watery liquid with some chartreuse-colored sediment. No exotherm.

E-3

WMC-EP-0701

E-4

WHC-EP-0701

E-5

E-6

WHC-EP-0701

APPENDIX F

DATA FOR TESTS WITH GENUINE TANK 101-SY RTW

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Ozonolysis of Genuine 101-SY (800 mL of 3:1 volume water:waste blend) on 16 April 1993
 Notebook WHC-N-656 1, pages 36 & 38.

Sample #	Time (h)	TOC (g/L)	TIC (g/L)	TC (g/L)	Cr(VI) (g/L)	TotCr(g/L)	Al(g/L)	Ca(g/L)	Fe(g/L)	Ni(g/L)	Na(g/L)	Sr(g/L)	Si(g/L)	Zn(g/L)	Ag(g/L)	Mn(g/L)	ET (hours) Temp(C)	
																	0	24
C-100B, R3811	0	5.400	2.800	8.200	0.0608	0.6780	7.94	0.0621	0.0471	0.0648	81	0.000563	0.153	0.00311	0.000399	0.0124	0.33	24.4
C-100, R3699	0	4.370	2.840	7.210	0.0426	0.0621	12.5	0.05	0.00509	0.0606	85.4	0.000178	0.135	0.000477	0.000185	0.000282	0.75	28.2
C-101, R3700	1	4.350	3.090	7.440	0.0055	0.0622	13.4	0.0498	0.00464	0.0612	92.2	0.000164	0.125	0.000536	0.000728	0.000112	1	29.2
C-102, R3701	2	4.120	3.180	7.300	0.0612	0.0659	13.3	0.0474	0.00474	0.06	91.7	0.000156	0.119	0.000327	0.00085	9.29E-05	1.5	29.8
C-103, R3702	3	3.930	3.310	7.240	0.0655	0.0732	13.1	0.0453	0.00471	0.0605	90.1	0.000126	0.124	0.000232	0.000945	0.000129	3	29
C-104, R3703	4	3.630	3.490	7.120	0.0698	0.0735	13.3	0.0415	0.00456	0.0591	91.3	0.000104	0.115	0.000323	0.000982	6.85E-05	3.33	29
C-105, R3704	6	3.570	3.530	7.100	0.0883	0.0949	13.5	0.0261	0.00458	0.0564	92.5	<0.000075	0.111	0.000224	0.00126	5.57E-05	4	29.2
C-106, R3705	8	1.630	5.510	7.140	0.545	0.4620	10.3	<0.00022	0.00401	0.00532	92.1	<0.000075	0.0932	0.000324	0.000859		5	30.2
C-107, R3706	10	2.060	6.060	8.120	1.49	1.62	8.59	<0.00022		0.00359	92	<0.000075	0.0742	0.000216	0.000528		6	30.2
C-108, R3707	12	0.864	6.140	7.004	1.67	1.81	8.64	<0.00022	0.00351	<0.00033	93.1	<0.000075	0.0719	0.000263	0.000697	0.00036	7	30.4
C-109, R3708	13.9	0.902	6.230	7.132	1.65	1.77	8.33	<0.00022	0.00343	<0.00033	93	<0.000075	0.0712	<0.0001	0.000819	0.00117	8	29.4
C-110, R3709	15.9	0.897	6.000	6.897	1.63	1.81	7.86	<0.00022	0.00355	<0.00033	94.8	<0.000075	0.0761	<0.0001	0.000689	0.00113	9	28.2

Sample #	Time (h)	HCO2(g/L)	HCO2 (gC/L)	C2H3O2 (g/L)	C2H3O2 (gC/L)	C2O4(g/L)	C2O4(gC/L)	Cl (g/L)	NO2 (g/L)	NO3 (g/L)	OH (g/L)	PO4(g/L)	SO4(g/L)	F(g/L)		
C-100B, R3811	0	2.69	0.717	1.78	0.724	1.24	0.3382	3.36	44.2	55.8	14.30	3.36	1.96	<4.14	13.9	27.4
C-100, R3699	0	2.550	0.680	1.810	0.736	1.36	0.3709	6.67	78.2	97	12.90	3.48	1.77	<0.04	15	27.2
C-101, R3700	1	2.630	0.701	1.780	0.724	1.4	0.3818	4	75.2	120	11.53	3.32	1.89	<0.04	15.9	27.6
C-102, R3701	2	2.650	0.707	1.720	0.700	1.38	0.3764	3.37	34.2	65.2	12.05	3.17	1.76	<0.04		
C-103, R3702	3	2.350	0.627	1.400	0.569	1.39	0.3791	3.18	24.7	73.6	10.50	3.31	1.79	<0.04		
C-104, R3703	4	2.400	0.640	1.460	0.594	1.51	0.4118	3.31	19.5	83.8	8.55	3.31	1.67	<0.04		
C-105, R3704	6	2.200	0.587	1.470	0.598	1.51	0.4118	2.97	3.99	97.5	7.00	3.18	1.65	<0.04		
C-106, R3705	8	0.213	0.057	0.376	0.153	2.14	0.5836	3.57	<0.4	115	6.80	3.38	1.99	<0.04		
C-107, R3706	10	<0.01	0.000	0.0638	0.026	1.86	0.5073	4.42	<0.4	109	6.09	3.2	2	<0.04		
C-108, R3707	12	<0.01	0.000	<0.01	0.000	1.51	0.4118	4.44	<0.4	119	5.73	2.98	1.89	<0.04		
C-109, R3708	13.9	<0.01	0.000	<0.01	0.000	1.6	0.4364	3.3	<0.4	110	5.76	3.36	2.05	<0.04		
C-110, R3709	15.9	<0.01	0.000	<0.01	0.000	1.63	0.4445	3.58	<0.4	116	5.90	3.42	3.11	<0.04		

Sample #	Time (h)	U(ug/mL)	Pu239,40 (nCi/mL)	Am241 (nCi/mL)	Cs137 (mCi/L)	Sr90 (uCi/L)	DSC	TGA
C-100B, R3811	0	3.32	0.293	0.515	153	2050	22.6J/g	76.96% H2O
C-100, R3699	0	4.55	<0.0568	0.161	145	1720		
C-101, R3700	1	2.33	<0.0949	0.1657	143	1680		
C-102, R3701	2	3.1	<0.128	0.217	147	1300		
C-103, R3702	3	1.71	<0.1	0.204	150	978		
C-104, R3703	4		<0.0939	0.132	152	840		
C-105, R3704	6	5.99	0.117	<0.127	150	170		
C-106, R3705	8	6.12	2.49	<0.127	149	<0.905		
C-107, R3706	10	6.97	2.54	<0.127	157	1.79		
C-108, R3707	12	8.78	5.65	<0.127	153	<1.07		
C-109, R3708	13.9	20.9	6.68	<0.127	148	<.818		
C-110, R3709	15.9	12.7	2.1	<0.127	152	0.662		
C-110C, R3968	15.9	6.08	0.238	0.474	152	220	no exother	77.63% H2O

Chromatolysis of Genuine 101-SY (800 mL of 3:1 volume water waste blend) on 18 April 1993
 Notebook WHC-N-656 1, pages 37 & 38

Sample #	Time (h)	TOC (g/L)	TIC (g/L)	TC (g/L)	Cr(VI) (g/L)	Tot Cr(g/L)	Al(g/L)	Ca(g/L)	Fe(g/L)	Ni(g/L)	Na(g/L)	Sr(g/L)	Si(g/L)	Zn(g/L)	Ag(g/L)	Mn(g/L)	ET (hours)	Temp(C)	pH
																	0	236	13.42
C-120B, R3812	0	7.200	2.590	9.790	0.0567	0.51	7.27	0.0537	0.0343	0.0584	73.3	0.000422	0.134	0.00252	0.00134	0.00895	0.33	25.6	13.36
C-120, R3688	0	4.060	2.110	6.170	0.0412	0.0617	11.7	0.0459	0.00464	0.054	76.7	0.000145	0.132	<0.0001	0.000542	0.000277	0.5	26.8	13.34
C-121, R3689	1	4.170	2.330	6.500	0.0515	0.0539	11.9	0.0447	0.00386	0.0522	79.8	0.00015	0.111	<0.0001	0.00203	<0.000075	1	28.2	13.3
C-122, R3690	2	3.720	2.470	6.190	0.0544	0.0607	12.1	0.0452	0.00405	0.0543	80.8	0.000139	0.109	<0.0001	0.00227	7E-05	1.5	28.6	13.28
C-123, R3691	3	3.670	3.010	6.680	0.0549	0.0626	11.8	0.042	0.00402	0.0523	78.3	0.000123	0.101	<0.0001	0.00239	8.95E-05	2	29	13.25
C-124, R3692	4	3.360	2.770	6.430	0.0617	0.0667	11.9	0.0402	<0.00038	0.053	78.8	0.000105	0.112	<0.0001	0.00272	7.49E-05	2.5	29	13.23
C-125, R3693	6	3.060	3.400	6.460	0.0723	0.0770	11	0.0258	0.00409	0.053	73.3	6.91E-05	0.103	0.000899	0.00355	5.39E-05	3	29	13.21
C-126, R3694	8	1.710	4.510	6.220	0.195	0.2010	8.78	<0.00022	0.00376	0.00613	73.8	<0.000075	0.0921	<0.0001	0.00393	5.35E-05	4	29.4	13.16
C-127, R3695	10	1.190	5.230	6.420	1.2	1.27	8.45	<0.00022	0.00333	<0.00032	81.2	<0.000075	0.0706	<0.0001	0.000484	<0.000075	4.75	29.2	13.14
C-128, R3696	12	0.979	5.440	6.419	1.49	1.6	7.78	<0.00022	0.00311	<0.00032	81.1	<0.000075	0.0639	<0.0001	0.00074	<0.000075	4.9	29.4	13.13
C-129, R3697	14	0.913	5.660	6.573	1.56	1.64	7.83	<0.00022	0.00321	<0.00032	81.6	<0.000075	0.0612	<0.0001	0.00089	0.000989	5.5	28.4	13.12
C-130, R3698	16	0.869	5.710	6.579	1.7	1.62	7.43	<0.00022	0.00311	<0.00032	81.3	<0.000075	0.0607	<0.0001	0.000928	0.00142	6	28.4	13.1

Sample #	Time (h)	HCO2(g/L)	HCO2 (g/L)	C2H3O2 (g/L)	C2H3O2 (g/L)	C2O4(g/L)	C2O4(g/L)	Cl (g/L)	NO2 (g/L)	NO3 (g/L)	OH (g/L)	PO4(g/L)	SO4(g/L)	F(g/L)	ET (hours)	Temp(C)	pH
C-120B, R3812	0	2.370	0.632	1.530	0.622	1.59	0.4336	2.83	38.1	45.9	12.5	3.06	1.79	<0.861	7.33	29.6	12.99
C-120, R3688	0	2.560	0.683	1.610	0.655	1.39	0.3791	7.01	46.7	56.7	11.87	2.56	1.4	<0.04	7.5	29.8	12.96
C-121, R3689	1	2.530	0.675	1.630	0.653	1.54	0.4200	2.85	34.4	50.8	10.10	2.71	1.47	<0.04	7.83	29.8	12.93
C-122, R3690	2	3.720	0.992	2.410	0.980	1.68	0.4582	3.16	32.1	63.3	9.070	2.82	1.64	<0.04	8	29.8	12.91
C-123, R3691	3	2.770	0.739	1.810	0.736	1.79	0.4882	4.23	29.5	83.8	8.755	2.78	1.64	<0.04	8.25	29.4	12.88
C-124, R3692	4	2.670	0.712	1.770	0.720	1.7	0.4636	3	17.8	74.2	8.160	2.73	1.57	<0.04	8.6	28.8	12.84
C-125, R3693	6	2.35	0.627	1.620	0.659	1.85	0.5045	2.95	5.9	92.5	6.732	2.86	1.58	<0.04	9	28.2	12.81
C-126, R3694	8	0.316	0.084	0.649	0.264	2.42	0.6600	2.15	<0.4		5.712	2.87	1.67	0.076	9.25	28	12.74
C-127, R3695	10	<0.010	0.000	0.134	0.055	2.71	0.7391	3.15	<0.4	98.8	5.832	3.09	1.87	<0.04	9.5	28	12.71
C-128, R3696	12	<0.010	0.000	0.0133	0.005	2.16	0.5891	3.16	<0.4	100	5.508	3.02	1.88	<0.04	10	27.8	12.6
C-129, R3697	14	<0.010	0.000	<0.010	0.000	2.03	0.5536	4.03	<0.4		4.488	2.96	1.84	<0.04	10.5	27.2	12.57
C-130, R3698	16	<0.010	0.000	<0.010	0.000	1.93	0.5264	3.19	<0.4	101	4.828	3.04	1.85	<0.04	11	26.8	12.56

Sample #	Time (h)	U(ug/mL)	Pu239.40 (nCi/mL)	Am241 (nCi/mL)	Cs137 (mCi/L)	Sr90 (uCi/L)	DSC	TGA		13.5	26.8	12.36
C-120B, R3812	0	4.05	0.296	1.84	135	1810	22.3J/g	79.41%H2O		14	27.2	12.34
C-120, R3688	0	2.24	<0.0894	0.138	127	1500				14.5	26.8	12.4
C-121, R3689	1	3.19	<0.0955	0.21	130	1560				15	26.6	12.33
C-122, R3690	2	3.79	<0.1	0.202	129	1250				15.5	26.6	12.32
C-123, R3691	3	5.98	<0.0864	0.194	131	898				16	26.8	12.31
C-124, R3692	4	3.98	<0.0942	0.159	126	761						
C-125, R3693	6	3.14	<0.0954	0.0863	128	253						
C-126, R3694	8	3.71	<0.126	<0.128	131	1.09						
C-127, R3695	10	8.95	0.749	<0.106	133	1.04						
C-128, R3696	12	7.62	2.27	<0.119	130	1.88						
C-129, R3697	14	8.61	2.23	<0.121	130	0.57						
C-130, R3698	16	4.7	2.4	<0.127	134	0.617						
C-130C, R3699	16	3.48	0.202	0.128	138	216	no exother	84.51%H2O				

WHC-EP-0701

Ozonolysis of Genuine 101-SY (800 mL of 3:1 volume water waste blend) on 18 April 1993.
 Notebook WHC-N-656 1, pages 37 & 38

Ozonolysis of Genuine 101-SY (800 mL of 3:1 volume water waste blend) on 18 April 1993																	ET (hours)	Temp(C)	pH
Notebook WHC-N-656-1, pages 37 & 38																	0	23.6	13.42
Sample #	Time (h)	TOC (g/L)	TIC (g/L)	TC (g/L)	Cr(VI) (g/L)	Tot.Cr(g/L)	Al(g/L)	Ca(g/L)	Fe(g/L)	Ni(g/L)	Na(g/L)	Sr(g/L)	Si(g/L)	Zn(g/L)	Ag(g/L)	Mn(g/L)	0.33	25.6	13.36
C-120B, R3612	0	7.200	2.590	9.790	0.0567	0.51	7.27	0.0537	0.0343	0.0584	73.3	0.000422	0.134	0.00252	0.00134	0.00895	0.5	26.8	13.34
C-120, R3688	0	4.060	2.110	6.170	0.0412	0.0617	11.7	0.0459	0.00464	0.054	76.7	0.000145	0.132	<0.0001	0.000642	0.000277	0.8	27.8	13.32
C-121, R3689	1	4.170	2.330	6.500	0.0515	0.0539	11.9	0.0447	0.00386	0.0522	79.8	0.00015	0.111	<0.0001	0.00203	<0.000075	1	28.2	13.3
C-122, R3690	2	3.720	2.470	6.190	0.0544	0.0607	12.1	0.0452	0.00405	0.0543	80.8	0.000139	0.109	<0.0001	0.00227	7E-06	1.5	28.6	13.28
C-123, R3691	3	3.670	3.010	6.680	0.0549	0.0626	11.8	0.042	0.00402	0.0523	78.3	0.000123	0.101	<0.0001	0.00239	8.85E-06	2	29	13.25
C-124, R3692	4	3.360	3.070	6.430	0.0617	0.0667	11.9	0.0402	<0.00038	0.053	78.8	0.000105	0.112	<0.0001	0.00272	7.45E-06	2.5	29	13.23
C-125, R3693	6	3.060	3.400	6.460	0.0723	0.0770	11	0.0258	0.00409	0.063	73.3	6.91E-06	0.103	0.000899	0.00355	5.39E-06	3	29	13.21
C-126, R3694	8	1.710	4.510	6.220	0.195	0.2010	8.78	<0.00022	0.00376	0.00613	73.8	<0.000075	0.0921	<0.0001	0.00363	5.35E-06	4	29.4	13.16
C-127, R3695	10	1.190	5.230	6.420	1.2	1.27	8.45	<0.00022	0.00333	<0.00032	81.2	<0.000075	0.0706	<0.0001	0.000484	<0.000075	4.75	29.2	13.14
C-128, R3696	12	0.979	5.440	6.419	1.49	1.6	7.78	<0.00022	0.00311	<0.00032	81.1	<0.000075	0.0639	<0.0001	0.00074	<0.000075	4.9	29.4	13.13
C-129, R3697	14	0.913	5.660	6.573	1.56	1.64	7.83	<0.00022	0.00321	<0.00032	81.6	<0.000075	0.0612	<0.0001	0.00089	0.000589	5.5	28.4	13.12
C-130, R3698	16	0.669	5.710	6.579	1.7	1.62	7.43	<0.00022	0.00311	<0.00032	81.3	<0.000075	0.0607	<0.0001	0.000928	0.00142	6	28.4	13.1
																	7	29	13.04
																	7.33	29.6	12.96
Sample #	Time (h)	HCO2 (g/L)	C2H3O2 (g/L)	C2H3O2 (g/L)	C2O4(g/L)	C2O4(g/L)	Cl (g/L)	NO2 (g/L)	NO3 (g/L)	OH (g/L)	PO4(g/L)	SO4(g/L)	F(g/L)						
C-120B, R3612	0	2.370	0.632	1.530	0.622	1.59	0.4336	2.83	38.1	45.9	12.5	3.06	1.79	<0.0001	7.33	29.6	12.96		
C-120, R3688	0	2.560	0.683	1.610	0.655	1.39	0.3791	7.01	46.7	56.7	11.87	2.56	1.4	<0.04	7.5	29.8	12.93		
C-121, R3689	1	2.530	0.675	1.630	0.663	1.54	0.4200	2.85	34.4	50.8	10.10	2.71	1.47	<0.04	7.83	29.8	12.91		
C-122, R3690	2	3.720	0.992	2.410	0.980	1.68	0.4582	3.16	32.1	63.3	9.070	2.82	1.64	<0.04	8	29.4	12.88		
C-123, R3691	3	2.770	0.739	1.810	0.736	1.79	0.4882	4.23	29.5	83.8	8.755	2.78	1.64	<0.04	8.6	28.8	12.84		
C-124, R3692	4	2.670	0.712	1.770	0.720	1.7	0.4636	3	17.8	74.2	8.160	2.73	1.57	<0.04	9	28.2	12.81		
C-125, R3693	6	2.35	0.627	1.620	0.659	1.85	0.5045	2.95	5.9	92.5	6.732	2.86	1.58	<0.04	9.25	28	12.74		
C-126, R3694	8	0.316	0.084	0.649	0.264	2.42	0.6600	2.15	<0.4		5.712	2.87	1.67	0.076	9.5	28	12.71		
C-127, R3695	10	<0.010	0.000	0.134	0.055	2.71	0.7391	3.15	<0.4	98.8	5.632	3.09	1.87	<0.04	10	27.8	12.6		
C-128, R3696	12	<0.010	0.000	0.0133	0.005	2.16	0.5891	3.16	<0.4	100	5.508	3.02	1.88	<0.04	10.5	27.2	12.57		
C-129, R3697	14	<0.010	0.000	<0.010	0.000	2.03	0.5536	4.03	<0.4		4.488	2.96	1.84	<0.04	11	26.8	12.56		
C-130, R3698	16	<0.010	0.000	<0.010	0.000	1.93	0.5264	3.19	<0.4	101	4.828	3.04	1.85	<0.04	11.5	27.2	12.51		
																	12	27.4	12.39
																	13	26.6	12.37
																	13.5	26.8	12.36
Sample #	Time (h)	U(ug/mL)	Pu239 40 (mCi/mL)	Am241 (mCi/mL)	Cs137 (mCi/L)	Sr90 (uCi/L)	DSC	TGA											
C-120B, R3612	0	4.05	0.286	1.84	1.35	1810	22.31/g	79.41% H2O											
C-120, R3688	0	2.24	<0.0894	0.136	1.27	1500													
C-121, R3689	1	3.19	<0.0955	0.21	1.30	1560													
C-122, R3690	2	3.79	<0.1	0.202	1.29	1250													
C-123, R3691	3	5.98	<0.0864	0.134	1.31	898													
C-124, R3692	4	3.98	<0.0942	0.159	1.26	761													
C-125, R3693	6	3.14	<0.0954	0.0863	1.28	253													
C-126, R3694	8	3.71	<0.126	<0.128	1.31	1.09													
C-127, R3695	10	8.95	0.749	<0.106	1.33	1.04													
C-128, R3696	12	7.62	2.27	<0.119	1.30	1.88													
C-129, R3697	14	8.61	2.23	<0.121	1.30	0.57													
C-130, R3698	16	4.7	2.4	<0.127	1.34	0.617													
C-130C, R3699	16	3.48	0.202	0.128	1.38	216	no exother	84.51% H2O											

WHC-EP-0701

Ozonolysis of Genuine 101-SY (800 mL of 3:1 volume water:waste blend) on 16 April 1993.
 Notebook WHC-N-656 1, pages 36 & 38.

Sample #	Time (h)	TOC (g/L)	TIC (g/L)	TC (g/L)	Cr(VI) (g/L)	Tot.Cr (g/L)	Al (g/L)	Ca (g/L)	Fe (g/L)	Ni (g/L)	Na (g/L)	Sr (g/L)	Si (g/L)	Zn (g/L)	Ag (g/L)	Mn (g/L)	ET (hours)	Temp (C)
																	0	24
C-100B, R3811	0	5.400	2.800	8.200	0.0608	0.6780	7.94	0.0621	0.0471	0.0648	81	0.000563	0.153	0.00311	0.000399	0.0124	0.33	24.4
C-100, R3699	0	4.370	2.840	7.210	0.0426	0.0621	12.5	0.05	0.00509	0.0606	86.4	0.000178	0.135	0.000477	0.000185	0.000282	0.75	28.2
C-101, R3700	1	4.350	3.090	7.440	0.0055	0.0622	13.4	0.0498	0.00464	0.0612	92.2	0.000164	0.125	0.000536	0.000728	0.000112	1	29.2
C-102, R3701	2	4.120	3.180	7.300	0.0612	0.0659	13.3	0.0474	0.00474	0.06	91.7	0.000156	0.119	0.000327	0.00085	9.29E-05	2.67	29
C-103, R3702	3	3.930	3.310	7.240	0.0655	0.0732	13.1	0.0453	0.00471	0.0605	90.1	0.000126	0.124	0.000232	0.000945	0.000129	3	29
C-104, R3703	4	3.630	3.490	7.120	0.0696	0.0735	13.3	0.0415	0.00456	0.0591	91.3	0.000104	0.115	0.000323	0.000982	6.85E-05	3.33	29
C-105, R3704	6	3.570	3.530	7.100	0.0883	0.0949	13.5	0.0261	0.00458	0.0564	92.5	<0.000075	0.111	0.000224	0.00126	5.57E-05	4	29.2
C-106, R3705	8	1.630	5.510	7.140	0.545	0.4620	10.3	<0.00022	0.00401	0.00532	92.1	<0.000075	0.0932	0.000324	0.000859		5	30.2
C-107, R3706	10	2.060	6.060	8.120	1.49	1.62	8.59	<0.00022		0.00359	92	<0.000075	0.0742	0.000216	0.000528		6	30.2
C-108, R3707	12	0.864	6.140	7.004	1.67	1.81	8.64	<0.00022	0.00351	<0.00033	93.1	<0.000075	0.0719	0.000263	0.000697	0.00036	7	30.4
C-109, R3708	13.9	0.902	6.230	7.132	1.65	1.77	8.33	<0.00022	0.00343	<0.00033	93	<0.000075	0.0712	<0.0001	0.000819	0.00117	8	29.4
C-110, R3709	15.9	0.897	6.000	6.897	1.63	1.81	7.86	<0.00022	0.00355	<0.00033	94.8	<0.000075	0.0761	<0.0001	0.000689	0.00113	9	28.2
																	10	28.2
																	11	27.5
																	12	27.6
																	13	27
																	13.9	27.4
																	15	27.2
																	15.9	27.6

Sample #	Time (h)	HCO2 (g/L)	C2H3O2 (g/L)	C2H3O2 (g/L)	C2O4 (g/L)	C2O4 (g/L)	Cl (g/L)	NO2 (g/L)	NO3 (g/L)	OH (g/L)	PO4 (g/L)	SO4 (g/L)	F (g/L)
C-100B, R3811	0	2.69	0.717	1.78	0.724	1.24	0.3382	3.36	44.2	55.8	14.30	3.36	1.96 <4.14
C-100, R3699	0	2.550	0.680	1.810	0.736	1.36	0.3709	6.67	78.2	97	12.90	3.48	1.77 <0.04
C-101, R3700	1	2.630	0.701	1.780	0.724	1.4	0.3818	4	75.2	120	11.53	3.32	1.89 <0.04
C-102, R3701	2	2.650	0.707	1.720	0.700	1.38	0.3764	3.37	34.2	65.2	12.05	3.17	1.76 <0.04
C-103, R3702	3	2.350	0.627	1.400	0.569	1.39	0.3791	3.18	24.7	73.6	10.50	3.31	1.79 <0.04
C-104, R3703	4	2.400	0.640	1.460	0.594	1.51	0.4118	3.31	19.5	83.8	8.55	3.31	1.67 <0.04
C-105, R3704	6	2.200	0.587	1.470	0.598	1.51	0.4118	2.97	3.99	97.5	7.00	3.18	1.65 <0.04
C-106, R3705	8	0.213	0.057	0.376	0.153	2.14	0.5836	3.57	<0.4	115	6.80	3.38	1.99 <0.04
C-107, R3706	10	<0.01	0.000	0.0638	0.026	1.86	0.5073	4.42	<0.4	109	6.09	3.2	2 <0.04
C-108, R3707	12	<0.01	0.000	<0.01	0.000	1.51	0.4118	4.44	<0.4	119	5.73	2.98	1.89 <0.04
C-109, R3708	13.9	<0.01	0.000	<0.01	0.000	1.6	0.4364	3.3	<0.4	110	5.76	3.36	2.05 <0.04
C-110, R3709	15.9	<0.01	0.000	<0.01	0.000	1.63	0.4445	3.58	<0.4	116	5.90	3.42	3.11 <0.04

Sample #	Time (h)	U (ug/mL)	Pu239,40 (nCi/mL)	Am241 (nCi/mL)	Cs137 (mCi/L)	Sr90 (uCi/L)	DSC	TGA
C-100B, R3811	0	3.32	0.293	0.515	153	2050	22.6J/g	76.96% H_2O
C-100, R3699	0	4.55	<0.0568	0.161	145	1720		
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