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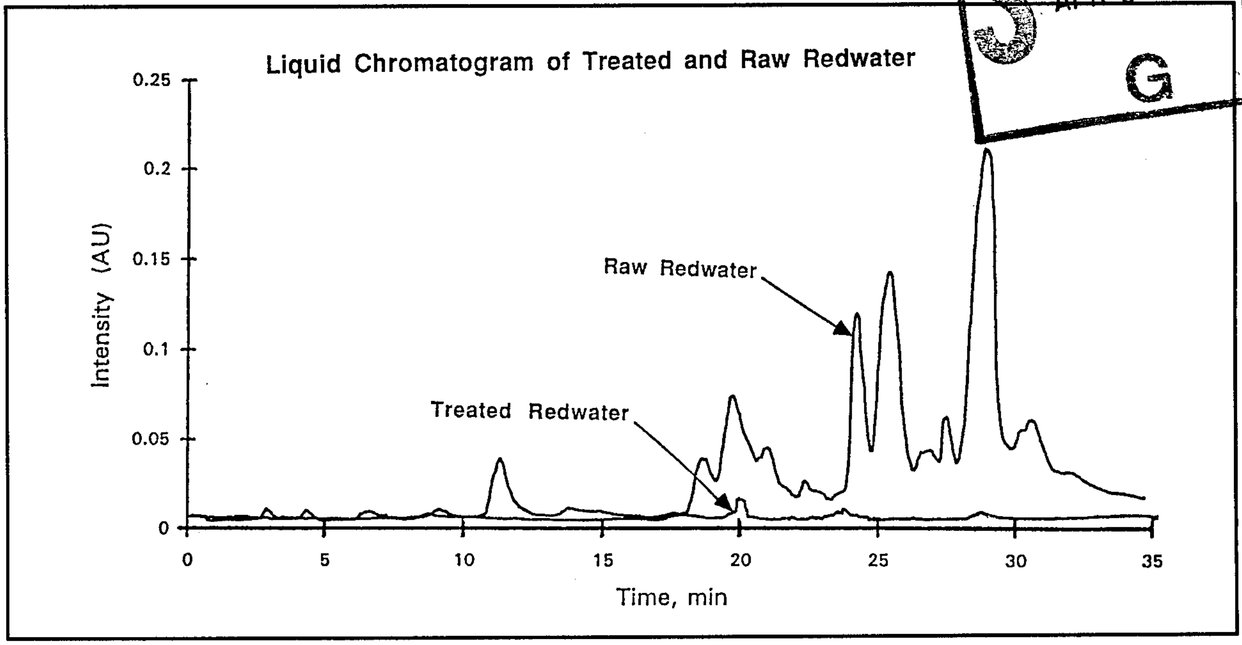
TNT Redwater Treatment by Wet Air Oxidation

by
Stephen W. Maloney, Veera M. Boddu, Kotu K. Phull, and Oliver J. Hao


Liquid Chromatogram of Treated and Raw Redwater

Trinitrotoluene (TNT) is one of the most widely used military explosives. The manufacturing process creates a highly toxic, reactive waste called "redwater." Increasingly stringent environmental regulations no longer allow the Army to dispose of redwater by burning it or selling it to the paper industry; alternate disposal solutions must be found. One feasible alternative is the oxidation of redwater at high temperatures and pressures, or wet air oxidation (WAO).

Oxidation temperatures between 225 °C and 300 °C may provide effluent that can be effectively treated using conventional biological wastewater treatment methods. A WAO temperature of 280 °C was proven by toxicity experiments in this report to be the optimal temperature for providing an effluent with the fewest remaining impurities that is best suited for biological treatment. The estimated cost of treating a gallon of redwater using WAO is \$0.35 if treated at 280 °C and \$1.02 if treated at 340 °C. A redwater treatment plant, designed for treating 16,000 gallons of redwater at a temperature of 280 °C, is estimated to cost \$3.9 million, with a total capital cost per year of \$730,000.

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13. ABSTRACT (Maximum 200 words)

Trinitrotoluene (TNT) is one of the most widely used military explosives. The manufacturing process creates a highly toxic, reactive waste called "redwater." Increasingly stringent environmental regulations no longer allow the Army to dispose of redwater by burning it or selling it to the paper industry; alternate disposal solutions must be found. One feasible alternative is the oxidation of redwater at high temperatures and pressures, or wet air oxidation (WAO).

Oxidation temperatures between 225 °C and 300 °C may provide effluent that can be effectively treated using conventional biological wastewater treatment methods. A WAO temperature of 280 °C was proven by toxicity experiments in this report to be the optimal temperature for providing an effluent with the fewest remaining impurities that is best suited for biological treatment. The estimated cost of treating a gallon of redwater using WAO is $0.35 if treated at 280 °C and $1.02 if treated at 340 °C. A redwater treatment plant, designed for treating 16,000 gallons of redwater at a temperature of 280 °C, is estimated to cost $3.9 million, with a total capital cost per year of $730,000.

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Executive Summary

The wet air oxidation (WAO) process is one of four technologies recommended for further evaluation by PEI Associates Inc. as a result of their evaluation of 30 different treatment technologies for redwater treatment (PEI Associates, 1990). Redwater is a wastewater listed as hazardous under the Resource Conservation and Recovery Act (RCRA), generated during the manufacture of trinitrotoluene (TNT). The evaluation was performed for the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, MD from October 1988 to December 1989.

As environmental regulations on air pollution and land disposal become more stringent, WAO appears to be promising as an efficient and cost-effective treatment process for redwater. This report summarizes the results of a laboratory WAO study on redwater, performed by personnel at the Department of Civil Engineering at the University of Maryland from May 1990 to October 1992. Part of the work was also performed at the Hazardous Waste Research and Information Center, Champaign, IL.

The main objectives of the research were to summarize the literature on WAO of redwater and similar wastes, perform WAO of redwater on a bench-scale system to obtain the oxidation kinetic information while proving the treatability of redwater, and subject the WAO-treated redwater to selected toxicity tests to determine the effectiveness of the WAO process. Specifically, the objectives of this research were to:

- conduct a literature review of WAO of redwater or similar wastes
- characterize the TNT redwater
- evaluate the feasibility of WAO for treatment of TNT redwater
- conduct a literature review of kinetic studies of WAO of hazardous wastes
- perform the WAO of diluted TNT redwater under various conditions to evaluate reaction rates
- perform carbon, sulfur, and nitrogen mass balances to determine their fate in the aqueous and gaseous phases
- determine the effects of catalysts/initiator on the WAO rate and find the optimum temperature, pressure, oxidant dose, and dilution
- obtain preliminary information on the toxicity of WAO-treated TNT redwater
- evaluate the WAO of redwater in terms of cost effectiveness and efficiency.

Analysis and characterization of redwater is important for understanding its behavior and treatment. To analyze the major redwater components, namely the dinitrotoluene sulfonates, an analytical method using reverse-phase, ion-pairing, high-pressure liquid chromatography (RPIPC) was developed for measuring dinitrotoluene sulfonic compounds. Only qualitative information could be obtained for the sulfonates in the raw and treated redwater because of unavailability of standards, the crude synthesis of the dinitritoluene sulfonates, and the uncertainty about the concentrations of the individual sulfonates used as standards. Analysis of the redwater is reported based on the information obtained from literature and laboratory experiments.

The WAO experiments were conducted using diluted orthonitrotoluene-produced redwater (1:100) at six different temperatures (200, 230, 260, 290, 320, and 340 °C)* and three initial oxygen pressures (PO_2 = 19, 90, and 190 pounds per square inch [psi] at 25 °C), with a 1-hour reaction time. At 340 °C and 2150 psi, almost 100 percent reduction was achieved for both total organic carbon (TOC) and chemical oxygen demand (COD), thus indicating a complete conversion and oxidation of the oxidizable materials present in the redwater. The dinitrotoluene (DNT) sulfonic salts were not detectable in the final WAO effluent, and only a trace amount of dinitrobenzene (DNB) remained. Accumulation of acetic acid was observed under lower WAO temperatures until an oxidation temperature of about 300 °C was reached, after which the acetic acid was further oxidized.

The results indicate that the contaminant removal efficiencies are a function of temperature, and, to a lesser extent, oxygen pressure. The kinetic rate studies included evaluation of the effect of redwater concentration, temperature, oxygen pressure, salt, and catalyst concentration on the rate of WAO. Analyses of the first sample collected within 5 minutes show a significant reduction of easily oxidizable COD. The amount of the rapid COD reduction is a function of experimental conditions: the more stringent the condition is, the greater the initial "flash" reduction. Thereafter, initial oxygen pressure exhibits no effect on the subsequent oxidation rate constant of the slowly oxidizable compounds, and the reaction proceeds at a first-order rate with respect to COD or TOC.

The substrate mass balance experiment was conducted using diluted redwater (1:100) at 260 °C and PO_2 = 0.69 megapascals [MPa] (100 psi at 25 °C), with a 1-hour reaction time. The results indicate that 85 percent of the initial organic C is accounted for: 44 percent CO_2; 4 percent CO; 33 percent dissolved CO_2; and 19 percent TOC remaining. The CO composition (0.33 percent) in the off-gases is approximately two orders of magnitude higher than National Ambient Air Quality

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* A table of metric conversion factors is located at the end of this report.

Standards, and the total hydrocarbons concentration (23 parts per million [ppm]) is close to that of Primary Air Quality Standards (U.S. Environmental Protection Agency). The amount of sulfate concentration in the treated sample is much higher than the sum of the measured inorganic sulfate and the organic sulfur associated with the DNT sulfonates initially present in the raw redwater. This indicates the presence of other unidentified S-containing organic compounds in redwater. The nitrogen analyses indicate a significant ammonium concentration (9 percent) in treated waste and a high N_2 concentration in the off-gas (72 percent); the others being NO_3^- (16 percent) and the residual nitroaromatics (3 percent). The extremely high percentage of NH_4^+ and N_2 clearly indicates that WAO is a complicated process involving both oxidation and reduction.

As for the catalyst addition, Cu(II) is effective not only in increasing the initial carbon reduction, but also in enhancing the overall rate and the extent of contaminant removal. However, the fate of Cu(II) and any toxic effects on biodegrading organisms remains to be investigated.

The preliminary toxicity results indicate that up to 75 percent volume fraction of treated redwater (320 °C, and $PO_2 = 90$ psi), i.e., 375 mL in a 500 mL sample size, does not produce any adverse effects on heterotrophic COD removal capability in a batch-activated sludge (BAS) system. However, there is a significant toxic effect on the enriched Nitrosomonas (bacteria) culture with the addition of the same fractions of treated redwater. The preliminary analysis indicates that the organic byproducts formed during the WAO of redwater are responsible for the observed adverse effects on nitrite production rates of the Nitrosomonas. The toxicity results reaffirm the preliminary findings that the WAO-treated redwater exerts toxic effects on Nitrosomonas and Acinetobacter growth, but has less impact on activated sludge (AS) in terms of COD removal. Further, treated samples at 340 °C appear to exhibit more inhibitory effect on both Acinetobacter and Nitrosomonas than those treated at 260 °C.

It is recommended that the use of WAO in conjunction with conventional biological treatment be investigated along with the investigation of the toxicity of treated redwater under different WAO or WAO/biotreatment conditions. Recommendations are also made to continue the research to investigate the fate of the nitro groups during WAO and to determine the effect of catalysts on reaction rates. If a significant amount of SO_x and NO_x gas is formed, increased capital and operations and maintenance (O & M) costs in meeting air quality regulatory standards would have to be considered in the overall evaluation of WAO treatment of TNT redwater. Catalyzed WAO of redwater might prove to be a cost-effective alternative for redwater treatment and disposal. Complete characterization of redwater components is deemed necessary not only because of its impact on the treatment process but also for an effective process performance evaluation. Recommendations are made to continue the investigation on the kinetics and possible reaction mechanisms of redwater treatment to gain a better understanding of the WAO process, and to establish optimum process parameters. Also, the identification and quantification of the byproducts present in the WAO-treated effluent is important in the case of direct discharge of treated redwater into receiving waters or to a sewage treatment plant. The maximum cost estimate for treating a gallon (gal) of redwater using WAO is $1.02 if treated at 340 °C, which compares well with the cost of contract disposal ($1.17). The estimated cost of treating a gallon of water using WAO if treated at 280 °C is $0.35.

This report can be used as guidance for additional research in this area or for scaleup studies.

Foreword

This study was conducted for the U.S. Army Corps of Engineers (USACE), under Project 4A162721D048, "Industrial Operations Pollution Control Technology"; Work Unit PE-TF3, "Redwater Treatment"; and Office of the Assistant Chief of Staff for Installation Management (OACS[IM]). The OACS(IM) technical monitor was Richard Eicholtz, SFIM-AEC-TSD.

The study was performed in part by the Department of Civil Engineering at the University of Maryland, College Park, MD, under contract to the Environmental Engineering Division (EP), Environmental Sustainment Laboratory (EL), U.S. Army Construction Engineering Research Laboratories (USACERL). Kotu K. Phull and Oliver J. Hao are with the University of Maryland. Dr. Edgar D. Smith is Acting Chief, CECER-EP, and William D. Goran is Chief, CECER-EL.

LTC David J. Rehbein is Commander and Acting Director, USACERL. Dr. Michael J. O'Connor is Technical Director.

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1 Introduction

Background

Trinitrotoluene, often referred to as TNT, is one of the most widely used military explosives. Conventionally, TNT is manufactured by successive nitration of toluene with mixed nitric and sulfuric acids. This process creates small quantities of unsymmetrical isomers and residual dinitrated species, which can result in potential differences in explosion properties of the TNT and make storage and handling difficult. Consequently, these products must be removed during the manufacturing process. The most common method of removing these *m*-substituted products from the mixture is to use a sellite solution (15 percent aqueous sodium sulfite) as a reactant. The spent sellite solution with all the unwanted products is dark red and is called "redwater."

Redwater is classified by the U.S. Environmental Protection Agency (USEPA) as a reactive waste (number K047, 40 CFR, 261.32) and must be treated properly before disposal. In the past, redwater was burned in rotary kilns or sold to the paper industry (PEI Associates, Inc. 1990). Increasingly stringent environmental regulations no longer allow the Army to use these disposal options; alternate solutions must be found.

Generally, pollutants may be removed/detoxified/degraded using various biological or physicochemical processes. However, some treatment processes may be too costly or result in "cross-media" pollution (e.g., the disposal problem of sludge, air-stripping of volatile organic compounds [VOCs]). To eliminate these hazardous waste compounds from the environment, they must be converted (e.g., oxidized) to relatively safe products. This can be accomplished by conventional incineration. However, the air pollution caused by incineration limits its practical applications. Like incineration, carbon adsorption is not only energy-intensive, but creates a polluted waste stream (spent carbon) that needs to be regenerated or disposed. Biological treatment, usually the method of choice for wastewater treatment, cannot successfully treat certain organic compounds due to their toxic, inhibitory, or refractory nature. Also, biological oxidation is quite sensitive to changes in waste concentrations (shock loads). Use of chemical oxidation for ultimate degradation of organics, i.e., complete destruction to CO_2 and H_2O, may be extremely expensive. Integration of partial chemical oxidation (i.e., structural change of parent compound) with biological treatment may represent a cost effective means of treating toxic wastes, including redwater.

U.S. Army regulations (e.g., Army Regulation [AR] 200-1) explicitly require the Army to maintain a leadership role in exploring and evaluating innovative environmental control technologies to treat wastes generated from its activities. For over a decade, the Army has been actively evaluating alternative technologies for environmentally sound and cost-effective treatment of TNT redwater. During the past several years, at least three independent studies have been conducted for the U.S. Army by private consultants to investigate potential technologies for the reduction and/or treatment of TNT redwater (Eckenrode et al. 1980; Foster Wheeler 1988; PEI Associates, Inc. 1990). PEI Associates, Inc. (1990) evaluated 30 technologies for treating redwater, identifying four for further evaluation: wet air oxidation (WAO), circulating bed combustion, slagging rotary Kiln combustion, and submerged combustion. The following criteria were used by PEI evaluators: (1) theoretical potential of technology for suitable treatment of redwater, (2) current application and status of the technology, (3) environmental impact, (4) time and cost to develop to implementation stage, and (5) complexity of process, system operation, and flexibility of operating parameters.

Wet air oxidation is the oxidation of chemicals at high temperatures (150-300 °C) and pressures (800-2500 psi). The process is typically used to oxidize sewage sludge, regenerate spent activated carbon, and treat process wastewaters. Wastewaters treated using this technology include pesticide wastes, petrochemical process wastes, cyanide-containing metal finishing wastes, spent caustic wastewaters containing phenolic compounds, and some organic chemical production wastewaters. Recently, the WAO technique has been successfully employed to treat a variety of hazardous wastes, including explosive wastes as discussed in Chapter 2. In 1984, the USEPA specified WAO as a "Best Demonstrated Available Technology" for many land-banned wastes under the Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA). During the past decade, WAO has proven to be an effective technology for ultimate destruction of a variety of hazardous wastes. However, its feasibility as a treatment for redwater is uncertain.

The results obtained in this study also have been published in Phull (1992) and Hao et al. (1993a, b).

Objectives

The main objective of this research was to evaluate WAO technology for the treatment of the TNT manufacturing wastewater, or redwater. Specifically, the goals were to:

- Conduct a literature review of redwater characteristics, the WAO process in general, and its success with hazardous compound destruction. Use pertinent literature to evaluate the feasibility of WAO for treatment of TNT redwater and to establish operating conditions such as temperature, pressure, reaction time, and oxidant dose.
- Perform bench-scale reaction studies to obtain the kinetic information required to determine optimum process conditions such as temperature, pressure, oxidant dose, and catalysts. Kinetic studies should also reveal the products formed by the WAO process.
- Subject the treated redwater to toxicity tests to ensure WAO success and safe disposal.
- Evaluate the WAO of redwater in terms of cost effectiveness and efficiency.

Approach

Pertinent literature relating to the WAO process was reviewed. Bench-scale experimentation was performed to test the feasibility of the technology. To achieve and quantify success in using the WAO process, the waste stream (and the initial components of redwater itself) must be characterized. To attempt this, TNT redwater was analyzed using existing analytical methods, e.g., gas chromatography (GC) for certain nitroaromatics, and by developing new methods to quantify DNT sulfonates, to the extent possible. The treated redwater was also tested for toxicity using three kinds of bacterial cultures. Preliminary estimates of WAO process plant and operating costs have been obtained from Zimpro-Passavant, Inc.

Scope

The techniques described and evaluated in this report apply to Army industrial activities in the United States responsible for manufacturing TNT destined for Army-specification explosives. The goals of treating reactive waste streams from past, present, and future activities, and avoiding cross-media pollution are addressed within the confines of the infrastructure of existing TNT production facilities of the Army.

Mode of Technology Transfer

It is anticipated that the findings and recommendations in this report will be used as a foundation for developing a large scale demonstration for treatment of TNT redwater by the U.S. Army Environmental Center.

2 Literature Review

This literature review includes a brief summary of TNT redwater generation and characteristics. A literature review of WAO kinetic studies, wet air oxidation reaction mechanisms, and toxicity tests of the oxidation products are also summarized.

TNT Production and Redwater Generation

The nitroaromatic compounds are an important class of explosive substances. One of these, the symmetrical 2,4,6-TNT is the most important and widely-used explosive. The advantages of TNT over other explosives are: low cost, safety in handling, excellent chemical and thermal stability, and favorable explosive properties.

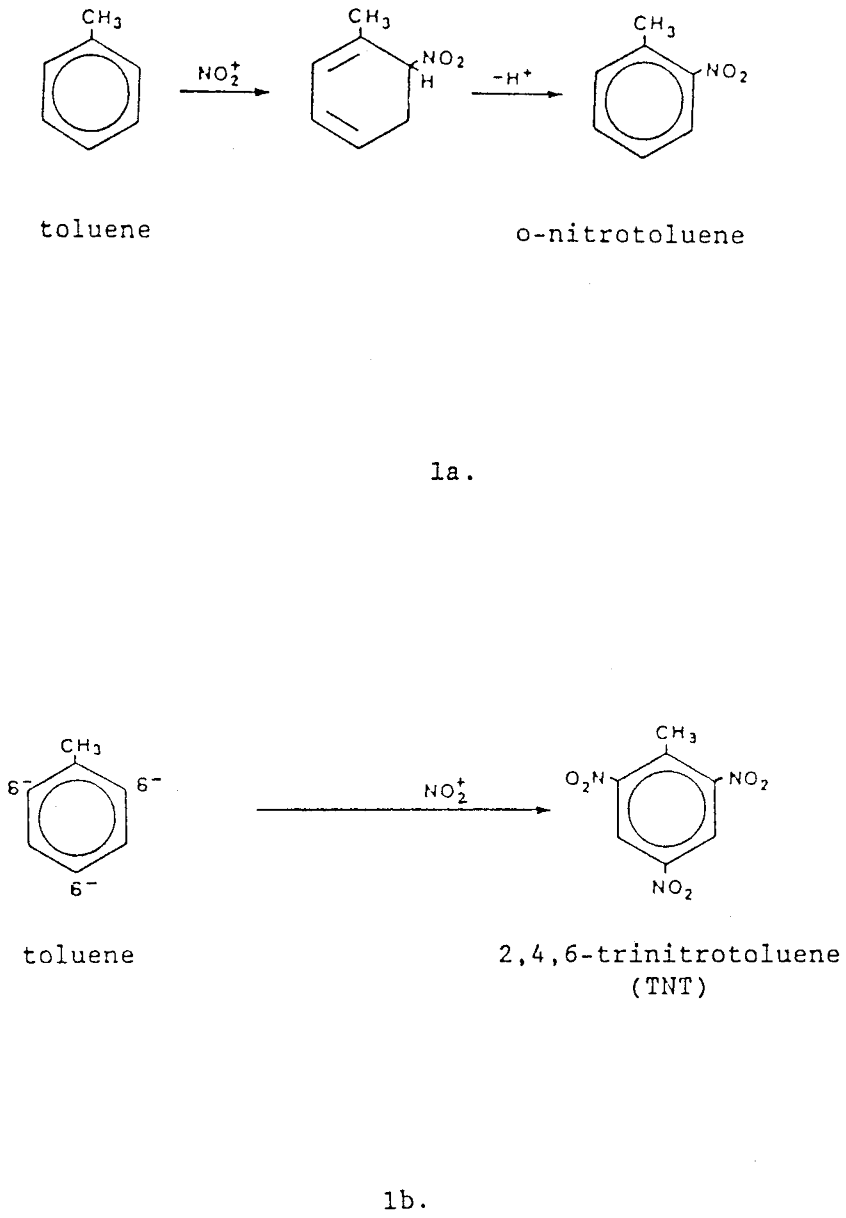
The manufacture of TNT consists of two main processes: (1) nitration of toluene to crude TNT, and (2) TNT purification to remove any unsymmetrical isomers. During the TNT purification process, the redwater is produced. Each of these processes is described below.

Nitration of Toluene to Crude TNT

The preparation of TNT occurs in three distinct nitration stages:

toluene → mononitrotoluene → dinitrotoluene → trinitrotoluene

Nitric and sulfuric acid together are used as the nitrating agent. The presence of a methyl group facilitates the formation of mononitrotoluene as a classic example of an electrophilic substitution reaction (Figure 2.1a). Because of increased electron density at the ortho and para positions in the benzene ring, further nitration results primarily in the production of 2,4,6-TNT (Figure 2.1b). Unfortunately, small amounts of unsymmetrical TNT isomers are also formed during nitration of toluene as shown in Table 2.1. This results in a lower purity of 2,4,6-TNT and hence a lower-grade TNT. In addition to the unsymmetrical TNT isomers, oxidative reactions of the methyl group and the aromatic ring occur, resulting in many additional products (Table 2.2). An example of oxidation of the



1a.

1b.

Figure 2.1. A classic example of electrophilic substitution.

Table 2.1. Typical concentrations of TNT and DNT isomers produced during the 3-stage nitration of toluene to TNT.

Isomer	% weight
TNT Isomers	
2,4,6-trinitrotoluene (α-TNT)	95.1
2,4,5- (or) 3,4,6-trinitrotoluene (γ-TNT)	2.69
2,3,4-trinitrotoluene (β-TNT)	1.36
2,3,5-trinitrotoluene (ε-TNT)	0.009
3,4,5-trinitrotoluene (δ-TNT)	0.002
2,3,6- (or) 2,5,6-trinitrotoluene (η-TNT)	0.29
DNT Isomers	
2,3-DNT	0.33
2,5-DNT	0.15
3,5-DNT	0.06

Source: Urbanski 1964.

methyl group to produce trinitrobenzyl alcohol (TNBOH), trinitrobenzaldehyde (TNBAL), and trinitrobenzoic acid (TNBA) is shown in Figure 2.2 (Kohlbeck et al. 1973). The oxidation of TNT to TNBAL is rapid. If the complete oxidation of TNBAL to TNBA is inhibited, a white compound is formed as shown in Figure 2.2.

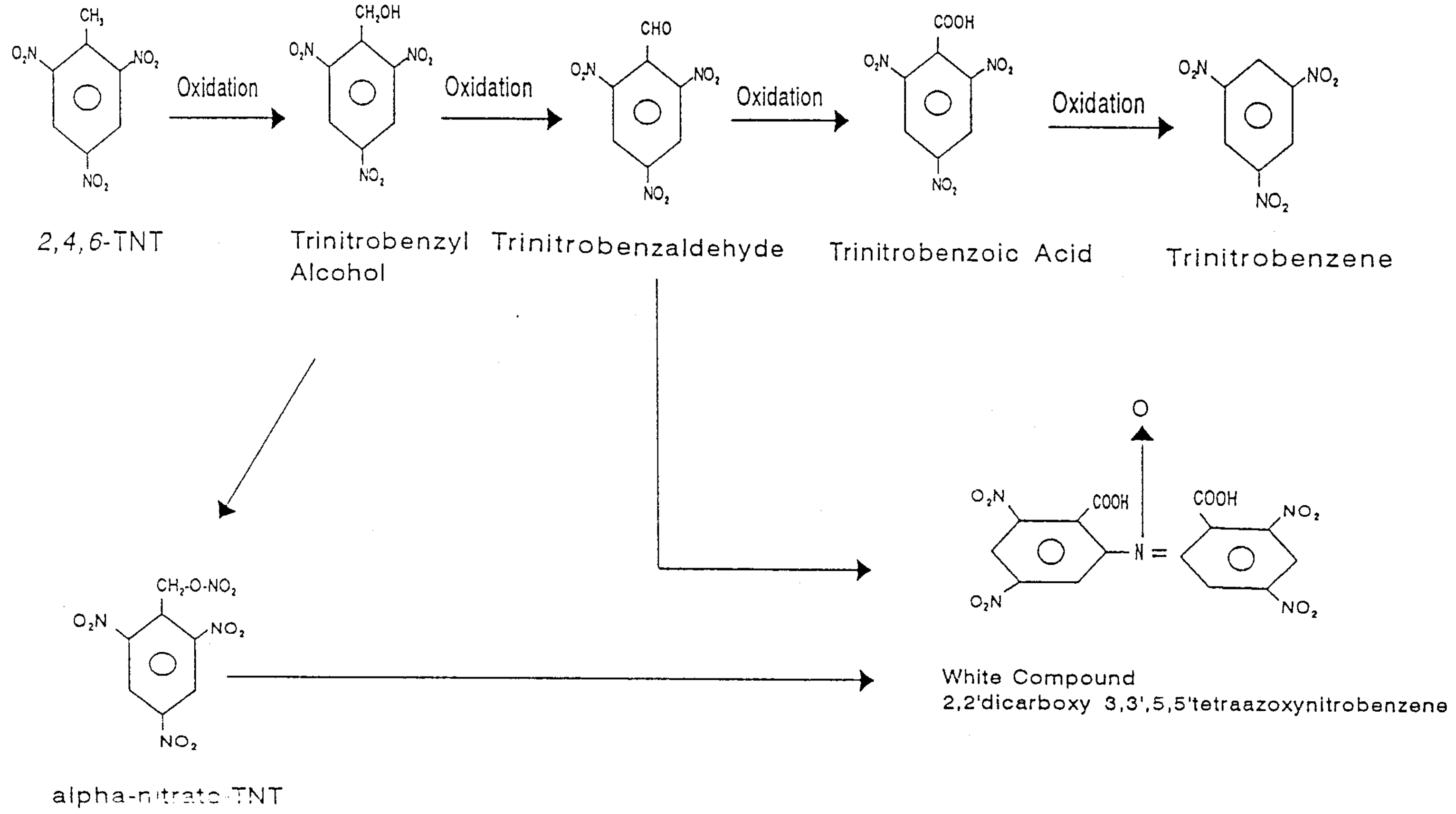
Purification of Crude TNT

The simplest and most frequently used method of removing unsymmetrical TNT isomers (4.5 percent by weight) from crude TNT to meet military specifications is

Table 2.2. Oxidation products formed during TNT production.

4,5-dinitro-o-cresol
2,6-dinitro-p-cresol
2,4,6-trinitro-m-cresol
2,4,6-trinitrophenol
2,4-dinitrobenzoic acid
3,4-dinitrobenzoic acid
2,4,6-trinitrobenzoic acid
2,4,6-trinitrobenzaldehyde
1,3-dinitrobenzene
1,3,5-trinitrobenzene
2,4-dinitro-5-hydroxy benzoic acid
2,2',4,4',6,6'-hexanitrobibenzyl (HNBB)
3-methyl-2,2',4,6,6'-pentanitrodiphenylmethane (MPDM)
2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene (White Compound)
2,2',4,4',6,6'-hexanitrstilbene (HNS)
3,3',5,5'-tetranitroazoxybenzene (TNAB)
nitrato-2,4,6-trinitrotoluene
tetranitromethane (TNM)

Source: Kohlbeck et al. 1973.



(Source: Kohlbeck et al. 1973.)

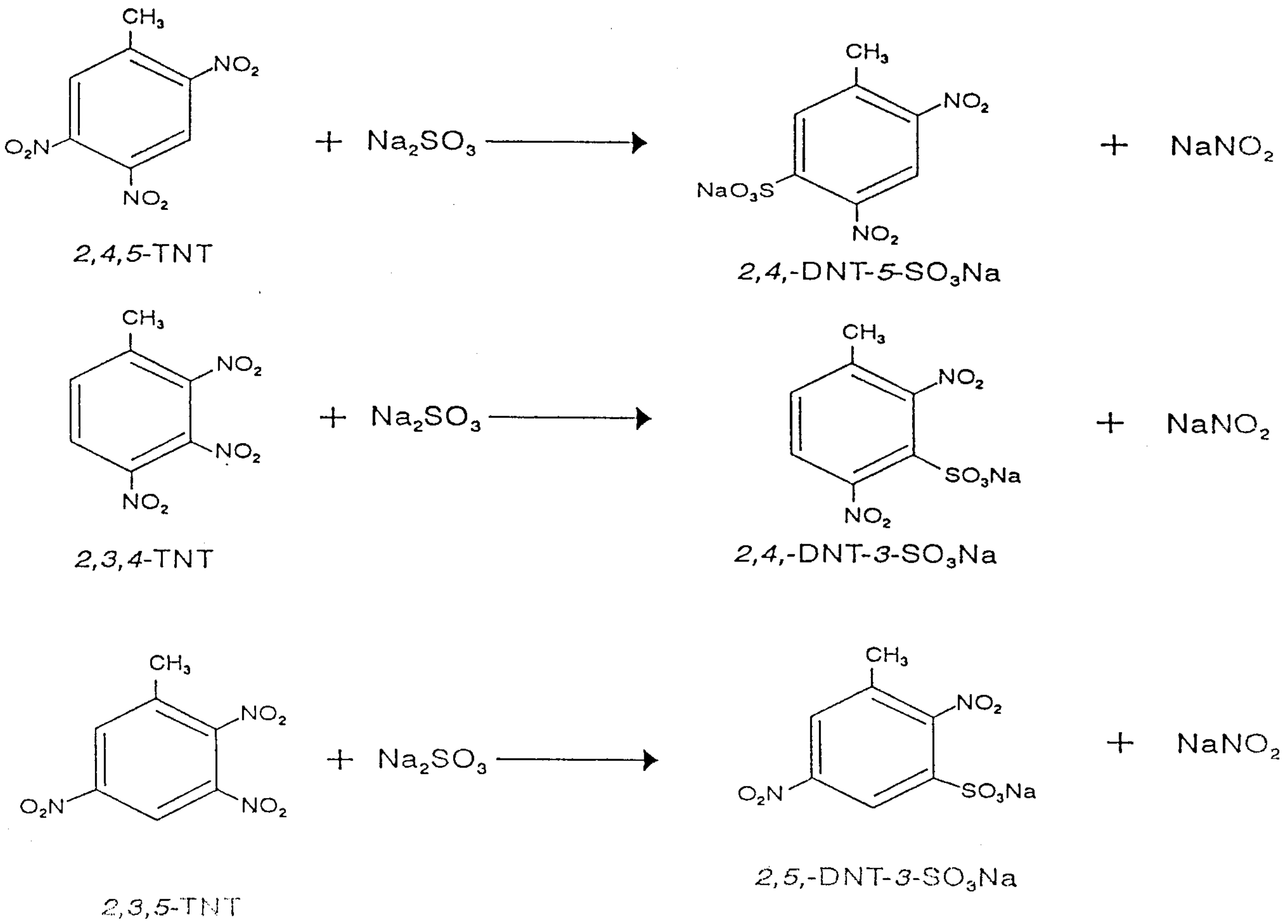
Figure 2.2. Oxidation of trinitrotoluene.

the reaction of crude TNT with sulfite solution (16 percent Na_2SO_3 and 0.2 percent NaHS). This is commonly referred to as the "selliting" process, and is shown in Figure 2.3 (Urbanski 1964). The DNT sulfonated compounds formed are water-soluble sodium salts and are easily separated from α-TNT by washing with water. The reaction is dependent on pH, temperature, and sulfite concentration. For example, as pH increases, the impurity concentration in TNT decreases significantly (Table 2.3, Hayes 1982). The α-TNT also reacts with sulfite, although the reaction is relatively slow compared to that of the unsymmetrical TNT isomers.

Redwater Characteristics

The addition of sodium sulfite to crude TNT yields a product with a deep "red" color, commonly known as redwater. An exact reason for the red color is not apparent based on the literature review. However, several investigators (Okamoto and Wang 1977; Jenkins and Schumacher 1990) have suggested that the trinitrobenzyl ion formed during the oxidation of the methyl group might be responsible for the appearance of red color. Other possible causes include the formation of the Meisenheimer complex (Urbanski 1964) and the formation of an α-TNT-sellite complex (Hall and Lawrence 1976).

Typical redwater composition is shown in Table 2.4. The data is estimated based on anticipated crude TNT composition, purification reaction mechanisms, and theoretical calculations (PEI 1990). It is expected that redwater contains a large quantity of nitrite from the sellite process (Figure 2.3), nitrate from HNO_3, sulfite from Na_2SO_3, and sulfate. As can be calculated from Table 2.4, the concentration of these inorganic solids amounts to about 6.8 percent (by weight) of the redwater, i.e., 45 percent of 15 percent total solids. In addition, the organic component contains all the DNT sulfonated compounds, salts of "white compound," and other complex products. The concentration of total nitrobodies from Table 2.4 is about 8.3 percent (92 percent of the nitrobodies are sulfonated compounds), and may be as high as 20 percent (Hayes 1982). Hall and Lawrence (1976) indicated that in addition to α-TNT, 1,3,5-trinitrobenzene (TNB), 2,4,6-TNBAL, and 2,4,6-TNBOH, the nonpolar fraction of redwater contained four other unidentified components. They further concluded that the polar organic content of redwater was 13.1 percent, about one third of which contained the DNT sulfonates (2.7 and 1.2 percent, respectively, of 2,4-DNT-5-sulfonate and 2,4-DNT-3-sulfonate). The remaining two-thirds of the polar organic content consisted of water-soluble red α-TNT-sellite complex and/or its degradation products. Wang et al. (1982) reported the presence of hexantrinitrodibenzyl (HNBB), tetranitromethane (TNM), cyanic acid, dinitocresol, and phenol in addition to some of the above-mentioned constituents.



(Source: Urbanski 1964.)

Figure 2.3. Removal of unsymmetrical TNT isomers by sellite purification.

Table 2.3. Effect of pH on the impurity concentration in TNT after reactions with Na_2SO_3.*

pH	Impurity Weight % (2,4,5- and 2,3,4-TNT)
7.0	0.64
7.6	0.18
8.0	0.08
9.0	0.07

*See also: Hayes 1982.

Sodium sulfite does not react with DNT or trinitrobanzoicacid (TNBA). Therefore, most oxidation products present during TNT production (shown in Table 2.2) remain after the TNT purification process with Na_2SO_3 (Table 2.4).

In 1979, the USEPA listed redwater as a hazardous waste based on its reactivity. This reactivity was measured using a method similar to that reported by the U.S. Bureau of Mines (Bajpayee and Mainiero 1988). Shortly thereafter, contractor personnel (Hercules Inc.) at the Radford Army Ammunition Plant (RAAP) reportedly tried to convince the USEPA that redwater was not reactive and should not be listed as a hazardous waste. Nevertheless, USEPA listed redwater as a hazardous waste because of its suspected toxicity or carcinogenicity. Redwater is toxic to aquatic life and animals (Nay et al. 1974; Smock et al. 1976; Burrows et al. 1989). Nay et al. (1972, 1974) reported that the increase in the color intensity of TNT manufacturing wastewater indicated more toxicity and had a derogatory effect on biological and physicochemical waste treatment. Besides α-TNT, the redwater does contain two of the USEPA priority pollutants, 2,4- and 2,6-DNT. Currently, redwater is a RCRA-regulated waste (K047) which must be handled as a hazardous waste.

RAAP Continuous TNT Process

The following describes the TNT manufacturing process at RAAP, VA.

Nitration. A counter-current eight-stage process was used (Figure 2.4). Each stage consists of a nitrator and a separator. Toluene is fed into Nitrators # 1 and 2, while the nitrating acids (Oleum, a solution of sulfur trioxide in sulfuric acid, and strong HNO_3) are fed into Nitrator # 8. As toluene passes through the nitration stages, it becomes progressively nitrated, emerging from Separator # 8 as crude TNT. Strong HNO_3 is also fed into Nitrators # 7, 6, 5, and 4, and weak HNO_3 is added to Nitrators # 3, 2, and 1 (the concentration decreasing as the numbers do). Dilution water is added to nitrator # 1 to control the final

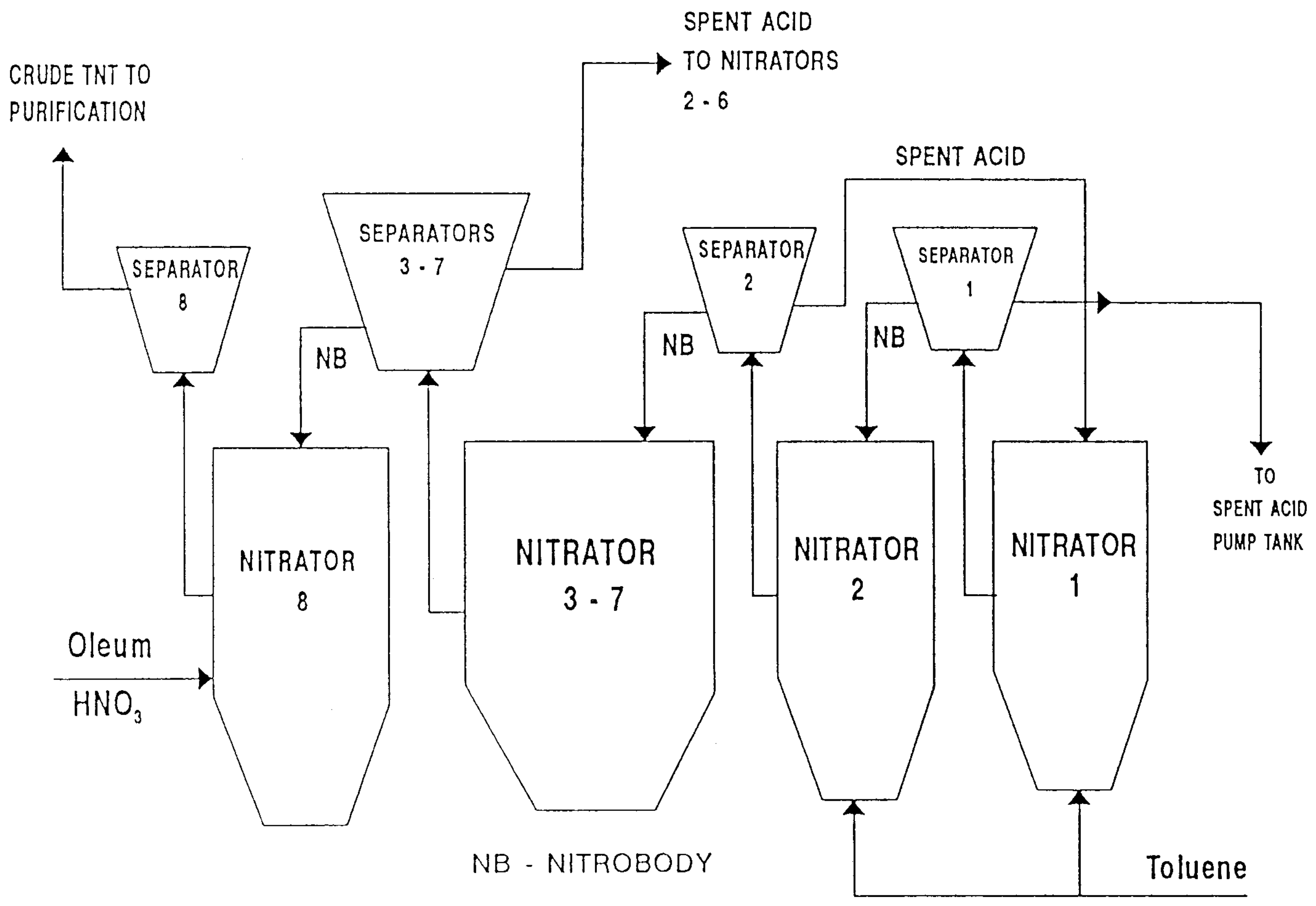
Table 2.4. Representative analyses of Radford Army Ammunition Plant (RAAP) redwater.

Solids, %	15
Water content (nominal), %	85
pH	7.0-9.7
Color	Dark red
Sp.Gravity	1.1
Solids heat value, BTU/lb	3200
Metal content, mg/L	
Calcium	346
Iron	307
Magnesium	90
Potassium	42
Aluminum	10
Chromium	4.9
Barium	3.0
Copper	2.3
Cadmium	0.7
Silver	0.4
Inorganic salts, wt. %	
Na_2SO_3-Na_2SO_4	32.3
$NaNO_2$ (sodium nitrite)	11.2
$NaNO_3$ (sodium nitrate)	1.5
Sodium sulfide (NaHS-Na_2S)	may be present
Sodium carbonate/bicarbonate	may be present
Subtotal inorganic salts	45.0
Nitrobodies, wt. %	
Sodium sulfonate of *2,4,5*-TNT	22.7
α-TNT-Sellite complex	16.2
Sodium sulfonate of *2,3,4*-TNT	9.6
Sodium sulfonate of *2,3,5*-TNT	2.0
Sodium sulfonate of *2,3,6*-TNT	Trace
2,4,6-TNBA (trinitrobenzoic acid) Na salt	1.0
White compound sodium salt	1.0
TNBAL-bisulfite addition compound (trinitrobenzaldehyde)	1.0
TNBOH (trinitrobenzyl alcohol)	1.0
Sodium nitroformate	0.5
3,4-DNBA (dinitrobenzoic acid) Na salt	Trace
2,3-DNBA (dinitrobenzoic acid) Na salt	Trace
TNB (trinitrobenzene)-Sellite complex	Trace
Dissolved *2,4*-DNT (dinitrotoluene)	Trace
Dissolved α-TNT (trinitrotoluene)	Trace
Subtotal nitrobodies	55.0

Source: PEI Associates Inc. 1990

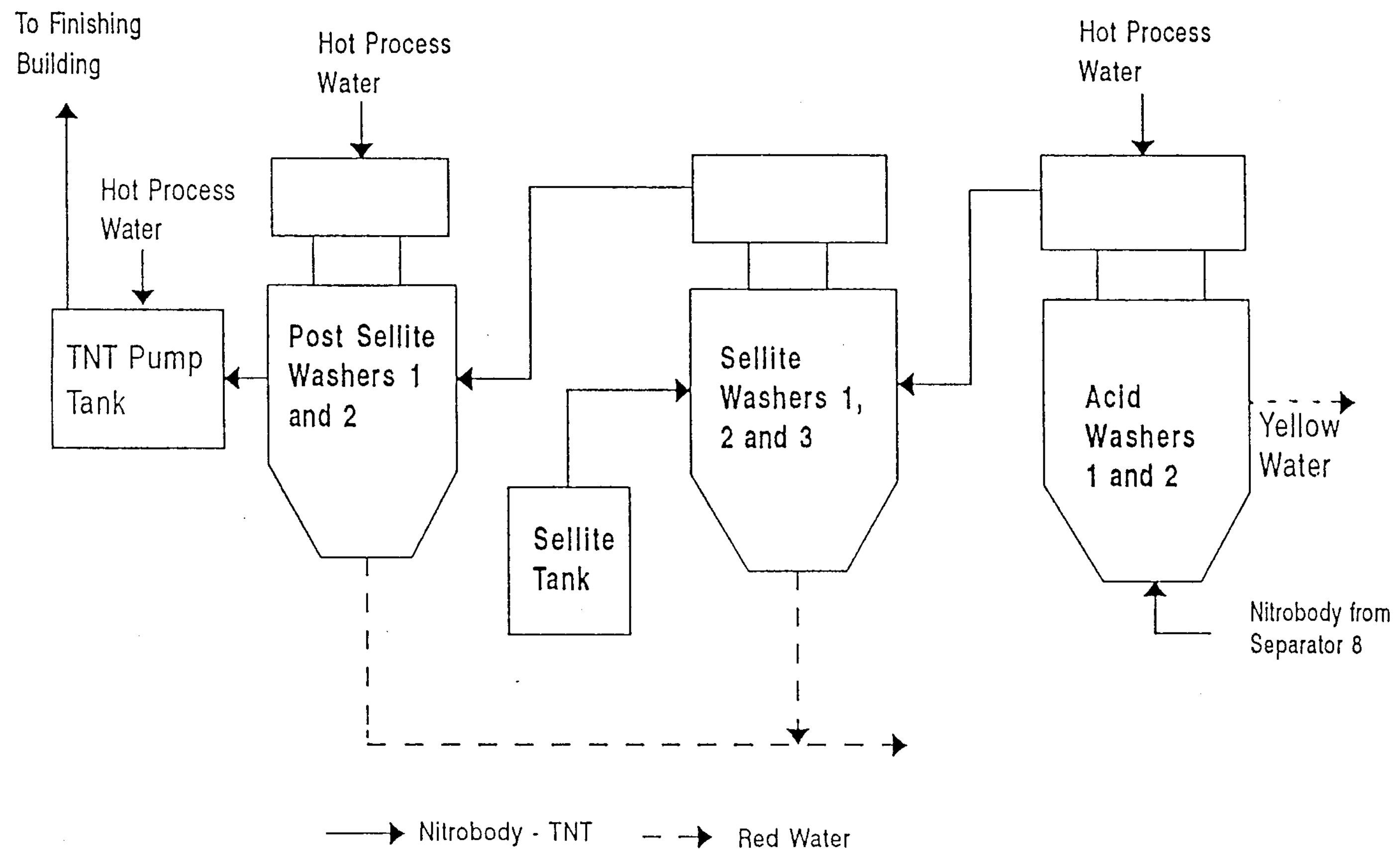
composition of spent acid leaving the nitration process. Typical temperature and substrate additions are shown in Table 2.5.

Sellite Purification. The crude TNT is purified in a series of countercurrent hot water and sodium sulfite wash systems (Figure 2.5). Crude TNT is first washed with hot water to remove entrained HNO_3 and H_2SO_4 in Washers # 1 and 2. Crude TNT is then reacted with sellite solution (16 percent Na_2SO_3 and 0.2



(Source: Phull 1992.)

Figure 2.4. Eight-stage continuous TNT process flow diagram.



(Source: Phull 1992.)

Figure 2.5. TNT purification process flow diagram.

percent NaHS) at a pH between 8.3 and 8.5 in Washers # 3, 4, and 5 to remove the unsymmetrical TNT isomers. The redwater generated from Washer # 3 is collected for treatment/disposal. After the sellite washers, the TNT receives two additional hot water washes and leaves Washer # 7 for further processing.

Processing of Purified TNT. The purified and washed TNT enters the TNT pump tank where recycled water or additional hot water is added to maintain a minimum 3:1 water to TNT ratio. The water/TNT slurry is then separated, dried, flaked, cut, packed, and loaded.

Redwater Disposal

There are four U.S. Army ammunition plants (AAPs) in the United States capable of producing TNT. The estimated amounts of redwater generated from these plants, when in operation, are: Joliet AAP, 23,000 gallons per day (gpd); Newport AAP, 19,200 gpd, Radford AAP, 15,400 gpd, and Volunteer AAP, 48,000 gpd. The exact amount of redwater generated would depend upon the manufacturing and purification processes used. An acceptable guideline, however, is 8 L (about 2 gal) of redwater per kilogram (about 2.2 lb) of TNT produced. The TNT has not been manufactured at Army AAPs since 1987, partially due to the redwater disposal problem.

Early (1940s) redwater disposal practices included direct discharge from TNT manufacturing plants into large streams where dilution was adequate, or into otherwise polluted streams not used as sources of drinking water supply. This practice was unacceptable to regulators and the public; subsequently, redwater was incinerated and the residual ash was disposed by land burial or in a landfill. In addition to the energy requirement, this presents a typical cross-media pollution problem—SO_2 and NO_x air pollution from the incineration operation, and water contamination with nitrobodies from the disposal of ash and condensate from the evaporation process.

Table 2.5. Typical temperatures and toluene/acid addition locations in the RAAP TNT production process.

Nitrator	Temp°C	Toluene	Weak HNO_3	Strong HNO_3	Oleum	Yellow Water
1	55	x	x			x
2	50	x	x			x
3	70			x		
4	80			x		
5	83			x		
6	90			x		
7	95			x		
8	100			x	x	

Redwater (about 35 percent concentration) was also sold to the paper industry as a supplemental source of sodium and sulfur. In 1986, USEPA withdrew exemption for redwater's sale to the paper industry.

Some researchers have investigated the possibility of eliminating the unwanted DNT isomers to minimize the amount of unsymmetrical TNT isomers formed (Schiff et al. 1978; Davis 1978). In contrast, however, very little information is currently available on economically and environmentally sound treatment technologies for the redwater itself. Biological, chemical, and thermal treatment schemes have been explored by some researchers to treat TNT redwater. Schott et al. (1943) found biological treatment to be ineffective for treating redwater, including diluted redwater containing high concentrations of DNT sulfonic compounds. Carbon adsorption was not found to be promising either. Experiments on chemical treatment found the waste stable and difficult to treat. Neutralization and precipitation, fractional distillation, and ozonation were found to be fruitless. Chlorination seemed promising only in reducing color.

Gilbert (1978) studied a number of possible direct and indirect methods to desulfonate the DNT sulfonates to DNTs which could, in turn, be recycled for nitration to TNT or removed by appropriate treatment. Spencer and Goldstein (1985) discussed the problems associated with the reuse of sodium sulfite recovered from the SONOCO sulfite recovery process which incorporates redwater destruction and sellite recovery.

Also, relatively more research has been undertaken to determine the biotransformation products of TNT and other nitroaromatics, as compared to the research on the chemical transformation products (McCormick et al. 1976; Spanggord et al. 1982; Burrows et al. 1989; Walsh, 1990). Supercritical water oxidation, a treatment technology claimed to be highly effective for the destruction of a broad spectrum of organic compounds (Modell 1985; Rofer 1987; Welch et al. 1987; Helling and Tester 1988; Yang and Eckert 1988; Rofer and Streit 1988; Eckert et al. 1990), is being considered for further investigation as a potential redwater treatment technology.

Other Wastewaters Generated During TNT Production

Besides redwater, other wastewaters are also produced during the TNT manufacturing process. "Pinkwater" is the wastewater generated from water-washing the purified TNT following the sellite purification step or from water-washing at the loading, assembly, and packing (LAP) facilities. Pinkwater contains up to 150 ppm TNT and other nitroaromatics, but little or no sulfonates. As a result of their study of the extractability of TNT, high-melting explosive

(HMX), and research department explosive (RDX) from spent carbon, Maskarinec et al. (1985) reported the presence of at least 80 gas chromatographable organic constituents in a methylene chloride extract. "Yellow-water" is produced when crude TNT is washed with water to remove excess nitric and sulfuric acids. Consequently, the yellow-water consists primarily of nitric and sulfuric acids, but also contains trace amounts of nitrobodies.

Significant research has been done to date on the physicochemical and biological treatability of pink- and yellow-waters. Ruchholft et al. (1945) found concentrations of α-TNT above 1 ppm in TNT wastewater from LAP operations (pinkwater) to have a detrimental effect on biological treatment processes. They also found that mixing activated carbon into the wastewater was more effective for TNT removal than filtration through carbon. Nay et al. (1972, 1974) concluded that TNT yellow-water could be biologically treated under certain conditions (e.g., combining it with domestic sewage), but also concluded that a combination of biological and chemical processes might be more practical and economical. Tatyrek (1976) discussed several concentration and destruction methods for pinkwater treatment. Bhattacharya et al. (1977) showed ultrafiltration to be feasible for removing nitrobodies from pinkwater. Okamoto et al. (1977) and Okamoto (1978) studied the use of surfactants to remove TNT from wastewaters generated at manufacturing plants and from LAP operations. They reported rapid removal of TNT in aqueous solutions using certain surfactants containing amino groups. Only trace levels of TNT were found in the filtrate after reacting the influent containing 120 to 140 ppm TNT with surfactants. However, the water-insoluble complexes formed were more potent mutagens than TNT (Kaplan and Kaplan 1982).

Brown and Jackson (1979) discussed the extraction of nitrobodies from pinkwater using white oil. Kaplan and Kaplan (1983) reported a potential for binding reactions between TNT and TNT-reduction products with soil. Freeman and Lehman (1990) recommended further evaluation of the powdered activated carbon/activated sludge (PAC/AS) treatment for wastewaters containing TNT and other explosives such as HMX, RDX, SEX, and TAX (octogen, cyclotrimethylene, 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, and 1-aceto-3,5-dinitro-1,3,5-triazocylohexane, respectively). The efficiency of WAO to treat these explosives could not be established during their study due to analytical problems.

This study was undertaken to assess the WAO process for the treatment of redwater. One of the proposed long-term aspects of this investigation is to see if partial WAO can produce an effluent that can be delisted as a hazardous waste and can then be treated using a conventional biological treatment process. Many researchers have been investigating the combined effect of WAO, biological, and/or physicochemical treatment (e.g., addition of PAC to a conventional activated sludge [AS] plant, WAO regeneration of spent carbon, etc.) of wastes containing hazardous organics (Knopp and Gitchel 1970; Meidl and Wilhelmi 1986; Meidl 1987; Meidl and Peterson 1987; Dietrich et al. 1988; Freeman and Lehman 1990). For example, Meidl and Peterson (1987) reported the use of WAO as a pretreatment step ahead of PAC/AS treatment to destroy RCRA-designated toxic wastes at a chemicals manufacturing plant. The WAO was also used for the regeneration of spent carbon and oxidation of biological sludge.

Analytical Methods

Although there are numerous chromatographic methods available for the separation and identification of many of the nitro and other aromatics believed to be present in redwater, e.g., DNT, TNT, DNB, etc. (Gehring and Shirk 1967; Kohlbeck et al. 1970; Chandler et al. 1972; Walsh et al. 1973; Jenkins et al. 1986; Bauer et al. 1986; Jenkins et al. 1989; Burrows et al. 1989; Jenkins and Schumacher, 1990), only a few have dealt with DNT sulfonates (Hall and Lawrence 1976; Gilbert 1978; DIONEX 1986; Brown et al. 1990).

Gehring and Shirk (1967) developed a gas chromatographic method for separation and quantification of low concentrations of unsymmetrical TNT isomers. The DNT isomers could also be separated using this method. Kohlbeck et al. (1970) reported use of thin layer chromatography (TLC) for process and product control by analyzing samples collected from the various stages of nitration and purification of TNT at the Radford AAP. Chandler et al. (1972) used TLC to measure the oxidation products formed during the nitration of toluene to TNT. Walsh et al. (1973) used liquid chromatography (LC) to monitor the results of the TNT wastewater treatment studies. For example, they demonstrated the application of LC in monitoring the color change in TNT solutions induced by pH and/or photochemical effects.

Jenkins et al. (1986) and Bauer et al. (1986) reported the development and interlaboratory evaluation, respectively, of a high performance liquid chromatographic (HPLC) determination of nitroorganics (DNT, TNT, HMX and RDX) in munitions wastewater. An LC-8 column was used with 50/38/12 (v/v/v) water/methanol/acetonitrile eluent. Detection was via ultraviolet (UV) absorbance at 254 nanometers (nm). Jenkins et al. (1989) developed a similar liquid chromatographic method to extract and quantify nitroaromatic and nitramine residues in soil. An excellent update of analytical techniques available for organic explosives and related is summarized by Burrows et al. (1989). Jenkins and Schumacher (1990) discuss development of a TNT field kit to measure the TNT concentrations in water and soil by forming a TNT complex with a basic oxide.

Hall and Lawrence (1976) used an elaborate extraction scheme to isolate the polar and nonpolar fractions of redwater. Both fractions were analyzed using TLC. For the analysis of sulfonic compounds, the TLC plates were coated with 0.3 millimeters (mm) silica gel and a fluorescent compound activated by 254 nm radiation. The extracted redwater samples and reference samples for the sulfonic compounds were spotted on the plates. The plates were subjected to programmed multiple development, using a developer consisting of a mixture of ethanol, ethyl ether, benzene, and concentrated ammonium hydroxide (54/50/84/12, v/v). The compounds scraped off the plates were extracted using dimethyl sulfoxide (DMSO). The silica gel was removed by centrifugation of the DMSO solution. The extracts were analyzed spectrophotometrically. They also reported infrared (IR) spectra for the red TNT wastewater, for the polar organic matter in the redwater, and for 2,4-DNT-5-SO_3Na.

In addition to providing details on the synthesis of pure DNT sulfonates, Gilbert (1978) developed a procedure to isolate the DNT sulfonates from redwater by extraction of the evaporated redwater residue with boiling dimethyl formamide or 90 percent isopropanol. He also reported IR spectra for 2,4-DNT-3- and 5-sulfonates, which were similar to those reported by Hall and Lawrence (1976).

Brown et al. (1990) reported an LC method that provided good separation for chlorinated aromatic sulfonates that were poorly resolved using the conventional reverse-phase high performance LC.

As indicated above, a large amount of information is available on analytical methods for nitroaromatics, the analytical information for DNT sulfonates is rather sparse. A summary of analytical methods discussed above is included in Table 2.6.

Wet Air Oxidation

The WAO process is the oxidation of soluble or suspended oxidizable materials by using air or pure oxygen in an aqueous phase under high temperature (150 to 350 °C) and pressure (300 to 3000 psi) conditions. High pressure is required to maintain water in the liquid state and to provide the minimum oxygen requirements for the oxidizable components in the waste stream. Insoluble organic matter is converted to simpler organic compounds, which are oxidized and converted to CO_2 and water; inorganics such as nitrogen and sulfur are oxidized to their highest states of oxidation. For example, inorganic nitrogen is converted to nitrate; organic amine nitrogen is converted to ammonia and ultimately to nitrate, and sulfur to sulfate (Hurwitz et al. 1965). One of the most stable

Table 2.6. Analytical methods for nitroaromatics and aromatic sulfonic compounds.

Parameter	Method	Reference
TNT, DNT Isomers	GC	Gehring and Shirk (1967)
TNT,DNT	TLC	Kohlbeck et al. (1970)
Oxidation products formed During nitration of toluene	TLC	Chandler et al. (1972)
TNT	HPLC	Walsh et al. (1973)
DNTSs and other Nitroaromatics	TLC/IR	Hall and Lawrence (1976)
DNTSs	TLC/IR	Gilbert (1978)
TNT, DNT, RDX, and HMX	HPLC	Bauer et al. (1986), Jenkins et al. (1986)
Nitroaromatic and Nitramine residues in soil	HPLC	Jenkins et al. (1989)
Aromatic sulfonic compounds	HPLC	Brown et al. (1990)
DNTSs	RPIPC	Present Study

*Note: An Abbreviations and Acronyms section can be found at the end of the report.

residual organic compounds prior to complete oxidation is acetic acid (Teletzke 1964; Teletzke et al. 1967; Day et al. 1973; Baillod 1982; Foussard et al. 1989). Teletzke (1964) reported that the concentration of acetate in the oxidized solution varied inversely with the oxidation temperature, with only traces remaining at temperatures above 320 °C.

Although WAO is a combustion process, it takes place at a much lower temperature than incineration (about 150 to 350 °C in contrast to about 1500 °C). The WAO is less energy-intensive than incineration of liquid wastes, because there is no phase change involved, thus saving the heat of vaporization. The nitrogen and sulfur oxides produced at the low WAO temperatures are negligible and the effluent can be completely controlled because the system is completely closed (Schaefer 1981; Rofer and Streit 1988). Although there is not much information available on WAO of the types of organic compounds present in TNT redwater, the literature does indicate that no nitrogen oxides, sulfur oxides, or particulate matter is generated from the WAO of high-sulfur coal, petroleum coke, or other low-grade fuels; at high enough temperatures, most organic compounds can be completely destroyed.

The degree of oxidation may be selected to suit specific local requirements, and can range from little to 100 percent (Pradt 1972). At around 150 °C, 5 to 10 percent of the COD may be oxidized and at 320 °C, nearly complete oxidation occurs for most substances.

The WAO is also attractive because it provides energy as a by-product. The oxidation reaction is self-sustaining and a net producer of thermal energy in the form of saturated steam, which would help defray the cost of operating the treatment process (Freese and Rolinski 1984). The WAO can proceed with less than 1 percent oxidizable organic materials in solution; sizeable amounts of energy would, of course, be required for more dilute solutions. Akse et al. (1987) described conditions under which WAO can become thermally and mechanically self-sustaining. The WAO process is also air-pollution free, and has no residual disposal problems since the resulting "ash" remains in solution.

In addition to the recovery of thermal or mechanical energy, WAO has chemical recovery applications such as: resource recovery of ammonium sulfate from WAO of coke oven gas scrubbing liquor from a foundry/steel manufacturing plant, recovery of filler clay (essentially titanium oxide and/or kaolin) from WAO of wastewater plant sludges at coated paper mills, etc. (Schaefer 1981).

In 1972, there were more than 70 WAO plants worldwide, but only six were treating pure industrial waste streams and none were in the United States (Pradt 1972). In 1979, there were over 200 Zimpro WAO units in operation at more than 160 locations throughout the world (Wilhelmi and Knopp 1979). More than six were engaged in destroying hazardous materials such as acrylonitrile, coke oven gas scrubbing wastewaters, and other hazardous wastes. Commercial-scale WAO systems designed and manufactured by Zimpro range in size from 6 gpm to multiple units with an aggregate capacity of 3000 gpm or more.

In addition to the WAO units designed and manufactured by Zimpro, the VerTech reactor, initially used for WAO of sludge, is now being used for treating industrial organic wastes, including hazardous and toxic wastes (Rappe 1985). The VerTech vertical tube reactor consists of a conventionally-drilled, cement-encased well just over 1 ft in diameter and about 1 mi deep. Under conditions of about 260 °C, 1400 psi, and sufficient oxygen, organic wastes pumped to the bottom are oxidized to water, carbon dioxide, dilute organic acids, and a small amount of sterile, inert ash. Removal efficiencies of 94 to 99 percent have been achieved for toluene, 1,2-dichloroethane, cyanide, and acrylonitrile. Further studies are needed before either configuration can be recommended.

Cheremisinoff (1988) lists many other processes besides WAO that can be used for thermal destruction of hazardous wastes. They include incineration (rotary kiln, liquid injection, multiple hearth, and fluidized bed), molten salt, circulating bed combustion, plasma arc, high temperature fluid wall, pyrolysis, supercritical water oxidation, and advanced electric reactor. The choice of which process is best suited to a waste stream will depend on the nature of the particular waste and the concentration of the stream. Roberts (1973) presented a conceptual relationship between process cost and concentration of organic pollutants. As summarized by Baillod (1979), chemical oxidation is suitable for treating wastes with low concentration of labile organics. Conventional biological oxidation processes such as AS may be most cost effective for biodegradable wastes. High temperature incineration becomes more practical for wastes containing 30 percent or more organics. The WAO process is ideally suited to liquid wastes that are too dilute to incinerate using dry combustion and too refractory to handle by conventional chemical and biological oxidation.

Historical Applications of WAO

Wet air oxidation is not a new process. Its origins can be traced to a patented process for the treatment of spent sulfite liquor from paper mills in 1915, to the zinc sulfide oxidation process of hydrometallurgy patented in 1927, and to the oxidation of paper mill effluents patented in Sweden in 1949 (Ploos van Amstel 1971). In the mid 1940s, WAO was used as a way to recover vanillin from spent pulping liquor. In addition to using WAO to treat pulping waste liquor, Zimmermann (1958, 1961) also used the process to treat primary, activated, and mixtures of sewage sludges, dairy and slaughterhouse wastes, and polluted chemical plant and oil refinery streams in the 1940s and 1950s. Redwater was subjected to WAO at 300 °C by Seidman and Hofman (1957). They found that COD for the redwater was reduced from 65.2 grams per liter (g/L) to 1.9~2.8 g/L (W.M. Copa, Zimpro Passavant, Rothschild, WI, personal communication, 1993).

After Zimmermann's patent, the WAO process was essentially used for sludge reduction and stabilization (Teletzke 1964; Hurwitz et al. 1965; Harding and Griffin 1965; Teletzke et al. 1967; USEPA 1974). Some researchers continue to investigate WAO's application to sludge treatment (Wu et al. 1987; Friedman et al. 1988); the use of WAO for sludge treatment, however, is not popular now because of high capital/operational costs and high organic concentration in the WAO effluent that has to be recycled back to the plants. The WAO of sludges is still recommended under low temperature conditions for easy sludge dewaterability. The reduced temperature/pressure significantly reduces capital and operational costs.

Current Applications of WAO

Since the 1970s, the WAO process has been applied to treat industrial wastewaters (Baillod et al. 1979; Randall and Knopp 1980; Freese and Rolinski 1984; McGinnis et al. 1984; Dietrich et al. 1984; Keen and Baillod 1985; Heimbuch and Wilhelmi 1985; Yoshida et al. 1986; Kalman et al. 1989) and propellants, and explosives (Fassell and Bridges 1975; Copa and Randall 1990). The presence of catalysts was shown to result in increased reaction rates or in the oxidation of organics under milder conditions compared to those experienced without the catalyst (Walsh and Katzer 1973; Sadana and Katzer 1974; Katzer et al. 1975; Randall and Knopp 1980; Miller et al. 1980; McGinnis et al. 1984; Yoshida et al. 1986; Immamura et al. 1986, 1988; Mitsui et al. 1989a, b, c, and d; Ito et al. 1989; Eckert et al. 1990).

Although much of the WAO literature regarding hazardous waste destruction describes the characteristic operating conditions and performances of existing WAO oxidation plants with the assumption that WAO will result in detoxification of a contaminated source water, few studies have been performed to confirm this assumption. Many of these studies were completed using proprietary processes for which information is not readily available, and it is difficult to compare data and interpret results. Furthermore, the kinetic information on compound destruction using WAO is sparse. Some examples of these WAO studies are discussed below.

Fassel and Bridges (1975) reported almost 95 percent destruction of different propellants and explosives by WAO. Randall and Knopp (1980) achieved greater than 99 percent destruction of several toxic compounds by WAO after 1-hour oxidation at 320 °C. The oxidation products were less toxic than the starting material by a factor of 15 to 4000, depending on the particular compound. In a field operation, a reduction of 99 percent of some compounds including phenols, cyanides, pesticides, and organic sulfides could also be attained (USEPA 1986). Keen and Baillod (1985) reported a similar reduction for phenol, 2-chlorophenol, and 4-nitrophenol. However, they concluded that byproducts were somewhat more toxic than the known concentration of initial compound remaining in the oxidized solution. Therefore, both the quantitative and qualitative identification of byproducts is very important to identify the major compounds that are responsible for the observed toxic effects.

Dietrich et al. (1985) found WAO to be very effective in treating a number of toxic and hazardous industrial wastewaters, particularly those containing phenols, pesticides, and herbicides. They reported WAO of 25 organic compounds, including 2,4-DNT which had a removal rate of 99.88 percent at 320 °C. Removal efficiencies were generally more than 97 percent for all the compounds studied, except for Kepone, Arochlor 1254, and 1,2-dichlorobenzene for which the removal efficiencies were 31 percent (at 280 °C/with catalyst), 63 percent (at 320 °C), and 69 percent (at 320 °C/with catalyst), respectively.

A recent study by Foussard et al. (1989) concluded that above 307 °C, almost all industrial wastes they studied were completely oxidized in less than 2 hours. They further noted that acetic acid was the major intermediate during oxidation of almost all of the wastes, and was the most difficult substance to oxidize. Copa and Randall (1990) studied WAO of various propellants and propellant wastewaters and reported complete destruction of double base propellants containing nitrocellulose and nitroglycerin, at 200 °C. They also reported almost complete destruction at 280 °C of propylene glycol dinitrate (component of OTTO Fuel), hydrazine, and 1,1-dimethyl-hydrazine (components of rocket fuel).

The WAO process has also been used for regenerating spent PAC. Knopp and Gitchel (1970) successfully demonstrated the effectiveness of partial WAO to restore the adsorptive capacity of PAC used for the removal of soluble organics from chemically treated or primary effluent sewage. Meidl and Wilhelmi (1986) reported the use of WAO as a pretreatment step ahead of PAC/AS treatment to destroy toxic wastes from a chemicals manufacturing plant.

Ding et al. (1987) and Wedeking et al. (1987) studied the effects of WAO regeneration time, temperature, and biomass on the capacity of the regenerated PAC with different surface oxygen characteristics. Recktenwalt et al. (1988) concluded that successively regenerated PAC showed decreased adsorption capacity for 2,4-dinitrophenol, but retained the same capacity for the organics present in secondary effluent. Larson et al. (1988) tentatively identified 15 intermediate products from the WAO of phenanthrene-loaded carbon by using gas chromatography-mass spectrometry (GC-MS). A tentative phenanthrene oxidation scheme involving hydroxyl radicals was proposed to hypothesize the destruction pathway from the three-ring phenanthrene to a one-ring phenol. Acetic acid concentration was increased by 3~4 fold between 10 and 60 minutes at 230 °C.

Very little is known about the possible intermediates in WAO of hazardous organics with the exception of the two heterocyclic compounds diphenylamine and mercaptobenzothiozole, as reported by Larson et al. (1988). Literature search efforts indicate that even less may be known about the chemistry of WAO of the nitroaromatics and sulfonated nitroaromatics.

The following summarizes the WAO literature review:

- Temperature is the most important process parameter. Reaction rates increase with temperature: several hours were required in one case for a reaction to reach equilibrium at low temperatures, but at 300 °C, the reaction was almost instantaneous.

- Pressure is required to maintain water in the liquid phase and to provide a minimum desired oxygen overpressure. Most literature indicates that the effect of pressure on the reaction rate is insignificant compared to the effect of temperature.

- Higher temperatures and pressures enhance oxygen transfer and reaction rates; however, there are higher equipment and compressor power costs.

- Excess oxygen does not affect the amount of organics removed.

- The high solubility and diffusivity of oxygen in aqueous solutions at elevated temperatures provide a strong chemical driving force.

- Reaction is catalyzed by CU (II) or other metal catalysts.

- Acidic conditions generally favor WAO of organic materials; alkaline conditions, however, enhance WAO of *o*-chlorophenol.

- Capital costs may be somewhat higher for WAO than for incineration systems, but WAO operating costs are lower, which offers opportunity to recover energy and inorganic chemicals.

Mechanisms, Kinetics, and Modeling

Although detailed mechanisms for the reactions in the WAO process are not readily available, oxidation studies of organic material in the liquid phase by molecular oxygen suggest a free radical mechanism. It is assumed that oxidation proceeds with the formation of peroxy radicals via hydroperoxides as intermediate products because of the relative ease with which peroxides are formed. The presence of molecules such as acetic acid in the product mixture (from WAO of compounds lacking methyl groups) has been put forth as evidence for this type of mechanism (Larson et al. 1988).

Only limited information was found in the literature search on the kinetics of the WAO process. Although some mechanistic and kinetic models have been proposed for WAO of different wastes, a universal model does not appear to exist that can describe the WAO of different compounds in different waste streams (Foussard et al. 1989; W.M. Copa, Zimpro Passavant, Rothschild, WI, personal communication, 1990, hereafter referred to as Copa 1990). Taylor and Weygandt (1974) studied the WAO reactions of oxygen with aqueous solutions of selected soluble alcohols, ketones, and acids. Saturated acids and methanol were not oxidized at pressures < 2000 psi and temperatures < 250 °C. The alcohols and ketones exhibited overall second-order kinetics, first-order with respect to organic compounds and first-order in oxygen. Day et al. (1973) proposed that WAO of propionic acid proceeded via two principal routes, half the acid being oxidized to carbon dioxide and the other half going to acetic acid via acetaldehyde as an intermediate. Other studies on kinetics, mechanistic considerations, and modeling include those by Ploos van Amstel and Rietma (1969), Takamatsu et al. (1970), Ploos van Amstel (1971), Sadana and Katzer (1974); Williams et al. (1975), Beyrich et al. (1979), Yang and Eckert (1988), Willms et al. (1988), and Foussard et al. (1989).

If WAO were assumed to proceed via a radical mechanism, the use of models obtained from studies of oxidation of individual hydrocarbons might not be easily possible for predicting mechanisms for streams containing a mixture of these compounds. The presence of other components will make the mechanisms of the chain process too complex to be modeled. Modeling may be practically impossible if all the components of a waste stream are not completely known, as in the case of TNT redwater.

Limited information is available on the kinetics of WAO of organics in general and of nitrated and sulfonated organics in particular. For example, Baillod et al. (1979) and Dietrich et al. (1985) discussed the WAO of nitrogen-containing organics, but only in terms of percent destruction of the compounds studied. In addition to reporting only percent destruction after a specified time, some of the WAO studies list proprietary processes, for which information is not readily available. This makes data comparison or results interpretation much more difficult. The literature describing the WAO reaction kinetics of compounds studied by different investigators is summarized in Table 2.7. As described in the following paragraphs, WAO reaction kinetics for phenol and substituted phenols have been studied extensively during the past 20 years; other compounds have not been studied as much.

Shibaeva et al. (1969) investigated the WAO of phenol at a pressure of 515 psi and temperatures of 140 to 210 °C. The initial oxidation rate of phenol was shown to be proportional to the phenol and oxygen concentrations. The dependence of the reaction rate on pH was described as complex. Sadana and Katzer (1974) studied

Table 2.7. Summary of WAO bench-scale, pilot-scale, and full-scale treatment of organics.

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Bench-Scale Studies				
Acenapthene	275/60	99.9+	pure compound	Dietrich et al. (1985)
	320/60	99.9+	organic in ww	Canney and Shaefer (1983)
Acetic acid	165/90	36	pure compound, catalyzed	Miller et al. (1980)
Acetone	280/60	99.4	in solvent recovery ww	Dietrich et al. (1985)
Acetonitrile	275/60	98.4	pure compound	Dietrich et al. (1985)
Acrolein	275/60	99.1	pure compound	Dietrich et al. (1985)
	320/60	99.4	pure compound	Canney and Schaefer 1983
Acrylonitrile	275/60	99.0	pure compound	Dietrich et al. (1985)
	275/60	99.5	pure compound, catalyzed	Canney and Schaefer (1983)
	320/60	99.9	pure compound	
Arochlor 1016	195/60	93	pure compound, catalyzed	Miller et al. (1980)
Arochlor 1254	275/60	99.6	pure compound, catalyzed	Canney and Schaefer (1983)
	320/120	2	pure compound, catalyzed	
	320/120	63	pure compound	Dietrich et al. (1985)
	250/120	95	pure compound, catalyzed,	Miller et al. (1980)
Carbon tetrachloride	275/60	99.7	pure compound	Dietrich et al. (1985)
	275/60	99.9+	pure compound, catalyzed	Canney and Schaefer (1983)
Chlorobenzene	275/60	72.0	pure compound, catalyzed	Dietrich et al. (1985)
	280/60	92.3	in spiked ww	
Chloroform	275/60	99.9	pure compound	Dietrich et al. (1985)
	275/60	99.9	pure compound, catalyzed	Canney and Schaefer (1983)
	280/60	99+	in spiked ww	Dietrich et al. (1985)
1-chloronaphathalene	275/60	99.9	pure compound, catalyzed,	Dietrich et al. (1985)
	280/60	99.5	in spiked ww	
2-chlorophenol	275/60	94.9	pure compound	Canney and Schaefer 1983)
	320/60	99.9		
	275/60	99.9	pure compound, catalyzed	Dietrich et al. (1985)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Cyanide	200/30	98.5-98.8	in ww	Canney and Schaefer (1983)
	275/60	99.9+	pure compound	
	275/60	99.4	in ww	
	275/60	99.9+	in ww, 1400 mg/L H_2O_2 added for post-treatment	
	280/60	97.6-99.8	in ww	
	280/60	99.7	in ww, 990 mg/L O_3 added for post-treatment	
	280/60	99.9+	in ww, 300 mg/L H_2O_2 added for post-treatment	
	280/60	98.3-99.6	metal plating and metal finishing ww from Casmalia Resources (California	Heimbuch and Wilhelmi (1985)
	300/60	99.8	in ww	
	300/120	99.7	in ww	Canney and Schaefer (1983)
(2,4-dichlorophenoxy) acetic acid or 2,4-D	165/15	65	pure compound, catalyzed	Miller et al. (1980)
Dibutylphthalate	275/60	99.5	pure compound	Dietrich et al. (1985)
2,4-dichloroaniline	275/60	99.8	pure compound, catalyzed	Dietrich et al. (1985)
1,2-dichlorobenzene	275/60	3	pure compound	Canney and Schaefer (1983)
	275/60	27.4-99.8	pure compound, catalyzed	
	320/60	69.1	pure compound, catalyzed	Dietrich et al. (1985)
	320/120	74.6	organic in ww	
2,6-dichlorobenzo-nitrile	280/60	92.1	in spiked ww	Dietrich et al. (1985)
1,2-dichloroethane	275/60	99.8	pure compound	Dietrich et al. (1985)
	275/60	99.9	organic in ww, catalyzed	Canney and Schaefer (1983)
Dichloromethane	280/60	99	in spiked ww	Dietrich et al. (1985)
1,2-dichloro-3-nitrobenzene	285/120	80.6	organic in ww	Dietrich et al. (1985)
2,4-dichlorophenol	280/60	98.4	in industrial ww	Dietrich et al. (1985)
	320/60	99.6	organic in ww	
DDT	275/60	99.9+	pure compound, catalyzed	Canney and Schaefer (1983)
Dimethylanaline	280/60	99.9	organic in ww	Dietrich et al. (1985)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
5,5-dimethylhydantoin	280/60	99.3	organic in ww	Dietrich et al. (1985)
2,4-dimethylphenol	275/60	99.9+	organic in ww	Dietrich et al. (1985)
	320/60	99.9+	pure compound, catalyzed	Canney and Schaefer (1983)
Dinitrobenzeneamine	285/120	90.6	organic in ww	Canney and Schaefer (1983)
Dinitrochlorobenzene Isomers	285/120	93.8-99.9+	organic in ww	Dietrich et al. (1985), Canney and Shaefer (1983)
Dinitrochlorophenol Isomers	285/120	99.9	organic in ww	Dietrich et al. (1985)
Dinitrophenol	285/120	82.5	organic in ww	Dietrich et al. (1985)
2,4-dinitrotoluene	275/60	99.7	pure compound	Dietrich et al. (1985)
	320/60	99.9	pure compound	Canney and Schaefer (1983)
Dioxin	200/240	99	pure compound, catalyzed	Miller et al. (1980)
1,2-diphenylhydrazine	275/60	99.9+	pure compound	Dietrich et al. (1985)
	320/60	99.9+	pure compound	Canney and Schaefer (1985)
Dipropylformamide	250/60	99.5	organic in ww	Dietrich et al. (1985)
Ethyl alcohol (ethanol)	280/60	57.2	in industrial ww	Dietrich et al. (1985)
	280/60	96.1	in solvent recovery ww	
	320/60	99.4		
Ethylene dibromide	165/60	51	pure compound, catalyzed	Miller et al. (1980)
Formic acid	300/60	98.3	pure compound	Dietrich et al. (1985)
Glycolic acid	165/30	99	pure compound, catalyzed	Miller et al. (1980)
Hexachlorocyclopentadiene	275/60	90-98	pure compound	Canney and Schaefer (1983)
	300/60	99.9+	pure compound	Dietrich et al. (1985)
Isophorone	275/60	99.4	pure compound	Dietrich et al. (1985)
Kepone	280/60	31	pure compound, catalyzed	Dietrich et al. (1985)
	250/360	93	pure compound, catalyzed	Miller et al. (1980)
Malathion	165/60	58	pure compound, catalyzed	Miller et al. (1980)
	200/60	99.9	pure compound	Canney and Schaefer (1983)
	300/60	99.9+		
	250/60	99.9	pure compound	Dietrich et al. (1985)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Mercaptans	225/60	99.3	organic in ww	Dietrich et al. (1985)
	280/60	99.9	in industrial ww	
Methyl alcohol (methanol)	280/60	57.2	in solvent recovery ww	Dietrich et al. (1985)
	320/60	91		
Methylethyl ketone	280/60	99.9+	in industrial ww	Dietrich et al. (1985)
	280/60	99.6	in solvent recovery ww	
	320/60	98.9		
2-(a-naphthoxy(-N,N-diethylpropionamide	280/60	99.8	in industrial ww	Dietrich et al. (1985)
Nitrobenzene	320/120	95.0	pure compound, catalyzed	Dietrich et al. (1985)
Nitrogen (organic)	280/60	77.7	pesticide rinsate	Heimbuch and Wilhemi (1985)
3-nitrophenol	285/120	99.9+	organic in ww	Dietrich et al. (1985)
4-nitrophenol	275/60	99.6	pure compound	Dietrich et al. (1985)
	320/60	99.9	pure compound	Canney and Schaefer (1983)
N-nitrosodimethylamine	275/60	99.6	pure compound	Dietrich et al. (1985)
	320/60	99.8	organic in ww	
	275/60	99.4	pure compound, catalyzed	Canney and Schaefer (1983)
Organonitrogen/ phosphorus compounds	260/60	99.5-99.6	in nonchlorinated pesticide ww	Canney and Schaefer (1983)
Organonitrogen/sulfur compounds	260/60	99.4	in nonchlorinated pesticide ww	Canney and Schaefer (1983)
Organonphosphorus compounds	300/60	94	in nonchlorinated pesticide ww	Canney and Schaefer (1983)
Pentachlorophenol	165/30	75	pure compound, catalyzed	Miller et al. (1980)
	275/60	82	pure compound	Canney and Schaefer (1983)
	320/60	99.9		
	275/60	97.3-99.9+	pure compound, catalyzed	Dietrich et al. (1985) and
Phthalimide compounds	225/60	99.0	in nonchlorinated pesticide ww	Canney and Schaefer (1983)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Phenol	275/60	99.8	pure compound	Dietrich et al. (1985)
	280/60	98.7-99.4	organic in ww	
	280/60	99.9+	organic in ww, 250-330 mg/L O_3 post-treatment	
	280/60	98.9-99.6	organic in ww, 900 mg/L H_2O_2 post-treatment	
	280/60	97.6	alkaline solvent at Casmalia Resources, CA	Heimbuch and Wilhelmi (1985)
	300/60	95.1	organic in ww	
	300/60	96.3	organic in ww, catalyzed	Dietrich et al. (1985)
	320/60	99.9+	pure compound	
	320/120	99.7	organic in ww	Canney and Schaefer (1983) Dietrich et al. (1985)
1,2-propanediol dinitrate	280/60	99+	in industrial ww	Dietrich et al. (1985)
2-propanol	280/60	98.3	in industrial ww	Dietrich et al. (1985)
	280/60	98.2	in solvent recovery ww	
	320/60	98.7	in solvent recovery ww	
Propionitrile	275/60	98.2	organic in ww, catalyzed	Dietrich et al. (1985)
Pyrene	275/60	99.9+	pure compound	Dietrich et al. (1985)
	275/60	99.9+	pure compound, catalyzed	Canney and Shaefer (1983)
Pyridine	320/120	85.4	pure compound, catalyzed	Dietrich et al. (1985)
Sulfide wastes	177/60	99.9+	sodium sulfide manufacturing ww	Canney and Schaefer (1983)
	177/60	99.9+	olefins production spent caustic scrubbing liquor	
	280/60	99.7	spent caustic at Casmalia Resources, Cailfornia	Heimbuch and Wilhelmi (1985)
Thiocyanate	275/60	99.9+	pure compound	Canney and Schaefer (1983)
Toluene	275/60	99.7	pure compound	Canney and Schaefer (1983)
	275/60	99.9+	pure compound, catalyzed	
	280/60	98.8	in solvent recovery ww	Dietrich et al. (1985)
	320/60	98.8	in solvent recovery ww	
	320/60	90	pure compound	

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
2,4,6-trichloroaniline	280/120	31.0	pure compound, catalyzed	Canney and Schaefer (1983)
	320/120	63.0	pure compound	
	320/120	99.9+	pure compound, catalyzed	Dietrich et al. (1985)
Trichloroethylene	280/60	99.3	in spiked ww	Dietrich et al. (1985)
	320/60	99.7	organic in ww	Dietrich et al. (1985)
2,4,6-trichlorophenol	285/120	99.9+	organic in ww	Dietrich et al. (1985)
2,4,6-trinitrophenol	285/120	99.9+	organic in ww	Dietrich et al. (1985)
Pilot-Scale Studies:				
Cresol	279/69	99.9+	coke plant ww, 6.3 gph, 1558 psi, catalyzed	Dietrich et al. (1985)
Cyanide	279/69	99	coke plant ww, 6.3 gph, 1558 psi, Cu^{2+} catalyzed	Dietrich et al. (1985)
	254/115	99.9+	acrylonitrile ww, 3.1 gph, 1050 psi, Cu^{2+} catalyzed	Canney and Schaefer (1983)
1,2-dichlorobenzene	314/128	98.7	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
2,5-dichloro-6-nitrobenzoic acid	281/60	99	herbicide production ww, 6.4 gph, 1558 psi, Cu^{2+} catalyzed	Dietrich et al. (1985)
2,5-dichloro-3-nitrobenzoic acid	281/60	99	herbicide production ww, 6.4 gph, 1558 psi, Cu^{2+} catalyzed	Dietrich et al. (1985)
Dipropyl formamide	224/131	95.9	herbicide ww, 4.2 gph, 1580 psi	Dietrich et al. (1985)
	243/130	99.0	herbicide ww, 4.2 gph, 1582 psi	Dietrich et al. (1985)
Isopropyl alcohol	314/128	76.6	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
Freon TF	314/128	99.9+	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
Methylethyl ketone	314/128	99.9+	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Methylene chloride	314/128	99.9+	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
Organonitrogen/phosphate	240/120	99.9+	pesticide ww, 4.5 gph, 848 psi	Dietrich et al. (1985)
	260/120	99.9+	pesticide ww, 4.5 gph, 1200 psi	Dietrich et al. (1985)
Organonitrogen/sulfur	240/120	99.9+	pesticide ww, 4.5 gph, 848 psi	Dietrich et al. (1985)
	260/120	99.9+	pesticide ww, 4.5 gph, 1200 psi	Dietrich et al. (1985)
Perchloroethylene	314/128	99.9+	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
Phenols	279/69	99.8	coke plant ww, 6.3 gph, 1558 psi, Cu^{2+} catalyzed	Dietrich et al. (1985)
	314/128	99.9	industrial ww, 2.6 gph, 1943 psi	Dietrich et al. (1985)
Quinoline	279/69	65.8	coke plant ww, 6.3 gph, 1558 psi, Cu^{2+} catalyzed	Dietrich et al. (1985)
Sulfide	174/56	99.9+	olefins production spent caustic scrubbing liquor, 150 psi	Canney and Shaefer (1983)
	200/47	99.9+	olefins production spent caustic scrubbing liquor	
	320/64	99.9+	olefins production spent caustic scrubbing liquor, 3000 psi	
Thiocyanate (SCN^-)	268/83	99.9+	coke oven gas waste liquor, 1365 psi	Canney and Schaefer (1983)
Thiosulfate ($S_2O_3^{2-}$)	268/83	99.9+	coke oven gas waste liquor, 1365 psi	Canney and Schaefer (1983)
Toluene	314/128	98.3	industrial ww, 2.6 gph, 1943 psi pressure	Dietrich et al. (1985)
Xylene	314/128	99.8	industrial ww, 2.6 gph, 1943 psi pressure	Dietrich et al. (1985)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Full-Scale Plants:				
Carbaryl	281/182	98.0	ww containing propylene glycol and organic ethers/ esters spiked with pesticides	Dietrich et al. (1985)
Cyanide	250/90	99.9+	acrylonitrile ww, 8700 gph, 1000 psi (Japan)	Chowdhury et al. (1984)
	257/80	99.7	cyanide ww, 450 gph, 1200 psi, air flow = 190 scfm	Heimbuch and Wilhelmi (1985)
	240-280/60-180	99.9+	metal plating ww	Chowdhury et al. (1984)
1,1-dimethylhydrazine	271/117	99.9+	in waste rocket fuel	Dietrich et al. (1985)
Dinoseb	281/182	99.5	ww containing propylene glycol and organic ethers/ esters spiked with pesticides	Dietrich et al. (1985)
Dipropyl formamide	240-280/60-180	99.8	herbicide ww	Chowdhury et al. (1984)
Herbicide by-product	245/60	98.2-99.3	herbicide production ww	Dietrich et al. (1985)
Hydrazine	271/117	99.9+	in waste rocket fuel	Dietrich et al. (1985)
Malathion	281/182	99.9	ww containing propylene glycol and organic ethers/ esters spiked with pesticides	Dietrich et al. (1985)
Methoxychlor	281/182	99.8	ww containing propylene glycol and organic ethers/ esters spiked with pesticides	Dietrich et al. (1985)
Phenols (total)	268/113	99.8	caustic ww from petroleum refineries, 318 gph, 1610 psi, air flow = 190 scfm	Heimbuch and Wilhelmi (1985)
Propylene glycol dinitrate	240-280/60-180	99.9+	Otto fuel waste	Chowdhury et al. (1984)

Table 2.7. (Cont'd)

Compound/Type of Compound Treated	Treatment Conditions (°C/minutes)	% Removal	Comments	Reference
Sulfide	177-260/39-60	99.1	olefins production spent caustic scrubbing liquor, 900-1380 gph, 1900 psi (USA)	Chowdhury et al. (1984)
	315-320/50	99.9+	olefins production spent caustic scrubbing liquor, 1080 gph, 1900 psi (USA)	Chowdhury et al. (1984)
	200/60	99.9+	ethylene plant spent caustic scrubbing liquor, 1320 gph, 500 psi (Japan)	Chowdhury et al. (1984)
Sulfur (organic)	268/113	94.0	caustic ww from petroleum refineries, 318 gph, 1610 psi, air flow = 190 scfm	Heimbuch and Wilhelmi (1985)
Thiocyanate (SCN^-)	260-270/60	97-99	coke oven gas desulfurization ww, 1060-4020 gph, 1065 psi (Japan)	Chowdhury et al. (1984)
	270/90	99.6	coke oven gas scrubbing liquor, 600 gph, 1250 psi (Canada)	Chowdhury et al. (1984)
Thiosulfate ($S_2O_3^{2-}$)	260/60	99	coke oven gas desulfurization ww, 1060 gpm, 1065 psi (Japan)	Chowdhury et al. (1984)

ww = waste/water
gph = gallons per hour
scfm = standard cubic feet per minute

catalytic WAO of phenol over supported copper oxide (Harshaw Cu-0803T 1/8 10 percent CuO on γ-alumina) at and above atmospheric pressure and between 96 and 146 °C. After an initial induction period, the reaction transitioned to a much higher activity regime. The rate dependence on phenol concentration was of first-order (reaction rate directly proportional to concentration) in both regimes, but the order of the reaction with respect to oxygen decreased from first-order in the induction stage to half-order in the second stage. The dependency of reaction rate was not first-order for catalyst loading. Katzer et al. (1976) reported similar results for complete oxidation of phenol to carbon dioxide and water at higher temperatures (114 to 200 °C) and at oxygen pressures between 50 and 250 psi.

Baillod et al. (1982) assessed the effectiveness of WAO on several different pollutants, including phenol, 2-chlorophenol, and 4-nitrophenol under temperature conditions of 204 to 260 °C and initial oxygen pressures of 288 to 360 psi. Second-order rate expressions (first-order both in organic and oxygen concentration) were used to model the removal rates of specific substances, TOC, and COD. Removal rates increased with temperature. Cupric ion catalyzed the reaction and increased the rate and extent of removal of specific pollutants and TOC. Alkaline pHs significantly increased the removal rate of specific pollutants, but only slightly increased the rate of TOC removal. However, significantly lower TOC and COD removals were obtained over a 1-hour reaction period. They also reported similar reaction kinetics for two other model compounds, 1,2-dimethylphthalate and 1,2-dichloroethane.

Willms et al. (1987) reported a two-step aqueous-phase oxidation of phenol at 200-275 °C and operational pressures of 1000-2500 psi. During the first stage (induction phase), the reaction was zero-order with respect to organic concentration and first-order in oxygen pressure. During the second stage (rapid activity phase), the reaction was first-order with respect to the organic and half-order in oxygen. They also reported similar kinetic data for the WAO of *m*-xylene.

Eckert et al. (1990) studied the WAO of *p*-chlorophenol under temperatures ranging from 310 to 400 °C and operational pressures of 1100 to 3525 psi. They found the reaction rate to be first-order in chlorophenol at low concentrations and second-order at high concentrations. Oxygen concentration, which was varied by as much as a factor of 11, showed no effect on the reaction rates. Use of copper(II) tetrafluoroborate as a catalyst did not seem to alter the reaction mechanisms. However, it increased the first-order rate constant by 37 percent and the second-order rate constant by 25 percent.

Joglekar et al. (1991) concluded that the WAO of phenol and substituted phenols took place in two steps. At temperatures of 150 to 180 °C and oxygen partial pressures of 43 to 218 psi, the oxidation reactions were found to be first-order in oxygen and the phenolic substrates in both steps. They also listed the WAO kinetics of phenol (first-order in both phenol and oxygen concentrations) described by others.

Using glucose solution as a model compound, Ploos van Amstel (1971) showed the WAO rate to be first-order in glucose and zero-order in oxygen. Experiments with AS, however, showed the chemical reaction rate to be first-order for both the organic matter and oxygen. At relatively high oxygen pressures, the oxygen dependency decreased to zero-order.

Day et al. (1973) studied liquid-phase oxidation of propionic acid solutions with concentrations in the range of 0.1 to 0.2 molar (M), or equivalent COD values of approximately 11 to 22 grams per liter (g/L). Temperatures ranged from 232 to 288 °C and the initial O_2 partial pressures ranged from 250 to 750 psi. Day et al. (1973) assumed an initial-rate kinetic expression of the power law form (rate = k $[C]^m$ $[O_2]^n$) and a regression analysis showed the reaction-rate orders of 1.42 and 0.41 with respect to the propionic acid and oxygen concentrations, respectively. Williams et al. (1975) extended the work of Day et al. (1973) to evaluate the kinetics of the oxidation of 0.1 to 0.2 M butyric acid solutions at temperatures of 238 and 257 °C, with partial pressures of oxygen of 350 to 750 psi. The orders with respect to the acid and oxygen were reported to be 1.40 and 0.46, respectively.

Taylor and Weygandt (1974) examined WAO of selected alcohols, ketones, and acids at temperatures up to 250 °C and at operating pressures up to 2000 psi. The short chain carboxylic acids (acetic, propionic, and acrylic acid) were inert under the conditions studied. The alcohols and ketones all showed second-order kinetics: first-order in organic compound and first-order in oxygen.

Wakabayashi and Okuwaki (1988) studied the kinetics of the oxidation of acetate at 250 °C with an oxygen pressure of 725 psi in a nickel reactor in the presence of 3 grams (g) of iron powder and 5 M NaOH. The base-catalyzed oxidation of the acetate was shown to be first-order in acetate concentration, second-order in OH concentration, and first-order in oxygen concentration. Foussard et al. (1989) developed a different rate expression for the oxidation of sodium acetate at temperatures and oxygen pressures ranging from 294 to 320 °C and 350 to 700 psi, respectively. The reaction obeyed a first-order law with respect to acetate: the oxygen order of reaction was 0.37.

Kalman et al. (1989) carried out WAO of cyanide solutions (about 40 g/L) under five different temperatures (160 to 240 °C) and showed that the reaction was first-order in cyanide concentration. Willms et al. (1985) developed a model to describe the WAO of *m*-xylene at 200 to 240 °C and 1000 to 2500 psi. The model considered the effects of vapor-liquid equilibrium in the reactor and the sample withdrawal from the reactor.

They showed that improper consideration (e.g., omission) of these factors can introduce significant errors in estimating the reaction rates.

Baillod et al. (1982) reported that cupric ion increased the reaction rate and removal of phenol, 2-chlorophenol and 4-nitrophenol under various WAO conditions (Temperature [T] = 200 to 260 °C, oxygen pressure [PO_2] = 2.09 - 2.48 MPa). Eckert et al. (1990) reported a significantly increased rate constant with Cu(II) tetrafluoroborate as a catalyst in the WAO of *p*-chlorophenol.

A number of WAO kinetic studies have been reported in the past few years; a summary is provided in Table 2.8. As shown in the summary, WAO kinetics for phenol and substituted phenols have been studied extensively during the past 20 years; other compounds have not been studied as much. It can be concluded from the summary that the kinetic rate orders are not universal, even for the same organics. Nonetheless, practically all investigators have reported the WAO rate dependence of phenol and substituted phenols as first-order, with respect to the organic concentration. The corresponding order in oxygen, however, varied from zero for *p*-chlorophenol, to 0.5 for phenol in the presence of a catalyst, to 1 for phenol and substituted phenols. In the case of glucose or AS, the rate dependence was first-order for both in concentration. The rate dependence was independent of oxygen concentration in the case of glucose. For acids, alcohols, and ketones, the rate dependence varied from 1 to 1.42 in organic concentration and 0.41 to 1 with respect to oxygen concentration. WAO of acetate showed first-order rate in acetate concentration and a variable order (0.37 to 1) in oxygen concentration. The rate dependence for WAO of a high cyanide waste was first-order in cyanide and independent of oxygen concentration. WAO of xylene was a first-order reaction, independent of oxygen concentration.

The studies summarized in Table 2.8 essentially involve a global reaction model of the general form, rate = k x $[\text{organic}]^m [\text{oxidant}]^n$. For complicated wastes, the observed pseudo-first-order rate (m = 1 with excess oxygen) may not represent the overall picture. Thus, many investigators have proposed a model by classifying the starting materials into different fractions: easy to oxidize; difficult to oxidize; and nonoxidizable parts in the case of sludge (Takamatsu et al. 1970; Ploos van Amstel 1971; Shanableh 1990) and organic compounds (Foussard et al. 1989). Other investigators (Beyrich et al. 1979; Foussard et al. 1989) further proposed that for the total reaction rate of a system containing different organics, A_i is the sum of the individual reactions:

$$r = \sum r_i \qquad \text{[Eq 2-1]}$$

$$\text{where, } r_i = k_i [A_i] [O_2]$$

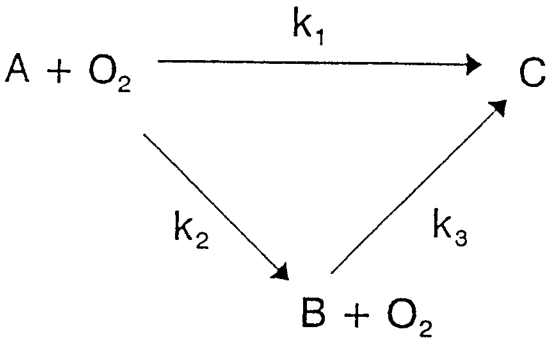
Table 2.8. Kinetic expressions for WAO of organic chemicals and wastes.

Compound	Rate Expression	Comments	Reference
Acetate (Na)	$r = k [C] [OH]^2 [O_2]$	Used a nickel reactor, and 3 g of iron powder.	Wakabayashi and Okuwaki (1988)
Acetate (Na)	$r = k [C] [O_2]^{0.37}$	-	Foussard et al. (1989)
Activated Sludge	$r = k [C] [O_2]$	O_2 dependency decreased to zero at high O_2 concentrations.	Ploos van Amstel (1971)
Butyric Acid	$r = k [C]^{1.40} [O_2]^{0.46}$	-	Williams et al. (1975)
Carboxylic acids, Alcohols, and Ketones	$r = k [C] [O_2]$	Short chain carboxylic acids were found to be inert under the conditions studied.	Taylor and Weygandt (1974)
Cyanide	$r = k [C]$	Waste from a wood carbonization factory.	Kalman et al. (1989)
Glucose	$r = k [C]$	-	Ploos van Amstel (1971)
Phenol	$r = k [C] [O_2]$	pH effect on rate dependence	Shibaeva et al. (1969a)
	$r = k [C] [O_2]$	CuO as catalyst, Induction stage.	Sadana and Katzer (1974)
	$r = k [C] [O_2]^{0.5}$	2nd stage.	
Phenol	$r = k [C] [O_2]$	-	Pruden and Le (1976)
	$r = k [C] [O_2]$	CuO as catalyst, Induction stage.	Katzer et al. (1976)
	$r = k [C] [O_2]^{0.5}$	2nd stage. High temperatures used for complete WAO of phenol to CO_2 and H_2O.	
	$r = k [C] [O_2]$	-	Harris et al. (1983)
	$r = k [O_2]$	Induction period.	Willms et al. (1985a)
	$r = k [C] [O_2]^{0.5}$	Rapid activity period.	

Table 2.8. (Cont'd)

Compound	Rate Expression	Comments	Reference
Phenol, *2*-chlorophenol, *1,2*-dichloroethane, *4*-nitrophenol, dimethylphthalate	$r = k [C] [O_2]$	-	Baillod et al. (1982)
4-chlorophenol	$r = k [C]$ $r = k [C]^2$	At low concentrations. At high concentrations. Copper tetrafluoroborate (catalyst) increased rate constants in both cases.	Eckert et al. (1990)
Phenol and substituted phenols (*2*-, *3*-, and *4*-chlorophenols, *2*-,*3*-cresols, *2*-,*4*-methoxyphenols, *2*-ethylphenol, and *2,6*-dimethylphenol)	$r = k [C] [O_2]$	In both induction and rapid activity stages.	Joglekar et al. (1991)
Propionic Acid	$r = k [C]^{1.42} [O_2]^{0.41}$	-	Day et al. (1973)
m-xylene	$r = k [C]$	Oxygen concentration was in great excess. Vapor-liquid equilibrium effects were considered in modelling.	Willms et al. (1985b)

Since acetic acid is the major end product, Li et. al (1991), following the approach used by Takamatsu et al. (1970), proposed a generalized kinetic model for WAO based on the formation and destruction of the rate-limiting intermediate, acetic acid. The schematic and simplified mathematical form of the model are shown below.



[Eq 2-2]

$$\frac{[A+B]}{[A+B]_o} = \frac{k_2}{k_1+k_2-k_3} e^{-k_3 t} + \frac{k_1-k_3}{k_1+k_2-k_3} e^{-(k_1+k_2)t}$$

$$\frac{[A + B]}{[A + B]_0} = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t} \qquad \text{[Eq 2-3]}$$

where A = all initial and intermediate organic compounds - acetic acid

B = acetic acid, and

C = oxidation end products

k = the Kinetic rate constants

The accumulation of acetic acid depends on the magnitude of k_2. For simplicity, the literature suggested that k_1 can be obtained from the initial reaction rates, and k_3 from the results of WAO of acetic acid performed by Foussard et al. (1989). The value of k_2 can be determined experimentally, or obtained from the point selectivity, α, defined as $\alpha = k_2/k_1$. The point selectivity can be determined from the ratio of the rate of formation of acetic acid to that of CO_2.

Intermediates and Reaction Pathways

Little is known about the types and concentrations of intermediates in WAO of hazardous organics. Even less seems to exist in the literature about the chemistry of WAO of nitroaromatics and sulfonated nitroaromatics. There is evidence however, that WAO-treated organic wastes are more toxic than the original compounds (Devlin and Harris 1984). Therefore, quantitative and qualitative identification of byproducts is important for identifying the major compounds present in WAO-treated effluents.

This will determine the compounds responsible for the observed toxic effects, and will help formulate the reaction pathways.

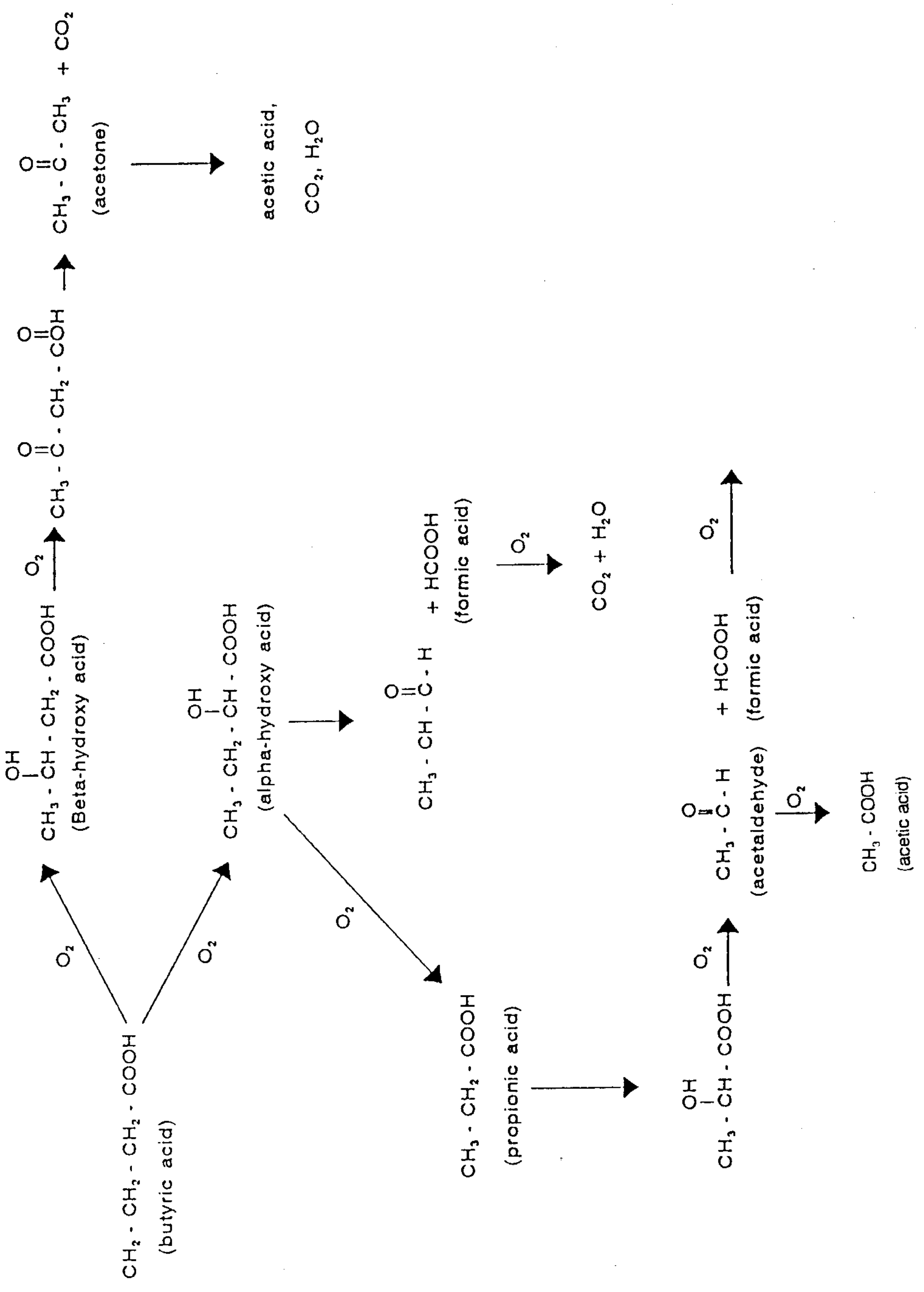
As reported by many investigators (Teletzke et al. 1967; Fisher 1971; Ploos van Amstel 1971; Day et al. 1973; Williams et al. 1975; Baillod et al. 1982; Keen and Baillod 1985; Wu et al. 1987; Friedman et al. 1988; Larson et al. 1988; Foussard et al. 1989), acetic acid appears to be a stable end product in the WAO of organics. Some examples of other WAO byproducts are listed in Table 2.9. For simple straight-chain organic compounds, the reaction pathways are relatively established to account for the accumulation of acetic acid. Day et al. (1973) proposed two parallel reaction pathways for the overall WAO of propionic acid. About half of the acid was completely oxidized to CO_2 and H_2O via a number of intermediates in the first pathway. The second route included the formation of acetic acid via acetaldehyde. Williams et al. (1975) presented the pathways for butyric acid and suggested that oxidation occurred at both α- and β-carbon by the hydroxyl radical (Figure 2.6). The α oxidation resulted in the formation of propionic acid and ß oxidation yielded acetone, which was rapidly oxidized to acetic acid. Taylor and Weygandt (1974) proposed two nonchain mechanisms for WAO of alcohols and ketones: 1) oxidation of alcohol first to the corresponding ketone or aldehyde, and subsequently to formic acid and CO_2; and 2) a keto-enol equilibrium resulting in the formation of acetic acid and CO_2. The considerable difference between the observed oxidative scission and that expected from the traditional free radical chain reactions involving elemental oxygen was given as the reason for the proposed nonchain mechanisms. However, the possibility of chain mechanisms were not completely ruled out.

The main end product for WAO of carbohydrates was formic acid (McGinnis et al. 1984): 1.5 mole/mole D-glucose at 190 °C, 1.1 mole/mole D-xylose at 190 °C, 1.3 mole/mole D-glucitol at 205 °C, and 1.4 mole/mole dextran at 227 °C. The other byproducts were acetic acid (0.19 to 0.23 molar ratios), methanol (0.5 percent), acetaldehyde, and acetone (< 0.5 percent).

For aromatic compounds, Sadana (1975) proposed a free radical mechanism for the aqueous phase oxidation of phenol via the formation of catechol and hydroquinone. Further oxidation of catechol to *o*-quinone and subsequent cleavage of *o*-quinone to *cis*-muconic acid, maleic acid, and oxalic acid were postulated as the intermediate steps before complete oxidation to CO_2 and H_2O. Devlin and Harris (1984) provided a detailed reaction pathway for oxidation of phenol via the formation of hydroquinone or catechol, benzoquinones, and several organic acids (Figure 2.7). Willms (1985a) proposed a free radical mechanism for WAO of xylene. Through computer simulations, he concluded that degenerate branching was an important step in the WAO of xylene. Yang and Eckert (1988) postulated a free radical mechanism for wet oxidation of *p*-chlorophenol. The rate expressions derived from the postulated

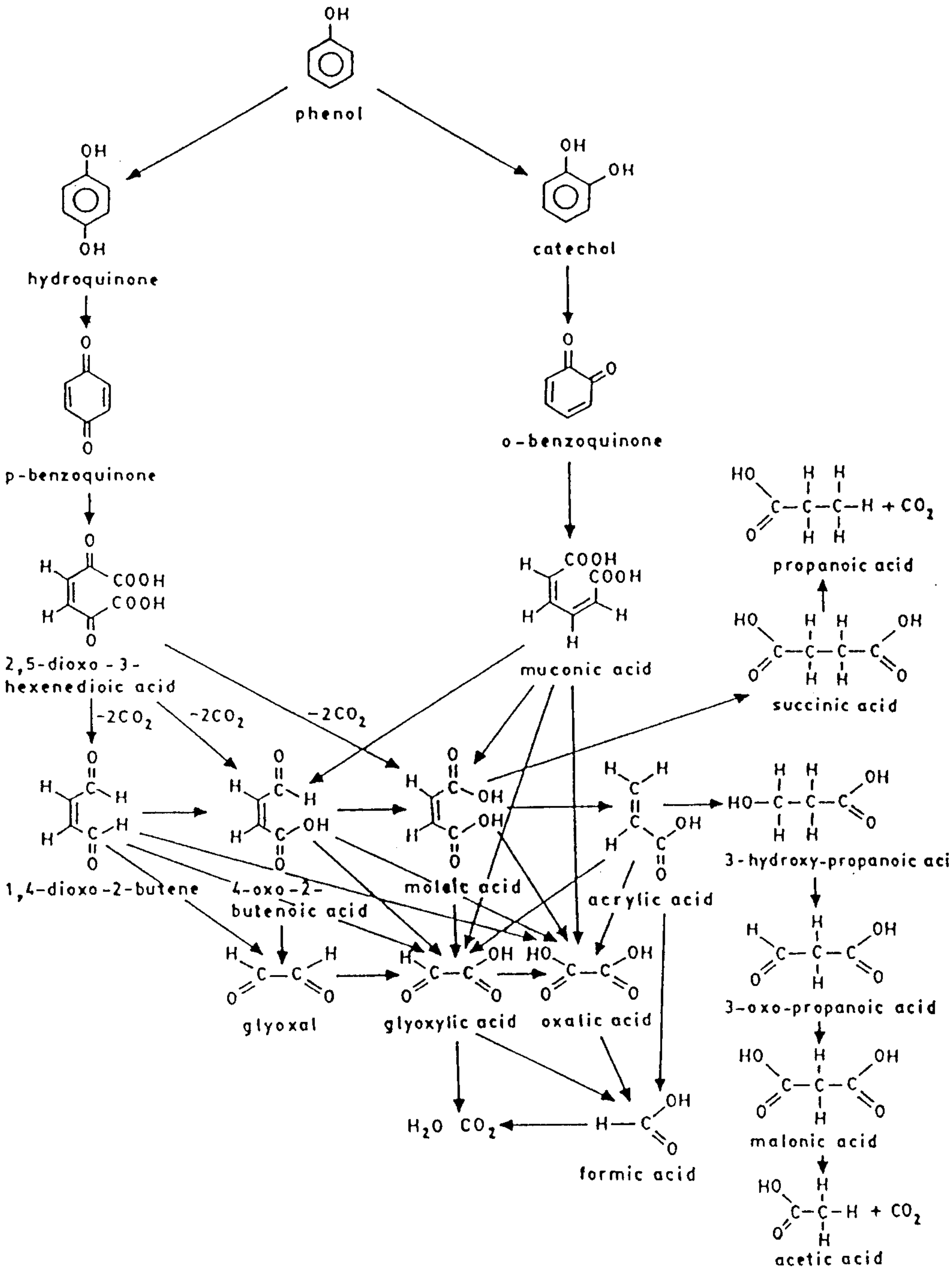
Table 2.9. Examples of end products formed from WAO of organics.

Starting Material/ WOP Conditions	End Product(s)	Reference
Propionic acid (14.8 g/L) 40% of PAC, 100 min, 245 °C, 500 psi PO_2	acetic acid, acetaldehyde methane, ethene (0.02%) ethylene (0.02%), CO_2	Day et al. (1973)
Phenol 1-hr, 232 °C	formic acid, acetic acid succinic acid, acetone acetaldehyde malaeic acid (disappeared after 15 min) oxalic acid (disappeared after 15 min)	Ballod et al. (1982)
4-chlorophenol	*1,4*-benzoquinone, HCl, CO_2, CO, methanol, ethane, and H_2	
Carbohydrate 171-227 °C, 240-480 psi PO_2, 30 min	formic acid, acetic acid, methanol, acetaldehyde, acetone, and several hydroxylated acids	McGinnis et al. (1984)
2-chlorophenol *4*-chlorophenol 204-260 °C, 565-1030 psi total pressure, 60 min	phenol, malaeic acid, oxalic acid, acetone, acetaldehyde, acetic acid	Keen and Baillod (1985)



(Source: Williams et al. 1975. Used with permission.)

Figure 2.6. Proposed oxidation pathway for butyric acid.



(Source: Devlin and Harris 1984. Reprinted with permission from *Industrial & Engineering Chemistry Fundamentals*, ©1984, American Chemical Society.)

Figure 2.7. Proposed reaction pathway for phenol oxidation.

mechanisms were independent of oxygen concentration. They concluded that the reaction *mechanism* was not affected by the addition of homogenous catalysts, although the reaction *rates* were significantly enhanced.

Phenanthrene was rapidly destroyed when phenanthrene-loaded carbon (250 milligrams [mg] in 5 g carbon) was subjected to WAO (230 °C and 400 psi PO_2) for carbon regeneration, as reported by Larson et al. (1988). Using GC-MS, they tentatively identified 15 byproducts (Table 2.10) after 1-hour WAO. A phenanthrene oxidation scheme involving hydroxyl radicals was proposed to hypothesize the destruction pathway from the three-ring phenanthrene to a one-ring phenol. Acetic acid concentration increased 3- to 4-fold between 10 and 60 minutes at 230 °C.

In general, free radical oxidation reactions (e.g., WAO) can be accelerated by increasing the initial rate of free radical formation. Various peroxides and azo compounds are commonly used as initiators (Emanuel et al. 1967) in liquid phase oxidation involving organic solvents. The effects of initiators can be seen more clearly in the case of WAO of compounds like phenol and xylene which exhibit an induction period, i.e., a period of slow reaction.

Table 2.10. Compounds tentatively identified in wet air regeneration of Nuchar PAC adsorbed with phenanthrene.

Phenol
Benzoic acid
o-hydroxybenzaldehyde
Salicylic acid
Phthalic acid
2-hydroxy-*2'*-carboxybiphenyl
2-(*2*-formylphenyl)benzoic acid
2-2'-diphenic acid
1,2-naphtholic anhydride
3,4-benzocoumarin
Fluorenone
Anthraquinone
Phenanthrenequinone
Dialdehyde $C_{14}H_{10}O_2$

(Reprinted from *Water Research*, Larson et al., "Some Intermediates in the Wet Air Oxidation of Phenanthrene Adsorbed on Powdered Activated Carbon," © 1988, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.)

The observed effect on the initial rate of COD/TOC reduction by the addition of H_2O_2 may be explained as follows (Emanuel et al. 1967). At the WAO conditions studied, H_2O_2 readily decomposes to produce $OH^{\cdot}$ radicals. With the added H_2O_2, the radical concentration in the reactor may exceed the equilibrium concentration of the radicals needed for the reaction to proceed. This causes an increase in the oxidation rate of the organics in redwater. As the free radical chain reactions proceed and the radicals are consumed in the propagation and termination stages, there is no longer an excess of radicals and the oxidation rates revert back to their normal, unenhanced rates.

Free Radical Mechanisms in WAO

WAO of organics with molecular oxygen is generally thought to proceed via free radical chain reaction mechanisms. The oxygen is involved in the formation of different radicals both in initiation (e.g., hydroperoxy ($HOO^{\cdot}$) and ($R^{\cdot}$) radicals) and propagation stages (e.g., $ROO^{\cdot}$). Yang and Eckert (1988), however, proposed that O_2 was only involved in the propagation stage. During the propagation stage, other radicals, such as $HO^{\cdot}$ (hydroxyl), $RO^{\cdot}$ (alcoxy), and $ROO^{\cdot}$ (peroxy), may be formed. These radicals are eventually involved in the formation of organic hydroperoxide (ROOH) and subsequent breakdown into other products including acetic/formic acid and CO_2.

An example of the four major steps of initiation, propagation, degenerate branching, and termination for free radical chain reactions is shown below (Emanuel et al. 1984):

INITIATION

$$RH + O_2 \rightarrow R^{\cdot} + HOO^{\cdot} \quad \text{[Eq 2-4]}$$

$$2RH + O_2 \rightarrow 2R^{\cdot} + H_2O_2 \quad \text{[Eq 2-5]}$$

PROPAGATION

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \quad \text{[Eq 2-6]}$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \quad \text{[Eq 2-7]}$$

DEGENERATE BRANCHING

$$ROOH \rightarrow RO^{\cdot} + HO^{\cdot} \quad \text{[Eq 2-8]}$$

$$ROOH + RH \rightarrow R^{\cdot} + RO^{\cdot} + H_2O \quad \text{[Eq 2-9]}$$

TERMINATION

$$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R \quad \text{[Eq 2-10]}$$

$$ROO^{\cdot} + R^{\cdot} \rightarrow ROOR \quad \text{[Eq 2-11]}$$

$$ROO^{\cdot} + ROO^{\cdot} \rightarrow ROH + R_1COR_2 + O_2 \quad \text{[Eq 2-12]}$$

Radicals produced in the various stages of the chain reactions described above play different roles depending on the substrate being oxidized, the oxidant used, and other experimental conditions. Only detailed kinetic experiments (e.g., continuous spectroscopic analysis to follow the disappearance of the specific radicals and the formation of intermediates and end products) may elucidate the role(s) of the various radicals (Mill and Hendry 1980).

The formation of H_2O_2 (Eq 2-5) indicates the existence of free radical mechanisms associated with WAO reactions. Shibaeva et al. (1969a) experimentally determined the presence of H_2O_2 (34 mg/L) during the WAO of phenol (T = 160 °C, dissolved oxygen = 640 mg/L, and phenol = 9.4 g/L), thereby confirming the involvement of free radicals in the liquid phase oxidation of phenol. Also, H_2O_2 can be formed from the direct reaction of $HOO^\bullet$ and the parent compound as (Shibaeva et al. 1969a):

$$RH + HOO^\bullet \rightarrow R^\bullet + H_2O_2 \qquad \text{[Eq 2-13]}$$

The radical $HOO^\bullet$ is extremely reactive, but is generally present in low concentrations in liquid phase oxidation. Nevertheless, it can play an important role, such as in the oxidation of carbohydrate (McGinnis et al. 1984), or phenol (Shibaeva et al. 1969a).

The radical $R^\bullet$ formed via equations 2-4 through 2-13 is involved in the formation of $ROO^\bullet$ radical (Eq. 2-6), R-R polymers (Eq. 2-10), and the production of oxidized compounds (Eq. 2-11).

The reactions listed in equations 2-4 through 2-13 are not the only radical reactions that occur in aqueous phase oxidation. For example, although the fate of $HO^\bullet$ is not explicitly shown in Emanuel's example, $HO^\bullet$ is involved in many chemical reactions, such as: the combustion process (Li et al. 1991), ozonation (Hoigné and Bader 1976), photocatalytic oxidation (Davis 1989), and Fenton-catalyzed process (Buxton et al. 1988). In WAO of butyric acid, Williams et al. (1975) suggested that the oxidation involved $HO^\bullet$; Shibaeva et al. (1969a) stated that $HO^\bullet$ facilitated the formation of $R^\bullet$ as:

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O \qquad \text{[Eq 2-14]}$$

In addition to thermal homolysis of the hydroperoxide (Eq 2-8), $HO^\bullet$ can also be formed as (Shibaeva et al. 1969a):

$$RH + H_2O_2 \rightarrow R^\bullet + H_2O + HO^\bullet \qquad \text{[Eq 2-15]}$$

The free radicals $R^\bullet$ and $ROO^\bullet$ are also reactive and rapidly disappear (Equations 2-7 to 2-13), resulting in an equilibrium concentration of these radicals; their formation rate is equal to their consumption rate. Although not shown above, the alcoxy radical,

$RO^\bullet$, can also participate in the chain reactions to produce an alcohol by interaction with the starting material, RH (Emanuel et al. 1967):

$$RO^\bullet + RH \rightarrow ROH + R^\bullet \qquad \text{[Eq 2-16]}$$

It has been established experimentally that $R^\bullet$ increases with PO_2, reaches some limiting value, and then remains constant (Emanuel et al. 1967). This relationship agrees well with the chain mechanism of oxidation. Dissolved Oxygen (DO) is low at very low PO_2. Reaction 2-6 is slower than reaction 2-7 resulting in $[R^\bullet] >> [ROO^\bullet]$, and chain termination takes place via reaction 2-10. The overall sequence results in reaction 2-6 being the rate limiting step. Consequently, the oxidation rate increases with $[O_2]$. Conversely, when DO is high, reaction 2-6 is rapid or $[R^\bullet] << [ROO^\bullet]$, the chain reaction terminates by reaction 2-11, and the rate of oxidation does not depend on $[O_2]$. In this case, oxidation is limited by reaction 2-7. For a general case, all three termination reactions must be considered to determine the oxidation dependency.

A critical concentration of radicals is required for free-radical reactions to proceed at reasonable rates (Emanuel et al. 1967). Such reactions can generally be accelerated by increasing the initial radical formation rate and concentration. Various peroxides and azo compounds can be used as initiators. For example, H_2O_2 would decompose under the WAO conditions and readily produce $HO^\bullet$. The increased radical concentration may exceed the critical value and shorten induction periods. Additionally, this may enhance the oxidation rate. As the reaction proceeds and the radicals are consumed in the propagation and termination steps, the radical concentration would eventually reach an equilibrium concentration and the reaction rates would revert back to the unenhanced rates (Emanuel et al. 1967).

Increases in the reaction rate that occur with metal compounds of variable valency are considered to be indicators that a particular reaction involves free radical mechanisms. Depending on their valency state, ions of metals (M) of variable valency may add or subtract one electron to/from any valence-saturated molecule, inevitably leading to the formation of free radicals and the acceleration of the chain oxidation process (Kamiya et al. 1964):

$$RH + M^{n+} \rightarrow R^\bullet + M^{(n-1)+} + H^+ \qquad \text{[Eq 2-17]}$$
$$ROOH + M^{n+} \rightarrow M^{(n+1)+} + OH^- + RO^\bullet \qquad \text{[Eq 2-18]}$$
$$ROOH + M^{n+} \rightarrow M^{(n-1)+} + H^+ + ROO^\bullet \qquad \text{[Eq 2-19]}$$

At higher catalyst concentrations, however, the reaction rates may be inhibited due to the formation of inactive products:

$$ROO^\bullet + M^{(n-1)+} = ROOM^{n+} \qquad \text{[Eq 2-20]}$$

Free radical mechanisms involve many pathways for the formation of intermediates and products. The intermediates themselves may enter into chain reactions in many ways. A lot of mechanistic-type information has been gathered on liquid phase oxidation of hydrocarbons; however, information on free radical reactions of hazardous wastes at elevated temperatures and pressures is relatively scarce.

Toxicity Tests

Although WAO has been extensively studied for a variety of hazardous wastes, only a few toxicity tests have been performed on WAO-treated wastes. Furthermore, these limited studies were conducted on a single species, the Daphnia magna (Randall and Knopp 1980; Keen and Baillod 1984), or Nitrosomonas (Hao and Phull 1992). Each test culture behaves differently; the validity of the results of one species when applied to others needs to be verified, and correlation among different species is of interest.

Friedman et al. (1975) attributed formaldehyde produced at 270 °C (WAO of sludge) to cause more toxic effects in batch bioassay tests than the insignificant toxicity produced by WAO at a temperature of 230 °C. Less toxicity tolerance at lower WAO temperatures is not unusual. The increased toxicity of redwater treated at high WAO temperatures was also reported by Gee (1992) using different bioassay techniques. Keen and Baillod (1985) reported that the enhancement factor (the ratio of the measured toxicity to the expected toxicity) of 4-nitrophenol towards Daphnia magma increased with increased WAO temperature. Based on the analysis of WAO results of several aromatics performed by Randall and Knopp (1980), Phull (1992) has shown that the enhancement factor increases from 275 to 320 °C for 7 out of 9 compounds. Clearly, byproducts generated at 320 °C may exhibit more inhibitory effects than those at 275 °C.

The toxicity data for possible intermediates associated with the oxidation of aromatic compounds are summarized in Table 2.11. Clearly, trace amounts of nitrobenzene (NB) and aminophenol would have exhibited a significant impact on Nitrosomonas. Hockenbury and Grady (1977) also reported that dodecylamine, aniline, and n-methylaniline at concentrations less than 1 mg/L would cause 50 percent inhibition of Nitrosomonas culture.

The determination of toxicity of WAO-treated redwater may be essential in the absence of complete elucidation of intermediates and end products. In some cases, nitroaromatics become less toxic with the introduction of a sulfonic acid (SO_3H) group which renders them water soluble. As shown in Table 2.12, however, some sulfonated compounds are more toxic than the parent compounds. Due to this tremendous variability, the toxicity of the WAO-treated effluent (which may contain varying

Table 2.11. Toxicity data (IC_{50}, mg/L) for related aromatic compounds.

Aromatic Compounds	Microtox	Nitrosomonas	Aerobic Heterotrophic
benzene	75	13	520
toluene	-	84	110
phenol	18	21	1100
NB	-	0.92	370
2,6-DNT	-	180	-
2-aminophenol	1.4	0.27	0.04
4-aminophenol	0.12	0.07	-
methylene chloride	-	1.2	320
2,4-dinitrophenol		37*	
quinolinol		1.5*	

* Hocknebury and Grady (1977)
Source: Blum and Speece, 1991.

amounts of sulfonates as well as the parent aromatic compounds) must be assessed for each compound.

Toxicity of Byproducts

Many state regulatory agencies now issue effluent permits to industrial waste treatment plants for specific toxic compounds. Discussed earlier, WAO can achieve greater than 90 to 99 percent destruction of almost all hazardous wastes and toxic

Table 2.12. Toxicity of sulfonated and parent compounds.

Chemical	Toxicity, mg/kg,LD_{50} (Oral - Rat)
Benzenesulfonic acid	890
Benzene	4,894
Toluenesulfonic acid	2,480
Toluene	5,000
Nitrobenzenesulfonic acid, sodium	11,000
Nitrobenzene	640
Nitrotoluenesulfonic acid	3,710
Nitrotoluene	2,144
Dinitrobenzenesulfonic acid	5,800
Dinitrobenzene	83

Source: RTECS, 1983
LD = lethal dose
Oral - Rat - oral toxicity to rats

compounds under appropriate conditions. Therefore, WAO-treated effluent may meet the specified regulations without difficulty. However, with stringent effluent-discharge regulations, bioassay tests are being required for publicly-owned wastewater treatment plants. Toxicity reduction evaluation is also needed for some industrial wastewater treatment plants. Because of the complicated nature of WAO involving free radical mechanisms, the transformation of starting materials to other intermediates occurs. Some of these intermediates and end products, such as amine-containing aromatics, may be more toxic than the parent compound(s). If WAO-treated wastes are to be discharged directly into the receiving waters, their impact on water quality must be quantified. Thus, the toxicity tests of WAO-treated wastes are of the utmost importance.

WAO of wood carbonization waste (COD = 50 to 190 g/L) resulted in 92 to 96 percent COD reduction (Kalman et al. 1989). The high residual COD (2000 mg/L) was not toxic to AS. Randall and Knopp (1980) showed that the WAO products of several organics examined using Daphnia magna were less toxic than the starting materials by a factor of 15 to 4000, depending on the particular compound. However, based on the WAO removal efficiencies of the starting materials, it is apparent that the observed toxicity of the WAO-treated compounds is due to end products. A toxicity factor (TF) is used to quantitatively describe their data, shown in Table 2.13. First, EC_{50} (percent by volume) is converted to EC_{50} (effective concentration for 50 percent of the population) in mg/L (C_x is the concentration of compound x) of the starting material as:

$$C_x \text{ (mg/L)} = (EC_{50}, \text{ percent by volume}) \\ \text{(final compound concentration, mg/L)} \qquad \text{[Eq 2-21]}$$

For example, C_x concentration of 0.043 mg/L (first row, acenaphthene data, 275 °C, Table 2.13) represents the acenaphthene concentration to which Daphnia reacts. Considering the EC_{50} of the untreated acenaphthene (3.5 mg/L), it is apparent that Daphnia reacts not to the small amount of acenaphthene, but more importantly, to the end products in the WAO-treated solution. TF is then classified as:

$$TF = (EC_{50} \text{ for original compound})/C_x \qquad \text{[Eq 2-22]}$$

In the case of WAO-treated acenaphthene at 275 °C, TF is 81. This factor, the same as the enhancement factor used by Keen and Baillod (1985), can be used to express the relative toxicity of intermediates and the original compound remaining after WAO. The greater this factor is, the more profound the toxic effect of the end products on the test species. Only one compound (pentachlorophenol) has a TF value of less than 1 at 275 °C; the starting compound was more toxic than WAO-generated byproducts. The others clearly indicate the toxicity of WAO byproducts to be higher than the

Table 2.13. Toxicity of raw and WAO-treated organics.*

Starting Material	48-hr EC_{50} for Starting Material (mg/L)	48-hr EC_{50} for WAO Effluent (% by Volume)		Concentration of Starting Material in WAO Effluent (mg/L)		48-hr C_x (mg/L)		Toxicity Factor (TF)	
		275 °C	320 °C	275 °C	320 °C	275 °C	320 °C	275 °C	320 °C
Acenaphthene	3.5	6.1	7.1	0.7	2.8	0.043	0.20	81	18
Acrolein	0.093	4.7	4.5	-	< 3	-	-	-	-
Acrylonitrile	11.0	1.7	4.8	80.6	73	1.37	0.35	8	31
2-chlorophenol	6.2	0.9	2.6	625	17.4	5.63	0.45	1	14
2,4-dimethylphenol	2.4	7.7	6.5	0.8	0.8	0.06	0.05	40	48
2,4-dinitrotoluene	26.2	3.4	4.0	26	12	0.88	0.48	30	55
1,2-diphenylhydrazine	2.2	6.6	7.2	1.0	1	0.066	e	33	31
Phenol	23.5	6.1	10.6	23	3	1.40	0.32	17	73
4-nitrophenol	20.0	6.4	7.7	40	4	2.56	0.31	8	65
Pentachlorophenol	1.0	1.1	0.3	952	6	10.47	0.018	0.1	56

* Raw data obtained from Randall and Knopp (1980). Used with permission.

starting materials. Furthermore, as WAO temperature increased from 275 to 320 °C, TF increased for 7 out of 9 compounds. In other words, byproducts generated at 320 °C exhibited more inhibitory effects than those at 275 °C.

Keen and Baillod (1985) also concluded that byproducts from the WAO of phenol and substituted phenols were somewhat more toxic than the known concentration of the initial compound remaining in the oxidized solution. Phull (1992) analyzed the results of Randall and Knopp (1980) and demonstrated that byproducts were more toxic than the starting aromatic compound. Eckenfelder (1989) also reported possible toxicity of WAO-treated wastes at 260 °C for 1 hour: the 48-hour IC_{50} (for mysid shrimp at 1:25 dilution) increased from 1.1 for concentrated waste to only 4.1 for treated waste, clearly showing that the end products were more toxic than the starting material. The term IC_{50} is defined as the concentration that inhibited the culture by 50 percent compared to the uninhibited controls (Blum and Speece 1991).

Larson et al. (1988) performed toxicity tests using a yeast strain (Saccharomyces cerevisiae) on the aqueous filtrates and carbon extracts of WAO (230 °C) of phenanthrene-containing PAC. The filtrate produced no toxicity; however, the carbon extract exhibited some degree of toxicity. Based on the fact that the extract of the non-regenerated carbon (loaded with 5 percent by weight phenanthrene) was only slightly toxic to yeast, the byproducts formed (still adsorbed on the PAC) during regeneration must be responsible for the observed toxicity. Nevertheless, as the regeneration proceeded, the byproducts were further oxidized and the toxicity effect decreased.

Costs

Detailed cost information is currently unavailable to compare WAO with other available treatment processes. Review of available literature (Heimbuch and Wilhelmi 1985) does indicate, however, that the capital cost for WAO would compare favorably with that of an incineration plant, but the operating costs for WAO would be much lower (Copa 1990, 1992), particularly since this technology offers a potential for resource recovery. Zimpro Passavant Environmental Systems, Inc. has completed a preliminary analysis of several WAO systems (see Appendix A), but more detailed studies are needed.

Since the cost of hazardous waste treatment is related to the degree of oxidation, (which is dependent on the pressure, temperature, organic concentration, contact time, and catalyst), results of proposed future studies will be used to determine optimum operational conditions for a desirable level of organic destruction. A detailed cost benefit analysis is needed to compare the WAO process with alternative treatment processes.

3 Experimental Details

In this chapter, materials used during the experiments are discussed, analytical procedures for identifying and quantifying the reactant and product components are described, and finally, the experimental procedures for WAO studies with different operating conditions and toxicity studies are presented.

Materials and Methods

TNT redwater is a complex mixture of many organic and inorganic constituents. Therefore, identification and quantification of individual components (e.g., dinitrotoluene sulfonates [DNTSs] and several nitroaromatics) required the use of separation techniques such as liquid and gas chromatography. Existing analytical methods were used for all the desired parameters with the exception of DNTSs. A review of pertinent literature and discussions with analytical laboratories indicated a need to develop an analytical method for DNTSs in redwater. Therefore, a reverse phase ion-pairing chromatography (RPIPC) method was developed and found to provide satisfactory results for DNTSs and other sulfonated nitroaromatics.

TNT Redwater

TNT redwater (1 gal) generated during the nitration of orthonitrotoluene was obtained in September 1990 from ICI-Explosives, Canada. The redwater was filtered through cotton, and as a safety precaution (Hulburt 1991), the filtrate was diluted to 1:100 for analysis and for most of the WAO experiments. Both raw and diluted redwater were placed in dark bottles and stored in a refrigerator at 4 °C.

Chemicals

The laboratory chemicals used in the analytical methods discussed below were acquired from different chemical suppliers. Analytical-grade reagents were used in all cases except for RPIPC, where chemicals of ultra-pure quality (acetonitrile and tetrabutylammonium hydroxide) were used.

Analytical Methods

Analytical methods used to characterize the various components of raw and treated TNT redwater are summarized in Table 3.1. A brief description follows for each except for the DNTSs method, which is discussed in detail. All analyses except COD were performed at the U.S. Army Environmental Hygiene Agency (USAEHA) laboratories in Edgewood, MD. The COD analyses were performed at the University of Maryland Environmental Engineering Laboratory. The USAEHA Laboratory is a USEPA-certified laboratory and maintains comprehensive, written standing operating procedures (SOPs) for various types of analyses and laboratory quality control. The SOPs were generally followed for the analyses of raw and treated samples.

TOC and COD

A TOC analyzer (Oceanographic International [O.I.] model 700) was used for TOC analysis. The method consists of acidification (5 percent H_3PO_4) to purge the inorganic carbon, followed by sodium persulfate (100 g/L) digestion of the sample at 100 °C for 5 minutes. The TOC analyzer measures the released CO_2 with an IR detector. Potassium hydrogen phthalate standards (0.2 to 10 mg/L) were used for calibration.

The dichromate reflux method (Standard Methods 1985) with a reflux time of 2 hours was used for COD measurement.

Table 3.1. Analytical methods used.

Parameter	Analytical Method
pH	pH Electrode and pH Meter
Solids	Standard Methods (1985)
TOC	O.I. TOC Analyzer Model 700
COD	Standard Methods (1985)
Nitrite, Nitrate, Sulfite, Sulfate, Acetic Acid, and Formic Acid	Ion Exchange Chromatography
α-TNT, DNTs, DNB, and TNB	Toluene Extraction and Gas Chromatography
DNTSs	Reverse Phase Ion Pairing High Performance Liquid Chromatography
Metals Spectrophotometry	Inductively Coupled Plasma

O.I.= Oceanographic International

Nitrite, Nitrate, Sulfite, and Sulfate

A DIONEX ion chromatograph (model 2020i) with an HPIC-AS4 analytical column and an HPIC-AG4 guard column was used for the analysis of the inorganic anions. The eluant composition and other experimental conditions are summarized in Table 3.2. The detection limits (DLs) for nitrite, nitrate, sulfite, and sulfate were 0.1, 0.5, 0.5, and 0.5 mg/L, respectively. Calibration standards were prepared by dissolving appropriate amounts of the sodium salts in deionized water.

Acetic Acid

Acetic acid was measured by ion exchange chromatography using a DIONEX ion chromatograph; experimental conditions are summarized in Table 3.2. Reagent-grade sodium acetate was used to prepare calibration standards of 0.5 to 5.0 mg/L as acetate; the DL was 0.5 mg/L for the acetic acid analysis.

pH

A pH electrode and meter (Orion, model 501) were used for pH measurements.

Solids

Crucibles with 5 to 10 glass beads were washed, cleaned, dried at 550 °C, and weighed. Samples (10 to 15 mL) were added into the crucibles for total solids determination at 103 °C and fixed solids at 550 °C. Volatile solids were obtained from the difference between the total solids and the fixed solids.

Metals

Analyses for total and soluble metals were performed using a Perkin-Elmer (model 6500) inductively coupled plasma (ICP) spectrophotometer. Soluble metals concentration was determined by first digesting a sample with concentrated sulfuric acid, filtering with a 0.8 micrometer (μm) Millipore filter, and analyzing the filtrate for metals.

Nitroaromatics

The USAEHA SOPs on analysis of explosives in wastewater were followed for the analysis of raw and treated samples. A Hewlett-Packard GC (model 5890) was used for the analysis of nitroaromatics (1,3-DNB; *2,4*-DNT; *2,6*-DNT; *1,3,5*-TNB; *α*-TNT). An 8 m DB1 (J & W Scientific) capillary column was used with electron capture detector. The following experimental conditions were used: oven temperature was 128

Table 3.2. Equipment and experimental conditions used for the analysis of inorganic anions, acetic acid, and DNTS.

Instrument: DIONEX Ion Chromatograph Model 2020i with Auto sampler and a Hewlett Packard Model 3396A Integrator

	Nitrite, Nitrate Sulfite, and Sulfate	Acetic Acid	DNTSs
Analytical Column	HPIC-AS4	HPIC-AS1	MPIC-NS1
Guard Column	HPIC-AG4	HPIC-AG1	MPIC-NG1
Anion Micromembrane Suppressor	AMMS-1	AMMS-1	AMMS-1
Eluant	0.0028 M $NaHCO_3$ + 0.0022 M Na_2CO_3	0.005 M Borate ($Na_2B_4O_7$)	28% ACN + 2 mM TBAOH
Eluant Flow Rate	1-2 mL/min	2 mL/min	1 mL/min
Regenerant	0.025 N Sulfuric Acid @ 2-3 mL/min	0.025 N Sulfuric Acid @ 2-3 mL/min	0.025 N Sulfuric Acid @ 2-3 mL/min
Column Pressure	870-920 psi	570-900 psi	1200-1600 psi
Sample Loop Size	100 μL	50 μL	100 μL
Background Conductivity	18.8 μS*/cm	5.5 μS	4.8-21 μS
Conductivity Range	10 μS	10 μS	10 μS
Analysis Run Time	25 min	12 min	30 min
Attenuation	7	7	7

*μS = microsiemens

to 220 °C at approximately 20 °C/min; injection port temperature was 270 °C; detector temperature was 280 °C; Helium flow was 6 mL/min; Argon/CH_4 flow was 30 mL/min; sample size was 2 microliters (µL); and direct on-column injection.

Samples were extracted by adding 2 mL toluene to a 100-mL aqueous sample in a 100-mL volumetric flask. The flask was carefully sealed and its contents mixed on a rotary shaker (at approximately 30 revolutions per minute [rpm]) for 30 minutes. After phase separation (approximately 10 minutes after mixing), 1 to 1.5 mL extract was pipetted from the top layer in the flask and stored in a 2-mL vial for later GC analysis. The DL was 0.05 mg/L for each nitroaromatic. Based on the extraction procedures used, the quantification limit for the samples was 0.001 mg/L for each nitroaromatic. Analytical standards for nitroaromatics were obtained from the Standard Analytical Reference Materials (SARM) maintained in the USAEC repository.

DNTSs

After discussion with several analytical chemists with experience in the characterization of explosives (DIONEX Corp., Sunnyvale, CA, personal communication, 1990; R. Gaffney, R. McKenzie, M. Hable, and K. Williams, AEHA, Aberdeen Proving Ground, MD, personal communication, 1990 and 1991), it was decided to develop a RPIPC method for the analysis of the highly polar, nonvolatile DNT sulfonic compounds (DNTSs). The commercial nonavailability of analytical standards for DNTSs necessitated their synthesis.

Reverse Phase Ion-Pairing Chromatography (RPIPC). Information published by DIONEX (Weis 1986) formed the basis of the method development for DNTSs. The RPIPC technique has been patented by DIONEX as mobile phase ion chromatography (MPIC); it includes detection via conductivity after reduction of the background conductivity using a micromembrane suppresser system. Both analytical and guard columns (stationary phase) used for this technique are made of a neutral macroporous polystyrene-divinyl benzene resin with a nonpolar character. Figure 3.1 presents an overall picture of the separation and detection processes involved in RPIPC.

There are two schools of thought concerning the physico-chemical concept governing the retention mechanism in RPIPC (Weis 1986). One proposes that the solute ions form neutral pairs with the lipophilic ions (tetrabutyl ammonium [TBA] cations in this case) in the aqueous phase which are adsorbed onto the neutral stationary phase. Lipophilic ions exhibit a high affinity for lipids (i.e., substances soluble in nonpolar organic solvents). The second hypothesis supports adsorption of the lipophilic ions onto the surface of the stationary phase, which in turn converts it into an ion-exchange material. The two hypotheses represent extreme cases and, as such, each fails to explain the retention processes under all chromatographic conditions. Organic

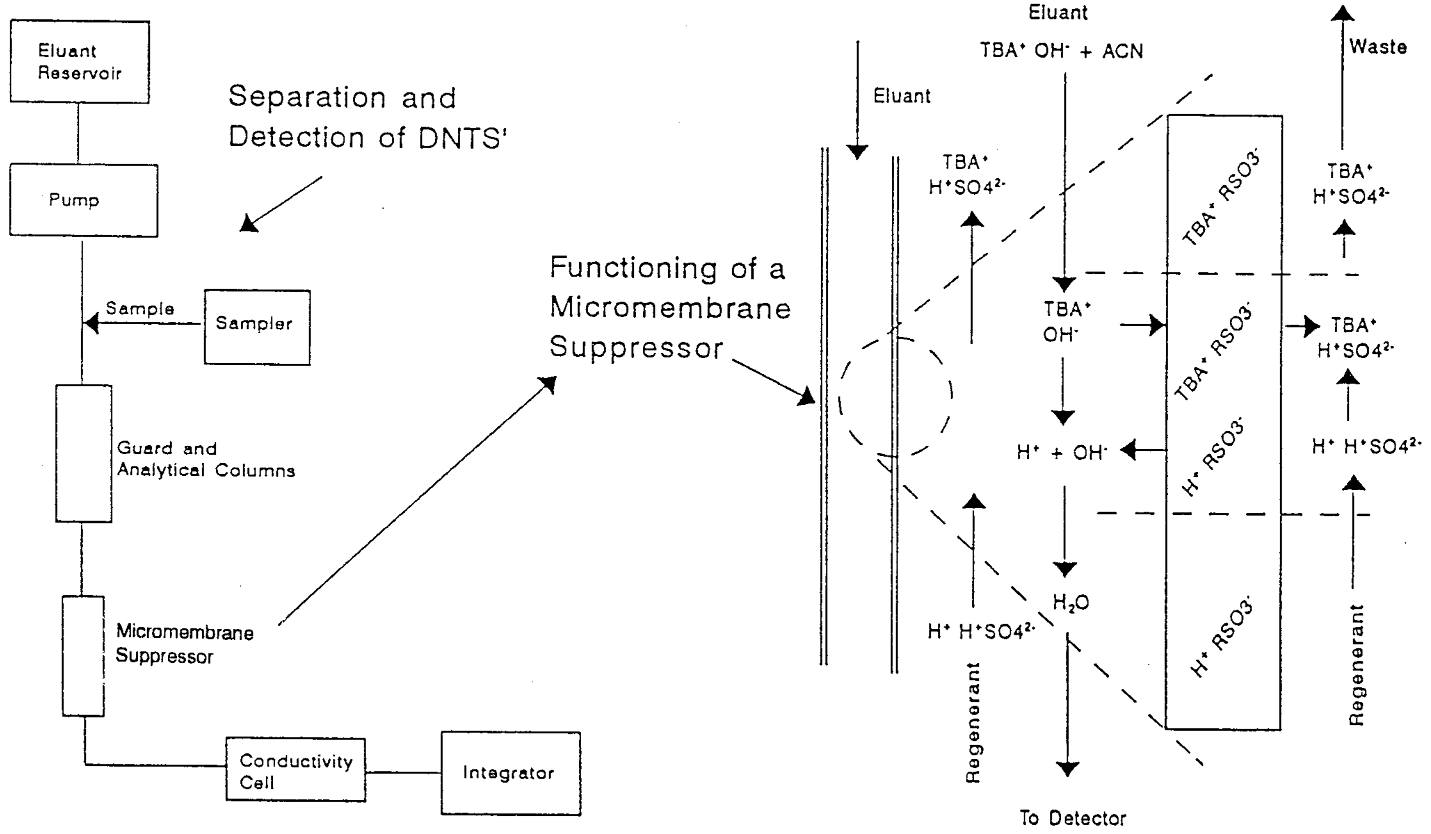


Figure 3.1. Conceptual diagram showing separation and detection of DNTS' using RPIPC.

modifiers, such as acetonitrile (ACN) as used in this study, or methanol (MeOH), serve to increase the rate at which ions elute. They become adsorbed on the resin surface and compete with the lipophilic ions in the adsorption equilibria.

Since sulfuric acid is used as the regenerating medium, the TBA ions are exchanged for protons during regeneration. A concentration gradient provides the driving force for the diffusion of protons through the wall of the suppresser membrane. Thus, anions being analyzed are converted into their acid form, allowing their sensitive detection via conductivity.

Procedures used for analytical method development for DNTSs are schematically presented in Figure 3.2. A list of equipment and experimental conditions used for the analysis of DNTSs was shown earlier in Table 3.2. Different concentrations of ACN and tetrabutyl ammonium hydroxide (TBAOH) were tested before a final selection of an eluant with 28 percent ACN and 2 millimolar (mM) TBAOH. This combination provided the optimum separation and reasonable retention times for the three DNTS isomers.

Synthesis of DNTSs. Analytical standards for DNTSs could not be obtained commercially, or from Army or private researchers who had previously worked on TNT redwater projects. Consequently, these compounds were synthesized in the laboratory. A TNT isomer mixture (*2,3,4-*; *2,4,5-*; and *2,3,6-*TNT) in ACN, which was used in the synthesis of the DNTS mixture, had been prepared in May 1985 at USAEHA. The bottle containing the TNT isomers was properly labeled and stored in a freezer with other analytical standards for explosives. Kaye (1980) noted that TNT showed no deterioration after 20 years storage in a magazine, or after two years as a liquid at 85 °C (i.e., just above the melting point). A GC analysis (same conditions as used for the analyses of nitroaromatics) yielded three distinct peaks (Figure 3.3), with retention times close to the retention time for *2,4,6-*TNT (about 1.9 minutes under similar GC operating conditions). The relative retention times of the three isomers and their concentrations based on the peak areas corresponded to their respective concentrations indicated on the bottle. A confirmatory identification of the three peaks could not be made, nor could they be quantified because of the nonavailability of analytical standards for all three isomers.

A known amount of the TNT isomers mixture was mixed with approximately 10 percent excess sodium sulfite at room temperature. The solution immediately turned red. Based on the location of the nitro groups in the three TNT isomers (*2,3,4-; 2,4,5-*; and *2,3,6-*TNT), their sulfonation should result in the formation of *2,4-*DNT-*3-*SO_3Na; *2,4-*DNT-*5-*SO_3Na; and *2,6-*DNT-*3-*SO_3Na isomers, respectively. A chromatogram from the RPIPC analysis of the sulfonate mixture is shown in Figure 3.4a. On a separate occasion, the TNT isomer mixture was again combined with sodium sulfite at room

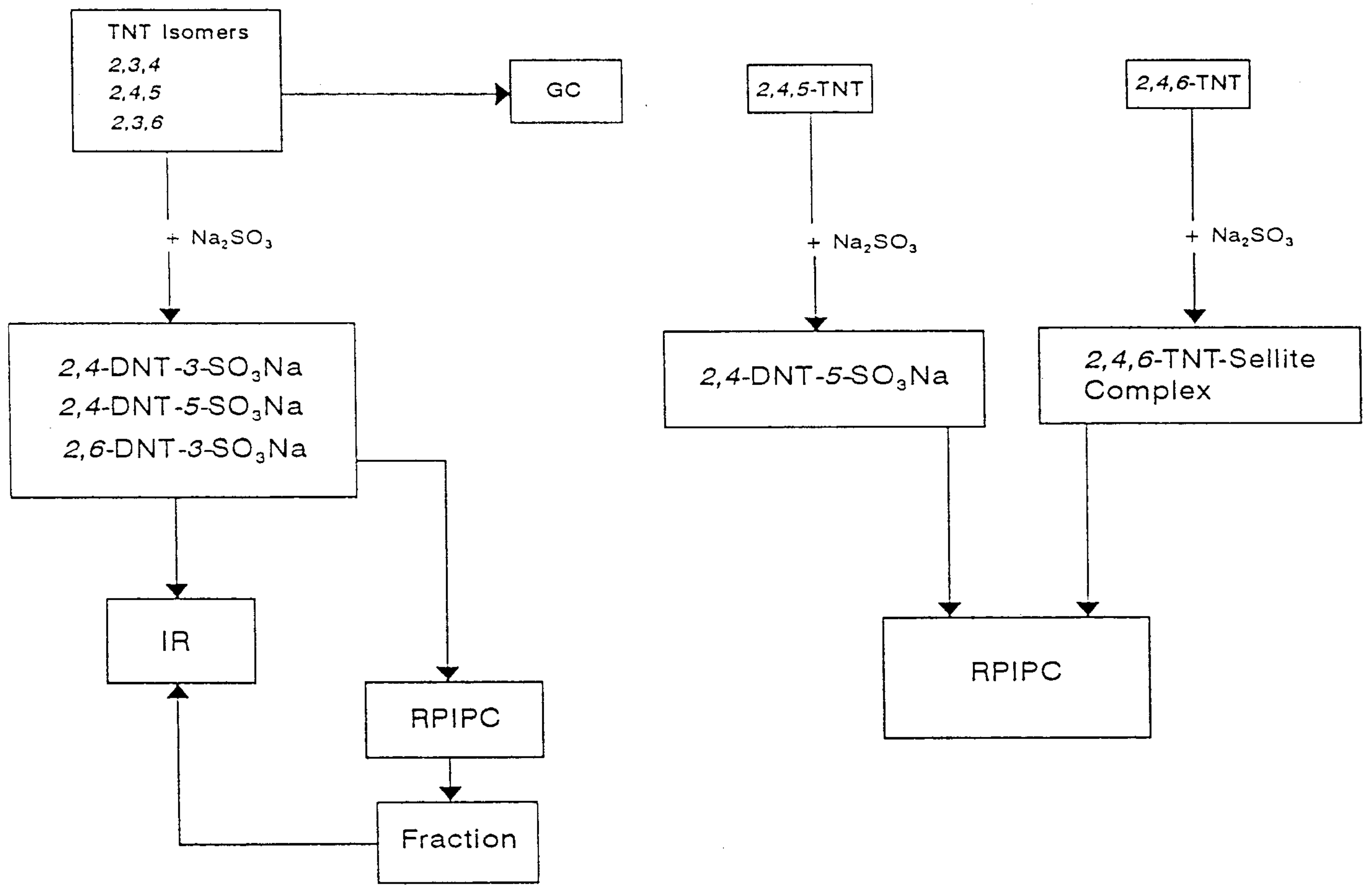


Figure 3.2. Analytical method development for DNTSs.

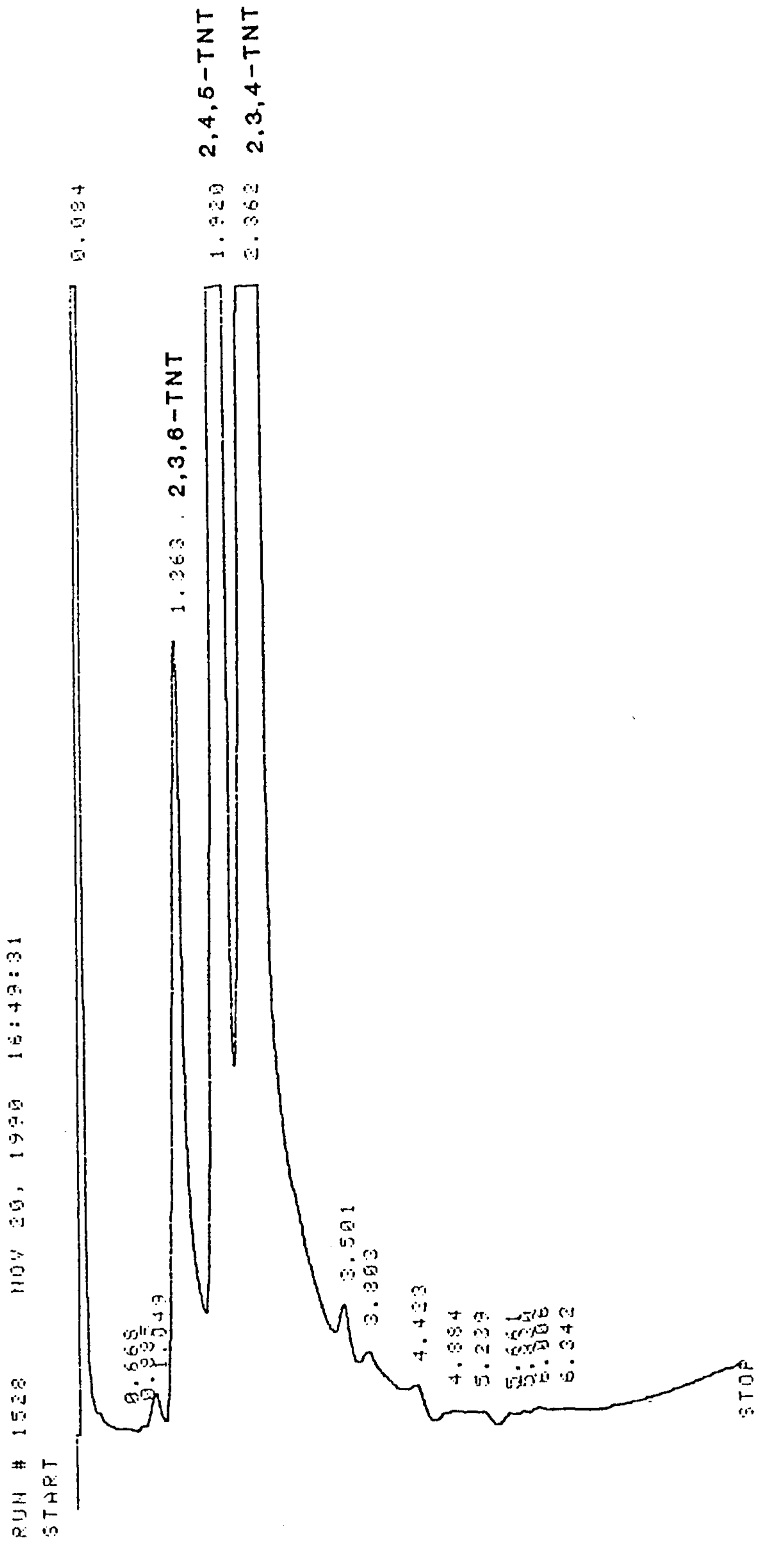


Figure 3.3. Chromatogram of TNT isomers used for synthesis of DNTSs.

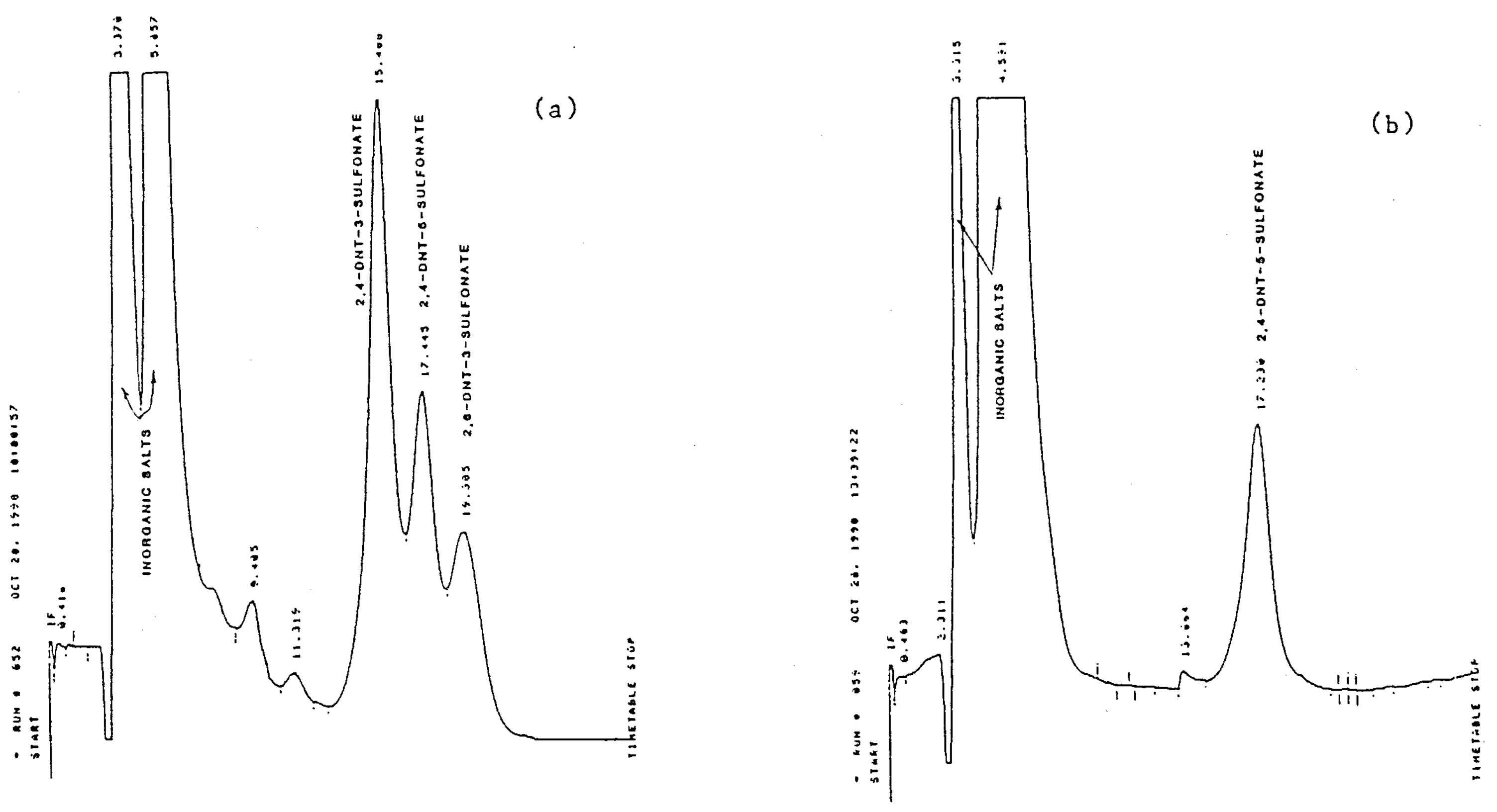


Figure 3.4. Chromatograms of (a) DNTS mixture and (b) 2, 4-DNT-5-SO_3Na.

temperature. When a stoichiometric amount of sodium sulfite was used, an orange color developed. However, a deep red color, similar to the color of actual redwater, developed when an excess amount of sodium sulfite was used. Chromatograms for the two DNTS mixtures using RPIPC showed one major difference. The sample with excess sodium sulfite (deep red color) had three peaks for the sulfonates, but the other sample (orange color) showed only two peaks. Reaction between TNT isomers and sodium sulfite conducted at elevated temperature (55 °C) also resulted in a red-colored solution and the chromatograms had three peaks.

The *2,4*-DNT-*5*-SO_3Na was similarly synthesized by reacting a known amount of pure *2,4,5*-TNT with excess sodium sulfite. The chromatogram (Figure 3.4b) had only one peak, assumed to be for *2,4*-DNT-*5*-SO_3Na. The other two DNTS isomers could not be synthesized individually due to the nonavailability of the required TNT isomers.

A known amount (0.1 g) of a-TNT was dissolved in about 5 mL of toluene and diluted to about 35 mL with deionized water. The solution was treated with an excess amount of sodium sulfite at about 60 °C to verify if the a-TNT-sellite complex formed also had a dark red color. Instead, the product(s) formed produced a slight pink color. Injections onto the MPIC-NS1 column produced no peaks (Figure 3.5). It is noted that a-TNT was dissolved in a toluene/water mixture, which might have affected its reaction with sodium sulfite. Further, the reaction of Na_2SO_3 with TNT isomers is pH-dependent and the product(s) formed with α-TNT might have yielded red color at higher pHs. These variations were not investigated further, because a systematic investigation was considered outside the scope of this work.

IR Analysis of DNTS Mixture and RPIPC Fraction. Internal reflectance IR spectroscopy was used to obtain an IR spectra of the concentrated synthetic DNTS mixture. A DIGILAB IR spectroscope (model FTS-15/90) equipped with a dueterated tri-glycine sulfate detector (DTGS) and a NOVA IV data station (Data General) was used. A 1/4-in. diameter zinc-selenide internal reflectance crystal and CIRCLE cell (Spectra Tech) were used. Fractions collected from the RPIPC analyses were evaporated at room temperature. Residue was mixed with potassium bromide (KBr) to obtain a KBr disc that was analyzed using straight transmission IR spectroscopy. A Perkin-Elmer Fourier Transformation Infra-red (FTIR) spectroscope (model 1760) was used. The spectroscope had a Perkin-Elmer data station (model 7700) and a wide-band mercury cadmium teluride (MCT) detector.

WAO Experiments—Feasibility Studies

Five experiments were performed at different WAO temperatures. A 1-hour reaction time (time between attainment of the desired reaction temperature and turning off the

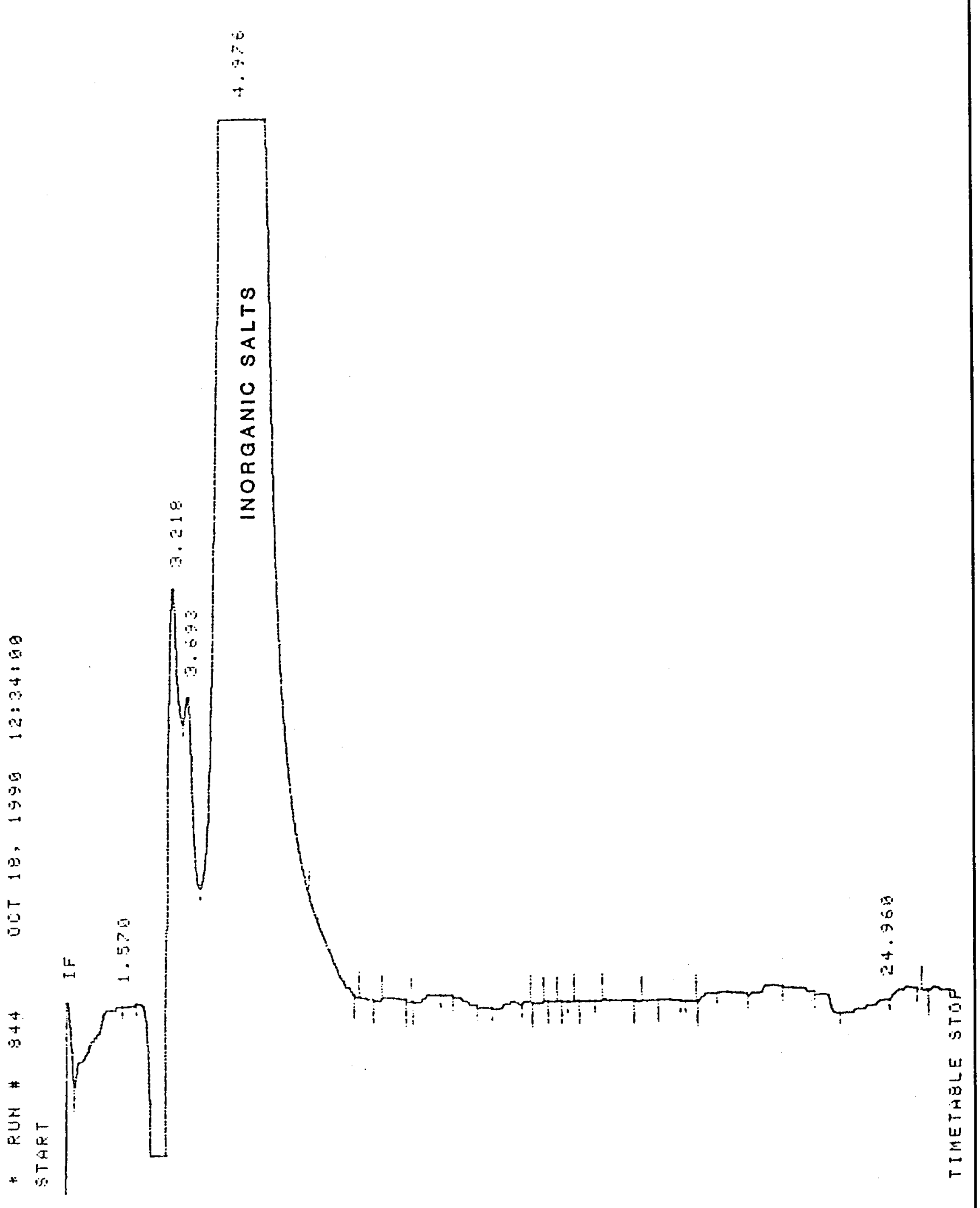


Figure 3.5. Chromatogram of TNT-satellite complex formed by reacting TNT with excess Na_2SO_3.

heater) was used. This provided a total contact time of about 95 to 135 minutes; that is, the time to reach the desired temperature (30 to 60 minutes), the reaction time (1 hour), and the cooling time (5 to 15 minutes) for the different experiments. Because the main objective of this study phase was to evaluate feasibility of WAO for redwater treatment, an excess amount of pure oxygen was used. Variable oxidant doses were used in the 1-hour experiments and kinetic experiments described later to establish optimum operational parameters for WAO of redwater. The experimental conditions used in this study phase are summarized in Table 3.3.

Apparatus

Experiments were carried out in either a 2-L or a 600-mL T-316 stainless steel reactor (Parr Instruments, Moline, IL). A schematic diagram of the apparatus is shown in Figure 3.6. Both reactors were rated for a maximum temperature of 350 °C, and were equipped with rupture discs rated at 3000 psi. However, the experiments were designed to operate the reactors at temperatures under 350 °C and at less than 70 percent of the rated pressure capacity, as recommended by the manufacturer, particularly for prolonged routine use.

The reactor temperature was regulated with a controller that regulated the output from a heater surrounding the reactor. An internal cooling coil, an integral part of the reactors, was used to control the temperature of the reactor contents (e.g., to cool down the contents quickly at the end of an experiment or in the case of an uncontrolled reaction resulting in a sudden increase in temperature). Both reactors had turbine-type impellers that were equipped with magnetic motors and provided stirring speeds of up to 750 rpm. A 1-gal stainless steel oxygen tank controlled the flow of oxygen into the reactor by using a pressure transducer for accurate tank pressure measurements (± 1 psi accuracy) before and after the discharge of oxygen into the reactor. Given the pressures in the auxiliary tank before and after the discharge of oxygen into the reactor and the sizes of the tank and the reactor, the amount of oxygen could be approximated assuming the ideal gas law. In addition to

Table 3.3. Experimental conditions for redwater WAO.

Condition	Temperature (°C)	Pressure (psig*)
Mild	225	900
Medium	300	1970
	325	2000
	325	2050
Harsh	340	2150

*psig = pounds per square inch gauge.

providing a continuous digital output for temperature, the controller also provided readouts for the mixing speed and the oxygen pressure in the 1-gal auxiliary oxygen tank via a transducer connected to the auxiliary O_2 tank. A pressure gauge mounted on the reactor provided the final operating pressure.

Procedures

All experiments were performed in a batch mode. One liter of the 1:100 dilution redwater sample (in the case of the 2-L reactor) or 300-mL sample (in the case of the 600-mL reactor) was introduced into the reactor. The auxiliary oxygen tank was filled with oxygen from a 150-lb oxygen cylinder. After sealing the reactor, the impeller motor was turned on and the speed was maintained at 200 rpm. Selecting a mixing speed of 200 rpm was based on published literature (e.g., no effect of mixing at 200 to 600 rpm on WAO of propionic acid [Day et al. 1973]). Mixing speeds between 100 and 650 rpm did not show any difference on the oxidation rate of a model compound, 5-nitro-*o*-toluenesulfonic acid.

A prescribed amount of oxygen was charged into the reactor to achieve a desired final operating pressure and a desired degree of oxygen overpressure. For example, if a particular experiment was planned for 300 °C and 1900 psi, the oxygen overpressure at 300 °C was calculated to be 654 psi (1900 psi to 1246 psi), where 1246 psi is the water vapor pressure at 300 °C. The oxygen charge pressure at room temperature (25 °C) was then calculated to be 340 psi. The heater was turned on after charging the reactor with oxygen. It took between 30 and 60 minutes for the reactor to reach the desired temperatures, between 225 and 340 °C.

The procedure of charging the reactor with oxygen at room temperature was adopted primarily for safety reasons. Thermal decomposition of redwater may occur when the reactor is heated. Since the reactor is a closed system, the thermally decomposed fractions would remain inside the reactor, and, with the introduction of oxygen, this could result in a runaway reaction and even an explosion. To avoid this, the reactor was loaded with both oxygen and the sample, and then heated. The volatile compounds are then oxidized as soon as they appear, eliminating their accumulation (Foussard et al. 1989). No sudden temperature surges were noted during any of the experiments, indicating that the reactions did not occur in an uncontrolled manner.

Analysis

At the end of 1-hour reaction time, the heater was turned off and the reactor contents were cooled with tap water via a cooling coil to quench the reaction quickly. It took 5 to 15 minutes to cool the reactor contents down to room temperature. After slowly venting the gas from the reactor, the reactor was disassembled. Samples were

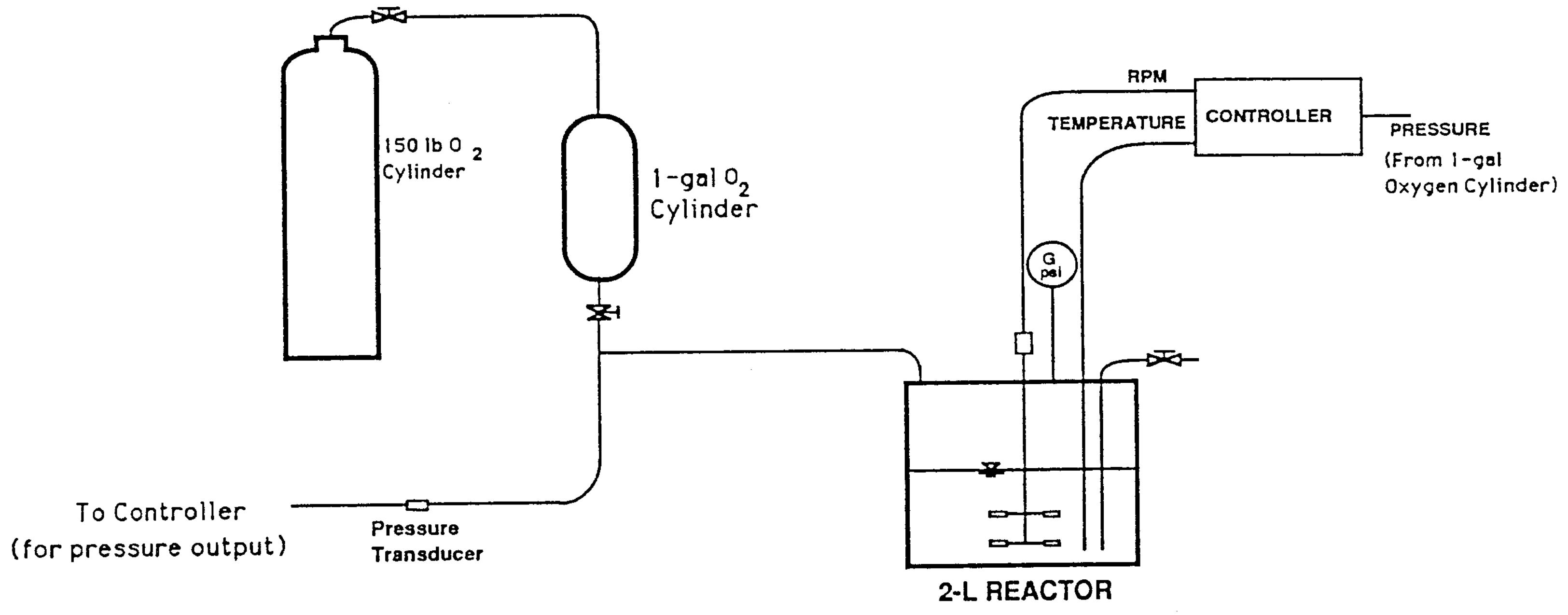


Figure 3.6. Schematic of WAO apparatus: 1 hour studies.

withdrawn from the reactor and analyzed for pH. Samples were preserved or extracted (*USAEHA Technical Guide 155*, 1991), as appropriate, for analysis for the following parameters: inorganic salts (sulfite, sulfate, nitrite, and nitrate), solids (total and volatile), COD, TOC, acetic acid, DNTSs, and five nitroaromatics [*1,3*-DNB *1,3,5*-TNB; *2,4*-DNT; *2,6*-DNT; and *a*-TNT].

The actual operating conditions are shown in Table 3.4. All experimental runs were conducted in the 2-L reactor, except for Run # 3, when the 600-mL reactor was used. In all cases, the theoretically calculated values for the final operating pressure were only slightly higher than those observed from the pressure gauge, except for Run # 3. The vast difference in the estimated and observed pressures for test Run # 3 was due to the malfunction of the pressure gauge for the 600-mL reactor.

The quantity of oxygen feed calculated from O_2 charge pressure (Table 3.4), varied from 6.4 g to 32 g O_2, far in excess of 685 mg COD of diluted redwater. Therefore, the oxidant (oxygen) dose was not considered the limiting parameter in the present study.

WAO Experiments—Kinetic Studies

The purpose of conducting these experiments was to quantify the effects of different operating conditions in the treatment of TNT redwater. The disappearance rates of different contaminants, such as DNTSs, and the concomitant appearance rate of products such as sulfates, should provide useful information on the fate of redwater components during WAO. Additionally, testing the use of a catalyst/initiator was of interest because it can significantly reduce capital and operational costs with lower temperatures and/or shorter contact times. Therefore, two sets of experiments were conducted to realize these objectives. The first set (1-hour experiments) was performed to assess WAO performance under different temperature and oxygen pressure conditions. The total contact time was about 100 to 135 minutes (i.e., the time to reach the desired temperature [30 to 45 minutes]; the reaction time [1 hour]; and the cooling time [5 to 15 minutes]) for the various test runs. The second set (kinetic experiments) was done to determine the fundamental kinetic parameters (e.g., reaction orders and rate constants) for WAO of redwater under varying conditions of temperature, oxygen pressure, catalyst addition, and other factors. These and toxicity tests performed on raw and WAO-treated redwater are described in the following paragraphs.

Apparatus

The 1-hour experiments were carried out in a 2-L, T-316 stainless steel reactor (Parr Instruments), as described in the previous Feasibility Studies section. The apparatus

Table 3.4. **WAO reactor operating conditions.**

	RUN #				
	1	2	3	4	5
Temperature, °C					
Set Temperature (S. T.), °C	225	300	325	335	340
Actual Temperature, °C	225-227	298-302	323-327	328-335	325-340
Pressure, psi					
O_2 Charge Pressure @ 25 °C	380	380	125	75	110
O_2 Pressure @ S. T.	635	730	250	155	225
Vapor Pressure @ S. T.	370	1250	1750	1990	2120
Total Theretical Pressure	1005	1980	2000	2145	2345
Actual Pressure	940-970	1950-1970	1650-1680*	1990-2050	1850-2150

* Pressure gauge not working. Pressure for this test was assumed to be 2000 psi.

was modified for the kinetic experiments to allow sample injection into the reactor at elevated temperatures and pressures.

Procedures

One-Hour Experiments. All 1-hour experiments were performed in a batch mode. A detailed description of the experimental apparatus and procedures was provided earlier under Feasibility Studies. The 2-L stainless steel reactor was filled with 1 L of diluted (1:100) redwater, sealed, charged with oxygen, and heated. The impeller speed was maintained at 200 rpm during the 1-hour reaction time. The sample collected after reactor cool-down was analyzed for pH, inorganic and organic anions (sulfite, sulfate, nitrite, nitrate, and acetate), solids (total and volatile), COD, TOC, DNTSs, six nitroaromatics [*1,3*-DNB; *1,3,5*-TNB; *2,4*-DNT; *2,6*-DNT; NB; and α-TNT], and UV/visible light (VIS) absorbance.

The operating conditions consisted of five different temperatures (200, 230, 260, 290, and 320 °C) and three oxygen partial pressures (19, 90, and 190 psi at 25 °C) with a total of 15 experimental runs. Due to the time differences in reaching the desired reaction temperatures, there is a slight variation in the total reaction time (including the heating and cooling periods) for the above experiments. Data for different temperature levels should, therefore, be compared with caution.

Kinetic Experiments. A schematic of the apparatus used for the kinetic experiments is shown in Figure 3.7. All kinetic experiments were performed using a 2-L stainless steel reactor. Initially, the reactor was filled with distilled water and the auxiliary oxygen cylinder (1 gal) was filled with oxygen (from the 150-lb oxygen cylinder). The sample and the rinsewater cylinders (each 50 mL capacity) were filled with raw redwater and distilled water, respectively. The amount of sample used depended on the sample concentration to be studied. For example, for a 1:25 dilution of redwater, the volumes of distilled water, raw redwater, and rinse distilled water were 910, 40, and 50 mL (respectively), in the reactor, sample cylinder, and rinsewater cylinder. After sealing the reactor, the stirrer was turned on to maintain a speed of 200 rpm. A desired amount of O_2 (e.g., PO_2 = 190 psi at 25 °C) was then charged into the reactor and the contents were heated to a predetermined temperature. Once the desired (set) temperature was reached, the raw redwater sample was discharged into the reactor via helium backpressure. The distilled water was then charged into the sample cylinder for rinsing, and finally to the reactor for a total liquid volume of 1 L. After the introduction of the sample and distilled water into the reactor, the temperature dropped slightly and the pressure increased a little; both stabilized within 2 to 3 minutes. The reaction time for the kinetic experiments varied from 2 to 4 hours.

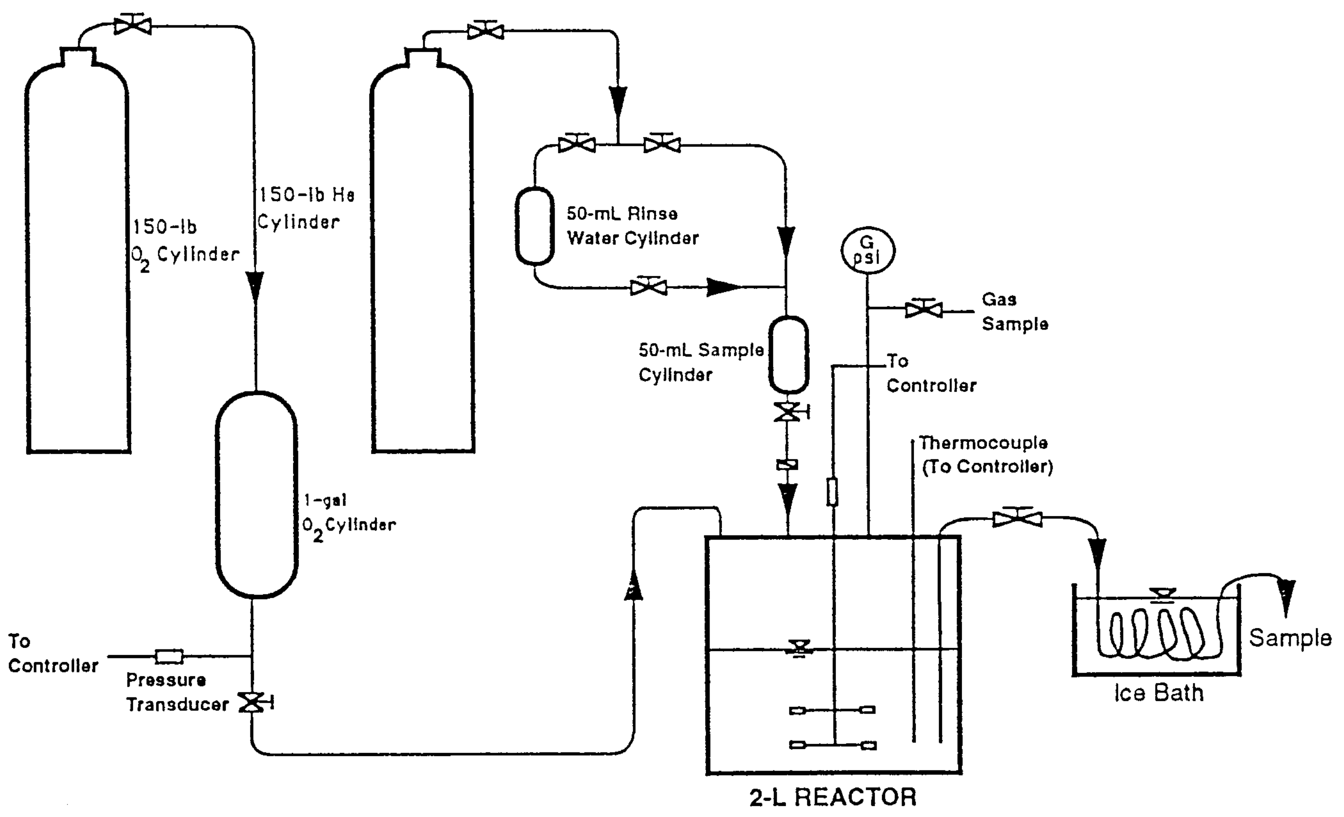


Figure 3.7. Schematic of WAO apparatus for kinetic experiments.

Samples were withdrawn through a stainless steel coil that was submerged in an ice-water bath. The first sample (10 to 15 mL) was obtained within 5 minutes of sample injection after the reactor contents returned to the set temperature; subsequent samples were collected at desired time intervals. Approximately 10 mL of liquid was discarded before each sampling event to minimize contamination of the sample from the liquid trapped in the sample loop from the previous sampling event. Samples were analyzed for COD, total volatile solids, pH, TOC, and other parameters to assess WAO performance. Several experiments were also performed to assess the effectiveness of catalyst or initiator addition on WAO reaction rates and the extent of organic removal. A radical initiator (20 and 150 mg/L H_2O_2) and two different catalysts [Mn(II), 10 mg/L; Cu(II), 5 and 10 mg/L)] were used. The initiator or the catalyst was added to the 50-mL distilled water cylinder and discharged into the reactor as described earlier.

The experimental conditions used for kinetic studies are summarized in Table 3.5. These conditions were chosen to obtain a broad range of data in terms of differences in temperature, PO_2, and initial redwater concentration.

Analysis

All raw and treated redwater samples were analyzed for pH, COD, TOC, solids, and DNTSs. In selected cases, samples were analyzed for inorganic and organic anions (nitrite, nitrate, sulfite, sulfate, and acetate), ammonium, and nitroaromatics. The analytical procedures for many of the different parameters monitored during the feasibility study phase were described earlier; additional methods used during this study phase are described below. As noted earlier, many of the analyses were performed using the analytical instruments at the USAEHA laboratories. The experiments and the analyses in the various phases were completed over a period of approximately 18 months. Because analytical instruments [e.g., a gas chromatograph (GC)] could not be exclusively dedicated to this research effort, it became necessary at times to use different instruments or different conditions for the same analyses. Such changes are noted in the text as appropriate.

Acetic Acid

Acetic acid was measured by GC in addition to ion exchange chromatography (discussed earlier in the chapter). A Perkin Elmer GC (Model 8500) was used and experimental conditions are summarized in Table 3.6. Sodium acetate, used as a standard for GC calibration, was prepared by mixing NaAc (5 to 100 mg/L) with an equal volume of 250 mg/L propionic acid in 0.015 N* HNO_3 as an internal standard.

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* N=normality

Table 3.5. Experimental conditions for kinetic experiments of WAO of TNT redwater.

Run #	Dilution	Temp. °C	PO_2, psi	Initial COD Reduction, %
1	1:100	260	175	64
2	1:100	300	175	87
3	1:50	260	225	-
4	1:25	260	45	39
5	1:25	260	90	64
6	1:25	260	175	69
7	1:25	260	280	73
8	1:25	260	225	69
9	1:25	260	320	73
10	1:25	230	90	52
11	1:25	280	90	70
12	1:25	300	90	73
13*	1:25	260	225	-
14*	1:25	260	225	-
15**	1:100	260	80	-

* with addition of $NaNO_3$ and Na_2SO_4

** with addition of catalyst/initiator

Duplicate samples were spiked with an equal volume of the internal standard (propionic acid) before directly injecting into the column. The detection limit (DL) was 5 mg/L.

Nitroaromatics

The instruments and experimental conditions used for the nitroaromatic analyses during this study phase are shown in Table 3.6. Sample extraction procedures were the same as described earlier. For on-column injections, the DL was 0.05 mg/L for each nitroaromatic. Based on the extraction procedures used, the quantification limit for the samples was 0.001 mg/L for each nitroaromatic. For splitless injections, the DL and quantification limits were 0.5 mg/L and 0.01 mg/L, respectively.

UV/VIS Absorbance

A Hewlett Packard Diode Array Spectrophotometer (model 8451A) was used to measure the UV/visible absorption for raw and treated redwater samples under

Table 3.6. Analytical methods and experimental conditions.

Equipment/Condition	1-Hr Experiments	WAO at 340 °C	Kinetic Experiments
Nitroaromatics:			
GC	HP* model 5890	HP model 5890	HP model 5890
Column	8 m DB1 capillary column with a silica pre-column	12 m (0.53 mm dia) DB1 210 column	10 m DB1 column w/o a pre-column
Carrier Gas (He), mL/min	5-6	8	5-6
Makeup Gas (Ar/CH_4) mL/min	30-35	30	30-35
Oven Temp.	75-140 °C @ 20 °C/min 140-170 °C @ 4 °C/min 170-200 °C @ 5 °C/min, 200 °C for 10 min	20-140 °C @ @ 20 °C/m 140-200 °C @ 6 °/min	125-175 °C @ 5 °C/min, 175 °C for 10 min
ECD			
Temp. °C	250	240	200
Injector Temp. °C	3 °C higher than initial oven temp. and tracked oven temp. during a run	250	190
Sample size, µL	1	1	1
Injection Technique	direct on-column injection	splitless injection	splitless injection
Detection Limit, mg/L	0.05	see text	0.05
Quantification Limit, mg/L	0.001	see text	0.01
Acetic Acid: Same equipment and conditions were used for all experiments.			
GC/column	Perkin-Elmer model 8500 with a 20 m Carbowax HP capillary column		
Oven Temp.	70 °C to 86°C @ 4 °C/min		
FID Temp.	150 °C		
Injector Temp.	150 °C		
He flow	35 mL/min		
Sample Size	5 µL		
Detection Limit	5 mg/L		

*HP = Hewlett Packard

different experimental conditions. A deuterium lamp was used as the light source to obtain a wave length range of 190 to 820 nm, with an accuracy of ± 2 nm. A 1-cm quartz cell was used. The samples were adequately diluted to obtain the absorbance readings between 0.1 and 2 absorbance units (au). Distilled water, used for sample dilutions, was also used as the blank for the UV/VIS absorbance analyses.

Gas Analysis

At the end of a run, the reactor off-gas was discharged into a 22-L TEDLAR bag and a 50-mL stainless steel cylinder for the following analyses: CO, CO_2, N_2, NO, NO_2, N_2O, SO_2, NH_3, and total hydrocarbons. The gas sample collected in the 50-mL cylinder was analyzed in a commercial laboratory for total hydrocarbons, CO_2, CO, N_2, NO_2, and N_2O. Gas analyses were also performed in the USAEHA laboratory for CO, CO_2, SO_2, NH_3, NO_2, N_2O, and NO. A Carle GC (Model 8700) was used for measuring CO_2, CO, O_2, N_2, and N_2O. The GC system consisted of two 6-ft stainless steel columns for separation of the various gases and detection via thermal conductivity detectors. The first column retained carbon dioxide, while the second column separated the other gases. The total hydrocarbons (as CH_4) were measured with a Perkin Elmer GC (Model 990). A MIRAN 1B2 Portable Ambient Air Analyzer was used for analyzing gas samples for CO, CO_2, SO_2, NH_3, NO, and N_2O. The sample size varied from 5 to 15 mL depending upon the type and concentration of gas being analyzed for. A 2000 Series Ecolizer (Energetics Science) was used for measuring NO_2, using an electrochemical sensor. The sensor produces an electric current output that is proportional to the level of NO_2 in the gas sample.

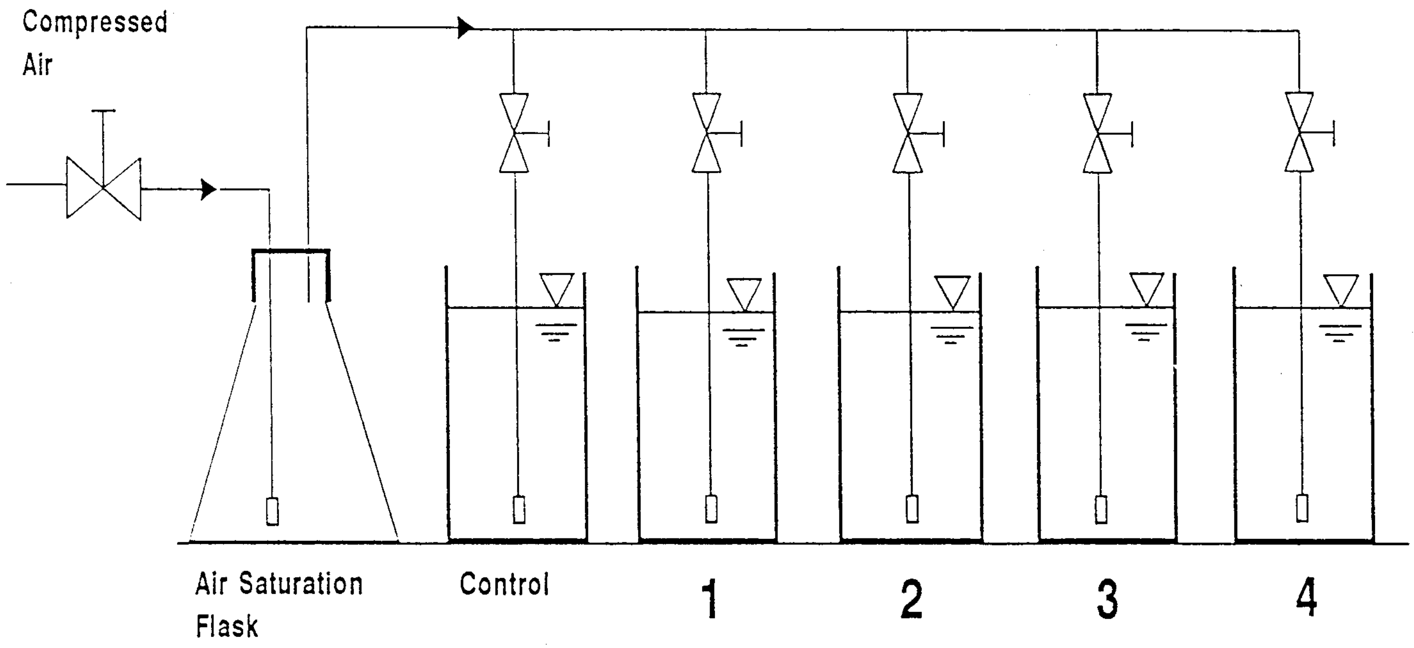
Preliminary Toxicity Study

Raw and treated redwater samples were tested for inhibitory effects on heterotrophic and autotrophic organisms. An unacclimated BAS system and an enriched Nitrosomonas culture were used to asses the effects of samples on COD degradation and nitrite production, respectively. Specifically, this phase of research was to subject raw and treated redwater to toxicity tests in terms of heterotrophic COD degradation and autotrophic oxidation of ammonia by enriched Nitrosomonas.

Materials—Activated Sludge and Nitrosomonas Culture

The AS used in the toxicity tests was obtained from an aeration tank at a local wastewater treatment plant and concentrated in the laboratory. The enriched Nitrosomonas cells were collected from a laboratory submerged nitrification column and subjected to batch feed (medium included bicarbonate, ammonium chloride, and other nutrients) for several days before use in the toxicity tests. Because the observed ammonium oxidation proceeded to nitrite only, the enriched nitrifiers were essentially Nitrosomonas.

The concentrated sludge sample was split into five 1-L reactors (50 mL AS), connected to individual air-diffuser systems (Figure 3.8). The pH of the treated sample (320 °C, PO_2 = 90 psi at 25 °C) was adjusted to 7 because of the initial low value (pH = 2 to 3).



CONDITIONS:

AS: 1000 mg/L Glucose and Primary Effluent

Nitrosomonas: 50 mg N/L, 500 mg/L $NaHCO_3$
as $CaCO_3$, and Other Nutrients

Figure 3.8. Schematic of batch AS system used for toxicity tests.

A fraction of treated redwater and deionized water were then added for a final volume of 500 mL. The mixture was supplemented with glucose and bicarbonate. An example of initial condition was: pH = 8.0; mixed liquor suspended solids (MLSS) = 2915 mg/L; mixed liquor volatile suspended solids (MLVSS) = 1910 mg/L; and alkalinity = 140 mg/L as $CaCO_3$. Sludge samples were taken periodically and filtrate samples (Whatman GF/C filter) were used for COD analysis.

The enriched Nitrosomonas cells were concentrated in a centrifuge and redissolved in the feed medium (Chen 1991). The experimental procedures were similar to those described above for heterotrophic COD degradation. An example experimental condition was: NH_4-N = 36 mg/L; alkalinity = 380 mg/L as $CaCO_3$; pH = 8.13; SS = 852 mg/L; and VSS = 584 mg/L. The filtrate samples were analyzed for nitrite using the N-(1-naphthyl)-ethylenediamine (NED) dihydrochloride method (*Standard Methods for the Examination of Water and Wastewater*, 1985).

4 Results and Discussion

In this chapter, the following results are discussed:

- The analytical method development for DNTSs and redwater characterization,
- feasibility experiments for WAO of diluted (1:100) TNT redwater,
- results of kinetic rate studies, and
- preliminary toxicity evaluation of redwater and treated redwater.

Analytical Method for DNTSs Characterization

A typical example of the chromatograms obtained using RPIPC for synthesized DNTSs was shown in Figure 3.4a. The first two peaks correspond to the inorganic anions (i.e., nitrite, nitrate, sulfite, and sulfate). The three distinct peaks at the retention times of approximately 15.5, 17.4, and 19.3 minutes are the three DNTS isomers produced from reactions between the three TNT isomers and sodium sulfite. These peaks were consistently obtained under different conditions [e.g., different ACN concentrations, different methods for synthesis of the DNTS isomers under room (25 °C) and elevated temperatures (55 °C)], although the relative retention times of these peaks shifted somewhat under different analytical conditions.

The IR spectra for the sulfonate mixture is similar to the spectra reported by Hall and Lawrence (1976). The comparison of IR data (wave numbers) between the present study and those of Hall and Lawrence (1976) is shown in Table 4.1. The IR spectra for a fraction (i.e., between retention times 14 and 21 minutes) collected from RPIPC analyses also compared well with those reported by Hall and Lawrence (1976). The slight differences in position and intensities of the average distances between bonded atoms (stretches) may be partly attributed to sampling techniques (i.e., a solid sample of DNTSs in the Hall and Lawrence study versus a liquid sample in the present study) and differences in the instrumentation used.

The peak corresponding to the retention time of 17.4 minutes in Figure 3.4a was assumed to be *2,4*-DNT-*5*-SO_3Na, since the retention time was essentially identical to that of *2,4*-DNT-*5*-SO_3Na (Figure 3.4b) synthesized from *2,4,5*-TNT and sodium sulfite. The first peak at 15.5 minutes in Figure 3.4a was inferred to be for *2,4*-DNT-*3*-SO_3Na

Table 4.1. IR spectra for the DNTS synthetic mixture and RPEPC fraction.

Stretch	Wave Number	
	This Study	Hall and Lawrence (1976)
DNTS MIXTURE		
C=N Stretch	1641.4(m)	1620(w)
NO_2 Symmetrical Stretch	1373.3(s)	1360(m)
$-SO_3$ Asymmetrical Stretch	1228.7(m)	1230(s)
C-O Stretch	1122.6(w)	1120(w)
$-SO_3$ Symmetrical Stretch	1049.3(s)	1050(s)
RPIPC FRACTION		
C=N Stretch	1635.6(m)	1620(m)
NO_2 Asymmetrical Stretch	1543(m)	1540(s)
NO_2 Symmetrical Stretch	1367.5(m)	1360(m)
$-SO_3$ Asymmetrical Stretch	1231(m)	1230(s)
$-SO_3$ Symmetrical Stretch	1055(s)	1050(s)
Z-N Stretch in $Z-NO_2$	837(m)	840(m)
S-O Deformation in -SO3	669(m)	660(m)

w = weak; m = medium; s = strong

based on the following rationale. Two of the peaks found in raw redwater (15.3 and 17.2 minutes, Figure 4.1) correspond to the first two sulfonate peaks found in the synthetic mixture (Figure 3.4a). Because only *2,3,4*-TNT and *2,4,5*-TNT are the *meta* isomers present in significant amounts in redwater, the corresponding sulfonates would be *2,4*-DNT-*3*- and *2,4*-DNT-*5*-SO_3Na, respectively. Only a trace amount of *2,3,6*-TNT isomer is present, resulting in an insignificant concentration of *2,6*-DNT-*3*-SO_3Na in redwater. Thus, Figure 4.1 was assumed not to have a peak for the *2,6*-DNT-*3*-sulfonate isomer. As a result, the first peak in Figure 3.4a (reaction time [RT] = 15.5 minutes) is assumed to be for *2,4*-DNT-*3*-SO_3Na, and the third peak (reaction time = 19.3 minutes) is for *2,6*-DNT-*3*-SO_3Na.

A linear relationship existed between the peak heights for *2,4*-DNT-*3*-SO_3Na and *2,6*-DNT-*3*-SO_3Na and the initial concentrations of the corresponding TNT isomers in the starting TNT mixture (i.e., the concentrations of *2,3,4*- and *2,3,6*-TNT). Assuming that RPIPC would give similar peak heights for comparable concentrations of different DNTS isomers, the above observation further aided the identification of the peak at 19.3 minutes to be *2,6*-DNT-*3*-SO_3Na.

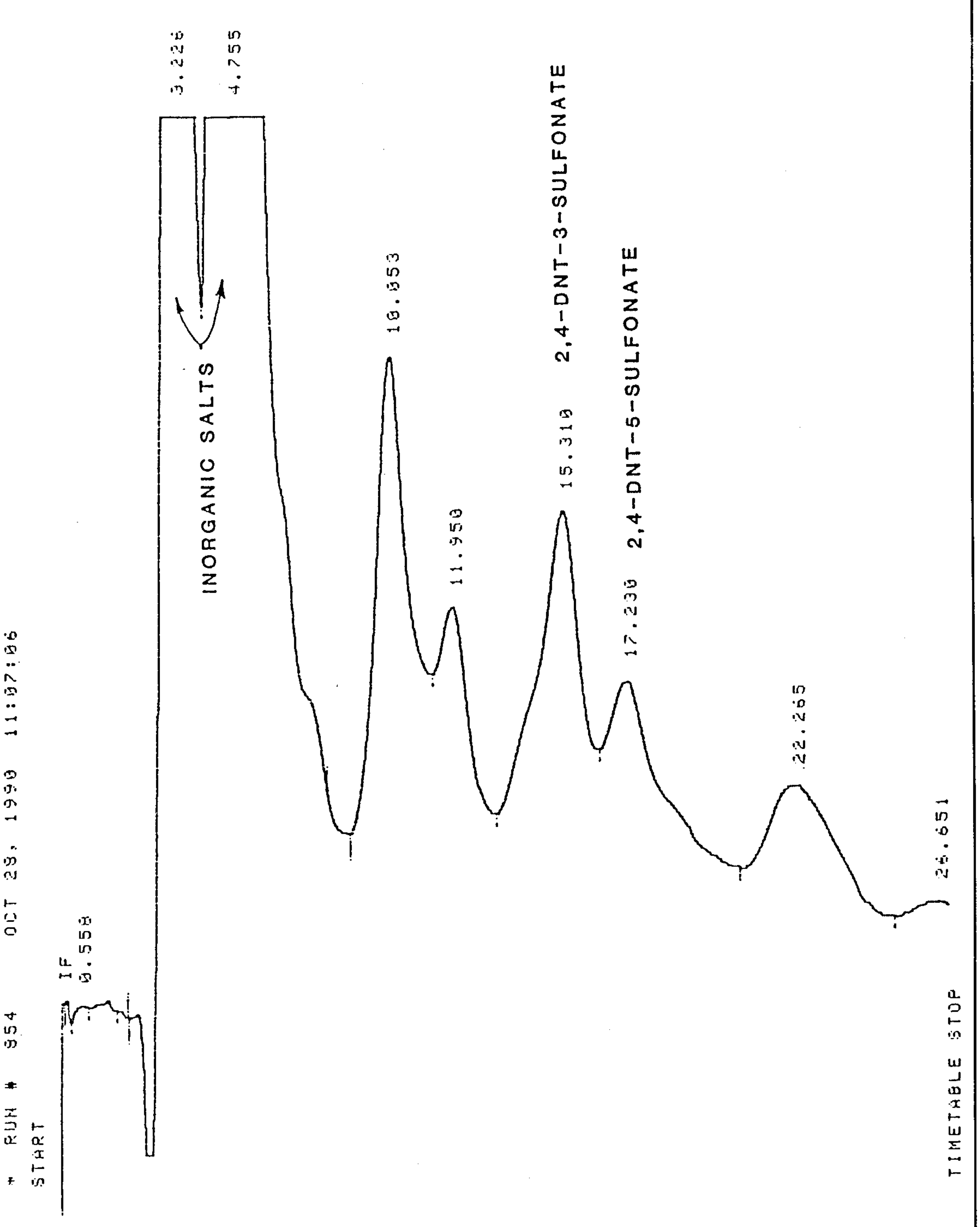


Figure 4.1. Chromatogram of raw redwater.

Despite the encouraging results discussed above, quantification of the synthesized DNTSs needs to be pursued to use the developed method. This remains incomplete as analytical standards are still not available for the three DNTS isomers.

Redwater Composition

The results of analyzing 1:100 diluted redwater during the present study and those reported by PEI (1990) are shown in Table 4.2. The PEI concentrations were divided by 100 for appropriate comparison. However, comparison must be made with caution, and for reference only, since redwater content may vary with the TNT manufacturing process. Furthermore, data obtained from PEI (1990) were partly based on anticipated crude TNT composition, purification reaction mechanisms, and theoretical calculations.

Based on present analyses, there is approximately 28.4 percent dissolved solids, 64 percent of which is the inorganic fraction (i.e., 18.2 percent) for undiluted raw redwater. Since the pH of redwater is 7.6, alkalinity exists primarily in the bicarbonate form (i.e., 43 mg/L as $CaCO_3$ or 72 mg/L $NaHCO_3$). The total concentration of the inorganic compounds in terms of nitrite, sulfite, sulfate, and bicarbonate is 8.5 percent—about half of the inorganic solids concentration. Apparently, the remaining inorganic solids must result from the combustion of DNTSs and other organic salts at 550 °C. As for the organic content, the surrogate parameters (i.e., COD and TOC) showed concentrations of 68,500 and 54,400 mg/L, respectively. Zimpro (Copa 1990) found the COD of TNT redwater to be about 65,000 mg/L in an earlier redwater study in 1957.

The two peaks at retention times of 15.3 and 17.2 minutes in Figure 4.1 were identified to be for *2,4*-DNT-*3*- and *2,4*-DNT-*5*-SO_3Na, respectively, in the chromatogram for untreated redwater. The exact concentrations of the DNTSs could not, however, be determined due to the nonavailability of analytical standards. Therefore, it was not possible to determine the fraction of COD or TOC contributed by DNTSs. Nevertheless, attempts were made to estimate the amounts of DNTSs in redwater, based on the assumption that the synthesis of the DNTSs from the TNT isomer mixture gave a quantitative yield. The TNT isomer mixture contained 6 mg total TNT per mL of water/ACN solution. According to the reactions shown in Figure 2.3, 6 mg/mL TNT isomer mixture should produce 7,510 mg/L total DNTSs (molecular weight [MW] 284; TNT MW = 227). Based on the concentrations of the three individual TNT isomers and use of excess sodium sulfite, and assuming a 100 percent yield for the reaction products, the synthetic mixture was assumed to contain the following sulfonates concentrations: *2,4*-DNT-*5*-sulfonate, 1790 mg/L; *2,4*-DNT-*3*-

Table 4.2. Redwater composition.

Parameter*	This study**	PEI (1990)***
pH, units	7.6	7.0-9.7
Specific Gravity	1.0	1.1
Solids		
Total	2840	1500
Volatile	1020	****
Fixed	1820	****
% Organics	36	****
Inorganic Salts		
$NaNO_2$	209	185
$NaNO_3$	0	25
Na_2SO_3	55	****
Na_2SO_4	514	****
Na_2SO_3-Na_2SO_4	569	533
Alkalinity (as $CaCO_3$)	43	****
Organic Content		
COD	685	****
TOC	544	****
Nitrobodies		
α-TNT	2.27	Trace
2,4-DNT	0.21	Trace
2,6-DNT	0.03	****
1,3,5-TNB	3.10	****
DNTSs*****		
2,4-DNT-*3*-SO_3Na	272	144
2,4-DNT-*5*-SO_3Na	228	341

* All results in mg/L (ppm), unless otherwise noted
** Based on diluted redwater (1:100)
*** Actual reported values for raw redwater were divided by 100
**** Value not reported
***** Estimated values

sulfonate, 3570 mg/L; and *2,6*-DNT-*3*-sulfonate, 2150 mg/L. Several dilutions of this synthetic mixture were analyzed. The results showed good linearity from 1.8 mg/L to 150 mg/L total DNTSs.

Using the synthetic mixture as the analytical standard, the concentrations of *2,4*-DNT-*5*-SO_3Na and *2,4*-DNT-*3*-SO_3Na in raw redwater were found to be 22,750 mg/L or 2.28 percent and 27,170 mg/L or 2.72 percent, respectively. These values are quite similar to those reported by Hall and Lawrence in 1976 (i.e., 2.7 percent and 1.2 percent, respectively), and by PEI (1990) as shown in Table 4.2 (i.e., 3.4 percent and 1.4 percent, respectively). The estimated values are, however, different than the 6 to

8 percent and 2 to 4 percent reported by Radford for *2,4*-DNT-*5*-SO_3Na and *2,4*-DNT-*3*-SO_3Na, respectively (Hall and Lawrence 1976).

There are two reasons for the differences in the reported values for the absolute and relative concentrations of the two sulfonates. First, the concentrations of the sulfonates and other products formed during the manufacture of TNT vary with plant operations (e.g., amount of sellite used; purity of the sellite used; operational conditions such as temperature, pH, etc.) For example, changing the amount of sodium sulfite during the synthesis of the DNTSs produced different chromatographic results. Not only were the products formed different, but the relative concentrations of the sulfonates changed. Second, the Canadian TNT plant that supplied the redwater used in this study does not use the same process as RAAP. The Canadian plant uses an orthonitrotoluene-rich mononitrotoluene as the starting material instead of the toluene used at RAAP or other U.S. AAPs. The purity of the o-nitrotoluene, particularly the amount of meta-nitrotoluene present, and operational conditions would significantly affect the amount of the unsymmetrical TNT isomers and their relative amounts and, therefore, the DNTSs in the redwater.

Undiluted redwater contains appreciable amounts of α-TNT (230 mg/L) and *2,4*-DNT (21 mg/L). The measured concentration of α-TNT far exceeds its reported solubility of about 130 mg/L at 20 °C. Large quantities of other chemicals present in TNT redwater appear to have cosolvent effect on the solubility of α-TNT in redwater. A significant amount of TNB (310 mg/L) is also present, mostly as a result of the oxidation of TNBAL, which is formed during the manufacture of TNT (Figure 2.2). The concentration of TNB measured during this study is close to a previously reported value of 500 mg/L (Hall and Lawrence 1976).

The results of metal analysis for diluted redwater are shown in Table 4.3. Sodium content is about 530 mg/L in diluted (1:100) redwater, or 5.3 percent in raw redwater. The sodium concentrations associated with nitrite, sulfite, sulfate, and bicarbonate anions are 70, 20, 170, and 10 mg Na/L, respectively, with a total sodium concentration of 270 mg/L. Assuming that the remaining sodium (260 mg/L) is present as organic salts, the total organic concentration in 1:100 diluted redwater would be 3210 mg/L expressed as DNTS (MW = 284), or 32.1 percent. This concentration (as DNTS) is extremely high compared to the previously reported values for the sulfonates. Based on the measured total concentration of DNTSs (500 mg/L; Table 4.2), only 40 mg/L sodium is associated with the DNTSs. The remaining sodium (220 mg/L) must be present as other unidentified organic sodium salts, such as α-TNT-sellite complex. PEI (1990) reported that this complex accounts for approximately 30 percent of the total nitrobodies in the redwater. Hall and Lawrence (1976) reported that DNTSs were only one-third of the polar organic content of redwater. For further comparison,

Table 4.3. Metals analysis for diluted TNT redwater (1:100).

Parameter	Concentration, mg/L	
	Cotton-filtered (1:100 Dilution)	0.8 μm-filtered (1:100 Dilution)
Ag	<0.001	<0.001
Al	<0.250	<0.250
As	<0.001	<0.001
Ba	0.0149	0.0126
Ca	0.477	0.411
Cd	0.0018	0.0021
Cr	<0.01	<0.01
Cu	0.0401	0.101
Fe	0.55	<0.050
K	0.506	0.638
Mg	<0.250	<0.250
Na	532	526
Pb	<0.001	<0.001
Zn	<0.010	0.011

TOC corresponding to a DNTS concentration of 3210 mg/L is 950 mg/L, as compared to the measured TOC of 540 mg/L.

Results of WAO Feasibility Studies

A summary of the experimental results under different operating conditions is shown in Table 4.4. The following sections address different parameters.

pH

After WAO of diluted redwater, solution pH values always decreased. The pH drop was probably due to the formation of free mineral acids, the production of acetic acid and other organic acids, and a high concentration of dissolved CO_2.

COD, TOC, and Acetic Acid

The significant decrease in both COD and TOC show a high degree of conversion and oxidation of organic contaminants present in redwater. The TOC removal ranged from 85 percent at 225 °C, to 92 percent at 300 °C, and 99.9 percent at 340 °C. The COD

Table 4.4. Results of experimental runs under different WAO conditions.

		RUN #				
		1	2	3	4	5
Temperature, °C		225	300	325	335	340
Pressure, psi		970	1970	2000	2050	2150
Parameter*	Redwater**					
pH, units	7.6	3.1	2.8	5.3	5.1	3.1
Sp. Gravity	1.0	***	***	***	***	***
Solids						
Total	2840	2045	1820	1855	1730	***
Volatile	1020	340	70	Trace	Trace	***
Fixed	1820	1705	1750	1875	1730	***
% Organics	36	16	4	0	0	***
Inorganic Salts						
$NaNO_2$ [0.1]+	209	BDL†	BDL	BDL	BDL	BDL
$NaNO_3$ [0.5]	BDL	181	466	278	261	376
Na_2SO_3 [0.5]	55	BDL	BDL	BDL	BDL	BDL
Na_2SO_4 [0.5]	514	1392	1641	1923	2088	1977
Na_2SO_3-Na_2SO_4	569	1392	1641	1923	2088	1977
Alkalinity (as $CaCO_3$)	43	BDL	BDL	BDL	BDL	BDL
Organic Content						
Acetic acid [0.5]	BDL	54	54	33	40	1
COD	685	114	8	5	8	Trace
TOC	544	80	42	26	27	4
Nitrobodies						
α-TNT [0.05]	2.27	BDL	BDL	BDL	BDL	BDL
2,4-DNT [0.05]	0.21	0.46	BDL	BDL	BDL	BDL
2,6-DNT [0.05]	0.03	7.74	BDL	BDL	BDL	BDL
1,3,5-TNB [0.05]	3.10	22.2	BDL	42	75	36
1,3-DNB [0.05]	BDL	BDL	16.3	1.85	0.57	0.26
DNTSs****						
2,4-DNT-*3*-SO_3Na	100	33.2	BDL	BDL	BDL	BDL
2,4-DNT-*5*-SO_3Na	100	5.0	BDL	BDL	BDL	BDL

* All results in mg/L (ppm), unless otherwise noted.

** Based on diluted redwater (1:100).

*** Not determined/reported.

**** Based on % remaining. See text for explanation.

† BDL - below detection limit.

\+ Numbers in [ ] refer to detection limits in mg/L (ppm).

reduction ranged from 83 percent at 225, °C, to 99 percent at 300 °C, and almost 100 percent at 340 °C. The values for COD reduction are slightly higher than those observed by Zimpro (Copa 1990) in the WAO experiments with redwater in the 1950s (COD reduction of 95 percent at 300 °C). Thus, organic compounds, detected as COD and TOC, are completely oxidized to a final product of CO_2 at 340 °C, indicating feasibility of WAO for initial redwater treatment. The treated effluents at higher temperatures ($\geq$ 325 °C) had only trace amounts of volatile solids, which corresponds well to the negligible amounts of COD and TOC present in these effluents.

It is interesting to note that the color of TNT redwater changed as a result of WAO. It varied from dark red (diluted redwater), to light yellow at 225 °C, to colorless at 340 °C.

The concentration of acetic acid increased with the oxidation temperature up to approximately 300 °C, at which point the acetic acid started to undergo further oxidation. Smaller amounts of acetic acid remained at the higher temperatures, with only a trace remaining at 340 °C. This observation is in agreement with the acetic acid accumulation and oxidation results previously reported by Foussard et al. (1989) for a variety of organic compounds. Acetic acid is a good substrate for microorganisms. The excellent degree of oxidation (approximately 83 percent COD reduction at 225 °C and 100 percent at 340 °C), together with the acetic acid data, indicates that a temperature range of between 225 and 300 °C might provide an effluent amenable to subsequent biological treatment. Acetic acid responds well to biological treatment.

α-TNT, DNTs, DNB, and TNB

Results show a dramatic decrease in the concentrations of α-TNT and DNTs at an oxidation temperature of 225 °C; a near complete destruction is observed at 300 °C. This finding agrees with a previous study performed by Dietrich et al. (1985) which concluded that a reduction of 99.7 percent for 2,4-DNT can be achieved at 275 °C after a 60-minute residence time. The residual nitroaromatics concentrations (Table 4.4, 4.5, 4.6, and 4.7) show a higher concentration of 2,6-DNT than 2,4-DNT. This appears to agree with Lee and Hunter (1985) who reported that the latter is relatively easier to oxidize by chlorination and ozonation. Still, small amounts of the other two nitroaromatics, 1,3,5-TNB (0.04 mg/L) and 1,3-DNB (0.26 mg/L), remained after 1-hour reaction time at 340 °C. The WAO-treated effluent was not analyzed for nitrobenzene (NB). Kinetic studies (reported on below) show the presence of this compound in redwater treated under similar conditions.

Table 4.5. Results of the WAO of diluted redwater at PO_2 = 19 psi (@ 25 °C) as a function of temperature.

Parameter		Test Run #*				
	Raw	1	2	3	4	5
Operational Conditions	(1:100)					
Set Temp.(S.T.) °C		200	230	260	290	320
$P_{Vap.}$, psi		225	406	680	1079	1638
PO_2 at S.T., psi		30	32	34	36	38
P_T at S.T., psi		255	438	714	1115	1676
Actual P_T, psi		240-260	420-430	700-740	1125-1130	1650-1700
Actual T, °C pH, unit		198-205	228-232	258-264	290-291	320-322
	7.12	5.10	5.24	4.46	5.43	5.64
Solids, mg/L						
TS	3087	2647	2353	2087	1973	1893
TVS	1353	1007	680	440	267	160
FS	1734	1640	1673	1647	1706	1733
TVS/TS, %	44	38	29	21	14	8
Inorganic Salts, mg/L						
NO_2^-	278	BDL**	BDL	BDL	BDL	BDL
NO_3^-	17	129	147	202	228	198
SO_3^{2-}	35	BDL	BDL	BDL	BDL	BDL
SO_4^{2-}	378	999	1103	1163	1235	1243
Organic Content, mg/L						
HAc	BDL	13	31	50	52	44
COD	816	418	238	118	52	18
TOC	454	317	225	147	75	35
Nitrobodies						
NB	BDL	0.07	0.03	0.16	0.17	0.25
α -TNT	0.80	0.14	0.11	0.11	0.04	0.03
2,4-DNT	0.17	0.24	0.15	0.06	0.08	0.04
2,6-DNT	0.02	0.81	0.90	0.37	BDL	BDL
1,3,5-TNB	1.46	5.33	0.94	0.33	0.25	0.11
1,3-DNB	0.05	8.12	23.70	20.18	16.74	2.51
DNTS'***						
2,4-DNT-*3*-SO_3Na	42.0	39.1	33.7	28.6	8.4	BDL
2,4-DNT-*5*-SO_3Na	28.0	24.9	9.8	BDL	BDL	BDL
UV/VIS Absorbance, au						
200 (nm wavelength)	1.25	0.880	0.670	0.460	0.360	0.260
346	0.23	BDL	BDL	BDL	BDL	BDL
362	BDL	0.090	0.045	0.023	0.010	0.006
400	BDL	BDL	BDL	0.010	0.003	0.003
432	0.127	0.034	0.014	0.008	0.003	0.002
488	0.110	0.016	0.008	0.007	0.002	0.005

*Run time 1 hr.

**BDL - below detection limit.

***Estimated values.

Table 4.6. Results of the WAO of diluted redwater at PO_2 = 90 psi (@ 25 °C) as a function of temperature.

Parameter	Test Run #*					
	Raw	1	2	3	4	5
Operational Conditions	(1:100)					
Set Temp.(S.T.) °C		200	230	260	290	320
$P_{Vap.}$, psi		225	406	680	1079	1638
PO_2 at S.T., psi		143	152	161	170	179
P_T at S.T., psi		368	558	841	1249	1817
Actual P_T, psi		350-360	530-550	790-820	1200-1220	1750-1760
Actual T, °C		200-201	230-231	259-261	290-291	320-322
pH, unit	7.10	3.37	3.41	3.27	3.13	3.05
Solids, mg/L						
TS	3147	2420	2290	1989	1833	1773
TVS	1347	867	693	393	247	127
FS	1800	1553	1607	1596	1586	1646
TVS/TS, %	43	36	30	20	13	7
Inorganic Salts, mg/L						
NO_2^-	291	BDL**	BDL	BDL	BDL	BDL
NO_3^-	17	230	275	271	338	336
SO_3^{2-}	35	BDL	BDL	BDL	BDL	BDL
SO_4^{2-}	360	1001	1068	1160	1208	1216
Organic Content, mg/L						
HAc	BDL	31	49	60	60	38
COD	800	278	178	72	30	8
TOC	495	255	228	112	72	30
Nitrobodies						
NB	BDL	BDL	0.11	0.06	0.10	0.13
α-TNT	0.79	0.16	0.17	0.11	0.06	0.01
2,4-DNT	0.18	0.25	0.35	0.07	0.05	0.01
2,6-DNT	0.02	0.49	0.72	0.36	BDL	BDL
1,3,5-TNB	1.35	12.31	3.74	0.91	0.83	0.32
1,3-DNB	0.04	7.02	21.50	21.33	17.55	5.68
DNT sulfonates***						
2,4-DNT-*3*-SO_3Na	42.0	38.6	32.3	25.6	10.9	BDL
2,4-DNT-*5*-SO_3Na	28.0	22.2	17.4	BDL	BDL	BDL

*Run time 1 hr.

**BDL - below detection limit.

***Estimated values.

Table 4.7. Results of the WAO of diluted redwater at PO_2 = 190 psi (@ 25 °C) as a function of temperature.

Parameter	Test Run #*					
	Raw	1	2	3	4	5
Operational Conditions	(1:100)					
Set Temp.(S.T.) °C		200	230	260	290	320
$P_{Vap.}$, psi		225	406	680	1079	1638
PO_2 at S.T., psi		302	321	340	359	378
P_T at S.T., psi		527	727	1020	1438	2016
Actual P_T, psi		480-520	680-720	980-1020	1380-1400	1900-1940
Actual T, °C		199-201	229-231	259-261	290-291	318-321
pH, unit	7.50	3.22	3.23	3.11	3.00	2.98
Solids, mg/L						
TS	3284	2784	2646	2278	2216	2128
TVS	1522	1032	834	422	362	268
FS	1762	1752	1812	1856	1854	1860
TVS/TS, %	46	37	32	19	16	13
Inorganic Salts, mg/L						
NO_2^-	236	BDL**	BDL	BDL	BDL	BDL
NO_3^-	18	307	331	339	334	314
SO_3^{2-}	35	BDL	BDL	BDL	BDL	BDL
SO_4^{2-}	391	1071	1104	1223	1263	1326
Organic Content, mg/L						
HAc	BDL	36	50	72	60	38
COD	830	275	175	79	38	20
TOC	477	275	224	115	71	50
Nitrobodies						
NB	BDL	0.09	0.01	0.06	0.08	0.13
α-TNT	0.67	0.22	0.40	0.41	0.11	BDL
2,4-DNT	0.24	0.42	0.47	0.51	0.03	0.02
2,6-DNT	0.02	0.56	0.78	0.60	BDL	BDL
1,3,5-TNB	1.84	19.92	5.47	0.92	0.36	0.35
1,3-DNB	0.05	8.32	16.67	15.93	14.16	10.04
DNT sulfonates***						
2,4-DNT-*3*-SO_3Na	42.0	31.1	29.4	23.1	8.8	BDL
2,4-DNT-*5*-SO_3Na	28.0	20.2	15.1	BDL	BDL	BDL
UV/VIS Absorbance, au						
200 (nm wavelength)	1.25	0.960	0.900	0.710	0.580	0.510
346	0.23	BDL	BDL	BDL	BDL	BDL
362	BDL	0.040	0.030	0.013	0.006	0.005
400	0.125	0.019	0.014	0.006	0.002	0.001
432	0.124	0.012	0.008	0.004	0.003	0.002
488	0.106	0.005	0.004	0.003	BDL	BDL

*Run time 1 hr.

**BDL - below detection limit.

***Estimated values.

DNTSs

Typical chromatograms for DNTSs in treated redwater at different temperatures (225 °C and 340 °C) and the chromatograms for untreated redwater and deionized water are shown in Figures 4.2 and 4.3. As shown in Figure 4.2b, four of the peaks, in addition to the first two peaks for the inorganic anions (originally present in the raw redwater) remained after treatment at 225 °C. The peaks at retention times of 17.2 and 19.4 minutes were identified as 2,4-DNT-3-SO_3Na and 2,4-DNT-5-SO_3Na, respectively; the other two peaks were not identified. No sulfonate peaks were noted in the redwater treated at 340 °C (Figure 4.3a). Again, due to the fact that analytical standards were not available for these compounds, the absolute concentrations could not be determined. Nevertheless, some conclusions can be drawn on the WAO destruction of the sulfonates by comparing the chromatograms for untreated redwater (Figure 4.2a) and the treated redwater (Figures 4.2b and 4.3a).

The comparison indicates reductions of 67 percent for 2,4-DNT-3-SO_3Na, and 95 percent for 2,4-DNT-5-SO_3Na at 225 °C. The sulfonates are undetectable at WAO operational temperatures $\geq$ 300 °C. However, there is a significant increase in the amount of inorganic sulfate, as can be seen from the change in the initial peaks in the chromatograms and from the measured sulfate concentrations (Table 4.4). This is due to the hydrolytic desulfonation of DNTSs to DNT and sulfuric acid discussed by Gilbert (1978), and the oxidation of DNTSs (discussed later in this chapter). The lower percent desulfonation of the 2,4-DNT-3-SO_3Na may have a lower desulfonation percentage than 2,4-DNT-5-SO_3Na because of its greater steric effects.

Nitrite, Nitrate, Sulfite, and Sulfate

As expected, WAO of the inorganic nitrite and sulfite present in redwater resulted in an increase in the levels of nitrate and sulfate (Figure 4.4). The sulfate increase, however, is mostly due to the oxidation of sulfonate (SO_3Na) groups associated with the organic DNTSs. Due to the nonavailability of complete data on the actual concentrations of the DNTSs and all other components of redwater except the five nitroaromatics analyzed), it is not possible to perform an accurate mass balance for nitrogen and sulfur. Nonetheless, a preliminary mass balance for sulfur was performed to explain the high level of sulfate which comes from: (1) the oxidation of inorganic sulfite, (2) the original sulfate present in raw redwater, and (3) the desulfonation of DNTSs. Based on the data shown in Table 4.4 and the estimated 3210 mg/L organics (as DNTS, previously discussed), the calculated Na_2SO_4 concentrations were 60, 510, and 1600 mg/L, respectively, for the three sources listed above. The total concentration is 2170 mg/L, as Na_2SO_4 compares favorably with the sulfate data at higher WAO temperatures (shown in Table 4.4).

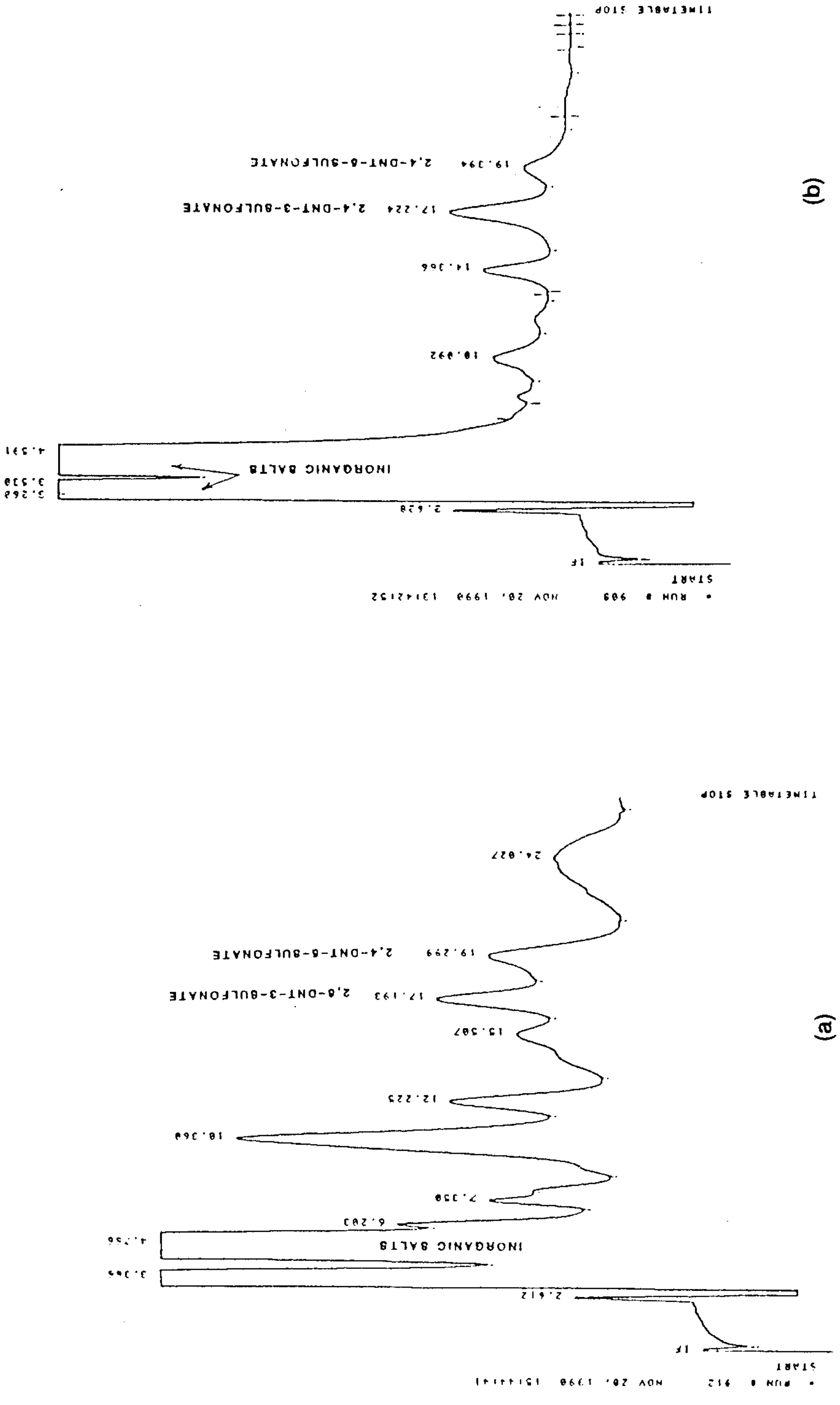


Figure 4.2. Chromatograms of (a) raw redwater and (b) treated redwater at 225 °C.

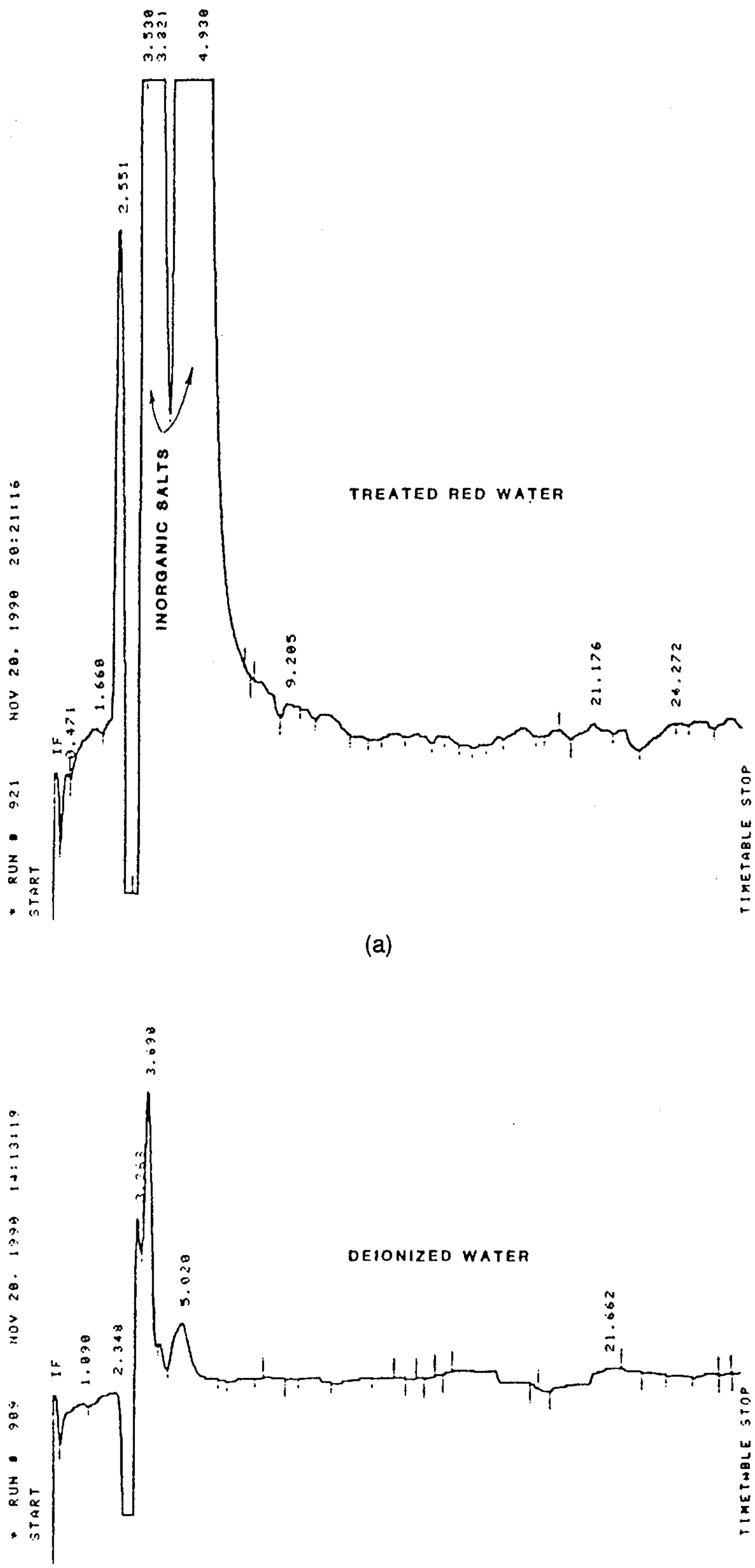


Figure 4.3. Chromatograms of (a) treated redwater at 340 °C and (b) deionized water.

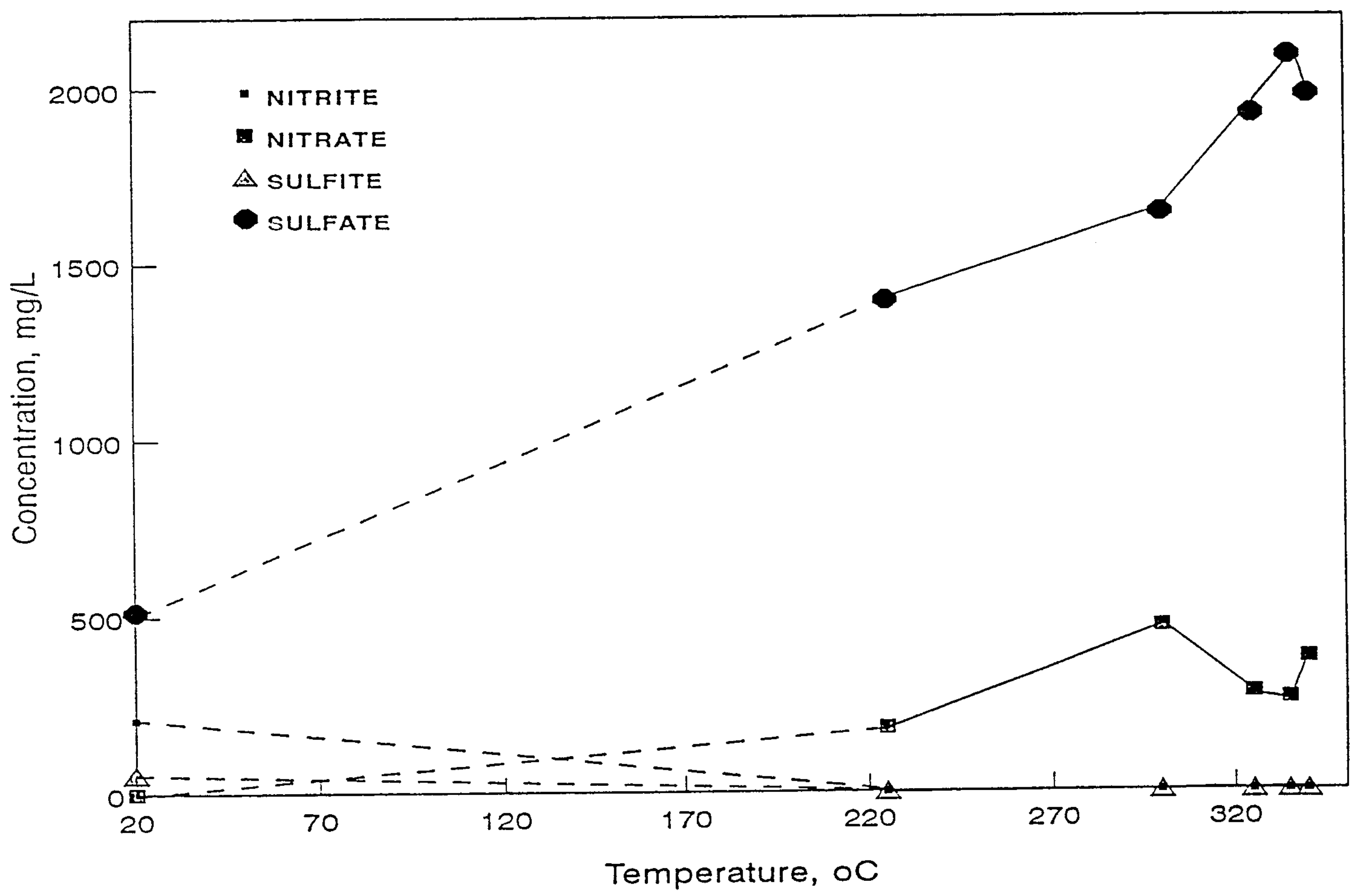


Figure 4.4. Results of WAO of redwater: nitrite, nitrate, sulfite, and sulfate.

A similar mass balance for nitrogen yielded the calculated $NaNO_3$ value that was one order of magnitude higher than the measured concentration (i.e., 181 to 466 mg/L $NaNO_3$, Table 4.4). Also, the net increase in the nitrate concentration (total nitrate concentration minus the original inorganic nitrite) is one order of magnitude less than that for sulfate. If all the nitro groups in DNTSs were oxidized to nitrate and the sulfonic groups to sulfate, the molar ratio of net nitrate formed to that of sulfate would be two. This is not the case, thus raising questions about the fate of the nitro groups in DNTSs.

Solids

The degree of reduction and nearly complete removal of volatile solids in redwater at higher oxidation temperatures (Table 4.4) compare well with the corresponding data on DNTSs, TOC, and COD.

Results of Kinetic Studies—1-Hour Experiments

The results of WAO of diluted redwater (1:100) under different temperature conditions as a function of pressure are tabulated in Table 4.5 (PO_2 = 19 psi at 25 °C), Table 4.6 (PO_2 = 90 psi), and Table 4.7 (PO_2 = 190 psi). Comparison of these results and those reported in Chapter 3 must be made with caution because of the uncertain stability of the compounds present in redwater, caused by prolonged sample storage in a refrigerator and the redissolving process. Although the effluent quality generally improved under harsher temperature and pressure conditions, the use of different WAO conditions in the two studies may make direct data comparison somewhat difficult. The differences in total run time for each experiment due to variable heating and cooling times and the use of different analytical equipment and procedures (e.g., on-column versus splitless GC injections) may further add to the difficulty. The following sections address different parameters.

pH

The degree of pH decrease is clearly a function of operating temperature and PO_2 (Figure 4.5). It varied from 5.64 (320 °C and PO_2 = 19 psi) to 2.98 (320 °C and PO_2 = 190 psi). The abrupt decrease in pH at 260 °C and 19 psi PO_2 may appear to be an anomaly, although the accumulation of acetic and other low molecular weight organic acids may be responsible for the observed pH drop. The final pH after 1-hour reaction differed little between the experiments at PO_2 90 and 190 psi. It is thought that the increased free mineral acids (e.g., H_2SO_4), low molecular weight organic acids, and aqueous CO_2 (all formed during WAO of redwater) contributed to the observed pH decrease.

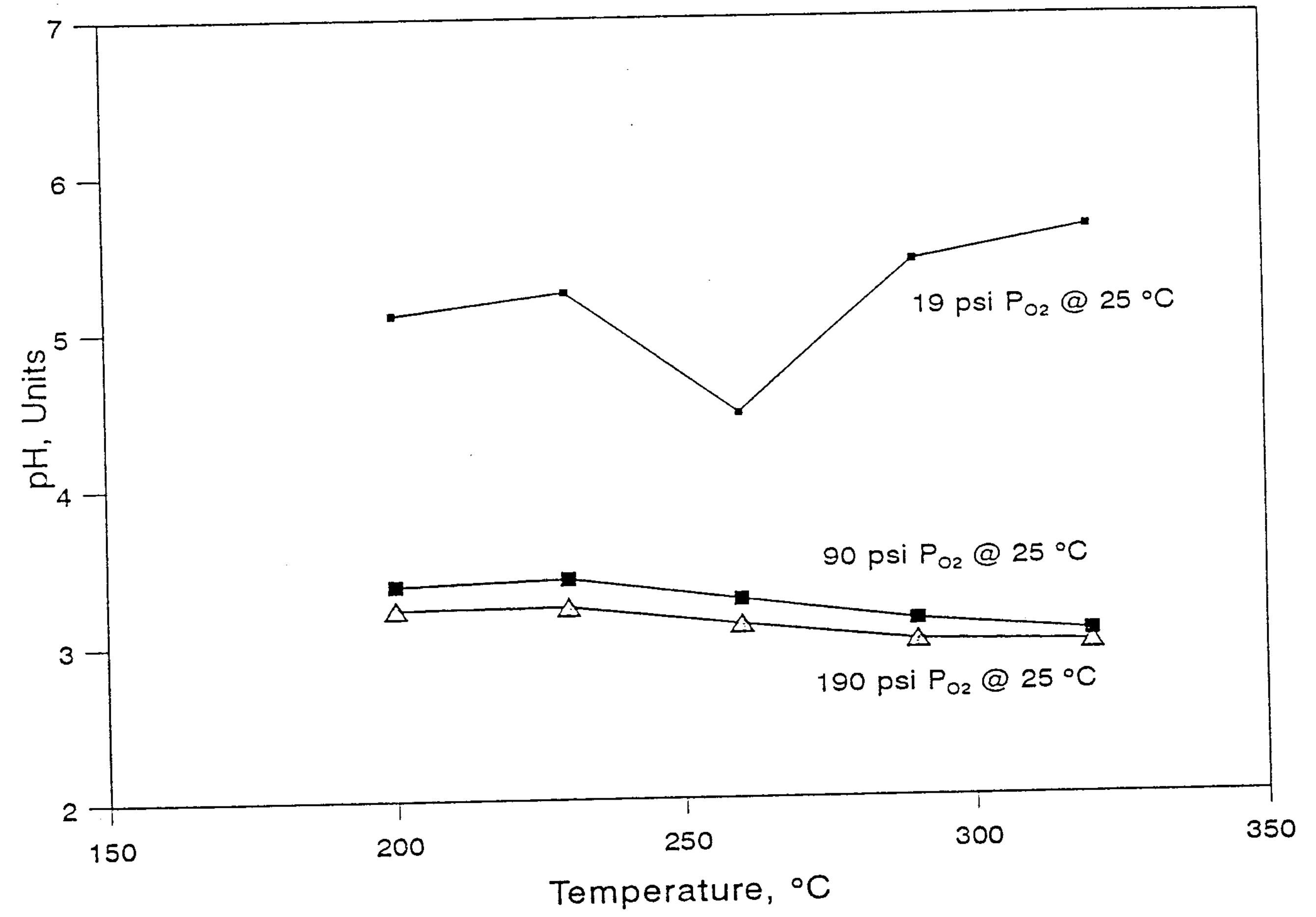


Figure 4.5. The pH of treated redwater as a function of temperature and PO_2.

COD, TOC, and Acetic Acid

A strong temperature dependence for COD and TOC removals is clearly shown in Figures 4.6 and 4.7. For example, COD removal efficiency increased from 65 percent at 200 °C to 96 percent at 290 °C in the PO_2 range of 90 to 190 psi. The values for COD reduction are similar to the value observed by Zimpro (Copa 1990) in WAO experiments with redwater in the 1950s (i.e., approximately 95 percent reduction at 300 °C). Oxygen pressure between 90 and 190 psi had little effect on COD and TOC removals. At higher temperatures ($\geq$ 260 °C), the effect of PO_2 on COD and TOC removal efficiencies became less noticeable even at 19 psi.

A precise oxygen demand is unknown for the starting materials present in redwater and the intermediates formed. This causes difficulty in explaining the observed differences in COD and TOC removals based on the quantity of the oxygen added in different experiments during this study phase. Compounding the problem is the fact that oxidation by molecular oxygen is complicated and not fully understood. The oxygen radicals formed at elevated temperatures can lead to the formation of H_2O_2, O_3, and $OH^{\bullet}$ (Joglekar et al. 1991). These, and the organic radicals formed, are capable of participating in the classical autooxidation chain reactions discussed in Chapter 2.

The bulk of the oxygen is transferred into the aqueous phase at the high temperatures during the startup period. However, as the reaction proceeds, the oxygen transfer rate might be lower than the oxygen consumption rate. The residual dissolved oxygen levels observed in the WAO effluents and the presence of oxygen in the reactor offgas (Hao and Phull 1992b) indicate that oxygen might not be limiting. The oxygen transfer under WAO conditions needs further evaluation to assess the potential for oxygen transfer limitations in the case of a complex wastewater such as TNT redwater, particularly at lower initial PO_2 conditions.

The ratio of TOC/COD increased as WAO temperature increased (Figure 4.8), probably due to the accumulation of the aromatic byproducts that cannot be measured by the COD dichromate oxidation method. Aromatic hydrocarbons, including many types of sulfonic acids such as benzene-, nitrobenzene-, chlorobenzene-, and toluene-sulfonic acid, are not oxidized under the COD test conditions (Hao, unpublished data). However, TOC can detect these sulfonated aromatic compounds as shown in Table 4.8. Consequently, COD alone is not a good "gross" parameter to assess either the WAO efficiency or the WAO effluent quality, and must be supplemented with other parameters to assess WAO efficiency for treating complex wastes such as redwater. For example, at 320 °C, COD values were below 20 mg/L for all three pressures studied, indicating a high degree of treatment, yet TOC concentrations were relatively high. Even samples treated at 320 °C exhibited a light yellow color that may indicate the presence of organics.

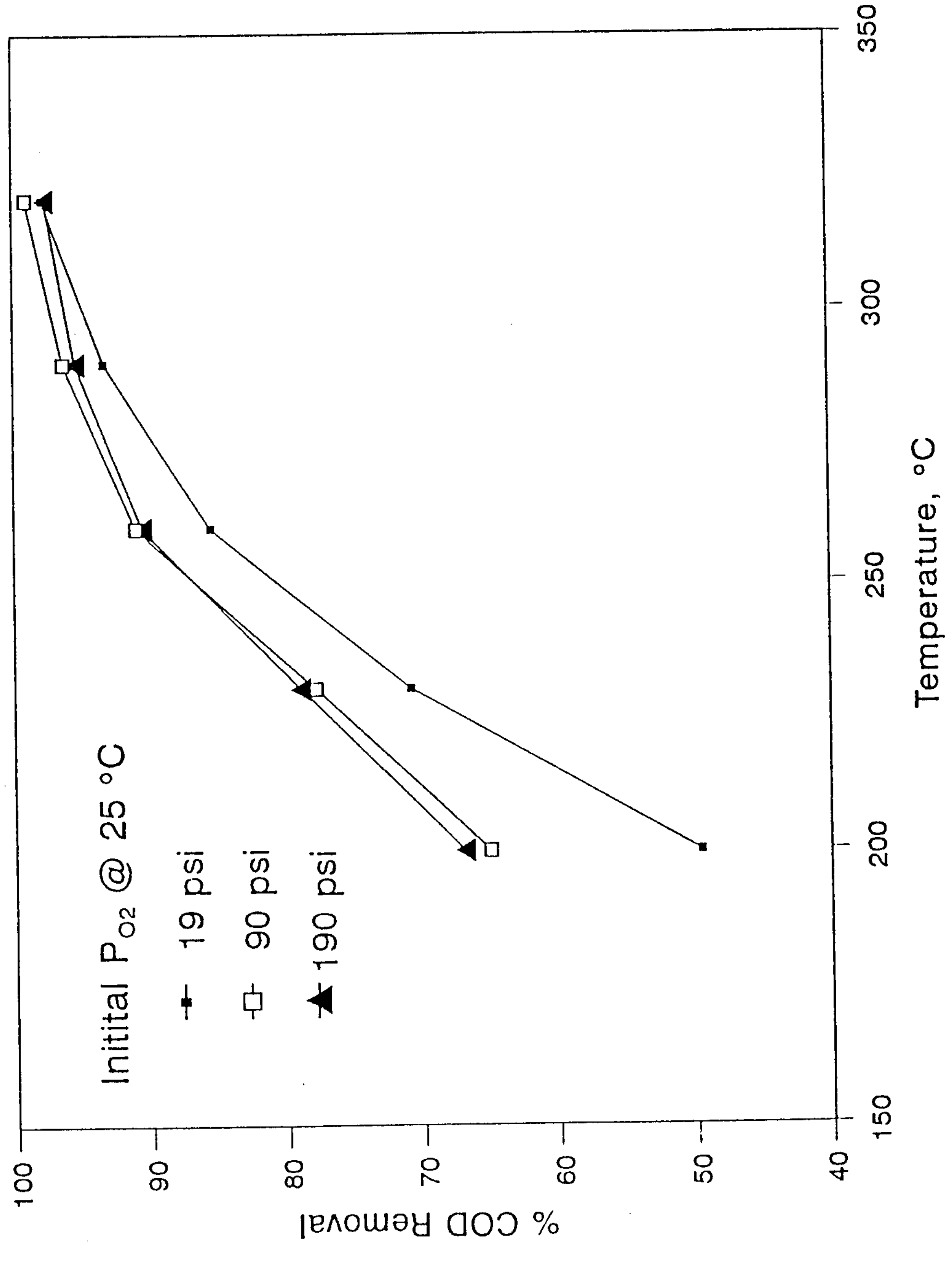


Figure 4.6. COD removal as a function of WAO temperature and PO_2.

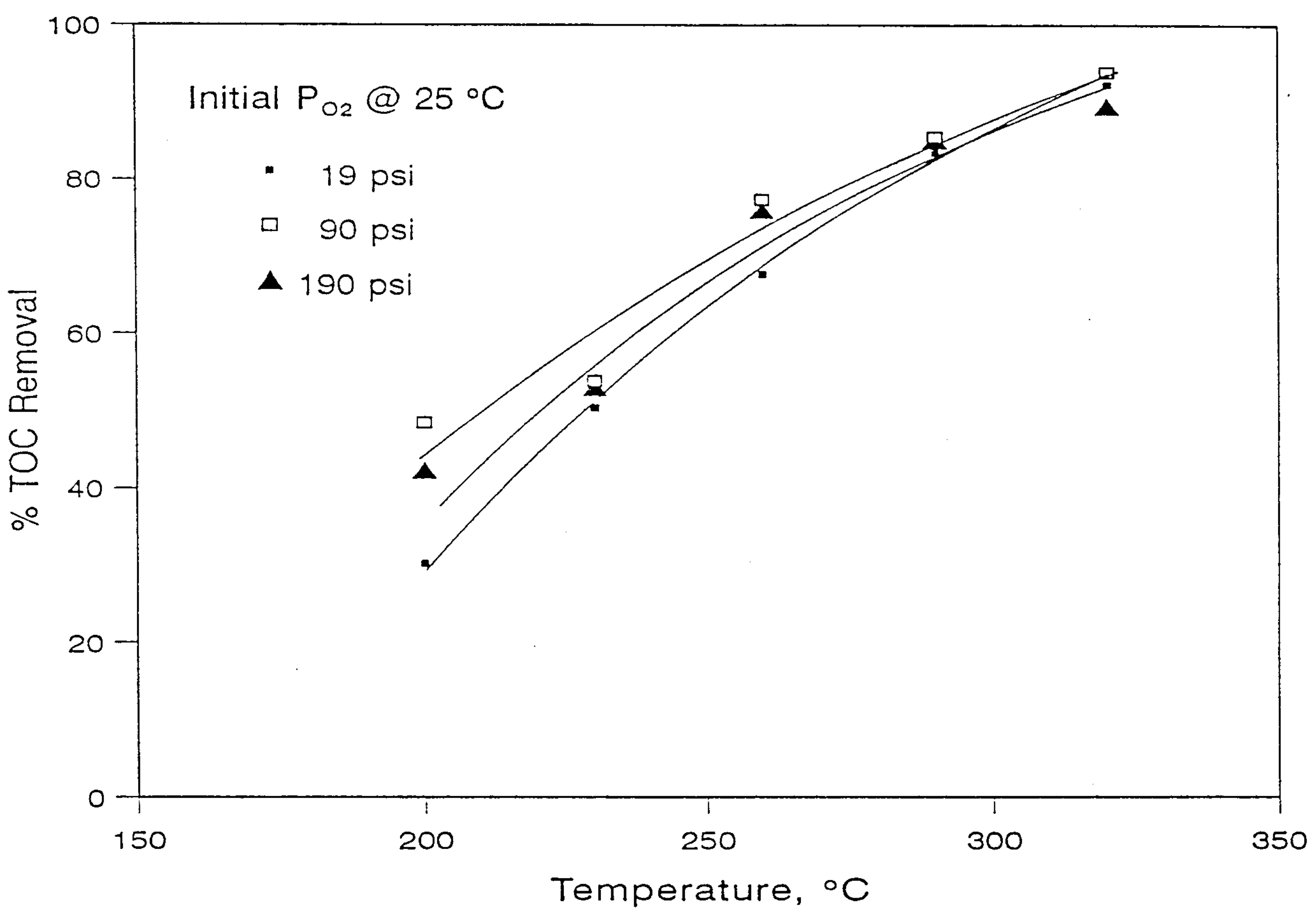


Figure 4.7. TOC removal as a function of WAO temperature and PO_2.

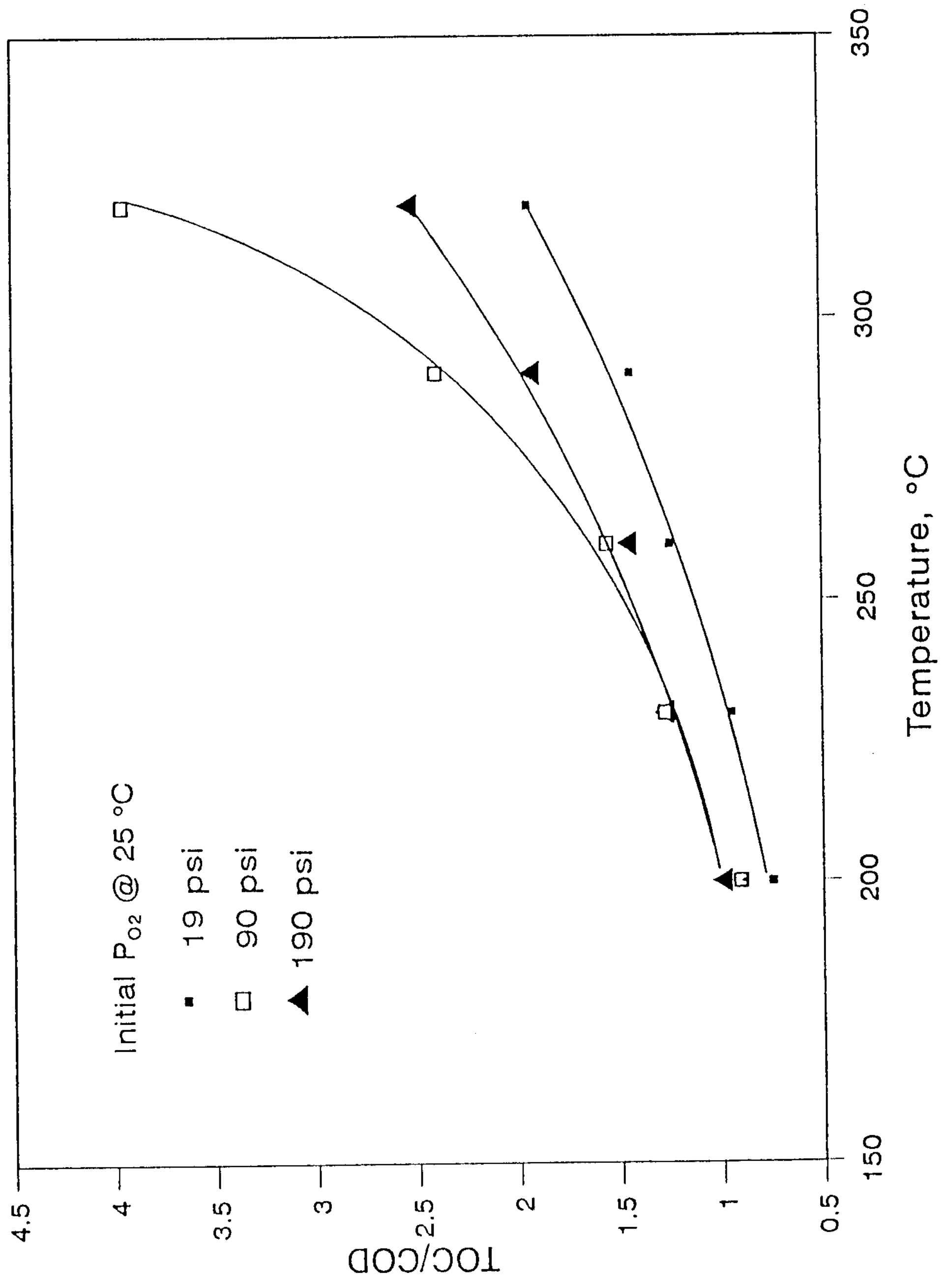


Figure 4.8. TOC/COD as a function of WAO temperature and PO_2.

Table 4.8. Experimental and theoretical TOC of sulfonated aromatics.

Compound	TOC, mg/L					
	Theoretical	Measured	% Difference	Theoretical	Measured	% Difference
Sodium *p*-toluene sulfonate	21.6	22.9	6	4.3	4.6	6
4-chlorobenzene sulfonic acid	18.7	18.9	0.8	3.7	3.9	6
Sodium *3*-nitrobenzene sulfonate	32.0	31.6	1	6.4	6.6	3
5-nitro-*o*-toluene sulfonic acid	16.6	15.8	5	3.3	3.4	3
Sodium *2,4*-dinitrobenzene sulfonate	26.7	26.6	0.3	5.3	5.4	2

Accumulation of acetic acid (HAc) as temperature increased up to 290 °C and the reduction in the HAc concentration thereafter are clearly shown in Figure 4.9. Acetic acid is one of the major end products of WAO of organic compounds before final oxidation to CO_2. At 260 °C and 190 psi PO_2, the concentration of HAc (72 mg/L, or an equivalence of 29 mg/L TOC) accounts for 25 percent of the measured TOC (115 mg/L). As temperature increased, the ratio of HAc/TOC also increased (e.g., HAc/TOC = 1.5 at 320 °C and PO_2 = 190 psi, or 61 percent TOC is associated with HAc; Figure 4.10) indicating a high degree of conversion of both original aromatic compounds and the intermediates to HAc. Foussard et al. (1989) observed a similar increase in the ratio of HAc to effluent total oxygen demand in the WAO of black liquor and concluded that acetic acid must be the last intermediate before complete oxidation.

The acetic acid data and the TOC/COD data indicate that partially treated redwater at lower WAO temperatures (e.g., 260 °C) may provide an effluent amenable to subsequent biological treatment. As shown later in this chapter, high inorganic salt concentrations (expected in a continuous redwater WAO operation) showed no adverse effect on the batch AS glucose COD removal capability.

Nitroaromatics

A recovery study was initiated to determine the sample matrix effect(s) on the analyses of the samples generated under different WAO conditions. Due to equipment restraints, however, a thorough recovery study could not be completed. Results of the recovery experiments conducted (Table 4.9) show that the percentage of recoveries in some instances are outside limits generally considered acceptable (70 to 130 percent) by USAEHA analysts. The wide variations in the percentage of recoveries, especially in the case of *2,6*-DNT and α-TNT, suggest either a significant sample matrix effect or an imperfect extraction or analytical technique. The reproducibility of the results obtained for *1,3*-DNB for the same samples on different days suggests that the extraction and analytical procedures are satisfactory. In light of this, the GC results reported herein should be used with caution. Their use to indicate trends may be acceptable, although their use to report precise concentrations may be somewhat questionable.

Typical chromatograms for standards, raw, and treated water samples using both on-column and splitless injection techniques are shown in Figures 4.11 through 4.14. As shown in Tables 4.5 to 4.7, the data for temperature dependence of the concentration of NB andα-TNT are somewhat scattered. However, the α-TNT concentration generally decreased with increasing WAO temperature, whereas the NB concentration increased at higher WAO temperatures. The concentrations of 1,3-DNB, 2,6-DNT, 2,4-DNT, and 1,3,5-TNB first increased and then decreased as the temperature varied from 200 to 320 °C. Accumulation and destruction of 1,3-DNB and 1,3,5-TNB at 90

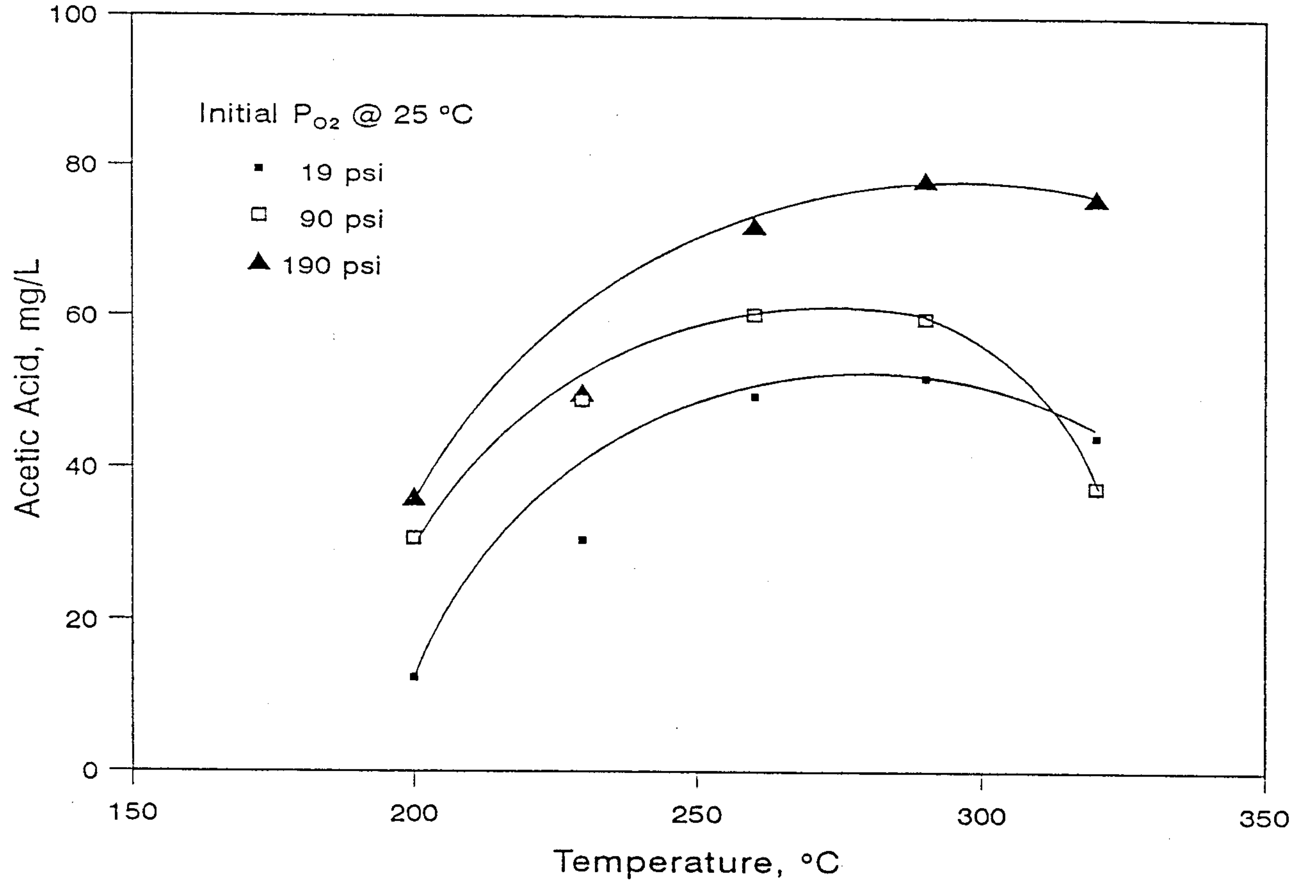


Figure 4.9. Accumulation and destruction of acetic acid as a function of WAO temperature and PO_2.

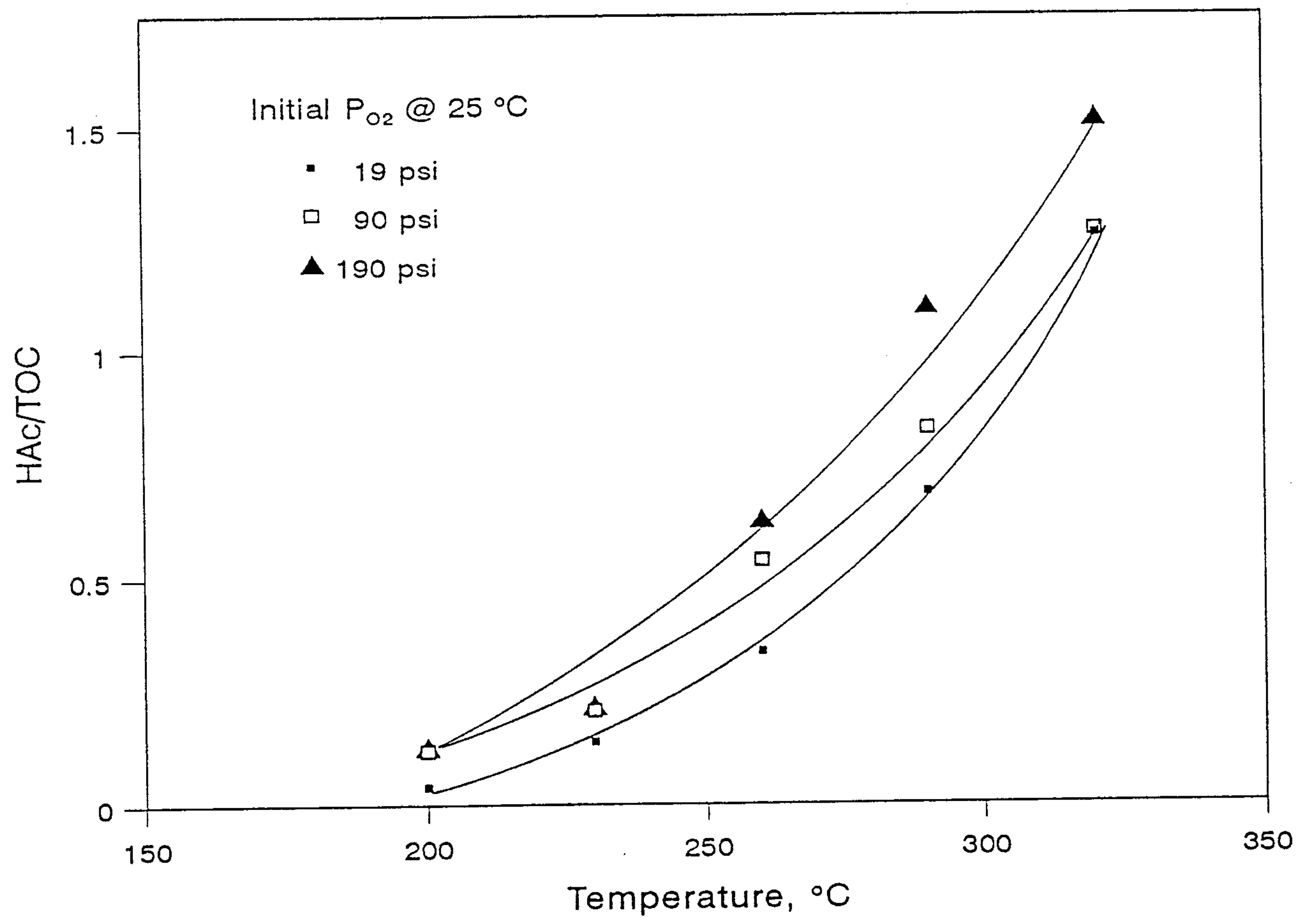


Figure 4.10. HAc/TOC as a function of WAO temperature and PO_2.

Table 4.9. Results of nitroaromatic recovery studies for sample matrix effects.

Sample ID	Amount Extracted in 2 mL Toluene from 100 mL Sample, µg					
	NB	*1,3*-DNB	*2,6*-DNT	*2,4*-DNT	*1,3,5*-TNB	α-TNT
Raw Redwater, w/ES*	0.620	1.998	0.240	0.638	1.828	0.854
w/o ES	BDL*	0.024	0.008	0.118	0.922	0.336
Difference	0.620	1.974	0.232	0.520	0.906	0.518
% Recovery	**103.3**	**109.7**	**116.0**	**130.0**	**151.0**	**86.3**
# 1, 200 °C, w/ES	0.592	5.174	0.446	0.650	10.202	0.752
w/o ES	0.044	4.158	0.282	0.210	9.958	0.112
Difference	0.548	1.016	0.164	0.440	0.444	0.640
% Recovery	**91.3**	**56.4**	**82.0**	**110.0**	**74.0**	**106.7**
# 2, 230 °C, w/ES	0.580	9.062	0.600	0.682	3.384	0.684
w/o ES	0.006	8.336	0.390	0.234	2.734	0.202
Difference	0.574	0.726	0.210	0.448	0.650	0.482
% Recovery	**95.7**	**40.3**	**105.0**	**112.0**	**108.3**	**80.3**
# 3, 260 °C, w/ES	0.586	8.76	0.488	0.674	0.604	0.542
w/o ES	0.032	7.966	0.300	0.254	0.462	0.204
Difference	0.554	0.800	0.188	0.420	0.142	0.338
% Recovery	**92.3**	**44.4**	**94.0**	**105.0**	**23.7**	**56.3**
# 4, 290 °C, w/ES	0.592	8.062	0.328	0.582	0.536	0.478
w/o ES	0.040	7.082	BDL	0.016	0.178	0.056
Difference	0.552	0.980	0.328	0.566	0.358	0.420
% Recovery	**92.0**	**54.4**	**164.0**	**141.5**	**59.7**	**70.4**
# 5, 320 °C, w/ES	0.622	5.822	0.286	0.508	0.472	0.438
w/o ES	0.064	5.020	BDL	0.010	0.174	BDL
Difference	0.558	0.802	0.286	0.498	0.298	0.438
% Recovery	**93.0**	**44.6**	**143.0**	**125.0**	**49.7**	**73.0**

* Diluted raw (1:100) and treated redwater samples were further diluted 1:200. Amounts of external standard (ES) added to diluted samples before extraction were: NB, *1,3,5*-TNB, and α-TNT (each 0.6 µg); *1,3*-DNB - 1.8 µg; *2,6*-DNT - 0.2 µg; and *2,4*-DNT - 0.4 µg. A 100 mL sample was then extracted in 2 mL toluene using the procedures described earlier.

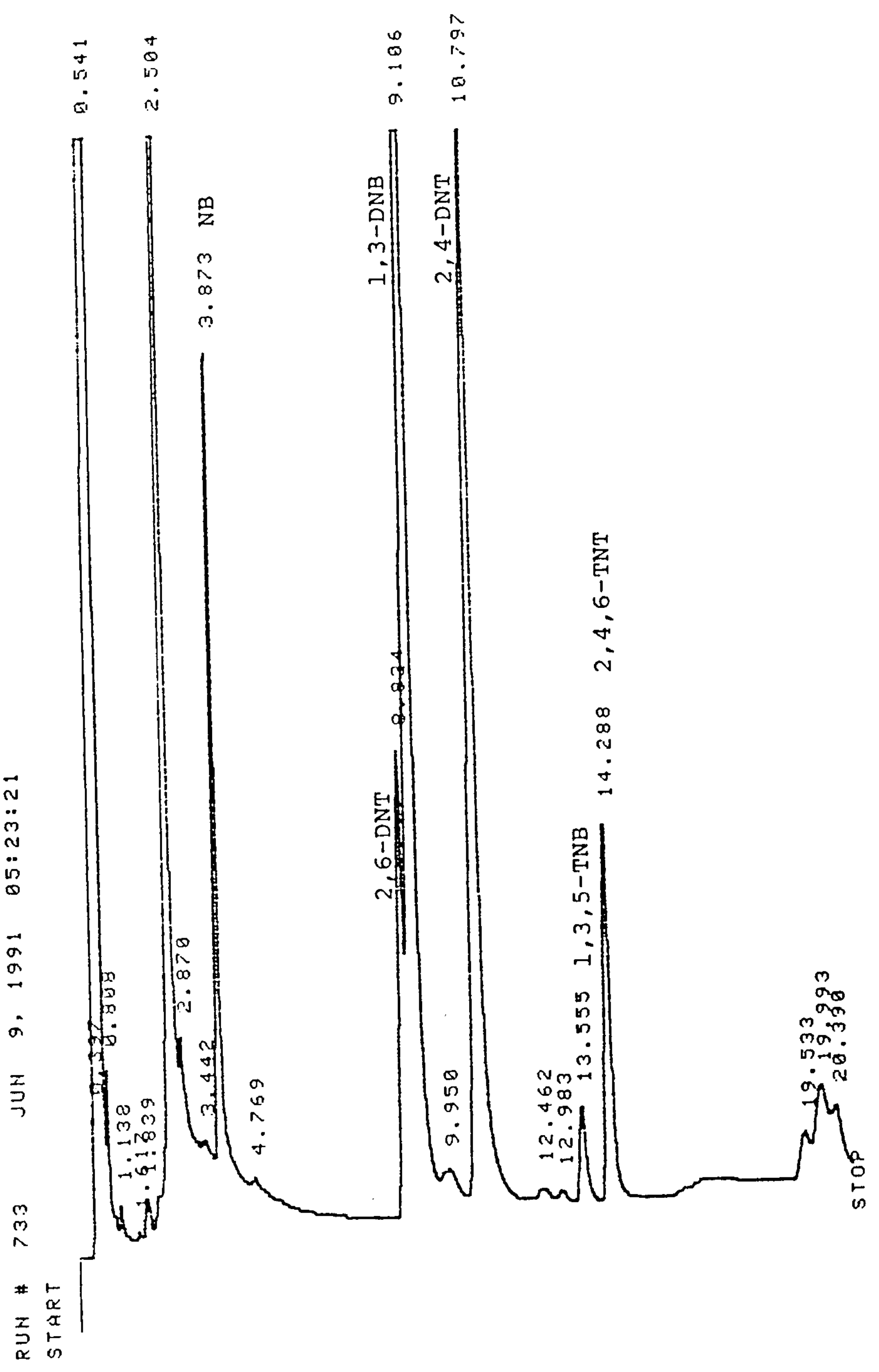


Figure 4.11. A typical gas chromatogram for standards using on-column injection.

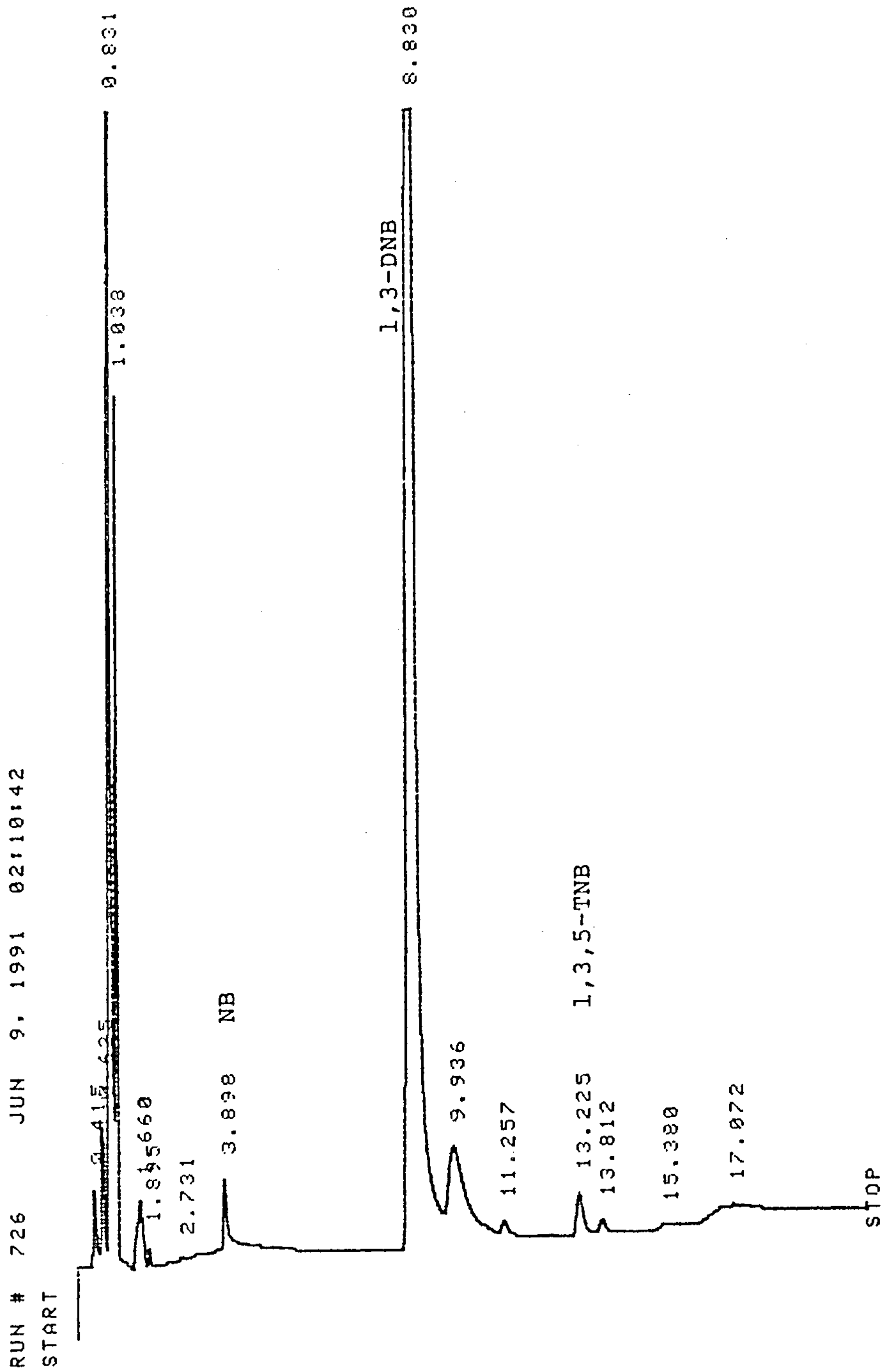


Figure 4.12. A typical gas chromatogram for treated redwater (320 °C and PO_2 = 190 psi) using on-column injection.

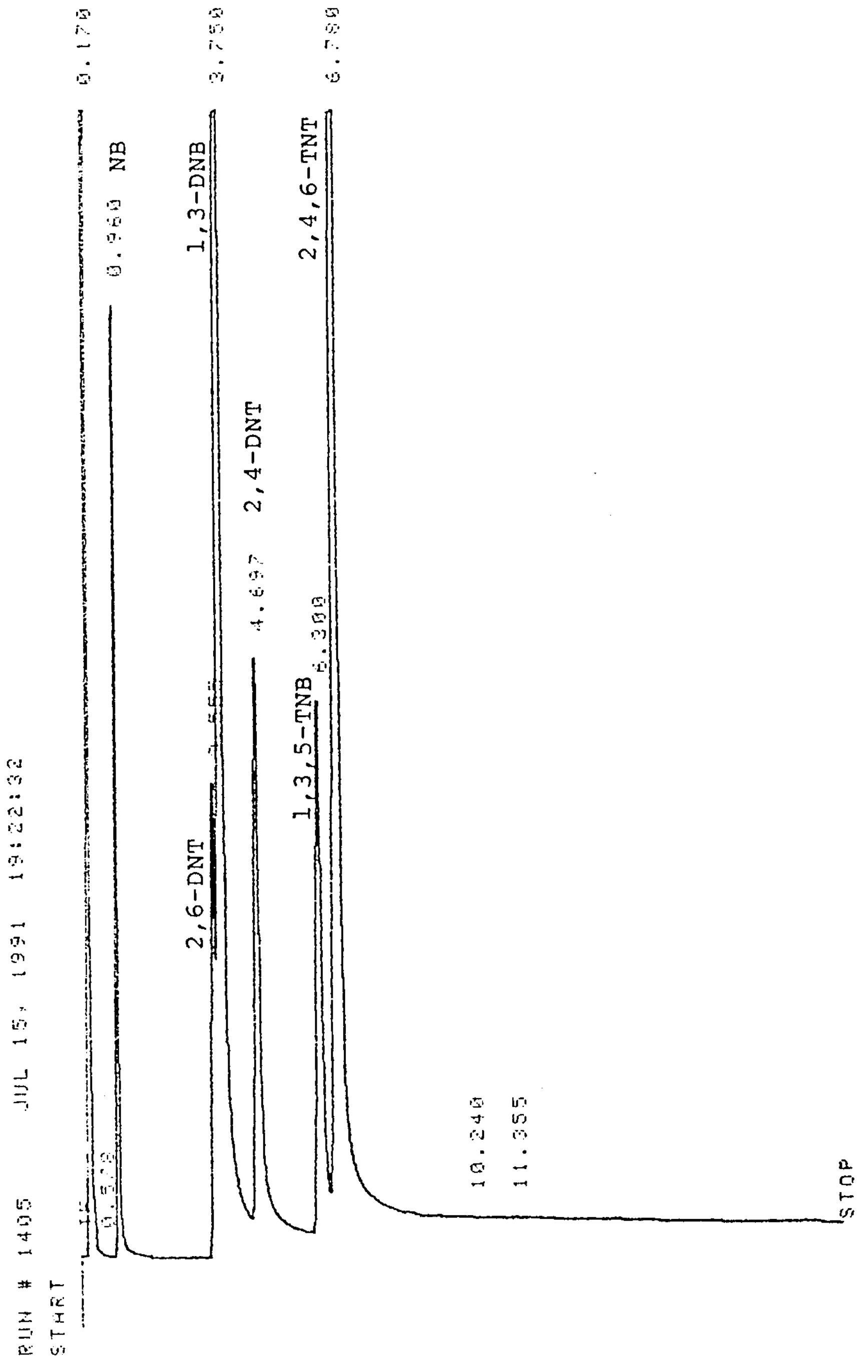


Figure 4.13. A typical gas chromatogram for standards using splitless injection.

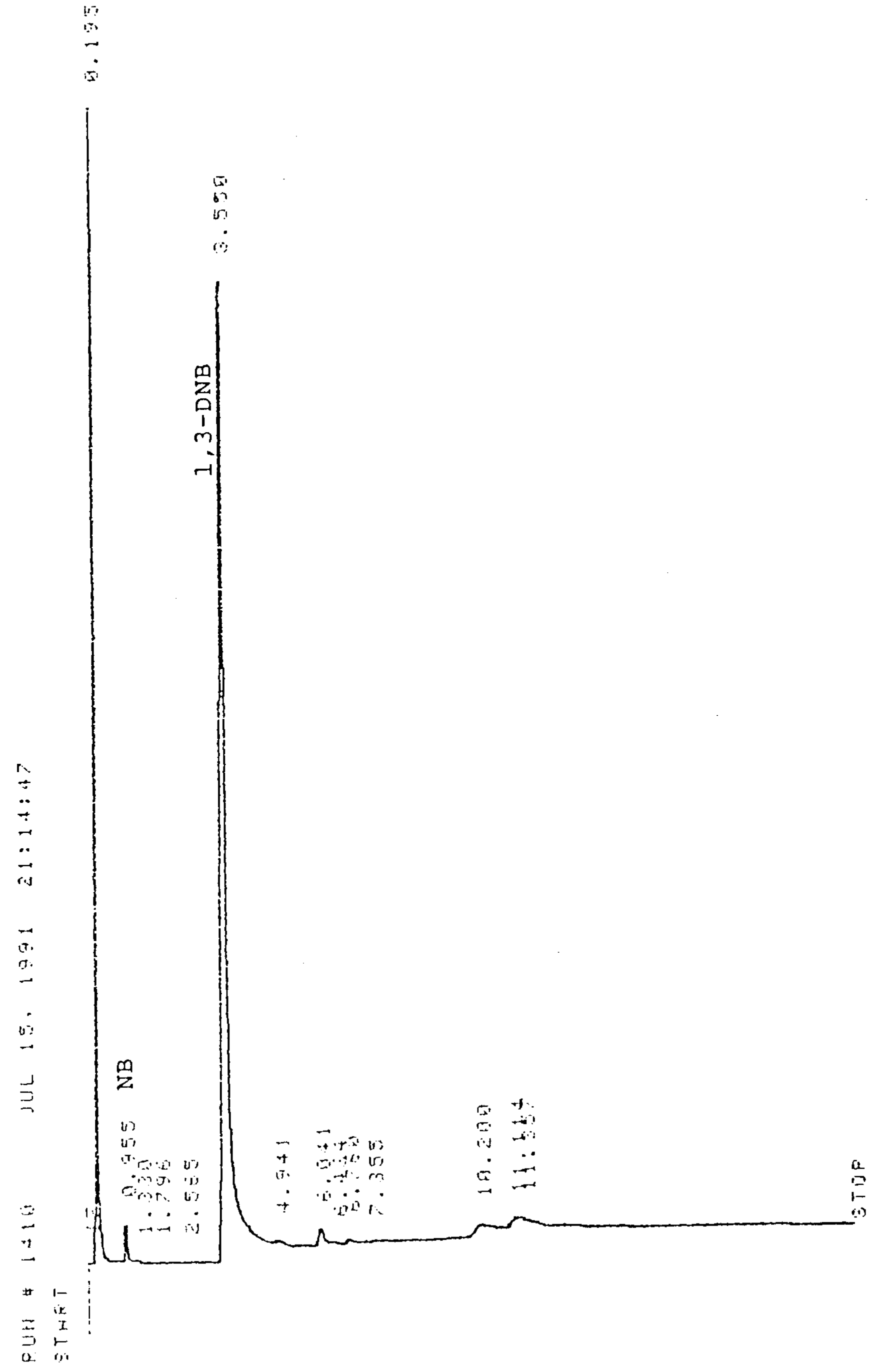


Figure 4.14. A typical gas chromatogram for treated redwater (300 °C and PO_2 = 90 psi) using splitless injection.

psi PO_2 are shown in Figure 4.15. For example, the 1,3-DNB concentration, which averaged about 0.05 mg/L in raw redwater, peaked between 16.7 and 23.7 mg/L at 230 °C before reducing to 2.5 to 10.0 mg/L at 320 °C (Tables 4.5 to 4.7). The 1,3-DNB is supposedly an intermediate compound formed by the elimination of the methyl group from the DNTs, which, in turn, are formed from the desulfonation of the DNTSs as: DNTSs → DNT → DN benzoic acid → DNB. However, 1,3-DNB may also originate from the breakdown of 1,3,5-TNB which, in addition to being initially present, is also formed during the WAO of redwater. The plots of 1,3,5-TNB and 1,3-DNB concentrations in Figure 4.15 indicate that accumulation and destruction of 1,3-DNB generally lags behind those of 1,3,5-TNB—a fact that tends to support the above statement. Considering the small amount of α-TNT (0.7 mg/L) initially present in raw redwater, the exact reason for the significant increase in *1,3,5*-TNB concentration is unclear. It might result from the breakdown of the so-called *a*-TNT-sellite complex, a major component present in redwater (PEI 1990) as:

$$\alpha\text{-TNT- complex} \rightarrow \alpha\text{-TNT} \rightarrow \text{TN benzoic acid} \rightarrow \text{TNB} \qquad \text{[Eq 4.1]}$$

The increase in 2,6-DNT concentration was higher than that for 2,4-DNT under all experimental conditions; both appear to be further oxidized at about 260 °C. The data in Tables 4.5 to 4.7 indicate that oxygen pressures do exhibit some influence on the pattern of reduction of the nitroaromatics concentrations; however, the data are too scattered to make meaningful interpretations.

The only nitroaromatic found in trace amounts in the redwater treated at 340 °C with excess oxygen was *1,3*-DNB; analysis was not performed for NB during the feasibility experiments. However, refer to Table 4.9 to see the results for NB in nitroaromatic recovery studies. It must be noted that NB, which is present in trace amounts in treated redwater, is listed as one of EPAs priority pollutants. The regulatory concentration for NB is 2 mg/L. NB is soluble in water (0.27 percent at 31 °C) and is very toxic. Its toxicity is due to its ability to convert hemoglobin to methemoglobin. It is readily absorbed through the skin and through inhalation (Kirk-Othmer 1983; Mcketta 1990). The presence of NB and a relatively high concentration of *1,3*-DNB in a WAO-treated effluent may cause it to be listed as a hazardous waste under the EPA RCRA Regulation, 40 Code of Federal Regulations (CFR), part 261, subpart D (e.g., U169-NB). Therefore, attempts must be made to eliminate the nitroaromatics from redwater to the extent possible and practicable. One possible alternative might be the use of biological treatment of the partially treated redwater.

DNTSs

A typical chromatogram for a standard (22.5 mg/L total DNTSs) synthesized in the laboratory is shown in Figure 4.16. The three peaks at retention times 14.0, 15.8, and

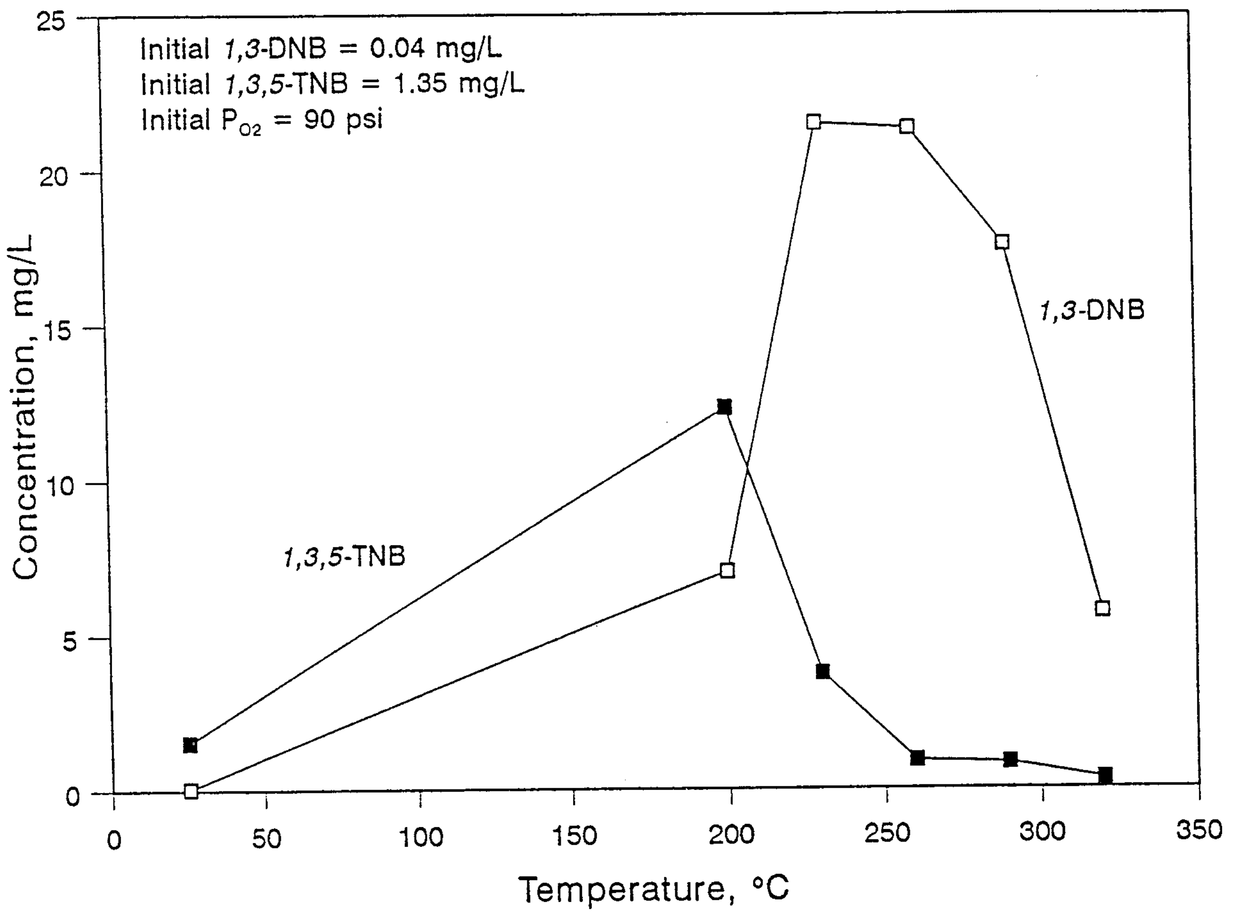


Figure 4.15. Concentrations of 1,3-DNB and 1,3,5 TNB as a function of WAO temperature.

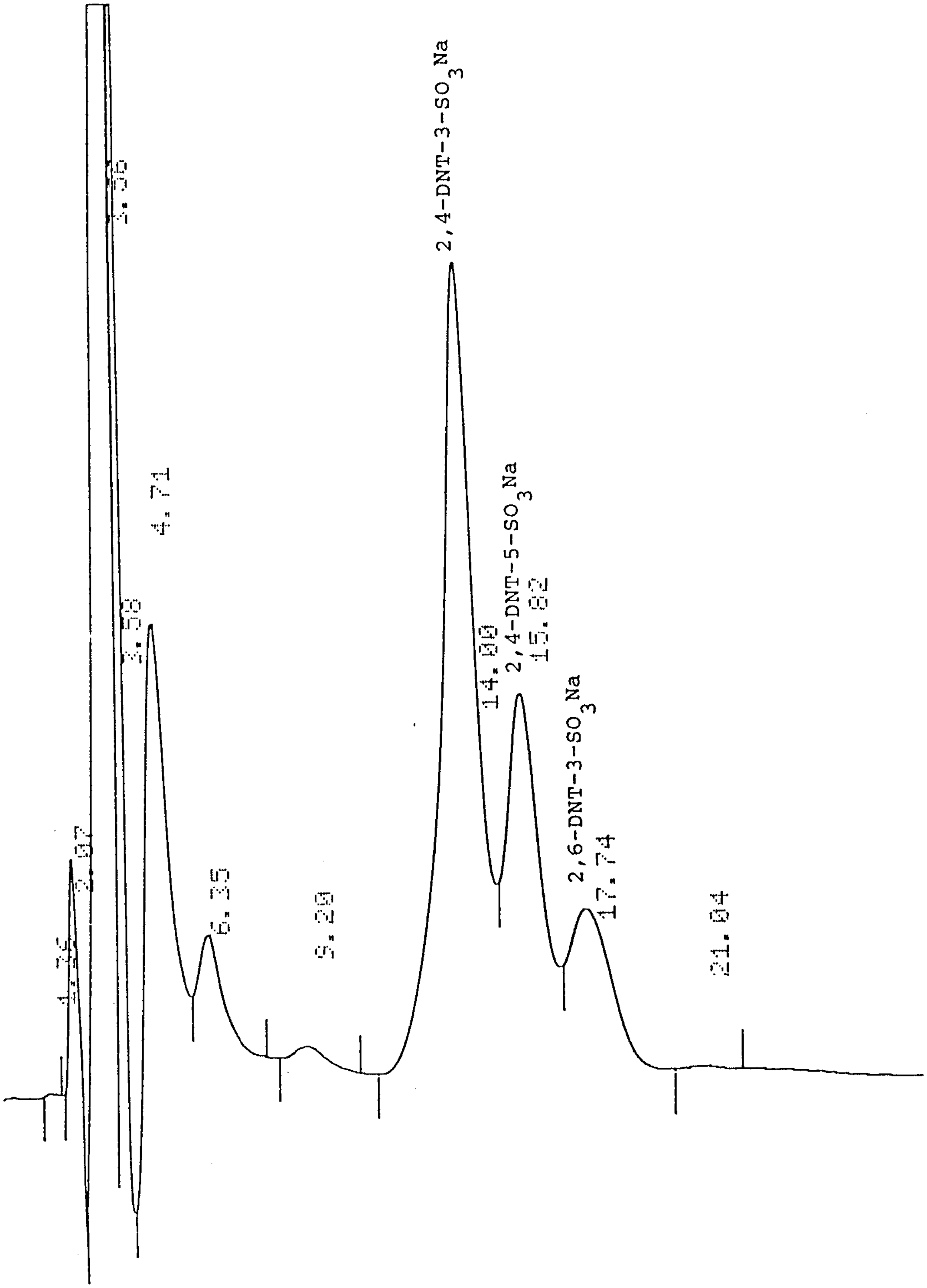


Figure 4.16. Chromatogram of DNTSs synthesized in the laboratory: mixture of 2,4-DNT-5-SO$_3$Na and 2,6-DNT-3-SO$_3$Na.

17.7 minutes were identified as *2,4*-DNT-*3*-SO_3Na, *2,4*-DNT-*5*-SO_3Na, and *2,6*-DNT-*3*-SO_3Na, respectively, using the rationale described in Chapter 3. Results of analyzing the standards for *2,4*-DNT-*3*-SO_3Na and *2,4*-DNT-*5*-SO_3Na, obtained from the State of Illinois' Hazardous Waste Research and Information Center (HWRIC) are shown in Figures 4.17 and 4.18. Similar peaks were observed for these DNTSs (Figure 4.17: 14.0 and 15.8 minutes respectively, for *2,4*-DNT-*3*-SO_3Na and *2,4*-DNT-*5*-SO_3Na; Figure 4.18: 15.6 minutes for *2,4*-DNT-*5*-SO_3Na). These standards were synthesized for HWRIC by the Stanford Research Institute, partly following the procedures described by Gilbert (1978). The major difference, reportedly, was that the standards synthesized for HWRIC were not fully purified, as recommended by Gilbert (1978).

A typical chromatogram for raw redwater is shown in Figure 4.19. A dilution factor of 1:10 was used for redwater sample (1:100) for a final dilution of 1:1000. After repeating the analyses several times, the DNTSs concentrations in raw redwater used in the present experiments were always much less than those previously noted in Chapter 3 (i.e., 42 and 28 mg/L presently compared to 272 and 228 mg/L found earlier for *2,4*-DNT-*3*-SO_3Na and *2,4*-DNT-*5*-SO_3Na, respectively). One plausible explanation for this discrepancy might be that DNTSs are not stable in aqueous solutions for extended periods. A similar observation regarding the instability of the DNTSs was also made by the chemists at the HWRIC (T. Chen, Illinois State Hazardous Waste Research and Information Center, Champaign, IL, personal communication, 1991).

Typical chromatograms for DNTSs in redwater treated under two different conditions are shown in Figure 4.20 (230 °C and PO_2 = 190 psi), and Figure 4.21 (290 °C and PO_2 = 190 psi); complete results are already summarized in Tables 4.5 to 4.7. The data show that *2,4*-DNT-*3*-SO_3Na and *2,4*-DNT-*5*-SO_3Na were not detected at 320 °C. Furthermore, *2,4*-DNT-*5*-SO_3Na was completely destroyed at or above 260 °C, whereas *2,4*-DNT-*3*-SO_3Na was eliminated only at a higher temperature of 320 °C. The relative removals of the two DNTSs are similar to those discussed in the Feasibility Studies. The effect of oxygen pressure on the removal of DNTSs is not easily discernible at the oxygen pressures studied.

Inorganic Sulfate and Nitrate

A typical ion chromatogram showing the analysis of nitrite, nitrate, and sulfate in raw and treated redwater samples is shown in Figure 4.22. After 1-hour WAO of the diluted redwater, there was a significant accumulation of the inorganic sulfate (Tables 4.5 to 4.7). The increased amount of sulfate (difference between the sulfate concentration in treated and raw redwater) represents the oxidation of inorganic sulfite and the desulfonation of SO_3 groups associated with DNTSs and other sulfur-bearing organic compounds in redwater. The increase in sulfate concentration is a function of temperature (Figure 4.23), similar to the temperature dependency for COD and

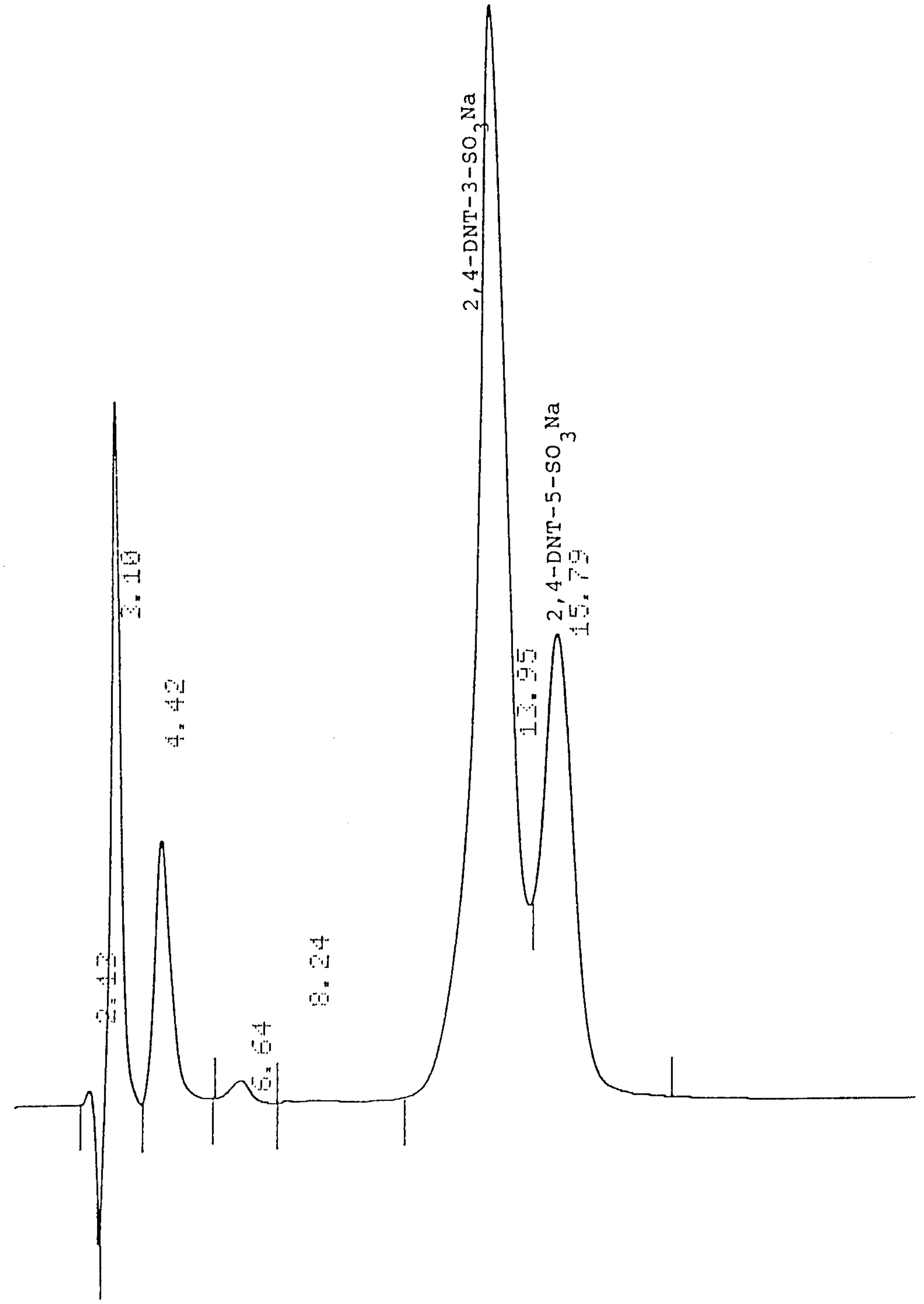


Figure 4.17. Chromatogram of DNTSs from the Hazardous Waste Research and Information Center, Champaign, IL: mixture of 2,4-DNT-3-SO$_3$Na and 2,4-DNT-5-SO$_3$Na.

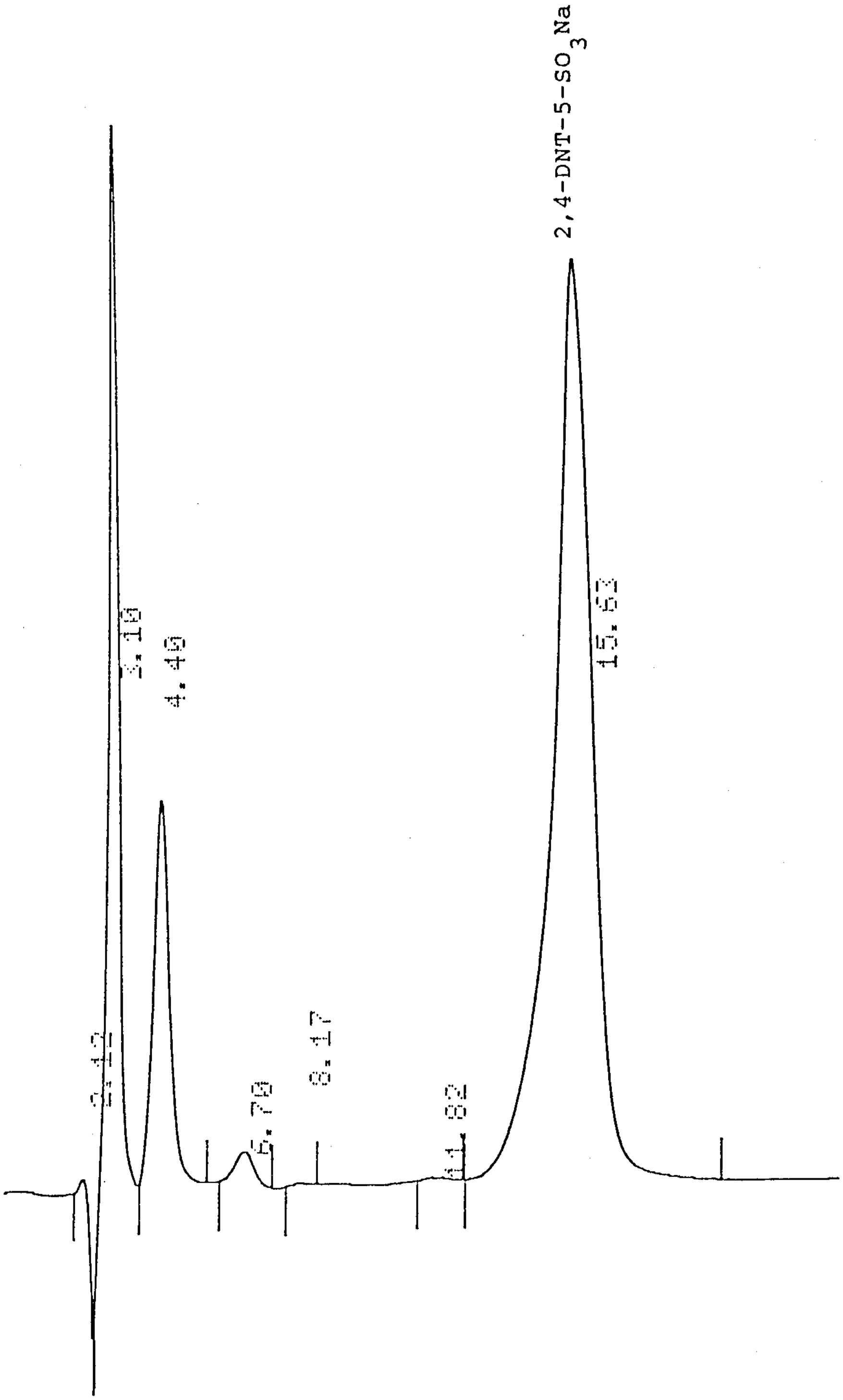


Figure 4.18. Chromatogram of DNTSs from the Hazardous Waste Research and Information Center, Champaign, IL: 2,4-DNT-5-SO$_3$Na.

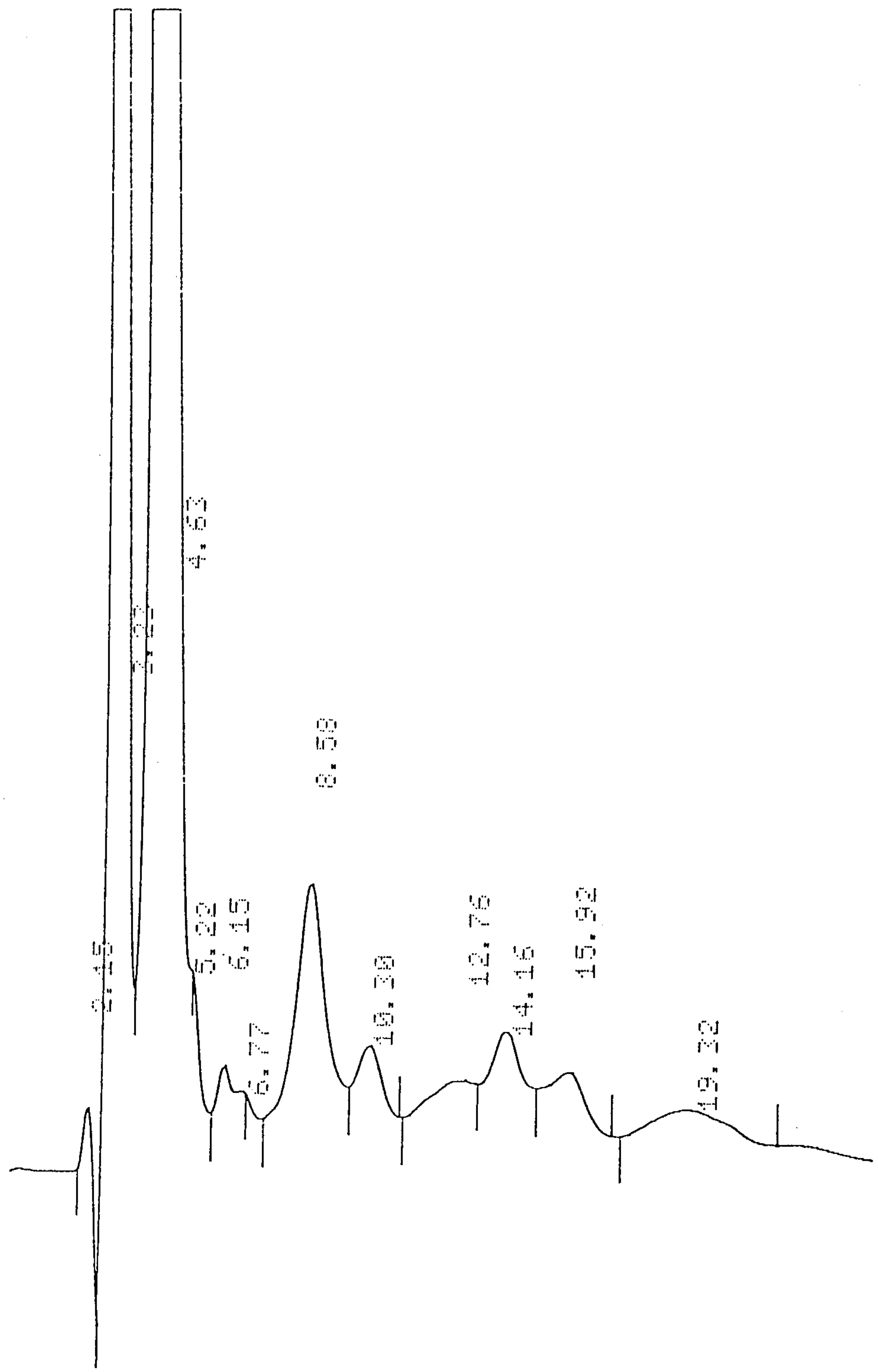


Figure 4.19. Chromatogram of raw redwater (dilution factor=1:100, sample dilution-1:10).

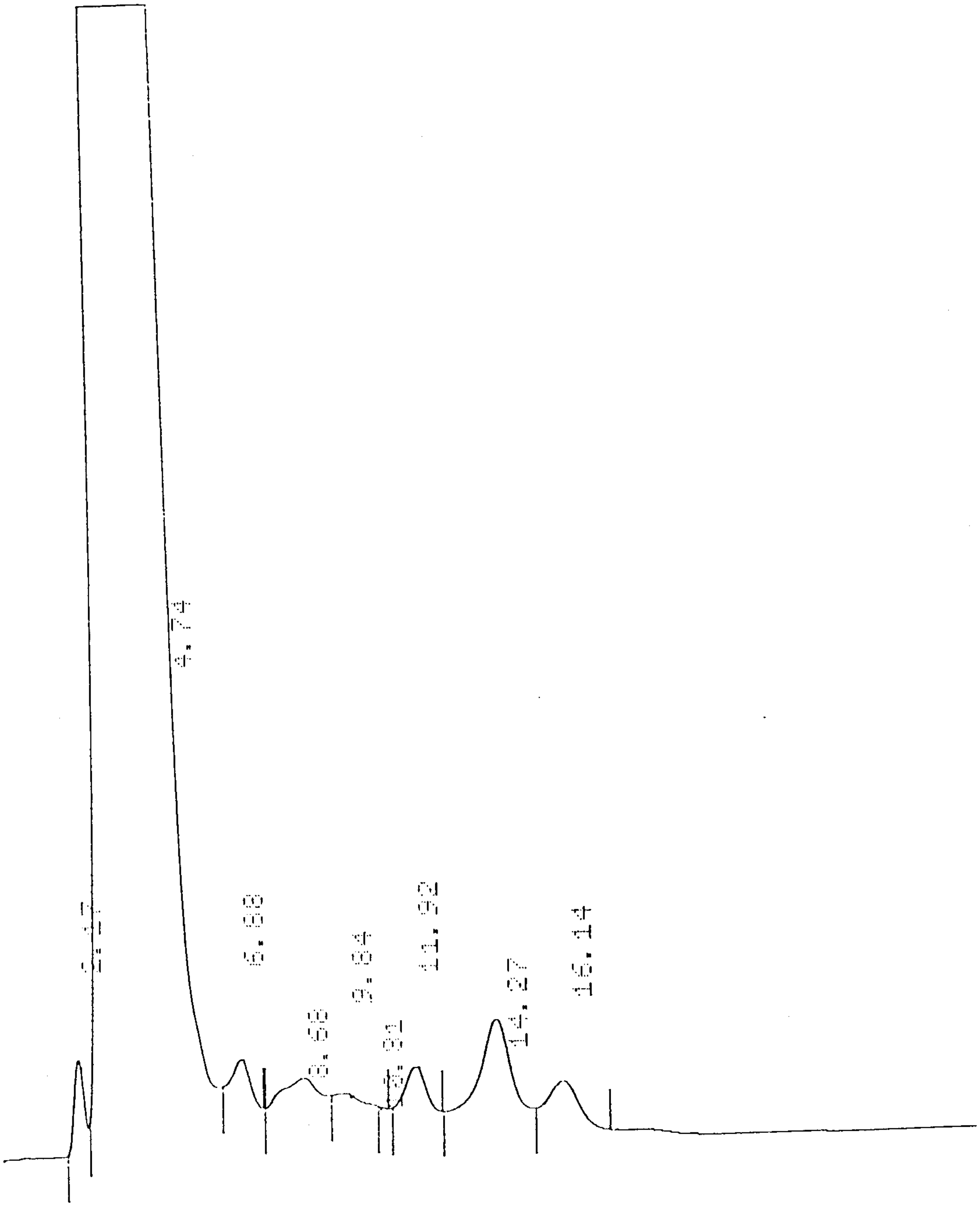


Figure 4.20. Chromatogram of treated redwater (1:1000 dilution): 230 °C and 190 psi PO_2.

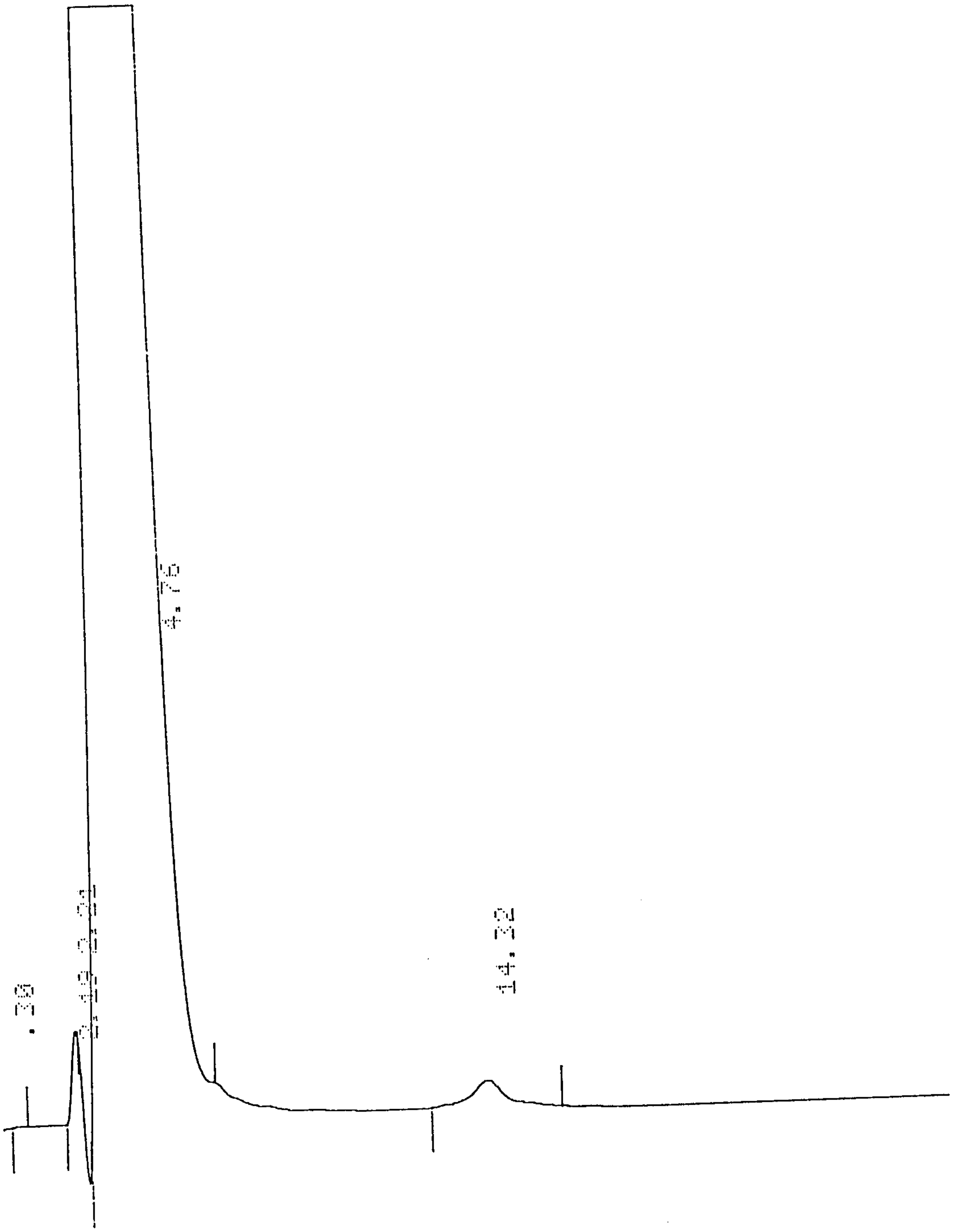


Figure 4.21. Chromatogram of treated redwater (1:100 dilution): 290 °C and 190 psi PO_2.

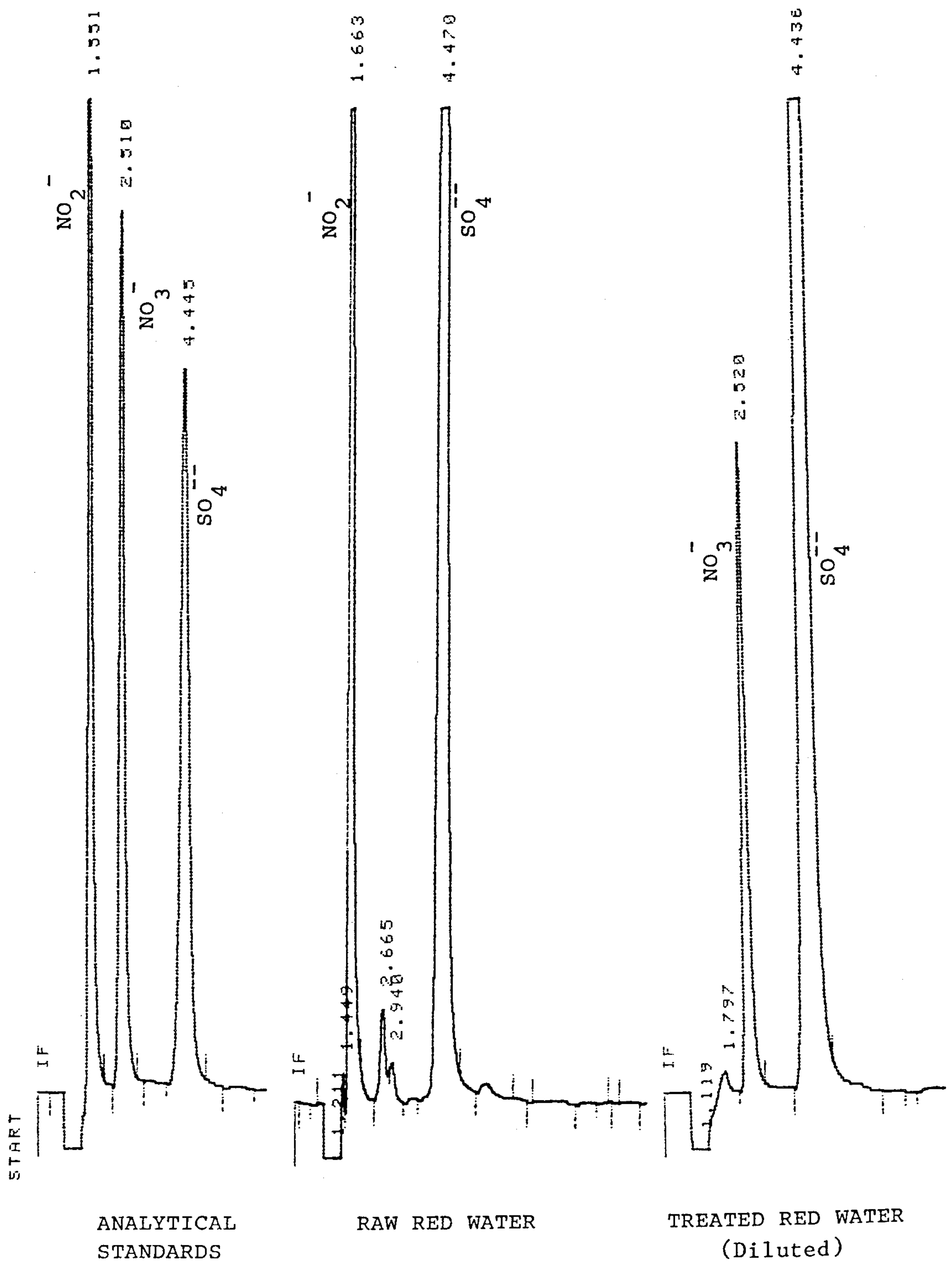


Figure 4.22. Typical chromatogram for nitrites, nitrates, and sulfates: standard, raw, and treated redwater.

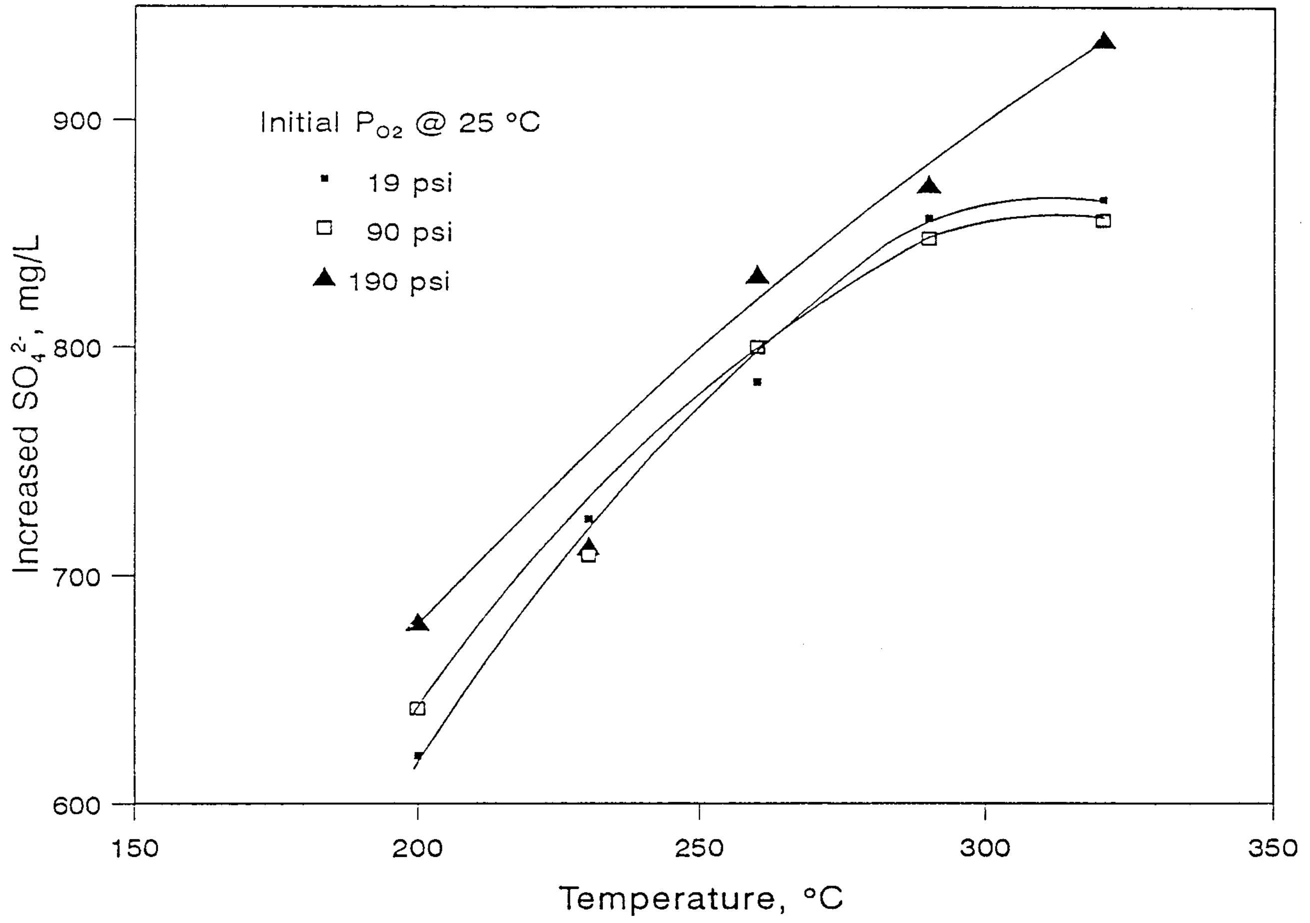


Figure 4.23. Increase in SO_4^{2-} concentration as a function of WAO temperature and PO_2.

TOC removal discussed earlier. The sulfate increase ranged from 856 to 935 mg/L as SO_4^{2-} at 320 °C. These sulfate concentrations are equivalent to 2530 to 2770 mg/L DNTSs (MW = 284) and are obviously almost two orders of magnitude greater than the combined estimated values of *2,4*-DNT-*3*- and *2,4*-DNT-*5*-SO_3Na. The difference must be due to other sulfonated compounds present in raw redwater (e.g., α-TNT-sellite complex). Consequently, it is difficult to compare the amount of sulfate increase to that of the DNTSs disappearance. Furthermore, the disappearance of the DNTSs may not only mean the loss of its SO_3 group, but may also be attributable to the formation of some intermediate compounds with the SO_3 group still intact (e.g., DNB sulfonic acid).

In many cases, the nitrate concentrations after WAO are less than the combined concentrations of inorganic nitrite and nitrate initially present in the diluted redwater; therefore, the fate of the nitro groups associated with the aromatic compounds is unknown. Since the SO_3 group is separated from the DNTSs and oxidized to sulfate, and the TOC concentration of treated redwater is low, the NO_2 group in DNTSs and intermediate nitro compounds must also be detached from these aromatic compounds. Therefore, the unaccountable nitrogen may possibly be present as nitrogen gases.

Solids

Total volatile solids (TVS) reductions (Figure 4.24) follow the same patterns as those for COD and TOC removals. The reduction averages about 48 percent at 230 °C and increases to 90 percent at 320 °C. Clearly, the organic compounds are oxidized to CO_2, otherwise the mere conversion of organic compounds to other organic byproducts would show up as TVS. The fixed solids remain essentially the same (a slight increase results from the conversion of nitrite to nitrate and sulfite to sulfate; Tables 4.5 to 4.7) and the corresponding TVS percentage decreases significantly as temperature increases (Figure 4.25).

The ratio of TVS/TOC reflects the oxidation state of organic compounds; that is, the larger the ratio, the higher the oxidized state of the compound (e.g., the TVS/TOC ratio for ethanol and acetic acid are 1.9 and 2.5, respectively). As temperature increases, the organic compounds are oxidized to higher oxidation states, resulting in an increased ratio of TVS/TOC, as shown in Figure 4.26.

UV/VIS Absorbance

The raw and treated samples were analyzed for UV/VIS absorption. As shown in Tables 4.5 and 4.7, the raw redwater exhibits a strong UV absorbance at a wavelength of 200 nm (au = 1.25) and weak visible absorbances at 432 nm (au = 0.12) and 488 nm

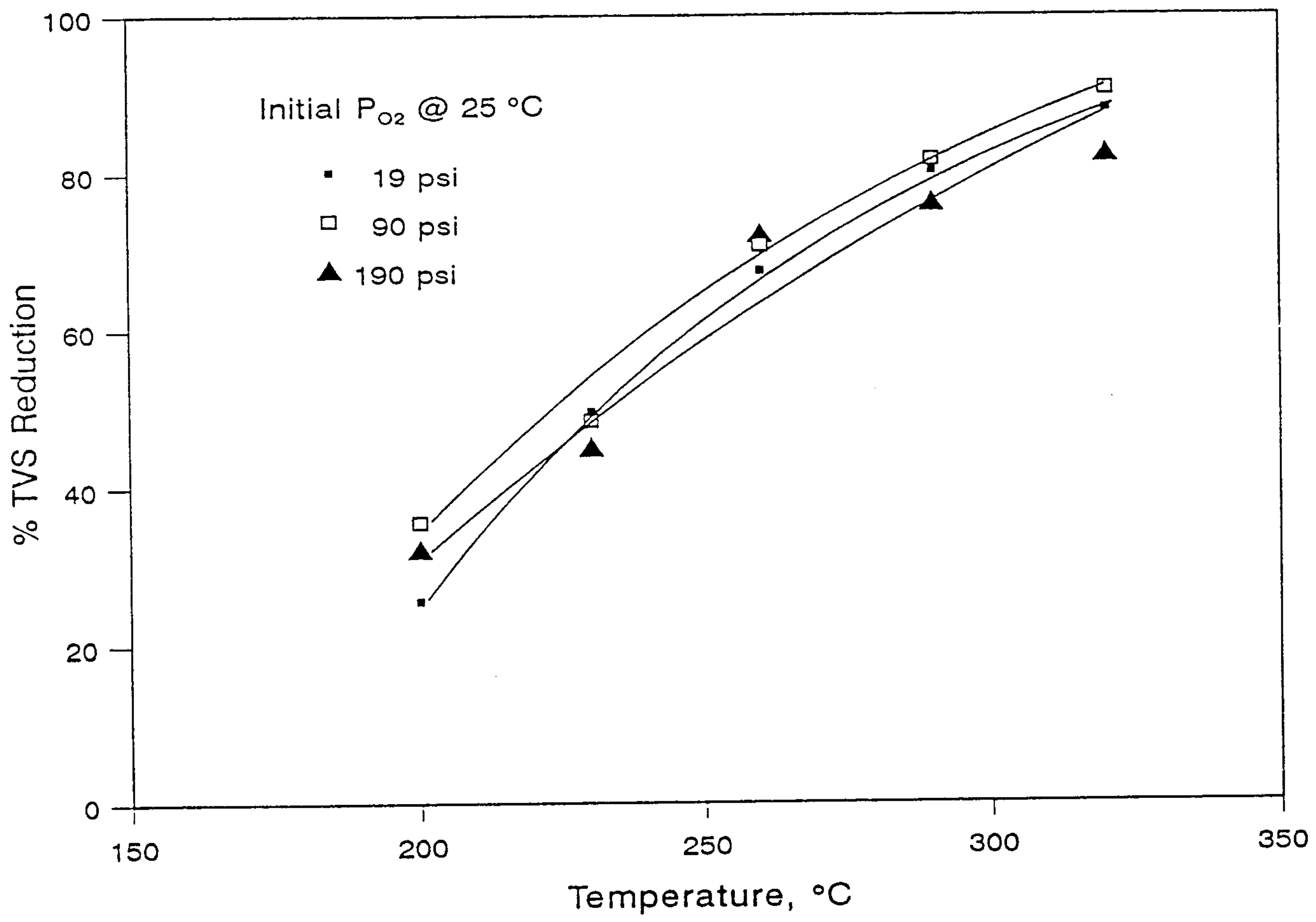


Figure 4.24. TVS reduction as a function of WAO temperature and PO_2.

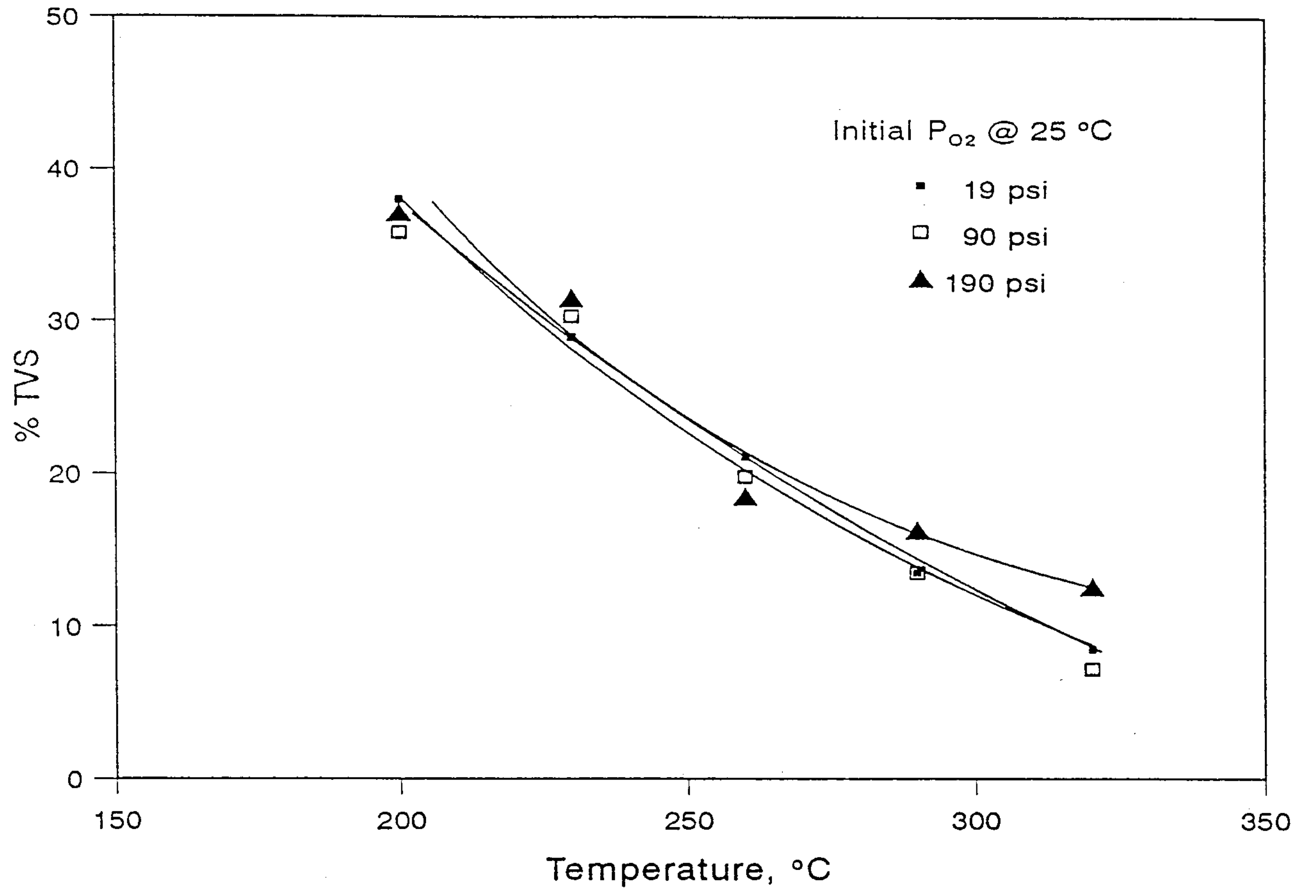


Figure 4.25. Reduction in volatile solids as a function of WAO temperature and PO_2.

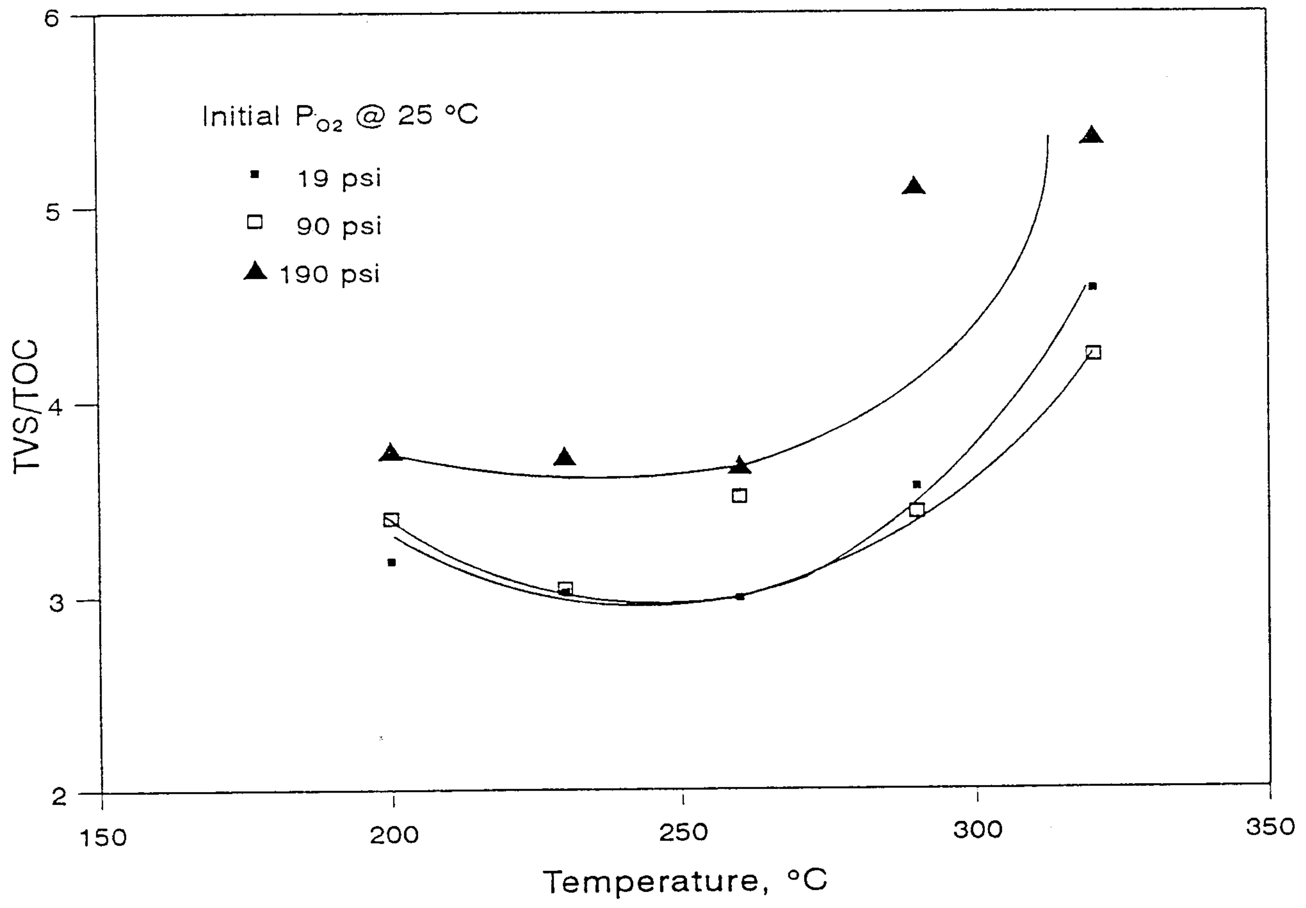


Figure 4.26. TVS/TOC as a function of WAO temperature and PO_2.

(au = 0.11). The absorbance results (au) were based on the diluted samples (1:100) of the diluted raw redwater (1:100) with a total dilution factor of 1:10,000. The compounds responsible for absorption at 346 nm are easily destroyed even at the lowest temperature of 200 °C. The reductions in the absorbance at 200 nm and other wavelengths are shown in Figure 4.27. The unknown byproducts (which absorb at 362 nm), accumulate up to 200 °C, at which point the concentration is reduced as the temperature increases.

Because of the complex organic composition of redwater, attempts were not made to identify or quantify compounds present in raw and treated samples that were responsible for absorption in the UV/VIS range. Instead, the absorption intensities at 200 nm were compared for raw and treated samples to observe changes in UV absorption under different experimental conditions.

WAO Run at 340 °C

None of the WAO conditions up to 320 °C and 190-psi oxygen pressure provided a complete treatment of redwater, as reflected by the residual concentrations of TOC and COD and high concentrations of the intermediates HAc and *1,3*-DNB. The harsh condition of 340 °C and 110 psi PO_2 used previously, indicated an almost complete removal of different contaminants, and was therefore repeated. The nitroaromatics analysis for the samples from this run was performed using a different GC, one dedicated exclusively to the detection of trace amounts of explosives contamination in groundwater. The analytical methods and instrument conditions are shown in Table 3.6. The DLs were: NB - 0.03 micrograms (µg)/L; *2,6*-DNT - 0.01 µg/L; *1,3*-DNB-0.09 µg/L; *2,4*-DNT-0.02 µg/L; α-TNT - 0.03 µg/L; and *1,3,5*-TNB - 0.03 µg/L. These DLs are based on the standards and samples extracted from a sample size of 100 mL into 0.5 mL toluene. The quantification limits are, therefore, the same as the DLs. The results indicate that the residual COD was 8 mg/L (or 98.5 percent removal of the initial COD of 540 mg/L), pH = 3.5, TOC = 30 mg/L (91 percent removal from the initial TOC of 327 mg/L), and only small amounts of NB (0.28 mg/L) and *1,3*-DNB (0.68 mg/L) were present. Trace amounts of *2,6*-DNT (0.002 mg/L), *2,4*-DNT (0.003 mg/L), and *1,3,5*-TNB (0.0008 mg/L) were also present. The DNTSs were not detected. The UV absorbance at 200 nm was 0.28 au compared to 1.25 au, for 1:100 diluted raw redwater.

Kinetic Experiments

The experimental conditions for the kinetic studies (i.e., PO_2 = 45-320 psi and T = 230-300 °C) were chosen to obtain a broad database. Typical semi-log plots of TVS, TOC, and COD versus reaction time (Figure 4.28; T = 260 °C, PO_2 = 45 psi, and dilution factor = 1:25) showed similar trends. There was a significant initial reduction of TOC,

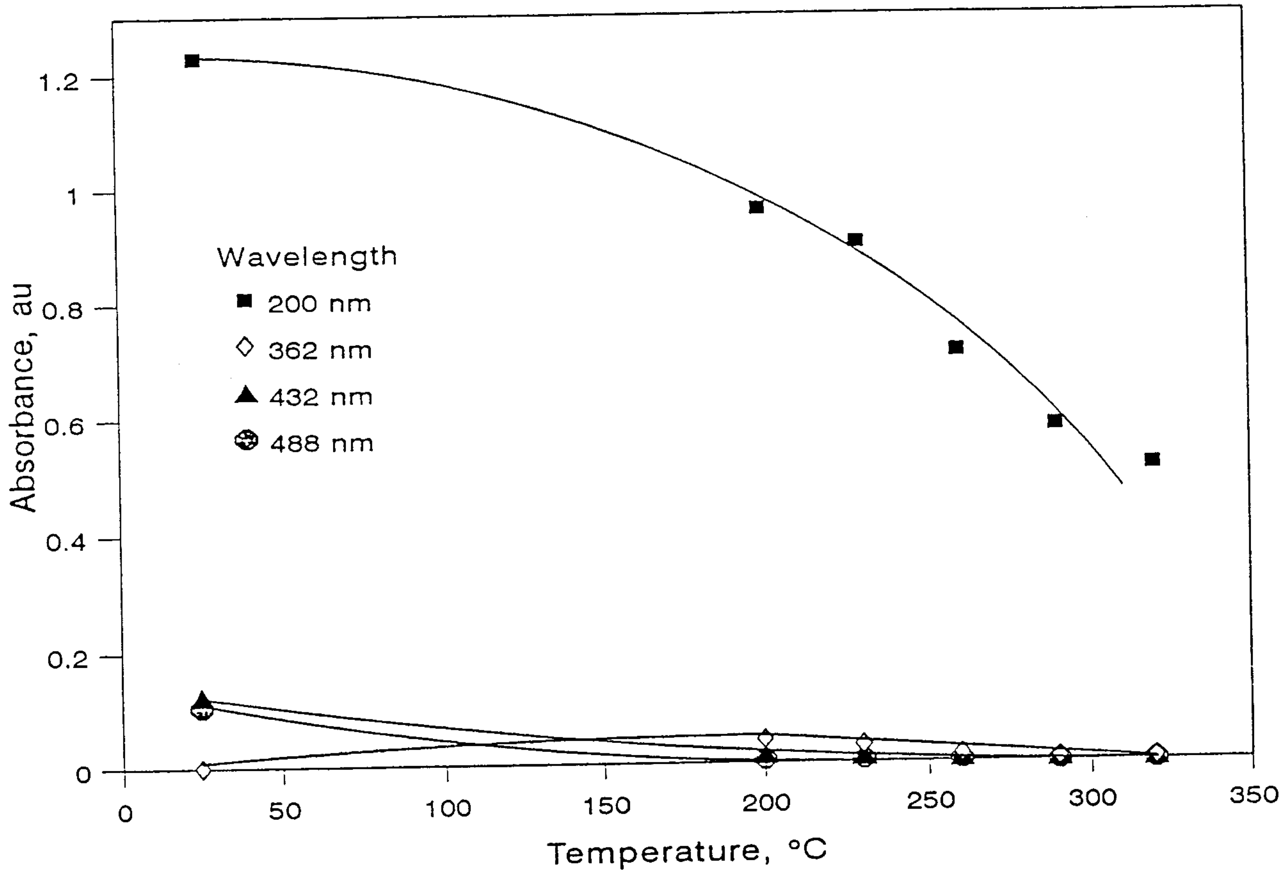


Figure 4.27. UV/VIS absorbance as a function of WAO temperature (PO_2=190 psi at 25 °C).

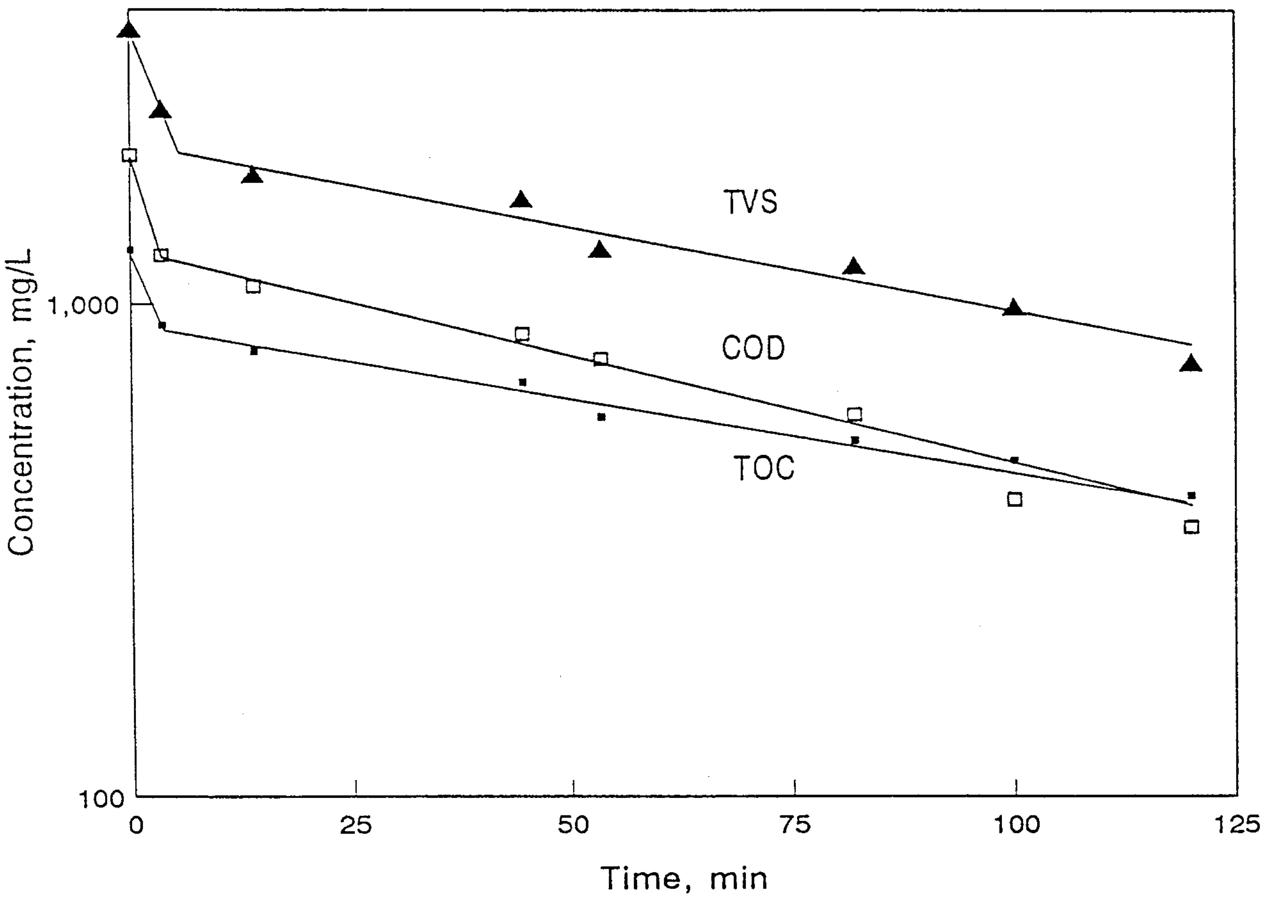


Figure 4.28. Typical COD, TOC, and TVS removal profiles at 260 °C, 45 psi PO_2, and 1:25 dilution.

COD, and TVS immediately after sample injection (within the first sampling event, usually < 5 minutes). After the initial "flash" destruction, the reaction proceeds as first-order:

$$r = - dC/dt = k\ C \qquad \text{[Eq 4-2]}$$

where r is the rate of reaction, d is the differential, C is the concentration (TOC, COD, or TVS), and k is the apparent (observed) first-order rate constant. From the semi-log plots, the rate constants were determined to be 6.5×10^{-3} ($R^2 = 0.98$), 1.1×10^{-2} ($R^2 = 0.97$), and 8.5×10^{-3} min^{-1} ($R^2 = 0.91$), respectively, for TOC, COD, and TVS. The first-order rate dependence with respect to a gross parameter of COD or TOC was also reported by Baillod et al. (1982) for WAO of phenol and nitrophenol and Joglekar et al. (1991) for phenol.

Samples were not withdrawn at time (t) = 0 minutes. Instead, the zero-minute TOC or COD was calculated from the known concentration of the redwater. As discussed later, tests performed to assess the accuracy of the sample injection technique showed the technique to be highly reliable. The measured concentrations of the organic compound and TOC were practically identical to the theoretical values based on the amounts injected.

The effect of sample withdrawal (done 6 times, at approximately 20 to 30 mL each with a total of 120 to 180 mL) on the reaction kinetics is unknown, but was presumed to be insignificant. The kinetic experimental data are shown in Appendix B. Effects of the various factors studied are discussed below.

Effect of Oxygen Pressure

For a 1:25 sample dilution factor, several different oxygen pressures were used at a constant temperature of 260 °C to evaluate the effect of oxygen pressure on the reaction rates. The results are shown in Figure 4.29 for COD. Within the first sampling period (less than 4.5 minutes), the initial COD (approximately 2020 mg/L) was significantly reduced. The degree of the initial "flash" destruction depends on pressure (Figure 4.29 and Table 3.5), as can be easily seen from the two extreme pressure cases. The data for the initial COD reduction shown in Table 3.5 were based on the difference between the initial COD concentration and the COD at a constant time of 5 minutes (extrapolated from the plots of concentration versus time). The reason for the initial rapid COD reduction is the presence of easily oxidizable compounds in the raw redwater. Furthermore, the organic compounds in a higher oxidation state may be destroyed during this "flash" phase. The increase in initial COD removal with an increase in PO_2 may be partially due to the higher dissolved oxygen concentrations at higher oxygen pressures.

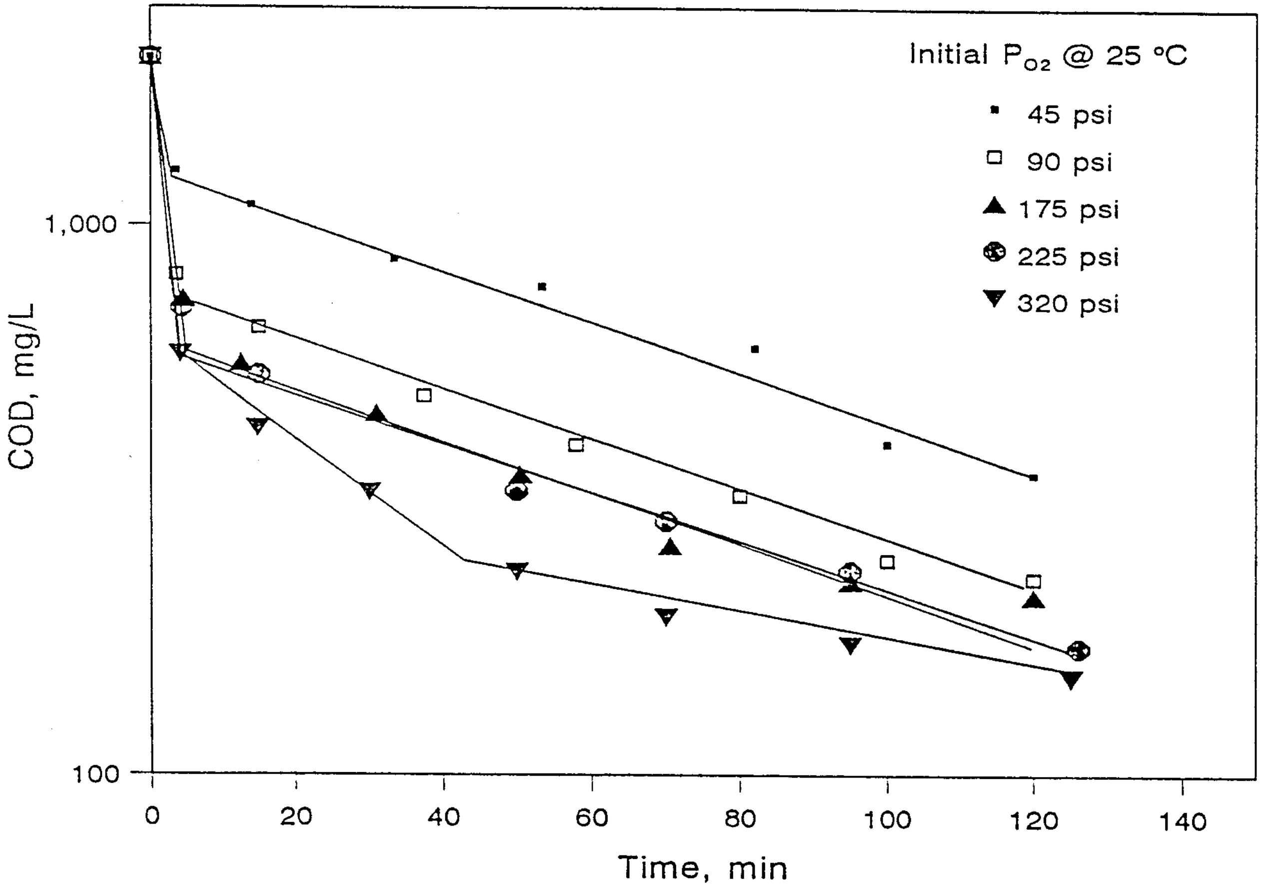


Figure 4.29. Effect of initial PO_2 on WAO rate at 260 °C and 1:25 dilution for COD.

After the initial COD reduction, the slowly oxidizable compounds then follow the typical first-order reaction rate (slopes are all parallel), and PO_2 has no further effect on the COD destruction rate constant. Eckert et al. (1990), in their WAO studies of *p*-chlorophenol, also reported that O_2 (varied by a factor of 11) did not exert any effect on the first-order reaction rate with respect to chlorophenol. However, at a higher pressure (320 psi), there appears to be two distinct first-order removal phases (Figure 4.29), with a higher rate constant of 2.2×10^{-2} min^{-1} with respect to COD for the first phase. The rate constant for the slower phase (the rate controlling step) was determined to be 5.7×10^{-3} min^{-1}.

Presence of two or more phases of reaction in WAO has been described by others. The model proposed by Ploos van Amstel (1971) to describe experimental findings of WAO of AS consists of three components: a more reactive component, a less reactive component, and a nonreactive component. Considering the conditions used in their experiments to be harsher than those used by Ploos van Amstel (1971) and Foussard et al. (1989) divided the organic loading in WAO of biological sludge into two parts: easily oxidized and not easily oxidized. They proposed first-order rate expressions in organic concentration for both parts. A two-phase reaction, first-order in each phase, was also presented by Joglekar et al. (1991) for WAO of substituted phenols. Other reactions with two distinct first-order phases include biological oxygen demand (BOD) and nitrification in streams (Deb and Bowers 1983), chlorine disinfection (Haas and Kana 1984), and endogenous nitrate respiration of AS (Kim and Hao 1990).

As discussed above and shown in Figure 4.29, the COD destruction rate at 260 °C is not affected by PO_2 except at 320 psi. Data in Figure 4.6, however, indicate that PO_2 may affect the COD reduction, especially at lower WAO temperatures (200 to 230 °C). The following explanation clarifies the apparent discrepancy. The extent of "flash" COD reduction varies with the initial oxygen pressure. The "starting" COD (the COD immediately after the "flash" destruction), therefore varies with PO_2. Despite the fact that the subsequent COD reduction rate constant is independent of the initial oxygen pressure (Figure 4.29), the COD concentration obtained after 1-hour reaction during the 1-hour experiments would vary inversely with the initial PO_2 (i.e., the final COD at PO_2 = 190 psi, would be lower than at 19 psi).

The ratio of COD/TVS during kinetic experiments decreased slightly with time—an indication of the formation of organic byproducts during WAO of redwater that are not accurately measured by the dichromate oxidation method of COD analysis.

The observed TOC destruction with time as shown in Figure 4.30 is similar to that of COD: initial rapid TOC removal (from 1260 to 600 mg/L within 4 minutes [260 °C and 320 psi]), initial rapid TOC destruction dependent on oxygen pressure, a first-order rate with respect to TOC for the subsequent reaction, no effect exerted by the

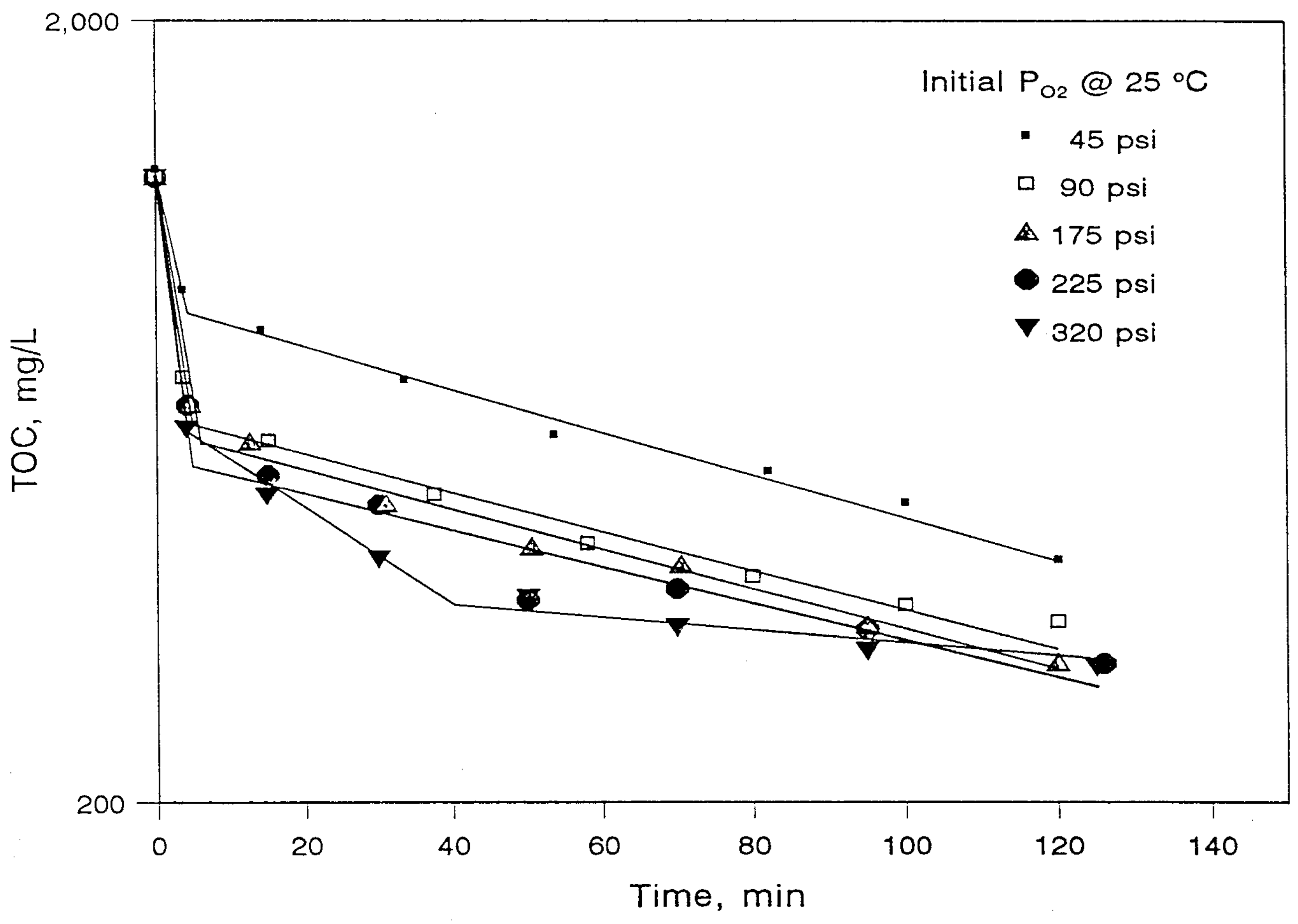


Figure 4.30. Effect of initial PO_2 on WAO rate at 260 °C and 1:25 dilution for TOC.

initial PO_2 on rate constants for this phase, and two distinct phases under the most stringent conditions.

Since a first-order reaction with respect to the organic compounds has been generally observed (Table 2.8, Chapter 2), a first-order rate reaction was used despite the scattered data in semi-log plots (Figures 4.29 and 4.30). Two sets of data from Figure 4.30 (260 °C, 45 psi and 320 psi) were statistically analyzed to fit the experimental data points to determine the exact order for the rate expression:

$$dC/dt = - k C^n \qquad \text{[Eq 4-3]}$$

The results using the Runge-Kutta method and a nonlinear, least-squares optimization are summarized in Table 4.10. They include predicted values from the best-fit approach (with the least sum of squares [SOS]) indicating particular n and k values, and those from the arbitrary first-order rate (n = 1). For Run A4, the best fit

Table 4.10. Results of data analysis for two different WAO runs.

Run A4: WAO Temp. = 260 °C, PO_2 = 45 psi at 25 °C. Redwater dilution = 1:25

Time, min	Measured TOC, mg/L	Predicted TOC, mg/L	
		Best fit n = 1.66 k = 10^{-4}	First-order Fit n = 1.0 k = $7.16\text{x}10^{-3}$
0	1290		
3.5	903	903	903
14	801	824	836
33.5	692	706	728
53.5	589	611	631
82	528	508	514
100	481	457	452
120	407	409	392
		(SOS = 2225)	(SOS = 5664)

Run A9: WAO Temp. = 260 °C, PO_2 = 320 psi at 25 °C, Redwater dilution = 1:25

Time, min	Measured TOC, mg/L	Predicted TOC, mg/L	
		Best fit n = 4.55 k = $4\text{x}10^{-12}$	First-order Fit n = 1.0 k = $8.1\text{x}10^{-3}$
0	1256		
4	598	598	598
14.8	490	484	547
30	407	415	484
50	363	366	412
70	333	335	350
95	311	310	286
125	297	288	224
		(SOS = 204)	(SOS = 17836)

(n = 1.66, k = 10^{-4} min^{-1}) has the least SOS of 2225, while the model assuming a first-order reaction yields a higher SOS value of 5664. Despite the different k and n values of these two methods, the predicted TOC concentrations for both methods are close to the measured concentrations. Also, an "n" value of 1.66 has no mechanistic meaning and is entirely empirical. A single rate expression was also fitted to the experimental data from Run A9. Again, a fractional reaction order of 4.55 provided the best fit; the k value was almost 9 orders of magnitude different than that for the first-order model. Yet, the predicted values for the first-order expression were close to the measured ones, especially in the earlier parts of the experiment. If the lower k value was used for the second part of oxidation, the overall fit would be much better. Consequently, for simplicity, the first-order rate expression was used to describe the WAO of redwater and to calculate kinetic parameters (reaction rate constants and activation energy). Because of the complex nature of the redwater components and the complicated WAO process, the use of gross parameters, such as COD and TOC, can only represent the trend and the degree of destruction of these parameters.

The effect of pressure on UV absorbance is not as obvious (not shown). Higher absorbances were noted at 200 nm for samples from experiments with the highest PO_2. It may be inferred that the higher pressures resulted in the chemical transformation of the complex redwater components to simple aromatics and other organic compounds, which, in turn, showed higher UV absorbance at 200 nm.

Effect of Temperature

At a constant initial pressure of 90 psi and a dilution factor of 1:25, the effect of WAO temperature on COD destruction is obvious (Figure 4.31). After the initial COD destruction, slowly oxidizable compounds follow first-order removal and the apparent (observed) rate constants are 5.4×10^{-3} and 1.1×10^{-2} min^{-1}, respectively, at 230 and 260 °C. However, at higher temperatures, two distinct phases are present, as previously observed in Figure 4.30 with the highest PO_2. The rate constants for the first phase were calculated to be 2.3×10^{-2} and 4.2×10^{-2} min^{-1}, respectively, at 280 and 300 °C. For the slower step, the rate constants at 280 and 300 °C were determined to be 9.8×10^{-3} min^{-1} and 1.0×10^{-2} min^{-1}, respectively.

The patterns for TOC reduction (Figure 4.32) and reduction in absorbance at 200 nm (Figure 4.33) as a function of temperature are similar to those for COD. For the two higher temperatures, there are two distinct reaction phases in each case. From the TOC data, the first-order reaction rate constants were calculated to be 2.7×10^{-3} min^{-1} and 5.9×10^{-3} min^{-1}, respectively, at 230 and 260 °C. At higher temperatures, the rate constants for the faster phase were 1.7×10^{-2} min^{-1} and 2.2×10^{-2} min^{-1} at 280 and 300 °C, respectively. The corresponding rates for the slower reaction phase were 4.4×10^{-3} min^{-1} and 6.8×10^{-3} min^{-1}.

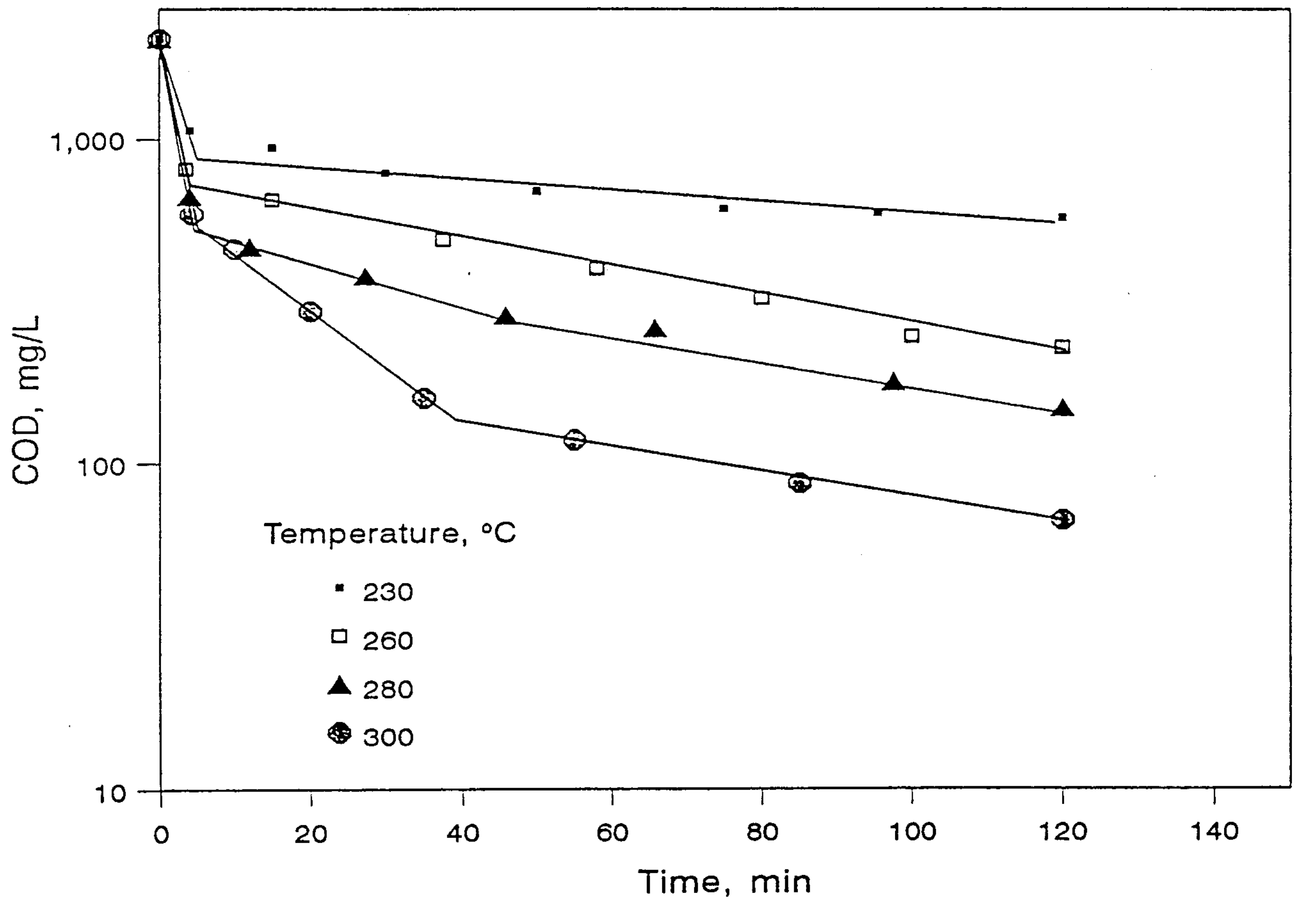


Figure 4.31. Effect of temperature on WAO rate at 90 psi PO_2 and 1:25 dilution for COD.

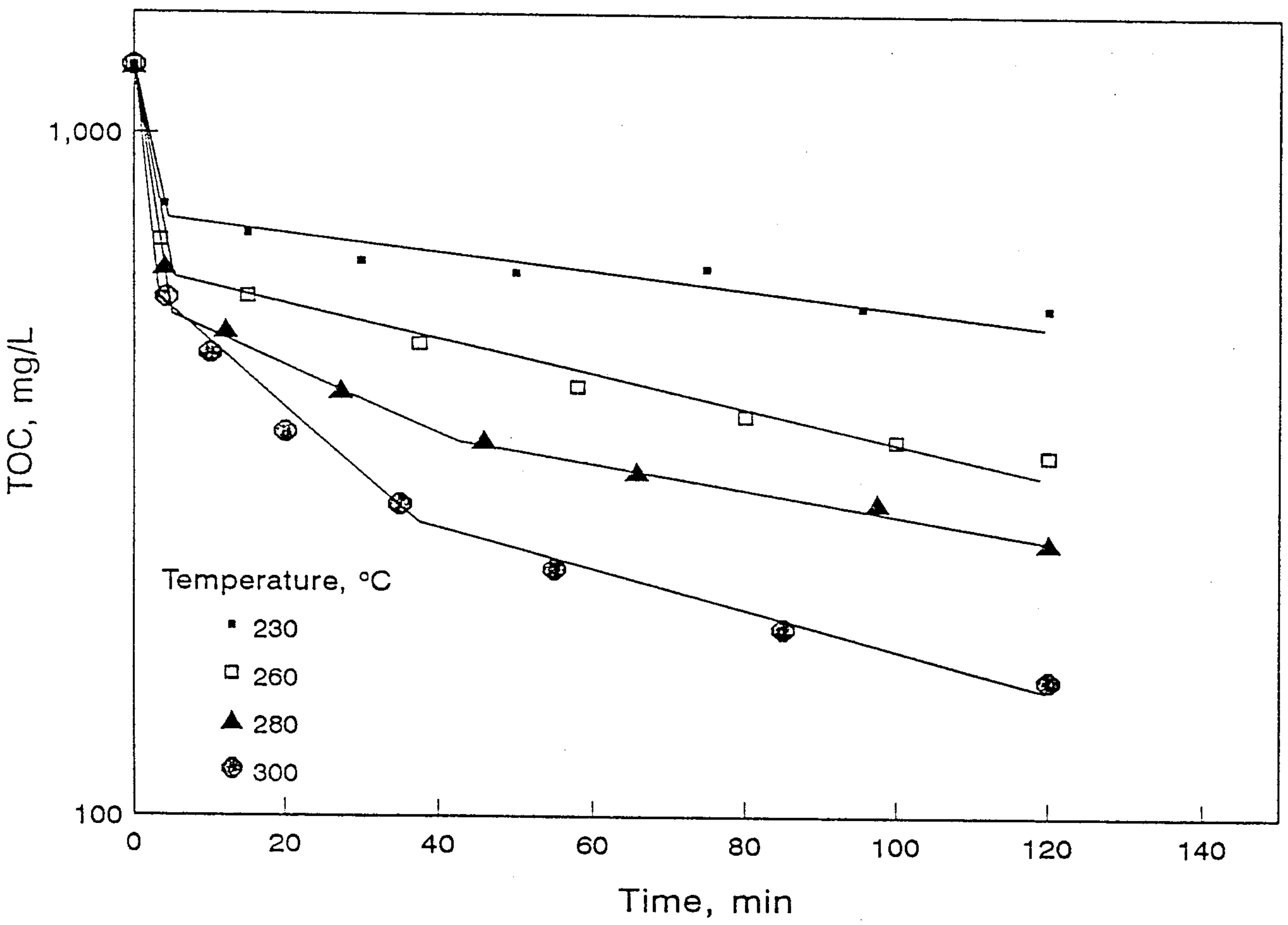


Figure 4.32. Effect of temperature on WAO rate at 90 psi PO_2 and 1:25 dilution for TOC.

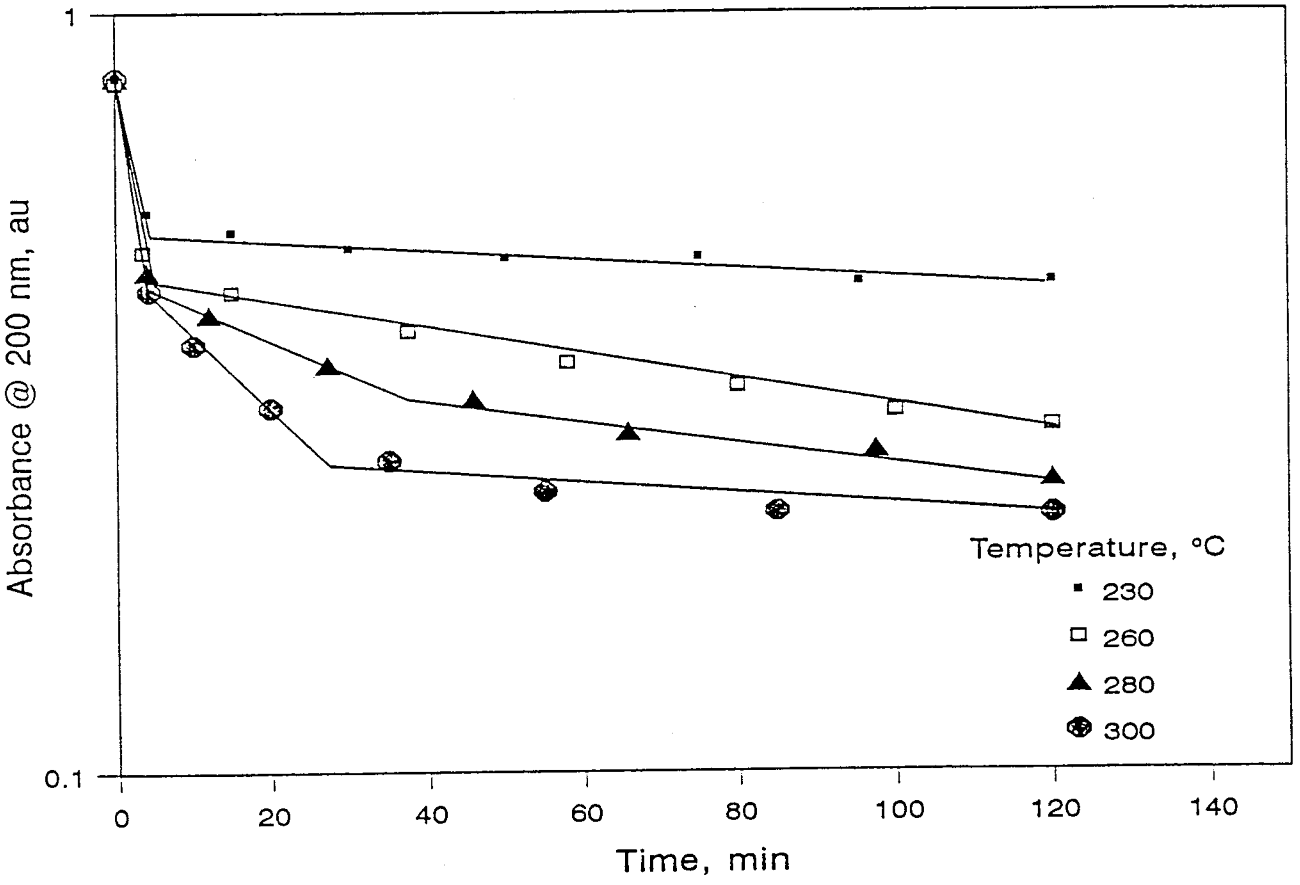


Figure 4.33. Effect of temperature on WAO rate at 90 psi PO_2 and 1:25 dilution for UV absorbance.

The Arrhenius plots for COD and TOC, using the rate constants for the faster reaction phases, are shown in Figure 4.34. The activation energies were calculated to be 17 kcal/mole (COD) and 18 kcal/mole (TOC). These values are quite similar to the values reported by other investigators for different compounds, e.g., 14 kcal/mole for both TNT (Urbanski 1984) and for catalytic oxidation of phenol (Katzer et al. 1976), 11 kcal/mole for phenol (Joglekar et al. 1991), and 16 kcal/mole for acetone (Taylor and Weygandt 1974).

Effect of Redwater Concentration

At a constant temperature of 260 °C, three different dilution factors were used to observe their effects on the reaction rates. The COD results (Figure 4.35) indicate essentially the same phenomena—the initial rapid COD destruction and a subsequent first-order COD removal rate. The semi-log plots have identical slopes, confirming a first-order reaction. The trends in the reductions in TOC and UV absorbance at 200 nm were similar to those observed for COD reduction.

Effect of Salt Concentration

Inorganic salts (e.g., Na_2SO_4) are not destroyed by WAO; in fact, their amounts increase as previously noted. The concentration of these salts in the case of a continuous WAO treatment of raw redwater would be much higher than the concentration present in diluted (1:100) redwater used in the present batch experiments. To determine the effects of high salt concentrations on WAO of redwater, two experiments were performed with the external addition of $NaNO_3$ and Na_2SO_4 to simulate higher salt concentrations under continuous treatment conditions. In the first experiment a 1.56 percent salt solution (15 g/L Na_2SO_4 plus 0.6 g/L $NaNO_3$) was added to the reactor; a 5.2 percent salt concentration (50 g/L Na_2SO_4 plus 2.0 g/L $NaNO_3$) was added in the other experiment. The COD results (Figure 4.36) indicate that the increased salt concentrations resulted in increased initial reaction rates, but the reaction rates decreased to that for the control as oxidation proceeded. The trace metals present as contaminants in the large quantities of $NaNO_3$ and Na_2SO_4 added might have catalyzed the reactions resulting in a slightly better overall COD removal.

The effects of salt concentration on TOC removal rates (Figure 4.37) are similar to those for COD. The low salt concentration (15 g/L Na_2SO_4 plus 0.6 g/L $NaNO_3$) appears to have only a minimal effect on the removal rate, but the higher salt concentration (50 g/L Na_2SO_4 plus 2.0 g/L $NaNO_3$) enhanced the TOC removal rate more noticeably. The effect of salt concentration on UV absorption characteristics of treated samples appears to be more complex. As compared to the control experiment, the UV absorbance at 200 nm increased with salt concentration; that is, the higher

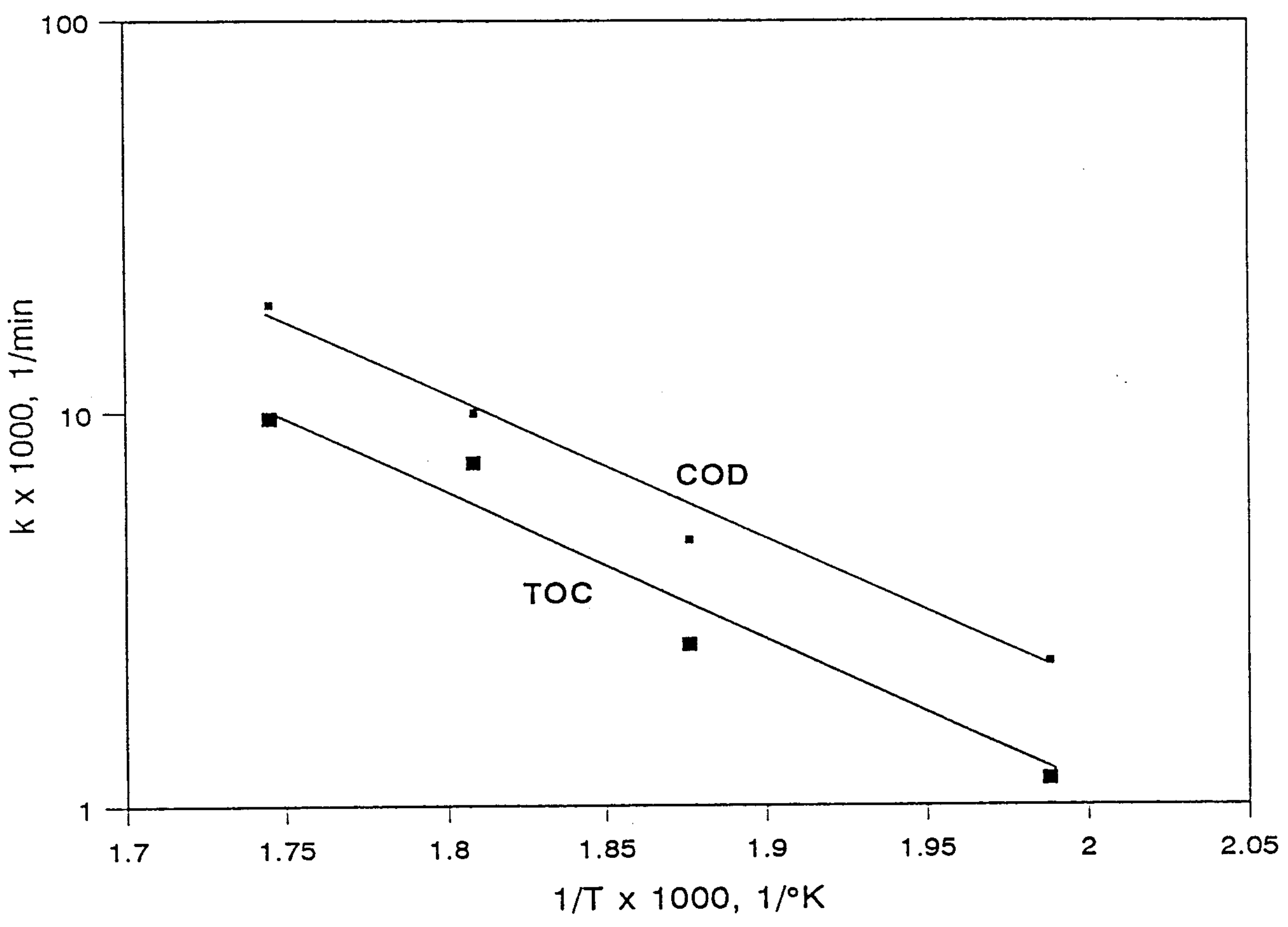


Figure 4.34. Arrhenius plots of the first-order rate constants for COD and TOC.

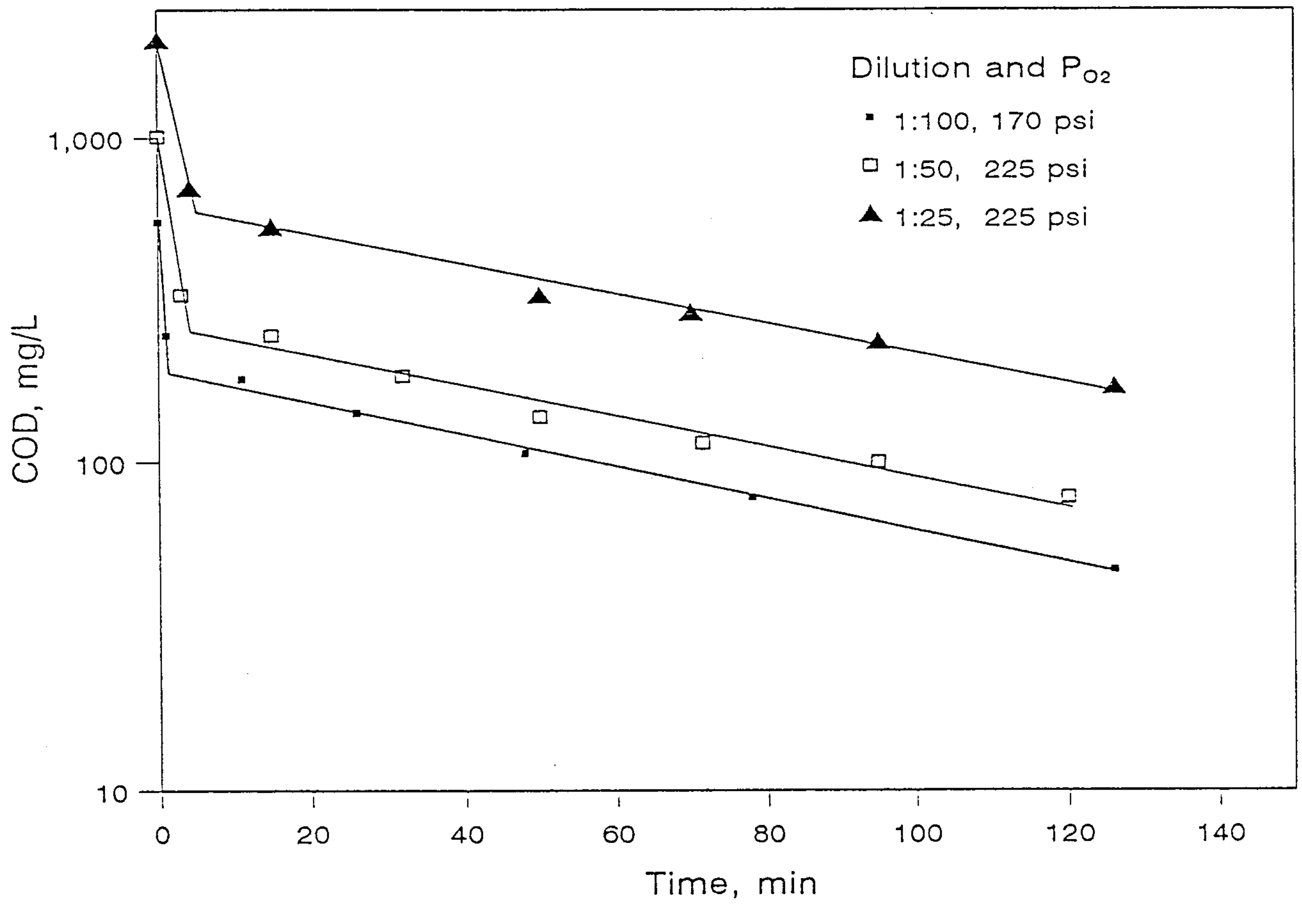


Figure 4.35. Effect of redwater concentration on WAO rate at 260 °C for COD.

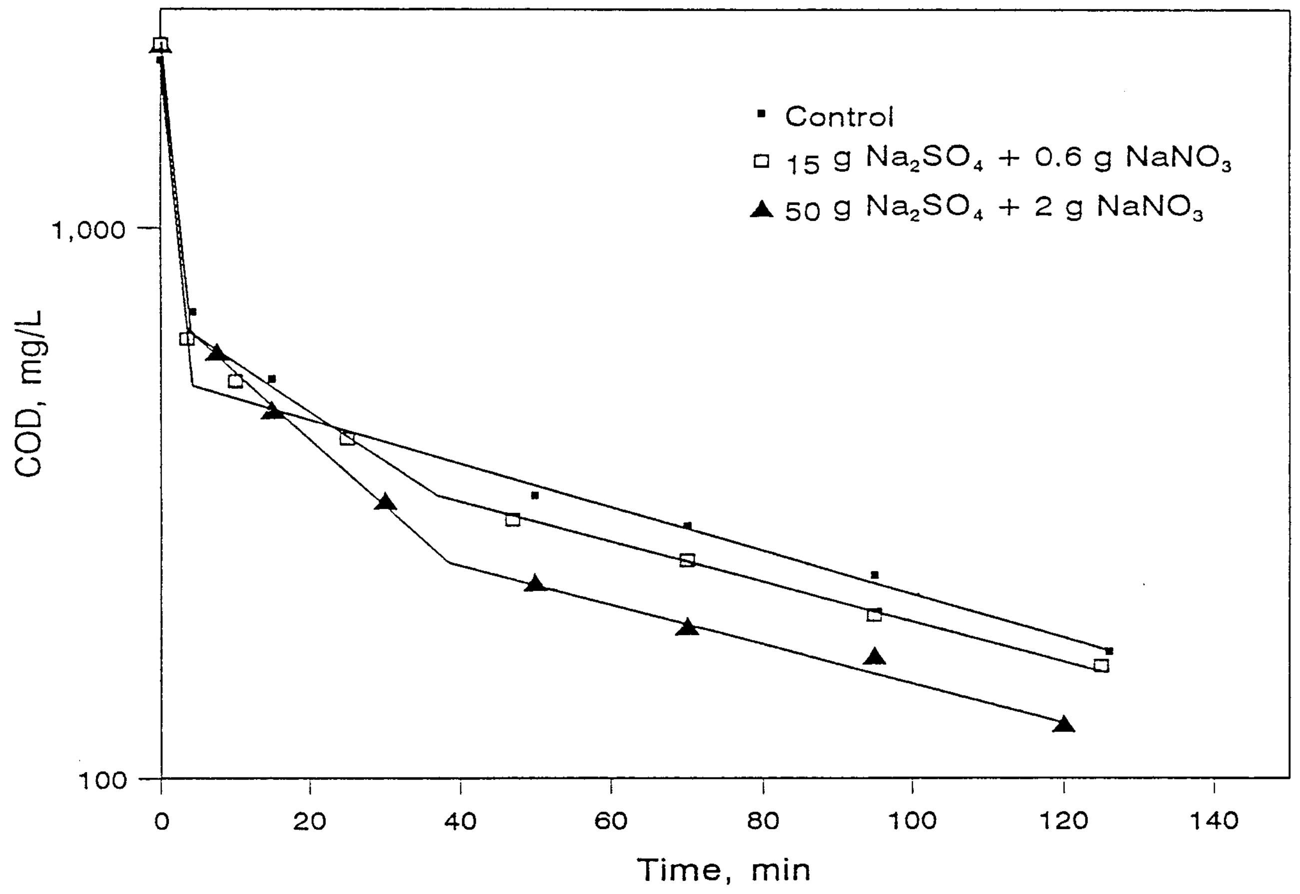


Figure 4.36. Effect of salt concentration on WAO rate at 260 °C, 225 psi PO_2, and 1:25 dilution for COD.

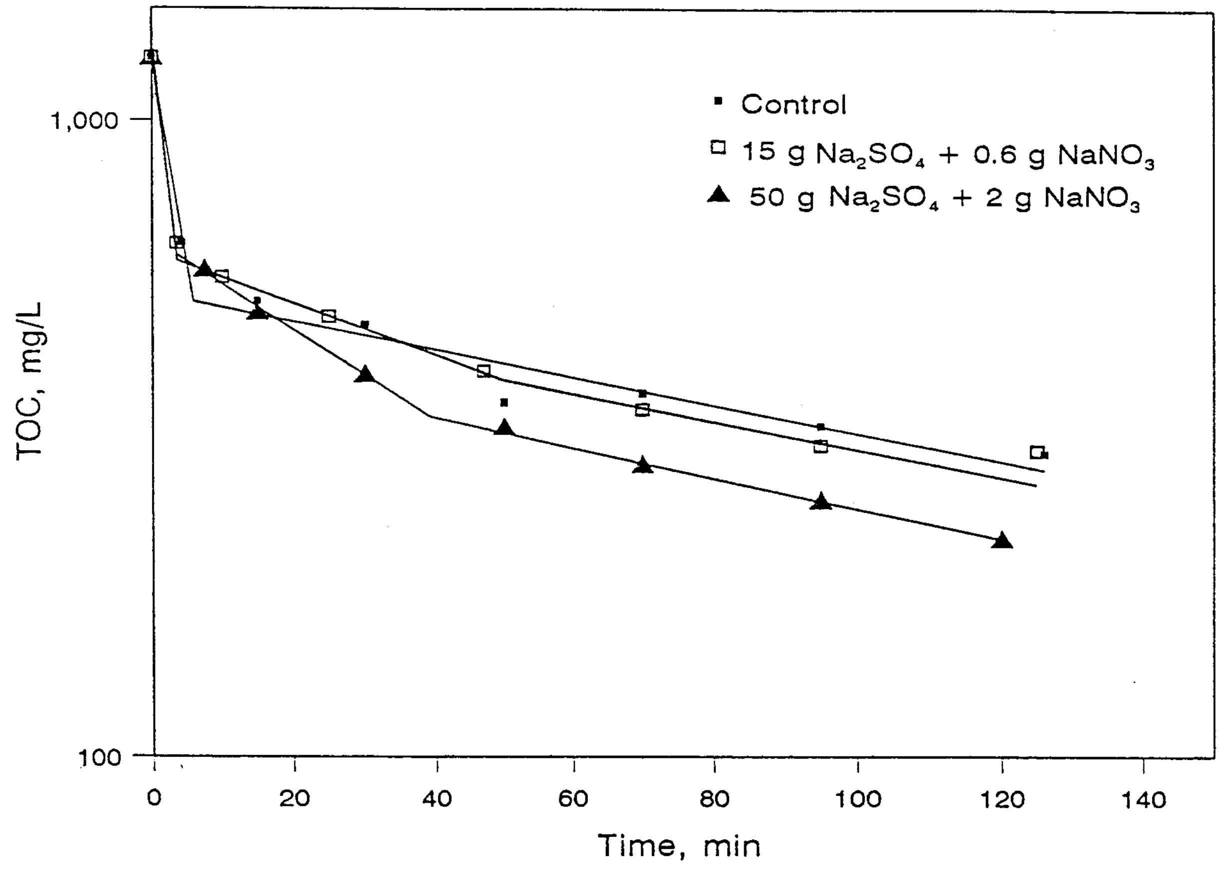


Figure 4.37. Effect of salt concentration on WAO rate at 260 °C, 225 psi PO_2, and 1:25 dilution for TOC.

salt concentrations do not enhance the removal of organics absorbing at 200 nm. With respect to the effects of pressure on UV absorbance (as discussed earlier), it may be that the salt concentration influences the mechanisms of chemical transformation of the complex redwater components into simpler aromatics. The byproducts resulting from these chemical transformations then exhibit higher absorbance at 200 nm.

Effect of Catalyst/Initiator

A mild WAO condition was selected to observe any enhanced rates upon the addition of a catalyst or an initiator. The results are summarized in Table 4.11 and shown in Figures 4.38 and 4.39. The initial rapid COD reduction was clearly affected by the addition of either the initiator (H_2O_2) or the catalyst [Cu(II) or Mn(II)]. For example, at t = 5 minutes, the residual COD for the control, 150 mg/L H_2O_2, 10 mg/L Mn(II), and 5 mg/L Cu(II) systems were 255, 198, 164, and 160 mg/L, respectively. This was an increase of COD removal from 62 percent (control) to 76 percent by adding 5 mg/L Cu(II). Further, both divalent metals appeared to enhance the overall reaction rates resulting in a lower residual COD. However, H_2O_2 addition at concentrations of 20 mg/L and 150 mg/L did not enhance the overall rates, resulting in approximately the same COD concentration, as with the control system, at the end of the experimental run (2 hours).

TOC concentration profiles in Figure 4.39 show a similar pattern, except that 150 mg/L H_2O_2 appears to have an adverse effect when compared to the control system. At high H_2O_2 concentrations, the nondecomposed H_2O_2 may act as a radical scavenger by reacting with radicals such as $HO^\bullet$, thereby inhibiting the reaction. Again, Cu(II) catalyst enhanced the overall TOC removal. The enhanced effect of Cu(II) on WAO of other organics has also been cited by others. Baillod et al. (1982) reported that cupric ion increased the reaction rate and extent of removal of phenol, *2*-chlorophenol, and *4*-nitrophenol under various WAO conditions (T = 200 to 260 °C, PO_2 = 300 to 360 psi). Eckert et al. (1990) reported a significantly increased rate constant with Cu(II) tetrafluoroborate as a catalyst in the WAO of *p*-chlorophenol under sub- and supercritical conditions.

The observed effect on the initial rate of COD/TOC reduction by the addition of H_2O_2 was explained by Emanuel et al. (1967). At the WAO conditions studied, H_2O_2 readily decomposes to produce $OH^\bullet$ radicals. With the added H_2O_2, the radical concentration in the reactor may exceed the equilibrium concentration of the radicals needed for the reaction to proceed. This causes an increase in the oxidation rate for the organics present in the redwater. As the free radical chain reactions proceed and the radicals are consumed in the propagation and termination stages, there is no longer an excess of radicals and the oxidation rates revert back to their normal, unenhanced rates.

Table 4.11. Effect of catalyst/initiator on WAO of diluted TNT redwater (1:100)* at 260 °C and 80 psi PO_2.

	CONTROL			10 mg/L Mn(II)			10 mg/L Cu(II)			5 mg/L Cu(II)		
TIME min	pH units	COD mg/L	TOC mg/L	pH units	COD mg/L	TOC mg/l	pH units	COD mg/L	TOC mg/l	pH units	COD mg/l	TOC mg/l
5	3.12	255	224	3.23	1164	220				3.29	160	211
8							3.01	80	140			
15	3.32	151	189	3.16	95	164	2.97	53	117	3.17	76	144
30	3.29	101	141	3.10	57	129	2.92	36	102	3.09	47	116
50	3.18	77	114	3.04	46	115	2.87	25	82	3.02	29	101
70	3.23	60	100	3.02	33	104	2.86	18	78	2.99	21	91
95	3.15	54	87	3.00	27	95	2.76	15	-	2.96	12	76
120	3.06	45	80	2.96	21	90	2.71	11	71	2.93	11	70

	CONTROL			20 mg/L H_2O_2			150 mg/L H_2O_2		
TIME min	pH units	COD mg/L	TOC mg/L	pH units	COD mg/L	TOC mg/L	pH units	COD mg/L	TOC mg/L
5	3.12	255	224	3.14	218	215	3.06	198	257
15	3.32	151	189	3.27	144	1204	3.13	161	239
30	3.29	101	141	3.03	109	161	3.12	124	191
50	3.18	77	114	3.24	74	137	3.03	96	-
70	3.23	60	100	3.18	68	121	2.98	70	149
95	3.15	54	87	3.15	53	102	2.93	45	133
120	3.06	45	80	3.23	43	98	2.88	37	119

* Initial redwater COD and TOC were 670 and 415 mg/L, respectively.

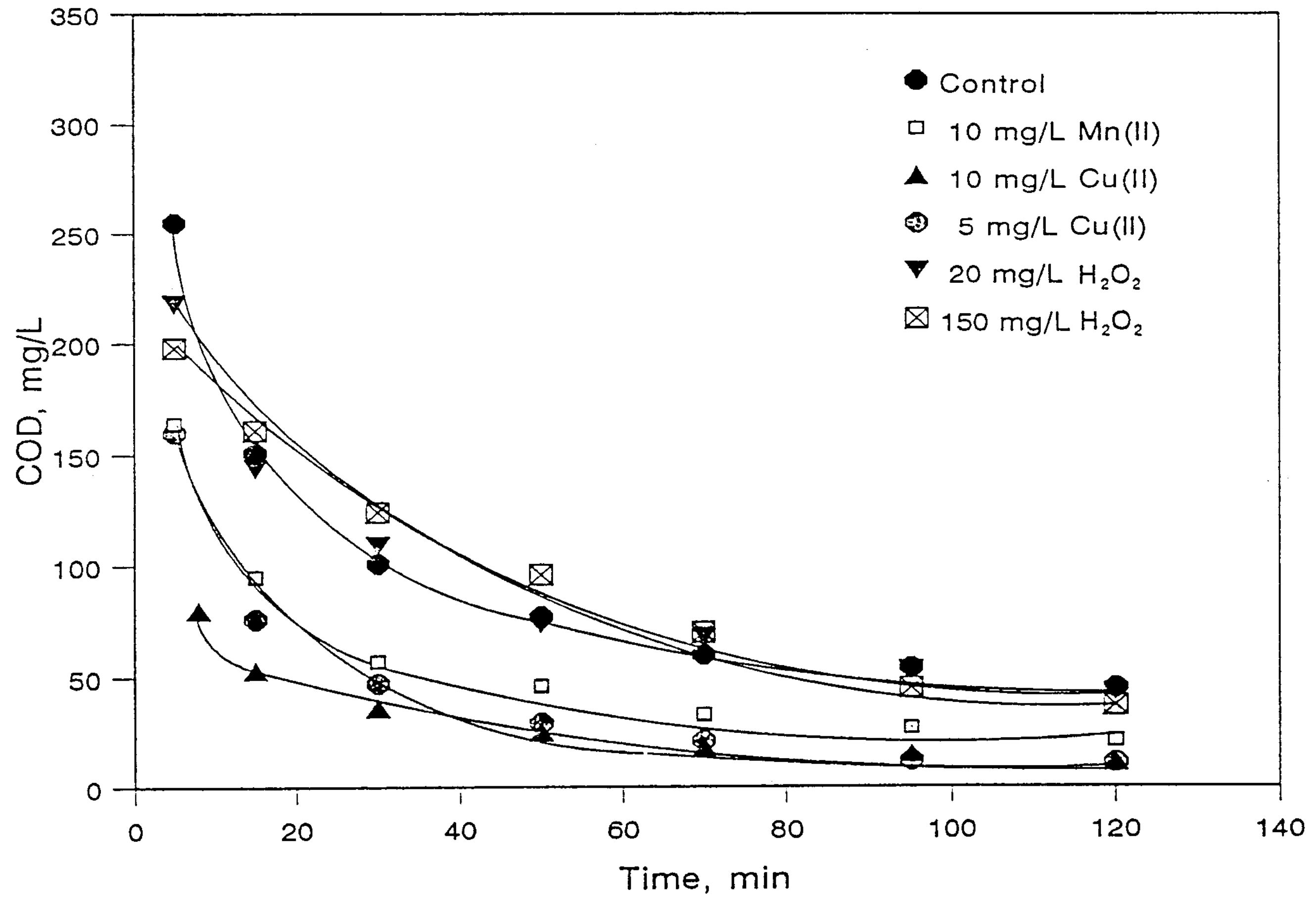


Figure 4.38. Effect of catalyst/initiator on WAO rate at 260 °C and 80 psi PO_2 for COD.

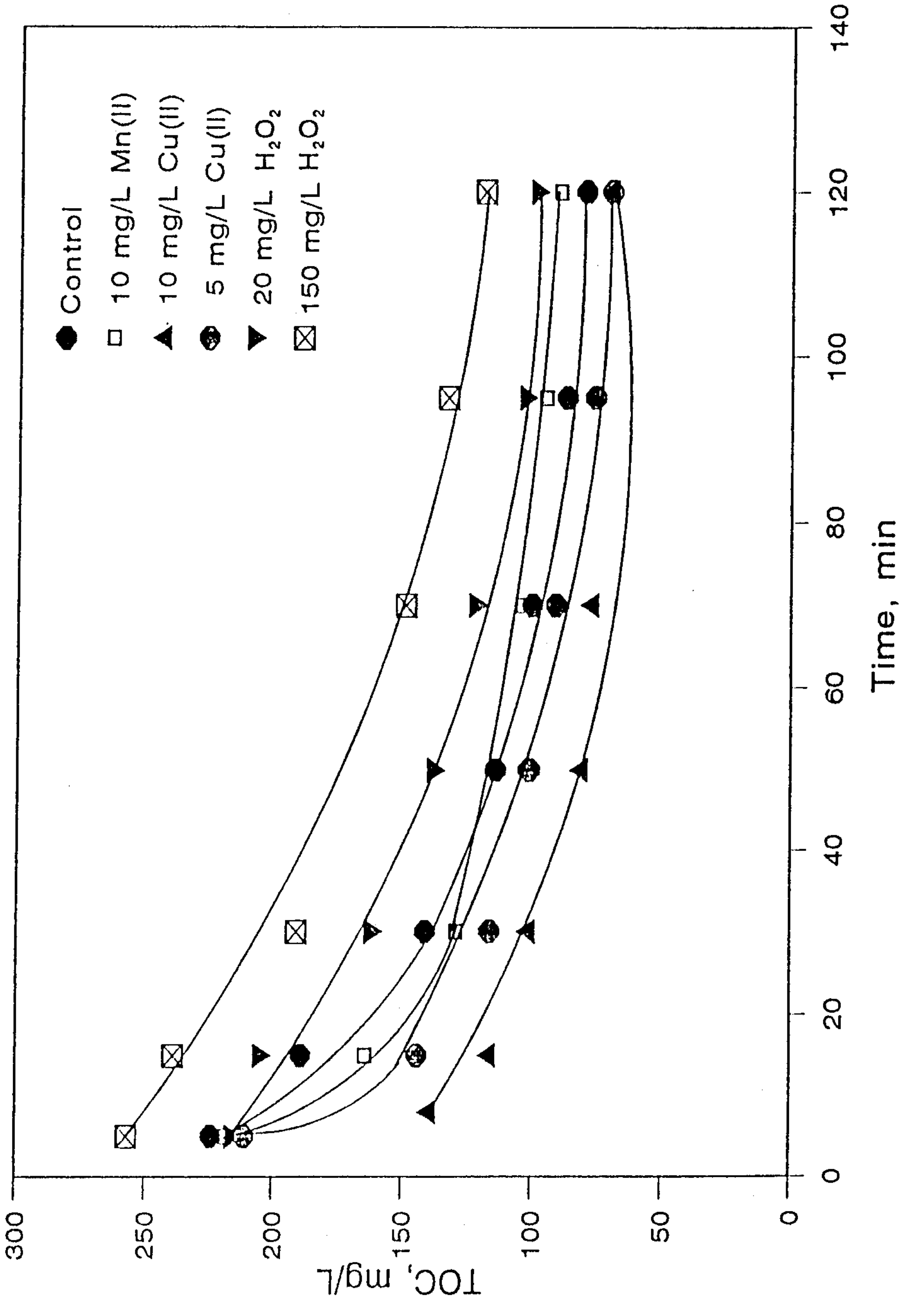


Figure 4.39. Effect of catalyst/initiator on WAO rate at 260 °C and 80 psi PO_2 for TOC.

Other Data

Typical pH profiles for WAO of redwater (1:25) are shown in Figure 4.40; data are shown in Figure 4.41 in Table A1, Appendix A. As expected, the solution pH after WAO is affected by the experimental conditions. It was significantly reduced from 7.6 to approximately 3.0 within the first sampling period (< 5 minutes) and remained constant after 20 minutes. This phenomenon corresponds to the initial rapid reduction in COD, TOC, or TVS as discussed earlier. The mineral acids (e.g., H_2SO_4), low molecular weight organic acids, and aqueous CO_2 formed as a result of the WAO of various organic components of redwater depress the pH of the treated redwater.

The concentration profiles for inorganic sulfate are shown in Figure 4.41. Again, there was a rapid increase in sulfate concentrations within the first 5 minutes (i.e., SO_4^{2-} concentration increased from the original 1500 to approximately 2970 mg/L at 300 °C at 90 psi PO_2). Since the initial inorganic sulfite (SO_3^{2-}) concentration is relatively insignificant (140 mg/L), the net change in sulfate concentration must be from the release of the SO_3 groups associated with different aromatics. Consequently, the so-called "flash" destruction of COD or TOC, as discussed above, must also include organic compounds that contain the SO_3 group.

As noted earlier, the measured nitrate concentrations were lower than the combined nitrite and nitrate concentrations initially present in redwater (Table A2, Appendix A). The unaccounted nitrogen is probably present as different nitrogen gases. The degree of WAO and the composition of gaseous byproducts influence capital costs as air-quality regulations may require further treatment of WAO offgas. Accurate characterization of the reactor offgas would, therefore, be needed under different WAO operational conditions.

The ratio of TOC and COD (Appendix A, Table A1) consistently decreased with time due to the formation of those intermediates that cannot be detected by the standard dichromate method for COD measurement.

The results of GC analyses for the *1,3*-DNB are shown in Appendix A, Table A3. After taking into account the difference between raw redwater dilution factors for the two cases (1:25 vs 1:100), the data compare well with data shown in Tables 4.5 to 4.7. The *1,3*-DNB concentration increases with temperature and time (DNTSs → DNT → DNB) and then decreases as a result of further oxidation.

The data for DNTS removal for the kinetic experiments (Appendix A, Table A4; Figure 4.42) at 260 °C, 225 psi PO_2 and 300 °C, 90 psi PO_2 show a trend similar to

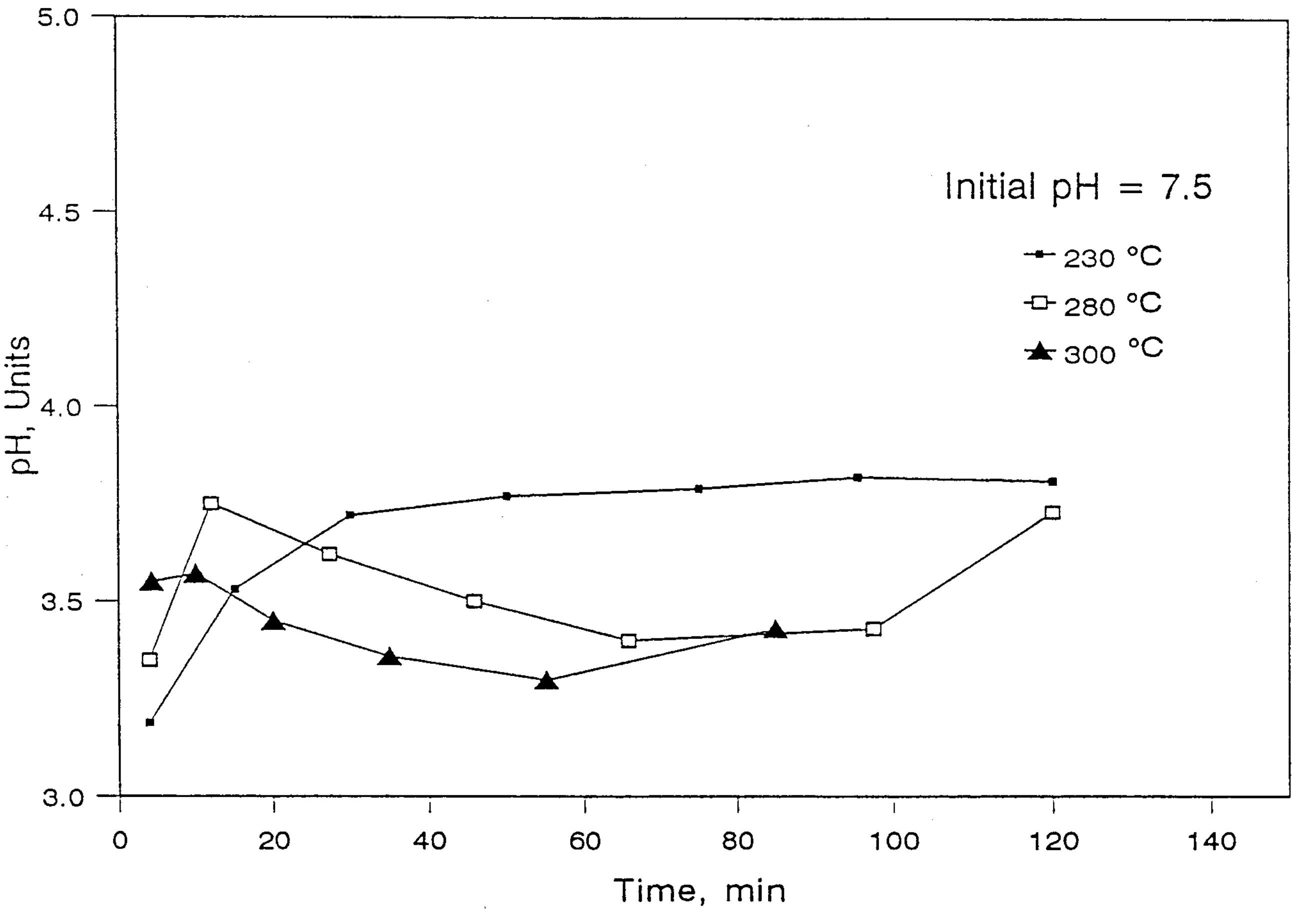


Figure 4.40. Typical pH profiles as a function of temperature at 90 psi PO_2 and 1:25 dilution.

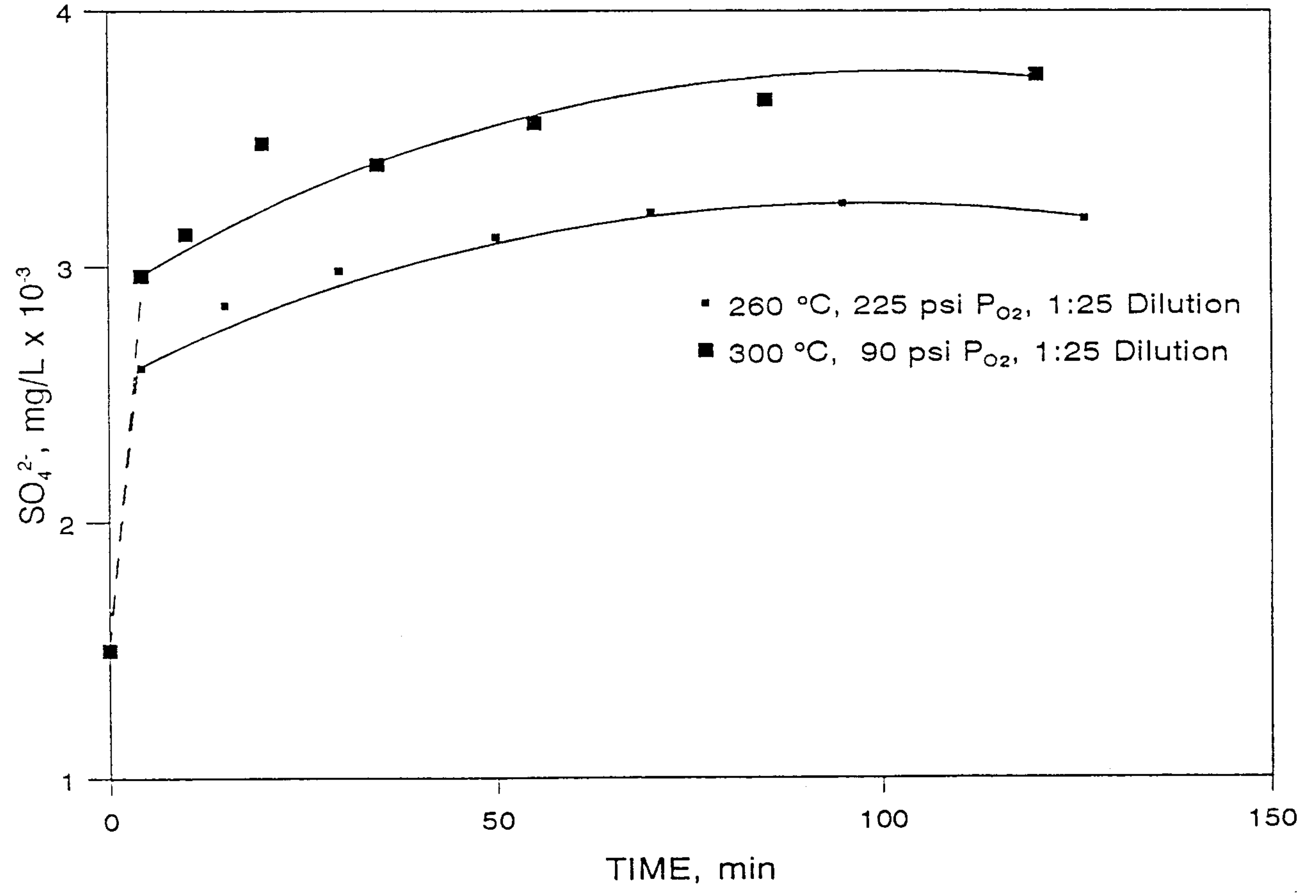


Figure 4.41. Accumulation of SO_4^{2-} during WAO of TNT redwater.

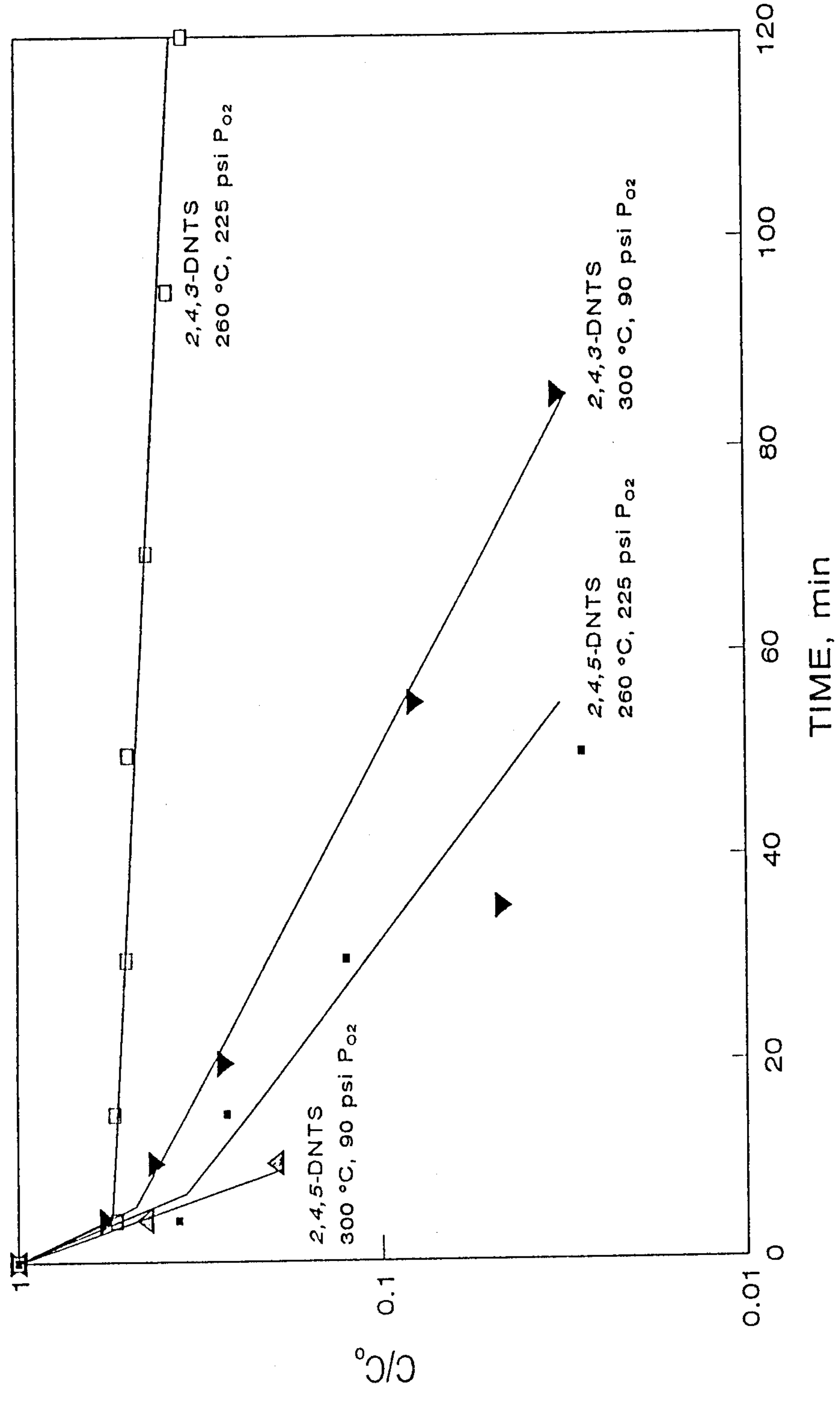


Figure 4.42. Effect of temperature and PO$_2$ on DNTS removal.

that observed for the 1-hour experiments. Specifically, *2,4*-DNT-*5*-SO_3Na is more easily oxidized than *2,4*-DNT-*3*-SO_3Na and temperature, rather than pressure, exhibits a significant effect.

The percent reductions in UV absorption at 200 nm under different experimental conditions are shown in Appendix A, Table A-5, with the corresponding TOC and COD removals. Although precise conclusions cannot be made from the UV absorption data, several general inferences can be drawn. First, aromatic compounds (benzene nucleus based on the strong absorption band at 200 nm) present in raw redwater are not completely destroyed at the WAO conditions studied. Second, the reduction in absorbance at 200 nm closely follows the patterns for TOC reduction. Third, specific experimental conditions often favor the formation of some intermediates that absorb at certain wavelengths (e.g., 362 nm). Finally, the intermediate compounds formed at lower temperatures (e.g., those showing absorbance at 362 nm) are further oxidized at higher WAO temperatures.

The UV absorption data (absorption maxima, λ_{max} and extinction coefficient, ε) for several nitroaromatics are shown in Table 4.12. Review of the current UV data indicates that the λ values for the compounds listed in Table 4.12 were not observed for raw and WAO-treated redwater samples. However, the UV absorption intensity for certain compounds in the presence of other chromophores and auxochromes often overlaps in a wide wavelength range. Yinon and Zitrin (1981) reported that the absorption band for *1,3,5*-TNB ranged from 233nm (in ethanol) to 410 nm when functional groups such as -Cl, $-CH_3$, and $-NO_2$, were added to *1,3,5*-TNB.

Off-Gas Analysis

Gas analysis was done for an experiment at 260°C and 100 pounds per square inch absolute [psia] PO_2 (initial oxygen at 25°C). The analysis gave the composition of 0.33 percent CO, 3.7 percent CO_2, <0.5 percent N_2O, 14.6 percent N_2, 77.7 percent O_2, and 23 ppm total hydrocarbons (expressed as methane). SO_2, NO_2, NO, and NH_3 were not detected in the gas phase. Nitrogen gas arises from the oxidation, because pure oxygen was used as the influent gas.

The value for total HCs is close to that of the Primary Air Quality Standard (24 ppm). The carbon monoxide (CO) composition of 0.33 percent (3300 ppm), however, is two orders of magnitude higher than the National Ambient Air Quality Standards, i.e., 9 ppm for an 8-hour average and 35 ppm for 1-hour average (Davis and Cornwell 1991). Consequently, a direct discharge of the off-gas may present environmental problems. At higher WAO temperatures, both CO and HC compositions may change because of further oxidation to CO_2. The off-gas composition as a function of WAO temperature should be investigated further.

Table 4.12. UV absorption maxima for some nitro compounds.

Compound	λ_{max} (nm)	e x 10^{-3} (L/mol-cm)
NB	267	6.9
1,3-DNB	244	15.4
1,3,5-TNB	229	28.1
2,4-DNT	252*	14.1*
α-TNT	233	15.8
ammonium nitrate	302	7.6

* in 5% ethanol in water

Source: Yinon and Zitrin 1981.

Preliminary Toxicity Study

Different fractions of treated and raw redwater were used to assess their effects on heterotrophic glucose COD removal capability and Nitrosomonas conversion of ammonium to nitrite. Nitrosomonas species were selected for the toxicity studies primarily due to their sensitivity to toxic substances in trace amounts. Diluted raw redwater (1:100) exhibited some inhibitory effect on the ability of the unacclimated AS to degrade glucose COD (Figure 4.43). Batch COD removal capability was practically identical for all four treated mixtures (320 °C and 90 psi PO_2 at 25 °C) and the control (Figure 4.44). The treated redwater, even up to the fraction of 75 percent, did not produce any toxic effect on heterotrophic COD removal efficiency. This was not surprising since the treated redwater at 320 °C and 90 psi PO_2 contained low concentrations of COD (8 mg/L) and TOC (30 mg/L), and AS has a large capacity to resist toxic effects from trace amounts of residuals.

The nitrite production as a function of time is illustrated in Figure 4.45 for different fractions of treated redwater added. For the control experiment, ammonium is completely oxidized to nitrite within a short period with a zero-order nitrite production rate of 0.28 mg N/L-minute (or 0.47 mg N/g volatile suspended solids [VSS]-minute). The nitrogen mass balance indicates that all ammonium initially present is accountable. Clearly, the zero-order nitrite production rates are significantly affected by the addition of treated redwater—the higher the fraction, the lower the nitrite production rate. The fraction of treated redwater is approximately 10 percent for a 50 percent reduction of the nitrite production rate (IC_{50}) as shown in Figure 4.46. Another toxicity run was conducted to evaluate the degree of the adverse effects of the raw redwater on enriched Nitrosomonas culture. It was found that the diluted raw redwater (1:100) up to 4 percent fraction did not exert any noticeable effect on the nitrite production rate (Figure 4.47). A slightly higher nitrite production rate of 0.55 mg N/g VSS-minute in Figure 4.47 is due to the viability of Nitrosomonas cells.

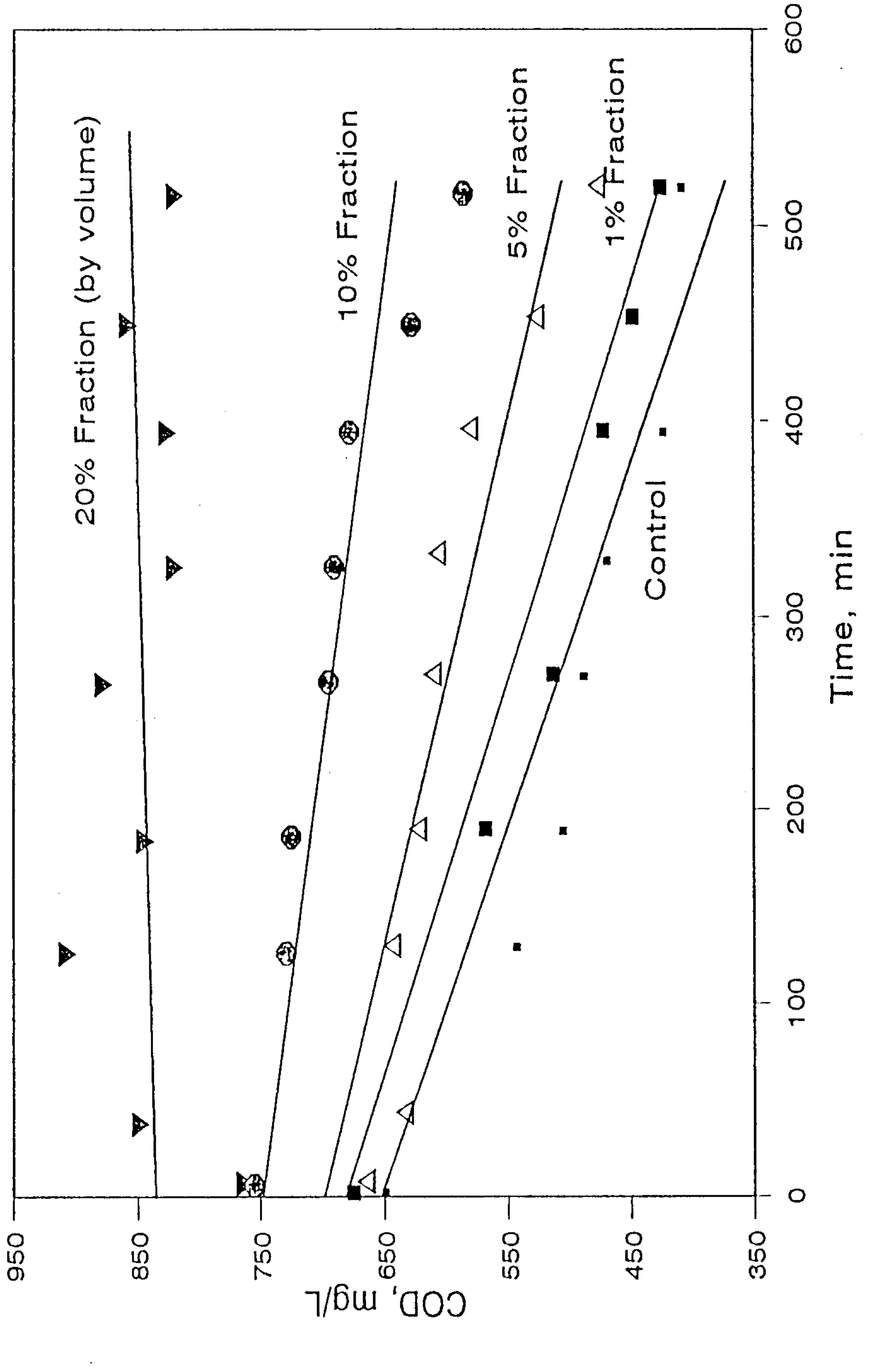


Figure 4.43. Effect of raw redwater (1:100) on glucose COD removal capability of unacclimated activated sludge.

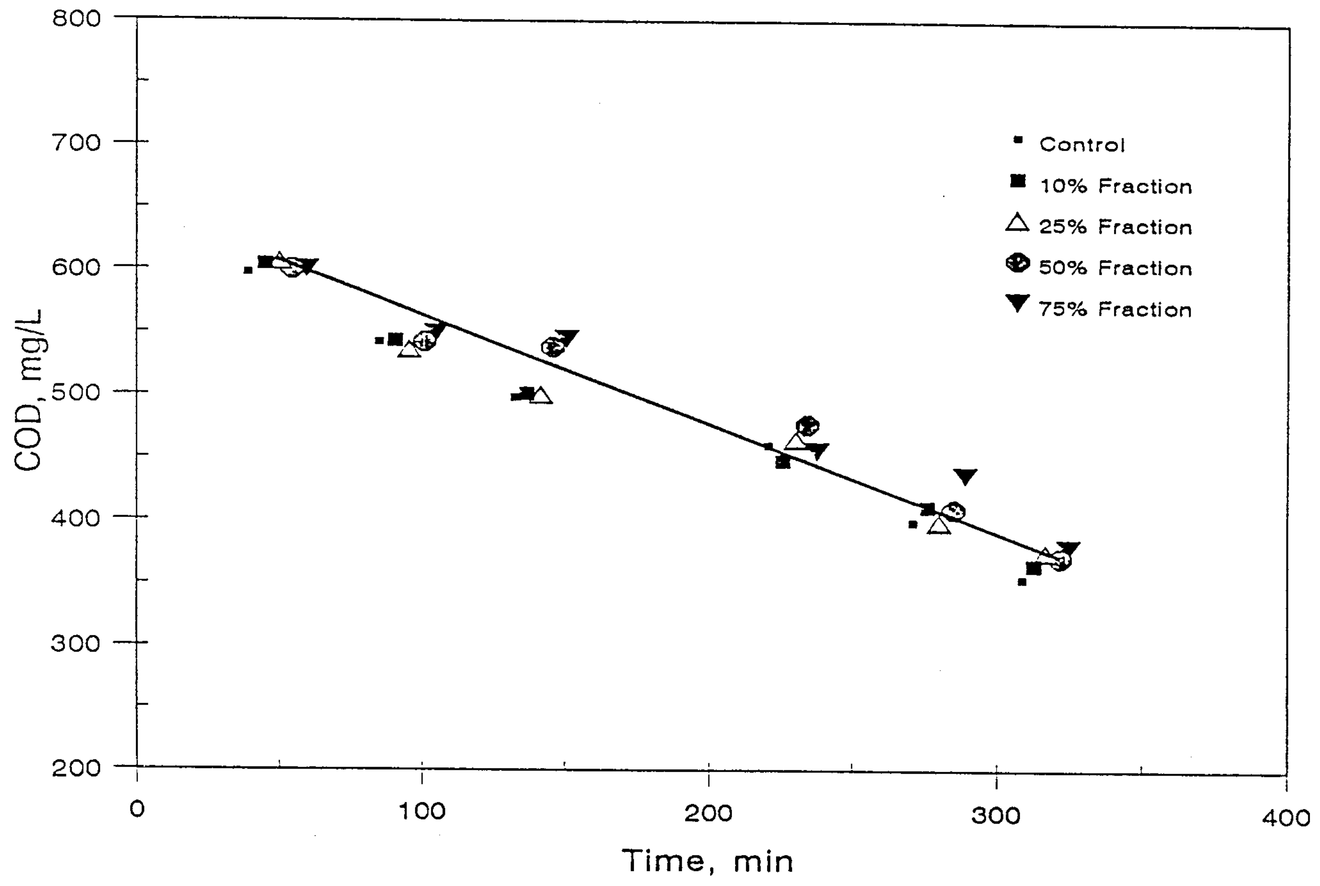


Figure 4.44. Effect of treated redwater on glucose COD removal capability of unacclimated activated sludge.

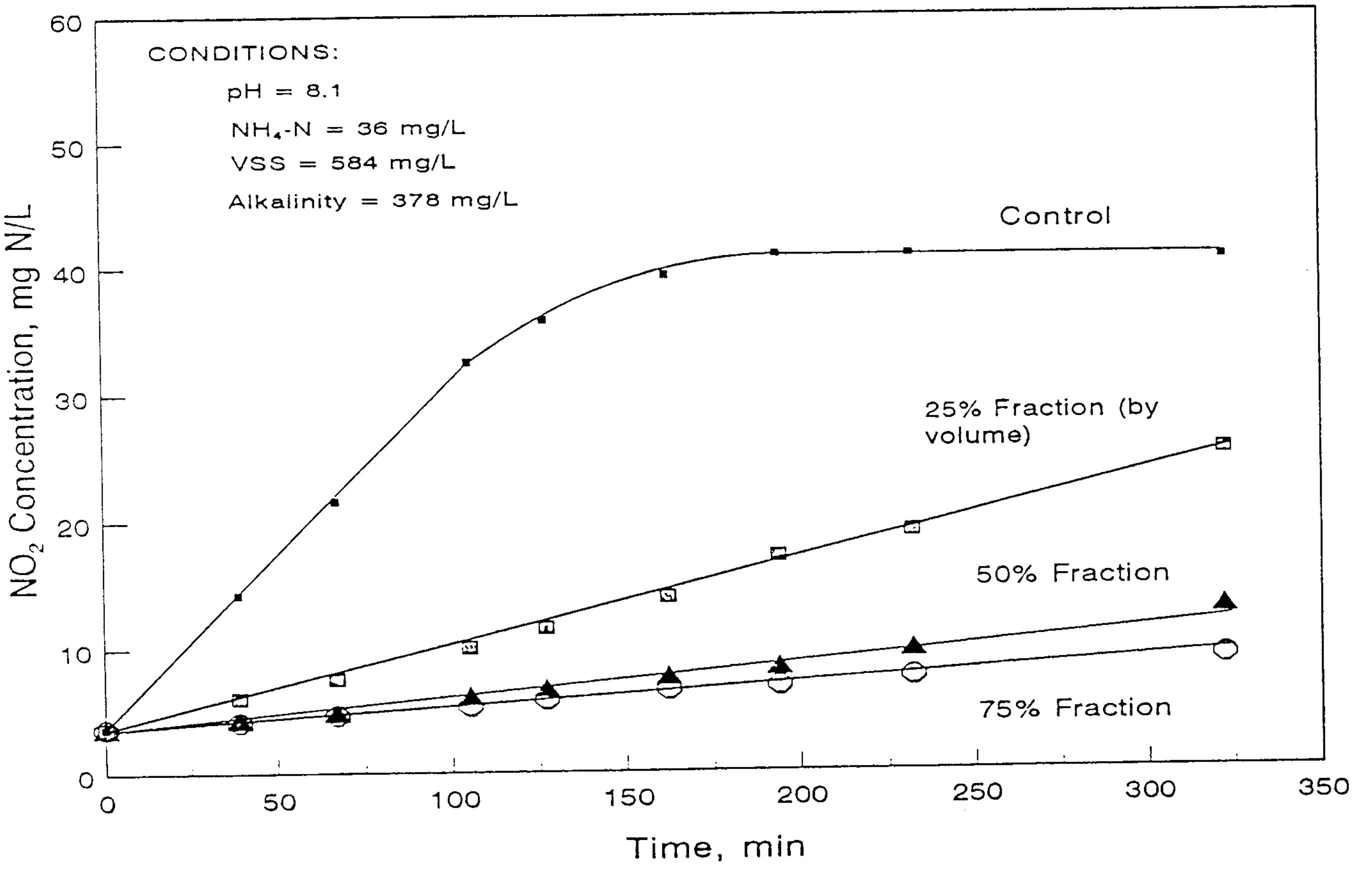


Figure 4.45. Effect of treated redwater on nitrite production of unacclimated Nitrosomonas culture.

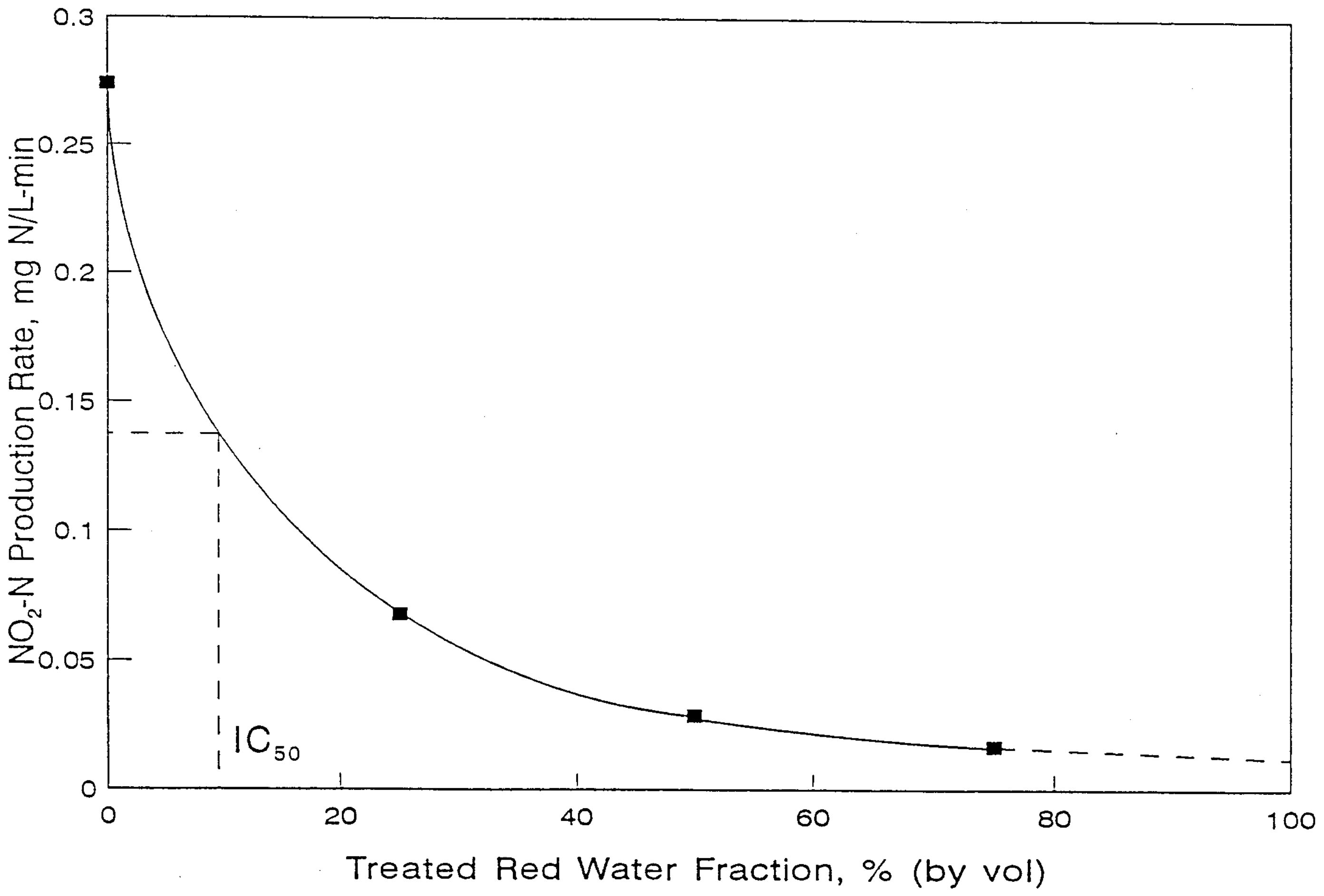


Figure 4.46. Inhibitory effect of treated redwater on nitrite production rate of unacclimated Nitrosomonas at different volume fractions.

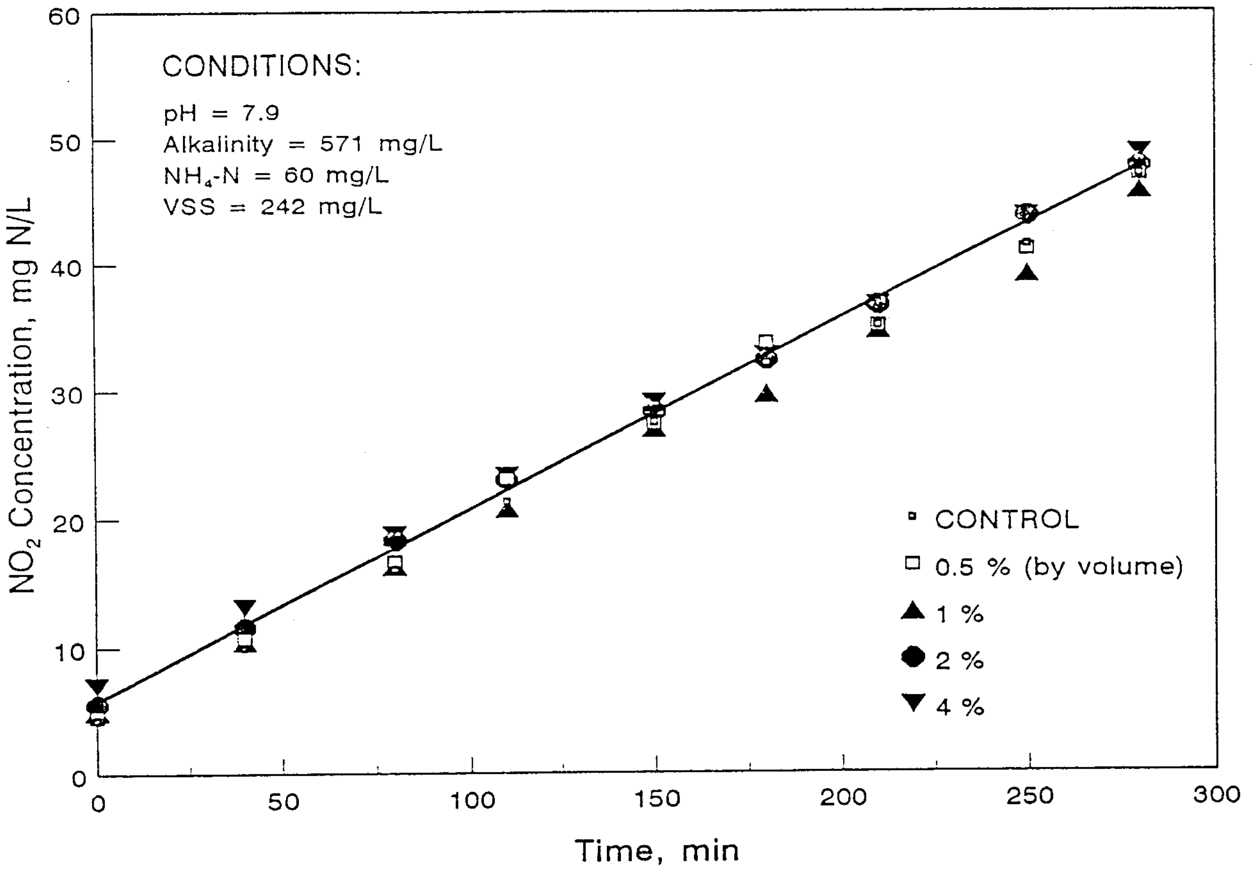


Figure 4.47. Effect of raw redwater on the nitrite production of unacclimated Nitrosomonas.

As discussed earlier, the WAO of redwater (320 °C, 90 psi) results in significant reductions in TOC (≈ 94 percent), COD (≈ 99 percent), α-TNT (≈ 99 percent) as shown in Table 4.6. A 4 percent fraction of the raw redwater had no adverse impact on Nitrosomonas culture; however, a 10 percent fraction of treated redwater reduced the Nitrosomonas activity by 50 percent. A 4 percent fraction of raw redwater would undoubtedly contain more of the organic compounds initially present in redwater than would the 10 percent fraction of treated redwater. Consequently, it is fair to state that the compounds originally present in the redwater are unlikely to cause the observed adverse effects on Nitrosomonas culture. Instead, the adverse effects must be due to the byproducts formed after WAO of redwater. The major byproducts are inorganic sulfate and nitrate and some unknown transformation organic products. To test whether the inorganic compounds had any effects, the addition of $NaNO_3$ (400 mg/L) and Na_2SO_4 (1500 mg/L) in a 1 percent fraction of diluted raw redwater (1:100) was tested on Nitrosomonas culture. The results (Figure 4.48) indicate that inorganic sulfate and nitrate exert no effect. Macfarlane and Herbert (1986) reported that the maximum rate of NH_4^+ oxidation was found at 1 percent NaCl concentration. A similar conclusion, that seawater concentration of up to 50 percent enhanced the nitrite production rate, was also reported by Kawasaki et al. (1986).

The organic products formed during WAO are therefore responsible for the observed effect. Out of the six measured nitroaromatics, IC_{50} data for Nitrosomonas were found only for NB and *2,6*-DNT, as reported by Blum and Speece (1991). They estimated an IC_{50} NB value of 0.9 mg/L for Nitrosomonas. The NB toxicity response to Nitrosomonas in terms of IC_{50} is similar to that of toxic chlorophenol, compared to a much higher value of 180 mg/L for *2,6*-DNT. Unfortunately, the toxicity response for *1,3*-DNB is unknown. Due to the complex redwater components, it is expected that the unidentified organic byproducts formed during WAO reactions must be responsible for inhibition of nitrite production. Keen and Baillod (1985) also reported that the end products of the WAO of phenol, *2*-chlorophenol, and *4*-nitrophenol were more toxic than expected, based on known concentrations of the starting compounds remaining after the WAO.

Detailed toxicity studies should be conducted to demonstrate the feasibility of direct discharge of treated redwater into receiving waters, or to investigate the integration of biological treatment with partial WAO of redwater (at lower temperatures).

Cost Analysis

A conceptual relationship between process cost and concentration of contaminants is shown in Figure 4.49 (Roberts 1973). Wet Air Oxidation appears to be ideally suited for liquid wastes that are too dilute to incinerate and too refractory to handle by

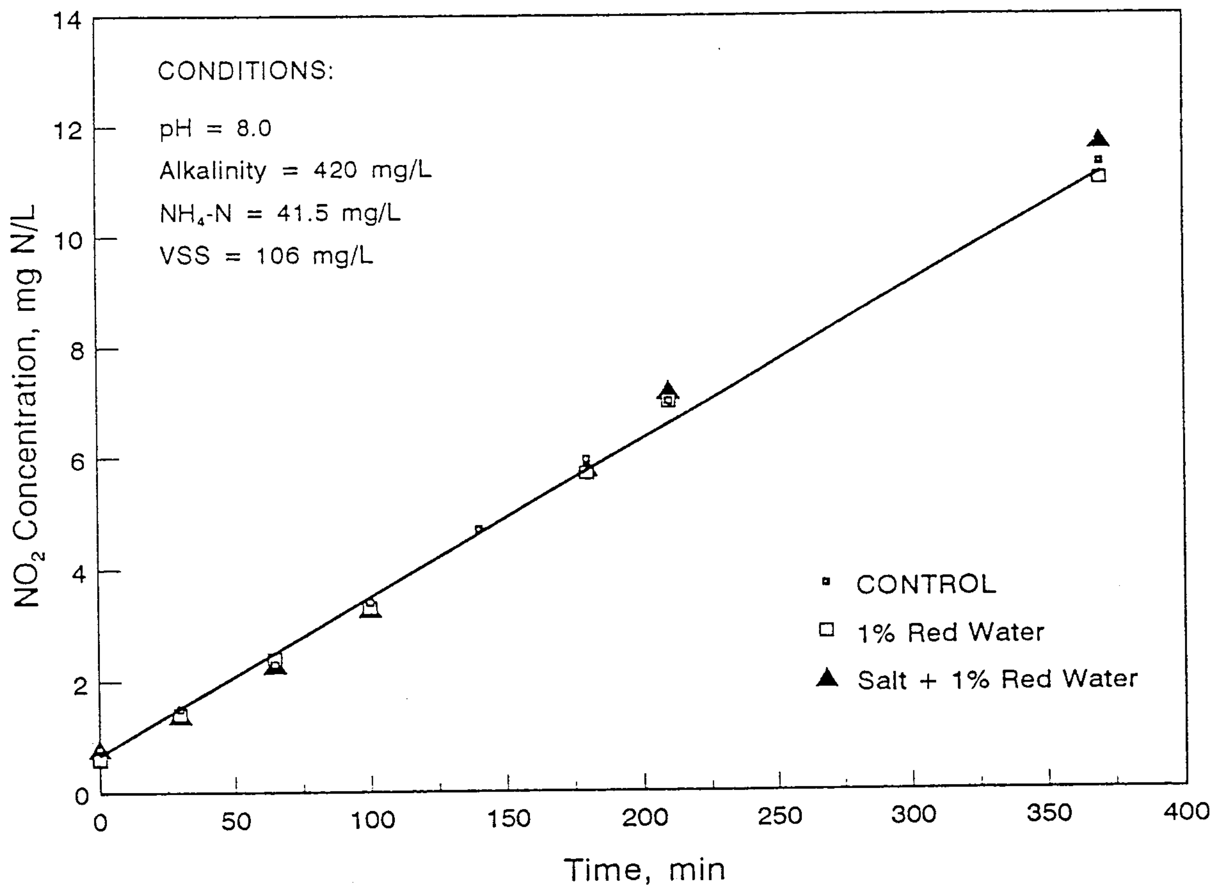
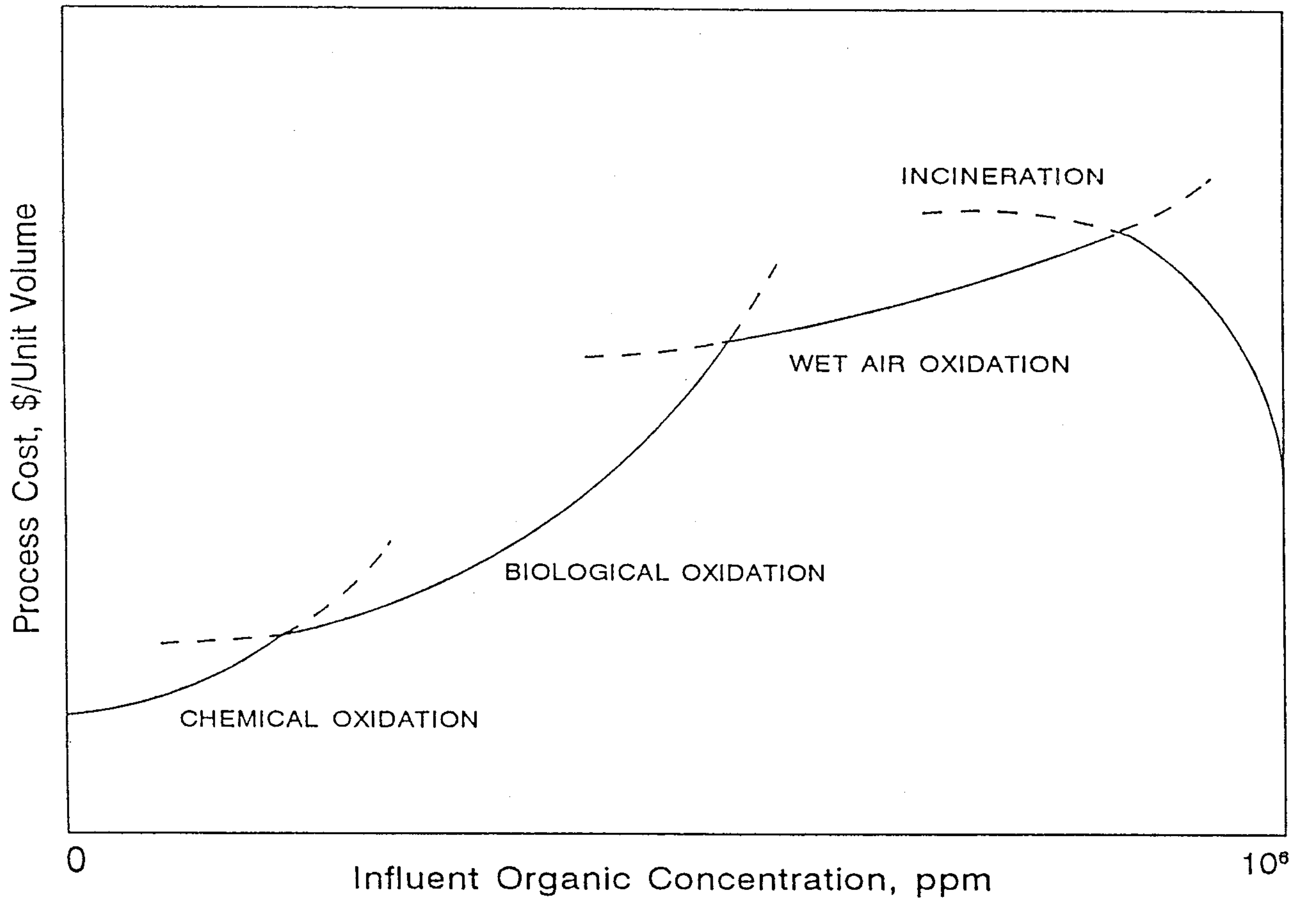


Figure 4.48. Effect of redwater (1:100) supplemented with $NaNO_3$ and Na_2SO_4 on nitrite production capability of enriched Nitrosomonas.



(Source: Roberts 1973. Used by permission of the American Institute of Chemical Engineers.)

Figure 4.49. Process cost as a function of organic concentration.

chemical and biological oxidation. As environmental (air, water, and land) discharge of harmful substances is further restricted by tighter regulations, the use of WAO as an efficient and cost-effective treatment process for hazardous waste may be a promising alternative. Integrating partial WAO as a pretreatment process with subsequent biological treatment may prove to be an effective means of treating redwater.

A cost estimate for disposal of 1 gal of redwater by the powdered activated carbon treatment (PACT) process (Contract disposal) is about $0.86. Transportation of redwater to the treatment site is $0.31/gal (Boddu and Maloney 1992). The remaining cost is for treatment, and the treatment costs could increase about 10 percent a year. Further, the treatment service reserves the right to refuse to accept the waste at any time.

A Budgetary Cost Proposal of a WAO system to treat 16,000 gpd of (undiluted) redwater was prepared by Zimpro Passavant Environmental Systems, Inc. (Appendix A). Two estimates, one for treating the redwater at 340 °C and the other at 280 °C, were developed. Appendix A contains the information on plant costs, and operations and maintenance costs. Assuming an operating life of 10 years and a down time of 165 days per year, the cost for treating 1 gal of redwater can be estimated. Also, one-time costs (civil works, insurance and license fees) are included. Using the information presented in Table 4.13 and in Appendix A, and assuming zero end-value of the plant, the cost for treating 1 gal of redwater is $1.02 (for 340 °C system) and $0.35 (for 280 °C system). This is a relatively conservative estimate because actual WAO plants have operated longer than 10 years.

Thus, Army WAO of TNT redwater is estimated to cost about the same that contract disposal would cost. In addition, onsite disposal eliminates the risk that long distance transport of waste introduces. Conversely, the actual cost of treatment at a fixed plant would increase if TNT is not produced on a regular basis, but the cost of contract disposal would not increase as rapidly (because no new fixed facilities are required for contract disposal).

Table 4.13. Cost estimate of WAO treatment systems operating at 340 °C and 280 °C to treat 16,000 gpd for 10 years.

Description	340 °C	280 °C
Plant Cost (K$) (Equipment and Installation)	12,300	3900
Civil Works, etc. (K$) (15% of plant cost)	1845	1845
Total Capital Cost (K$)	14,145	4485
Capital Recovery Factor (10 Years, 10%)	0.1627	0.1627
Capital Cost per year (K$)	2301	730
O&M Cost per hour ($)	203	82
Hours of Operation per year (200 days @ 24 hours/day)	4800	4800
O&M Cost per year (K$)	974	394
Total Cost per year (K$)	3276	1123
Redwater Flow Rate per day (kgal)	16	16
Redwater Quantity per year (kgal) (200 days operation)	3200	3200
Treatment Cost per gallon	$1.02	$0.35

5 Conclusions and Recommendations

Feasibility Studies

The following conclusions can be made from the results of the feasibility studies:

- WAO is a feasible technology for TNT redwater treatment.
- The analytical method using reverse RPIPC can be used to analyze the DNTSs present in raw and treated redwater.
- TNT redwater contains 28.4 percent solids of which 36 percent is organic; inorganic $NaNO_2$ and $NaNO_3$ are 20.9 g/L and 51.4 g/L, respectively. A relatively low COD to TOC ratio indicates that some redwater components cannot be accurately detected by the standard COD test. The concentrations of α-TNT and *1,3,5*-TNB are 230 mg/L and 310 mg/L, respectively, while *2,4*-DNT and *2,6*-DNT concentrations are 21 and 3 mg/L, respectively.
- Oxidation temperatures higher than 325 °C may provide almost 100 percent organic oxidation in terms of COD and TOC removal in diluted redwater. A nearly complete destruction of the nitroaromatics and complete removal of DNTSs is also achieved. WAO of redwater results in an increase in inorganic sulfate and nitrate concentrations due to oxidation of the inorganic sulfite and nitrite present in raw redwater and the oxidation of organically-bound sulfur to sulfate. The exact fate of organic nitrogen upon WAO is unclear.
- Accumulation of acetic acid occurs at lower temperatures. Thus, oxidation temperatures between 225 and 300 °C (closer to 300 than 225) may provide an effluent that may be effectively treated using conventional biological wastewater treatment, if the necessary dilution can be achieved to eliminate the adverse effect of high inorganic solids content. This might be easier to achieve using catalysts/initiators to obtain enhanced reaction rates.
- Less is known about the chemical transformation products of TNT and other nitroaromatics, than is known about their biotransformation products (McCormick et al. 1976; Spanggord et al. 1982; Burrows et al. 1989; Walsh

1990). Therefore, the identification and quantification of products from chemical transformations during WAO of TNT redwater are important.

Kinetic Studies

- The results of WAO experiments with diluted redwater (1:100) at five different temperatures and three oxygen pressures indicate that contaminant removal efficiencies are a function of temperature, and to a lesser extent, oxygen pressure. At the highest temperature of 320 °C and 90 psi PO_2, only a small amount of COD (8 mg/L) remained after 1-hour reaction; the other contaminants were still present in high concentrations [e.g., TOC (30 mg/L), HAc (38 mg/L), TVS (127 mg/L), and other byproducts, such as *1,3*-DNB (5.7 mg/L), and NB (0.13 mg/L)]. Because of organic destruction, significant amounts of inorganic sulfate accumulate. Acetic acid also accumulates up to a temperature of 320 °C.

- Kinetic experiments revealed several interesting points. An initial rapid organic destruction in terms of TOC, COD, and TVS was observed in each experiment immediately after the injection of the sample into the reactor. This is due to the oxidation of easily oxidizable compounds initially present in the redwater. The degree of this "flash" COD or TOC reduction is related to the operating conditions. The higher the temperature and/or pressure, the more the COD or TOC reduction. After this initial fast activity, PO_2 has little effect and reaction of the slowly oxidizable compounds proceeds at a typical first-order rate with respect to COD, TOC, or TVS. Under harsher conditions, however, there appear two distinct first-order rate phases.

- Temperature, as expected, significantly affects kinetic rates and the activation energies based on first-order kinetics are approximately 17 kcal/mole (COD) and 18 kcal/mole (TOC).

- Catalyst [Cu(II) and Mn(II)] and initiator (H_2O_2) addition enhanced the reaction rates. High salt concentrations also showed slight enhancement in the WAO rate of redwater.

- For a 1-hour WAO of diluted redwater (1:100) at 260 °C and 0.69 MPa, the removal efficiencies of the organic matter in terms of TOC, COD, and organic nitrogen and four measured nitro-compounds (α-TNT, 2,4-DNT, 2,6-DNT, and 1,3,5-TNB) were all greater than 84 percent. The DNT sulfonates, 2,4-DNT-5-SO_3Na and 2,4-DNT-3-SO_3Na, were not detected.

- There was a significant accumulation of inorganic sulfate (1414 mg/L as Na_2SO_4) and NH_4^+ (32 mg N/L), as well as acetic acid (28 mg/L) and 1,3-DNB (14 mg/L). The off-gas yielded a high concentration of N_2 (net increase of 4.6 percent), CO_2 (3.7 percent), and CO (0.33 percent).

- The carbon balance analysis indicates that 85 percent of the initial organic C is accounted for: 44 percent CO_2, 4 percent CO, 33 percent dissolved CO_2, and 19 percent TOC remaining, all expressed as C. The sulfate concentration in the treated sample was much higher than would be expected from complete oxidation of the measured inorganic sulfate and organic DNT sulfonate concentrations in raw redwater. Thus, a significant amount of S-containing organic compounds present in the redwater are not accounted for. The nitrogen analyses indicate a significant ammonium concentration (9 percent) in the treated waste and high N_2 concentration in the off-gas (72 percent); the others are NO_3^- (16 percent) and residual nitrocompounds (3 percent). The extremely high percentage of NH_4^+ and N_2 clearly indicates that WAO is a complicated process involving both oxidation and reduction.

- As for catalyst addition, Cu(II) enhanced both the initial rapid carbon reduction and the overall WAO rate. The radical initiator H_2O_2 at two concentrations only enhanced the initial COD reduction.

Toxicity Studies

- The raw and treated redwater were tested for toxicity using heterotrophic Activated Sludge (AS). Raw redwater was only slightly inhibitory to the ability of the mixed culture to degrade glucose COD, while up to a 75 percent fraction by volume of the treated redwater (320 °C and PO_2 = 90 psi) showed no adverse effects. However, the same sample definitely affected the ability of the enriched Nitrosomonas culture to convert ammonium to nitrite. A 10 percent fraction of treated sample reduced the nitrite production rate by half. Up to 1 percent and 4 percent fractions of the diluted raw redwater (1:100), with and without the supplemental addition of $NaNO_3$ (400 mg/L) and Na_2SO_4 (1500 mg/L), respectively, did not exert any noticeable adverse effects on the Nitrosomonas culture. The resulting conclusion is that the organic byproducts formed during the WAO of redwater are responsible for the observed toxic effects. Consequently, a direct discharge of WAO-treated redwater into receiving waters may exert toxic effects on aquatic life.

- To minimize the variability of the bioassay tests, the WAO-treated redwater was evaluated using three different microbial cultures. The results reaffirm the preliminary finding that WAO-treated waste exerts toxic effect on Nitrosomonas and Acinetobacter growth, but has less impact on AS capability in COD removal. Further, treated samples at 340 °C appear to exhibit a more toxic effect than those at 260 °C for both Acinetobacter and Nitrosomonas. Apparently, organic byproducts generated at higher temperatures are responsible for the observed adverse effects.

Costs

- The estimated cost for treating a gallon of redwater is $1.02 if treated at 340 °C, and $0.35 if treated at 280 °C. The cost for a 340 °C plant treating 16,000 gpd of redwater was estimated at $12,300,000. A plant treating the same amount of redwater at 280 °C costs $3,900,000. Total capital cost per year at 340 °C is $2,301,000; per year at 280 °C is $730,000.

Recommendations

- The complete characterization of redwater components is necessary to determine its impact on the treatment process and to evaluate process performance. The identification and quantification of the byproducts present in the WAO-treated sample are also important. Currently, there is no known technology that can accomplish a complete identification and quantification of redwater components and WAO-treated byproducts.

- Additional studies, preferably in flow-through mode, on large quantities of redwater, are necessary to extract sufficient quantities of byproducts for identification.

- The CO concentration in the off-gases from the WAO process is two orders of magnitude higher than National Ambient Air Quality Standards. The value of total hydrocarbons (23 ppm as CH_4) is close to that of Primary Air Quality Standards. The quality of the off-gas may vary as a function of WAO temperature as well as pressure, and must be considered in the further evaluation of WAO technology for the treatment and disposal of redwater.

- Based on the feasibility, kinetic, and preliminary toxicity studies conducted for this project, redwater can be treated with WAO. A treatment process with WAO followed by AS treatment may be useful for disposal of redwater.

- Further tests and developmental work are recommended for the sludge treatment step.

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Appendix A: Budgetary Proposal for Wet Air Oxidation Systems for the Destruction of TNT Redwater at 536 °F and 645 °F

PREPARED FOR
U.S. ARMY CONSTRUCTION RESEARCH LAB
CONTRACT NO. DACA88-93-M-0668

BY
ZIMPRO ENVIRONMENTAL, INC.
21-2803-93.0

AUGUST 27, 1993

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SECTION I

INTRODUCTION

INTRODUCTION

The production of TNT using standard Army procedures generates a waste stream high in dinitrotoluene sulfonates, complexed TNT and inorganic salts (sodium nitrate, nitrite, sulfate and sulfite) which has been designated a hazardous waste by the Environmental Protection Agency. This wastestream is commonly called redwater, due to its dark red coloration. This poses a problem in the production of TNT, whereby acceptable, cost-effective disposal of redwater is currently unavailable.

Wet air oxidation (WAO) has been demonstrated for removing TNT redwater constituents in terms of COD (chemical oxygen demand), TOC (total organic carbon), and TVS (total volatile solids) reduction. Wet air oxidation is an aqueous phase oxidation of organic compounds by dissolved molecular oxygen at elevated temperatures and pressures. Depending on the overall desired treatment level, the oxidation reactions will occur at moderate temperatures (300°F - 600°F) and at pressures ranging from 150 to over 3000 pounds per square inch (psig). As the oxidation temperature is increased, a larger portion of the organic compounds will be oxidized which will correspond to a higher overall COD reduction. Organic compounds are oxidized to carbon dioxide and water with some complex compounds being partially oxidized to compounds such as acetate which are more readily biodegradable.

Zimpro Environmental, Inc. has been requested by U. S. Army Construction Engineering Research Lab, reference Contract DACA88-93-M-0668, to provide budgetary capital and operating cost estimates for high pressure wet air oxidation systems designed to destroy the TNT redwater. Two (2) budgetary cost estimates were devolved to treat 16,000 gallons per day of redwater, one (1) at an operating temperature of 536°F and one (1) at an operating temperature of 645°F.

DISCUSSION

The untreated redwater may contain up to fifteen percent (15%) dissolved salts composed primarily of sodium sulfate. Additional sodium sulfate will be formed as reaction products from the oxidation of sodium sulfite and organic sulfonic acids contained in the redwater waste. The wet air oxidized redwater effluent could contain as much as 165 grams per liter of sodium sulfate if it were not diluted prior to treatment by wet air oxidation. Sodium sulfate is one of the few inorganic salts that exhibit an inverse solubility at elevated temperatures. Sodium sulfate has a relatively high solubility between 86°F and 482°F. The solubility of sodium sulfate increases rapidly as the temperature is increased from ambient to 86°F and decreases rapidly as the temperature is increased from 480°F to 645°F. The solubility of sodium sulfate is approximately 40 grams per liter at 645°F. It is necessary to dilute the redwater waste before it can be treated at 645°F in a wet air oxidation system to avoid solubility limit problems.

The system designed for operation at 536°F also includes the addition of some dilution water. Dilution of the redwater is necessary to allow for better control of the wet air oxidation system due to the high strength of the waste.

PROCESS DESCRIPTION

Figure 1 presents the basic flow scheme for the proposed wet air oxidation systems. The proposed flow scheme begins with a waste storage tank. The design and supply of this waste storage tank is beyond the scope of the systems being offered by ZIMPRO.

A low pressure centrifugal feed pump is used to transfer the waste mixture from a storage tank provided by the Purchaser to the to the inlet of the high pressure pump. Pressurized dilution water is directed to the discharge of the low pressure feed pump. A separate metering pump is also used to inject sodium hydroxide at the discharge of the waste feed pump to maintain the pH of the oxidized effluent above 4.5. A static mixer is provided to insure adequate mixing of the waste, dilution water and caustic prior to entering the system.

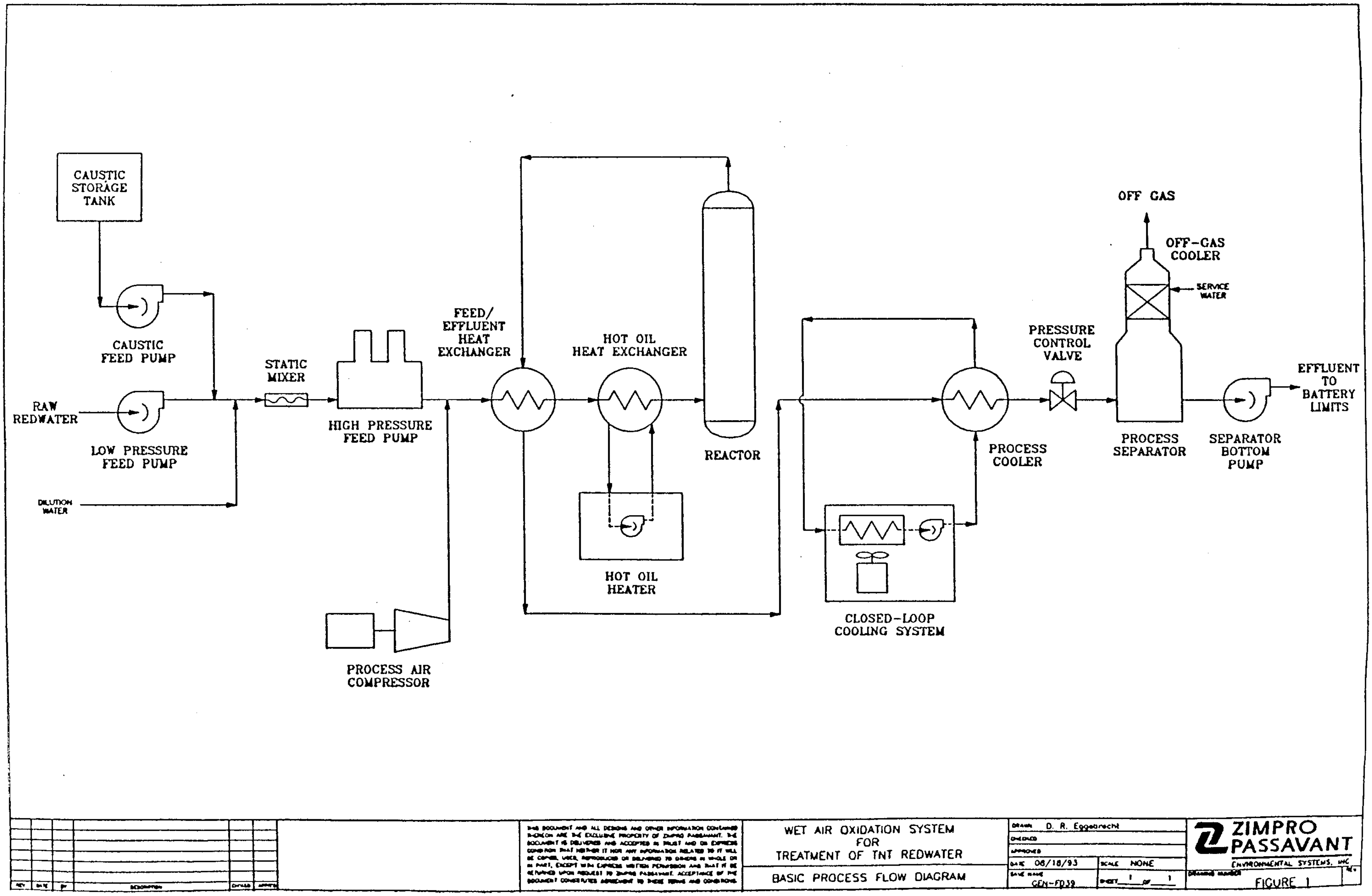
The pressurized discharge from the high pressure pump is combined with the air stream from the process air compressor thereby forming a two-phase stream. The two-phase air/waste stream passes through the tube-side of the feed/effluent heat exchanger. The feed/effluent heat exchanger is used to transfer thermal energy from the hot oxidized effluent to the un-reacted waste and air mixture. The heated mixture is then routed through the hot oil heat exchanger. The hot oil heat exchanger is used to supplement the thermal energy transferred to the air/waste mixture from a closed-loop hot oil system.

The heated air/waste mixture is introduced to the bottom of the reactor which is a vertically oriented column type pressure vessel. The reactor contents are mixed by the action of the gas phase rising through the liquid. As the gas phase rises and mixes with the liquid, oxygen is dissolved into the liquid which takes part in the oxidation reactions. The reactor is designed to provide sufficient detention time to allow the oxidation reactions to reach the desired level. These reactions liberate sufficient heat to allow the reactor to operate at the 645°F (or 536°F) operating temperature.

The oxidized liquid, oxidation product gases, and spent air are routed through the shell side of the feed/effluent heat exchanger, as mentioned above, to preheat the incoming air-wastewater stream. Temperature control of the oxidation system is achieved by varying the heat duty to the hot oil heat exchanger.

Substantial cooling of the reactor effluent is achieved in the feed/effluent heat exchanger. Additional cooling is accomplished by the process cooler. Additional thermal energy is transferred from the reactor effluent to a closed loop cooling system to achieve the desired treated waste discharge temperature. It should be noted that the system is still at an elevated pressure at this point.

The cooled reactor effluent is throttled through a pressure control valve into the separator thereby creating separate liquid and vapor phase waste streams. The vapor phase is separated from the liquid and passes upward through a packed bed tower where water is used to further cool the gases and condense some of the water vapor contained therein. The gases are then conveyed to the proposed boundary limits for receipt by the Purchaser. The oxidized wastewater is pumped via separator bottoms pump to the boundary limit.


CAUSTIC STORAGE TANK
CAUSTIC FEED PUMP
RAW REDWATER
LOW PRESSURE FEED PUMP
DILUTION WATER
STATIC MIXER
HIGH PRESSURE FEED PUMP
PROCESS AIR COMPRESSOR
FEED/ EFFLUENT HEAT EXCHANGER
HOT OIL HEAT EXCHANGER
HOT OIL HEATER
REACTOR
CLOSED-LOOP COOLING SYSTEM
PROCESS COOLER
PRESSURE CONTROL VALVE
OFF GAS
OFF-GAS COOLER
SERVICE WATER
PROCESS SEPARATOR
SEPARATOR BOTTOM PUMP
EFFLUENT TO BATTERY LIMITS
WET AIR OXIDATION SYSTEM
FOR
TREATMENT OF TNT REDWATER
BASIC PROCESS FLOW DIAGRAM
DRAWN D. R. Eggebrecht
CHECKED
APPROVED
DATE 08/18/93
SCALE NONE
SAVE NAME GEN-FD39
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ZIMPRO PASSAVANT
ENVIRONMENTAL SYSTEMS, INC.
DRAWING NUMBER
FIGURE 1
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SECTION II

DESIGN BASIS

DESIGN BASIS

Wastewater Characteristics

The proposed wet air oxidation system designs are based on laboratory scale wet air oxidation tests performed on a sample of redwater provided by USACERL in 1991. The test results were presented in a report titled "Bench-Scale Shaking Autoclave Results for Wet Air Oxidation System Treatment of a TNT Process Waste (Red Water) From The U.S. Army" dated February 16, 1992. The waste characteristics used in the preliminary full scale design are listed in TABLE II-1 below.

TABLE II-1: RAW REDWATER WASTEWATER CHARACTERISTICS

Characteristic	Units	Value
Design Flowrate	gpd	16,000
COD	g/l	120
Sodium Sulfate	g/l	165
Soluble Chloride	mg/l	< 100
Specific Gravity	--	1.10
pH	--	7-10

Oxidized Effluent

The proposed wet air oxidation systems shall be designed to oxidize the redwater waste with the characteristics as defined above and will produce both aqueous and gaseous product streams as characterized in TABLE II-2 below. It has been assumed that the COD reductions will be approximately 90% and 99.5% at 536°F and 645°F respectively as reported in the laboratory scale test report. The values indicated in TABLE II-2 represent the anticipated conditions at the wet air oxidation boundary limits.

TABLE II-2: OXIDATION PRODUCT CHARACTERISTICS

LIQUID EFFLUENT

Characteristic	Units	Value	Value
Reactor Operating Temperature	°F	536	645
Total Flow Rate	gpm	16.7	66.7
Maximum Pressure	psig	30	30
COD	g/l	7.8	<1
pH	--	≈7	≈7

GASEOUS EFFLUENT

Characteristic	Units	Value	Value
Flow Rate (Dry Basis)	lb/hr	3420	4010
Pressure	psig	≈1	≈1
Temperature	°F	≈100	≈100
Oxygen Concentration	Percent	5	5
Hydrocarbon Content	ppm	nil	nil
NO_x	ppm	nil	nil
SO_x	ppm	nil	nil

Mechanical Design Parameters

The mechanical design of the proposed wet air oxidation systems are based on the parameters listed in TABLE II-3.

TABLE II-3: MECHANICAL DESIGN PARAMETERS

Parameter	Units	Value	Value
Reactor Operating Temperature	°F	536	645
Reactor Operating Pressure	psig	1800	3500
Mechanical Design Temperature Minimum Maximum	°F	 32 600	 32 670
Mechanical Design Pressure	psig	2200	4250
System Hydraulic Processing Rate	gpm	16.7	66.7
Dilution Water Flow	gpm	5.6	55.6
Residual Oxygen In Off-Gas	Percent	5	5
Corrosion Allowance for Wetted Alloy Components	mm	0.38	0.38

Instrument/Electrical Design

All electrical and instrumentation systems shall be provided based on the parameters and/or standards specified in TABLE II-4.

TABLE II-4: INSTRUMENTATION/ELECTRICAL DESIGN PARAMETERS

Parameter	Usage	Type
Classification	Panel Instruments	Unclassified
Instrument Philosophy		Control, alarm, and shutdown can originate from same point, instruments not redundant. Programmable logic controller. Not redundant. Electronic, small case instruments.
Enclosure Types	Junction Boxes	NEMA 12
	Control Panel	NEMA 12
	Motor Control Centers.	NEMA 1

Site Conditions and Utilities

It has been assumed that utilities and conditions listed below shall exist at the installation site. It shall be the responsibility of the Purchaser to provide all utility services necessitated by the proposed system.

TABLE II-5: SITE CONDITIONS AND UTILITY SERVICES

Parameters	Units	Value
Ambient Temperature		
Low	°F	32
High	°F	90
Temperature For Winterizing	--	Freeze Protection Shall Not Be Included
Earthquake Zone	--	No Seismic Zoning
System Location	--	Indoors
Process Water		
Minimum Supply Pressure	psig	50
Mechanical Design Pressure	psig	100
Supply Temperature	°F	85
pH	--	5.5-8.0
Solids	--	low
Hardness	--	low
Electrical Service		
Area classification		Non-hazardous
Power Supply		
Motor Size < 3/4 HP		220 V, 1Ø, 60 Hz
Motor Size > 3/4 HP to 500 HP		440 V, 3Ø, 60 Hz
Control Circuits		110 V, 1Ø, 60 Hz

Specifications and Codes

The codes and specifications listed in TABLE II-6 shall be utilized in the design of the proposed wet air oxidation systems in addition to ZIMPRO's standard engineering practices and methodologies.

TABLE II-6: SPECIFICATIONS AND CODES

System Component	Code or Specification
Pressure Vessel	ASME Section VIII, Div. 1
Heat Exchanger	ASME Section VIII, Div. 1
Centrifugal Pump	ANSI B73.1
Metering Pump	API 675
Air Compressor	Manufactures Standard
High Pressure Pump	ZIMPRO'S Standard
Piping	ANSI B31.3
Electrical	National Electrical Code As Published By The National Association Of Fire Engineers
Instrumentation	ZIMPRO's Standard Practice
Safety Equipment	U.S.A. Occupational Safety and Health Administration

SECTION III

645°F OPERATING TEMPERATURE SYSTEM

SCOPE OF OFFERING 645°F OPERATING TEMPERATURE SYSTEM

ZIMPRO proposes to provide all engineering, design, equipment procurement, installation of equipment in Purchasers building, and field services necessary to install and start-up the wet air oxidation system. The proposed services are limited to the components of the wet air oxidation system and does not include any civil type work such as buildings, foundations, sewers, etc.

Services Supplied by ZIMPRO

Design Services

The design services included in the budgetary price stated hereinafter are as follows:

- Process Design, Equipment Sizing
- Logic Diagrams
- Wiring Diagrams
- Process and Instrument Diagrams
- Process Flow Diagrams
- Equipment Installation Drawings
- Operation and Maintenance Manuals

Installation Service

The selling price stated hereinafter includes the on-site services of a qualified ZIMPRO field construction supervisor to supervise the installation of the wet air oxidation system in the Purchasers building. ZIMPRO shall employ the services of independent contractors (mechanical, electrical, insulation etc.) to install the components according to ZIMPRO prepared installation drawings and specifications. ZIMPRO's construction supervisor shall remain on site as necessary until the wet air oxidation system is completed and the equipment is ready for check out and start-up. It is anticipated that the installation period shall require approximately four (4) to six (6) months duration following free access to the Purchasers building.

Start-up Services

The hereinafter stated selling price includes four (4) consecutive weeks (7 days per week, 24 hours per day) of on site services of three (3) ZIMPRO field operation technicians to assist in the system check-out and start-up and to provide training in the operation of the wet air oxidation system. Should additional services be deemed necessary by the Purchaser, additional services may be procured from ZIMPRO on a per diem basis.

Equipment Supplied by ZIMPRO

TABLE III-1 lists the major equipment pieces and/or system components to be furnished and installed by ZIMPRO and so included in the proposed selling price, as stated hereinafter.

TABLE III-1 : MAJOR EQUIPMENT LIST

Item	Quantity	Material of Construction If Applicable
Low Pressure Feed Pump	2 (1 spare)	316 L Stainless Steel
High Pressure Feed Pump	1	316 L Stainless Steel
Process Air Compressor	1	Manufacturer's Standard
Feed/Effluent Heat Exchanger	1	316 L Stainless Steel
Hot Oil Heat Exchanger	1	316 L Tubes, CS Shell
Hot Oil Heater System	1	Manufacturer's Standard
Hot Oil Recirculating Pump	2 (1 spare)	Manufacturer's Standard
Process Reactor	1	316 L Clad Carbon Steel
Process Cooler	1	316 L Tubes, CS Shell
Pressure Control Valve	2 (1 spare)	316 L Stainless Steel
Process Separator	1	316 L Stainless Steel
Off-Gas Cooler	1	316 L Stainless Steel
Separator Bottoms Pump	2 (1 spare)	316 L Stainless Steel
Caustic Metering Pump	2 (1 spare)	Manufacturer's Standard
Caustic Day Tank	1	Carbon Steel
Closed Loop Cooling System	1	Manufacturer's Standard
Cooling System Recirculating Pump	1	Manufacturer's Standard
Motor Control Center	1	Manufacturer's Standard
Control Panel/Instrumentation	1 Lot	Manufacturer's Standard
Instrument Air Compressor	1	Manufacturer's Standard

TABLE III-1 : MAJOR EQUIPMENT LIST

Item	**Quantity**	**Material of Construction If Applicable**
Solvent Tank	1	316 L Stainless Steel
Solvent Pump	1	316 L Stainless Steel

Items Excluded from ZIMPRO's Scope

The following items are excluded from ZIMPRO's scope of supply and the Purchaser will need to make arrangements for the completion of each of these tasks.

- Design, supply and installation of equipment foundations, civil works, sumps, pads and external supports, as required.
- Building design and construction.
- Design, supply, and installation of all utility services (process water, space heating, fuel supply, electrical service, etc.) and their respective distribution systems.
- Design, supply and installation of any facilities for additional treatment of the wet air oxidation process effluent and/or off-gas.
- Design, supply, or installation of equalization or storage tanks.
- Any operational spare parts with the exception of spare operating equipment as defined in this proposal.

Utilities

Utilities required by the wet air oxidation system and to be supplied by the Purchaser to a battery limit defined as one (1) foot inside the building designed to house the wet air oxidation system include: 480 Volt 3 Phase electrical service, 220 Volt 1 Phase electrical service, natural gas and/or No. 2 fuel oil, fifty percent caustic, process water and potable water. ZIMPRO estimates that the proposed wet air oxidation system shall impose the utility duties presented in TABLE III-2.

TABLE III-2: ESTIMATED UTILITY DUTIES

Utility	Units	Quantity
Operating Electrical Power	kw·hr/hr	710
Service Water	gpm	30
Hot Oil Boiler Fuel (No. 2 Fuel Oil)	gal/hr	34
Caustic (50%)	gal/hr	3.5

Estimated Operating and Maintenance (O&M) Cost

The estimated O&M cost for the treatment of red water by wet air oxidation at 340°C is presented in Table III-3. The unit cost for each cost element is shown in the cost table. The maintenance cost is based on an annual cost of four (4) percent of the equipment cost prorated to a hourly rate based on 200 days of operation per year.

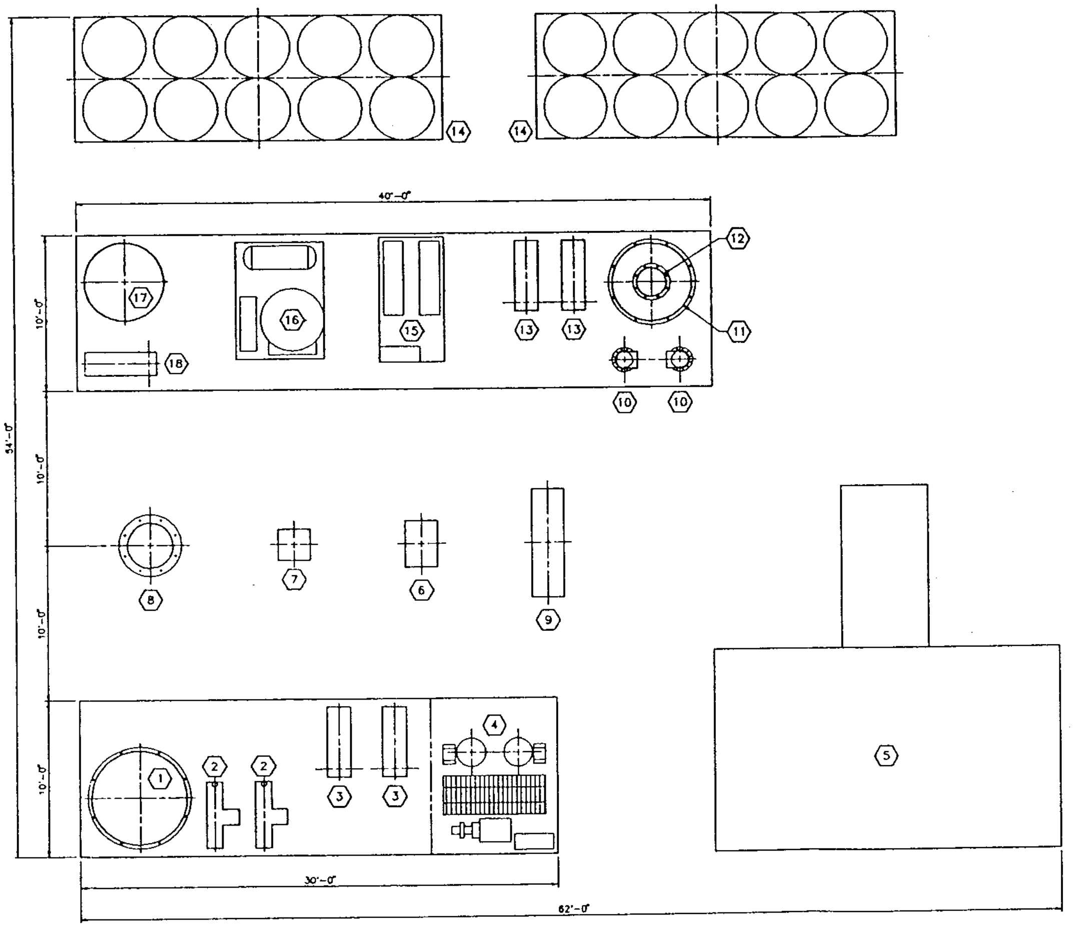
TABLE III-3: ESTIMATED O & M COST

Cost Element	Unit Cost	Cost/Hr.
Operating Labaor	$20.00/hr	$20.00
Electric Power	$0.05/KWH	$35.50
Service Water	$1.00/1000 gal	$1.80
No. 2 Fuel Oil	$1.00/gal	$34.00
Caustic (50% NaOH)	$2.00/gal	$7.00
Maintenance (Labor and Materials)	-	$105.00
Total O & M Cost	-	$203.30

Budgetary Installed System Price

ZIMPRO offers to provide, on a budgetary basis, the equipment, services and installation for the 645°F operating temperature wet air oxidation system, as defined under Section III of this proposal, for the sum of Twelve Million, Three Hundred Thousand and No/100 Dollars ($12,300,000.00), F.O.B. job site, assuming United States location.

The price quoted above **does not** include any applicable state, local, or federal taxes, permits, bonds, or fees.



EQUIPMENT LIST

ITEM	DESCRIPTION
1	CAUSTIC STORAGE TANK
2	CAUSTIC FEED PUMP
3	LOW PRESSURE FEED PUMP
4	HIGH PRESSURE FEED PUMP
5	PROCESS AIR COMPRESSOR
6	FEED/EFFLUENT HEAT EXCHANGER
7	HOT OIL HEAT EXCHANGER
8	REACTOR
9	PROCESS COOLER
10	PRESSURE CONTROL VALVE
11	SEPARATOR
12	OFF-GAS COOLER
13	SEPARATOR BOTTOM PUMP
14	CLOSED LOOP COOLING HEAT EXCHANGER
15	CLOSED LOOP COOLING SYSTEM PUMP SKID
16	HOT OIL BOILER SKID
17	SOLVENT TANK
18	SOLVENT PUMP

REV	DATE	BY	DESCRIPTION	CHKED	APPR'D

1 - 17 GPM, 536 °F
WET AIR OXIDATION UNIT
FOR
TREATMENT OF TNT REDWATER

PRELIMINARY PLANT LAYOUT

DRAWN D. R. Eggebrecht
CHECKED
APPROVED
DATE 08/18/1993 SCALE 1/4" = 1'-0"
SAVE NAME 4001A-01 SHEET 1 OF 1

ZIMPRO
ENVIRONMENTAL, INC.
An Affiliate of the Black Clawson Co.

DRAWING NUMBER 13.0-2803-D-4001A
REV

SECTION IV

536°F OPERATING TEMPERATURE SYSTEM

SCOPE OF OFFERING 536°F OPERATING TEMPERATURE SYSTEM

ZIMPRO proposes to provide all engineering, design, equipment procurement and start-up services necessary for the Purchaser to install, start-up and operate the 536°F wet air oxidation system. The proposed services are limited to the components of the oxidation system and do not include any civil type work such as buildings, foundations, sewers, etc.

Services Supplied by ZIMPRO

Design Services

The design services included in the budgetary price stated hereinafter are as follows:

- Process Design, Equipment Sizing
- Logic Diagrams
- Wiring Diagrams
- Process and Instrument Diagrams
- Process Flow Diagrams
- Equipment Layout Drawing
- Interconnecting Process Piping Design
- Operation and Maintenance Manuals

Installation Inspection Service

The hereinafter stated selling price includes four (4) weeks (5 days per week, 8 hours per day) of on-site installation inspection service by a qualified ZIMPRO field construction supervisor to assist and make recommendations concerning the wet air oxidation system installation. Should additional services be deemed necessary by the Purchaser, additional services may be procured from ZIMPRO on a per diem basis.

Start-up Services

The hereinafter stated selling price includes three (3) consecutive weeks (7 days per week, 24 hours per day) of on-site services by a qualified ZIMPRO field operator technician to assist in the system check-out and start-up and to provide training in the operation of the wet air oxidation system. Should additional services be deemed necessary by the Purchaser, additional services may be procured from ZIMPRO on a per diem basis.

Equipment Supplied by ZIMPRO

TABLE IV-1 lists the major equipment pieces and/or system components to be furnished by ZIMPRO and so included in the proposed selling price, as stated hereinafter.

TABLE IV-1 : MAJOR EQUIPMENT LIST

Item	Quantity	Material of Construction If Applicable
Low Pressure Feed Pump	2 (1 spare)	316 L Stainless Steel
High Pressure Feed Pump	1	316 L Stainless Steel
Process Air Compressor	1	Manufacturer's Standard
Feed/Effluent Heat Exchanger	1	316 L Stainless Steel
Hot Oil Heat Exchanger	1	316 L Tubes, CS Shell
Hot Oil Heater System	1	Manufacturer's Standard
Hot Oil Recirculating Pump	2 (1 spare)	Manufacturer's Standard
Process Reactor	1	316 L Clad Carbon Steel
Process Cooler	1	316 L Tubes, CS Shell
Pressure Control Valve	2 (1 spare)	316 L Stainless Steel
Process Separator	1	316 L Stainless Steel
Off-Gas Cooler	1	316 L Stainless Steel
Separator Bottoms Pump	2 (1 spare)	316 L Stainless Steel
Caustic Metering Pump	2 (1 spare)	
Caustic Day Tank	1	Carbon Steel
Closed Loop Cooling System	1	Manufactures Standard
Cooling System Recirculating Pump	1	Manufacturer's Standard
Control Panel/Instrumentation	1 Lot	Manufacturer's Standard
Solvent Tank	1	316 L Stainless Steel
Solvent Pump	1	316 L Stainless Steel

Equipment Skids

The majority of the process equipment listed under TABLE IV -1 shall be skid mounted to facilitate system placement and installation by the Purchaser. All skid mounted equipment, instrumentation and valves shall be pre-piped and pre-wired to the extent practical. Skid mounted instruments and start-stop stations shall be pre-wired to skid mounted terminal strip/boxes. ZIMPRO shall supply a control system for the proposed wet air oxidation system. Wiring between the control panel and field instrumentation and Purchaser supplied motor control center shall be the responsibility of the Purchaser.

The Purchaser shall be required to provide all necessary foundations and equipment pads for the equipment skids. TABLE IV-2 lists the sizes and quantities of the equipment skids anticipated to be supplied for the proposed system.

TABLE IV-2: EQUIPMENT SKIDS

Description	Quantity	Approx. Dimension L x W x H (feet)	Approx. Weight lbs.
Main Equipment Skid	1	40 X 10 X 12	30,000
Process Compressor	1	22 x 23.5 x 9	90,000
Pump Skid	1	30 x 10 x 12	25,000

Non-Skid Equipment

Individual items and/or system components such as the process reactor, feed/effluent heat exchanger, hot oil heat exchanger, process cooler, field valves, and field instrumentation will require mounting by the Purchaser on separate concrete foundations to be provided by the Purchaser. TABLE IV-3 is a list of major equipment items being offered in the proposed wet air oxidation system which require independent mounting and/or installation.

TABLE IV-3: MAJOR INDEPENDENTLY MOUNTED EQUIPMENT

Description	Quantity	Approx. Dimension L x W x H (feet)	Approx. Weight lbs.
Reactor	1	3'∅ x 30	32,000
Feed/Effluent Heat Exchanger	1	3 x 2 x 20	6,000
Process Cooler	1	7 x 2 x 20	8,500
Hot Oil Heat Exchanger	1	2 x 2 x 20	1,400
Closed Loop Cooling System Heat Exchangers	2	23 x 8 x 5	3,700

Items Excluded from ZIMPRO's Scope

The following items are excluded from ZIMPRO's scope of supply and the Purchaser will need to make arrangements for the completion of each of these tasks.

- Installation of all process equipment, instrumentation, piping, etc. required to complete the wet air oxidation system.
- Design, supply, and installation of skid interconnecting piping. ZIMPRO shall provide the design only for the skid high temperature/pressure process interconnecting piping.
- Design, supply and installation of equipment foundations, civil works, sumps, pads and external supports, as required.
- Building design and construction.
- Design, supply, and installation of all utility services (process water, space heating, fuel supply, electrical service, etc.) and their respective distribution systems.
- Motor control center.
- Design, supply and installation of any facilities for additional treatment of the wet air oxidation process effluent and/or off-gas.
- Design, supply and installation of waste equalization or storage tanks.
- Supply/installation of power and control wiring.

Utilities

Utilities required by the wet air oxidation system and to be supplied by the Purchaser include: 480 Volt 3 Phase electrical service, 220 Volt 1 Phase electrical service, natural gas and/or No. 2 fuel oil, fifty percent caustic, process water and potable water. ZIMPRO estimates that the proposed wet air oxidation system shall impose the utility duties presented in TABLE IV-4.

TABLE IV-4: ESTIMATED UTILITY DUTIES

Utility	Units	Quantity
Operating Electrical Power	kw·hr/hr	370
Service Water	gpm	24
Hot Oil Boiler Fuel (No. 2 Fuel Oil)	gal/hr	0*
Caustic (50%)	gal/hr	3.5

*Unit is autothermal at design conditions.

Estimated Operating and Maintenance (O & M) Cost

The estimated O & M cost for the treatment of red water by wet air oxidation at 280°C is presented in Table IV-5. The unit cost for each cost element is shown in the cost table. The maintenance cost is based on an annual cost of four (4) percent of the equipment cost prorated to a hourly rate based on 200 days of operation per year.

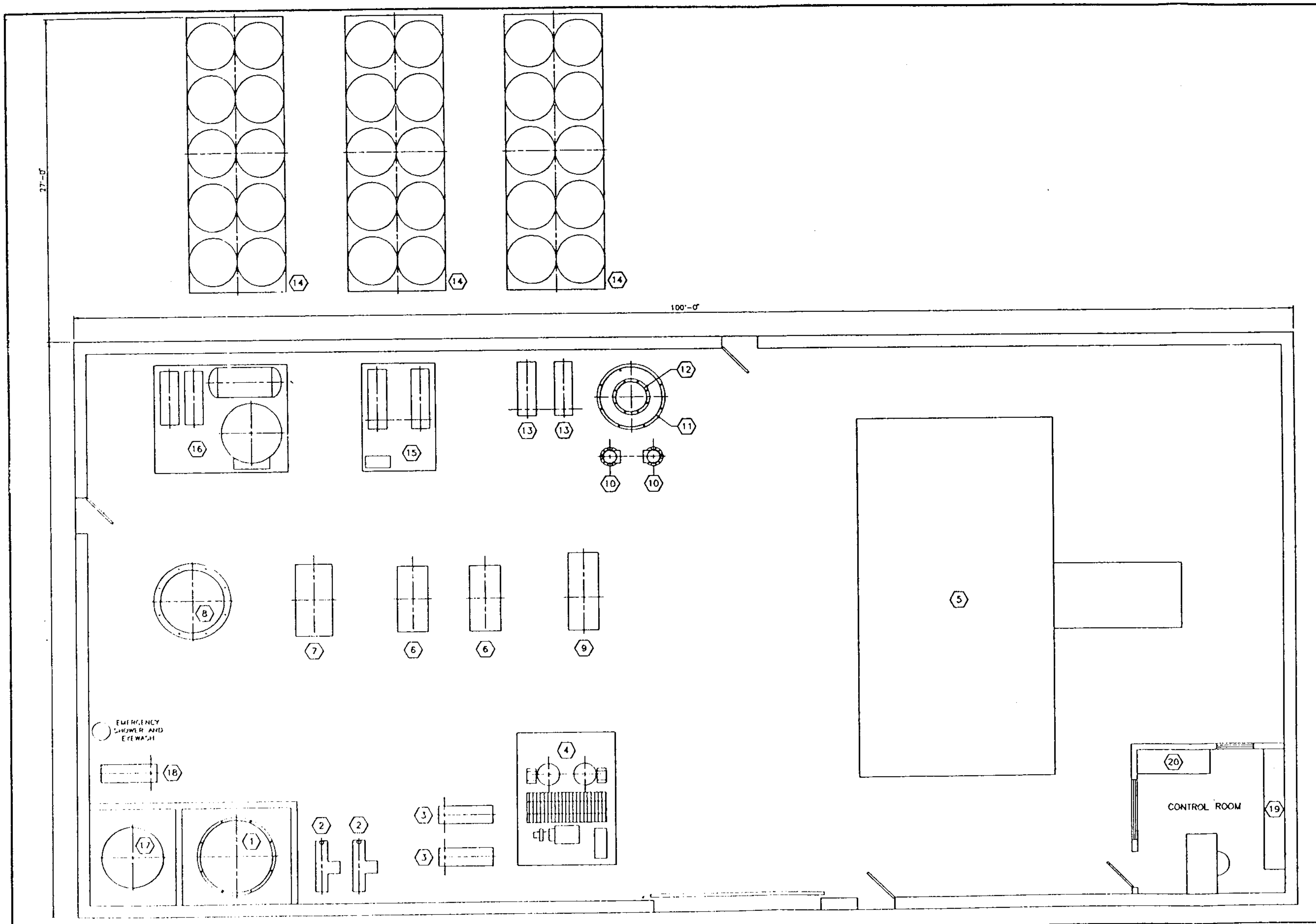
TABLE IV-5: ESTIMATED O & M COST

Cost Element	Unit Cost	Cost/Hr.
Operating Labaor	$20.00/hr	$20.00
Electric Power	$0.05/KWH	$18.50
Service Water	$1.00/1000 gal	$1.44
No. 2 Fuel Oil	$1.00/gal	$0.00
Caustic (50% NaOH)	$2.00/gal	$7.00
Maintenance (Labor and Materials)	-	$35.00
Total O & M Cost	-	$81.94

Budgetary System Price

ZIMPRO offers to provide, on a budgetary basis, the equipment and services for the 536°F operating temperature wet air oxidation system, as defined under Section IV of this proposal, for the sum of Three Million, Nine Hundred Thousand and No/100 Dollars ($3,900,000.00), F.O.B. job site, assuming United States location.

The price quoted above **does not** include any applicable state, local, or federal taxes, permits, bonds, fees or duties.



EQUIPMENT LIST

ITEM	DESCRIPTION
1	CAUSTIC STORAGE TANK
2	CAUSTIC FEED PUMP
3	LOW PRESSURE FEED PUMP
4	HIGH PRESSURE FEED PUMP
5	PROCESS AIR COMPRESSOR
6	FEED/EFFLUENT HEAT EXCHANGER
7	HOT OIL HEAT EXCHANGER
8	REACTOR
9	PROCESS COOLER
10	PRESSURE CONTROL VALVE
11	SEPARATOR
12	OFF-GAS COOLER
13	SEPARATOR BOTTOM PUMP
14	CLOSED LOOP COOLING HEAT EXCHANGER
15	CLOSED LOOP COOLING SYSTEM PUMP SKID
16	HOT OIL BOILER SKID
17	SOLVENT TANK
18	SOLVENT PUMP
19	MOTOR CONTROL CENTER
20	CONTROL PANEL

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1 - 67 GPM, 645°F
WET AIR OXIDATION UNIT
FOR
TREATMENT OF TNT REDWATER

PRELIMINARY PLANT LAYOUT

DRAWN D. R. Eggebrecht
CHECKED
APPROVED
DATE 06/18/1993
SCALE 1/4" = 1'-0"
SAVE NAME 4001-01
SHEET 1 OF 1

ZIMPRO
ENVIRONMENTAL, INC.
An Affiliate of the Black Clawson Co

DRAWING NUMBER 3.0-2803-D-4001
REV

Appendix B: Data From Kinetic Experiments

Table B1. Results of kinetic experiments - pH, COD, TOC, and TVS.

B1.1: 260 °C, 175 psi PO_2 @ 25 °C, 1:100 Dilution			B1.2: 300 °C, 175 psi PO_2 @ 25 °C, 1:100 Dilution			B1.3: 260 °C, 225 psi PO_2 @ 25 °C, 1:50 Dilution			
Time min	TVS mg/L	COD mg/L	Time min	TVS mg/L	COD mg/L	Time min	COD mg/L	TOC mg/L	pH units
0	1147	550	0	1147	550	0	1010	628	7.50
1	687	244	1	365	106	3	327	331	2.86
11	-	179	13	293	60	15	244	277	3.00
26	500	141	31	253	39	32	183	233	3.02
48	433	106	51	247	29	50	137	204	2.91
78	300	78	71	227	-	71.5	114	182	2.95
126	200	47	91	-	20	95	100	160	2.91
			121	170	11	120	78	156	2.95

B1.4: 260 °C, 45 psi PO_2 @ 25 °C, 1:25 Dilution				B1.5: 260 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution				B1.6: 260 °C, 175 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	TVS mg/L	COD mg/L	TOC mg/L	Time min	TVS mg/L	COD mg/L	TOC mg/L	Time min	TVS mg/L	COD mg/L	TOC mg/L
0	3660	2020	1290	0	3660	2020	1261	0	3660	2020	1261
3.5	2510	1257	903	3.5	2070	810	697	4.5	2170	731	644
14	1850	1087	801	15	1370	647	578	12.5	1555	559	577
33.5	1650	867	692	37.5	1170	487	493	31	1320	453	480
53.5	1300	772	589	58	800	397	427	50.5	1380	350	423
82	1200	596	528	80	820	321	387	70.5	1210	260	401
100	990	400	481	100	730	245	356	95	1045	224	336
120	760	351	407	120	700	227	339	120	910	211	301

Table B1. (Cont'd)

B1.7: 260 °C, 180 psi PO_2 @ 25 °C, 1:25 Dilution				B1.8: 280 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution				B1.9: 260 °C, 320 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	TVS mg/L	COD mg/L	TOC mg/L	Time min	TVS mg/L	COD mg/L	TOC mg/L	Time min	pH units	COD mg/L	TOC mg/L
0	3660	2020	1261	0	3660	2020	1256	0	7.50	2020	1256
1	2100	670	673	4.2	2120	703	642	4	3.19	579	598
11	1700	507	437	15	1705	532	521	14.8	3.53	425	490
31	1405	312	425	30	1480	-	478	30	3.72	325	407
51	1245	214	411	50	1050	327	361	50	3.77	233	363
71	990	171	328	70	1060	288	373	70	3.79	193	333
96	805	144	437	95	980	234	331	95	3.82	172	311
121	-	114	271	126	850	170	300	125	3.81	150	297

B1.10: 230 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution				B1.11: 280 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution				B1.12: 300 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	pH units	COD mg/L	TOC mg/L	Time min	pH units	COD mg/L	TOC mg/L	Time min	pH units	COD mg/L	TOC mg/L
0	7.50	2020	1256	0	7.50	2020	1256	0	7.50	2020	1256
4	3.19	1064	786	4	3.35	664	639	4.3	3.55	585	574
15	3.53	942	713	12	3.75	463	516	10	3.57	456	476
30	3.72	786	651	27.3	3.62	376	422	20	3.45	292	366
50	3.77	690	627	45.8	3.50	284	357	35	3.36	159	287
75	3.79	608	636	65.8	3.40	259	322	55	3.30	118	231
95.5	3.82	589	558	97.5	3.43	178	290	85	3.43	87	189
120	3.81	568	557	120	3.73	148	254	120	-	67	159

Table B1. (Cont'd)

B1.13: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution, Addition of 15 g/L Na_2SO_4 and 0.6 g/L $NaNO_3$				B1.14: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution, addition of 50 g/L Na_2SO_4 and 2.0 g/L $NaNO_3$			
Time min	pH units	COD mg/L	TOC mg/L	Time min	pH units	COD mg/L	TOC mg/L
0	7.50	2160	1308	0	7.50	2160	1308
3.5	3.4	629	641	7.5	3.28	595	574
10	3.15	527	567	15	3.31	467	476
25	3.13	414	492	30	3.32	320	366
47	3.12	295	404	50	3.34	227	287
70	3.10	249	352	70	3.33	189	231
95	3.10	198	309	95	3.32	167	189
125	3.09	160	303	120	3.32	126	159

Table B2. Results of kinetic experiments - inorganics.

B2.8: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution				B2.12: 300 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution			
Time, min	Concentration, mg/L			Time, min	Concentration, mg/L		
	Nitrite	Nitrate	Sulfate		Nitrite	Nitrate	Sulfate
0	1048	68	1504	0	1048	68	1504
4.2	-	683	2603	4.3	-	431	2965
15	-	586	2846	10	-	441	3127
30	-	583	2981	20	-	466	3484
50	-	607	3113	35	-	447	3400
70	-	625	3211	55	-	473	3562
95	-	614	3245	85	-	480	3653
126	-	607	3187	120	-	500	3751

* Concentrations are expressed as NO_2^-, NO_3^-, and SO_4^{2-}

Table B3. Results of WAO kinetic experiments - *1,3*-DNB.

B3.8: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution		**B3.12: 300 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution**	
Time, min	*1,3*-DNB, mg/L	Time, min	*1,3*-DNB, mg/L
0	<0.05	4.3	89.6
4.2	82.3	10	98.1
15	78.9	20	90.3
30	92.5	35	82.1
50	89.5	55	77.8
70	89.4	85	66.5
95	86.9	120	57.5
126	85.6		

Table B4. Results of WAO kinetic experiments - DNTS'.

B4.8: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution			**B4.12: 300 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution**		
Time, min	% Removal		Time, min	% Removal	
	2,4-DNT-5-SO_3Na	2,4-DNT-3-SO_3Na		2,4-DNT-5-SO_3Na	2,4-DNT-3-SO_3Na
0	0	0	0	0	0
4.2	63.8	46.3	4.3	55.1	43.3
15	73.4	45.7	10	80.3	58.4
30	87.5	49.6	20	100	73.2
50	97.2	50.2	35	100	95.4
70	100	56.1	55	100	92.0
95	100	61.7	85	100	96.8
126	100	65.4	120	100	100

Table B5. Percent reduction in TOC, COD, and UV absorbance at 200 nm: kinetics experiments.

B5.3: 260 °C, 225 psi PO_2 @ 25 °C, 1:50 Dilution				B5.4: 260 °C, 45 psi PO_2 @ 25 °C, 1:25 Dilution				B5.5: 260 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	Absorbance @ 200 nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD
3	28	47	67	3.5	39	30	38	3.5	40	45	60
15	34	56	77	14	45	38	46	15	47	54	68
32	40	63	82	33.5	51	46	57	37.5	53	61	76
50	44	68	86	53.5	54	54	62	58	57	66	80
70.5	47	71	89	82	60	59	71	80	60	69	84
95	48	74	90	100	63	63	80	100	63	72	88
125	51	76	92	120	68	68	83	120	65	73	89

B5.6: 260 °C, 175 psi PO_2 @ 25 °C, 1:25 Dilution				B5.8: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution				B5.9: 260 °C, 320 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	Absorbance @ 200 nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD
4.5	40	50	64	4.2	39	49	65	4	38	52	71
12.5	42	55	72	15	44	59	74	14.8	43	61	79
31	49	63	78	30	48	62	-	30	47	67	84
50.5	54	67	83	50	57	71	84	50	50	71	89
70.5	56	69	87	70	56	70	86	70	52	74	90
95	59	74	89	95	57	74	88	95	54	72	92
120	61	77	90	126	59	76	92	125	54	76	93

Table B5. (Cont'd)

B5.10: 230 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution				B5.11: 280 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution				B5.12: 300 °C, 90 psi PO_2 @ 25 °C, 1:25 Dilution			
Time min	Absorbance @ 200nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD
4	34	37	47	4	45	49	67	4.25	48	54	71
15	38	43	53	12	51	59	77	10	56	62	77
30	41	48	61	27.3	58	66	81	20	63	71	86
50	42	50	66	45.8	62	72	86	35	69	77	92
75	42	49	70	65.8	66	74	84	55	72	82	94
95.5	46	56	71	97.5	68	77	91	85	73	85	96
120	46	56	72	120	71	80	93	120	74	87	97

B5.13: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution, Addition of 15 g/L Na_2SO_4 and 0.6 g/L $NaNO_3$				B5.14: 260 °C, 225 psi PO_2 @ 25 °C, 1:25 Dilution, Addition of 50 g/L Na_2SO_4 and 2.0 g/L $NaNO_3$			
Time min	Absorbance @ 200nm	TOC	COD	Time min	Absorbance @ 200 nm	TOC	COD
3.5	31	51	71	7.5	26	55	73
10	33	57	76	15	26	62	78
25	36	62	81	30	28	69	85
47	39	69	86	50	28	75	90
70	41	73	89	70	29	78	91
95	43	76	91	95	28	81	92
120	43	77	93	120	29	83	94

Abbreviations and Acronyms

AAP	Army ammunition plant
ACN	acetonitrile
AR	Army Regulation
AS	activated sludge
au	absorbance unit
BAS	batch activated sludge system
BDL	below detection limit
BOD	biological oxygen demand
COD	chemical oxygen demand
DL	detection limit
DMSO	dimethyl sulfoxide
DNB	dinitrobenzene
DNT	dinitrotoluene
DNTS	dinitrotoluene sulfonate
DO	dissolved oxygen
DTGS	dueterated tri-glycine sulfate detector
FS	fixed solids
FTIR	Fourier Transformation Infra-red
GC	gas chromatography/gas chromatograph
GC-MS	gas chromatography coupled with mass spectrometry
gpd	gallons per day
HAc	acetic acid
HMX	high-melting explosive
HNBB	2,2',4,4',6,6'-hexanitrobibenzy
HNS	2,2',4,4',6,6'-hexanitrstilbene
$HO^{\bullet}$	hydroxyl radical
$HOO^{\bullet}$	hydroperoxy radical
HPLC	high performance liquid chromatography
HWRIC	Hazardous Waste Research and Information Center (Illinois)
ICP	inductively coupled plasma (spectrophotometer)
IR	infrared
KBr	potassium bromide
LAP	load, assembly, and packaging
LD	lethal dose
M	molar

MCT	mercury cadmium teluride
MeOH	methanol
MLSS	mixed liquor suspended solids
mM	multimolar
MPa	megapascal
MPIC	mobile phase ion chromatograph
MPDM	3-methyl-2,2’,4,6,'-pentanitrodiphenylmethane
MW	molecular weight
N	normality
NB	nitrobenzene
O.I.	Oceanographic International
O&M	operations and maintenance
Oral-rat	oral toxicity to rats
PAC	powdered activated carbon
PACT	powdered activated carbon treatment
PO_2	oxygen pressure
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
RCRA	Resource Conservation and Recovery Act
RDX	cyclotrimethylene
$RO^{\bullet}$	alcoxy
$ROO^{\bullet}$	peroxy
ROOH	organic hydroperoxide
RPIPC	reverse-phase ion-pairing chromatography
RT	reaction time
SARM	Standard Analytical Reference Materials
SEX	1,-aceto-3,5,7 trinitro 1,3,5,7 tetriazo cyclooctane
SOP	standing operating procedure
SOS	sum of squares
S.T.	set temperature
T	temperature
t	time
TAX	1,-aceto-3,5, dinitro 1,3,5-triazo cyclohexane
TBA	tetrabutyl ammonium
TBAOH	tetrebutyl ammonium hydroxide
TF	toxicity factor
TLC	thin layer chromatography
TNAB	3,3’,5,5’-tetranitroazoxybenzene
TNB	1,3,5-trinitrobenzene
TNBA	trinitrobenzoic acid

TNBAL	trinitrobenzaldehyde
TNBOH	trinitrobenzyl alcohol
TNM	tetranitromethane
TNT	trinitrotoluene
TOC	total organic carbon
TS	total solids
TVS	total volatile solids
USACERL	U.S. Army Contruction Engineering Research Laboratories
USAEC	U.S. Army Environmental Center
USAEHA	U.S. Army Environmental Hygiene Agency
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet radiation
VIS	visible light
VOC	volatile organic compound
VSS	volatile suspended solids
WAO	wet air oxidation

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