

**Technical Report**

**CRWR 238**

**A SURVEY: DESTRUCTION OF CHEMICAL AGENT  
SIMULANTS IN SUPERCRITICAL WATER OXIDATION**

**by**

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## ABSTRACT

The supercritical water oxidation (SCWO) process exhibits distinct advantages for destruction of toxic wastes. Examples of these wastes are two chemical agent simulants, dimethyl methylphosphonate (DMMP) and thiodiglycol (2,2'-thiodiethanol). DMMP is similar to the nerve agent GB Sarin in structure, and thiodiglycol is a hydrolysis product of the blister agent HD Sulfur Mustard. Both simulants are miscible in water and relatively non-toxic in comparison to the actual chemical agents.

Using a laboratory-scale, batch reactor, three temperatures were investigated: 425°C, 450°C, and 500°C using an initial concentration of one percent by volume, (11,450 mg/L, of DMMP and 12,220 mg/L of thiodiglycol). Residence times investigated were: 1, 2, 3, 6, and 8 minutes. Reactor heat-up (H.U.) was determined to be one minute. Both pyrolysis and oxidation tests were conducted. Oxygen levels were uniformly set at 200% of stoichiometric requirements for the parent compounds. The pressure was calculated as a function of reactor temperature and density. In these studies, the density was kept constant to provide a larger sample volume while continuing to achieve supercritical conditions. Both the mass and the sample volume remained constant. The performance of the SCWO system was evaluated as follows: measurement of total organic carbon destruction by TOC analyses; determination of effluent sulfate and phosphate concentrations by ion chromatography analyses; and monitoring the pH.

Increases in reactor residence time and temperature resulted in greater destruction of TOC for DMMP and thiodiglycol. The rate and degree of thermal destruction (pyrolysis), oxidation, and hydrolysis, as based on TOC and for similar conditions, were greater for thiodiglycol as compared with DMMP. The strength of

the P-methyl bond in DMMP was suggested as the reason for this greater TOC destruction.

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## 1.0 INTRODUCTION

With the drawdown of military forces and weaponry, the disposal of weapons and associated hazardous wastes requires serious attention. The development of capable technologies to treat and dispose of such unique wastes is a difficult task. There are no treatment methods currently in use that are both scientifically and publicly accepted.

With immediate action necessary to handle the disposal problem, the federal government passed wide-ranging legislation. Initially, the U.S. Congress passed the National Environmental Policy Act (NEPA) in 1985, Public Law 99-145, requiring the Department of Defense (DOD) to destroy the stockpile of chemical munitions by September 30, 1994 (Carnes, 1989). The U.S. Army acting as the executive agent for the DOD and the lethal munitions arsenal established the Program Manager for Chemical Demilitarization (PM Cml Demil) to implement a disposal program (Carnes, 1989). After evaluating the problem, the Army informed the Congress in 1988 that disposal of the arsenal would be delayed until 1997. The Congress extended the deadline until April 1997 (Capaccio, 1990). The Army indicated that the additional experience gained from monitoring the chemical weapon destruction facility on Johnston Atoll in the Pacific Ocean would aid in the design of similar systems in the continental U.S. (CONUS) (Carnes, 1989). In 1990, the Army requested a second extension due to operational difficulties at Johnston Atoll (Capaccio, 1990). These delays resulted in further program extensions, 1999 or later (Picardi et al., 1991).

There were also international deadlines agreed upon by the United States and the former Soviet Union. These countries initiated agreements to reduce chemical agent stockpiles to 5,000 tons over a ten-year period, beginning in 1992 (Ember, 1990). The development and reduction in nuclear arsenals over the past five to ten years created the need for safe and innovative waste disposal technologies.

There are eight locations in the continental U.S. where chemical weapon stockpiles exist. These locations are: Umatilla Depot, Oregon; Tooele Army Depot, Utah; Pueblo Depot, Colorado; Pine Bluff Arsenal, Arkansas; Anniston Army Depot, Alabama; Newport Army Ammunition Plant,

Indiana; Lexington Blue Grass Army Depot, Kentucky; and Aberdeen Proving Ground, Maryland (Ember, 1990). Also, there are stockpiles at Johnston Atoll in the central Pacific Ocean which received the stockpiles from the Federal Republic of Germany, November of 1990 (Picardi et al., 1991). Tooele Army Depot, contains the largest percentage of chemical munitions, 42% by agent tonnage. Due to the diverse geographic distribution of these stockpiles and the difficulties in transporting such wastes to a centralized location, the need is apparent for cost-effective mobile or local treatment systems.

Supercritical water oxidation (SCWO) is an innovative waste treatment technology and subject to engineering design considerations, has great potential for adaptation as an effective system for destroying chemical agents. SCWO conditions occur above the supercritical point of water which is 374°C and 22.1 MPa. The increased solubilities of organic compounds in supercritical water make SCWO a unique environment for treating organic wastes. SCWO operates as a closed system that allows for complete control of the effluent.

Experimental investigations require the use of chemical agent simulants due to the toxicity and exorbitant cost of testing with the actual chemical agents. The expense is due to the safety precautions that must be taken to test these wastes. Safety concerns in any future full-scale treatment of the chemical agents with SCWO will necessitate a remotely controlled treatment system. A malfunction at a full-scale SCWO system treating chemical agent or propellant wastes may result in serious injury or loss of life. Handling such unique wastes requires extensive testing. Therefore, pilot-scale testing of a waste treatment system is an important part of system development.

A limited amount of treatability data involving chemical agent simulants are available. Additional data are needed before a full-scale SCWO plant can be designed to treat chemical agent and propellant wastes.

## **1.1 Objective**

The objective of this study was to evaluate the effectiveness of SCWO as a viable treatment option for chemical agent wastes. Specifically, the purpose was to test the potential destruction of two chemical agent simulants, DMMP and thiodiglycol. A secondary objective was to analyze the relevant

literature as to: 1) characteristics of chemical agents and propellants and 2) available disposal alternatives.

## 1.2 Scope

Two chemical agent simulants, dimethyl methylphosphonate and thiodiglycol, were selected. Batch tests were conducted with U-tube reactors and a fluidized sand bath heater. The following influent and effluent characteristics were measured:

- 1) total organic carbon (TOC);
- 2) phosphate and sulfate, respectively, for DMMP and thiodiglycol using an ion chromatograph; and
- 3) pH.

The test conditions and procedures were limited to variations of temperature, reactor residence time, pressure, and oxidant. Three temperatures (425°C, 450°C, and 500°C) and four reactor residence times (one, two, three, six, and eight minutes) were used. A heat-up period of one minute was selected based on a temperature calibration of the sand bath and temperature profiles obtained during preliminary test runs. The reactor residence times do not include the heat-up time. The pressure was calculated as a function of temperature while the density remained constant with no change in the mass or volume. Oxygen, 200% stoichiometric, served as the oxidant. To measure thermal destruction, pyrolysis tests were also conducted for the three minute residence time at each temperature. Initial concentration of the parent compounds was limited to a one percent by volume solution or 11,450 mg/L for DMMP and 12,220 mg/L for thiodiglycol. To evaluate reproducibility of technique and analyses, duplicate samples were obtained for every test at one, two, and three minute residence times. If the relative percent difference (RPD), calculated based on the percent organic carbon removed, varied by as much as  $\pm 10\%$  for any duplicate test, a third test was performed. The performance of the SCWO system was evaluated by 1) measuring the destruction of total organic carbon using a TOC analyzer, 2) determining the effluent sulfate and phosphate concentrations using an ion chromatograph, and 3) monitoring the pH.

### 1.3 Rationale

Chemical agents and propellants are extremely hazardous substances and require destruction prior to disposal. The currently accepted technology is incineration. However, the public has questioned this technology and put increasing pressure on the DOD to explore alternative methodologies. The greatest concern with incineration is the release of oxidized by-products and toxic contaminants to the atmosphere. This concern has expanded the opportunities for alternative technologies. Undoubtedly, there will be a continued role for incineration in waste disposal, but the search for more efficient and economical methodologies must continue.

SCWO has the capability to fulfill stringent requirements for the treatment of specific chemical agent and propellant wastes. Although SCWO cannot destroy the casing materials that contain these weapons, SCWO does have the capability of destroying the actual chemical agents and propellants, and based on preliminary studies, is cost-effective. Therefore, a mobile SCWO treatment unit specifically designed and constructed for the destruction of chemical agent and propellant wastes would serve a useful purpose. A mobile treatment unit would allow for the movement of the unit to any of the eight sites in the contiguous U.S. that currently store chemical agents or to the sites where propellant wastes are targeted for destruction. The DOD has initiated multiple programs to develop pilot plants and mobile systems especially designed to destroy toxic, propellant, and chemical agent wastes (Shaw et al., 1991).

## 2.0 LITERATURE EVALUATION

The literature evaluation provides an overview of SCWO and a general characterization of selected munitions wastes. The advantages for using SCWO for the destruction of chemical agent and propellant wastes are discussed. Two chemical agent simulants, DMMP and thiodiglycol, are described and reasons for choosing each surrogate are presented. Treatment alternatives for the destruction of these wastes are evaluated. A summary of SCWO research and alternative technologies provides a basis for process evaluation. Finally, future directions for the treatment of chemical agent and propellant wastes are considered.

### 2.1 Supercritical Water Oxidation

For the destruction of organic wastes containing less than 20% by weight organics, SCWO becomes a viable alternative to such traditionally accepted practices as incineration and carbon adsorption (Thomason and Modell, 1984). One of the unique properties of a supercritical fluid is that it is a single-phase medium. This phenomenon occurs because the gas and the liquid phases, become more and less dense, respectively, as the temperature increases. When this distinction is no longer apparent, the critical point of the fluid has been reached and substances are referred to as "supercritical" fluids (Shaw et al., 1991). As shown in Figure 2-1, the supercritical fluid region for water occurs at 221 bars (22.1 MPa) and 374°C. Complete mixing is possible in this single-phase, supercritical medium, which means that reaction kinetics are not diffusion limited (Buelow et al., 1989). A direct result of these conditions is that SCWO has the capability to treat mixed wastes that may include toxic organic, inorganic, and radiological waste streams (Bramlette et al., 1990).

The SCWO process occurs in a completely enclosed reactor that allows for complete control of the effluent. The majority of reactions are exothermic and the process can be designed to recover process heat or to co-generate electricity (Buelow et al., 1989). The SCWO process has been demonstrated as capable of destroying a number of hazardous organic compounds. These compounds are completely oxidized in the supercritical water, eliminating the need for auxiliary off-gas processing (Thomason and Modell, 1984).

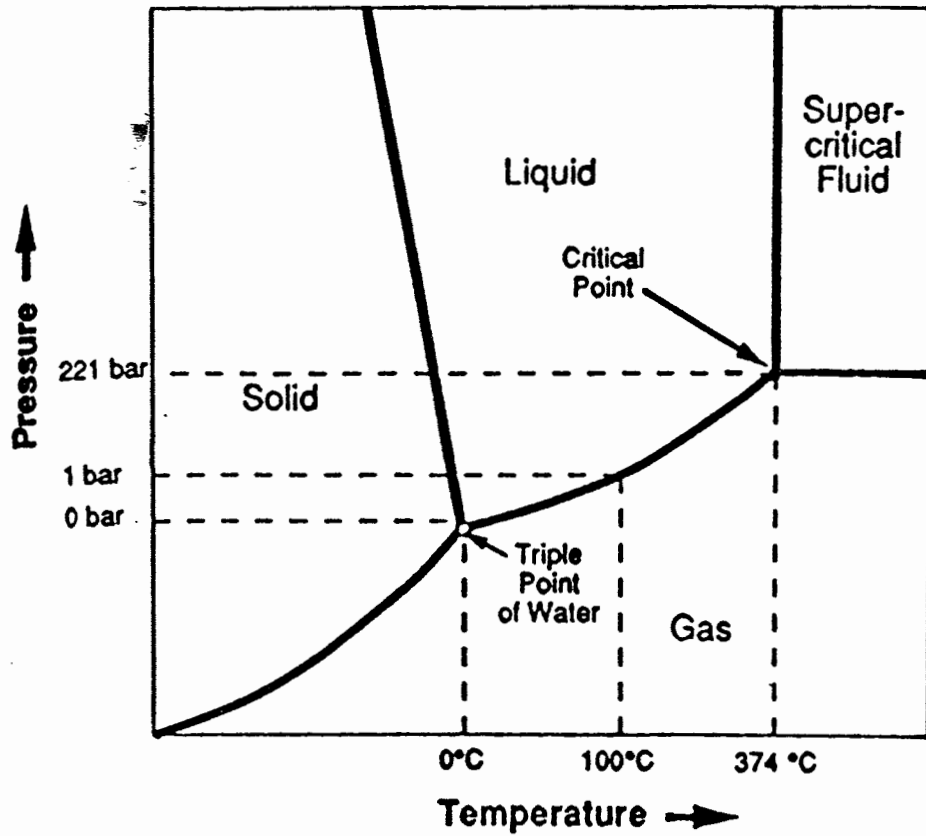


Figure 2-1. Phase Diagram for Water  
(Josephson, 1982)



Sometimes organic compounds and oxidizers are converted to simple, less toxic compounds (Buelow et al., 1989). The product of organic carbon destruction is an inorganic form of carbon, carbon dioxide ( $\text{CO}_2$ ) (Buelow et al., 1989). Hydrogen ions ( $\text{H}^+$ ) will combine to form water molecules, nitrogen will react to produce ammonia ( $\text{NH}_3$ ) and dinitrogen ( $\text{N}_2$ ), phosphorus will revert to phosphoric acid ( $\text{H}_3\text{PO}_4$ ), sulfur will react to form sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and halogenic compounds will produce their corresponding halogen acids (Buelow et al., 1989). Typical oxidants used in SCWO are oxygen ( $\text{O}_2$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Oxidants are more effective under SCWO conditions because the single-phase, SCWO medium has no surface tension; this allows the oxidant to penetrate much smaller pores than possible under standard conditions for water. The result is complete oxidation of organic materials (Freeman, 1989).

Other important characteristics are associated with supercritical phenomena. For example, the dielectric constant measures the degree of molecular association (Thomason and Modell, 1984). Water has a fairly high dielectric constant, 78.5, at  $25^\circ\text{C}$  and one atm, due to hydrogen bonding (Shaw et al., 1991; Thomason and Modell, 1984). This value drops sharply as the temperature of water increases while the density remains fairly constant up to the critical point. At the critical point of water, the density falls off rapidly and the dielectric constant of water is five (Thomason and Modell, 1984). A low dielectric constant means a reduced level of hydrogen bonding as a result of the increased thermal energy contained in the water molecules (Freeman, 1989). The result is that in supercritical water, nonpolar organic compounds are miscible while salts are immiscible.

Another significant advantage with SCWO is the rapid increase in oxidation kinetics above the critical point of water. The oxidation kinetics are a function of reactor residence time and temperature. With increasing reactor residence time and temperature, there is a corresponding increase in the oxidation kinetics and therefore, increased conversion of organic matter to inorganic end-products.

SCWO design must consider corrosion and salt characteristics. The corrosion problems result from the high temperature and aggressive SCWO reactor environments. Salts containing chloride, sulfate, or carbonate appear

to present the greatest difficulties (Barner et al., 1991). However, precipitated oxide solids do not adhere to surfaces as readily. A tubular reactor has been found to be effective in controlling the generation and adherence of salts and solids while producing beneficial flow properties.

## 2.2 Characterization of Problem Wastes

The disposal of propellant and chemical agent wastes poses a unique problem. Recent legislation mandates the eventual destruction and disposal of the munitions. The difficulty lies in finding a disposal method effective enough to satisfy an increasingly sensitive public. Open burning of weapons containing propellants has resulted in disapproval from those concerned about the release of possible toxic emissions. Future methods of disposal must limit toxic emissions and, in particular, find ways to treat gaseous reaction products. Another consideration is the age of many munitions containing propellants. With each passing year, the risk of munitions exploding unexpectedly increases.

Similarly, the age of chemical agent munitions approaches the age of propellant munitions. The production of chemical weapons came to a halt in 1969 upon an Executive Order from President Nixon (Carnes, 1989). Age estimates of chemical munitions vary between 21 to 45 years (Capaccio, 1990). Little is known about the physical-chemical changes that have occurred during storage. The possibility of leaking chemical munitions heightens the concerns of the public and the lawmakers who represent them (Capaccio, 1990). The Bush administration promised the Germans that the removal of chemical weapons would be accelerated by two years. This promise has made the chemical agent stockpile destruction program a high priority item (Capaccio, 1990).

### 2.2.1 Propellant Wastes

There are three components of solid rocket propellants: fuel, oxidizer, and binder. These three components contain mixtures of low molecular weight prepolymers (i.e., less than 2,000 g/mole), curatives, plasticizers, bonding agents, stabilizers, aluminum fuel, and oxidizer salts (Schreuder-Gibson, 1979). Solid rocket propellants represent the majority of propellant wastes. Liquid rocket propellants represent a smaller fraction and do not contain the rubbery binder of solid rocket propellants.

There are three classes of propellants; single, double, and triple-base propellant mixtures (Wang et al., 1982). The problems with the disposal of these wastes are their unstable and corrosive characteristics. Bondline failures in the solid propellant rocket motors have been reported due to rapid chemical changes, processing problems, and the accumulation of damaging stress (Schreuder-Gibson, 1979). The existing sources of propellant wastes requiring disposal include 1) existing stockpiles, 2) on-going production, 3) remanufacturing programs, 4) excess missile inventory disposition, and 5) the excess weapons resulting from the Strategic Arms Reduction Talks (START) (Rofer and Wander, 1989). The major concerns in the disposal of propellant wastes are impact on the environment, the aging of weapons containing propellants, treaty provisions which may override other considerations, the reclamation of the contents of the propellant wastes, and the possible reuse of the weapon containing the propellant (Rofer and Wander, 1989).

Before the treatment of the propellant waste can be accomplished, the solid fuel contained in the solid rocket propellant requires removal. To remove the solid fuel, a rubber-like material, from solid rocket propellants, researchers have found success in spraying or immersing the solid fuel with cold liquid nitrogen that reduces the solid fuel to a powder. The use of a high-pressure stream of hot water has also been investigated, but the presence of nitroglycerin that may explode under the application of the heat restrains the applicability of this method. Previous methods of removing the solid fuel used a high-pressure stream of cool water, but these were inefficient (Broad, 1991). Safe and more effective methods of removing the solid fuel from solid rocket propellants are needed.

Major constituents of propellant manufacturing processes include nitrocellulose (cellulose nitrate), nitroglycerin (glyceryl trinitrate), 2,4,6-trinitrotoluene (TNT), and phosphorus. Nitrocellulose is a principal ingredient in single-, double-, and triple-base propellants. Nitrocellulose, an original compound in single-base propellants, is combined with nitroglycerine to form double-base propellants, and it is combined with nitroglycerin and nitroguanidine to form triple-base propellants. To manufacture nitrocellulose, 16 to 22 gallons of process water are required to produce one pound of nitrocellulose (Wang et al., 1982). The resulting wastewater contains significant concentrations of fine particles of

nitrocellulose and nitric and sulfuric acids. The fine particles of nitrocellulose are not water-soluble and occur as colloids in wastewater; this makes physical-chemical treatment necessary before the waste can enter a biological treatment system.

Nitroglycerin is a principal ingredient in double- and triple-base propellants. Nitroglycerin is soluble in water to 1800 mg/L at 25°C and is miscible in the majority of organic solvents (Wang et al., 1982). Nitroglycerin manufacturing occurs in either a batch or a continuous process. The batch process requires about 0.50 gallons of process water/lb nitroglycerin produced. The continuous process requires 2.5 gallons of process water/lb nitroglycerin produced (Wang et al., 1982). The TNT manufacturing process, including phosphorus addition, requires additional amounts of process water similar to that required for nitrocellulose and nitroglycerin.

The current industrial process for dealing with propellant wastes involves removal, collection, transportation, recovery and reuse, disposal and destruction, and residue disposition (Rofer and Wander, 1989). The current techniques of disposing of propellants are open pit burning, use of a detonation chamber, and static firing of the weapons containing propellants. In the 1970s, open pit burning and detonation were used to dispose of 68 million lbs/yr at 54 separate facilities (Rofer and Wander, 1989). Although open pit burning and detonation have been the lowest cost disposal methodologies, these processes have become unacceptable because of their transportation, storage, and environmental impacts. Currently, for unstable materials, a detonation chamber is the only available method (Rofer and Wander, 1989). The detonation chamber method is not capable of disposing of large quantities of propellant wastes, and there are safety concerns. The static firing of weapons containing propellant presents environmental concerns similar to that of open pit burning and detonation. Additionally, the high cost and inadequate potential for substantial inventory reduction eliminate static firing as an alternative (Rofer and Wander, 1989).

Techniques that have shown potential for the disposal of propellants in the next five years are incineration and the use of solvent extraction (Rofer and Wander, 1989). Incineration occurs in any of three types of incinerators, which include: 1) the rotary kiln, 2) the fluidized bed, and 3) molten salt incinerators (Rofer and Wander, 1989). High destruction efficiencies of

propellant wastes are achievable with incineration temperatures exceeding 2000°C, but the recurrent problems with incineration have hurt its acceptance among many in the public. Air emissions are a major concern with incinerators and often require air pollution control measures to treat the stack gases. These measures often take the form of air scrubber or air stripping equipment. With the current push for cleaner air, propellant waste disposal through incineration techniques may be limited. Other problems with incineration include corrosion and the possibility of detonations within the incinerator leading to equipment damage.

Solvent extraction attempts to reclaim the valuable materials in propellant munitions. The difficulty is that the valuable materials are present only in trace quantities. Also, the reuse of many constituents in propellants is currently prohibited.

Potential propellant waste disposal methodologies during the next five to ten years are solvolysis and wet air oxidation (WAO). Solvolysis is a process that uses organic solvents to convert the wastes to a form that is acceptable for existing wastewater treatment. The major difficulty with solvolysis is the required long reaction time (Rofer and Wander, 1989). WAO is a demonstrated technology in the area of municipal sludge treatment. The difficulties with the WAO process are the long retention times and oxidation rates of insoluble ingredients (Rofer and Wander, 1989).

Other technologies that could play a significant part in the future disposal of propellant wastes include biodegradation, ozonolysis, peroxide oxidation, and SCWO (Rofer and Wander, 1989). Biodegradation is a cost-effective approach but cannot achieve the necessary destruction efficiencies for the disposal of propellant wastes. Also, at high enough concentrations, certain components of propellant wastes are toxic to microorganisms. Ozonolysis and peroxide oxidation require long retention times, which limits their future applicability. However, before the implementation of any disposal technique, the following considerations must be evaluated: safety, economics, operability, environmental regulations, legal ramifications, and the compliance with political mandates such as existing treaties (Rofer and Wander, 1989).

The current objectives of studies in the destruction of propellant wastes

using SCWO include 1) safe loading of propellant components into an SCWO reactor, 2) determination of destruction efficiencies, 3) evaluation of reaction products, and 4) reaction rate studies (Buelow et al., 1989). SCWO of aqueous propellant wastes has the ability to sustain a high degree of reaction and to recycle the energy content. SCWO performance with energetic materials requires verification, and a number of reaction rate models require validation (Rofer and Wander, 1989).

Tests with propellant wastes under SCWO conditions have shown over a 99.8% destruction of ammonium perchlorate, a compound often present in propellant wastes, with a residence time of 15 seconds at a temperature of 500°C (Buelow et al., 1989). Over 99% destruction of nitromethane, another ubiquitous component of propellant wastes, at 500°C with a residence time of 30 seconds has been achieved (Buelow et al., 1989). Both compounds have been destroyed by SCWO without an explosive energy release (Buelow et al., 1989).

The distinct advantage of SCWO is its ability to use oxygen rather than air. A concentrated oxidant minimizes the quantity of gaseous effluent requiring disposal. The Modell Development Process claims the ability to eliminate particulate emissions and acid gases using in situ scrubbing techniques (Modell, 1991). Similarly, Eco Waste Technologies addresses important design considerations concerning solid, liquid, and gas separation, corrosion control and other design requirements (Eller, 1992).

Tables 2-1 and 2-2 provide an overview of some of the typical constituents of solid rocket propellants. A large fraction of the solid propellants consists of complex organic chemicals and explosive chemicals such as nitroglycerin. It is possible to remove the binder for separate treatment. This action may be required due to the explosive nature of the binder materials. The oxidizer contains ammonium perchlorate, which is extremely reactive and explosive. The fuel, typically an aluminum powder, does not pose serious treatment problems.

### 2.2.2 Chemical Agent Wastes

The U.S. stockpile of chemical agents includes the organophosphate (OP) or nerve agents G(German)A Tabun, GB Sarin, and VX, and the vesicant or blister agents H, HD, HT, and Lewisite, which are different forms of sulfur

**Table 2-1. Main Components of Class 1.1 Composite  
Propellant--Composite Modified Double-Base (CMDB) (O'Brien, 1991)**

<u>INGREDIENTS</u>	<u>WEIGHT (%)</u>
<b>Fuel:</b>	
Powdered Aluminum	18.0
<b>Oxidizer:</b>	
Ammonium Perchlorate	4.0
HMX	52.5
<b>Binder:</b>	
Nitroglycerin	17.67
Polyethylene Glycol	5.86
Nitrocellulose	0.06
Aliphatic Polyisocyanate	0.7
NMNA	0.56
Carbon Black	0.5
2-NDPA	0.15

**Table 2-2. Main Components of Class 1.3  
Composite Propellant--HTPB and PBAN (O'Brien, 1991)**

<u>INGREDIENTS</u>	<u>WEIGHT (%)</u>	
	HTPB	PBAN
<b>Fuel:</b>		
Powdered Aluminum	20	16
Iron Oxide	0.9	0.23
<b>Oxidizer:</b>		
Ammonium Perchlorate	68.1	67.77
<b>Binder:</b>		
HTPB Prepolymer	8.05	
IsoDecyl Pelarginate	2.0	
Isophorone Diisocynate	0.545	
HX-752	0.3	
Protech 3105	0.1	
Triphenyl Bismuth	0.005	
PBAN Prepolymer		10.076
DER-332 Epoxy		2.956
Diocetyl Adipate (DOA)		2.4
Nadic Methyl Anhydride		0.568



mustard (Watson et al., 1989). The lethality of nerve agents based on a dose or concentration value is much greater as compared to the blister agents. Blister agents are carcinogens and as such, pose potential long-term health problems if accidental exposure occurs. The chemical munitions stockpile in the U.S. is estimated at greater than 25,000 tons (Carnes, 1989).

The configuration of munitions while in storage is in either an explosive or non-explosive mode depending on its wartime function. Bulk containers represent 60% of the stored tonnage (Carnes, 1989). Ton capacity containers, spray tanks, and bombs are examples of bulk containers. Examples of explosive configurations are M55 rockets, M23 land mines, mortars, cartridges, and projectiles (Carnes, 1989). The explosive configurations are kept in earth-bermed bunkers or igloos. Ton-capacity containers, used to store mustard agents are stored in the open, this storage of mustard agents is the only open-air munition storage in the U.S. (Carnes, 1989).

Table 2-3 outlines some of the physical properties of the principal chemical agents. The high variability of these properties is an underlying problem in designing an effective disposal system. For example, GB is miscible in water at 25°C while VX and HD, respectively, require a dilute mineral acid and an organic solvent to improve solubility levels. Although the heterogeneity of chemical agents represents a significant problem, mixed hazardous waste streams occasionally found at superfund sites pose even greater problems.

The solids content of an agent may present a problem in SCWO. Solubilization of the agents may be necessary before entry into the SCWO reactor. For example, VX has a heat of combustion that is three times higher than HD or GB, and this large variation could cause overheating and reduced operating efficiency.

### **2.3 Chemical Agent Simulants**

The selection of a chemical agent simulant involves mirroring, as closely as possible, the physical and chemical properties of the chemical agent. The most probable choices, based on chemical properties, are the hydrolysis and thermal decomposition products of the chemical agents. Simulants with similar physical properties are necessary to accurately depict initial mixing and mass transfer during heat-up and the reaction period (Carney, 1991). For

example, since GB is completely miscible in water, the simulant also should be equally miscible in water.

**Table 2-3. Select Physical Properties of Chemical Agents**  
(Carney, 1991)

	<u>GB</u>	<u>VX</u>	<u>HD</u>
Molecular Weight	140.1	267.4	159.1
Boiling Point (°C)	158	298	218
Freezing Pt. (°C)	-56	-39	14.5
Heat of Combustion (kcal/mole)	784	2254	756
Density (g/ml) <sup>a</sup> @ 25°C	1.09	1.01	1.27
Solubility in Distilled Water (g/100g) @25°C	miscible	3.0 7.5 @ 15°C miscible < 9.4°C	0.092
Best Solvent	N/A	dilute mineral acid	organic solvent
Readily Soluble	N/A	organic solvent	92.5% ethanol at > 28.6°C acetone

The critical properties of concern in selecting a chemical simulant include density, viscosity, molecular weight, and solubility (Carney, 1991). Similarly, the critical property in the simulation of the appropriate homogeneous or heterogeneous conditions during initial mixing and heat-up is solubility. The homogeneity or heterogeneity of a chemical agent will differ based on its solubility in water or an organic solvent. Certain chemical simulants may have to be studied as a slurry, which would result in a more heterogeneous mixture. Both chemical agent simulants selected for this study are miscible with water at 25°C.

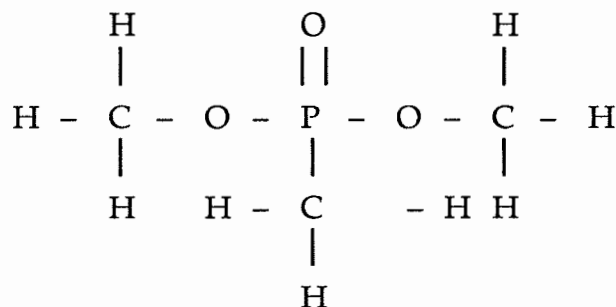
Density and viscosity, along with the diffusion coefficient, help determine diffusion. The diffusion coefficient is a function of molecular weight, molar volume, and ionic mobility (Carney, 1991). Density and viscosity are the physical properties that characterize the flow conditions. The

high dilution and rapid destruction of inorganic reaction products, as well as the general properties of supercritical water, will determine the density and viscosity of fluid in the reactor. The chemical structure of the simulant should include the most difficult cleavage groups of the actual agent. For example, GB Sarin contains phosphorus-methyl (P-CH<sub>3</sub>) bonds, which are difficult to cleave, and the simulant, dimethyl methylphosphonate (DMMP), also contains P-methyl bonds.

Previous SCWO research, Section 2.5.1, suggests that the effective reaction rate is mass transfer limited rather than kinetic. A mass transfer limited reaction rate places less emphasis on precise simulation of chemical structure and more emphasis on obtaining the characteristic physical properties responsible for diffusional and hydrodynamic processes (Carney, 1991).

### 2.3.1 Dimethyl Methylphosphonate

Dimethyl methylphosphonate is analogous in structure and molecular weight to GB Sarin and is relatively non-toxic in comparison to the actual agent. DMMP is the transformation product of all chemical agents and their associated decomposition products containing the P-methyl bond (Verweij et al., 1985). The molecular formula for DMMP is C<sub>3</sub>H<sub>9</sub>O<sub>3</sub>P. The compound has the following structure:



The presence of phosphorus in DMMP permits investigation of this heteroatom. However, DMMP does not contain fluorine. GB Sarin does contain fluorine and will present challenging corrosion problems and a different set of physical and chemical interactions. Specifically, the phosphonate structure will be dissimilar in GB Sarin due to differences in the



## 2.4 Treatment Alternatives

Treatment alternatives exist for the destruction of chemical agent and propellant wastes. The treatment alternatives for propellant wastes were discussed in Section 2.2.1. Incineration was adopted as the preferred method of disposing of chemical agents in 1982 (Picardi et al., 1991). However, this policy is under review. The Army's previous claims were that biodegradation, nuclear detonation, etc., were "problematic" and "premature" methods not worthy of consideration (Carnes, 1989). However, recent studies indicate that the incineration of these wastes may present some special problems. Incineration requires rigorous control over the fire box, secondary chambers, air cleaning systems, and solids disposal. Also, it is nearly impossible to transport these toxic munitions across state and local governmental boundaries. Treatment alternatives to supplement incineration are under development and will help ease the amount of wastes requiring treatment by incineration methods.

### 2.4.1 Supercritical Water Oxidation

Many researchers believe SCWO, as compared to incineration, can treat aqueous waste streams at a substantial reduction in cost (Modell, 1991). One estimate involving an aqueous hazardous waste, (which has a total organic carbon content of 100,000 mg/L) suggests that incineration would cost \$0.35/gallon whereas, SCWO would cost \$0.10/gallon (Modell, 1991). SCWO operates at temperatures of 400°C to 600°C as compared to 1000°C to 1500°C for incineration. The SCWO process is also capable of recovering exothermically developed process heat.

Aqueous waste streams susceptible to SCWO treatment include a host of liquid organic wastes and biological or organic sludges. Additionally, SCWO can accommodate incinerator stack scrubbing liquors, chemical agent equipment wash waters, and mixed low-level radioactive wastes. There are also advantages to treating chemical agents and propellants in an aqueous waste stream. For propellant wastes, dispersion of ammonium perchlorate and nitroglycerin in an aqueous stream promotes extraction of these compounds (Modell, 1991). The hydrolysis of chemical agents will result in the production of hydrolysis products that are far less toxic than the original agent (Modell, 1991). For example, thiodiglycol is a natural hydrolysis product

of HD Sulfur Mustard and represents a substantial reduction in toxicity of the original chemical agent.

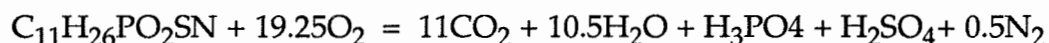
Another significant advantage of SCWO over other treatment technologies is that SCWO operates under homogeneous, single-phase conditions. These conditions promote excellent mixing along with elevated mass and heat transfer rates in the reaction vessel. In addition, the presence of solids in the reactor is not thought to be of concern by some researchers, which would alleviate one of the potential problems with the SCWO system (Carney, 1991).

Destruction of chemical agents or their simulants may occur due to hydrolysis, thermal decomposition (pyrolysis), and oxidation. The first stage of this destruction will involve the conversion to lower molecular weight compounds, which will occur during the heat-up period (Carney, 1991). The predominant destruction mechanism will differ for each chemical agent due to varying molecular structures. The following reactions are the predicted oxidation reactions for GB, VX, and HD under SCWO conditions:

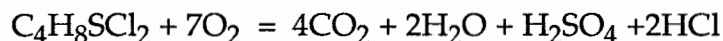
**GB:**



**VX:**



**HD:**



(Modell, 1991).

The preceding expected oxidation reactions of the chemical agents suggest that corrosion is a major concern. All three reactions produce strong acids. Production of phosphoric, sulfuric, and hydrochloric acids are all expected in the oxidation reactions, and consequently the pH will be lowered. SCWO of GB, VX, and HD will require special corrosive-resistant materials. The final inorganic products are the precursors of the corrosion problem and include  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{NH}_3$ , and  $\text{CO}_2$  (Carney, 1991). A reaction mixture with a pH of less than one is not uncommon and requires

neutralization before discharge to the environment.

GB is completely miscible with water; VX has a limited solubility; but HD is nearly insoluble. Solids may present a challenge in SCWO. Therefore, in some cases the solubility of the agents must be increased before they enter the reactor. A water-miscible organic solvent or surfactant may be necessary to improve the solubility of the agents VX and HD (Carney, 1991).

#### 2.4.2 Biological

Biological processes include the biodegradation of chemical agents and the use of bioreactors. The biodegradation of chemical agents is in the laboratory stage of development. For example, at the Sunflower Army Ammunition Plant in Desoto, Kansas, pilot- and bench-scale biological treatment systems are being tested for the treatment of an explosive nitroguanidine waste (Picardi et al., 1991). Bioreactors for the destruction of chemical agents have been successfully demonstrated on a pilot scale and are in the production stage of development.

Biological methods are applicable only to wastes consisting of organic substances such as the organophosphorous nerve agents. In particular, the biological degradation of the nerve agents Soman and Sarin has been demonstrated by using immobilized enzymes from microorganisms and invertebrates (Picardi et al., 1991). The direct C-P bond is a rare, nonreactive bond existing in unsubstituted alkyl- and aryl-phosphonate nerve agents and is the cause of conjecture about the effectiveness of biological methods. The C-P bond resists cleavage by the microorganisms often capable of degrading complex organic molecules with their enzyme systems. Also, at high enough concentrations, chemical agents are toxic to microorganisms. Clearly, the capability of biological methods to destroy chemical agent wastes is not proven. Even the widest use of biological methods to destroy chemical agent wastes would apply to only a small percentage of the overall stockpile.

#### 2.4.3 Chemical

Chemical processes under development include the following: 1) SCWO and WAO, 2) Synthetica steam gasification process, 3) molten salt reactor, 4) metallic couples, 5) dechlorination, 6) Goodyear Sodium Naphthalide Process, 7) Acurex Process, 8) Sun Ohio PCBX, and 9) the Galson

Remediation technologies (Picardi et al., 1991). The SCWO process was discussed in detail in Section 2.4.1. Technologies 4) through 9) are either at the early stages of development or their practical application to chemical agent wastes are not yet determined.

To achieve an acceptable level of destruction with chemical processes, a combination of processes will be necessary. For example, the Synthetica steam gasification process can operate in a field mode with a variety of liquid and solid waste feeds by exposing the vaporized waste to superheated steam. The Synthetica steam gasification process could serve to detoxify chemical munitions and their casings but produces toxic emissions in the process. The toxic emissions will require further treatment using an exhaust gas scrubber. The SCWO, WAO, and molten salt reactor processes in theory are considered nonspecific according to waste feed, making these processes attractive for further development. In practice, SCWO, WAO and molten salt reactor processes will be limited by organic loading, solids content, economics, etc. The molten reactor process has demonstrated the ability to treat organophosphorous compounds similar in structure to the organophosphorous nerve agents (Picardi et al., 1991).

#### 2.4.4 Photochemical

Two broad categories exist for the classification of photochemical processes; processes designed for treatment of dilute aqueous waste streams and processes designed for vapor waste streams. Photochemical methods have the following perceived advantages: 1) ability to operate using a closed loop system with controlled discharge and 2) potential of vapor phase processes to directly treat undiluted chemical agents. Photochemical applications include: 1) ozonization, 2) ultraviolet radiation (UV), 3) a laser photochemical system, 4) gamma irradiation, 5) the Sandia/SERI Soltox and Photox Processes, and 6) the Sandia/SERI Solcat Process (Picardi et al., 1991). All of the photochemical processes are currently in the laboratory stage of development with the exception of the Sandia/SERI Solcat Process, which is in the pilot-plant stage (Picardi et al., 1991).

Applications for aqueous waste streams typically use sunlight in conjunction with a titanium dioxide ( $\text{TiO}_2$ ) catalyst operating at solar concentration ratios from 1 to 20 and a nearly ambient temperature. The



removal of the  $\text{TiO}_2$  particles from the effluent aqueous waste stream appears to pose the most difficulty.

Processes designed for vapor-phase waste streams operate at solar concentration ratios from 300 to 1,000 and temperatures between  $700^\circ\text{C}$  to  $1100^\circ\text{C}$ . The vapor-phase processes are designed to operate in the absence of catalysis. Processes designed to operate in the vapor phase will require significantly more energy.

#### 2.4.5 Electrochemical

Applications for electrochemical techniques for waste treatment fall under two categories, electrodialysis and electrochemical treatment (Picardi et al., 1991). Electrodialysis involves concentrating the waste stream through removal of ions, which results in a reduced volume of waste. A direct electric current is applied to the waste stream, selectively transporting ions across a semi-permeable membrane. Electrodialysis could be used to remove heavy metal contamination found in chemical agent waste streams and is in the production phase of development.

In electrochemical treatment, organic waste materials and energy supplied to an electrochemical cell use metal ions to act as a coupling agent to oxidize the waste materials. The oxidation occurs in one of two ways: 1) direct electrochemical oxidation reaction of the waste materials at the anode or 2) indirect oxidation through formation of oxidizing species with the addition of  $\text{NaCl}$  or  $\text{HOCl}$ . With indirect oxidation, the  $\text{NaCl}$  or  $\text{HOCl}$  results in the propagation of free chlorine, which functions as the oxidizing species. In addition, indirect oxidation does not restrain the electrochemical oxidation reaction to a two-dimensional interface of waste material and electrode. The disadvantage with indirect oxidation and free chlorine as the oxidizing species is the likely production of chlorinated organics.

Two electrochemical processes under development are the SYDOX Process and AEA Process (Picardi et al., 1991). The SYDOX Process is in laboratory-scale development undergoing catalyzed oxidation reaction testing. Terminal oxidizing agents used in the SYDOX process are hypochlorite and persulfate. Funding for a pilot installation using the SYDOX Process has been requested. The AEA Process is under pilot-plant study. The process involves direct oxidation of organic material at the anode in a highly efficient

electrochemical reaction. The AEA Process has been tested with the organophosphorous solvent tributyl phosphate,  $(C_4H_9)_3PO_4$ , and is able to treat solid waste materials. Uncertainties in its ability to handle chlorinated organics are the source of concern with the AEA Process. For example, vesicant agents Lewisite and Agent T are highly chlorinated, and performance of the AEA Process with these compounds is unpredictable.

#### 2.4.6 Neutralization

In the past, the Army concluded that chemical neutralization, as compared to incineration, would require the disposal of three to four times the amount of hazardous waste. Due to the addition of chemicals required to neutralize the waste. Chemical neutralization required reaction times on the order of days instead of the predicted reaction times, which were in terms of hours. These prolonged reaction times resulted in the need for additional caustic solution, NaOH, which translates into additional cost. Suggestions have been made that the neutralization process might be reversible under certain conditions for the agent GB. No major research-demonstration effort appears to have been undertaken to address this reversibility notion, but it could result in a major drawback for using neutralization.

The only neutralization technologies under development involve the processes of hydrolysis and oxidation (Picardi et al., 1991). Hydrolysis with organic compounds involves a reaction between water molecules and the organic compound whereby hydrogens replace carbon functional groups and hydroxide ions ( $OH^-$ ) are left in solution. The degree of solubility of the chemical agent is the determining factor for use of hydrolysis technology. While GA and GB are miscible with water, the nerve agent VX and mustard agents are characterized by low solubility with water, which constrains the use of hydrolysis. Organic solvents such as monoethanolamine (MEA) are used to increase solubility levels but at the same time can slow the hydrolysis reaction rate.

For oxidation, the Army prefers adding HOCl as the oxidizing agent in an aqueous waste stream for detoxification of mustard agents and the nerve agent VX. Decontamination agents are also added to assist in the propagation of the oxidation reactions and completion of the decontamination process. Sodium hypochlorite, calcium hypochlorite, and the organic N-chloramine

are examples of decontamination agents (Picardi et al., 1991).

Hydrolysis and oxidation technologies are in the production stage of development. Before implementation of hydrolysis and oxidation technologies, a full characterization of end-products must occur in order to ascertain a method to treat process residues. Complete retainment of process residues is the distinct advantage of hydrolysis and oxidation processes.

#### 2.4.7 Chemical Reprocess

Technology applications in the area of chemical reprocess include chlorinolysis and catalytic hydrodechlorination. Chlorinolysis involves exhaustive chlorination using a series of columns containing assorted chlorine-based compounds ( $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{HCl}$ , etc.) at various temperatures and pressures to produce usable raw materials, carbon tetrachloride, and possibly other hazardous compounds. Carbon tetrachloride presents problems due to its atmospheric half life of 40 years and because it is a carcinogen, a contributor to ozone depletion, and a "Greenhouse Gas" (Picardi et al., 1991). The most significant question with chlorinolysis is waste generation and subsequent waste disposal.

The intent of catalytic hydrodechlorination is the production of compounds susceptible to biodegradation through partial or total dechlorination. Solvents, fuels, and chemical intermediates are potentially useful end-products resulting from the process. The applicability of catalytic hydrodechlorination lies with the vesicants or chlorine-based agents. A separation system would be necessary to remove partially dechlorinated end-products. The most encouraging application for catalytic hydrodechlorination is in the hydrogenation and reuse of hazardous organic wastes in the form of petroleum products. Applications to decontaminate chemical agents appear limited. Both of these processes are in the production stage of development (Picardi et al., 1991).

#### 2.4.8 Thermal

Technologies utilizing thermal treatment or heat treatment include: 1) plasma microwave, 2) plasma torch, 3) radio frequency (RF), 4) SHIRCO IR Process, and 5) incineration processes (Picardi et al., 1991). There are inherent dangers in the application of the intense heat necessary to initiate the thermal processes. The explosive nature of munitions may result in severe damage to

thermal process elements. If the explosive contents of the munition can be removed and treated separately, the risk created by the contaminated casing material is minimal.

The plasma microwave and plasma torch technologies are in laboratory-scale development. Liquid and solid organic wastes, refractory organic compounds, and metal-containing wastes can be treated with plasma technologies. Plasma technologies use a process similar to incineration with different methods of supplying process heat. The plasma microwave process uses microwave radiation, and the plasma torch process uses a torch to supply process heat. The shortcomings of plasma technologies are similar to those associated with incineration processes; concern over air emissions and susceptibility to process upsets.

Radio frequency technology uses an RF electrode exciter array containing tubular electrodes placed in the soil. The heating of the soil volatilizes the soil contaminants, which are collected in a cover placed over the area of contamination. After collection of the soil contaminants, further treatment using a separate technology is necessary. RF technology has applications in the treatment of soils contaminated by chemical agents. This process is in the pilot-scale stage of development.

The SHIRCO IR Process uses electrically produced infrared radiation via silicon carbide rods. The process uses primary and secondary combustion chambers and is a refinement of various incineration processes. The SHIRCO IR Process is designed as a mobile unit for operation at remote sites. Before full-scale implementation of the SHIRCO IR Process, problems with air emissions, including the inability to operate in a closed system, must be addressed. Both the SHIRCO IR Process and incineration processes are in the production phases (Picardi et al., 1991).

## **2.5 Previous Treatment**

Chemical agent and propellant waste treatment has a limited history. Chemical neutralization of the nerve agent GB occurred in the mid 1970s. Propellant wastes were disposed of with incineration in the 1970s, and the Army has built two chemical agent disposal facilities, the Chemical Agent Munitions Disposal System (CAMDS) pilot plant at Tooele Army Depot, Utah, and the Johnston Atoll Chemical Agent Disposal System (JACADS).

Prior to 1969, open pit burning, ocean dumping, land burial, and atmospheric dilution of the wastes were accepted treatment methods.

In 1982, the Defense Nuclear Agency proposed destroying chemical agents by using nuclear explosives in an underground cavity (Clark, 1992). The perceived advantages included: 1) no requirement for disassembly or preparation of the agents prior to disposal and 2) no residue disposal. The method was rejected by the Army in favor of incineration.

In 1984, the Army's plan was to construct six demilitarization facilities for munitions targeted for disposal (Sides and Spafford, 1984). For modified munitions (drained of active ingredients) exposed to chemical warfare agents, but a level of decontamination called 3X was required. The 3X level of decontamination can be achieved using chemical decontamination with sodium hydroxide or sodium hypochlorite solutions. After achieving a 3X level of decontamination, the munitions could be cleared for movement between government installations but not for release from government control (Sides and Spafford, 1984). Further decontamination to a 5X level was necessary before release to the public. A 5X level of decontamination could be achieved by heating the materials to 1000°F for 15 minutes. Upon reaching a 5X level of decontamination, the material was considered free of any trace chemical agents and could be released for public use (Sides and Spafford, 1984). The 3X and 5X decontamination processes ran into difficulty. Presently, neither are considered to be acceptable levels of treatment.

### 2.5.1 SCWO

Pilot-scale SCWO systems have demonstrated the capability of destroying hazardous wastes, including chemical agent or propellant wastes. No full-scale SCWO treatment system exists. Bench-scale SCWO studies with chemical agent simulants showed little increase in destruction efficiency with increasing temperature (Carney, 1991). Slight increases in destruction efficiency with increasing temperature indicate mass transfer limited reactions, which include mixing and diffusional processes, rather than kinetically limited reactions.

Brief residence times, less than 10 seconds, have resulted in high destruction efficiencies. For example, a 99.9999% destruction efficiency for the nerve agent VX was achieved in 3.5 seconds at 450°C (Carney, 1991).

However, there is an important distinction between destruction efficiency and complete removal of hazardous compounds. Destruction efficiency is often reported based on the degree of destruction of the parent compound and not for the destruction of potentially hazardous transformation products. Therefore, the level of TOC destroyed is often a better measure of the complete destruction of hazardous organic wastes.

### 2.5.2 Technologies Exclusive of SCWO

More than 6 million lbs of mustard agent and over 8 million lbs of nerve agent GB were chemically neutralized in the early to mid-70s at the Rocky Mountain Arsenal, Denver, Colorado (Carnes, 1989). The U.S. Army Toxic and Hazardous Materials Agency was the agency responsible for the destruction of these agents. The current agency responsible for implementing a disposal program is the Program Manager for Chemical Demilitarization (PM Cml Demil), established by the Department of the Army (DOA). The DOA is the acting executive agent for the DOD in the disposal of chemical agents.

Incineration technology was used to treat propellant wastes at the Radford Army Ammunition Plant in 1972 (Forsten, 1973). The propellant waste was fed as a slurry, 12.5% solids by weight, to the combustion region. About 27,300 lbs of propellants, 1,065 lbs of HMX, and 273 lbs of TNT were disposed of in a rotary kiln incinerator at a feed rate of 250 lbs solids/hr (Forsten, 1973). To facilitate in the preparation of the slurry, a ball mill grinder was used to grind the HMX, TNT, and propellant materials into a uniform particle size.

At Tooele Army Depot, the Army used chlorine as the oxidizing agent to decontaminate the nerve agent VX in 100 lb lots. The munitions were dissolved in 1.5N HCl and chlorine until the formation of a green color. A 99.999999% destruction was reportedly achieved with the conversion of the munitions to drum dried salts (Picardi et al., 1991).

In 1981, testing was conducted with an activated sludge system to biodegrade Agent Orange at the Utah State College of Engineering Water Resource Laboratory (Picardi et al., 1991). Reductions of Agent Orange in the range of 64% to 73% were achieved with aqueous mixtures of Agent Orange at concentrations ranging from 230 to 3,450 mg/L incubated at 18°C.

## 2.6 Present Status

Officially, incineration remains the technology of choice by the DOD to destroy the chemical agent and propellant waste stockpiles. However, public pressure and operational delays with the incinerator currently dedicated to the destruction of the stockpile have forced the DOD to investigate using alternative technologies to assist in the process. SCWO is an alternative technology that has received a significant amount of recent attention. The attention is a result of the capability of the SCWO process to sufficiently destroy hazardous organic wastes while operating in a closed-system configuration at a reasonable cost. Before a full-scale SCWO plant becomes operational for chemical agent destruction, the following engineering tasks need to be addressed:

- design and scale-up of the reactor;
- evaluate salts deposition and scaling;
- select most appropriate construction materials, considering life expectancy; and
- establish environmental and safety requirements (Barner et al., 1991).

## 2.7 Future Directions

If delays and problems continue to slow the incineration of chemical agent munitions, the Army will have to implement an alternative technology for the disposal of the munitions. As a prelude to future disposal difficulties, the Under Secretary of the Army disallowed marine transport of munitions from Aberdeen, Maryland. Concern has been expressed over possible contamination of the Chesapeake Bay in the event of an accident resulting from transportation or handling activities (Carnes, 1989). It has been suggested that site-specific conditions should dictate the applicable technologies. Consideration should be given to the chemical composition and configuration, bulk containers or munitions, at each site. Other factors that should be considered include the site-specific geography, geology, hydrology, and meteorology (Picardi et al. 1991). Public awareness is essential to ensure public trust.

### 3.0 EXPERIMENTAL PROCEDURES

A batch-scale SCWO reactor system and a U-tube reactor were used for all of the treatability runs. The following sections describe the experimental apparatus, procedure, and preliminary calculations.

#### 3.1 Batch Reactor System

The U-tube reactor, as shown in Figure 3-1, was connected to a reactor vessel and shaker assembly. A control switch was used to move the reactor vessel either horizontally or vertically. The horizontal transfer cylinder was used to move the reactor to and from the sand and water baths, and the vertical transfer cylinder transferred the reactor into and out of the sand and water baths. The fluidized sand bath was heated electrically, and temperatures were recorded continuously. Oxygen was added at the beginning of each test. As a safety measure, a shield constructed of transparent, impact-proof polycarbonate sheets surrounds the batch reactor.

#### 3.2 U-tube Reactor

As shown in Figures 3-2 and 3-3, the U-tube reactor contained two plugs. The plugs served to minimize dead volume. Also, one plug was fitted with a type-J thermocouple for temperature measurement while the other plug provided an inlet for oxygen. The reactor used throughout the treatability tests was constructed of Stainless Steel 316. As shown in Figure 3-3, the outer and inner diameter dimensions, respectively, were 12.7 mm (0.5 in.) and 8.128 mm (0.32 in.). The internal volume of the U-tube reactor was 20 mL. The flat bottom portion of the reactor, 6 mL, helps to minimize the effect of temperature gradients. For these tests, the upper part of the reactor vessel remained above the heated sand.

#### 3.3 Methods and Materials

A typical experiment consisted of the following procedures:

- using a clean syringe, a 6 mL sample of either DMMP or thiodiglycol, at a known initial concentration, was injected into the U-tube reactor vessel;



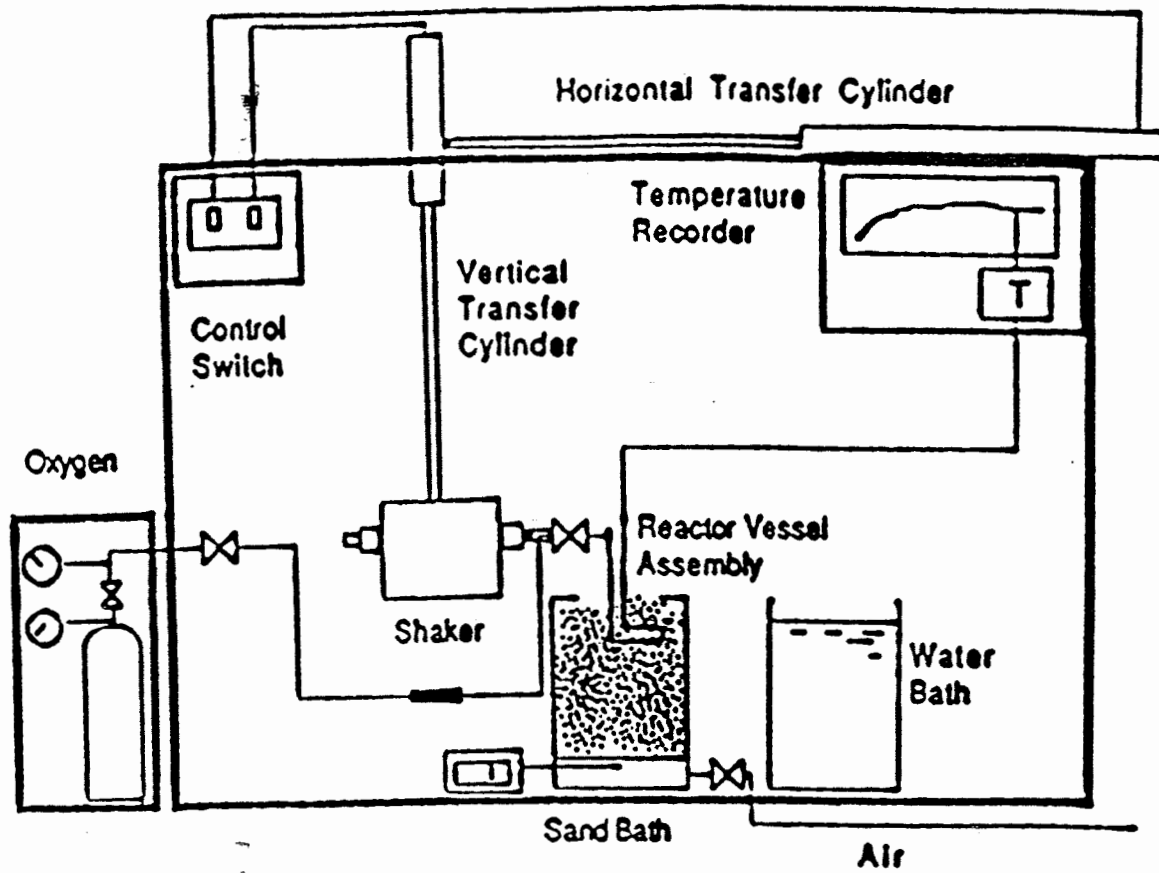


Figure 3-1. SCWO Batch Reactor System  
(Lee et al., 1990)

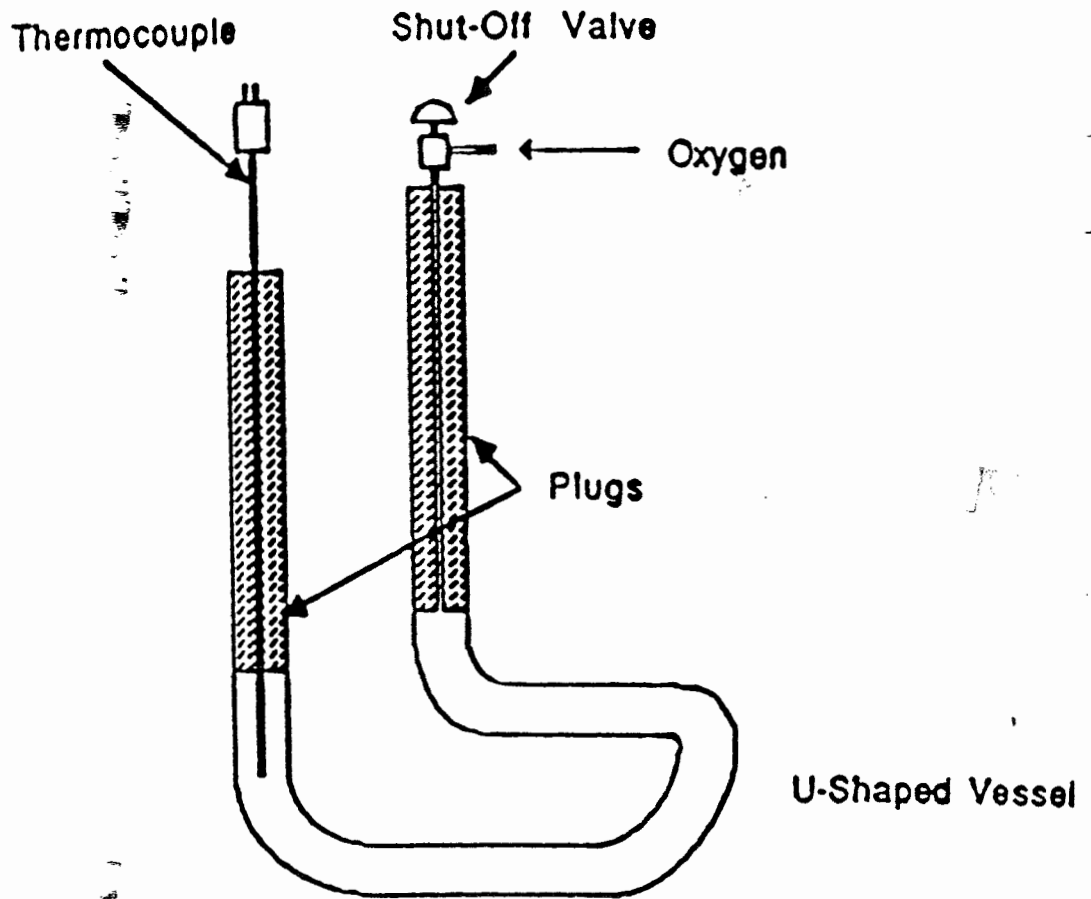
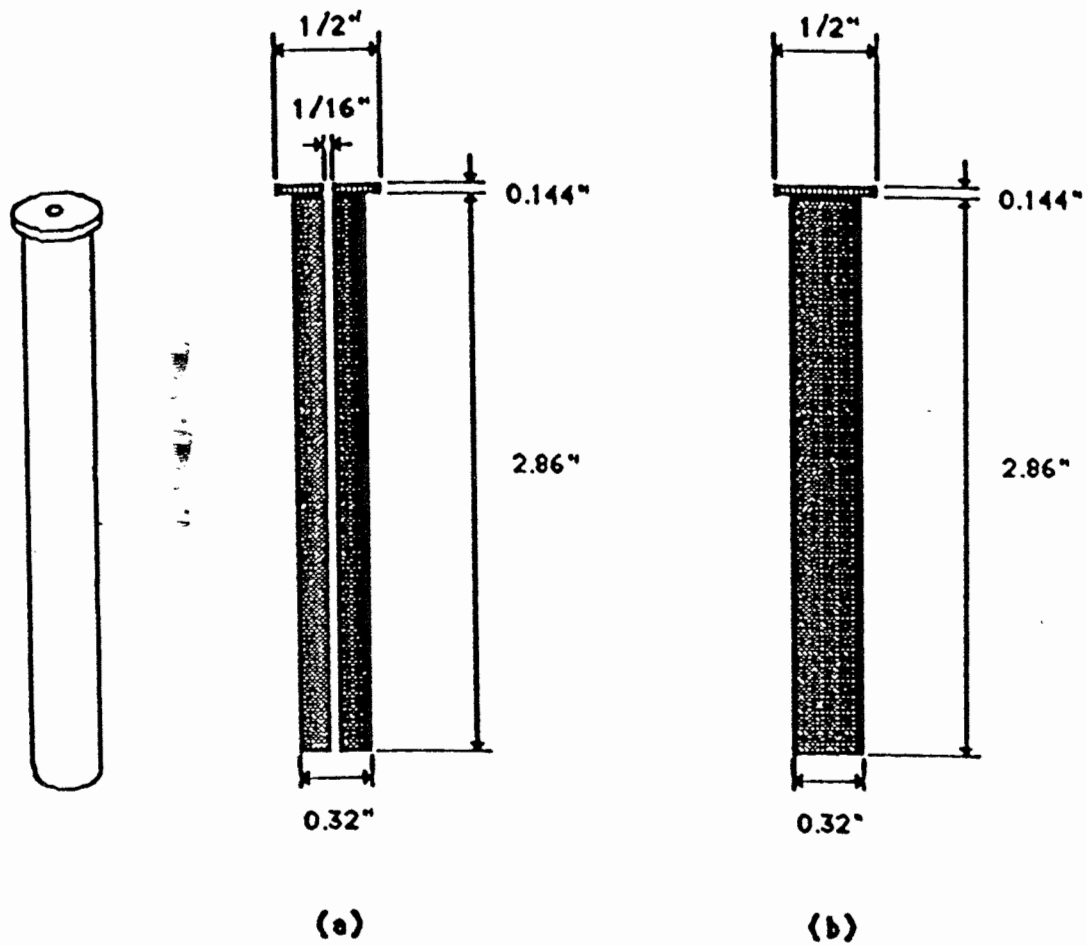


Figure 3-2. U-tube Reactor Vessel  
(Lee et al., 1990)



(a) Thermocouple reactor plug

(b) Oxygen reactor plug

Figure 3-3. Reactor Plugs

- reactor plugs were inserted into the U-tube reactor and the reactor sealed;
- in non-pyrolysis experiments, oxygen was then added at a predetermined pressure through the shut-off valve on the oxygen reactor plug;
- the shut-off valve was closed;
- the reactor was connected to the side-shaft of a wrist-action shaker;
- the thermocouple was connected to the pyrometer;
- the timer on the wrist-action shaker was set and started (the set time covered the entire test period);
- the reactor was transferred using the horizontal transfer cylinder to a position directly above the fluidized sand bath using the control switch and immersed in the sand bath with the help of the vertical transfer cylinder;
- a 60 second heat-up period was used;
- while the reactor remained in the sand bath, both the temperature and pressure were recorded;
- following the pre-set residence time, the reactor was removed using the vertical and horizontal transfer cylinders;
- the reactor was quenched in a water bath;
- the reactor contents were collected for analysis; and
- the reactor plugs were cleaned, rinsed with distilled water, and prepared for reuse.

Calibration data were recorded. The temperature of the sand bath is depicted in Table A1 (Appendix A) and Figure B1 (Appendix B).

The reactor vessels were cleaned after each experiment to remove corrosion products and encrusted materials. The cleaning solution contained a mixture of H<sub>2</sub>O (50%) and 0.1N HNO<sub>3</sub> (50%). Each reactor was rinsed initially with hot tap water and filled with a 0.1N HCl solution. After a reaction of 30 minutes, the reactor was again rinsed with hot tap water, filled with a 0.1N NaOH solution, and subjected to a 30-minute reaction period.

The reactor was sequentially rinsed with hot tap water and distilled water (room-temperature). Finally, the reactor was dried overnight at 120°C.

### 3.3.1 DMMP

The procedures and analytical tests used in both the DMMP and thiodiglycol experiments were similar. The estimated O<sub>2</sub> requirements, 200% of stoichiometric, were calculated based on a probable reaction. A constant density, in contrast to pressure, was selected because this technique provided a uniformly large volume for analytical purposes. With a calculated density and temperature, the pressure could be determined.

The calculations for density and oxygen pressure for a DMMP concentration of one percent (by volume) were as follows:

1. Given;

$$\text{reactor volume} = 20 \text{ mL,}$$

$$\text{sample volume} = 6 \text{ mL,}$$

$$\rho_{\text{water}} = 1 \text{ g/mL,}$$

$$\rho_{\text{DMMP}} = 1.145 \text{ g/mL}$$

The feed solution was prepared in a 100 mL volumetric flask.

2. Simplified DMMP reaction;



3. Density calculation;

$$\rho = \left( \frac{[(1\text{mLDMMP}) (1.145\text{gDMMP/mL}) + (99\text{mLH}_2\text{O}) (1\text{gH}_2\text{O/mL})]}{100\text{mL}} \right) \left( \frac{6\text{mL}}{20\text{mL}} \right)$$

The 6 mL over 20 mL factor corrects for the fact that the sample volume resides in only 6 mL of the 20 mL (reactor volume).

$$\rho = 0.3 \text{ g/cm}^3 \text{ or } 0.3 \text{ g/mL}$$

4. Pressure calculation using the ideal gas law;

$$\text{O}_2 \text{ pressure: } PV = nRT \rightarrow P = \frac{nRT}{V}$$

$$R, \text{ gas constant} = 0.08205 \text{ L-atm/K-mole}$$

$$T = 298 \text{ K (room temperature)}$$

$$V_{\text{sample}} = 6 \text{ mL} = 0.006 \text{ L}$$

$$V_{\text{dead}} = 14 \text{ mL} = 0.014 \text{ L}$$

$$\text{Molecular weight of DMMP} = 124.07 \text{ g/mole}$$

$$n = \text{moles of O}_2 \text{ required} \times 2 \text{ (200\% stoichiometric O}_2 \text{ requirements)}$$

$$n = \frac{5 \text{ moles O}_2}{1 \text{ mole DMMP}} \frac{(11.450 \text{ g DMMP/L}) (0.006 \text{ L})}{(124.07 \text{ g/mole DMMP})} \times 2 = 5.54 \times 10^{-2} \text{ moles}$$

$$P = (5.54 \times 10^{-2} \text{ moles}) \left( 0.08205 \frac{\text{L-atm}}{\text{K-mole}} \right) \left( \frac{298 \text{ K}}{0.014 \text{ L}} \right) (14.7 \text{ psi/atm})$$

$$P = 142 \text{ psi}$$

The percentage of oxygen in the ambient air was assumed to be 21% (standard temperature and pressure).

$$\text{atmospheric O}_2 \text{ pressure} = (0.21) (14.7 \text{ psi}) = 3.1 \text{ psi}$$

$$P = 142 - 3.1$$

$$P = 138.9 \text{ psi}$$

The oxygen pressure initially applied under ambient temperature was 140 psi. The density,  $0.3 \text{ g/cm}^3$ , was constant for all DMMP tests. The 200% stoichiometric oxygen requirements were not recalculated for the varying influent concentrations. For example, the pressure resulting from the lowest influent concentration, 11,500 mg/L, and the 200% stoichiometric O<sub>2</sub> requirement was 140 psi, as contrasted to 147 psi resulting from 12,066 mg/L and the 200% stoichiometric O<sub>2</sub> requirement. The reason for using 200% stoichiometric O<sub>2</sub> was to insure sufficient oxygen to oxidize the primary organic compounds and the transformation by-products. The error resulting from using the above technique was less than 5%. Temperature and reactor residence time were dominant factors in TOC destruction. Duplicate experiments were performed with different initial concentrations under the same conditions of temperature, pressure, and reactor residence time; these yielded similar results.

### 3.3.1.1 TOC

The level of organic destruction was based on total organic carbon (TOC). TOC, in contrast to chemical oxygen demand (COD), permitted a more

direct measurement of the total organic carbon content. TOC is independent of the oxidation states of the organic matter, whereas the COD test is dependent on the oxidation states of the organic matter. TOC is defined by *Standard Methods for the Examination of Water and Wastewater*, 17th ed., as "all carbon atoms covalently bonded in organic molecules." The inorganic carbon (IC) fraction is defined as "the carbonate, bicarbonate, and dissolved CO<sub>2</sub>."

There are some limitations to the TOC test. For example, because TOC is independent of the oxidation state of the organic matter, the test provides no measure of other organically bound elements, such as nitrogen and hydrogen. The test also does not measure the contribution of inorganics to the oxygen demand (Clesceri et al., 1989).

A Beckman TOC Analyzer, Model 915, was used for all samples containing DMMP. A Beckman Infrared Analyzer, Model 215A, served as the measuring instrument for the total carbon (TC) and IC analyses. Standards were run according to *Standard Methods for the Examination of Water and Wastewater*, 17th ed., section 5310-B, Combustion-Infrared Method. The only deviation from *Standard Methods for the Examination of Water and Wastewater*, 17th ed., was that CO<sub>2</sub>-free water was not used in the preparation of the organic and inorganic carbon stock solutions used to develop the calibration curves. The potential error from not using CO<sub>2</sub>-free water in either standard solutions, TC or IC, should have subtracted out in the calculation for influent and effluent TOC, where  $TOC = TC - IC$ . Calibration curves are provided in Figures B6 through B9, Appendix B. The influent and effluent TOC was based on these TC and IC calibration curves. Before performing a TOC analysis, three or four standard solutions were used to validate the calibration curves for the total and inorganic carbon channels. Also, the TC and IC of distilled, deionized (DDI) water was tested using both the TC and IC channels. This procedure ensured that there was no analytical bias resulting from the infrared analyzer.

### 3.3.1.2 Ion Chromatograph

A Dionex Ion Chromatograph, System 14, equipped with anion separator columns and a conductivity detector served as the analytical tool for the analysis of the conversion of phosphorus for DMMP. Phosphate (PO<sub>4</sub><sup>-3</sup>)

standards were prepared prior to IC analyses. These standards were based on the expected production of phosphoric acid. The resulting calibration curve was used to translate IC data into mg/L, as phosphate. After the phosphate to phosphorus translation was made, the percent phosphorous conversion, as based on influent to effluent analyses, was calculated as follows:

$$\%P \text{ conversion} = \left( \frac{P_{DMMP} - P_{PO_4}}{P_{DMMP}} \right) \times 100$$

The reproducibility of the IC analysis based on periodic duplicate injections was excellent.

### 3.3.1.3 pH

The influent pH, for one percent by volume DMMP and thiodiglycol solutions, was determined using ColorpHast<sup>®</sup> pH paper. The ColorpHast<sup>®</sup> paper was sensitive within 1±0.5 pH units. A syringe was used to extract approximately two milliliters of influent solution, four to five drops were placed onto the paper, and finally the syringe was purged with distilled, deionized water.

Similarly, the effluent pH of each sample was determined by using pH paper. However, pHydrion Controls pH paper was used because of greater sensitivity (±0.2 pH units). The pH ranges selected, 0.0 to 1.5 and 1.2 to 2.4 units, were chosen based on the influent pH of DMMP (≅ 5.0) and the fact that phosphoric acid in the effluent would lower the pH. The range of anticipated effluent pH values was 0.5 to 2.0.

### 3.3.2 Thiodiglycol

The procedures for monitoring the destruction of thiodiglycol (TDG) to inorganic by-products were similar to those used in the investigation of DMMP. The calculations for a one percent (by volume) solution of TDG were as follows:

1. Given;

reactor volume = 20 mL,

sample volume = 6 mL,

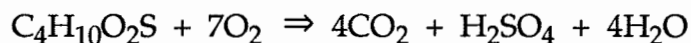
$\rho_{water} = 1 \text{ g/mL}$ ,

$\rho_{TDG} = 1.221 \text{ g/mL}$



The test solution was prepared in a 100 mL volumetric flask.

2. Simplified thiodiglycol reaction;



3. Density calculation;

$$\rho = \left( \frac{[(1\text{mLTDG})(1.221\text{gTDG/mL}) + (99\text{mLH}_2\text{O})(1\text{gH}_2\text{O/mL})]}{100\text{ mL}} \right) \left( \frac{6\text{ mL}}{20\text{ mL}} \right)$$

The 6 mL over 20 mL factor accounts for the fact that the sample volume resides in only 6 mL of the 20 mL reactor volume.

$$\rho = 0.3 \text{ g/cm}^3 \text{ or g/mL}$$

4. Pressure calculation using the ideal gas law;

$$O_2 \text{ pressure : } P V = n R T \rightarrow P = \frac{n R T}{V}$$

$$R, \text{ gas constant} = 0.08205 \text{ L-atm/K-mole}$$

$$T = 298 \text{ K (room temperature)}$$

$$V_{\text{sample}} = 6 \text{ mL} = 0.006 \text{ L}$$

$$V_{\text{dead}} = 14 \text{ mL} = 0.014 \text{ L}$$

$$\text{Molecular weight of Thiodiglycol} = 122 \text{ g/mole}$$

$$n = \text{moles of } O_2 \text{ required} \times 2 \text{ (200\% stoichiometric } O_2 \text{ requirements)}$$

$$n = \frac{7 \text{ moles } O_2}{1 \text{ mole TDG}} \frac{(12.221 \text{ g TDG/L})(0.006 \text{ L})}{(122 \text{ g/mole TDG})} \times 2 = 8.4 \times 10^{-3} \text{ moles}$$

$$n = (8.4 \times 10^{-3} \text{ moles}) \left( 0.08205 \frac{\text{L-atm}}{\text{K-mole}} \right) \left( \frac{298 \text{ K}}{0.014 \text{ L}} \right) (14.7 \text{ psi/atm})$$

$$P = 216 \text{ psi}$$

The percentage of oxygen in the ambient air was assumed to be 21% (standard temperature and pressure).

$$\text{atmospheric } O_2 \text{ pressure} = (0.21) (14.7 \text{ psi}) = 3.1 \text{ psi}$$

$$P = 216 - 3.1$$

$$P = 212.9 \text{ psi}$$

The oxygen pressure initially applied under ambient temperature was 215 psi. The density,  $0.3 \text{ g/cm}^3$ , was constant for all thiodiglycol tests. The lowest TDG

influent concentration (12,285 mg/L) and the 200% stoichiometric O<sub>2</sub> requirement resulted in a pressure of 214 psi as contrasted to 227 psi for the highest influent concentration, 13,004 mg/L. The pressure differential represents an error of less than 5.6%. As with DMMP, temperature and reactor residence times were the dominant factors in limiting TOC destruction of thiodiglycol. Duplicate experiments were performed with different initial concentrations under the same conditions of temperature, pressure, and reactor residence time and yielded similar results.

### 3.3.2.1 TOC

The TOC analyses for thiodiglycol were performed as outlined in Section 3.3.1.1 for DMMP. There was no deviation in the methods of TOC analysis for thiodiglycol in comparison to DMMP.

### 3.3.2.2 Ion Chromatograph

The IC analyses for thiodiglycol were performed as outlined in Section 3.3.1.2. In this case, sulfate standards were prepared based on the expected production of sulfuric acid, and calibration curves reflected the concentration of the SO<sub>4</sub><sup>-2</sup> anions present. The reproducibility of the IC analyses for thiodiglycol was excellent.

### 3.3.2.3 pH

The influent and effluent pH of each sample was measured as outlined in Section 3.3.1.3 for DMMP. The pH of the influent thiodiglycol solution was ≅ 5.0. The range of expected effluent pH values was 0.5 to 2.0.

## 3.4 Applicability of Results and Sources of Error

Sources of potential experimental error were defined. Similarly, completeness calculations were undertaken. To assess the mutual agreement of independent experiments for duplicate runs a Relative Percent Difference (RPD) calculation for TOC was performed. RPD is a data quality indicator that is a determination of the precision of the experiments. The RPD was calculated as follows:

$$RPD (\%) = \frac{(C_1 - C_2) \times 100}{\frac{(C_1 + C_2)}{2}}$$

where,

$C_1$  = the larger of the two observed values

$C_2$  = the smaller of the two observed values

The calculation was made based upon the percent organic carbon removed rather than the percent organic carbon remaining. If the RPD value exceeded  $\pm 10\%$  for any duplicate test, a third test was performed to verify the agreement of the experiments.

To measure the amount of valid data from the batch tests with DMMP, the completeness of the experiments were calculated. Completeness is a data quality indicator to assist in determining the legitimacy of the data. If the data reinforced the predicted trends, the data was considered valid. For example, the amount of TOC destroyed was predicted to increase with increasing temperature and reactor residence time. If a data point reinforced this prediction, the data was considered valid. A completeness calculation was made for the TOC results from the TOC analyzer and percent phosphorous conversion results from the ion chromatograph. The calculation was made as follows:

$$\text{Completeness (\%)} = 100 \times \left( \frac{V}{T} \right)$$

where,

V = number of measurements judged valid

T = total number of measurements

The completeness values for the batch tests with DMMP were judged as 92.9% for the TOC results and 82.1% for the percent phosphorous conversion results. The completeness values for the batch tests with thiodiglycol were judged as 92.3% for the TOC results and 85.2% for the percent sulfur conversion results. The completeness values for thiodiglycol are higher due to greater familiarity with experimental technique.

The potential sources of experimental error are: 1) inconsistent heating of the batch reactor, 2) instrument error, 3) the dilution error associated with those samples where dilution was necessary to complete an accurate sample analysis, 4) contamination of samples from insufficiently cleaned glassware, reactors, reactor plugs, etc., 5) consistency of sampling analysis, and 6) errors in experimental technique. Steps were taken to minimize the potential error

in each source.

The most significant source of potential error is the inconsistent heating of the batch reactor. There is inevitably some variability in the heat-up and cooldown temperature profiles for independent experiments. A temperature calibration of the fluidized batch reactor attempted to minimize the error by providing a basis for selection of a thermocouple temperature to target the desired reactor temperature.

Instrument error was minimized by achieving intimate familiarity with the analytical equipment. The TOC analyzer consistently measured only 70% to 80% of the theoretical influent TOC for both compounds. The percent TOC destroyed was calculated as follows:

$$\% \text{ TOC destroyed} = \frac{\text{TOC}_{\text{influent}} - \text{TOC}_{\text{effluent}}}{\text{TOC}_{\text{influent}}} \times 100$$

For the varying influent concentrations, the measured  $\text{TOC}_{\text{influent}}$  was determined using the TOC analyzer. The theoretical  $\text{TOC}_{\text{influent}}$  was calculated based on the molecular structure of the parent compounds. For example, DMMP has the molecular formula  $\text{C}_3\text{H}_9\text{O}_3\text{P}$  and a molecular weight of 124.07 g/mole. Therefore, the theoretical TOC for DMMP is:

$$\frac{36 \text{ g C}}{\text{mole DMMP}} \div \frac{124.07 \text{ g DMMP}}{\text{mole DMMP}} \text{ or } \frac{0.29 \text{ g C}}{\text{g DMMP}}$$

The percent TOC destroyed equation indicates that the instrument error decreases with increasing TOC destruction because the difference of  $[\text{TOC}_{\text{influent}} - \text{TOC}_{\text{effluent}}]$  increases. The increasing difference reduces the effect the disparity between  $[\text{measured } \text{TOC}_{\text{influent}} - \text{measured } \text{TOC}_{\text{effluent}}]$  and  $[\text{theoretical } \text{TOC}_{\text{influent}} - \text{measured } \text{TOC}_{\text{effluent}}]$  has on percent destroyed values, which decreases the TOC destroyed error. Because the values reported for TOC destroyed were based on measured  $\text{TOC}_{\text{influent}}$  and  $\text{TOC}_{\text{effluent}}$  values, the values are conservative. For the highest (98.4%) and lowest (15.0%) levels of TOC destruction (DMMP), the percent error for TOC destroyed was 0.32% and 63.5%, respectively. Similarly, for thiodiglycol, the percent error in TOC destroyed was 0.44% and 4.40%, respectively, for the highest values of TOC (98.2%) and for the lowest values of TOC (83.5%).

As discussed in Section 3.0, standard procedures were implemented to

minimize the effects of contamination. With regard to consistency of sampling analysis, the TOC and pH analyses were conducted within 24 to 48 hours following a test. Errors in experimental technique refer to familiarity with the experimental procedures and improved with time and experience.

## 4.0 EXPERIMENTAL RESULTS

The experimental results, Sections 4.1 through 4.3, summarize the data. Detailed data and experimental conditions are contained in Appendices A and B. Experimental results reinforced the prediction that SCWO environments can effectively destroy potentially hazardous organic compounds.

### 4.1 DMMP

A total of 28 DMMP experiments were conducted. Of these, twenty-five were conducted with oxygen and three without an oxidant.

Table 4-1 summarizes the oxidation data obtained from DMMP tests. The percentage of TOC destroyed and the conversion of phosphorus (P) were analyzed for three temperatures (425°C to 500°C) and reactor residence times ranging from one to eight minutes. For these conditions, the percentage of TOC destroyed varied from 15.0% to 98.4%. Similarly, the percentage P conversion varied from 2% to 79%. Phosphorous conversion results include only phosphorus measured as phosphates in the effluent. Phosphorus was also present in the effluent in the form of methylphosphonic acid but was not quantified. Both the TOC destruction and P conversion data showed a high degree of variability with respect to temperature and reactor residence time.

#### 4.1.1 Residence Time Effects

Increases in reactor residence time correspond with increases in TOC destruction and production of phosphoric acid. Longer residence times permitted greater demarcation of reaction pathways for by-product formation and transformation. Figures 4-1 and 4-2 show the results of the oxidation experiments with DMMP.

Figure 4-1 depicts TOC Destruction vs. Residence Time. Considerable scatter occurs at shorter residence times and lower temperatures. In particular, at a temperature of 425°C and a reactor residence time of one minute there is considerable dispersion. This variability at low temperatures and residence times is a function of two factors. First, short-term stability with this reactor design is difficult to achieve. Second, the reaction pathways for by-product formation and transformation are less defined.

Table 4-1. TOC and Ion Chromatograph Data--Oxidation of DMMP

Run #	Temp. (°C)	Time (minutes)	TOC Destyd. (%)	PO <sub>4</sub> Conc. <sup>1</sup> (mg/L)	P Conver. <sup>2</sup> (%)
1	415	1	15.0	200	2.0
2	425	1	28.7	350	4.0
3	425	1	67.7	2900	32
4	425	1	70.4	2900	31
5	435	1	68.6	1600	17
6	425	2	61.0	1500	17
7	425	2	66.4	2600	29
8	425	3	76.3	2600	29
9	425	3	70.6	750	8.0
10	425	8	73.0	600	7.0
11	450	1	63.3	3500	39
12	450	1	63.6	3000	34
13	460	1	74.7	3800	43
14	450	2	72.1	4700	53
15	450	2	68.5	2000	22
16	450	3	74.7	3800	43
17	465	3	84.9	5400	62
18	450	8	86.9	1100	12
19	500	1	78.9	4700	53
20	510	1	86.6	5300	60
21	500	2	88.3	5900	66
22	520	2	94.5	7300	79
23	480	3	89.0	5900	66
24	490	3	88.6	6200	70
25	500	6	98.4	3700	40

<sup>1</sup>Concentration of phosphates measured in the effluent.

<sup>2</sup>Includes only phosphorus measured as phosphates in the effluent.

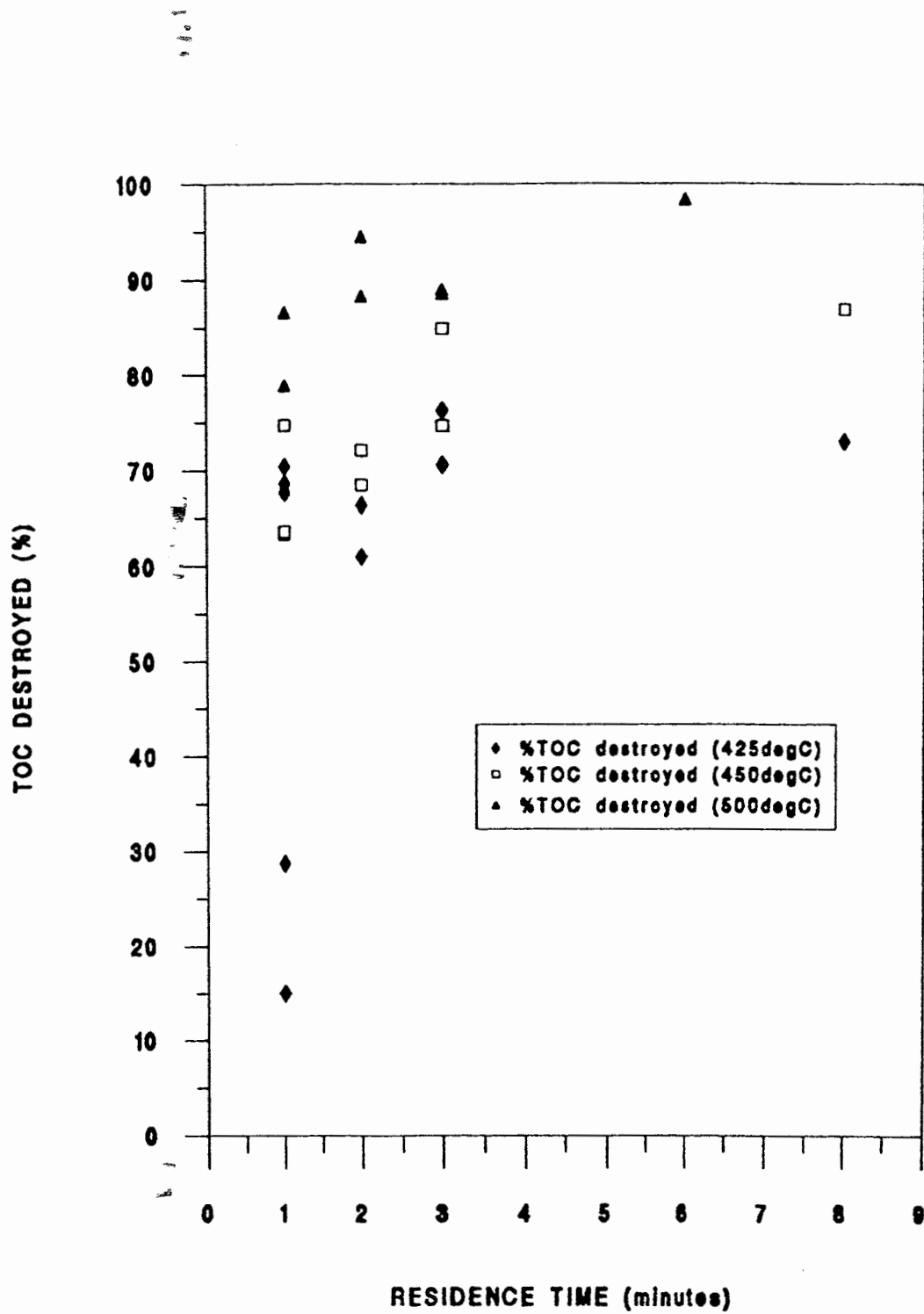


Figure 4-1. TOC Destroyed vs. Residence Time for DMMP



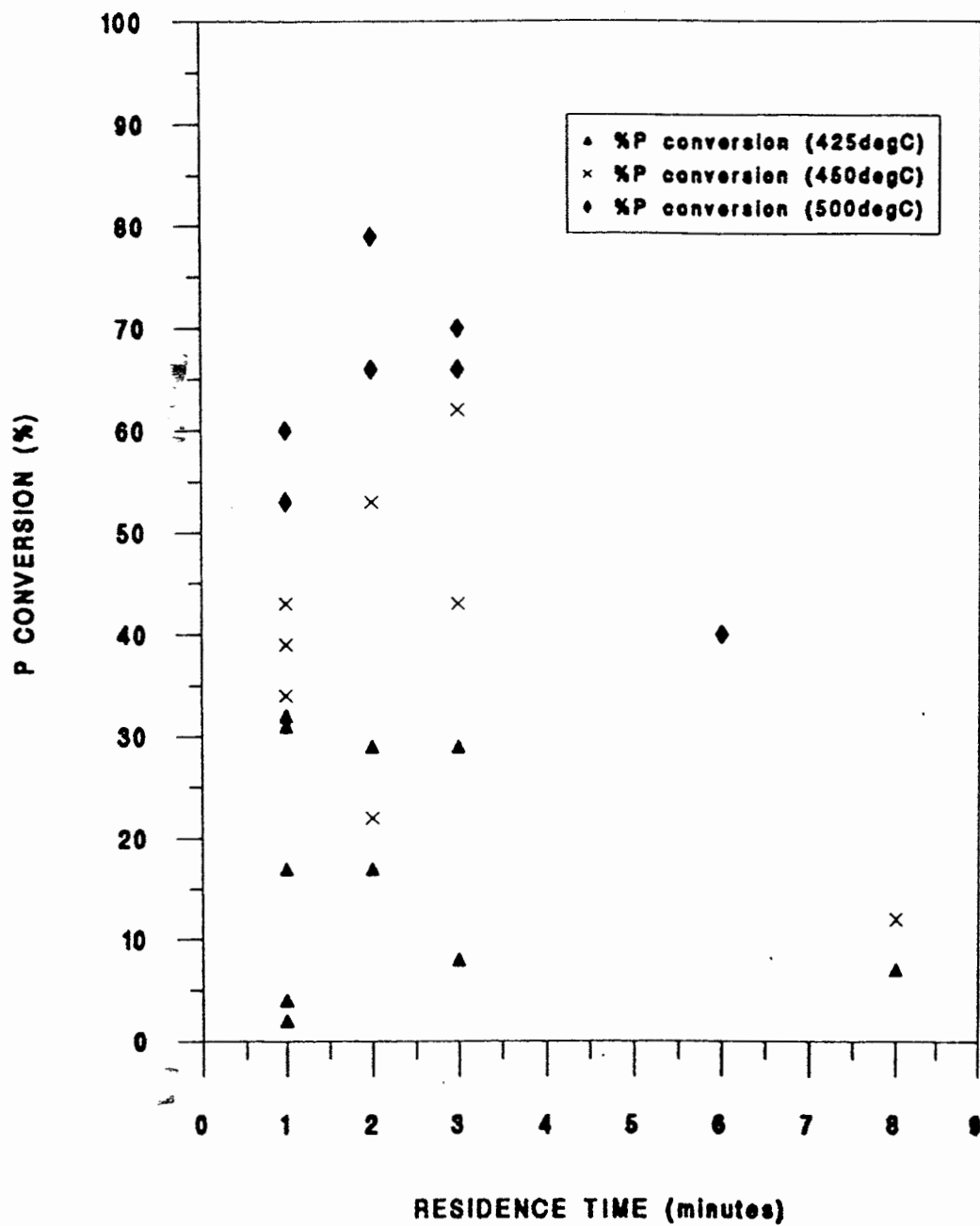


Figure 4-2. P Conversion vs. Residence Time for DMMP

Figure 4-2 reveals that percent phosphorus converted from DMMP increases with increasing reactor residence time. The three data points for the longer residence time at each temperature, 425°C, 450°C and 500°C, do not fit the general trend. A possible explanation could be the impact resulting from the use of a contaminated reactor. The three experiments conducted at longer residence times for each temperature were with reactors previously used for thiodiglycol tests. The thiodiglycol samples had contaminated the reactors, even after cleaning, with substantial concentrations of sulfates measured in IC analyses. The interference of the sulfate contamination probably led to the irregularity seen in the phosphorous conversion results.

#### 4.1.2 Temperature Effects

Originally, the three temperatures chosen for the DMMP and thiodiglycol experiments were 400°C, 450°C, and 500°C. These temperatures were chosen to provide adequate separation between temperatures and thus avoid overlapping temperature profiles due to the inconsistent heating of the batch reactor. The 425°C temperature was substituted for the 400°C temperature because of the inconsistency of experimental conditions when operating near the critical point of water. A change to the experimental conditions that should have been made was to replace the 450°C with a temperature between 460-470°C to restore adequate separation of the temperature profiles. For that reason, the manifestation of the temperature effect was more difficult to demonstrate when comparing 425°C and 450°C tests and caused more anomalies in the data.

Figures 4-3 and 4-4, respectively, are graphs of TOC Destroyed and P Conversion vs. Temperature. These include data developed at one, two, and three minute reactor residence times. Only three tests were run at reactor residence times other than one, two, and three minutes.

Longer residence times resulted in higher TOC removal and greater production of phosphoric acid for most experiments. The greatest variability occurred at 425°C and one minute reactor residence time. At 500°C, the activation energies of most compounds are exceeded and as a result the trends are more consistent. For 500°C tests, triplicate experiments were unnecessary based on a relative percent difference (RPD) calculation for TOC results.

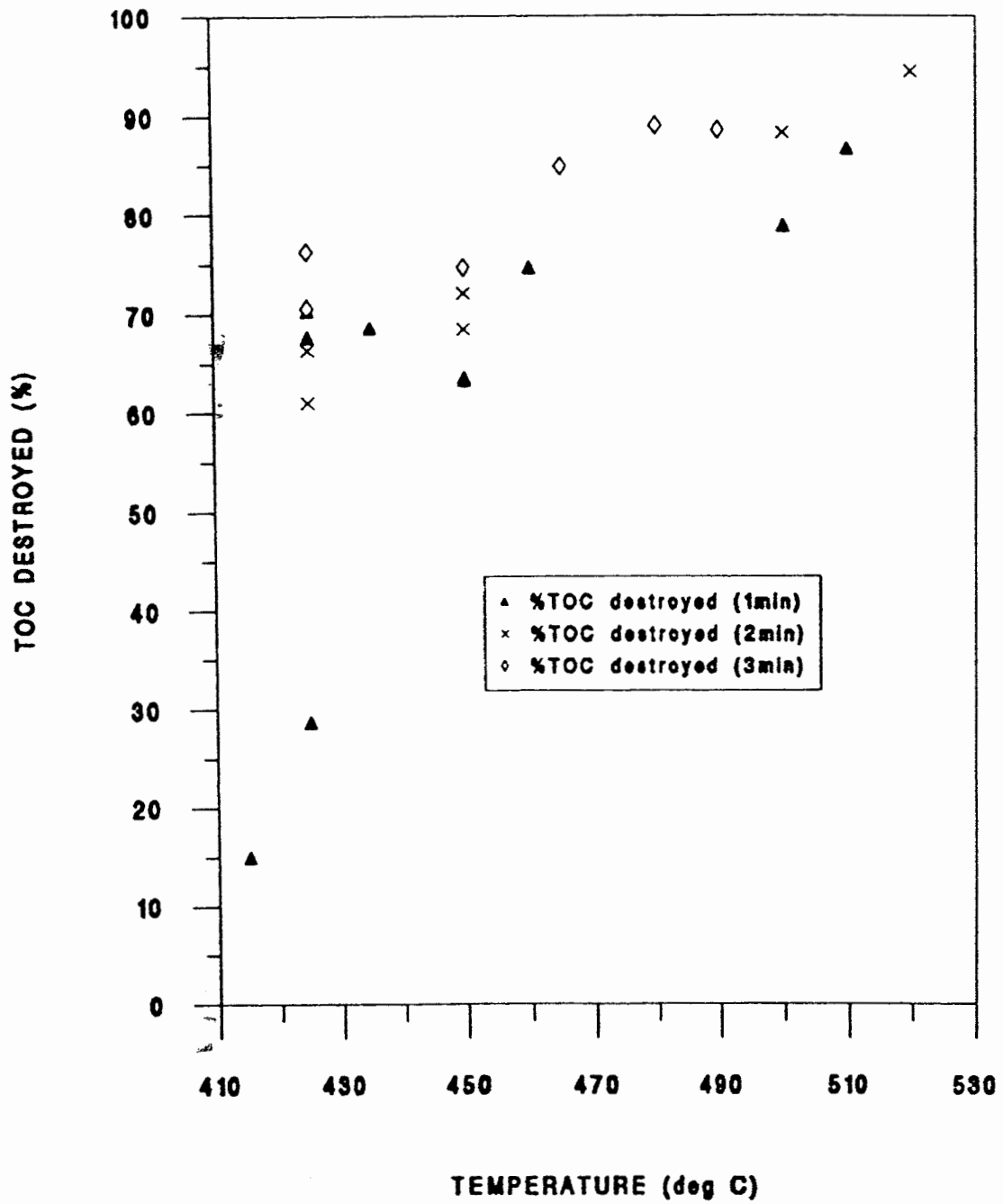


Figure 4-3. TOC Destroyed vs. Temperature for DMMP

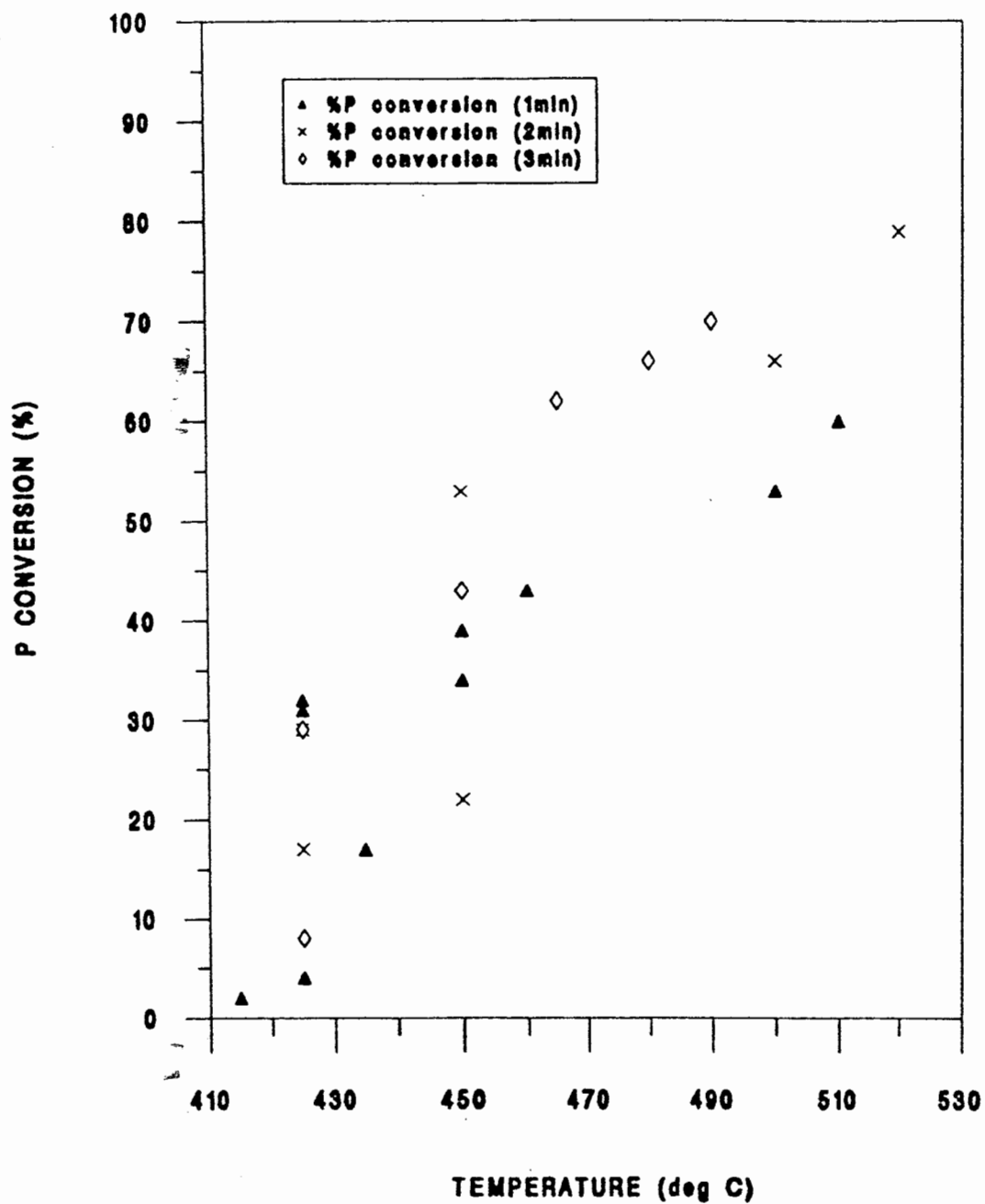


Figure 4-4. P Conversion vs. Temperature for DMMP

### 4.1.3 Oxidant Level Effects

It was necessary to compare the thermal effects on DMMP destruction. Therefore, three pyrolysis tests were conducted using a three minute reactor residence time. Figure 4-5 clearly shows that pyrolysis destruction was slower as compared to oxidation. The percentages of thermal destruction, based on TOC destroyed, and three minute reactor residence time at 425°C, 450°C and 500°C, respectively, were 8.10%, 13.5% and 21.7%. The percent conversion of phosphorus to phosphoric acid was one percent or less for the pyrolysis tests.

It should be noted that some oxygen was present during pyrolysis runs. Ambient air in the reactor contained approximately 21% oxygen. Oxygen was present as dissolved oxygen and oxygen atoms in water molecules, and organically bound oxygen was associated with both the DMMP and thiodiglycol. However, the IC results for both compounds indicated little thermal oxidation in the form of phosphoric or sulfuric acids. Table 4-2 summarizes the thermal and oxidation data at a three minute reactor residence time.

**Table 4-2. DMMP Data for Three Minute Residence Time With and Without Oxidant**

Run #	Temperature (°C)	Oxidant (% Stoich.)	TOC Destroyed (%)	P Conversion <sup>1</sup> (%)
8	425	200	76.3	29
9	425	200	70.6	8.0
16	450	200	74.7	43
17	465	200	84.9	62
23	480	200	89.0	66
24	490	200	88.6	70
26	425	0.02	8.10	1.0
27	450	0.02	13.5	2.0
28	500	0.02	21.7	1.0

<sup>1</sup>Includes only phosphorus measured as phosphates in the effluent.

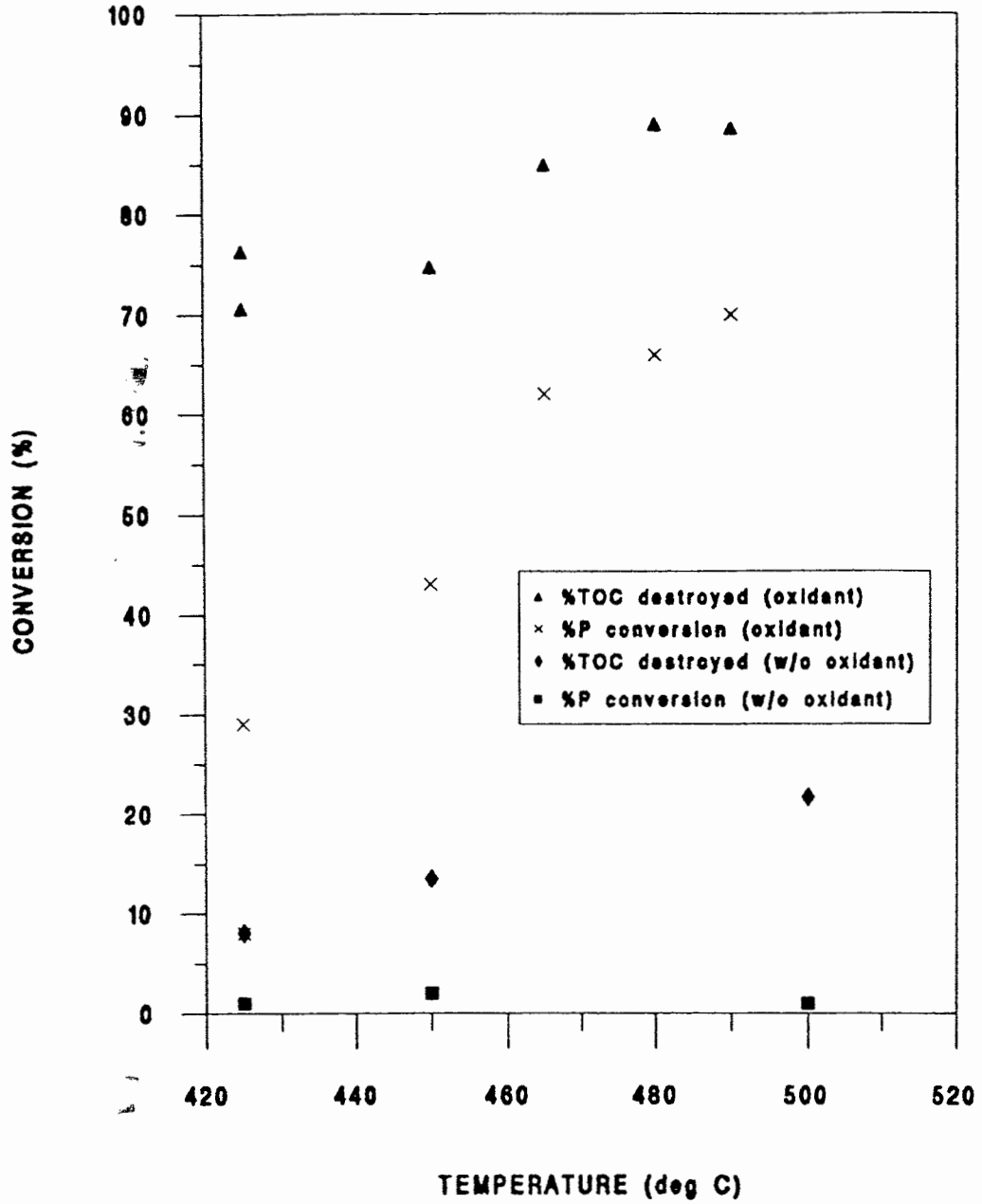


Figure 4-5. Conversion vs. Temperature for DMMP at Three Minute Residence Time With and Without Oxidant

## 4.2 Thiodiglycol

A total of 26 experiments were conducted with thiodiglycol. Twenty-three oxidation experiments and three pyrolysis experiments were conducted.

Table 4-3 summarizes the oxidation data obtained from thiodiglycol tests. The percentage of TOC destroyed and the conversion of sulfur (S) were analyzed for three temperatures ( $\cong 425^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ ) and reactor residence times ranging from one to three minutes. For these conditions, the percentage of TOC destroyed varied from 83.5% to 97.8%. Similarly, the percentage S conversion varied from 17% to 87%. Sulfur conversion results include only sulfur measured as sulfates in the effluent. Sulfur was also released in the form of effluent sulfur gases. The S conversion data showed a high degree of variability with respect to temperature and reactor residence time.

### 4.2.1 Residence Time Effects

As shown in Figures 4-6 and 4-7, the amount of TOC destroyed and the percent of sulfur conversion for thiodiglycol increased with increasing reactor residence time and temperature. The variation of TOC destruction, Figure 4-6, was significant only at the lowest temperature. Figure 4-7, S Conversion vs. Residence Time, contains one significant anomaly in the data. These TOC and sulfur results were about 10% higher than corresponding DMMP data. A more complete oxidation of sulfur as opposed to the phosphorus was not expected. One conceivably would expect the phosphorus to be oxidized more rapidly because the phosphorus present in DMMP is at its highest oxidation state, while the sulfur in thiodiglycol is not. The greater percentage of TOC destroyed in the thiodiglycol tests indicates the relative strength of the C-P bond. Presumably, the strength of the C-P bond is greater than that of the C-S bond. In addition, this bond strength may account for the greater completeness of the sulfur oxidation.

### 4.2.2 Temperature Effects

Figures 4-8 and 4-9, respectively, are graphs of TOC Destroyed and S Conversion vs. Temperature. These include data for one, two, and three minute reactor residence times.

**Table 4-3. TOC and Ion Chromatograph Data--Oxidation of Thiodiglycol**

Run #	Temp. (°C)	Time (minutes)	TOC Destyd. (%)	SO <sub>4</sub> Conc. <sup>1</sup> (mg/L)	S Conver. <sup>2</sup> (%)
1	425	1	83.5	5500	54
2	425	1	87.2	6200	61
3	425	2	89.8	6700	66
4	430	2	92.9	6300	62
5	435	2	90.1	5600	55
6	425	3	92.1	6000	59
7	425	3	88.3	4400	43
8	425	3	87.8	5500	54
9	425	3	90.5	5200	51
10	450	1	88.0	5300	52
11	460	1	92.0	5700	57
12	450	2	94.3	5500	55
13	450	2	91.1	6600	68
14	450	2	94.3	7200	70
15	470	2	97.1	6800	67
16	450	3	96.1	7000	69
17	450	3	96.6	6200	64
18	500	1	94.0	1700	17
19	515	1	95.6	8000	83
20	500	2	97.0	6300	65
21	500	2	97.5	8400	87
22	500	3	97.8	7900	82
23	500	3	97.0	8000	83

<sup>1</sup>Concentration of sulfates measured in the effluent.

<sup>2</sup>Includes only sulfur measured as sulfates in the effluent.



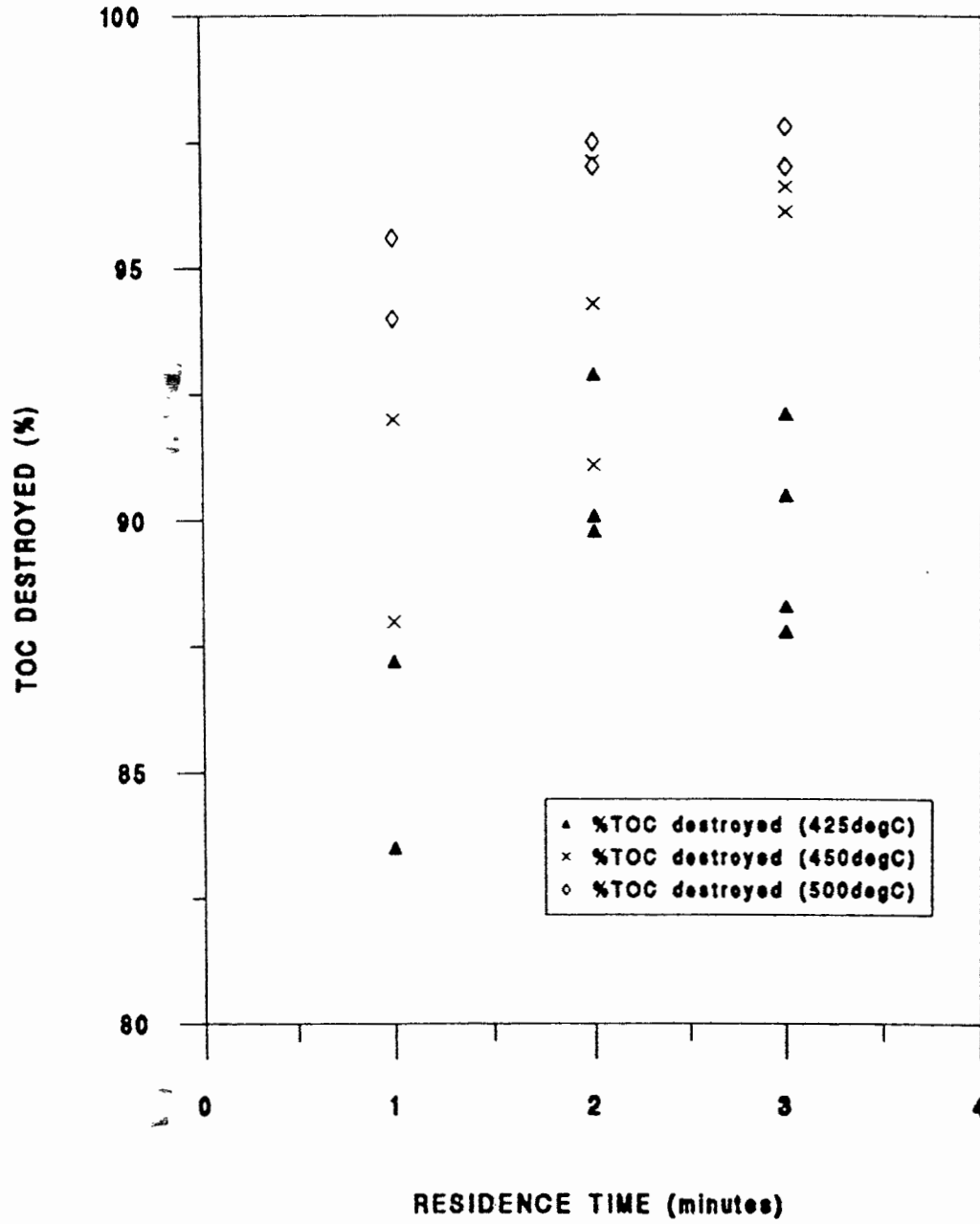


Figure 4-6. TOC Destroyed vs. Residence Time for Thiodiglycol

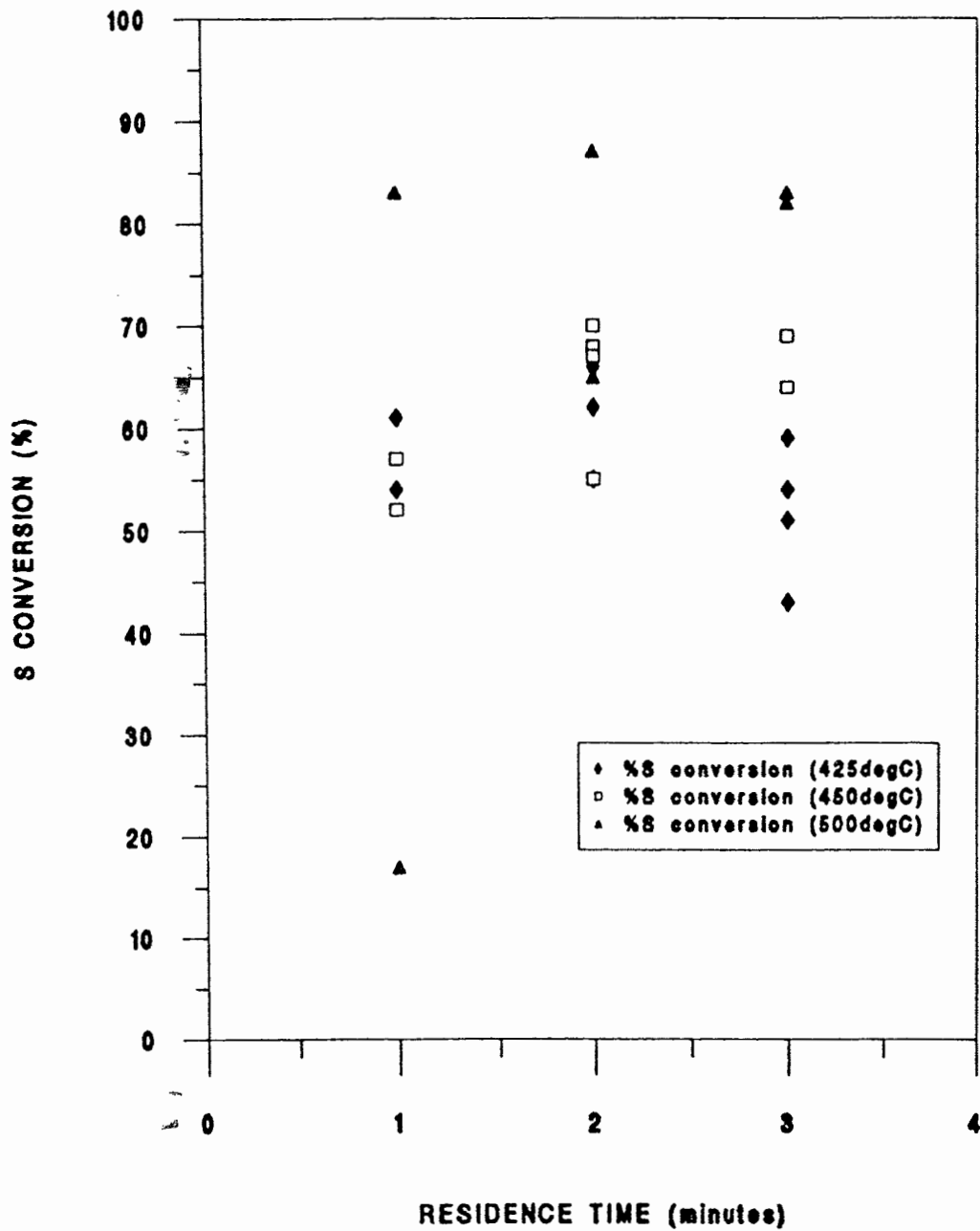


Figure 4-7. S Conversion vs. Residence Time for Thiodiglycol

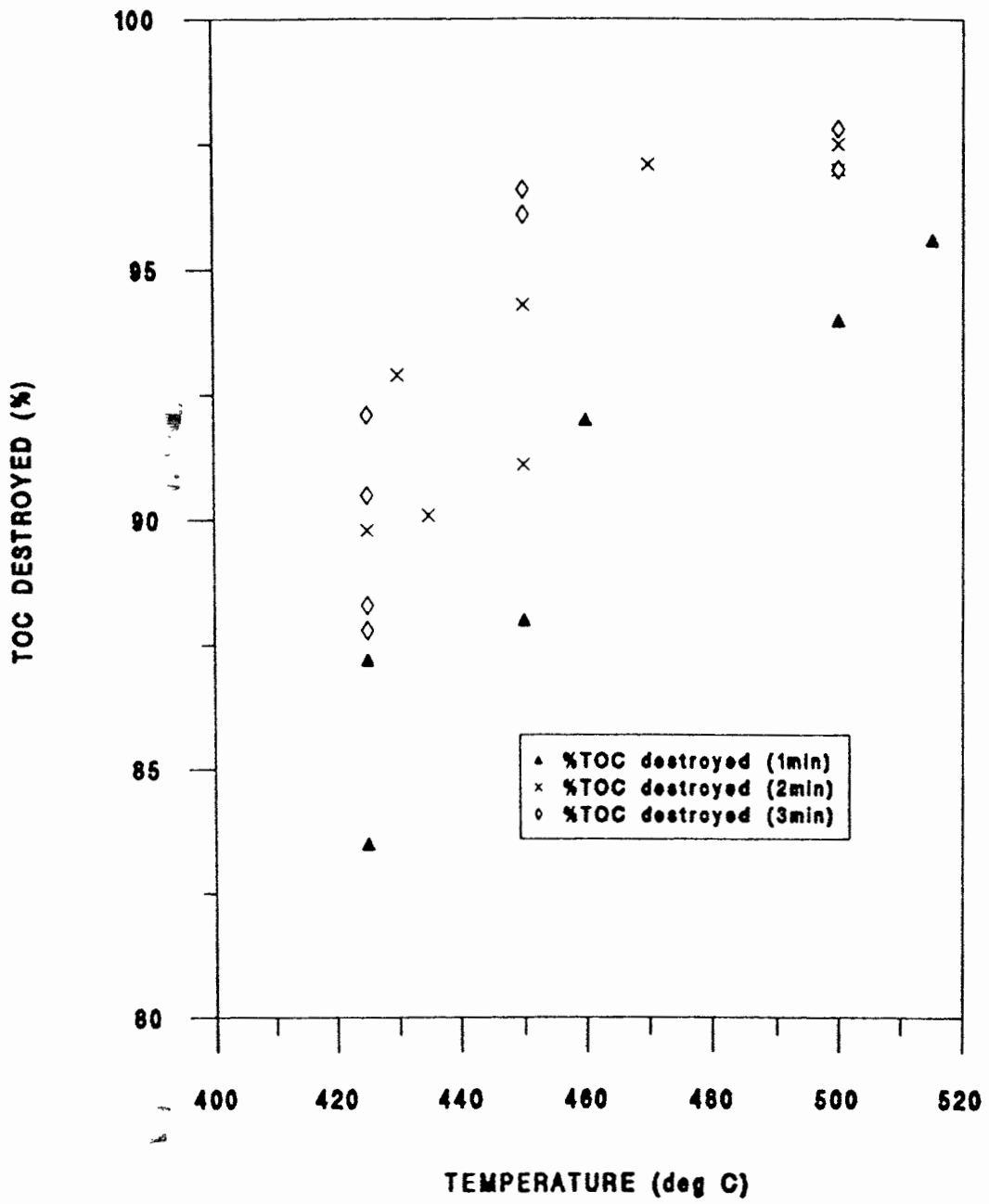


Figure 4-8. TOC Destroyed vs. Temperature for Thiodiglycol

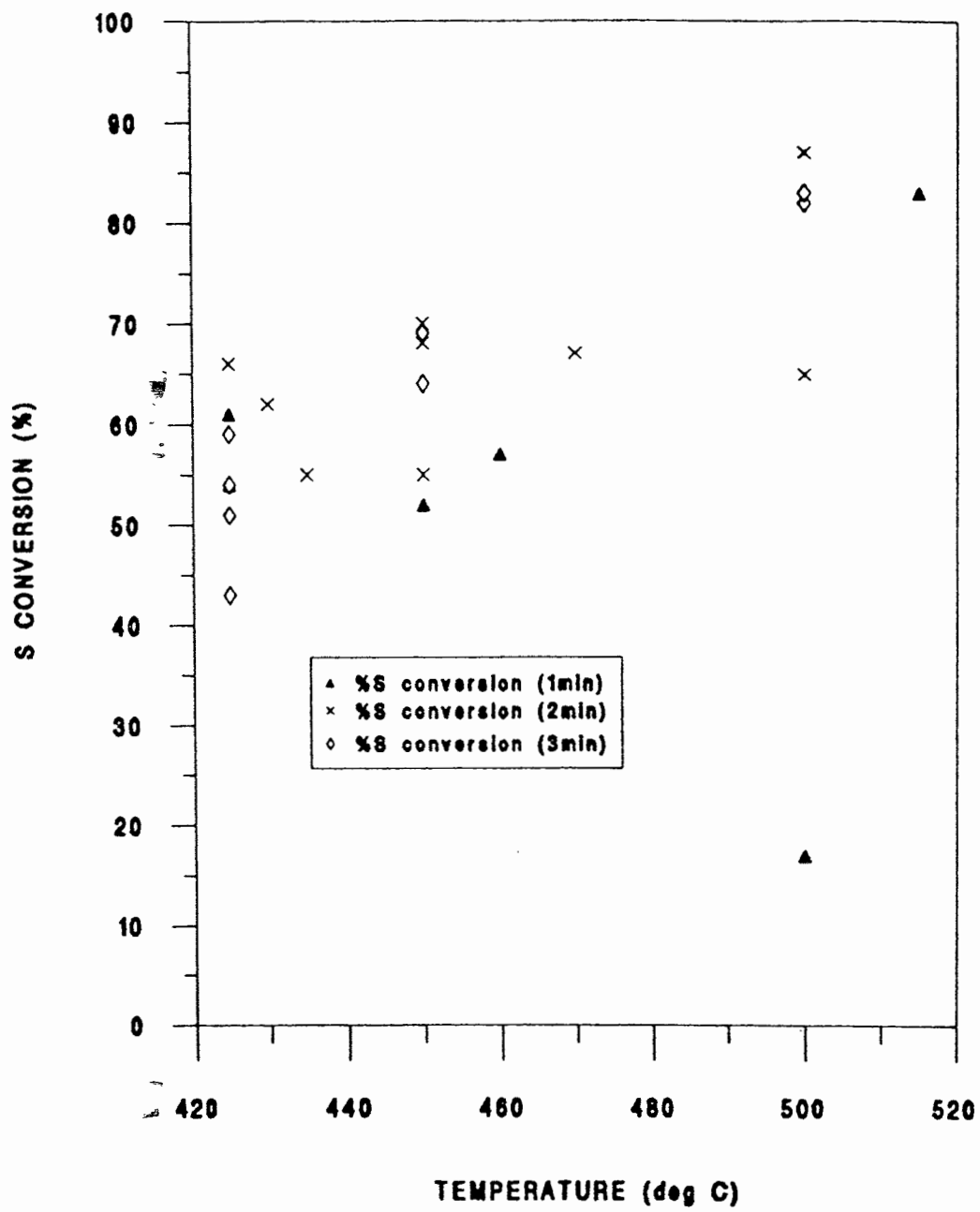


Figure 4-9. S Conversion vs. Temperature for Thiodiglycol

Higher temperatures resulted in increased TOC destruction and greater production of sulfuric acid. The greatest variability in TOC destruction and conversion of sulfur occurred at 425°C and a three minute reactor residence time. At 500°C, the activation energies of most compounds are exceeded and as a result the trends are more consistent. For 500°C tests, triplicate experiments were unnecessary based on a relative percent difference (RPD) calculation for TOC results.

#### 4.2.3 Oxidant Level Effects

Three pyrolysis tests were conducted for the longest residence time. The percentages of thermal destruction based on TOC destroyed, with three minute reactor residence time were 89.7%, 90.2% and 92.7%, respectively, for temperatures of 425°C, 450°C and 500°C. The percent conversion of sulfur to sulfuric acid was one percent or less for the pyrolysis tests. Figure 4-10 indicates that thermal destruction based on TOC destroyed proceeded almost as rapidly as the combined thermal and oxidation destruction. The wide differences in the sulfur conversion might indicate that the thermal decomposition of thiodiglycol occurs under a separate reaction pathway. Reports have been made on the complete destruction of HD for pyrolysis experiments that were conducted in a nitrogen atmosphere at 450°C for an unspecified amount of time (Sides and Spafford, 1984). Table 4-4 summarizes the oxidation and pyrolysis data at a three minute reactor residence time.

#### **4.3 pH effects**

Both DMMP and thiodiglycol influents exhibited a pH of about five. The effluent pH values ranged from 1 to 1.6 for both compounds. This drop in pH resulted from the production of phosphoric and sulfuric acids, respectively, for DMMP and thiodiglycol. The only exception was the pH reduction for the three pyrolysis tests with thiodiglycol, which resulted in pH values of four. Although similar pH reductions occurred for the oxidation tests of both compounds, the presence of solids, possibly from reactor sidewalls, in thiodiglycol samples might indicate that sulfuric acid produced a more corrosive environment as compared to phosphoric acid.

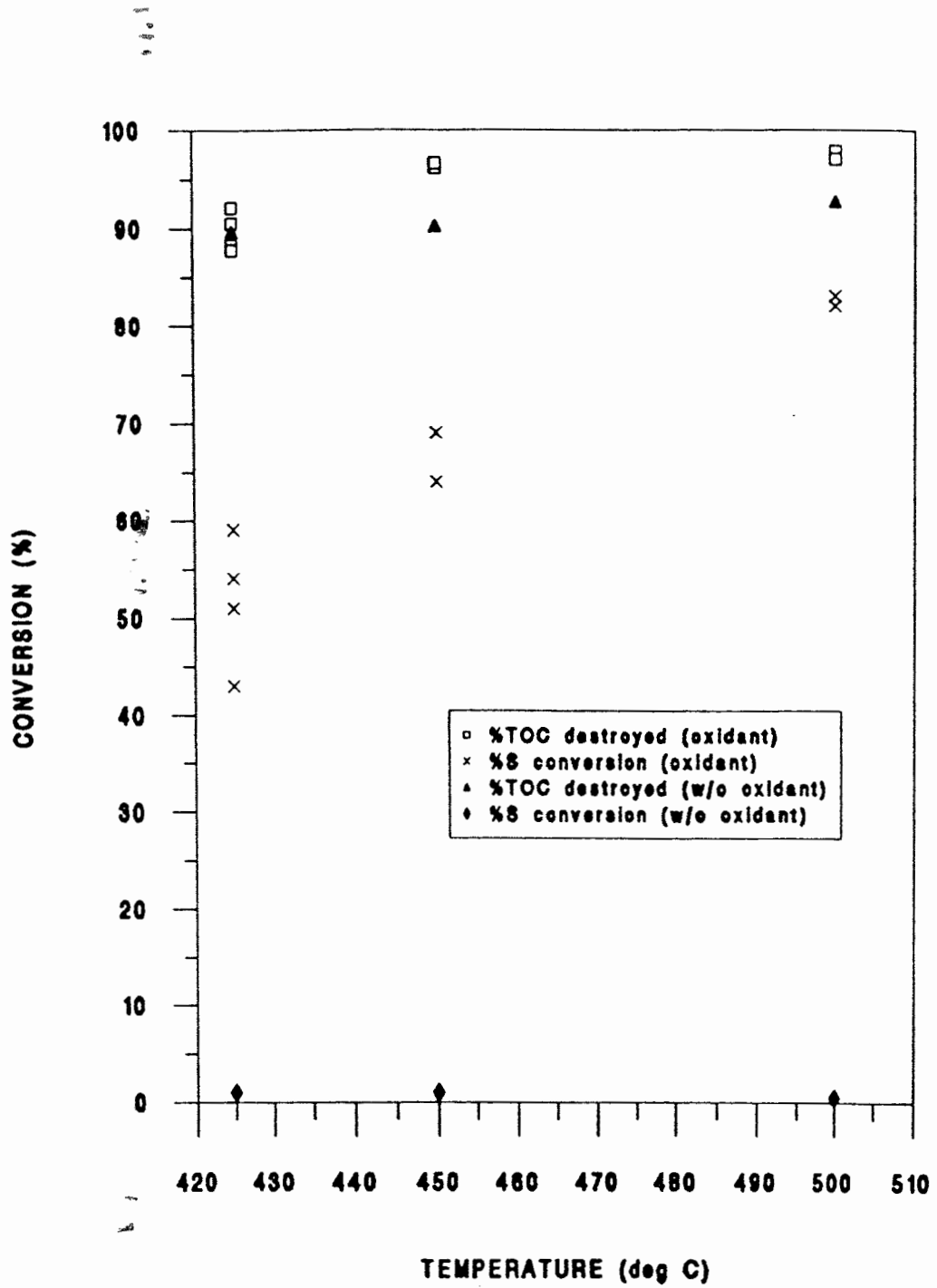


Figure 4-10. Conversion vs. Temperature for Thiodiglycol at Three Minute Residence Time With and Without Oxidant

**Table 4-4. Thiodiglycol Data for Three Minute Residence Time  
With and Without Oxidant**

Run #	Temperature (°C)	Oxidant (% Stoich.)	TOC Destroyed (%)	S Conversion <sup>1</sup> (%)
6	425	200	92.1	59
7	425	200	88.3	43
8	425	200	87.8	54
9	425	200	90.5	51
16	450	200	96.1	69
17	450	200	96.6	64
22	500	200	97.8	82
23	500	200	97.0	83
24	425	0.014	89.7	1.0
25	450	0.014	90.2	1.0
26	500	0.014	92.7	0.5

<sup>1</sup>Includes only sulfur measured as sulfates in the effluent.

## 5.0 DISCUSSION

Barner et al. (1991) cited that the rate of oxidation of large organic molecules under SCWO conditions is controlled by smaller, partially oxygenated compounds. This may explain why a significant amount of the TOC was removed at shorter reactor residence times and lower temperatures. Increases in reactor residence time and temperature, although destroying more TOC, removed TOC at a reduced rate.

The results indicate there is a direct relationship between TOC destruction and conversion of phosphorus and sulfur. For all conditions of temperature and reactor residence time, increases in TOC destruction were coupled with increases in conversion of phosphorus and sulfur, respectively, to phosphoric and sulfuric acids. The lower percentage of phosphorous and sulfur conversion as compared to TOC destroyed indicates that in the SCWO of both compounds the carbon groups (methyl groups in DMMP and ethanol groups in thiodiglycol) were detached before the conversion to phosphoric and sulfuric acids.

The destruction of the parent compounds occurred through hydrolysis, thermal destruction or pyrolysis, and thermal oxidation. Previous research has indicated that most of the chemical agents react to form lower molecular weight compounds in the heat-up to SCWO conditions (Carney, 1991). Although previous studies indicated no effect of water density on the destruction rate (Lee et al., 1990), the density was maintained at a uniform level.

### 5.1 DMMP

The hydrolysis reaction with GB is pH dependent, and under acidic conditions will form isopropylmethylphosphonic acid (IMPA) plus fluoride. The IMPA will yield methylphosphonic acid (MPA) at a reduced rate with the loss of isopropanol (Verweij et al., 1982). The IC results with DMMP showed significant peaks for the phosphate and methylphosphonate anions, which are the anions associated with the compounds phosphoric acid and MPA, respectively. Analyses of methylphosphonates were not included in this study.



The structural similarities of DMMP with GB suggests that MPA might be produced during the hydrolysis of DMMP. The high resistance of the P-methyl bond to hydrolysis would indicate that the breakdown of the MPA, if present, would occur due to thermal oxidation and pyrolysis (Verweij et al., 1982). With the exception of the fluoride ion, the hydrolysis products of GB Sarin are non-toxic (Clark, 1989). Therefore, the hydrolysis products of DMMP are presumably non-toxic because of the absence of fluorine in the structure of DMMP.

The following is a list of probable by-products produced in the SCWO of DMMP (Turner, 1992):

carbon dioxide, $\text{CO}_2$	phosphoric acid, $\text{H}_3\text{PO}_4$
carbon monoxide, $\text{CO}$	dimethylphosphinic acid, $(\text{CH}_3)_2\text{P}(\text{O})\text{OH}$
methanoic acid (formic acid), $\text{HCOOH}$	dimethylphosphite, $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$
methanol, $\text{CH}_3\text{OH}$	methylphosphonic acid, $\text{CH}_3\text{P}(\text{O})(\text{OH})_2$
ethanal, $\text{CH}_3\text{CHO}$	phosphonoacetic acid, $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{H}$
ethanediol, $\text{HOCH}_2\text{CH}_2\text{OH}$	trimethylphosphate, $(\text{CH}_3\text{O})_3\text{P}(\text{O})$
ethanoic acid (acetic acid), $\text{CH}_3\text{COOH}$	trimethylphosphonoformate, $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CO}_2\text{CH}_3$
ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	trimethylphosphonoacetate, $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{CH}_3$
methanal (formaldehyde), $\text{HCHO}$	

Carbon dioxide and carbon monoxide constitute the inorganic carbon content of the reacted DMMP. Acetic and formic acids could result from the combination of the single-carbon radicals. The formation of other carboxylic acids is possible, but past research with SCWO has indicated that the most commonly formed and remaining carboxylic acids are acetic and formic acids. Phosphoric acid is a predicted end-product in the SCWO of organic compounds where the heteroatom phosphorus is present. Methylphosphonic acid is a predicted hydrolysis product of DMMP. In the hydrolysis of DMMP, the methyl groups attached to the oxygens on DMMP might be replaced with hydrogens. The resulting transformation is methylphosphonic acid.

## 5.2 Thiodiglycol

Hydrogen sulfide,  $H_2S$ , is a reported principal decomposition product of HD sulfur mustard at higher temperatures,  $350^\circ C$  to  $450^\circ C$  (Sides and Spafford, 1984). Because thiodiglycol is a natural and final hydrolysis product of HD sulfur mustard, hydrogen sulfide gas formation should be expected under SCWO conditions. The presence of hydrogen sulfide, sulfur dioxide, or an associated gas containing a mercaptan bond, H-S bond, was detected during the studies reported herein. All testing with thiodiglycol must be undertaken beneath a protective and vented hood.

The four toxic thermal decomposition products of HD sulfur mustard are all halogenated (Sides and Spafford, 1984). Thiodiglycol is not halogenated, and it is probable that the thermal decomposition products produced in the SCWO batch experiments might be relatively non-toxic. However, solids, possibly derived from reactor sidewalls, were present in the effluent samples. Therefore, the existence of a highly corrosive environment might indicate the possible presence of toxic thermal decomposition products. Removal of solids from reactor sidewalls did not occur in the SCWO of DMMP.

The following is a list of probable by-products produced in the SCWO of thiodiglycol (Turner, 1992):

carbon dioxide, $CO_2$	ethanal, $CH_3CHO$
carbon monoxide, $CO$	ethanediol, $HOCH_2CH_2OH$
diethylsulfate, $(CH_3CH_2O)_2SO_2$	ethanoic acid, $CH_3COOH$
diethylsulfite, $(CH_3CH_2O)_2SO$	ethanol, $CH_3CH_2OH$
diethylsulfone, $(CH_3CH_2)_2SO_2$	methanal, $HCHO$
diethylsulfoxide, $(CH_3CH_2)_2SO$	methanethiol, $CH_3SH$
dimethylsulfate, $(CH_3O)_2SO_2$	methanoic acid, $HCOOH$
dimethylsulfite, $(CH_3O)_2SO$	methanol, $CH_3OH$
dimethylsulfone, $(CH_3CH_2)_2SO_2$	sulfuric acid, $H_2SO_4$
dimethylsulfoxide, $(CH_3)_2SO$	hydrogen sulfide, $H_2S$
sulfur dioxide, $SO_2$	

Carbon dioxide and carbon monoxide constitute inorganic carbon content of the reacted thiodiglycol. The production of acetic and formic acids would arise from the combination of the single-carbon radicals. The ethanol groups ( $\text{CH}_3\text{CH}_2\text{OH}$ ) in thiodiglycol, as opposed to the methyl groups in DMMP, account for the increase in the probable list of by-products. The distinct odor of hydrogen sulfide, sulfur dioxide, or an associated mercaptan bond was present in all effluent samples with thiodiglycol. The odor was even more distinct for the pyrolysis tests.

## 6.0 CONCLUSIONS

1. It is concluded that supercritical water oxidation (SCWO) is a viable treatment option for the chemical agent simulants dimethyl methylphosphonate (DMMP) and thiodiglycol. Based on total organic carbon (TOC) tests, including the parent and all organic transformation compounds, TOC destruction during batch tests was as high as 98%. For this maximum destruction of DMMP, the temperature and reactor residence times, respectively, were 500°C and six minutes. At the same temperature and level of TOC destruction, the residence for thiodiglycol was only three minutes.
2. Increases in reactor residence time and temperature in the SCWO of DMMP and thiodiglycol resulted in increased TOC destruction and greater production of phosphoric and sulfuric acids. For DMMP at 450°C and one, two, and three minute reactor residence times, the average TOC destruction and conversion of phosphorus to phosphoric acid, respectively, were 63%, 71% and 75%, and 36%, 38% and 43%. At a two-minute reactor residence time and 425°C, 450°C, and 500°C temperatures, the average TOC destruction and conversion of phosphorus to phosphoric acid, respectively, were 64%, 71% and 88%, and 23%, 38% and 66%. Similar results were reported for thiodiglycol.
3. The rate and degree of destruction (oxidation, hydrolysis, and pyrolysis), as based on TOC changes and similar experimental conditions, were greater for thiodiglycol as compared to DMMP. The greater degree of destruction suggests that the strength of the P-methyl bond is a better indicator of expected destruction than the initial oxidation states of phosphorus and sulfur. For example, the level of TOC destroyed at 450°C and two minute reactor residence time was 71% and 93%, respectively, for DMMP and thiodiglycol. At a temperature of 500°C and reactor residence time of three minutes, the level of TOC destroyed was 90% and 98%, respectively, for DMMP and thiodiglycol.
4. The relatively high percentage of TOC destruction observed during the pyrolysis tests involving thiodiglycol (90% to 93% at 425°C to 500°C and three minutes) indicates that the degradation of chemical agents and

chemical agent simulants containing sulfur will undergo rapid destruction. Within a batch reactor, this may allow for complete destruction of TOC during reaction periods of five minutes or less. In continuous-flow reactors, it is anticipated that the reaction rate will be uniformly faster and more complete.

5. Previous studies with chemical agent simulants noted that increases in temperature had little effect on the destruction efficiency of parent compounds (Carney, 1991). Based on this preliminary study of percentage of TOC destroyed, it was unclear whether temperature or reactor residence time had a more significant effect. For example, the percentage of TOC destroyed (DMMP) using a three-minute reactor residence time at temperatures of 450°C and 500°C, respectively, was 75% and 90%. At 500°C, the TOC reductions (DMMP) for one and three minute residence times were 79% and 90%, respectively. Similarly, at 450°C, the TOC destructions (DMMP) at one and three minute residence, respectively, were 63% and 75%. These results indicate that temperature, as based on the absolute difference of temperature and residence time, may have had a greater effect. However, when results for DMMP at the 425°C and 450°C temperatures were compared in a similar manner, residence time had a greater effect. Similar results were reported for thiodiglycol experiments. Therefore, determination of which parameter had a more significant effect depends on the conditions chosen for comparison.
6. It is concluded that kinetic analyses should be performed to determine specific reaction orders. Continuous-flow reactor experiments should be undertaken. Also, special attention should be directed to carbon and phosphate mass balances. Carbon dioxide and carbon monoxide releases should be evaluated. Similarly, carbon and sulfur mass balances need to be validated. Determining thiodiglycol mass balance will be more difficult, as compared to DMMP, because of the anticipated sulfur gas or gases.

**APPENDICES**

APPENDIX A. Data

Table A1. Temperature Calibration of the Sand Bath

Time (secs)	620°C (set temp.)	550°C (set temp.)	500°C (set temp.)	450°C (set temp.)
15	367	329	302	274
30	460	420	392	371
45	507	460	423	392
60	525	473	435	403
75	531	485	447	406
90	541	487	450	409
105	548	490	454	411
120	547	497	456	411
135	546	499	454	412
150	548	502	458	412
165	548	505	460	413
180	552	504	459	413
210	555	505	460	412
225	553	507	461	413
240	557	510	460	413
255	560	510	-	415
270	559	510	-	415
285	559	510	-	414
300	561	512	462	415
360	563	518	463	412
420	560	522	464	413
480	563	525	464	415
540	568	528	464	412

**Table A2. Summary of All Data for the Batch Experiments With DMMP**

**Conditions:**

Reaction Density = 0.3 g/mL

Initial Oxygen Conc. = 200% of Stoichiometric Demand

Run #	InitConc (mg/L)	Temp. (°C)	Time (min)	Pres. (MPa)	TOC (%)	PO <sub>4</sub> Con (mg/L)	P Conv. (%)	Effluent pH
1	11940	415	1	32.7	15.0	200	2.0	1.6
2	11740	425	1	35.3	28.7	350	4.0	1.2
3	12066	425	1	35.3	67.7	2900	32	1.2
4	12066	425	1	35.3	70.4	2900	31	1.2
5	11970	435	1	38	68.6	1600	17	1.2
6	11740	425	2	35.3	61.0	1500	17	1.2
7	11970	425	2	35.3	66.4	2600	29	1.2
8	11740	425	3	35.3	76.3	2600	29	1.2
9	11970	425	3	35.3	70.6	750	8.0	1.2
10	12066	425	8	35.3	73.0	600	7.0	1.2
11	11550	450	1	41.9	63.3	3500	39	1.2
12	11500	450	1	41.9	63.6	3000	34	1.2
13	11500	460	1	44.6	74.7	3800	43	1.2
14	11500	450	2	41.9	72.1	4700	53	1.2
15	11970	450	2	41.9	68.5	2000	22	1.2
16	11500	450	3	41.9	74.7	3800	43	1.2
17	11500	465	3	45.9	84.9	5400	62	1.2
18	12066	450	8	41.9	86.9	1100	12	1.2
19	11550	500	1	55.2	78.9	4700	53	1.2
20	11550	510	1	57.8	86.6	5300	60	1.2
21	11550	500	2	55.2	88.3	5900	66	1.2
22	12066	520	2	60.4	94.5	7300	79	1.2
23	11550	480	3	49.9	89.0	5900	66	1.2
24	11550	490	3	52.5	88.6	6200	70	1.2
25	12066	500	6	55.2	98.4	3700	40	1.2

**Conditions:**

Reaction Density = 0.3 g/mL

Initial Oxygen Conc. = Oxygen in Ambient Air

26	12066	425	3	35.3	8.1	130	1.0	1.2
27	12066	450	3	41.9	13.5	200	2.0	1.2
28	12066	500	3	55.2	21.7	83.6	1.0	2.0



**Table A3. Summary of All Data for the Batch Experiments With Thiodiglycol**

**Conditions:**  
 Reaction Density = 0.3 g/mL  
 Initial Oxygen Conc. = 200% of Stoichiometric Demand

Run #	InitConc (mg/L)	Temp. (°C)	Time (min)	Pres. (MPa)	TOC (%)	SO <sub>4</sub> Con (mg/L)	S Conv. (%)	Effluent pH
1	12877	425	1	35.3	83.5	5500	54	1.0
2	12877	425	1	35.3	87.2	6200	61	1.0
3	12877	425	2	35.3	89.8	6700	66	1.2
4	12877	430	2	36.7	92.9	6300	62	1.2
5	13004	435	2	38.0	90.1	5600	55	1.0
6	12877	425	3	35.3	92.1	6000	59	1.0
7	12877	425	3	35.3	88.3	4400	43	1.0
8	13004	425	3	35.3	87.8	5500	54	1.6
9	13004	425	3	35.3	90.5	5200	51	1.0
10	12877	450	1	41.9	88.0	5300	52	1.2
11	12877	460	1	44.6	92.0	5700	57	1.0
12	12877	450	2	41.9	94.3	5500	55	1.2
13	12285	450	2	41.9	91.1	6600	68	1.0
14	13004	450	2	41.9	94.3	7200	70	1.0
15	12877	470	2	47.2	97.1	6800	67	1.0
16	12877	450	3	41.9	96.1	7000	69	1.0
17	12285	450	3	41.9	96.6	6200	64	1.0
18	12285	500	1	55.2	94.0	1700	17	1.2
19	12285	515	1	59.1	95.6	8000	83	1.0
20	12285	500	2	55.2	97.0	6300	65	1.2
21	12285	500	2	55.2	97.5	8400	87	1.0
22	12285	500	3	55.2	97.8	7900	82	1.0
23	12285	500	3	55.2	97.0	8000	83	1.0

**Conditions:**  
 Reaction Density = 0.3 g/mL  
 Initial Oxygen Conc. = Oxygen in Ambient Air

24	12285	425	3	35.3	89.7	50	1.0	4.0
25	12285	450	3	41.9	90.2	50	1.0	4.0
26	12285	500	3	55.2	92.7	40	0.5	4.0

APPENDIX B. Figures

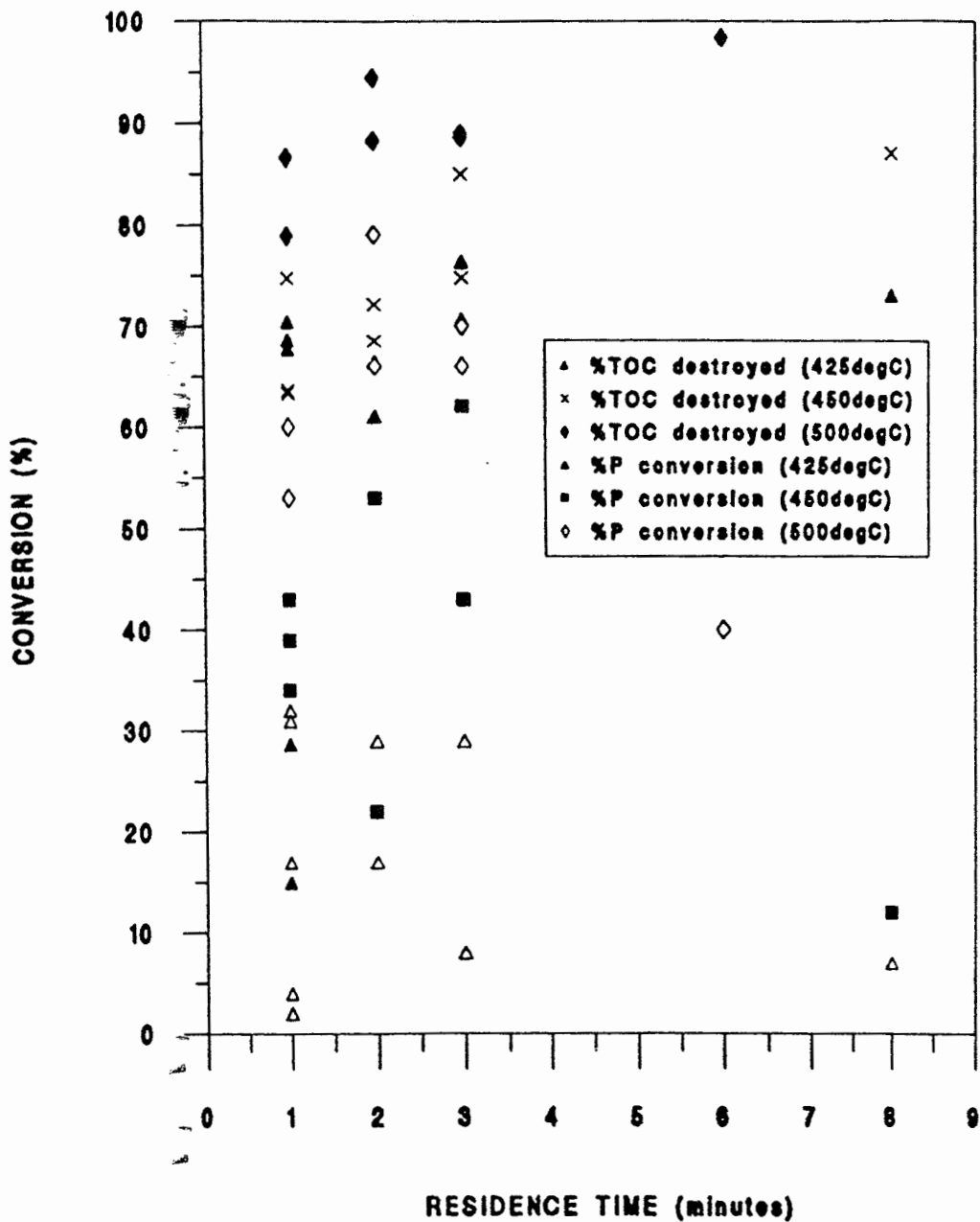


Figure B1. Conversion vs. Residence Time for All DMMP Oxidation Tests

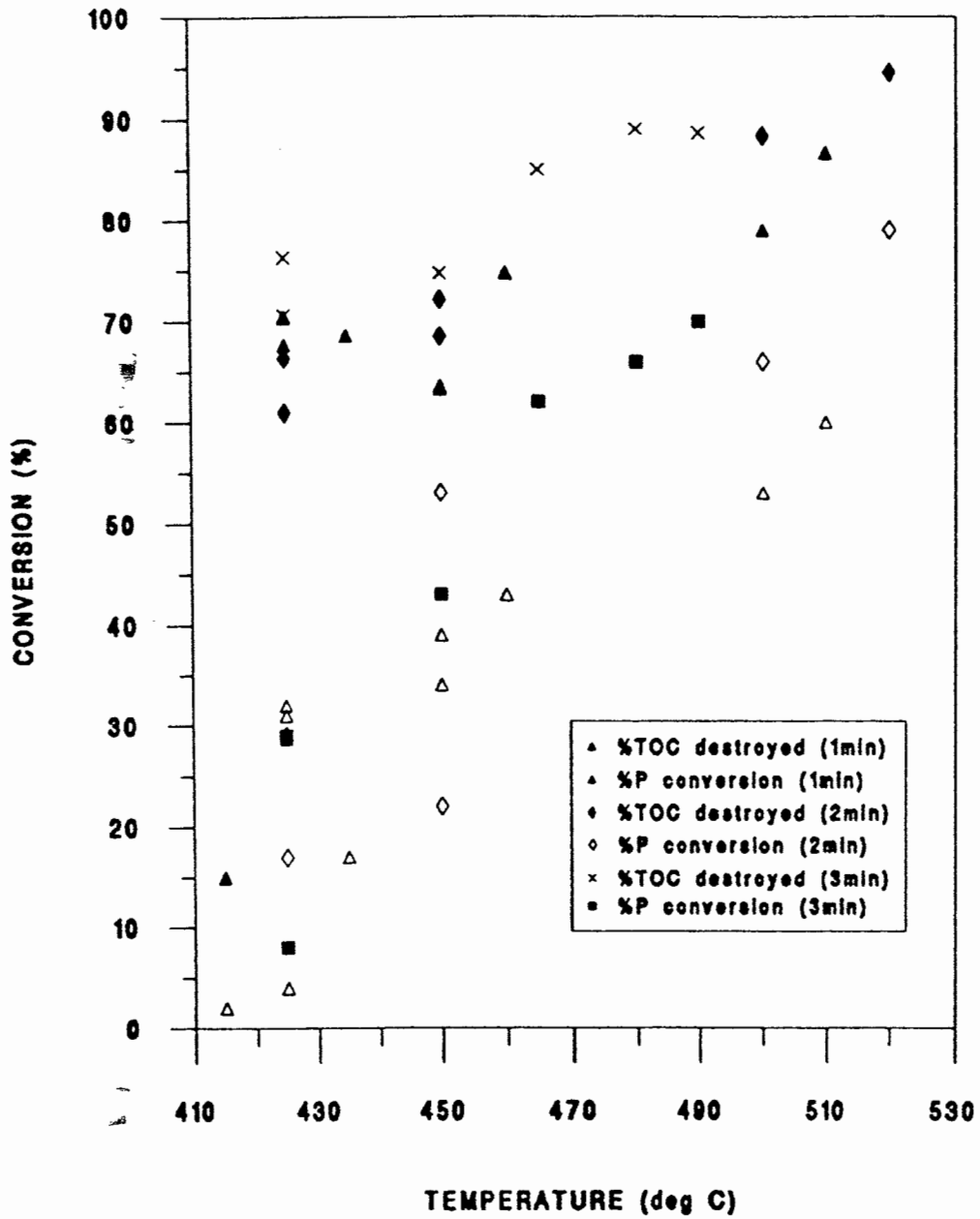


Figure B2. Conversion vs. Temperature for All DMMP Oxidation Tests

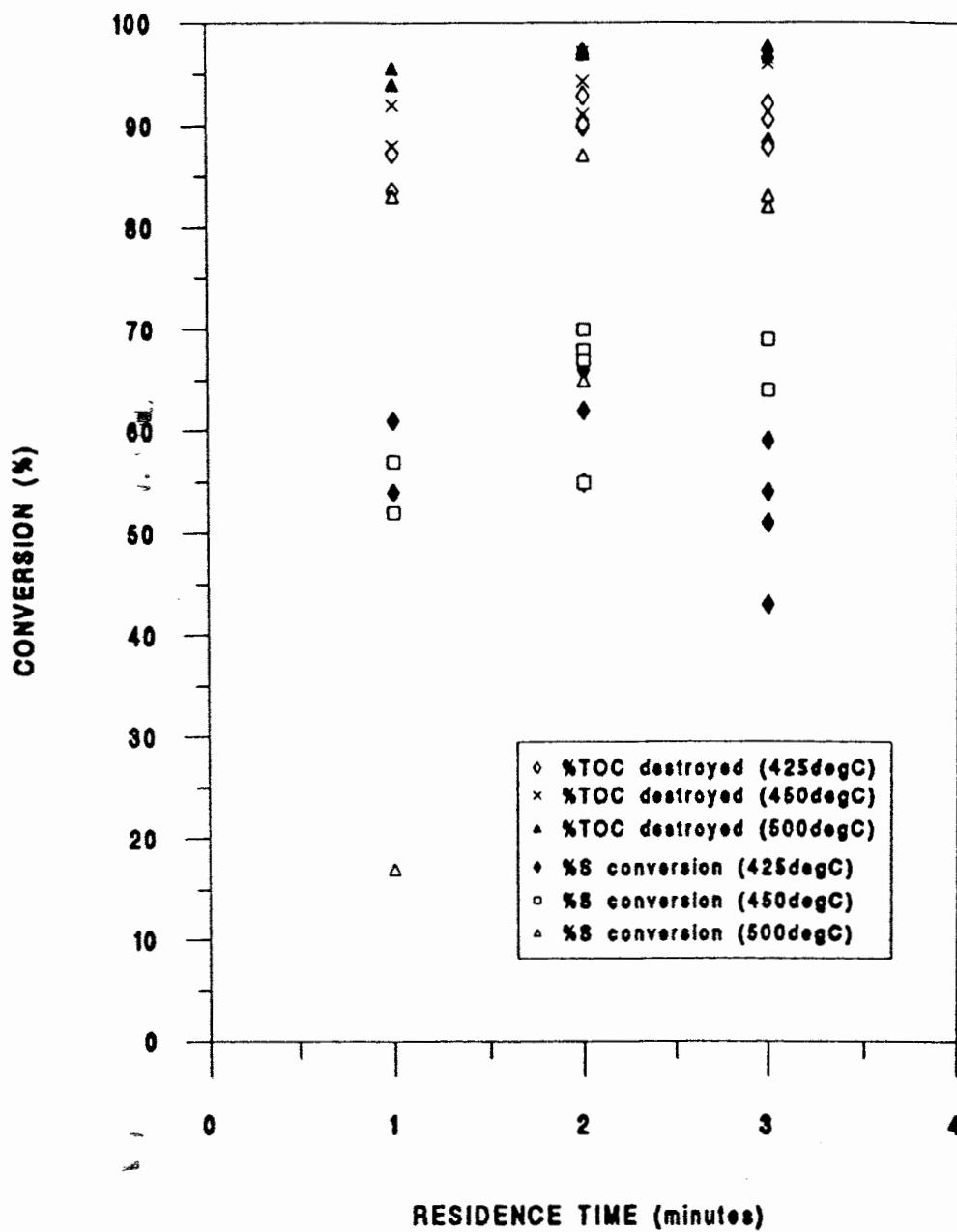


Figure B3. Conversion vs. Residence Time for All Thiodiglycol Oxidation Tests

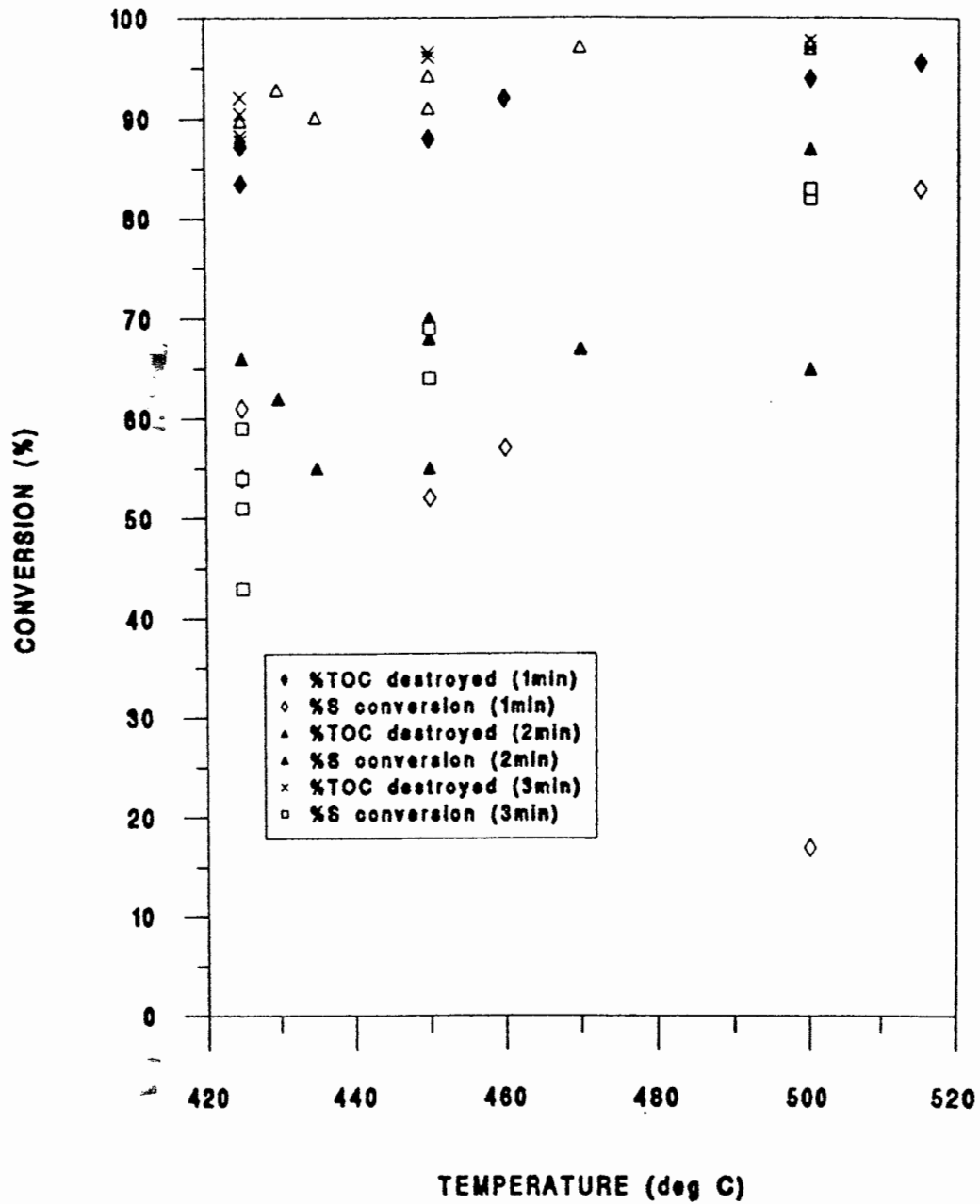


Figure B4. Conversion vs. Temperature for All Thiodiglycol Oxidation Tests

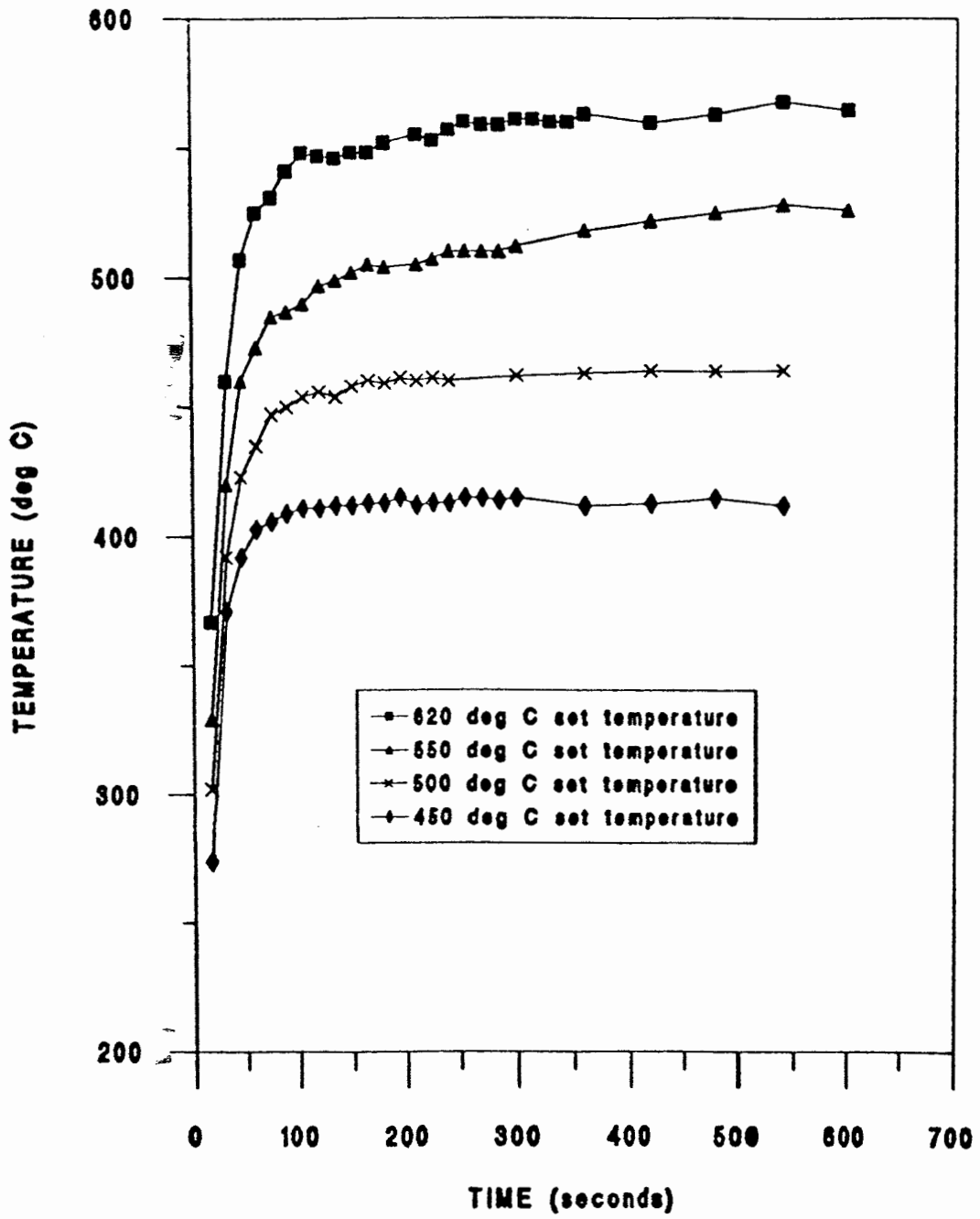


Figure B5. Temperature Calibration Curve for Sand Bath

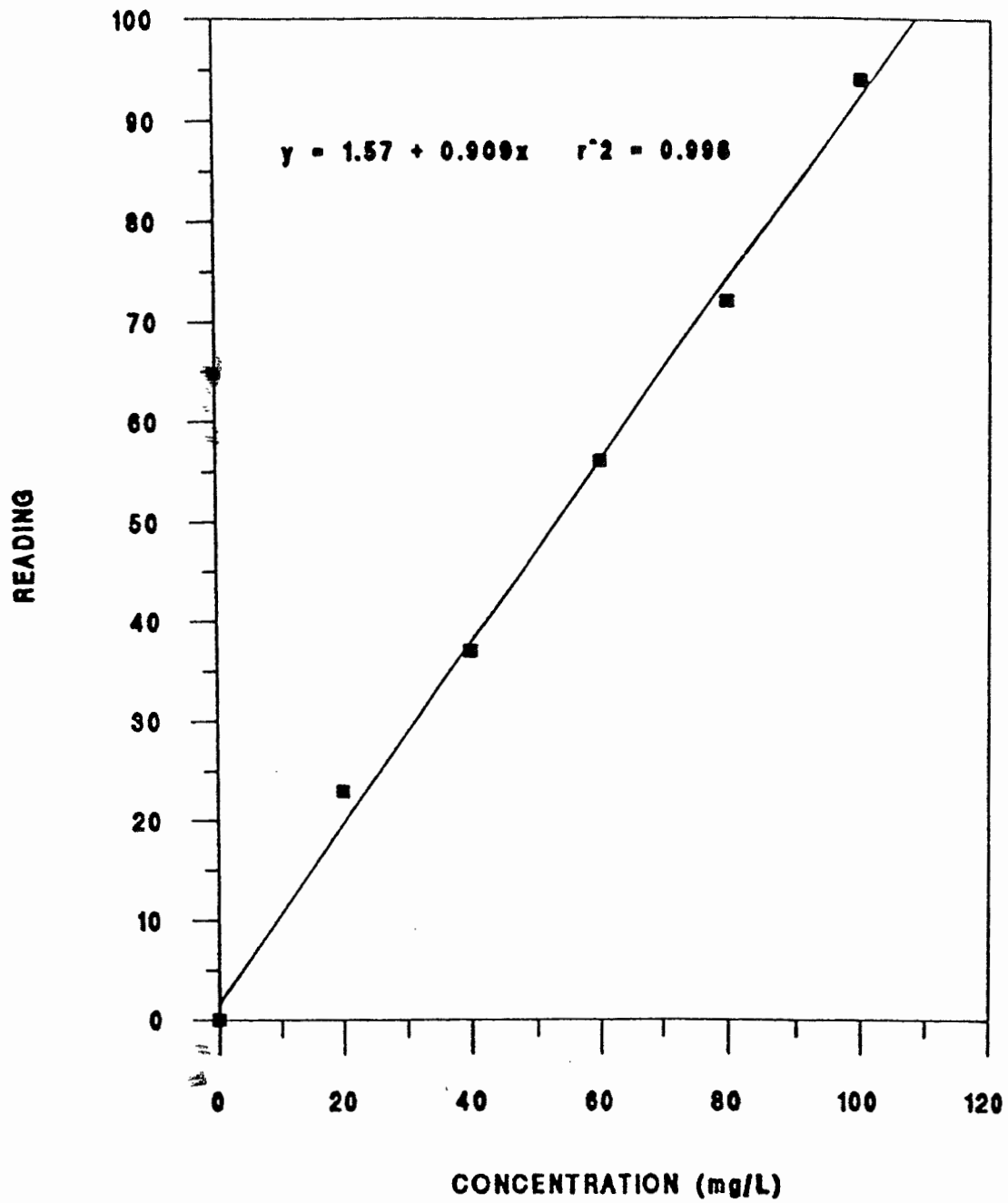


Figure B6. Total Carbon Standard for TOC Analysis (Low Scale)

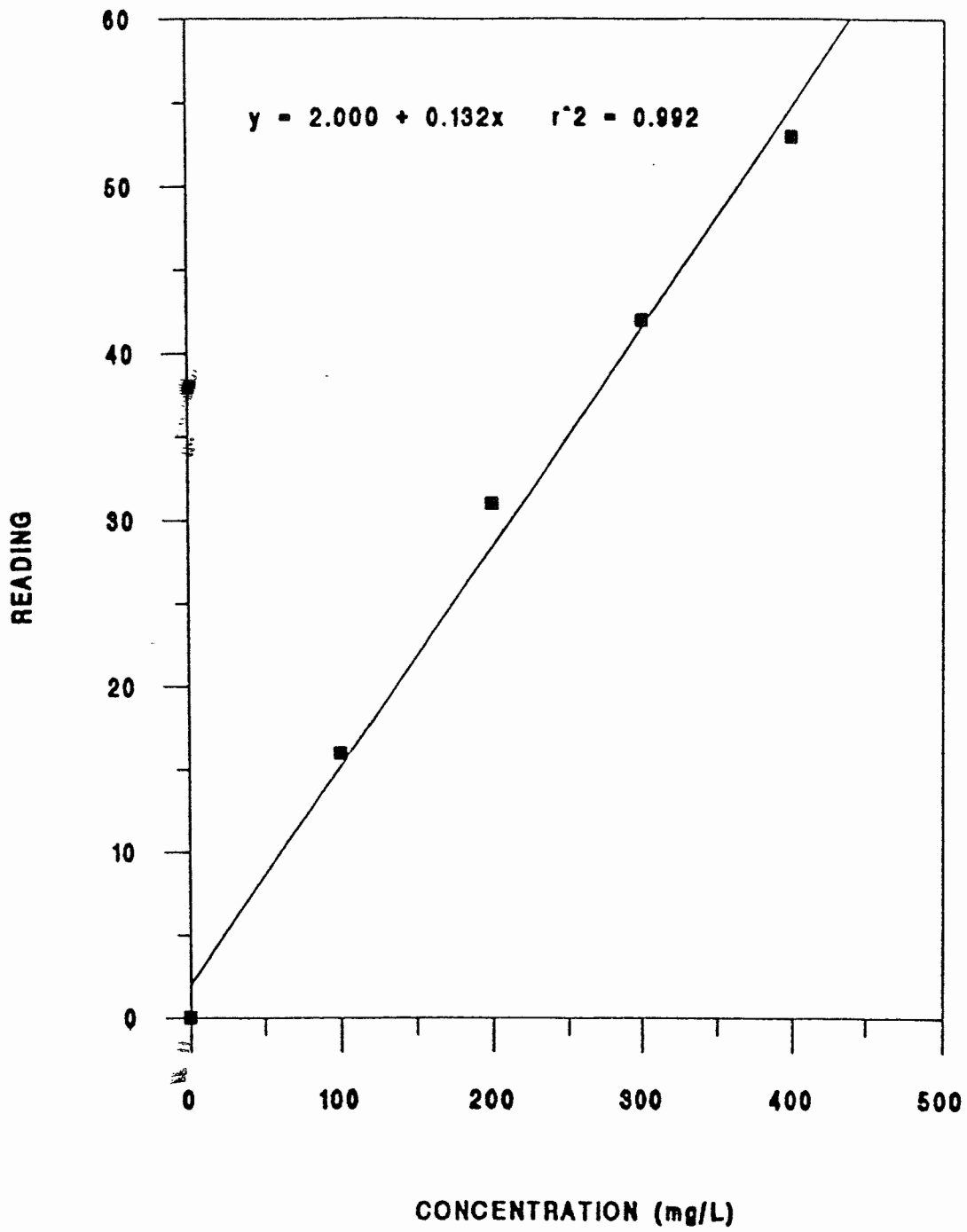


Figure B7. Total Carbon Standard for TOC Analysis (High Scale)



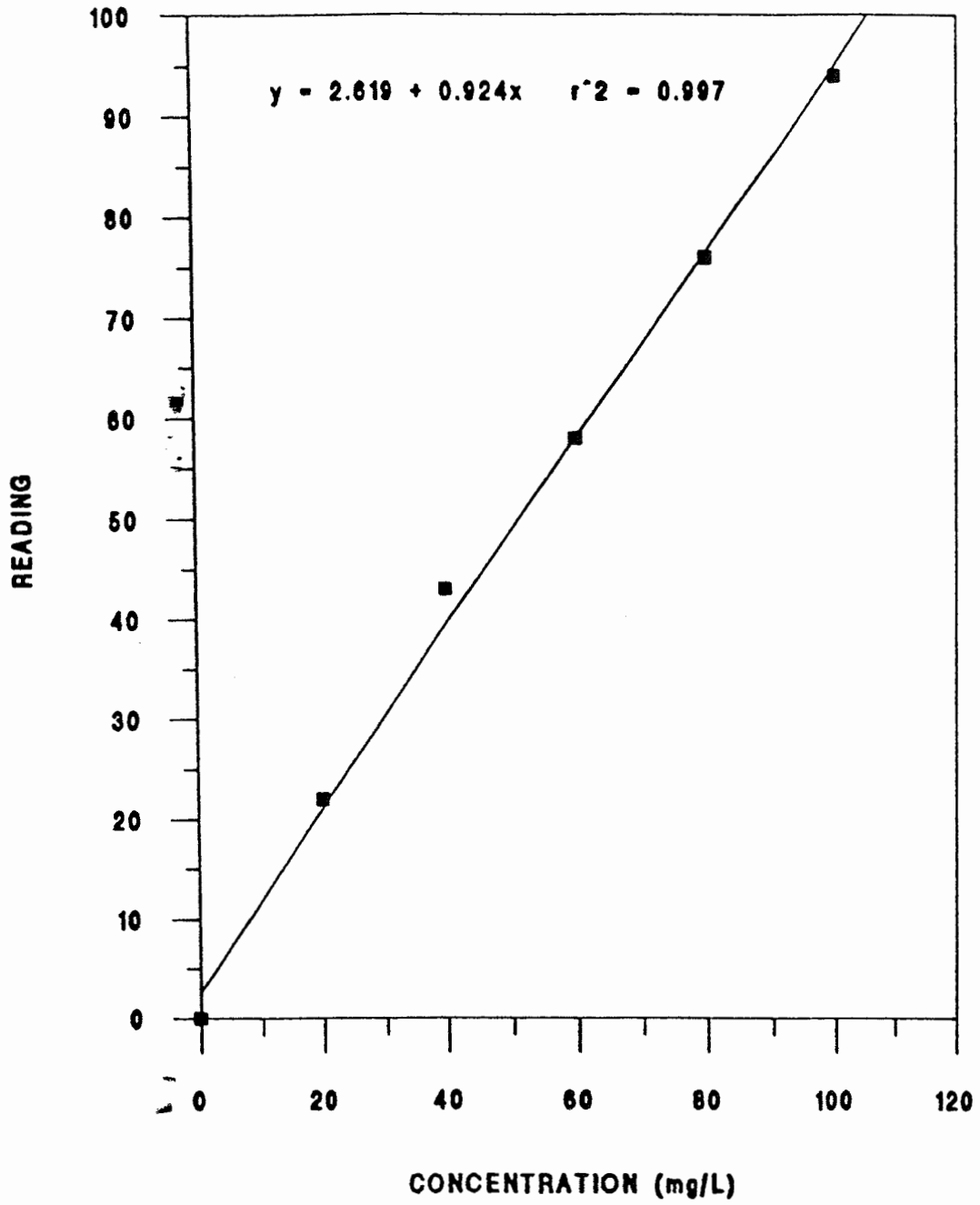


Figure B8. Inorganic Carbon Standard for TOC Analysis (Low Scale)

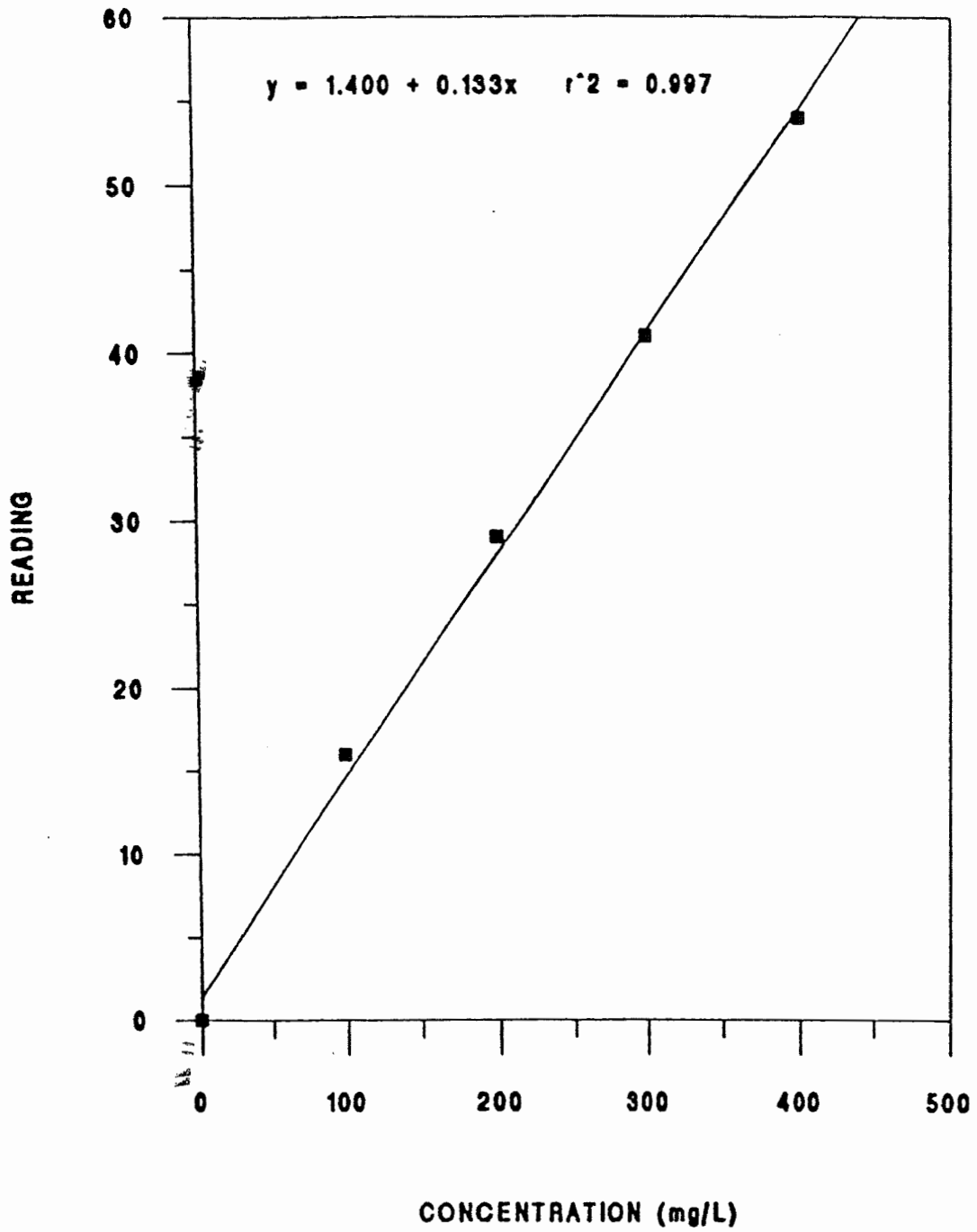


Figure B9. Inorganic Carbon Standard for TOC Analysis (High Scale)

## REFERENCES

- Barner, H.E., et al., Supercritical Water Oxidation: An Emerging Technology, *ACHEMA*, June 1991.
- Bramlette, T.T., et al., Destruction of DOE/DP Surrogate Wastes with Supercritical Water Oxidation Technology, Sandia Report, Albuquerque, NM, SAND90-8229, Nov. 1990.
- Broad, W.J., New Methods Sought to Dispose of Rockets with No Harm to Earth, *New York Times*, Sep. 17, 1991.
- Buelow, S.J., et al., Advanced Techniques for Soil Remediation: Destruction of Propellant Components in Supercritical Water, Los Alamos National Laboratory, NM, August 1, 1989.
- Capaccio, T., Army Hit by Added Delays on Chemical Weapons Cleanup, *Defense Week*, 28(11), 1, 1990.
- Carnes, S.A., Disposing of Chemical Weapons: A Desired End in Search of an Acceptable Means, *Environmental Professional*, 11, 179, 1989.
- Carney, H.C., Personal Communication, Internal Correspondence GA 1076, Chemical Agent Simulants for SCWO Program, July 12, 1991.
- Chang, Y., et al., Polymer Sorbents for Phosphorus Esters: I. Selection of Polymers by Analog Calorimetry, *Polymer Engineering and Science*, 27(10), May 1987.
- Clark, D.N., Chemical Weapons Disposal, *Science*, 257, 11, 1992.
- Clark, D.N., Review of Reactions of Chemical Agents in Water, Battelle, Avail. NTIS, Order No.: AD-A213287 GRAI U.S., Washington, D.C., January 1, 1989.
- Clesceri, L.S., et al., eds., *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; APHA, AWWA, and WPCF; Washington, D.C., 1989.

- Eller, J. Personal Communication, Eco Waste Technology, Austin, Texas, 1992.
- Ember, L.R., Chemical Weapons Disposal: Daunting Challenges Still Ahead, *Chemical and Engineering News*, 11, Aug. 13, 1990.
- Forsten, I., Pollution Abatement in a Munitions Plant, *Environmental Science and Technology*, 7(9), 806, 1973.
- Franck, E.U., Thermophysical Properties of Supercritical Fluids with Special Consideration of Aqueous Systems, *Fluid Phase Equilibria*, 10, 211, 1983.
- Freeman, H.M., ed., *Standard Handbook of Hazardous Waste Treatment and Disposal*, McGraw-Hill, New York, NY, 1989.
- Josephson, J., Supercritical Fluids, *Environmental Science and Technology*, 16(10), 548A, 1982.
- Lee, D.S., et al., Efficiency of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> in Supercritical Water Oxidation of 2,4-Dichlorophenol and Acetic Acid, *Journal of Supercritical Fluids*, 3, 249, 1990.
- Modell, M., Detoxification and Disposal of Hazardous Organic Chemicals by Processing in Supercritical Water, Modar Inc., Avail. NTIS, Order No.: AD-A179-005 GRAI U.S., DAMD-17-80-C-0078, Washington, D.C., Nov. 6, 1985.
- Modell, M., et al., Supercritical Water: Testing Reveals New Process Holds Promise, *Solids Waste Management*, 26, Aug. 1982.
- Modell Development Corporation, Supercritical Water Oxidation: An Alternative to Incineration for High Risk Wastes, Briefing for Los Alamos National Laboratory, NM, Feb. 28, 1991.
- O'Brien, R.L., Tables of Solid Rocket Motor Propellant Composition, Personal Correspondence, Oct. 29, 1991.
- Picardi, A., et al., *Alternative Technologies for the Detoxification of Chemical Weapons: An Information Document*, Prepared for Greenpeace International, May 24, 1991.

- Rofer, C.K., and Wander, J.D., Proceedings of the Workshop on Supercritical Fluid Processing of High Risk Wastes, Los Alamos National Laboratory, NM, August 1, 1989.
- Schreuder-Gibson, H.L., Adhesion of Solid Rocket Materials, *Rubber World*, 34, Nov. 1990.
- Shaw, R.W., et al., Supercritical Water: A Medium for Chemistry, *Chemical and Engineering News*, Dec. 23, 1991.
- Sides, G.D., and Spafford, R.B., Literature Review of Thermal Decomposition Studies of the Agents GB, VX, and HD, Southern Research Institute, SoRI-EAS-84-817, October 11, 1984.
- Thomason, T.B., and Modell, M., Supercritical Water Destruction of Aqueous Wastes, *Hazardous Waste*, 1(4), 453, 1984.
- Turner, M.D., Personal Communication, The University of Texas at Austin, Austin, TX, 1992.
- USAFA, Chemical Warfare Handout, Department of Civil Engineering, USAF Academy, Fall 1990.
- Verweij, A., et al., Isolation, Concentration and Subsequent Analysis by Capillary Gas Chromatography of Trace Amounts of Organophosphorus Compounds from Aqueous Samples, *International Journal of Environmental and Analytical Chemistry*, 21, 63, 1985.
- Verweij, A., et al., Hydrolysis of Some Methylphosphonites and Methylphosphinates, *Analytica Chimica Acta*, 151(1), 221, 1982.
- Wang, L.K., et al., Pollution from U.S. Explosives and Propellants Production, *Effluent and Water Treatment Journal*, 222, June 1982.
- Watson, A.P., et al., Health Effects of Warfare Agent Exposure: Implications for Stockpile Disposal, *Environmental Professional*, 11, 335, 1989.

## GENERAL REFERENCES

- Arendale, W.F., *Chemistry of Propellants Based on Chemically Crosslinked Binders, Propellants Manufacture, Hazards, and Testing*, American Chemical Society, Washington, D.C., 67, 1969.
- Bader, A., et al., *Aldrich*, Aldrich Chemical Company, Inc., New York, NY, 1990.
- Bailin, L.J., *Microwave Plasma Detoxification Process for Hazardous Wastes. Phase II. Systems Application, Evaluation, Avail. NTIS, Order No.:PB-284652 GRAI U.S., 78(25), Washington, D.C., 177, 1978.*
- Barlow, J.W., et al., *Development of Flow Through Detectors For Phosphorous Esters, Proceedings of the 1984 CRDC Scientific Conference on Chemical Defense Research, Aberdeen, MD, Nov. 13, 1984.*
- Barlow, J.W., et al., *Polymer Sorbents for Phosphorous Esters: II. Hydrogen Bond Driven Sorption in Fluoro-Carbinol Substituted Polystyrene, Polymer Engineering and Science, 27(10), 1987.*
- Belcher, D.W., *Spray Drying of War Gas Residue, Chemical Engineering Progress, 73(7), 101, 1977.*
- Budavari, S., ed., *The Merck Index*, 11th ed., Merck and Co., Inc., Rahway, NJ, 1989.
- D'Agostino, P.A., and Provost, L.R., *Gas Chromatographic Retention Indices of Chemical Warfare Agents and Simulants, Journal of Chromatography, 331(1), 47, 1985.*
- Demilitarization Plan: *Operation of the Chemical Agent Munitions Disposal System (CAMDS) at Tooele Army Depot. Inclosure Number 1. Design Criteria, Avail. NTIS, Order No.: AD-A062-372 GRAI U.S., 79(9), Washington, D.C., 169, 1979.*
- Deneau, K.S., *Pyrolytic Destruction of Hazardous Waste, Plant/Operations Progress, 2(1), 34, 1983.*

- Dustin, D.F., et al., Applications of Molten Salt Incineration to the Demilitarization and Disposal of Chemical Material, Report 1977, EM-TR-76099, Avail. NTIS, Order No.: AD-B016376 GRAI U.S., 79(10), Washington, D.C., 209, 1979.
- Dutch, P.H., Developing an Enzymatic Method of Decontaminating Water Containing Chemical Warfare Nerve Agents, Report 1985, Avail. NTIS, Order No.: AD-A155639 GRAI U.S., 85(19), Washington, D.C., 1985.
- Edmundson, R.S., *Dictionary of Organophosphorus Compounds*, Chapman and Hall, New York, NY, 1988.
- Eringen, A.C., Liebowitz, H., Koh, S.L., and Crowley, J.M., eds., *Mechanics and Chemistry of Solid Propellants*, Pergamon, New York, NY, 1967.
- Franck, E.U., Experimental Investigations of Fluids at High Pressures and Elevated Temperatures, *High Pressure Chemistry*, 221, 1978.
- Gay, R.L., Molten Salt Destruction, *Hazardous Waste Consultant*, 8(6), 4-38, 1990.
- Hancock, J.R., and Peters, G.R., Retention Index Monitoring of Compounds of Chemical Defence Interest Using Thermal Desorption Gas Chromatography, *Journal of Chromatography*, 538(2), 249, 1991.
- Helling, R.K., and Tester, J.W., Oxidation of Simple Compounds and Mixtures in Supercritical Water: Carbon Monoxide, Ammonia, and Ethanol, *Environmental Science and Technology*, 22(11), 1319, 1988.
- Landel, R.F., and Rembaum, A., eds., *Chemistry in Space Research*, American Elsevier, New York, NY, 1972.
- Lawhorne, S., Demilitarization Plan; Operation of the Chemical Agent Munitions Disposal System (CAMDS) at Tooele Army Depot, Inclosure Number 2, Statistically Significant Sampling Program, Avail. NTIS, Order No.: AD-A062-378 GRAI U.S., 79(9), Washington, D.C., 169, 1979.

- Lee, D.S., et al., Supercritical Water Oxidation of Hazardous Organic Compounds, Presented at AIChE Annual Meeting, Los Angeles, CA, November 1991.
- Levelt Sengers, J.M.H., Solubility Near the Solvent's Critical Point, *Journal of Supercritical Fluids*, May 3, 1991.
- Lindsten, D.C., and DesRoches, P.R., Decontamination of Water Containing Chemical and Radiological Warfare Agents by Reverse Osmosis, AD Rep. 1977, Avail. NTIS, Order No: AD-A046203 GRAI U.S., 78(2), Washington, D.C., 177, 1978.
- Mesmer, R.E., et al., Thermodynamics of Aqueous Association and Ionization Reactions at High Temperatures and Pressures, *Journal of Solution Chemistry*, 17(8), 699, 1988.
- Mink, W.H., Application of the Sodium Dual Alkali Scrubbing Process to High Chloride Gas Streams, *ACS Division of Fuel Chemistry Preprints*, 30(2), 162, 1985.
- Ogata, Y., and Sawaki, Y., Kinetics of the Catalytic Hydrogen Peroxide Oxidation of Thiodiglycol in Aqueous Solutions, *Chemical Society of Japan Bulletin*, 68, 1484, 1946.
- Pouchert, C.J., *The Aldrich Library of Infrared Spectra*, 3rd ed., Aldrich Chemical Company, Inc., 1981.
- Robinson, J.P.P., *Chemical and Biological Warfare Developments: 1985*, Oxford Univ. Press, New York, NY, 1986.
- Ross, S.D., The Rate of Oxidation of Thiodiglycol and Triethylamine by Hydrogen Peroxide, *Journal American Chemical Society*, 68, 1484, Aug. 1946.
- Sass, S., and Fisher, T.L., Chemical Ionization and Electron Impact Mass Spectrometry of Some Organophosphonate Compounds, *Organic Mass Spectrometry*, 14(5), 257, 1979.



- Sehnai, V.M., et al., Diffusion in Liquid and Supercritical Fluid Mixtures, AIChE Annual Meeting Symposium on Supercritical Fluids, Los Angeles, CA, November 1991.
- Small, M.J., Compounds Formed from the Chemical Decontamination of HD, GB, and VX and their Environmental Fate, 1984, USAMBRDC-TR-8304, Avail. NTIS, Order No.: AD-A149575/9/GAR GRAI U.S., 85(8), Washington, D.C., 158, 1985.
- Smith, J.G., et al., A Convenient Synthesis of Dimethyl [(Alkylthio)methyl]phosphonates and Dimethyl [(Arylthio)methyl]phosphonates, *American Chemical Society*, 48, 1110, 1983.
- Spiers, E.M., *Chemical Weaponry: A Continuing Challenge*, St. Martin's Press, New York, NY, 1989.
- Stearns-Roger, Inc., Final Process Design for the Agent Destruction System (ADS) for CAMDS [Chemical Agent Munitions Disposal System] at Tooele Army Depot, Tooele, Utah, Avail. NTIS, Order No.: AD-A062-358 GRAI U.S., 79(9), Washington, D.C., 169, 1979.
- Subramaniam, B., and McHugh, M.A., Reactions in Supercritical Fluids A Review, *Industrial Engineering Chemistry Process Design and Development*, 25, 1, 1986.
- Swallow, K.C., et al., The Modar Process for the Destruction of Hazardous Organic Wastes—Field Test of a Pilot-Scale Unit, *Waste Management*, 9, 19, 1989.
- Templeton, M.K., and Weinberg, W.H., Decomposition of Phosphonate Esters Adsorbed on Aluminum Oxide, *Journal American Chemical Society*, 107(4), 774, 1985.
- Van Der Veken, B.J., and Herman, M.A., An Infrared Study of the Gas-Phase Conformation of Dimethyl methylphosphonate, *Journal of Molecular Structure*, 96, 233, 1983.

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