

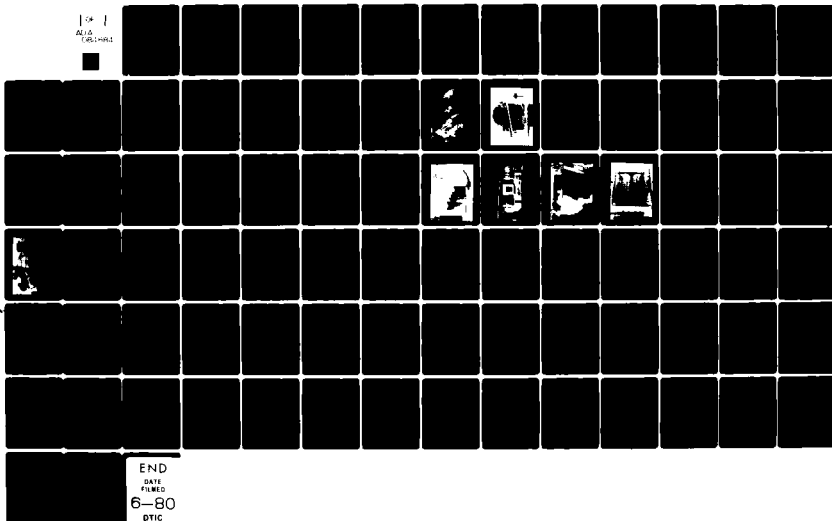
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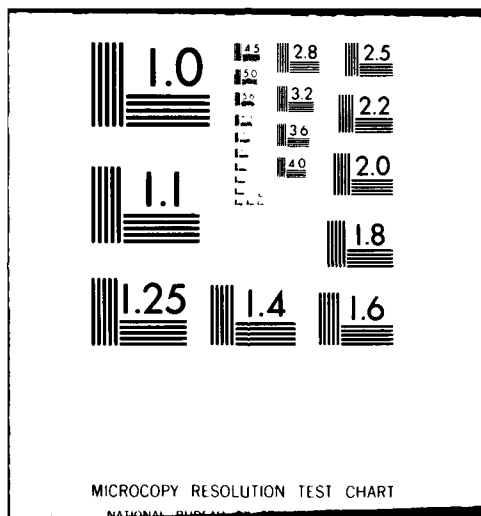
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Photooxidative Treatment
of TNT Contaminated Waste Waters

A Project of the
Manufacturing Technology Program
of the Naval Sea Systems Command

FINAL REPORT

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MAY 27 1980

Prepared by
Catherine C. Andrews
Weapons Quality Engineering Center
Naval Weapons Support Center, Crane, Indiana

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	Explosive contaminated water																
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See page 1 408811 Jm																	

ABSTRACT

Photooxidative Treatment of TNT Contaminated Wastewaters

This project demonstrated the feasibility of treating explosive contaminated wastewaters using an oxidant (hydrogen peroxide) in conjunction with short wavelength UV light. The process achieves a high degree of decontamination without any troublesome by-products. Water contaminated with trinitrotoluene (TNT) and cyclonite (RDX) was successfully treated using this photooxidative method. The parameters for the design of an ultraviolet light chamber for large scale treatment of TNT and RDX contaminated wastewaters were ascertained as a result of these studies. A pilot-scale system was designed and tested at a load, assemble and pack (LAP) facility at the Naval Weapons Support Center, Crane, Indiana.

In general, when compared with two other processes (UV-ozonation and carbon adsorption), the UV-H₂O₂ (hydrogen peroxide) treatment appears to be the simplest, most direct and most economical process available for the treatment of explosive contaminated wastewaters.

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
List of Tables	v
List of Figures	vi
 I INTRODUCTION	 1
 II PRELIMINARY LABORATORY WORK	 1
A. General Discussion	1
B. The pH Factor	3
C. Summary: Bench-Scale UV System	5
 III BASIC MECHANISM OF H_2O_2 IN THE PHOTOOXIDATIVE PROCESS	 5
 IV TESTING OF COMMERCIAL UV UNITS	 6
A. General Introduction	6
B. Methodology	6
C. Results of Studies with Commercial Units	8
D. Mechanism of Oxone Reaction	12
E. Objections to Oxone Use	12
 V FILM DEPTH, UV INTENSITY AND TRANSMISSION	 13
 VI UV-PILOT SCALE SYSTEM	 14
A. General Introduction	14
B. Methodology and Results	17
C. Problems	20
 VII SUMMARY AND RECOMMENDATIONS	 21

TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
VIII GENERAL COMPARISON OF AVAILABLE TREATMENT PROCESSES	23
IX COMPARISON OF CAPITAL AND OPERATING COSTS FOR UV H ₂ O ₂ , UV-OZONE, AND CARBON ADSORPTION TREATMENTS	24
A. Basis of Cost Estimates	24
B. Equipment	26
C. Energy	26
D. Oxidizer (H ₂ O ₂)	27
E. Combined Costs	28
X POTENTIAL USE -- UV-H ₂ O ₂ SYSTEM (TREATMENT OF WASTE EXPLOSIVE D AND MILITARY DYE MARKERS)	29
XI GENERAL SUMMARY	30
XII ACKNOWLEDGEMENTS	30
XIII REFERENCES	31
XIV APPENDIX OF METHODS	32
1. Gas Chromatographic (GC) Analysis of TNT	32
2. Thin-layer Chromatographic (TLC) Analysis of Polynitroaromatics	33
3. Total Organic Carbon (TOC) Analysis	35
4. Liquid Chromatographic (LC) Analysis of Explosives: TNT, RDX, HMX and TNB	36

TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
5. Gravimetric Analysis of Sulfate With Ignition of Residue .	38
6. Potassium Permanganate Tetraton of H_2O_2	38
7. Modified Brucine Method for $N-NO_3$	38
8. IR Analysis of Jacket Film -- KBr Pellet Method	38
XV DISTRIBUTION LIST	39

LIST OF TABLES

TABLE	<u>Page</u>
1 The effects of pH on the photooxidation of 100 ppm TNT solutions in the bench-scale unit	4
2 Comparison of the UV-2000 and UV-500 systems using oxone and/or H ₂ O ₂ in the treatment of 1:4 diluted pink water	9
3 Comparison of oxidants in the treatment of diluted pink water in the UV-2000 system	10
4 Comparison of oxidants in the treatment of pink water in the UV-500 system	11
5 Results of UV pilot study (2 gpm flow)	19
6 Comparison of initial explosive concentration and pH before and after irradiation	21
7 Cost of major equipment for UV-H ₂ O ₂ , UV-ozone and carbon adsorption systems	25
8 Operating cost for UV-H ₂ O ₂ treatment	25
9 Cost comparisons of major consumables for UV-H ₂ O ₂ , UV-ozone and carbon adsorption systems	26

LIST OF FIGURES

FIGURE	Following <u>Page</u>
1 Bench-Scale UV System	1
2 Comparison of Initial Peroxide Concentration and Average Residual TNT Concentration after One Hour Exposure in Bench-Scale Unit	2
3 Effect of Initial H ₂ O ₂ Concentration on TOC Reduction . . .	2
4 Effect of Prolonged Exposure on TOC of TNT Solution	2
5 Ultradynamics UV-2000 Units Connected in Series	6
6 Ultradynamics UV-500 Unit	6
7 Chemical Structures	6
8 Details of Photodegradation Reactor Unit	15
9 Path of Flow Through UV Unit	15
10 Top View of UV Reactor	15
11 UV Reactor in Trailer Outside Carbon Treatment Facility . .	15
12a Electrical Control Cabinet -- Pilot System	15
12b Lamp Wiring Arrangement	15
13 Route of Contaminated Effluent to UV Pilot System	16
14 Photooxidative System's Influent Lines	17

LIST OF FIGURES (Continued)

FIGURE	Following Page
15 Relationship of Absorbance (Color), Explosive and TOC Concentrations in the UV Pilot System at 2 gpm (Study A) .	18
16 Relationship of Absorbance (Color), Explosive and TOC Concentrations in the UV Pilot System at 1 gpm (Study B) .	18
17 Comparison of Residual Trinitrobenzene Concentration With Exposure and Original TNT Concentrations in the Pilot System	20
18 Comparison of pH and NO ₃ Concentration With Exposure in the Pilot System (Study A)	20
19 Comparison of pH and NO ₃ Concentration With Exposure in the Pilot System (Study B)	20
20 Comparison of pH and NO ₃ Concentration With Exposure in the Pilot System (Study C)	20

I. INTRODUCTION

Explosive contaminated wastewaters is a definite environmental problem at Department of Defense bomb production and demilitarization facilities. Laboratory studies were performed to evaluate the capability of using a photooxidative process to treat effluents contaminated with trinitrotoluene (TNT) alone or with TNT and cyclonite (RDX). The process incorporates the combination of short wavelength ultraviolet (UV) light and an oxidizer such as hydrogen peroxide as the treatment for these wastewaters. Studies using bench-scale and small commercial UV units have shown the feasibility and potential of the treatment. Additional work involving the testing of a large UV reactor system at a bomb production facility was performed to determine if the process could be scaled-up.

II. PRELIMINARY LABORATORY WORK

A. General Discussion

Initial laboratory studies incorporated a bench-scale UV unit and hydrogen peroxide in the treatment of TNT contaminated water. Synthetic solutions of 100 ppm TNT were made by dissolving 100mg of recrystallized TNT in one liter of distilled water with overnight mixing. This concentration was selected for the bench-scale studies because it approximates the limits of solubility of TNT in water at room temperature. The explosive solutions were mixed with hydrogen peroxide (Fisher Co., 35% H_2O_2) immediately before irradiation to yield the desired peroxide concentration. The solutions were irradiated in a UV apparatus consisting of a 30 watt mercury vapor lamp (primary wavelength, 254 nm) encased by a Pyrex glass sleeve designed with two ports for filling and emptying or recycling. See Figure 1 for an illustration of the apparatus. The liquid to be irradiated was trapped between the lamp and the glass. The film depth (maximum distance of the liquid from the UV source) was 5 mm. The total liquid capacity of the unit approximated 150 ml. Tests were performed with the unit operating

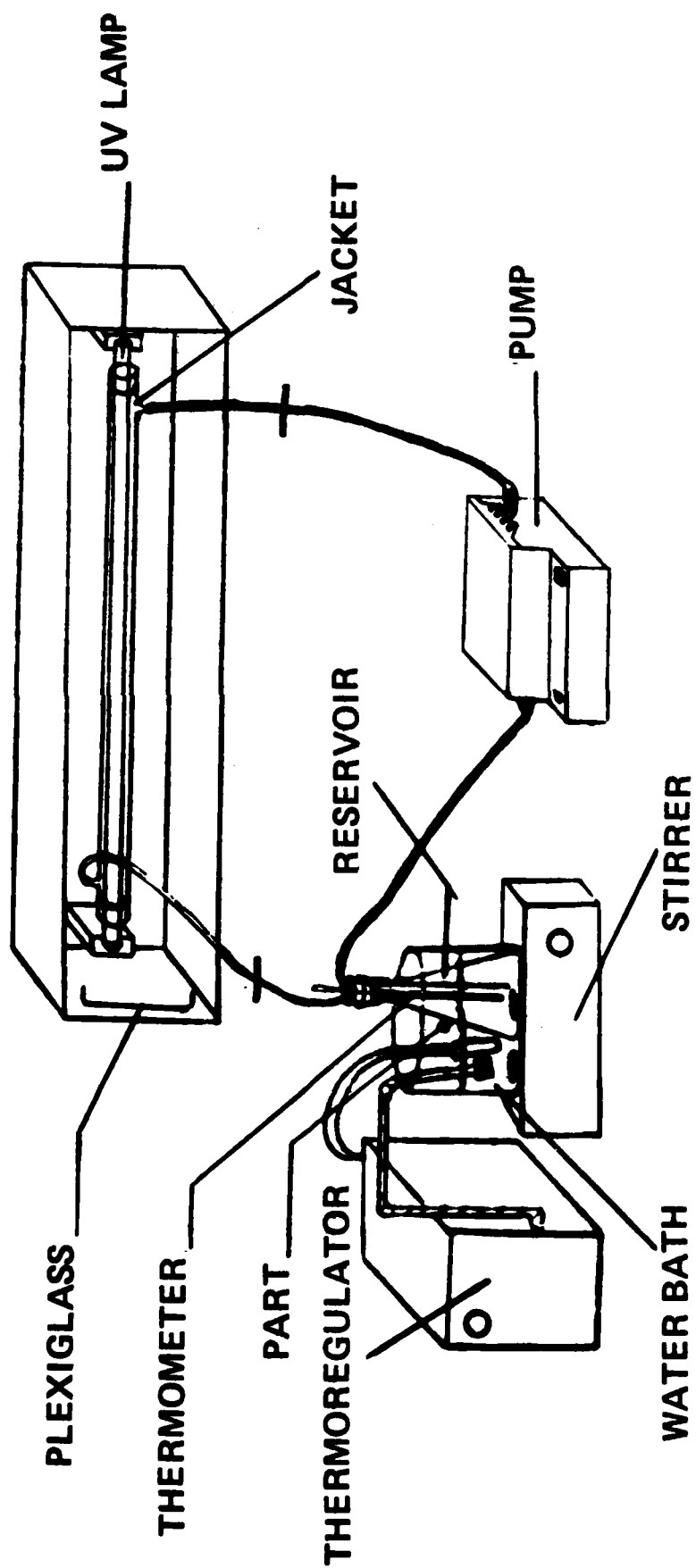


FIGURE 1. BENCH-SCALE UV SYSTEM

in recirculating mode with temperature regulation as depicted in Figure 1 or in static mode by filling the unit and irradiating the solution after clamping the influent and effluent ports.

Tests were performed to determine the exposure time and peroxide concentration required to efficiently and effectively destroy the explosive. Figure 2 illustrates the relationship between the initial hydrogen peroxide concentration tested and the average TNT concentration detected after irradiation of 100 ppm TNT solutions one hour in the bench-scale system. TNT concentrations were determined quantitatively by gas chromatography (GC), as described in Method 1, appendix. The presence of TNT and other polynitroaromatics was determined qualitatively by thin-layer chromatography (TLC) (Method 2, appendix).

The results of this study have shown that introducing concentrations of hydrogen peroxide at 0.5% or greater can have an adverse effect on the efficiency of the system. Maximum efficiency is achieved at 0.05% to 0.1% H_2O_2 . This is confirmed by comparing the reduction in TOC concentration (Method 3, appendix) with the initial H_2O_2 concentration in Figure 3. Based on the above, 0.1% H_2O_2 was selected for future studies. Limited experimentation has also shown that exposure beyond one hour in the bench-scale unit does not contribute significantly to the reduction in TOC concentrations of the 100 ppm explosive solutions (Figure 4).

The photooxidative mineralization of the TNT has been confirmed by studies involving the irradiation of solutions of 1, 3 and 5 labeled ^{14}C -TNT. $^{14}CO_2$ was recovered after the irradiation process indicating that the TNT ring was broken and that the TNT was being destroyed and not merely converted to related compounds by the photooxidative process (1, 2).

TLC analyses of these irradiated 100 ppm TNT solutions have supported the above results. No polynitroaromatic products were detected

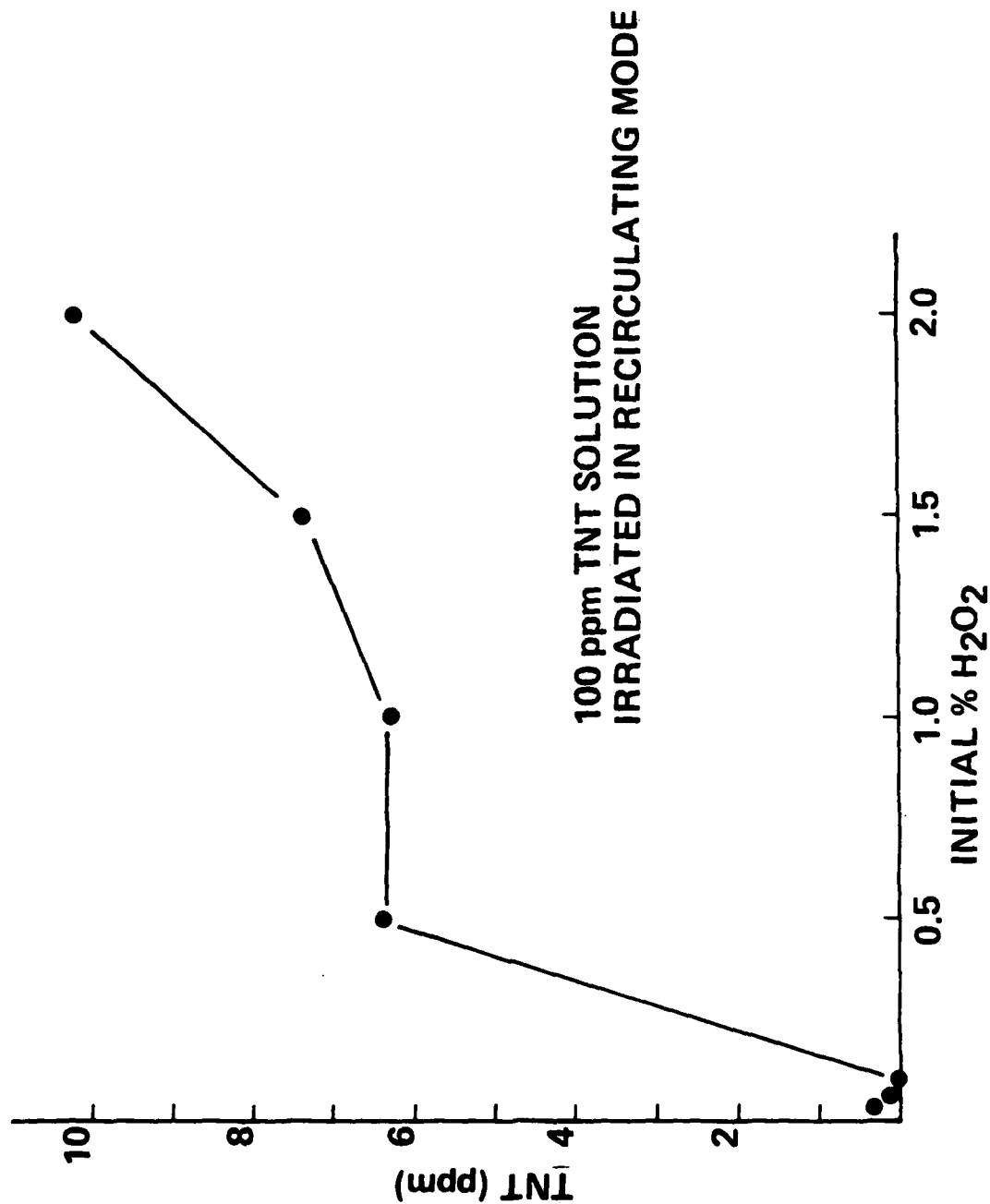


FIGURE 2. COMPARISON OF INITIAL PEROXIDE CONCENTRATION
AND AVERAGE RESIDUAL TNT CONCENTRATION
AFTER 1 HR. EXPOSURE IN BENCH-SCALE UNIT

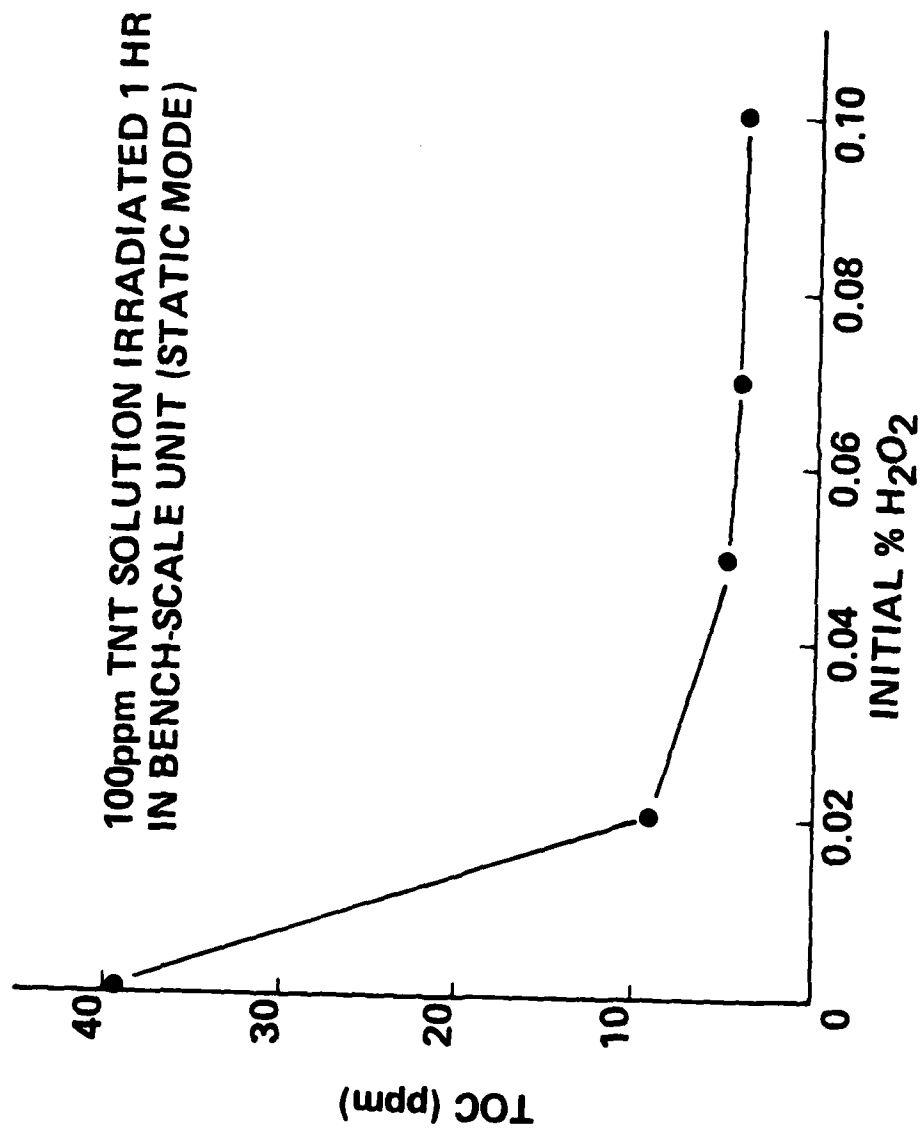


FIGURE 3. EFFECT OF INITIAL H_2O_2 CONCENTRATION
ON TOC REDUCTION

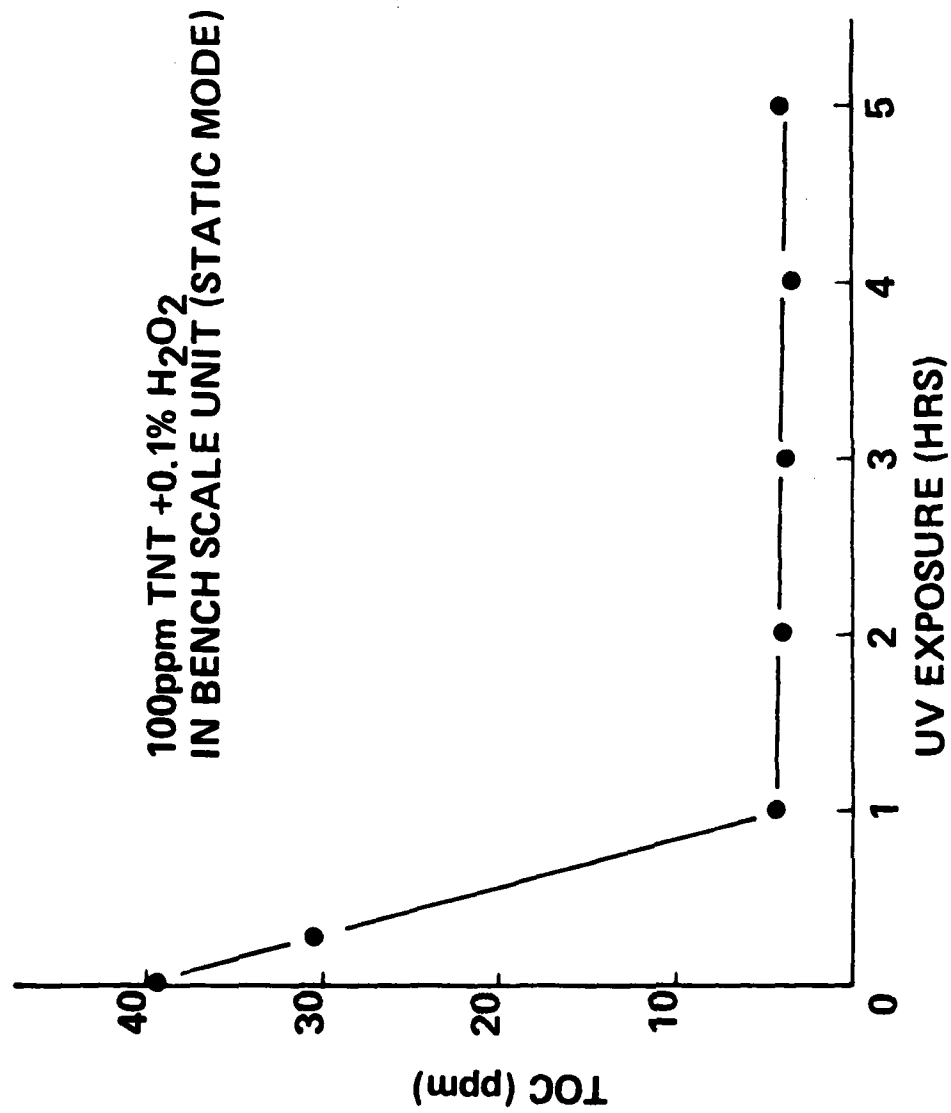


FIGURE 4. EFFECT OF PROLONGED IRRADIATION ON TOC OF
TNT SOLUTION

in these solutions by thin-layer chromatography after sufficient irradiation in the system.

As determined by peroxide test strips (E. Merck & Co., W. Germany) less than 10 ppm of the initial 1000 ppm (0.1%) H_2O_2 employed remained in solution after one hour of irradiation in the bench-scale system.

B. The pH Factor

The pH of the synthetic 100 ppm TNT water solutions varied between 6.5 and 7.0 after addition of sufficient H_2O_2 to achieve a 0.1% H_2O_2 concentration. After one hour of irradiation the pH of these solutions varied between 3.3 and 3.5. In a series of studies the pH of 100 ppm TNT solutions was adjusted with HCl or NaOH before irradiation to provide a pH range from one to ten to determine if the adjusted pH influenced the photooxidative reaction. Hydrogen peroxide was added in equal increments to the solutions after 0, 15 and 30 minutes of exposure. After the three additions a total of 0.06% hydrogen peroxide had been added. The pH of each of seven solutions was adjusted to 1, 2, 4, 7, 8, 9 or 10 after the addition of the first aliquot of H_2O_2 . Each of the solutions was irradiated for one hour. With addition of peroxide as noted, TNT solutions without pH adjustment were irradiated as controls. It was determined (Table 1) that an extremely acid pH (pH 1 or 2) negatively affected the reaction (note the large residual TNT and TOC concentrations after one hour of exposure). Such results could be attributed to the fact that extremely acidic environments stabilize the H_2O_2 . At least 100 ppm of the original 0.06% H_2O_2 concentration remained in these strongly acidified solutions after irradiation. Thin-layer chromatography of these acidic solutions illustrated that high concentrations of TNT as well as three other polynitroaromatic compounds were detected in the irradiated solutions adjusted to pH 1 or 2. Such results were unique as compared with the solutions having a higher initial pH values.

Table 1. The Effects of pH on the Photooxidation of 100 ppm TNT Solutions After One Hour of Irradiation in the Bench-Scale Unit (Multiple H_2O_2 additions yield 0.06% H_2O_2).

INITIAL pH	FINAL pH	INITIAL ppm TNT ^a	FINAL ppm TNT ^a	INITIAL ppm TOC ^b	FINAL ppm TOC ^b	FINAL ppm H_2O_2 ^c
6.9 ^d	---	98.2	---	41.5	---	---
1.0	1.1	---	32.1	---	32.8	100
2.0	1.9	---	22.5	---	21.2	100
4.0	3.4	---	0.15	---	23.9	12-50
6.9 ^d	3.5	---	≤ 0.01	---	3.7	50
7.0	3.4	---	≤ 0.2	---	10.9	50
8.0	3.5	---	$\leq 0.1^e$	---	1.0	50-100
9.0	3.5	---	$\leq 0.1^e$	---	3.2	50-100
10.0	3.6	---	$\leq 0.1^e$	---	4.3	12-50

^a GC Analysis - Method 1 in appendix

^b TOC Analysis - Method 3 in appendix

^c H_2O_2 - Semi-quantitative determinations using peroxide test strips (E. Merck & Co., Darmstadt, W. Germany) - color reaction

^d pH not adjusted

^e Limits of detection of this series of GC analyses was 0.1 ppm because of problems with interferences.

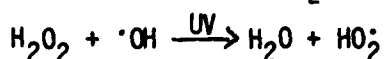
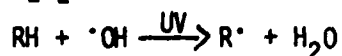
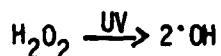
Overall, pH adjustment did not positively enhance the photooxidative process when such results are compared with the control. The solutions adjusted to neutrality by the addition of base also yielded poorer average results than that of the nonadjusted control which had an initial pH of 6.9.

C. Summary - Bench-Scale UV System

In view of the results with the bench-scale UV unit, the photooxidative process using short wavelength UV light and hydrogen peroxide appeared to be a very feasible treatment for TNT contaminated wastewaters. Patent #4,038,116 entitled "Method for Degrading Aromatic Explosive Solutions" was issued for this process on 26 July 1977. Since that time testing has been performed on larger UV systems to determine the applicability of such systems at a full scale demilitarization or production facility.

III. BASIC MECHANISM OF THE PHOTOOXIDATIVE PROCESS

In the presence of UV light hydrogen peroxide is broken down into radicals ($\cdot\text{OH}$, $\text{HO}_2\cdot$) which are ultimately responsible for the oxidation of the explosive structure. TNT strongly absorbs UV at the wavelength used in these studies, and so is probably in an "excited", or less stable, state during irradiation, thus tending toward a greater reaction with the free radicals. An incomplete but basic conception of this proposed reaction is presented below. RH represents the explosives.



IV. TESTING OF COMMERCIAL UV UNITS

A. General Introduction

Commercially available short wavelength ultraviolet units were incorporated in a test program to determine their effectiveness as reactor chambers for the photooxidative treatment process. Two types of UV light units were tested. They differed in size, lamp number and maximum film depth. Both units were manufactured by the Ultradynamics Corporation of Santa Monica, California. See Figures 5 and 6 for photographs of these units. The Ultradynamics UV-2000 unit (Figure 5) was the larger of the two types tested. It houses four 40 watt mercury vapor (UV) lamps (primary wavelength 254 nm) each surrounded by a quartz sleeve which is continuously cleaned by a hydraulically operated wiper assembly. The maximum film depth in this chamber is about 6.5 cm. Its liquid capacity is approximately 6 gallons (22.7 l). The smaller of the two units, the Ultradynamics UV-500 unit houses a single 40 watt mercury vapor lamp (254 nm primary wavelength) surrounded by a quartz sleeve. It is equipped with a manually operated wiper assembly. The maximum film depth of the UV-500 is 2.5 cm and it has a liquid volume of approximately 3/4 of a gallon (2.84 l). Both of the Ultradynamics units are made of 304 stainless steel.

B. Methodology

TNT Contaminated Effluent ("pink water") obtained from a bomb load and steamout operation at NAVWPNSUPPCEN Crane served as the source of the explosive contaminated effluent. The effluent is also known as pink water since TNT contaminated water upon exposure to sunlight becomes pink in color. The wastewaters contain the explosives TNT, RDX and hemicyclonite (HMX) from Comp B used in the bomblet production. The chemical structures of these compounds are illustrated in Figure 7. Before combination with the oxidizer and passage through the UV system, the effluents were filtered through 5 μ and 0.8 μ filters to remove suspended particulates. The water was then diluted with one or three

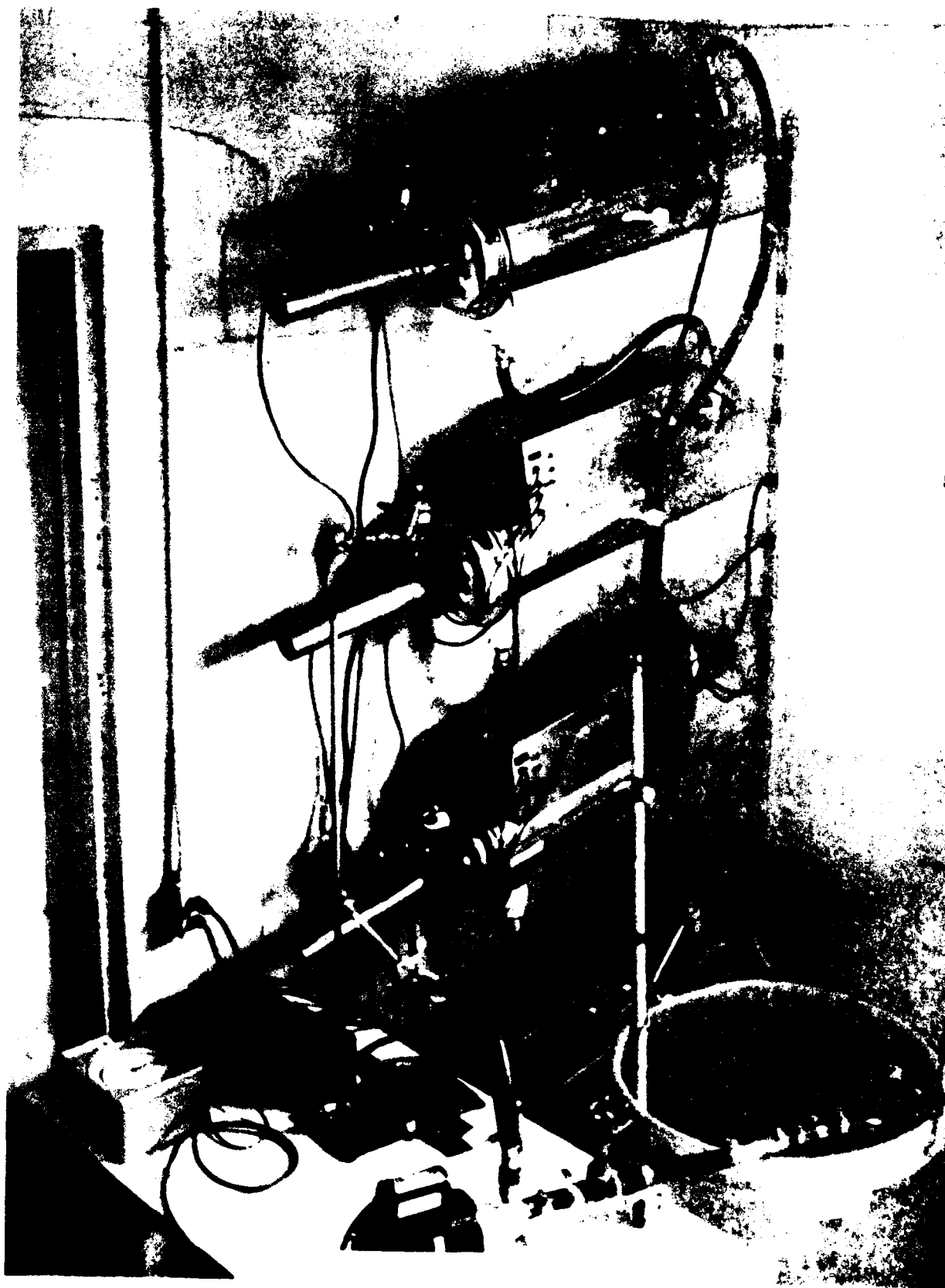


FIG. 5 ULTRADYNAMICS UV-2000
UNITS CONNECTED IN SERIES

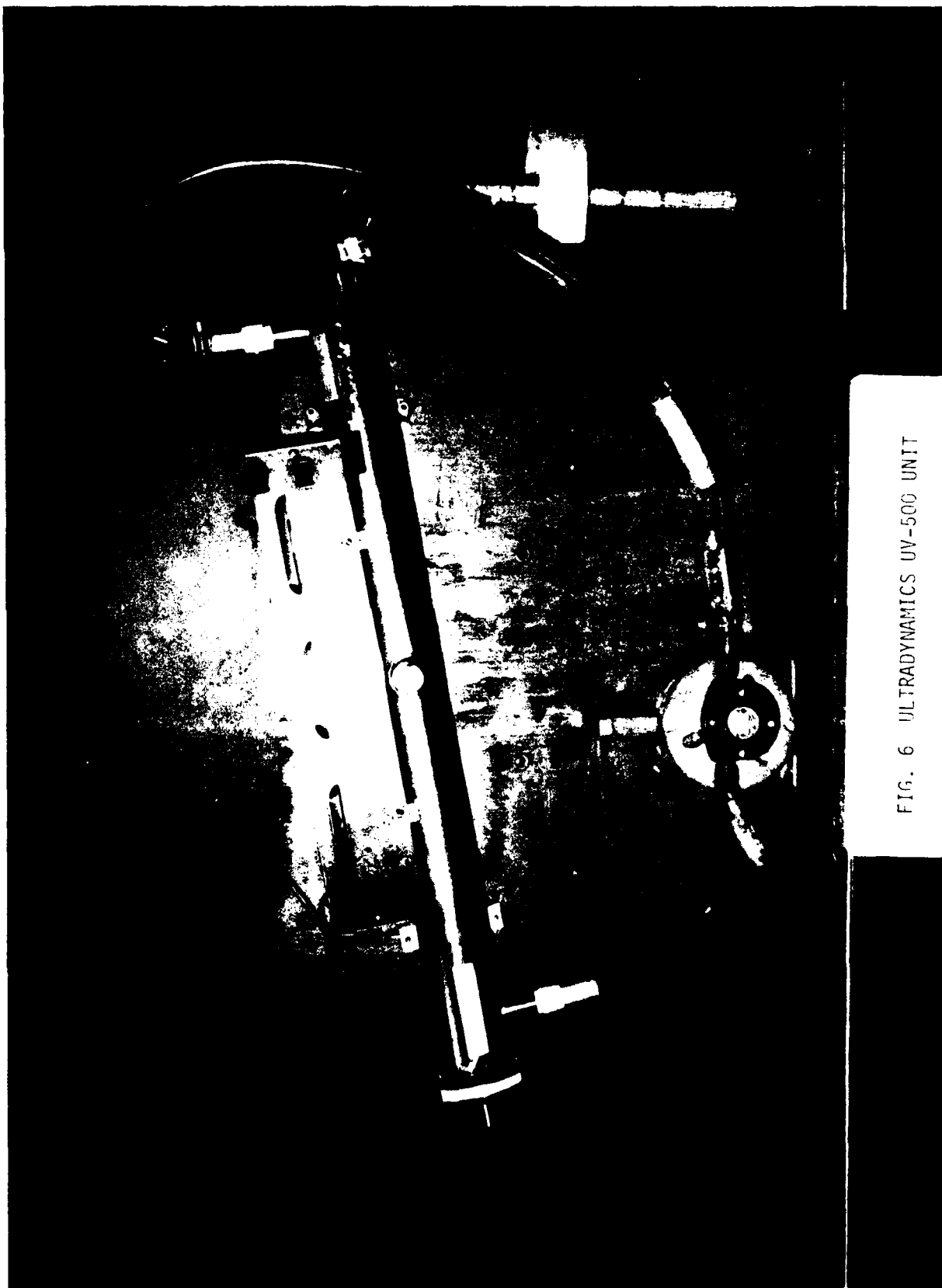
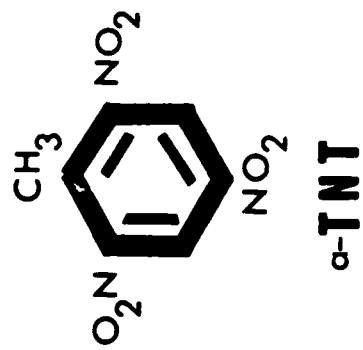
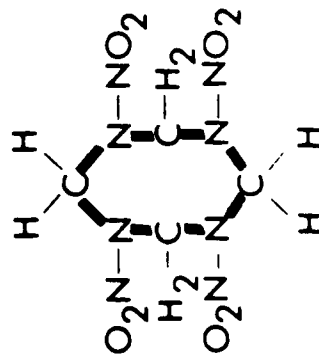


FIG. 6 ULTRADYNAMICS UV-500 UNIT



HMX



RDX

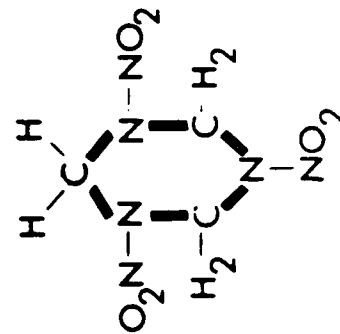


FIGURE 7. CHEMICAL STRUCTURES

parts tap water to yield 1:2 and 1:4 dilutions before treatment. Dilution was necessary since the initial color of the effluent was so intense that it would negatively affect the photooxidative process. Much of the UV energy would be lost to color absorption and thus unavailable for initiating the photochemical reactions. Before and after irradiation the water was analyzed by gas, liquid and/or thin-layer chromatography (Methods 1, 2, 4, appendix) to determine explosive concentrations. Total organic carbon (TOC) concentrations were determined according to Method 3 (appendix).

Based on the work discussed earlier 0.1% hydrogen peroxide was employed in all testing. A 35% H_2O_2 (Fisher Chemical) solution was diluted and mixed with the effluent to be treated to yield a concentration of 0.1% H_2O_2 before irradiation. After mixing with the peroxide the effluent was treated "in batch mode" by recirculating the liquid by means of centrifugal pump from a reservoir through the UV-2000 or UV-500 units. Only negligible amounts of solution remained in the reservoir and tubing at any one time and because of the rapid recirculation rate (identical for both units) actual contact time was assumed to approximate recirculation time.

Another oxidizing agent, a monopersulfate mixture*, was substituted for or used in conjunction with H_2O_2 in a number of studies involving the commercial units. The concentration of oxone was varied during the testing. Preweighed amounts of the oxone solids were dissolved in the effluent to obtain the desired concentrations. A special study was undertaken to examine the effects of using a combination of H_2O_2 and oxone in equivalent concentrations as part of the testing. Concentrations of 0.2% and 0.3% oxone in the effluent were

* Oxone - (Tradename - E. I. DuPont Nemours, Inc.) mixture of potassium monopersulfate, potassium sulfate and potassium hydrogen sulfate.

examined in the UV-2000 system and concentrations of 0.2%, 0.3% and 0.7% oxone were examined in the UV-500 system. A 0.1% oxone/0.1% H_2O_2 combination was tested in the UV-500 system as well.

C. Results of Studies With Commercial Units

Table 2 summarizes a study comparing the UV-2000 and UV-500 systems on the treatment of 1:4 diluted pink water. Hydrogen peroxide and oxone were used as the oxidizers. Based on the results of this study, oxone appears to yield better overall results with respect to explosive oxidation as determined by reductions in TOC concentrations.

Table 3 illustrates the results of studies comparing H_2O_2 , oxone and a combination of oxone and H_2O_2 on the treatment of diluted pink water solutions in the UV-2000 system. Based on the efficiency of the process with respect to TOC reduction and explosive destruction per unit time, it appears that oxone or the oxone/ H_2O_2 combination is more effective than H_2O_2 alone in treating these diluted pink water effluents. Treatment of 1:4 and 1:2 dilutions with 0.2% oxone required less exposure time than that of the same dilutions treated with 0.1% H_2O_2 . The combination oxone/peroxide treatments yielded comparable results. Trinitrobenzene does not appear to be a significant by-product of the oxone photooxidative reaction as it is with the peroxide treatment.

The treatment of pink water in the UV-500 system has also shown that oxone is more effective than H_2O_2 (Table 4). Far less exposure time was required in the UV-500 system than in the UV-2000 system to achieve comparable results. This is a result of some combination of factors involved, including differences in volume of material exposed, depth of film around the bulbs, number of bulbs, etc.

Utilizing the UV-500 system with a large concentration of oxone (0.7% oxone), a large exposure time was required to obtain explosive elimination and significant reduction in TOC in treating a supersaturated

Table 2. Comparison of the UV-2000* and UV-500* Systems Using Oxone or H₂O₂ as the Oxidizers on a 1:4 Diluted Solution of Pink Water

System	Oxidizing Agent	Total UV Exposure (hrs)	Decolorization Time (hrs)	Explosives Concentration (ppm)			TNB** Concentration (ppm)	TOC (ppm)	PNA*** (number present)
UV-2000	0.1% H ₂ O ₂	0	---	30.0	26.8	3.0	0	24.8	TNT + 2
		3	(~3)	≤ 0.01	≤ 0.01	≤ 0.02	2.53	5.6	TNB** + 3
		5	---	≤ 0.01	≤ 0.01	≤ 0.02	2.8	1.6	TNB + 3
UV-2000	0.3% oxone	0	---	34.0	27.4	2.8	0	24.2	TNT + 2
		3	(~1)	≤ 0.01	≤ 0.01	0	0	1.0	none
		5	---	≤ 0.01	≤ 0.01	≤ 0.02	0	1.0	none
UV-500	0.1% H ₂ O ₂	0	---	29.0	20.6	3.1	0	23.0	TNT + 2
		0.5	---	0.8	0.01	0.02	0.9	17.4	TNT, TNB + 4
		1.5	(~1.5)	0.05	≤ 0.01	≤ 0.02	2.8	8.0	TNB
UV-500	0.3% oxone	0	---	29.0	20.6	3.1	0	23.0	TNT + 2
		0.5	(~0.5)	0.3	≤ 0.01	≤ 0.02	1.5	7.6	TNT, TNB + 2
		1.5	---	≤ 0.01	≤ 0.01	≤ 0.02	0.06	1.8	none

*UV-500 system contains 2.84 liters of contaminated water; UV-2000 system, 22.7 liters

**TNB = trinitrobenzene - appears to be an intermediate in the reaction

***PNA = polynitroaromatic compounds as detected by thin-layer chromatography. All compounds were present at barely discernible levels in most cases. Except for TNB (trinitrobenzene) the other polynitroaromatics remain to be identified.

Table 3. Comparison of Oxidants in the Treatment of Diluted Pink Water in the UV-2000 System

DILUTION	OXIDANT	HOURS UV EXPOSURE	EXPLOSIVE (ppm)				TLC	TOC
			TNT	RDX	HMX	TNB ^a		
1:4	0.1% H ₂ O ₂	0	30.0	26.8	3.0	0	TNT + 2 PNA ^b	23.0
		5	≤ 0.01	≤ 0.01	≤ 0.02	2.08	TNB	1.6
1:4	0.3% oxone	0	28.0	26.0	2.7	trace	TNT + 2 PNA	22.8
		3	≤ 0.01	≤ 0.01	≤ 0.02	0	0	1.0 ^c
1:4	0.2% oxone	0	23.0	19.0	2.4	trace	TNT + 2 PNA	21.8
		3	≤ 0.01	≤ 0.01	≤ 0.02	0	0	1.0
1:2	0.1% H ₂ O ₂	0	64.0	48.0	6.9	0	TNT + 2 PNA	45.4
		5	≤ 0.01	≤ 0.05	≤ 0.05	2.5 0.9	TNB + 2 PNA	13.0
1:2	0.3% oxone	0	64.0	55.0	8.5	trace	TNT + 2 PNA	46.1
		3	≤ 0.01	≤ 0.01	≤ 0.02	0.4	TNB	3.4
1:4	0.1% H ₂ O ₂ + 0.1% oxone	0	23.0	20.0	2.5	trace	TNT + 2 PNA	25.0
		3	≤ 0.01	≤ 0.01	≤ 0.02	0.1	0	1.0

^a TNB - Trinitrobenzene

^b PNA - Polynitroaromatic product - unidentified

^c Limits of detectability of TOC 1.0 ppm

Table 4. Comparison of Oxidants in the Treatment of Pink Water in the UV-500 System

DILUTION	OXIDANT	HOURS UV EXPOSURE	EXPLOSIVE (ppm)				TLC	TOC
			TNT	RDY	HMX	TNB ^a		
1:4	0.1% H ₂ O ₂	0	29.0	20.6	3.1	0	TNT + 2 PNA ^b	23.0
		1.5	0.01	0.01	0.02	2.8	TNB	8.0
1:4	0.3% oxone	0	29.0	20.6	3.1	0	TNT + 2 PNA	23.0
		1	0.01	0.01	0.02	0	0	1.0 ^c
0	0.7% oxone ^d	0	138.0	128.6	15.0	---	TNT + 3 PNA	86.6
		6	0.02	0.02	0.02	1.1	TNB + 1 PNA	9.0

^a TNB = trinitrobenzene

^b PNA = polynitroaromatics - as yet, unidentified

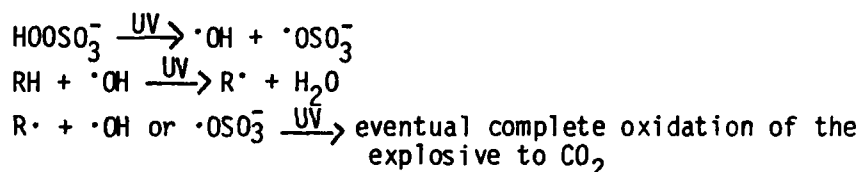
^c Limits of detectability of TOC = 1.0 ppm

^d Smaller oxone concentrations were tested without decolorization even after 7 hours of exposure

pink water solution. Nonetheless, after this treatment only trinitrobenzene and one unidentified polynitroaromatic compound were detected by thin-layer chromatography.

D. Mechanism of Oxone Reaction

The basic mechanism of the oxone photooxidative reaction is theorized to be essentially similar to that of the H_2O_2 mechanism discussed earlier. The primary reactive species of the oxone is the monopersulfate ion* existing in the water solution. This species is broken down to hydroxyl and sulfate radicals upon irradiation with UV light. Both the hydroxyl and sulfate radicals seek a more stable state and oxidize the explosives to achieve this. The basic theoretical reaction is summarized below:



Obviously, the reaction is far more complex. For a better understanding of the monopersulfate oxidative mechanism consult reference 3.

E. Objections to Oxone Use

There are two major drawbacks in the use of oxone as an oxidizer. A significantly large residual amount of sulfate (residual concentration dependent on initial amounts employed) was detected in these solutions after treatment. Concentrations of sulfate ranging from 1,000 to 3,000 ppm were detected when concentrations of 0.1%, 0.2% and 0.3% were initially employed. (Method 5, appendix). Although not specifically measured, large amounts of potassium were probably also present since oxone is composed of a variety of potassium sulfate salts and the potassium should not be involved in the reaction. The inorganic

* Monopersulfate ion = HSO_5^-

salts in the effluent could be a major problem in recycling the treated wastewater or for direct discharge if it cannot be sufficiently diluted.

Oxone is also relatively more expensive than peroxide on a weight by weight cost comparison.

V. FILM DEPTH, AND UV INTENSITY AND TRANSMISSION

The transmission of light through a solution containing light absorbing material depends upon the nature of the substance, the wavelength of the light, and the amount of light absorbing material in its path. This last factor depends upon the concentration of the substance and the depth of solution through which the light passes. The relationship at a given wavelength of light may be written

$$-\log T = Klc$$

in which T is percent of transmitted light, l = depth of solution through which the light passes, and c is the concentration of the absorbing material.

In a system which depends upon light absorption for reaction to occur, it is obvious that reaction rates are a function of the depth of the film through which the light is transmitted.

Trinitrotoluene, RDX and H_2O_2 , all components of reaction in the wastewater systems, all absorb strongly at 254 nm, the primary wavelength of light emitted by the lamps used in these studies. An aqueous solution containing 7 ppm TNT transmits only 46.5 percent of the incident UV light through a distance of 1 cm; 0.1% aqueous hydrogen peroxide, only 13.5%. In a solution containing 4 to 5 times as much TNT, some RDX, and 0.1% H_2O_2 , it is obvious that less than one percent of the UV light would be transmitted through a distance of 1 cm. A ten-fold decrease in film depth should increase transmission to between 60 and 70 percent at 254 nm.

Obviously, however, as the reaction proceeds the concentration of absorbant (TNT, H_2O_2) decreases, with a concomitant increase in distance the light travels before extinction. Also, in a flowing system, there will be continual mixing of the reacted and unreacted materials. There obviously must be trade-offs in selecting path length (film depth).

Also, the amount of UV energy available to the explosive-peroxide reaction will contribute significantly to reaction rates. UV lamps of the same general size and geometry but with different energy outputs are not, at present, available. However, it is possible to increase the number of bulbs in a system. The greater the number of UV sources per unit area maintaining this thin film, the greater the energy generated per unit of space and the greater the intensity. This energy can then be more effectively and efficiently used in the reaction process.

VI. UV - PILOT SCALE SYSTEM

A. General Introduction

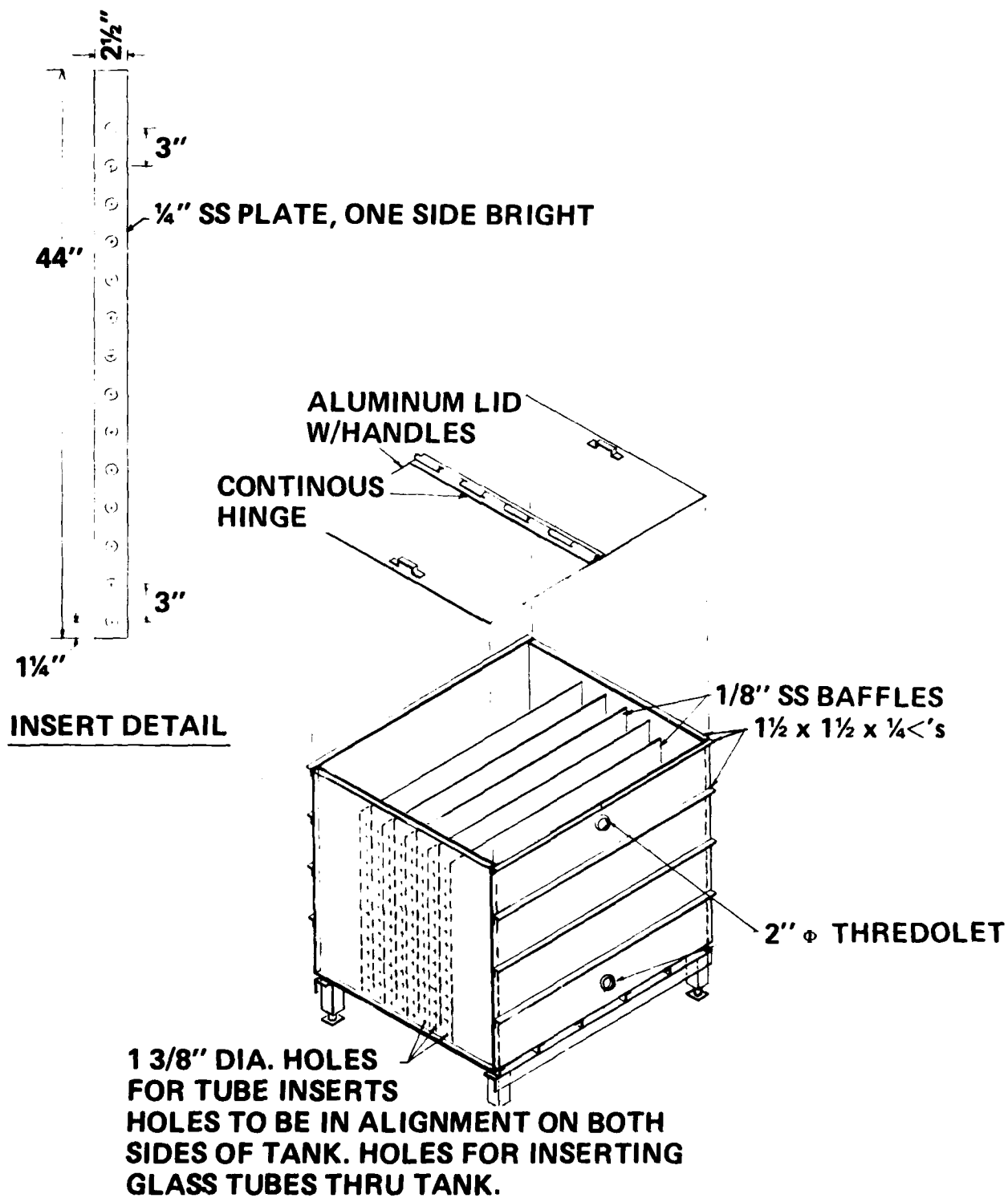
The previous studies illustrated the potential of the photooxidative process and provided the impetus to investigate the possibility of treating explosive contaminated effluents on a large scale using hydrogen peroxide as the oxidizer. To scale up to a pilot operation a large UV reactor was needed to provide sufficient exposure and a small enough film depth to achieve a relatively efficient operation.

As a result of a series of trade-offs involving economics and efficiency, the reactor was designed and built to provide a maximum film depth of 2.5 cm. Eight baffled rows of lamps provide the necessary contact time. This type of arrangement should provide greater efficiency than the single lamp commercial unit of the same film depth tested earlier.

The test chamber is made of 316 stainless steel plate. It is 4' x 4' x 5' and contains a total liquid volume of 550 gallons with 240 gallons of this volume exposed to the lamps at any given time. Reservoirs on either side of the baffled area contain respectively the contaminated influent and treated effluent water. See Figure 8 for detailed drawings of the unit. Figure 9 illustrates the path of flow of the liquid through the reactor. The photograph represented by Figure 10 displays a top view and the baffling of the unit.

The UV reactor houses a total of 112 64 inch (1.6 m), 65 watt ultraviolet lamps (primary wavelength 254 nm). The lamps have single pin contacts on either end and are 1.5 cm in diameter (American Ultraviolet, Chatham, New Jersey). Each of the lamps is surrounded by a seamless quartz jacket, 64 inches (1.6 m) long, 2.2 cm i.d., 2.5 cm o.d., (General Electric Co., Cleveland, Ohio) to allow maximum penetration of the UV energy and to provide for an air space around the lamp to allow the lamp to operate at peak efficiency. The jacket also provides a margin of safety if the lamp should shatter or break. Parker Hannifin stainless steel fittings and O-ring assemblies were used to seal the quartz jackets in the unit. Steel angle braces were used on the outside of the unit for support. For an illustration of the side view of the UV reactor unit and a general idea of its size, see Figure 11.

The lamps are divided into eight banks by polished stainless steel baffles. The lamps in each bank are set apart from each other to provide a maximum film depth of 2.5 cm. Each of two lamps is independently powered by a 120V, 60 Hz dual ballast (Jefferson Electric Co., Bellwood, Illinois). The ballasts and switches for operating the lamps are housed in a cabinet separate from the UV reactor. See Figure 12a. Each lamp is controlled individually by a corresponding switch on the cabinet panel. Pilot lights indicate when the lamps and ballasts are operational. This system allows for flexibility in controlling the number of lamps operating at any one time. Figure 12b illustrates the lamp wiring arrangement outside the reactor unit.



TEST TANK ISOMETRIC

FIGURE 8. DETAILS OF PHOTODEGRADATION REACTOR UNIT

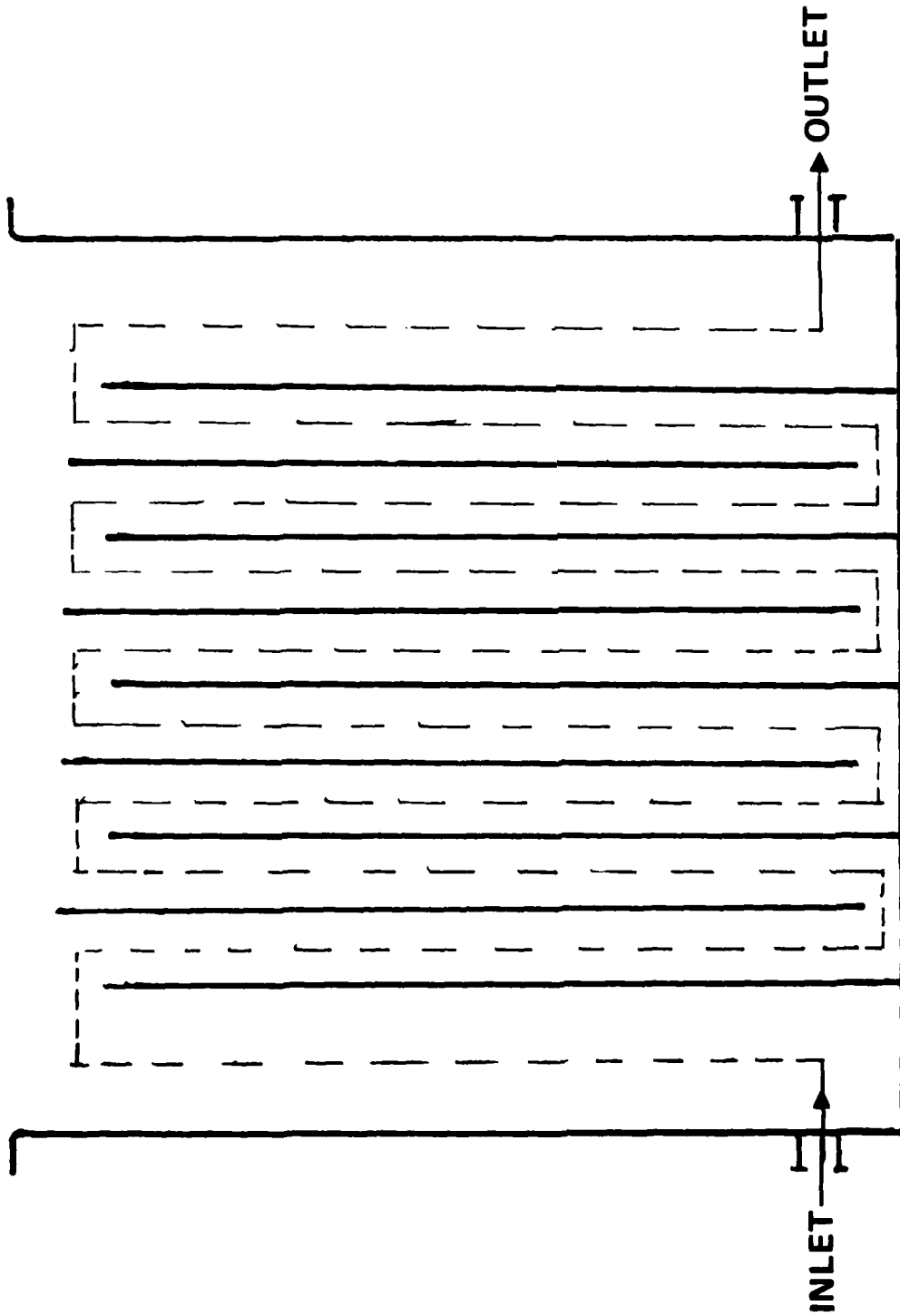


FIGURE 9. PATH OF FLOW THROUGH UV UNIT



FIG. 10 TOP VIEW OF UV REACTOR

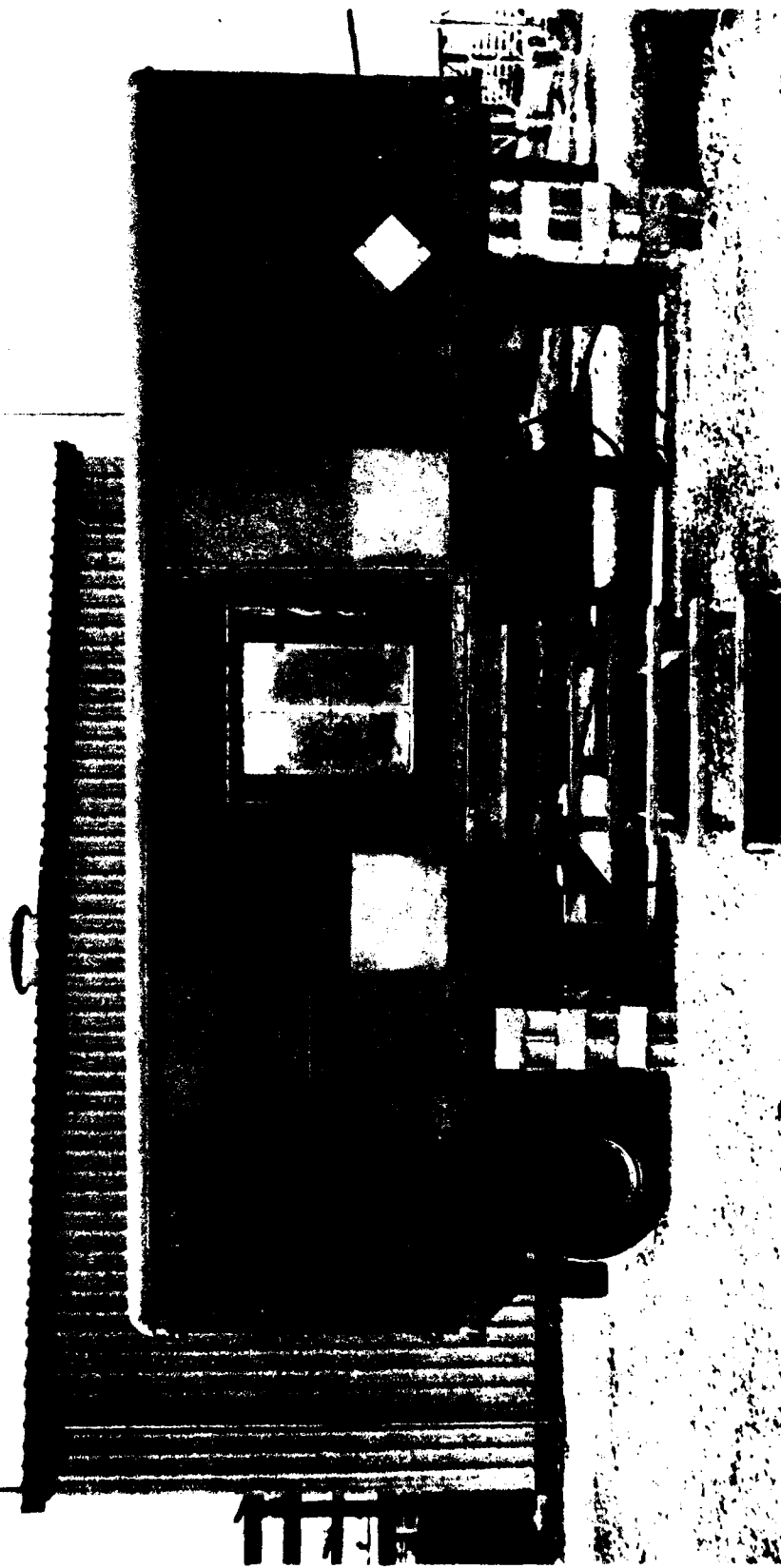


FIG. 11 UV REACTOR 1'3"
TYPICAL OUTSIDE CAPTION TREATMENT FACILITY

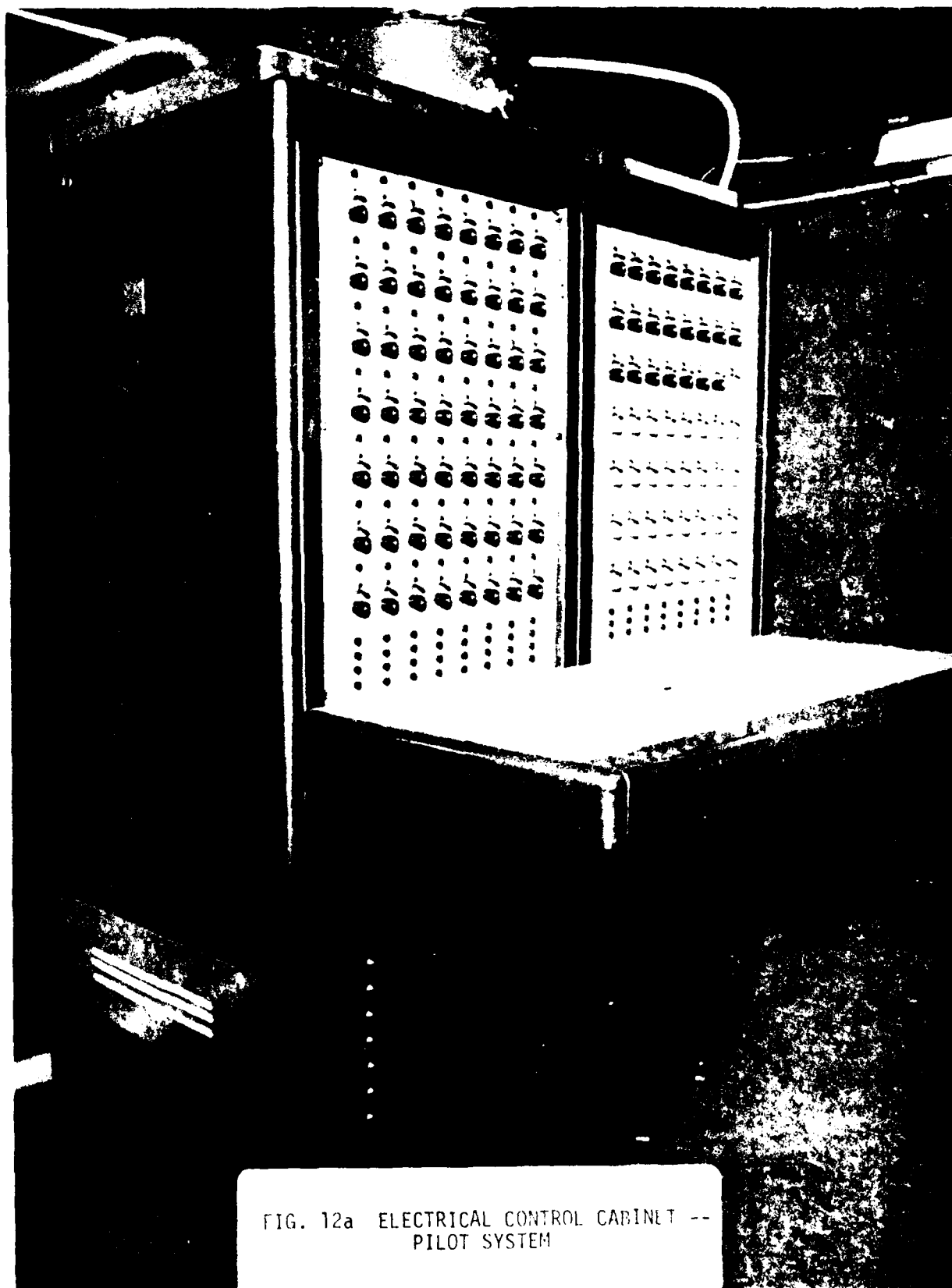


FIG. 12a ELECTRICAL CONTROL CABINET --
PILOT SYSTEM

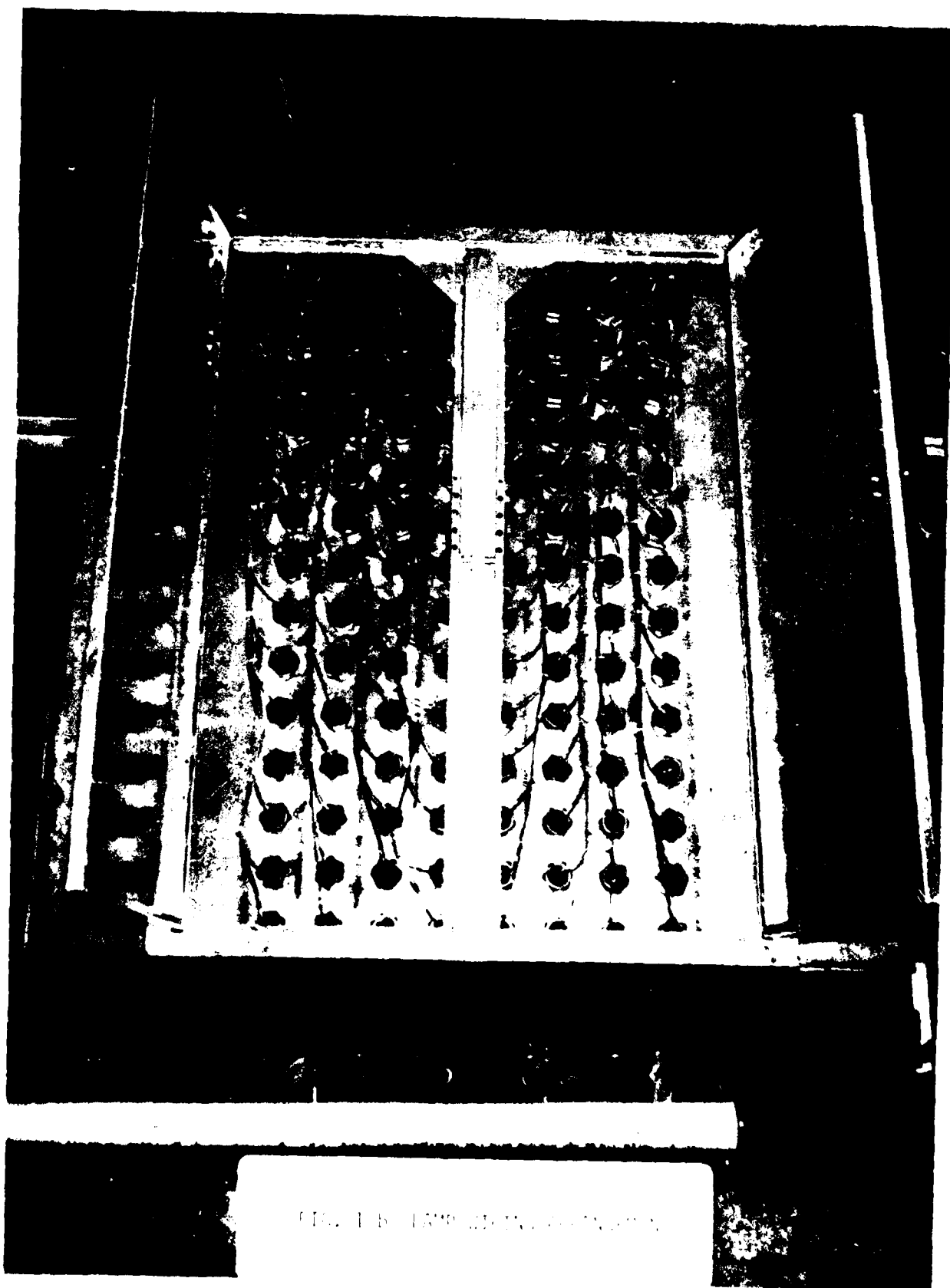


FIG. 1. B. LAMP. (20X, 100X, 100X)

Four sampling valves (one below each of four sets of baffled areas in the UV reactor) allow for sampling at various points in the unit to determine what the status of the liquid is at four different levels of exposure in the system. The valves are pictured near the bottom of the page in Figure 12b.

The UV reactor was tested at one of the Army's bomb load, assemble and pack (LAP) facilities operated by the Crane Army Ammunition Activity at the Naval Weapons Support Center Crane. The washout and steamout operations there provided a source of TNT and RDX (Comp B) contaminated wastewaters. This facility was also the source of explosive contaminated water (pink water) used for the earlier work.

The photooxidative pilot test system was installed in a trailer (5 ft x 17 ft) adjacent to the carbon treatment plant for the LAP facility. The explosive contaminated wastewater from the steamout and washdown operations was piped into a holding tank. This tank has a chiller which cooled the water to remove the wax which is used as a desensitizer in some explosive operations. The "chilled" water was then fed into a mobile fiber filter assembly in the carbon treatment building to remove suspended particulates (greater than 10 μ in size). After filtration the wastewater was channeled into a sump which was the source of the contaminated water for the UV treatment system as well as the carbon absorption system. See Figure 13 for an illustration of the route of the wastewater from the LAP facility to the UV system. The chilling and filtration processes removed the wax and most of the suspended particles from the water before it entered the UV reactor unit. However, as an additional precaution, the water was also filtered through a polypropylene filter assembly (Serfilco (#SF 05P10 μ filters), Glenville, Illinois) to remove particles greater than 5 μ in size before the water entered the reactor.

Only plastic or stainless steel pipe, fittings and valves were used in the system. Other materials could not be used because any

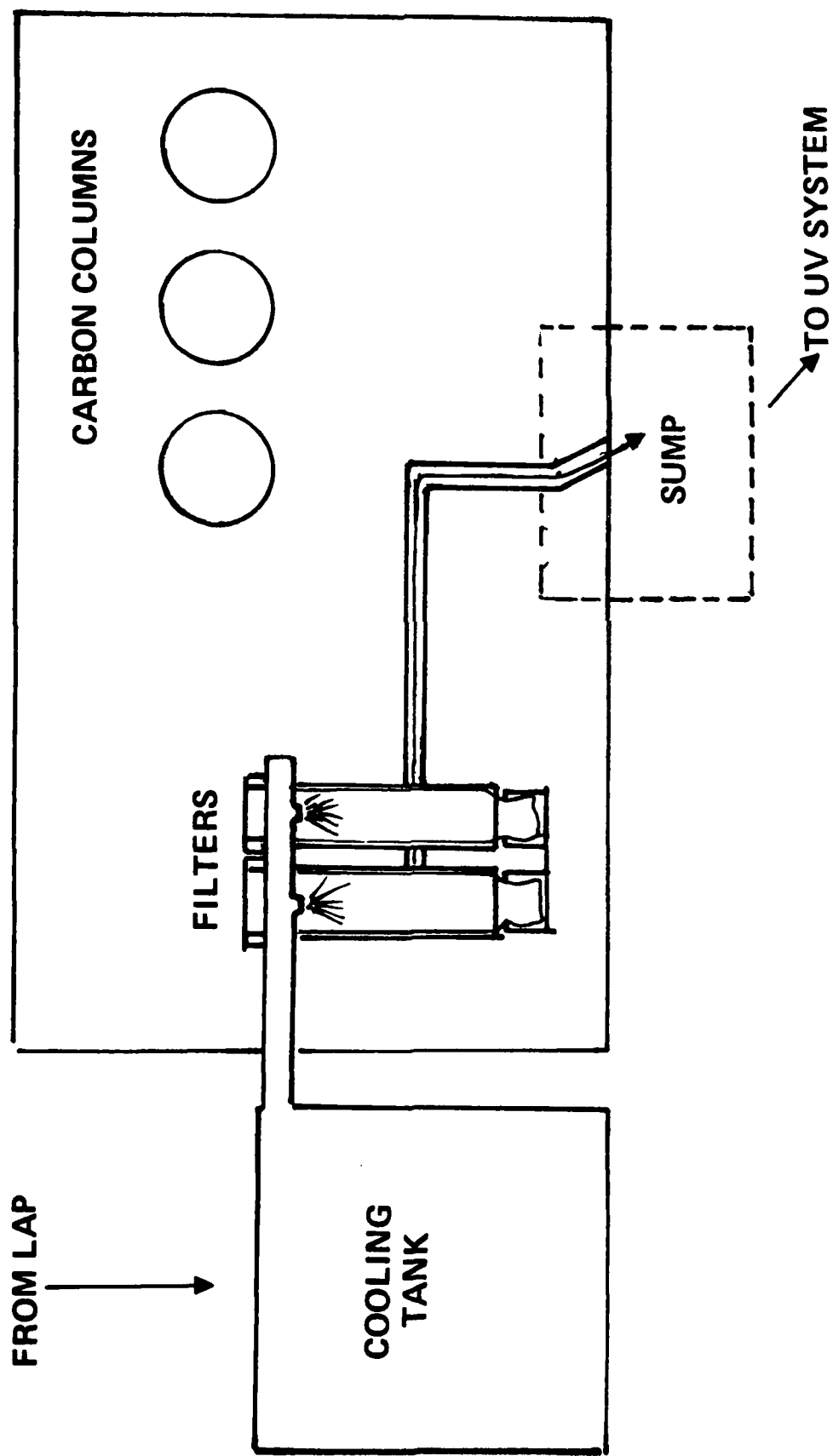


FIGURE 13. ROUTE OF CONTAMINATED EFFLUENT TO UV
PILOT SYSTEM

contaminants such as manganese, copper or iron could result in corrosion of these materials or could even initiate a violent reaction in the presence of a strong oxidizer such as hydrogen peroxide.

B. Methodology & Results

The contaminated water from the sump entered the pipe system in the trailer housing the pilot system through a pipeline situated just above the filter unit. See Figure 14. It was then filtered and mixed with hydrogen peroxide in an inline mixer (Kenics Corporation, North Andover, Massachusetts) to yield a concentration of 0.1% H_2O_2 (the adapted test concentration) before it entered the UV reactor. The H_2O_2 was metered into the system at the desired rate by a Pulsafeeder Model 7120SE (Interspace Corp., Rochester, New York) metering pump situated to the left of the filter. (It cannot be seen in Figure 14.) The source of the hydrogen peroxide was DuPont Tysul WW50 (50% H_2O_2). Because of pump limitations, it was diluted to a concentration of 4% before being pumped into the system at the necessary rate to achieve the desired 0.1% H_2O_2 concentration.

Flow rates were monitored periodically to ascertain reproducibility. Peroxide concentration was measured by a potassium permanganate method (Method 6, appendix). Flow rates of the influent water were monitored by flow meters after filtration and before entry into the UV reactor.

Explosive analysis and TOC analysis were routinely performed on the influent water - H_2O_2 mixture before, during and after treatment. Methods 1 through 4 describe the procedures used for these analyses.

The initial concentrations of the explosives in the wastewater varied considerably from day to day. This was primarily due to the backwashing of the carbon columns. This backwash water was fed back into

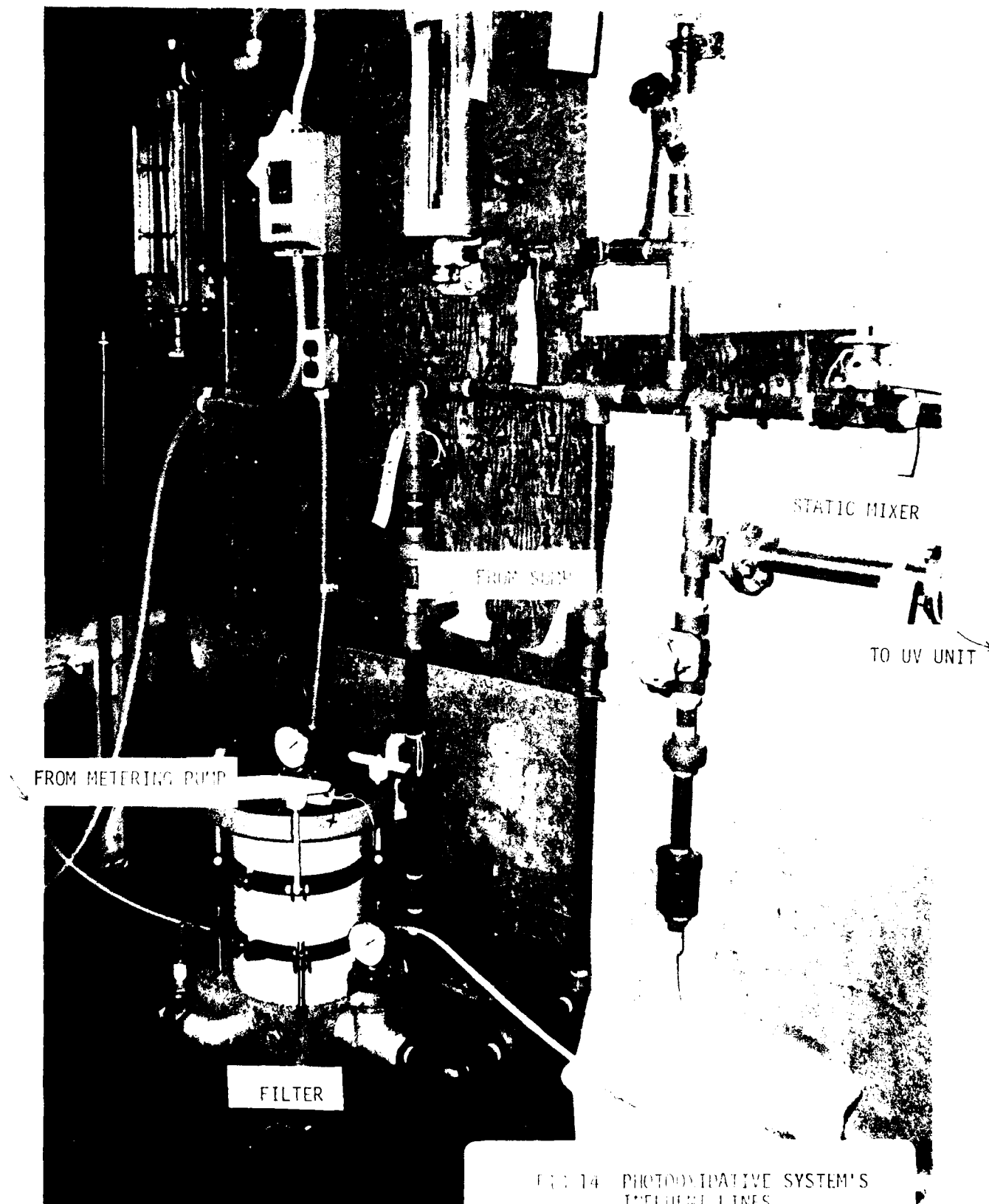


FIG. 14 PHOTODYNAMIC SYSTEM'S
INFLUENT LINES

the holding tank thus diluting the water already there from the steamout and washdown operations. The explosive concentrations ranged from 8 to 80 ppm TNT and from 6 to 52 ppm RDX.

For test purposes flow rates in the pilot system were varied from one to four gallons per minute (gpm). Table 5 represents the average results of some studies undertaken at a flow rate of 2 gpm. The variability of the initial explosive concentrations can be clearly seen in this table. Samples from baffles 1, 2, 3, and 4 had been irradiated for 30, 60, 90, and 120 minutes, respectively. In the first study (study A) presented, it can be seen that a significant drop in TOC concentration only occurred between 0 and 30 minutes and between 90 and 120 minutes of exposure. This can be associated with color changes as is seen in Figure 15. TNT is eliminated earlier but is probably converted to (an) intermediate(s) responsible for the color of the solution. After the colored intermediate(s) is (are) destroyed, the TOC level is significantly reduced. RDX is eliminated more rapidly than the TNT. This could be attributed to initial concentration differences and/or sensitivity of the explosive to the photooxidative reaction. In the other studies presented (Table 5), TNT and RDX are eliminated and the TOC level of the solutions are reduced by 120 minutes of exposure represented by samples from Baffle 4.

The relationship between the TNT concentration, absorbance and TOC concentration with irradiation at a flow of 1 gpm is displayed in Figure 16. The initial TNT concentration of this study was 80 ppm. Because of increased contact time in each baffled area in the UV reactor, the reduction in TOC concentration does not appear to be as dependent on color elimination as in the earlier case (Figure 15, 2 gpm) presented. Also, as seen in Figure 16, RDX is once eliminated before the TNT is. In this case, the required exposure time was doubled with a doubling of the initial concentration of explosives in the effluent. (See Figures 15 and 16 for comparison.)

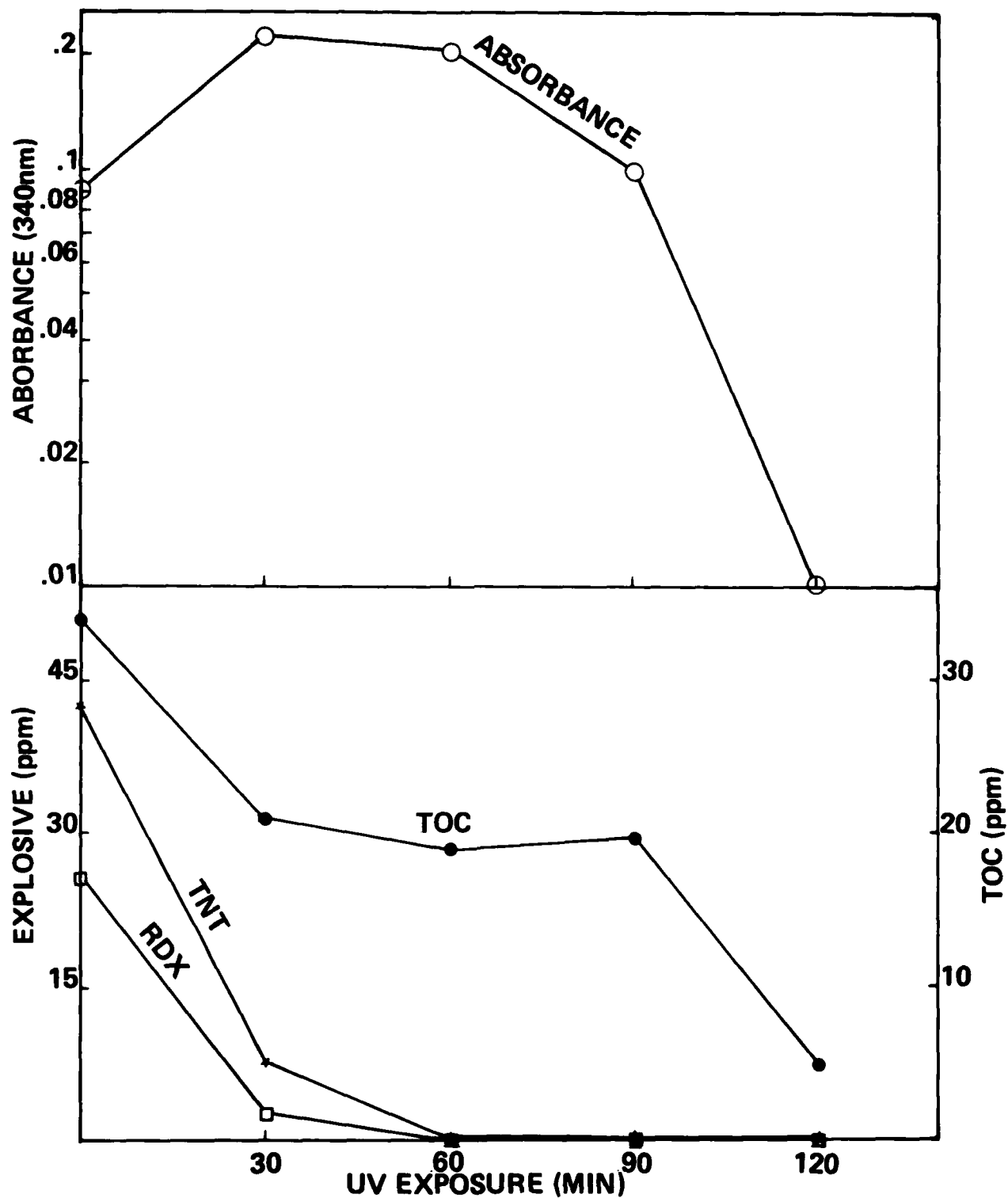


FIGURE 15. RELATIONSHIP OF ABSORBANCE (COLOR), EXPLOSIVE AND TOC CONCENTRATIONS IN THE UV PILOT SYSTEM AT 2 GPM (STUDY A)

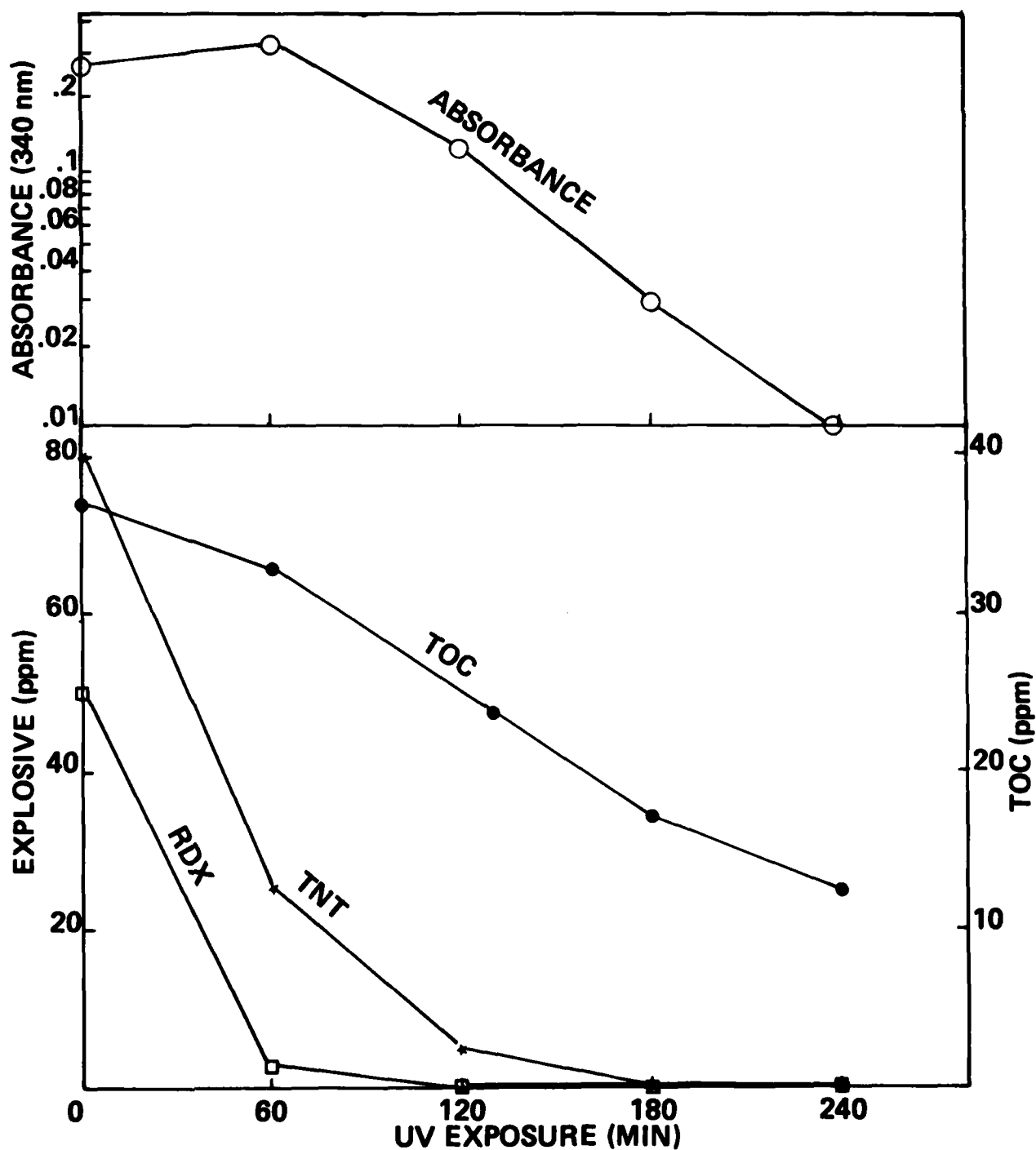


FIGURE 16. RELATIONSHIP OF ABSORBANCE (COLOR), EXPLOSIVE AND TOC CONCENTRATIONS IN THE UV PILOT SYSTEM AT 1 GPM (STUDY B)

Table 5. Results of UV-Pilot Study (2 gpm)

Sample	TNT	ppm RDX	TOC
0-Time	41.5	24.9	34.0
Baffle 1	8.1	2.9	20.4
Baffle 2	0.4	0.08	18.5
Baffle 3	≤ 0.02	≤ 0.08	20.0
Baffle 4	≤ 0.02	≤ 0.08	7.0
0-Time	8.6	6.6	14.5
Baffle 4	≤ 0.02	≤ 0.08	6.9
0-Time	28.0	17.4	25.5
Baffle 4	≤ 0.02	≤ 0.08	8.3

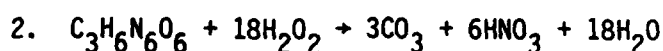
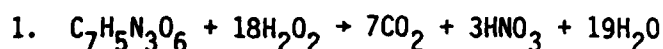
Studies were also performed on the treatment of pink water effluent at flow rate of 4 gpm. This flow rate provides the solution with a maximum UV contact time of one hour. It was determined that for this unit the flow was too high for water containing over 25 ppm TNT.

Thin-layer chromatographic analysis (Method 3, appendix) of all the treated samples in the pilot study indicated that trinitrobenzene (TNB) was the only detectable product present. Quantitative determinations of TNB in the irradiated samples were performed with

liquid chromatography (Method 4, appendix). Earlier studies with the bench-scale UV system have shown that residual TNB can be destroyed with sufficient irradiation. The pilot scale studies also indicate this (Figure 17). The concentrations of TNB peak and begin to fall with prolonged exposure.

The final pH of the irradiated samples varied with the initial explosive concentrations. The initial pH of the pink water effluent varied between 6.9 and 7.5. Table 6 illustrates a comparison between initial explosive concentration and final pH. It appears that the pH is directly related to the concentration of nitrate in the solution. In these treated aqueous explosive effluents, weak solutions of nitric acid (dependent on original explosive concentrations) are formed resulting in the acidic pH. See Figures 18-20 for an illustration of the relationship of pH and detected nitrate levels (Method 7, appendix) of these irradiated solutions.

Looking at the expected reactions of the explosives with H_2O_2 (if the reactions totally go to completion) the formulation of nitric acid is expected.



Peroxide concentrations were monitored throughout the study of the UV reactor pilot treatment. Titrations were performed on all samples according to reference 5. It was found that an average of 80% of the initial concentration of H_2O_2 was consumed during the treatment process.

C. Problems

A major difficulty experienced in the photooxidative treatment of the explosive solution in the UV pilot reactor was the depositing of film

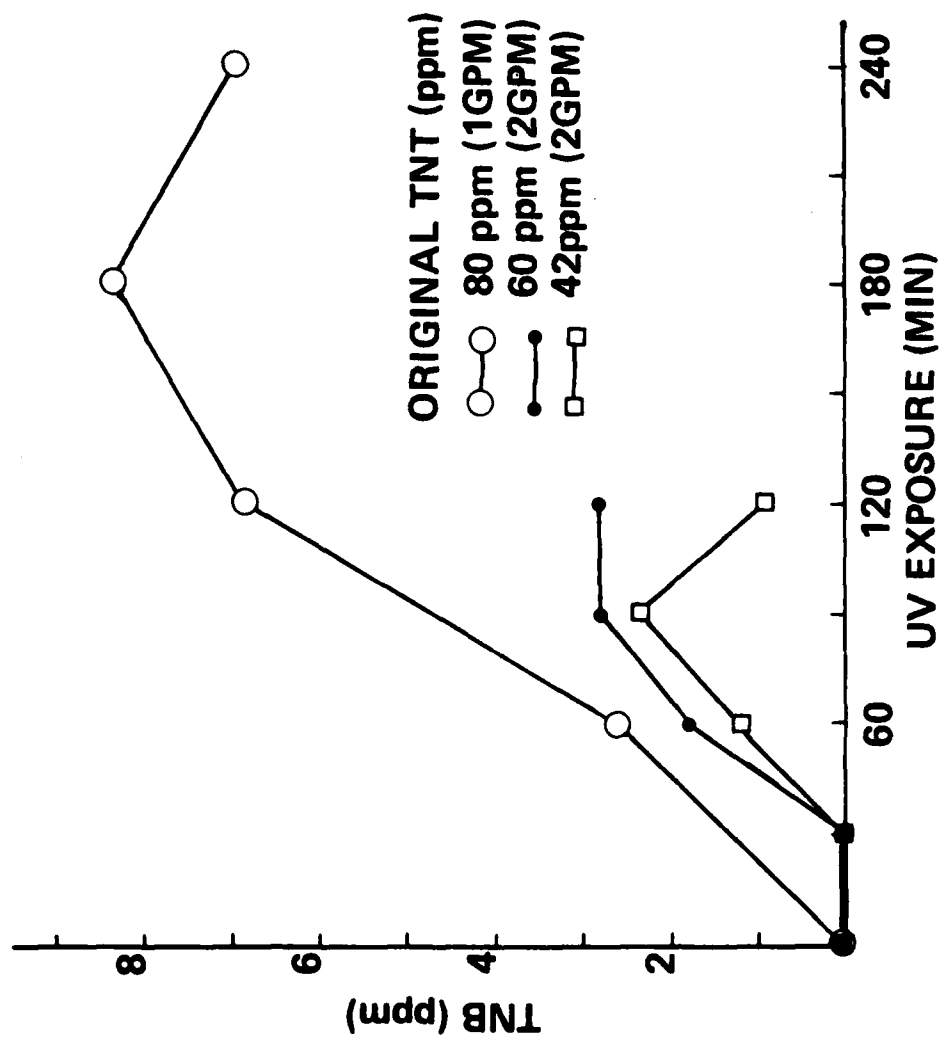


FIGURE 17. COMPARISON OF RESIDUAL TRINITROBENZENE (TNB) CONCENTRATION WITH EXPOSURE AND ORIGINAL TNT CONCENTRATIONS IN PILOT SYSTEM

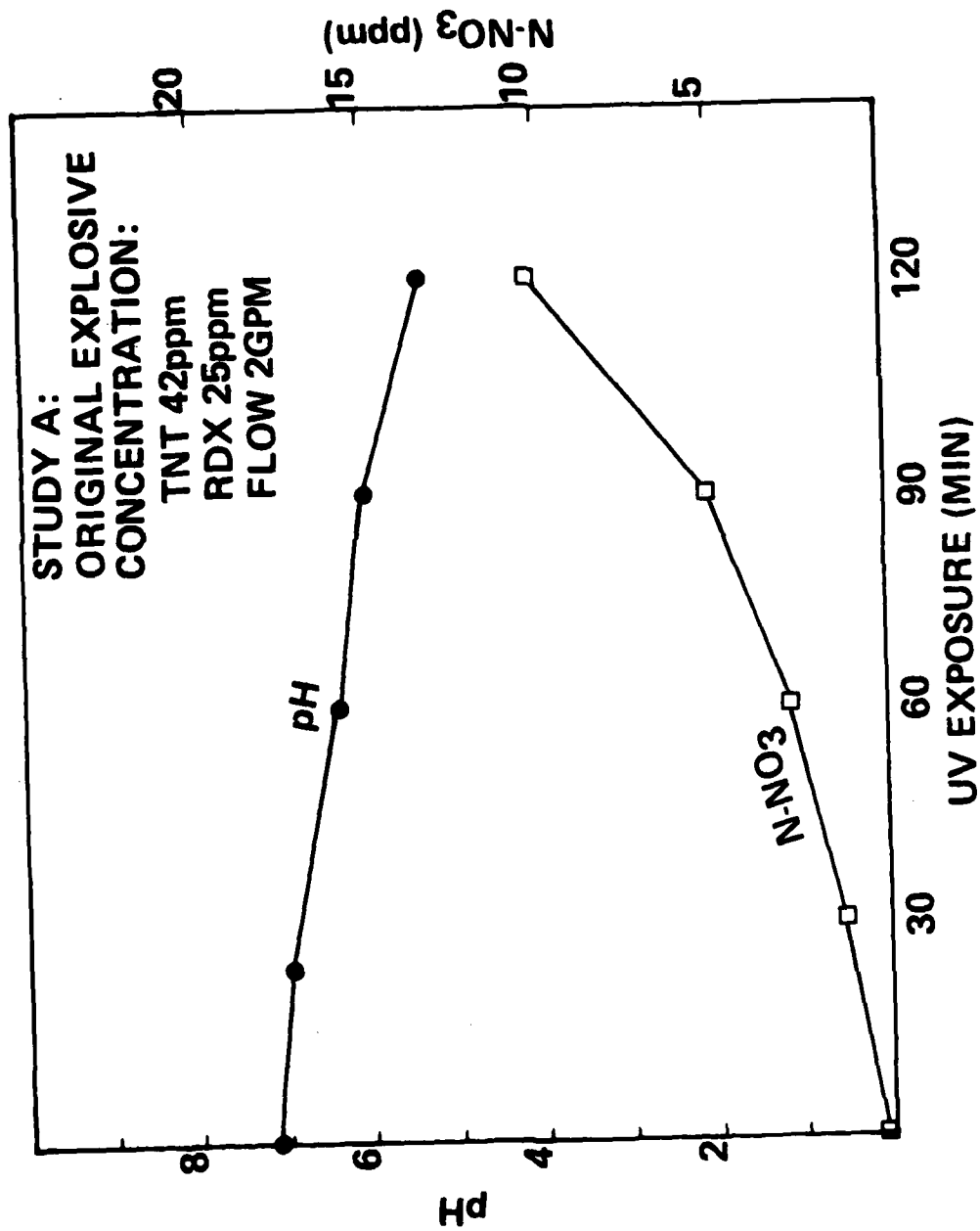


FIGURE 18. COMPARISON OF pH AND NO₃ CONCENTRATION WITH EXPOSURE IN PILOT SYSTEM (STUDY A)

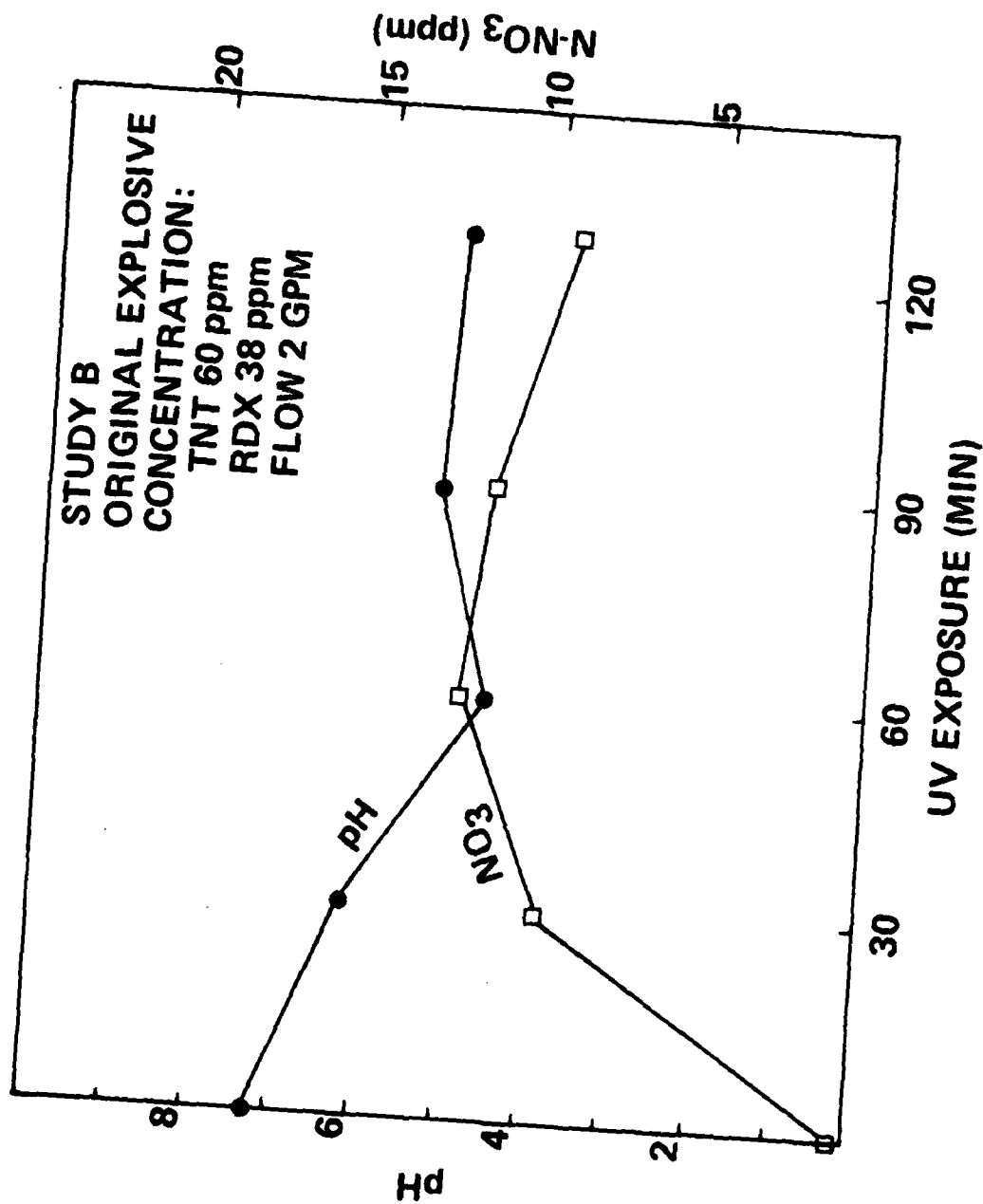
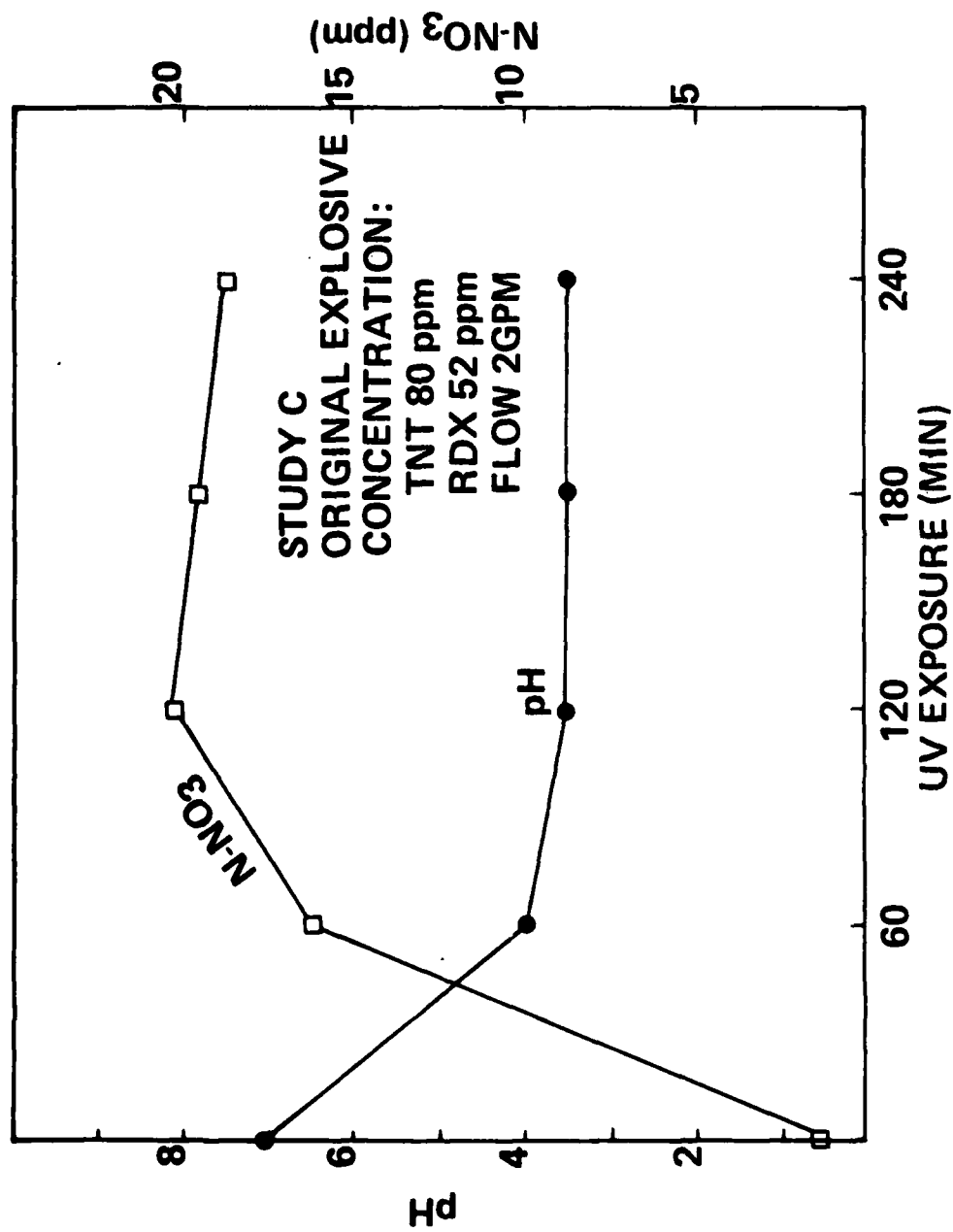


FIGURE 19. COMPARISON OF pH AND NO₃ CONCENTRATION WITH EXPOSURE IN PILOT SYSTEM (STUDY B)



**FIGURE 20. COMPARISON OF pH AND NO₃ CONCENTRATION
WITH EXPOSURE IN PILOT SYSTEM (STUDY C)**

Table 6. Comparison of Initial Explosive Concentration
and pH Before and After Irradiation

Initial Explosive Conc. (ppm)		pH	
TNT	RDX	Initial	Final
27.5	17.4	7.3	6.8
41.0	24.9	7.2	5.3
60.0	38.2	7.3	5.2
80.0	52.0	7.1	3.6

(from contaminants in the water) on the quartz sleeves. This film prevented the passage of much of the UV energy necessary to effect the reactions. Infrared (IR) analysis (Method 8, appendix) of the film showed that it was primarily composed of silicone, which is a release agent used in the bomb production. The silicone also was mixed with fine carbon particles which probably entered the system from the backwashing operation and from carbon replacement in the towers. The test operations were suspended for a period of time to allow the reactor jackets to be manually cleaned. Although coating is a major problem for any such photooxidative process, it can be eliminated by the use of automatic wiper assemblies which operate continuously throughout the process to wipe the jackets clean. The motion of the wiper would also provide mixing for the solution in the reaction and would inevitably increase the efficiency of the process.

VII. SUMMARY & RECOMMENDATIONS - BASED ON PILOT SYSTEM

These studies have demonstrated the feasibility of the photooxidative process in the treating of explosive contaminated waters. Although the large pilot scale UV reactor tested in these studies was restricted in

efficiency because of film depth and film deposits, valuable information was gained from the work with the unit. This work did illustrate the potential of the process as well as its weaknesses. Efficiency can be increased by decreasing the maximum film depth and by increasing the UV intensity. This can be achieved by increasing the number of lamps in a given space to provide the required thin film depth and necessary contact time. The establishment of parameters for large-scale treatment of TNT contaminated effluents should be based on the information obtained from all the work presented in this report and not on the pilot-scale system alone. The flow rates on the pilot unit were varied primarily to determine required exposure time (at a film depth of 2.5 cm) to significantly reduce to the TOC concentration which is illustrative of explosive mineralization and not mere photochemical conversion. The optimum film depth to incorporate in the UV reactor should be tailored to specific needs. That is, the chosen film depth should be dependent on economics and the volumes of wastewater to be treated per unit time. In general, the thinner the film depth, the greater the efficiency.

Based on the results of all these studies, it is recommended that for the efficient treatment of saturated TNT contaminated solutions, when H_2O_2 is incorporated as the oxidizing agent, the maximum allowable film depth should be about 5 mm. The unit should be designed to yield a retention time of one hour for a given flow rate to effect the best possible treatment. The reactor should be designed to allow lamps to be operated individually. This would allow for flexibility if it were determined that one hour of UV contact was not required for average treatment and this would provide for potential energy savings as well. The system would, therefore, be designed for the "worst possible" situation, but could be modified according to actual need, as it arises. The UV reactor unit should also be equipped with an automatic wiper assembly to maintain a high level of UV transmission. This would also secondarily provide for improved efficiency because of mixing. A chiller and some type of filtration process is required for removing wax, crystallized explosives and suspended particulates from the wastewater before it enters the UV reactor.

Obviously other factors should be considered in the optimization of design parameters to achieve good efficiency with minimum energy consumption. Such factors as reduction in lamp numbers in the last stage(s) of the reactor unit, increasing flow rates and/or decreasing film depth as the concentrations of contamination in the water decrease should be investigated.

VIII. GENERAL COMPARISON OF AVAILABLE TREATMENT PROCESSES

There are three major methods that are in use or are currently being tested for the treatment of explosive contaminated wastewaters. These are carbon adsorption, UV-ozone and UV-peroxide.

By its very nature the UV-H₂O₂ process is the simplest, most direct treatment available for explosive contaminated effluents. The water can be recirculated after treatment or directly discharged with the knowledge that given sufficient irradiation the explosives have been mineralized to CO₂, H₂O and NO₃ or other nitrogenous inorganic compound(s). After the UV-H₂O₂ treatment there is no additional solid waste to dispose of as in the case of the carbon treatment. Given sufficient irradiation there should be no breakthrough of explosives to accumulate or contaminate the environment if the treated effluents are directly discharged. This is a major problem with the carbon adsorption treatment. Even fresh carbon allows at least 1 ppm TNT to break through the system. Also, organic contaminants drastically alter the efficiency of the carbon adsorption process since these contaminants deplete adsorption sites available for the explosives. The presence of organic contaminants (other than explosives), in general, should not alter the efficiency of the UV-H₂O₂ process unless they interfere with transmission. In all probability, these contaminants are likely to be destroyed in the photooxidative system. The carbon adsorption system concentrates the explosives and presents a costly disposal problem. Incineration is the recommended and expensive choice of disposal for the spent carbon.

UV-ozonation, another possible method of treating explosive contaminated effluents, uses short wavelength UV light with ozone as the oxidizer. Operating costs are higher for this system than the UV-H₂O₂ treatment. Although comparable results can be achieved with UV-ozonation, this process requires bulky, space-consuming ozone generators which utilize large amounts of electrical energy during operation. This is a critical feature to consider in times when energy costs are at a premium. Also, because of the complexity of the system, breakdown and maintenance problems and costs are likely to be higher for this process than the UV-H₂O₂ treatment.

IX. COMPARISON OF CAPITAL AND OPERATING COSTS FOR UV-H₂O₂, UV-OZONE AND CARBON ADSORPTION TREATMENTS

Cost determinations for the UV-H₂O₂ treatment are based on modified version of the pilot UV-reactor system described earlier in this report. Each modified unit (of the same external dimensions^a) would contain four times the number of lamps in each baffled area to provide a 5 mm film depth and each would be equipped with automatic wiper assembly. Based on the average results of all the testing the laboratory performed, it is estimated that ten of these modified units installed in parallel could treat at least 19,200 gallons per day (40 gpm) of water contaminated with saturated levels of explosives.

A. Basis of Cost Estimates

Cost estimates of the major equipment and consumables required for the UV-H₂O₂ system are found in Tables 7, 8 and 9. All operations are based on a 40 gpm flow rate, 8 hour day, and an average of

^a Increasing the number of lamps and jackets in the modified unit would reduce the liquid volume in the baffled area. To maintain the same liquid volume in this area and the same overall dimensions of the unit, the reservoirs on both sides of the baffled area could be reduced in size.

Table 7. Cost of Major Equipment and Supplies for UV-H₂O₂,
UV-ozone and Carbon Adsorption Systems^a

	UV-H ₂ O ₂ ^b	UV-ozone ^c	Carbon Adsorption ^d
Equipment	\$608,000	\$640,000	
Materials ^e	25,000	60,000	
Labor - Installation	50,000	50,000	
Totals	<u>\$683,000</u>	<u>\$750,000</u>	<u>\$854,330^f</u>

^a All estimates based on current 1980 prices of equipment required for a 40 gpm treatment system of explosive contaminated wastewaters.

^b Equipment includes 10 UV-reactors and electrical components, in-line static-mixer, metering pump for H₂O₂ transfer.

^c Equipment includes four ozonators (each with 40 lb ozone capacity) and four UV-reactors. Costs are based on information from communications with military and industrial representatives.

^d Equipment includes three stainless steel towers, vacuum system, pumps, and carbon. Costs are based on information from communications with military and industrial representatives.

^e Pipes, valves, controls, meters, hardware . . .

^f Breakdown unavailable. Includes total construction costs.

Table 8. Major Operating Costs for UV-H₂O₂ Treatment

Energy	\$1.69/1000 gal	(81.3 kwh/reactor)
H ₂ O ₂	\$2.00 + 3.00/1000 gal ^a	(0.05% + 0.075% H ₂ O ₂)
Total	<u>\$3.69 + \$4.69/1000 gal</u>	

^a dependent on explosive concentration

Table 9. Cost Comparisons of Major Consumable for
UV-H₂O₂, UV-ozone and Carbon Adsorption Systems

	UV-H ₂ O ₂	UV-ozone	Carbon Adsorption
per 1000 gal	\$3.69 → \$4.69	\$4.93	\$7.11
per year ^a	\$15,587 → \$19,811	\$20,824	\$90,000

^a Operations based on time periods discussed earlier in the report.

220 work days per year. Comparisons of capital and operating costs of UV-ozone and carbon adsorption treatments with UV-H₂O₂ are also presented in Tables 7 and 9.

B. Equipment

The major pieces of equipment required for the UV-H₂O₂ method and their potential costs are outlined in Table 7. Cost comparisons with th UV-ozone and carbon adsorption systems are also presented here.

C. Energy

Energy costs for the UV-H₂O₂ system are based on power consumption for the reactor units alone. This includes the operation of the lamps, dual ballasts and fans for the electrical control cabinet. A single modified unit with 448 lamps and 224 ballasts would consume about 81.3 kwh/day (10.16 kw x 8 hrs/day). Assuming a rate of \$0.04/kwh (NAWPN SUPPCEN Crane rate \$0.039), it would cost \$3.25 to operate each unit per day, with 10 units costing \$32.50. At 40 gpm the energy costs would amount to \$1.69/1000 gallons.

This UV-H₂O₂ system would require far less energy for operation than the UV-ozone system. Ozone generation requires as much as 15 kwh of power to produce one pound of ozone. See reference 10. Based on previous studies cited in reference 10 approximately 38 lbs. of ozone are required to treat 5,000 gallons of TNT saturated wastewater. Therefore, approximately 2280 kwh would be consumed in the treatment of 20,000 gallons of this type wastewater per day. Because of the large amounts of heat generated by the production of ozone (of the total power utilized only 10% can be accounted for as ozone, much is lost as heat, reference 10) the system must be cooled by air or water. If air is selected, additional energy must be expended for this cooling process. Also, the energy consumption by the UV lamps must be considered in addition to these other factors, although it will be relatively small in comparison with the power requirements for ozone generation.

Essentially, the energy requirements of the carbon adsorption system are negligible by comparison, since a gravity feed is employed too in the process.

D. Oxidizer (H₂O₂)

Based on previous work with the bench-scale UV unit having a 5 mm film depth, it was determined that a range of 0.05% to 0.1% H₂O₂ was acceptable for the treatment of TNT contaminated wastewaters. By maintaining that film depth and increasing the number of lamps per given area (as would be done in the modified UV reactor unit) intensity would be increased and efficiency increased accordingly. Less oxidizer may be required since more would be efficiently utilized in the reaction and less wasted in the system. Based on the chemical equations for the reactions of explosive with peroxide cited earlier in this report, (1 mole explosive requires 18 moles of H₂O₂) if the reaction were 100% efficient only 0.0269% H₂O₂ would be required to treat each 100 ppm explosive.

Given a reasonably efficient system 0.05% H_2O_2 should be more than sufficient to treat 100 ppm TNT and 0.075% H_2O_2 should be more than sufficient to treat a solution containing 100 ppm TNT and 50 ppm RDX (solubility limits of these explosives at room temperature). The cost of the oxidizer, therefore, will be based on a required range of 0.05% to 0.075% H_2O_2 (dependent on need). At \$0.20/lb of 50% H_2O_2 , the cost of one gallon of H_2O_2 would be \$1.98 (9.9 lbs H_2O_2 /gal). Within this range of 0.05% to 0.075% H_2O_2 19.4 to 29.1 gallons of 50% H_2O_2 could be required to treat 19,200 gallons of wastewater (40 gpm/8 hr day). The daily cost would then range from \$38.40 to \$57.62 for oxidizer, given that 100 to 150 ppm explosive is present in the wastewater. This equals \$2.00 to \$3.00/1000 gallons of explosive contaminated water.

E. Combined Costs

The combined cost for energy and oxidizer in the UV- H_2O_2 treatment could range from \$3.69 to \$4.69/1000 gallons or \$15,587 to \$19,811 per year.

The cost of ozone generation alone for explosive saturated water (15 kwh/lb, \$0.04/kwh, 150 lbs/day) amounts to \$4.69/1000 gallons or \$19,811 per year. This does not include the cost of UV lamp operation which would probably add on additional \$0.24^a/1000 gallon or an additional \$1,013 per year.

The major operating cost for a carbon adsorption system capable of handling 40 gpm (24 hr/day, 5 days/week) averages \$7.10/1000 gallons (\$90,000 per year) for consumables and disposal of spent carbon^b. This

^a Cost based on the operation of four UV units described in reference 11.

^b Cost based on information obtained from communications with representatives of a local Army facility with a carbon adsorption system (40 gpm).

figure does not include labor in order to be consistent with the other cost comparisons.

Cost comparison summaries of all major operating expenses (excluding labor which would probably be comparable for all systems) for the UV-H₂O₂, UV-ozonation and carbon adsorption systems are found in Table 9.

It appears that of all available treatments the UV-H₂O₂ is not only the simplest but is also the most economically feasible for the treatment of explosive contaminated wastewaters.

X. POTENTIAL USE - UV-H₂O₂ SYSTEM (TREATMENT OF WASTE EXPLOSIVE D AND MILITARY DYE MARKERS)

The UV-H₂O₂ treatment process has exhibited much potential in the treatment of military wastes. Bench-scale work and work with the Ultradynamics UV-500 unit described earlier in this report show that the process is effective in treating water solutions of 2,4-dinitrotoluene; 2,6-dinitrotoluene (reference 2); Explosive D (Yellow D); and military dye markers (MIL-D-16627 dyes). A report entitled "The Photo-oxidative Treatment of MIL-D-16627 Dyes and Explosive D" was submitted to Naval Sea Systems Command, Code 04J23, 25 January 1979. The work performed on the compounds has shown that the UV-H₂O₂ process is more efficient in treating such wastes than TNT wastes, e.g., 500 ppm Explosive D was destroyed in 30 minutes in the bench-scale UV unit using 0.1% H₂O₂. This is one-half the time required to treat 100 ppm TNT solutions under identical conditions. Even the most recalcitrant dye treated (500 ppm Orange Dye 2G) only required 40 minutes of exposure with 0.1% H₂O₂ to achieve the same results. A UV-H₂O₂ system based on using the modified UV-reactors described earlier in this report can be designed to

treat such wastes. The design of the system (number of required units) would be dependent on the concentrations of these materials to be treated per unit time. The actual potential of the UV-H₂O₂ process in the treatment of other military and industrial wastes has yet to be explored but appears to be very promising.

XI. SUMMARY

The UV-H₂O₂ process for the treatment of explosive contaminated wastewaters is simple and economical. The process actually destroys the explosives in question (TNT, RDX, Explosive D, . . .) allowing for direct discharge of the effluent or recirculation of the treated water. Of all the treatment processes available for explosive contaminated effluents the UV-H₂O₂ treatment appears to be the simplest, the most versatile and the most cost effective method in existence today.

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XIV. APPENDIX OF METHODS

Method 1

Gas Chromatographic Analysis of TNT and TNB in Water

Sample Preparation

Transfer 3 milliliters (ml) of water sample to a 18 x 150 mm disposable test tube. Add 3 ml of toluene containing 1 µg/ml of 2,4,6 trinitro-1-tertbutyl-3,5 dimethyl benzene internal standard. Mix well on a vortex mixer. For samples expected to contain more than 10 µg/ml trinitrotoluene (TNT) and/or trinitrobenzene (TNB) use 0.4 ml sample and 4 ml of toluene plus internal standard. Prepare standard TNB-TNT solutions in water using a small amount of acetone to dissolve the explosives. Extract the standards with the toluene plus internal standard in the same manner as samples.

GC Analysis

Inject a 3 µl aliquot of the toluene extract into a Hewlett-Packard 5713A gas chromatograph with electron capture detector. (Nickel-63).

GC parameters:

Column - 5% QF-1 on Gas Chrom Q 100/120 mesh
6 ft x 2mm ID glass column

Column temp - 180°C

Injection port temp - 200°C

Detector temp - 250°C

Carrier - 24 cc/min 5% CH₄/95% Ar v/v

Calculation of TNB Concentration

$$\text{Concentration} = \frac{\text{pk. hgt. Int. Std. in Std.}}{\text{pk. hgt. Int. Std. in sample}} \times$$

$$\frac{\text{pk. hgt. TNB in sample}}{\text{pk. hgt. TNB in Std.}} \times \mu\text{g/ml TNB in std} \times \text{dilution factor}$$

Method 2

TLC Analysis of TNT and (Polynitroaromatic) Derivatives Procedure Based on WQEC Standard Test Method QTM-TLC4

All glassware is chromic acid washed prior to use.

TLC plates are LQDF silica thin-layer chromatography plates from Quantum Industries. Plastic plate covers should remain intact until use. Plates should be exposed to air and humidity as little as possible.

Sample Preparation

All samples are aqueous solutions.

Benzene* Solubles

Two ml of sample + two ml of benzene are mixed on a tube mixer. Time is allowed for the layers to separate. The benzene (top) layer is withdrawn by pipet and transferred to a small tube. Benzene is evaporated with a gentle stream of dry air. Residue is dissolved in 50 microliters (μl) of acetone. Twenty μl of each sample is applied

*Toluene has since been substituted for benzene because of benzene's toxic properties.

1.5 cm from bottom of TLC plate and allowed to completely dry. One sample or standard is spotted in each channel.

A covered glass tank with approximately 1/4 inch (90 ml) of Chandler's #1 solvent system is used to develop the spotted plates. Chandler's #1 solvent system formula is:

50 parts benzene*
45 parts cyclohexane
5 parts ethyl acetate

Sides of the chamber are covered with Whatman #1 filter paper to insure chamber saturation. Chamber is left to equilibrate 1/2 hour before use. TLC plates are developed until the solvent front has traveled 12 to 13 cm. Solvent front is marked immediately after taking plates from chamber.

The plate is then sprayed with a 1:5 ethylenediamine (EDA) dimethylsulfoxide (DMSO) mixture which is specific for polynitroaromatics. Color and location of the spots are noted.

Acetone Solubles

Calcium chloride dihydrate (0.47 g/ml) is dissolved in the aqueous portion remaining from the benzene extraction. Two ml of acetone are added and sample mixed. Time is allowed for the layers to separate. The acetone (top) layer is withdrawn by pipet and transferred to a small tube.

Proceed as with the benzene solubles except use Chandler's #2 solvent system.

Chandler's #2 formula is:

50 parts benzene*
30 parts ethyl ether

20 parts ethanol

1/4 part H₂O

Sensitivity of the procedure ~0.3 ppm TNT with concentration of 2 ml extracts.

Standards

The following TNT acetone standards are used:

25 ppm

50 ppm

100 ppm

200 ppm

500 ppm

Twenty µl of each standard is spotted directly onto the TLC plate with both the benzene and acetone solubles.

Method 3

Total Organic Carbon (TOC) Analysis

Analysis is based on instructions and calibration for the Beckman 915 Total Organic Carbon Analyzer, Beckman Instruction 015-082355.

Beckman Instruments, Inc.
Process Instruments Division
Fullerton, CA 92634

Method 4

WQEC CHEMICAL STANDARD TEST METHOD QTM-LC2

LIQUID CHROMATOGRAPHIC ANALYSIS OF TNT, HMX AND TDX IN SOIL AND WATER

Introduction

This method was developed for explosive analysis of water and compost samples submitted by the Biological Sciences Branch.

The method was adapted from a separation procedure obtained from C. D. Chandler, Radford Army Arsenal, Virginia.

Sample Preparation

Water Samples

Approximately one ml of the water sample is filtered through a 0.45 micron filter to remove suspended material. The filter is discarded if low concentrations of explosives are being measured.

The filter is washed with one ml of acetone and the acetone is transferred to a ten ml volumetric flask when it is necessary to analyze the suspended material for explosives. The flask is filled to the mark with distilled water. One ml of the solution is filtered as described above for explosive analysis

Liquid Chromatographic Analysis

Liquid Chromatograph Parameters:

Column: DuPont Permaphase Eth, 1 m long by 2.1 mm I.D.

Column Temperature: 54°C

Mobile Phase: Distilled Water/2-Propanol (90:10)

Flow Rate: 0.8 ml/minute

Sensitivity: Dependent on sample concentration 0.02 or 0.16
absorbance units fill scale

Detector: UV, 254 nanometers

Chart Speed: .4 inch/minute

Sample Size: Dependent on sample concentration - 5 microliters
to 1 ml

Standard Curve

Four standards are prepared in the explosive concentration range indicated on the analysis request.

The recorded peak heights of standards are plotted versus the ppm concentration of explosive.

Sample Analysis

An aliquot of the filtered sample is injected in the liquid chromatograph.

The retention times of the recorded peaks are measured to determine if explosives are present.

Peak heights of explosives are measured.

$$\begin{array}{l} \text{(PPM explosive)} = \text{(PPM from the)} \times \text{(dilution)} \\ \text{(in the sample)} \quad \text{(standard curve)} \quad \text{(factor)} \end{array}$$

N.B. The analysis of RDX + HMX was based on a procedure found in "The Analysis of Explosives by High Performance Liquid Chromatography and Chemical Ionization Mass Spectroscopy," Analytical Chemistry, Vol. 49, 1977. pp. 1039-1043.

Method 5

Gravimetric Analysis of Sulfate with Ignition of Residue

See Reference 4.

Method 6

Titration of H_2O_2

See Reference 5. A certified one N potassium permanganate solution (Fisher Co., Fairlawn, N.J.) was used for the titration.

Method 7

Modified Brucine Method for NO_3 -N Determination

Reference 6 was modified by the addition of catalase (from bovine liver, Sigma Chemical Co., St. Louis, 0.1 mg/ml sample) to eliminate interferences caused by the presence of the H_2O_2 .

Method 8

IR Analysis of Contaminants

See References 7 and 8 for procedure describing the potassium bromide pellet method and equipment parameters.

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Philadelphia, PA 19112
108. Commander
Kansas AAP
Parsons, KS 67357
109. Commander
Lake City AAP
Independence, MO 64050

110. Commander
Lone Star AAP
Texarkana, TX 75501
111. Commander
Longhorn AAP
Marshall, TX 75670
112. Commander
Louisiana AAP
Shreveport, LA 71130
113. Commander
Crane AAP
Crane, IN 47552
114. Commander
McAlester AAP
McAlester, OK 74501
115. Commander
Hawthorne AAP
Hawthorne, NV 89415