

AD-A159 416

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DEVELOPMENT OF
DESIGN PARAMETERS FOR
AN EXPLOSIVE CONTAMINATED
WASTEWATER TREATMENT SYSTEM

Report No. WQEC/C 85-297

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER WQEC/C 85-297	2. GOVT ACCESSION NO. AD-A159 416	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEVELOPMENT OF DESIGN PARAMETERS FOR AN EXPLOSIVE CONTAMINATED WASTEWATER TREATMENT SYSTEM		5. TYPE OF REPORT & PERIOD COVERED Final
7. AUTHOR(s) Explosive Sciences Branch		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS NAVWPNSUPPCEN Code 3025, Building 2707 Crane, IN 47522-5030		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS COMNAVSEASYSOM SEA-6423 Washington, DC 20361		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 3204 Program Number 3204
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE June 1985
		13. NUMBER OF PAGES 41
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Unlimited		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Ultraviolet TNT Hydrogen peroxide RDX Wastewater Treatment		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Design parameters for the construction of an ultraviolet light-hydrogen peroxide system for the treatment of explosive contaminated wastewater have been developed. Studies were performed both with commercial ultraviolet light systems designed for water sterilization and with a continuous flow laboratory system. It has been determined that TNT, RDX and HMX can be completely destroyed, singly or in combination, by the system. The critical factors are optimum (0.05 to 0.15%) hydrogen peroxide concentration and a minimum of 10 megawatt-minutes of ultraviolet light at 254 nm.		

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DEVELOPMENT OF
DESIGN PARAMETERS FOR
AN EXPLOSIVE CONTAMINATED
WASTEWATER TREATMENT SYSTEM

Prepared by: Explosive Sciences Branch

Report No. WQEC/C 85-297

June 1985

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SUMMARY

Design parameters for the construction of an ultraviolet light-hydrogen peroxide system for the treatment of explosive contaminated wastewater have been developed. Studies were performed both with commercial ultraviolet light systems designed for water sterilization and with a continuous flow laboratory system. It has been determined that TNT, RDX and HMX can be completely destroyed, singly or in combination, by the system. The critical factors are optimum (0.05 to 0.15%) hydrogen peroxide concentration and a minimum of 10 megawatt-minutes of ultraviolet light at 254 nm per mole of explosive. Under these conditions all traces of explosives and their organic reaction products are destroyed. Inorganic products of the reaction include ammonia, nitrates and carbon dioxide. The effluent water may develop an acidity as low as pH 3. Because of interactions between the reactants (explosives and peroxide) and certain structural materials it is recommended that quartz, glass or stainless steel be utilized in all components of the system which will come into contact with the wastewater. The incoming wastewater will contain particulate matter which must be removed prior to its injection into the light system.

INTRODUCTION

Many military installations, during ordnance production and demilitarization processing, produce wastewaters contaminated with 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-hydrotriazine (RDX) or other explosives. It is the Navy's goal that all demilitarization (and other) processes be accomplished as safely and inexpensively as possible, and with minimum adverse impact on the environment. This includes decontamination of wastewaters prior to release.

At present, the explosive contaminated wastewater from the Navy's various demilitarization operations is treated by a combination of mechanical filtration and carbon adsorption, considered "state-of-the-art" in reducing explosive contaminants to an environmentally acceptable level. The process involves extensive maintenance monitoring and maintenance costs. In addition it creates a hazardous waste (explosive contaminated carbon and other filter media) which results itself in a difficult disposal problem.

Previous studies by the Navy have indicated that a photooxidative treatment, involving ultraviolet light and hydrogen peroxide, may provide a simple, effective and economical method of destroying explosive-related contaminants of wastewater, allowing for direct discharge of the treated effluent.

This report explores the engineering parameters necessary for final design and construction of a photooxidative wastewater treatment system for treating explosive contaminated wastewaters.

HISTORY OF THE ULTRAVIOLET-PEROXIDE TREATMENT SYSTEM

Ultraviolet (UV) light, at a 240 to 260 nm wavelength range, in combination with hydrogen peroxide, has been reported (1,2,3) as an effective method for treating water contaminated with explosives such as TNT, RDX, HMX, 2,4-DNT (dinitrotoluene), 2,6-DNT and ammonium picrate. The process also has been successful in treating pink water effluents from ammunition load, assemble and pack (LAP) operations.

These studies indicated that maximum efficiency of reduction of explosive content and reduction of Total Organic Carbon (TOC) was achieved at peroxide concentrations of 0.05 to 0.10 per cent. Peroxide concentrations above 0.5 per cent have an adverse effect on explosive destruction rates. In the absence of peroxide, however, TNT is chemically modified by UV light to highly colored compounds, with no significant reduction in total organic carbon (TOC).

These studies also indicated, through use of radiocarbon labeled TNT, that the explosive ring structure was being broken. The TNT was being mineralized, not merely converted to modified but related compounds that could be environmentally as undesirable as the explosive.

The above studies have since been verified and amplified (4). Thin layer chromatography (TLC), which can detect extremely low levels of chemical compounds, did not detect any polynitroaromatic compounds, thus supporting the radiocarbon findings. TOC levels as low as 3 ppm (part per million) were reached when 100 ppm TNT solutions (approximately 40 ppm TOC originally) were processed.

This report also examined the effect of acidity on the rate of reaction. Normally, solutions of nominal 100 ppm TNT at an initial unadjusted pH 6.9 will, during treatment, become acidic, reaching pH levels between 3.3 and 3.5. It was determined that extremely acidic solutions (adjusted to pH 1 or 2 prior to treatment), had large TNT and TOC concentrations at the end of the reaction. Such results could be attributed to the fact that extremely acidic environments stabilize the peroxide.

Another oxidizing agent, a commercial mixture of potassium monopersulfate, potassium sulfate and potassium hydrogen sulfate, was at least as effective as hydrogen peroxide in mediating the destruction of the explosive pollutants. However, hydrogen peroxide was more satisfactory from both cost and environmental considerations and was selected for further study.

The report also detailed the scale-up of the reaction. Two commercially available short wavelength UV units, designed for water disinfection, and a larger system designed and constructed for the project were utilized.

The smaller of the commercial units housed one 40 watt mercury vapor lamp (254 nm primary light output) and held 2.84 liters (1). The larger housed four lamps and had a nominal volume of 22.7 l. Both were made of stainless steel. All bulbs were surrounded by quartz sleeves. Both had wiper assemblies to clean the quartz sleeves. Both were made by the same manufacturer.

The unit designed and constructed for the project was constructed of stainless steel, contained 112 1.6-meter, 65-watt mercury vapor bulbs, each housed in a quartz jacket. This system did not contain a wiper assembly for cleaning the quartz tubes. The lamps were divided into 8 banks by stainless steel baffles. Water flow was directed in a sinuous manner under and over the baffles. This unit held 240 gallons (908.5 l) in the reaction chamber. There were also reservoir chambers at each end of the reaction chamber. The total volume of the unit was 550 gallons (2082 l).

All units, when operated in a recirculating mode, were able to destroy TNT, RDX and HMX, and to effectively reduce TOC. They did not yield sufficient data, however, to allow final design of a system for use in the Navy's steamout plants. It was noted, however, that the absence of a wiper assembly detracted from the efficiency of the custom built system.

All of the explosives studied which are destroyed by this system strongly absorb UV light at 250 to 260 nm, as does hydrogen peroxide.

It has been speculated that the mechanism of reaction for this system involves dissociation of the hydrogen peroxide, through the mediation of UV light, to free radicals (.OH and explosive structure. The explosives also absorb UV light in the wavelengths used, and so are probably in an "excited" or more reactive state during irradiation. It should be noted that TNT changes to colored compounds as a result of UV irradiation alone (5). The "excited" explosives--if indeed these occur--react rapidly with the free radicals generated from the peroxide to yield unstable compounds which are quickly destroyed.

CURRENT TECHNOLOGY

Currently, explosive contaminated wastewater is treated almost exclusively by filtration through a rough roll filter followed by removal of the dissolved explosives by treatment through carbon adsorption systems. Such systems have problems:

they are expensive to operate. The carbon must be replaced at intervals either with new carbon or with regenerated carbon. It is possible to regenerate spent carbon thermally, but the cost of a regeneration system is sufficiently prohibitive to make it impractical for any but an extremely large user. The Navy does not have any facilities with sufficiently large usage rates to warrant the expense. (The transport of explosive contaminated carbon must be done by a licensed explosive waste handler, precluding economical sharing of a common regeneration facility.)

they require constant monitoring. Although carbon towers may reduce the explosive concentration of effluents to near 0.1 parts per million (ppm) in the wastewater, the life of the tower is difficult to predict because of the variability of the explosive concentration of the influent water (see Table 1). In our experience, as the effluent wastewater explosive content approaches 1 ppm, catastrophic breakthrough is imminent. Although automated monitoring equipment is available for some towers the effectiveness of this equipment is debatable. The equipment usually monitors TNT content. RDX is usually the first explosive to evade removal by the system.

TABLE 1.

AVERAGE INFLUENT WASTEWATER SAMPLE ANALYSES

WPNSTA Yorktown, Virginia Steamout Facility

May - October 1982

Analytical Parameter	High	Low	Norm
Explosive Concentration:			
TNT (ppm)	217.4	12.3	84.4
RDX (ppm)	157.8	6.1	45.6
HMX (ppm)	12.7	0.05	3.6
Total Organic Carbon (TOC) (ppm)	91.7	8.7	42.7
Suspended Solids (ppm)	70	8	36.2
Dissolved Solids (ppm)	432	260	352
Temperature (C)	33.3	21.1	

the spent carbon must be treated. As mentioned above, it is possible, but not practical to regenerate it. A general practice is to dry it, mix it with combustible material and burn it. A water pollution problem becomes an air pollution problem. There is also some evidence to indicate that burning does not completely destroy all of the entrapped explosives.

There are several other methods which have been proposed, but to date have not been developed sufficiently to be put into use. All require filtration prior to use to remove insoluble material from the system. These include, but are not necessarily limited to, collection on polymeric adsorption resins (6), ozonolysis under the influence of UV irradiation (7), foam separation (8), and simultaneous treatment with hydrogen peroxide and UV light.

This last method was developed in the laboratories at the Naval Weapons Support Center. Its use has been verified in larger systems (4). The development of engineering parameters for design and production of a full size system for use at a Navy steamout facility form the basis for this report.

ENVIRONMENTAL CONSIDERATIONS

Wastewater discharge criteria are regulated by the United States Environmental Protection Agency and by state/local environmental agencies. The federal National Pollutant Discharge Elimination System (NPDES), under the Clean Water Act, covers point discharge sources including steamout plant wastewater. A NPDES permit is required for wastewater discharge.

Federal regulations governing effluent limitation for explosive manufacturing and explosive load, assemble and pack facilities are contained in Parts 457.10 and 457.30 of Title 40 of the Code of Federal Regulations (40 CFR). These limitations are concerned only with COD/BOD-5, total suspended solids, pH and oil and grease. National limitations for explosives in wastewater do not currently exist. However, because state and local environmental agencies may enact limitations which are equivalent to or more strict than the national limits suggested, the U. S. Army's Surgeon General has proposed limits for both TNT and RDX for Department of Defense facilities. The proposed limits are 0.04 mg/l (40 parts per billion) TNT and 0.03 mg/l (30 parts per billion) RDX.

Although steamout facilities are not, in the strictest sense, load, pack, assemble or manufacturing operations, these proposed limits are the standards which the equipment and processes discussed herein are to meet.

The discharge of even treated wastewater to either the natural environment or to a sewer system is regulated for any source. The discharge requires a NPDES permit or must meet sewer pretreatment standards. Discharge standards of this type are understood to be site specific.

WASTEWATER CHARACTERIZATION

Many ordnance items are loaded with castable explosives. Castable explosives are primarily TNT to which has been added the explosives RDX or HMX (octahydro-1,3,5,7-tetrazocine), or aluminum, charcoal, wax or other ingredients. When the ordnance item becomes obsolete, surplus or otherwise no longer of use to the Navy, it becomes a candidate for demilitarization, reclamation or disposal. If the explosive load is present in amounts allowing for cost effective reclamation, the ordnance items are usually processed through a "steam-out plant". In such a plant, steam is applied directly to the explosive load either by means of steam lances inserted into the explosive loaded cavity, or by surrounding the item with steam in a steam cabinet. The steam causes the explosive load to melt and flow from the item for dewatering and further processing. Wastewater is produced from condensation of steam, from dewatering, from air scrubbing equipment, and from clean-up water. A diagram of a typical steamout plant is presented as Figure 1.

The amount of water generated and the nature of the contaminants is basically a function of the plant/process design and the exact composition of the explosives being reclaimed. A summary of the constituents of influent wastewater was presented previously in Table 1.

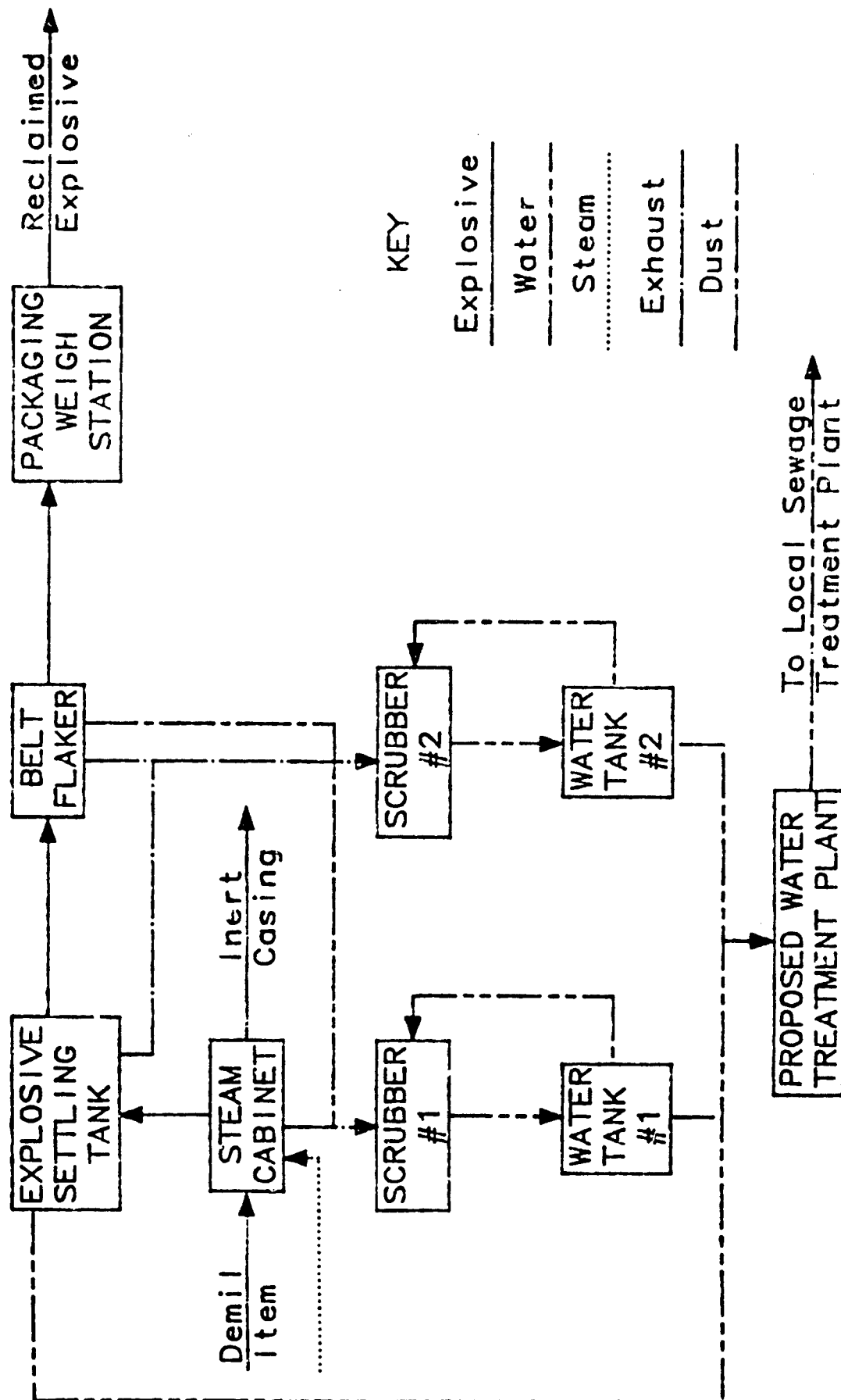
Some generalizations concerning the wastewater may be made inasmuch as most of the explosive loads are similar. The principle water soluble pollutants in wastewater from steamout plants are TNT, RDX or HMX. There may also be, in small amounts, some degradation products of these explosives. Other explosive ingredients are essentially insoluble and can be removed mechanically by filtration.

Wastewater from operations involving TNT is often characterized as "pink water" or "red water" because of the color of such effluents. The color is a result of the exposure of the TNT to sunlight (UV light) or alkali solutions. The color usually represents only an insignificant percentage of the TNT present. As will be discussed later, the system being described is effective not only in treating the explosives involved but also degradation and reaction products of these explosives.

The temperature of the wastewater as it leaves the facility is also a function of the plant design. Wastewater temperatures as high as 90°C have been observed. The solubilities of the explosives increase significantly as temperatures increase.

FIGURE 1.

Typical Steamout Plant Layout



See Table 2. Cooling of the solution by a period of prolonged standing (e.g., 24 hours) at ambient temperatures produces a filterable (0.5 micron) precipitate of crystalline TNT and an aqueous solution to be processed which approaches the ambient saturation level of 130 to 140 ppm TNT. This holding period also facilitates the removal by filtration of other insoluble ingredients.

METHODOLOGY: Equipment

These studies were primarily conducted with commercially available ultraviolet (UV) light reactors which have been, in some cases, modified to provide specific parameters. These units were the UV-500, manufactured by the Ultradynamics Corporation, Santa Monica, California, and the TD-5 System, from Purewater Systems, Inc., Fairfield, New Jersey. A third, custom made miniature constant flow unit was fabricated for additional testing.

The original UV-500 unit houses a single 40 watt mercury vapor lamp (13.8 watt at 254 nm) surrounded by a quartz sleeve. It is equipped with a manually operated wiper assembly to remove fouling from the quartz sleeve. The reaction chamber is constructed of polished stainless steel. The maximum film depth is 2.5 cm. The reaction chamber has a liquid volume of 2.84 liters. The system was modified by addition of a stainless steel heat exchanger and a bottom-drained stainless steel holding tank. Stainless steel was utilized for plumbing in the additional equipment. The final system has a total capacity of 7 liters. A schematic diagram of the UV-500 is included as Figure 2.

The TD-5 unit houses 66 lamps, each surrounded by a quartz sleeve. Total output capacity of the lamps is 1.5 KW, of which 574 watts (8.7 w per lamp) is at 254 nm. The lamps are housed in a 304 stainless steel reaction chamber (volume 21.4 l) equipped with an automatic mechanical wiper. The configuration of the lamps establishes a maximum film depth of 6.3 mm. The system has a capacity of approximately 114 liters. A diagram of the TD-5 system is included as Figure 3.

The miniature constant flow unit, assembled in the laboratory, was constructed as follows: a quartz tube, 2.2 cm inside diameter, was notched at both ends to provide fluid paths. An Ultradynamics Corporation P-247 AL-BAC Lamp was inserted into the quartz tube. Seals were placed over the ends of the lamp and seated against the quartz tube. The assembly was held together by two modified Swagelock large tubing connectors. Inlet and outlet ports were provided in the connectors. See Figure 4. The distance between the bulb and the jacket was 3.5 mm. Reaction liquor was pumped through the system, bottom to top, at pre-selected rates.

TABLE 2.

SOLUBILITIES OF TNT AND RDX IN WATER

Temperature (C)	TNT (ppm)	RDX (ppm)
10	110	no data
20	140	10
26.7	190	55
40	300	150
60	750	470
76.7	1300	1000

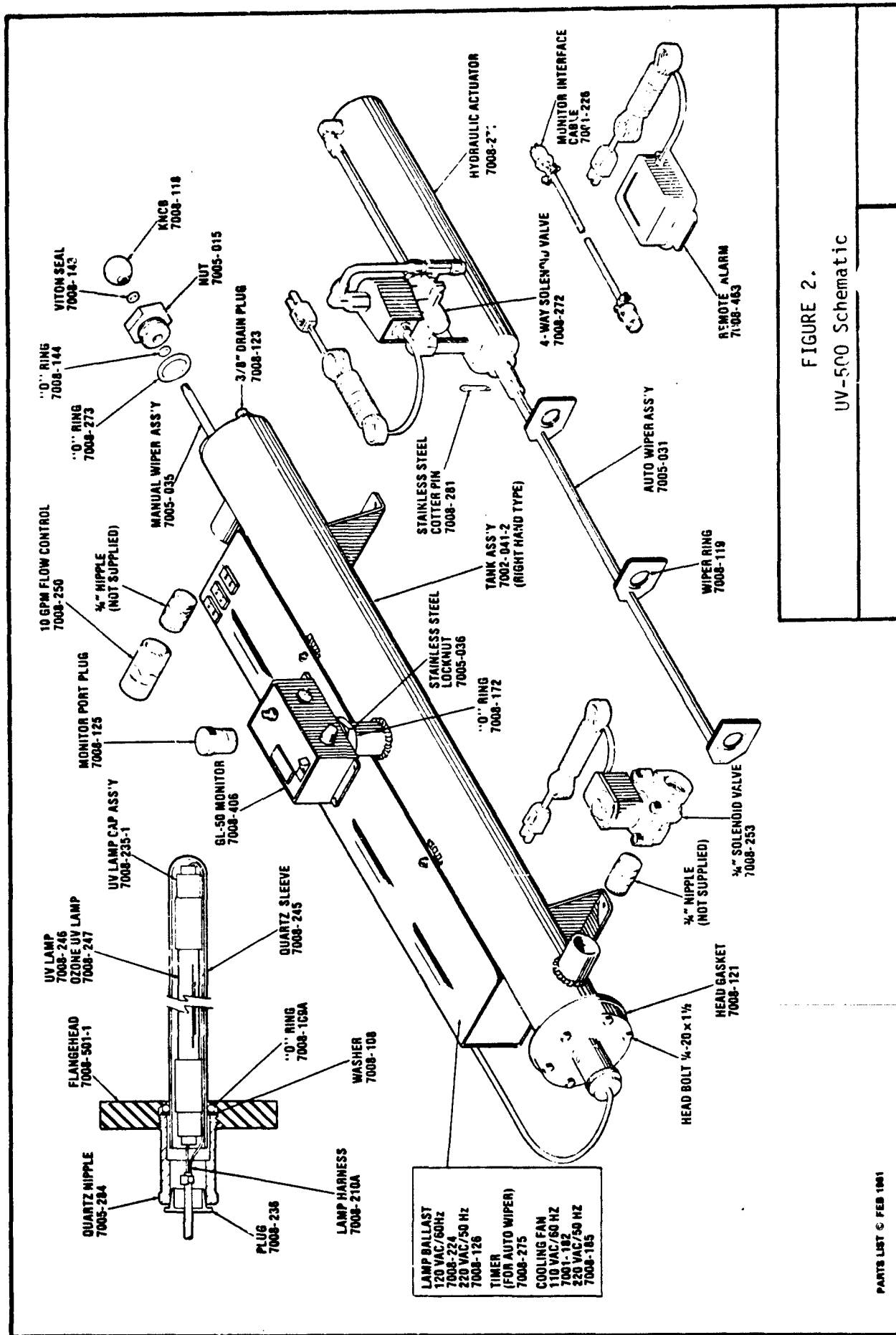


FIGURE 3.

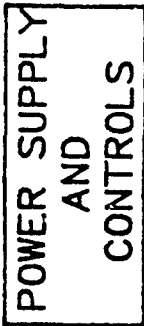
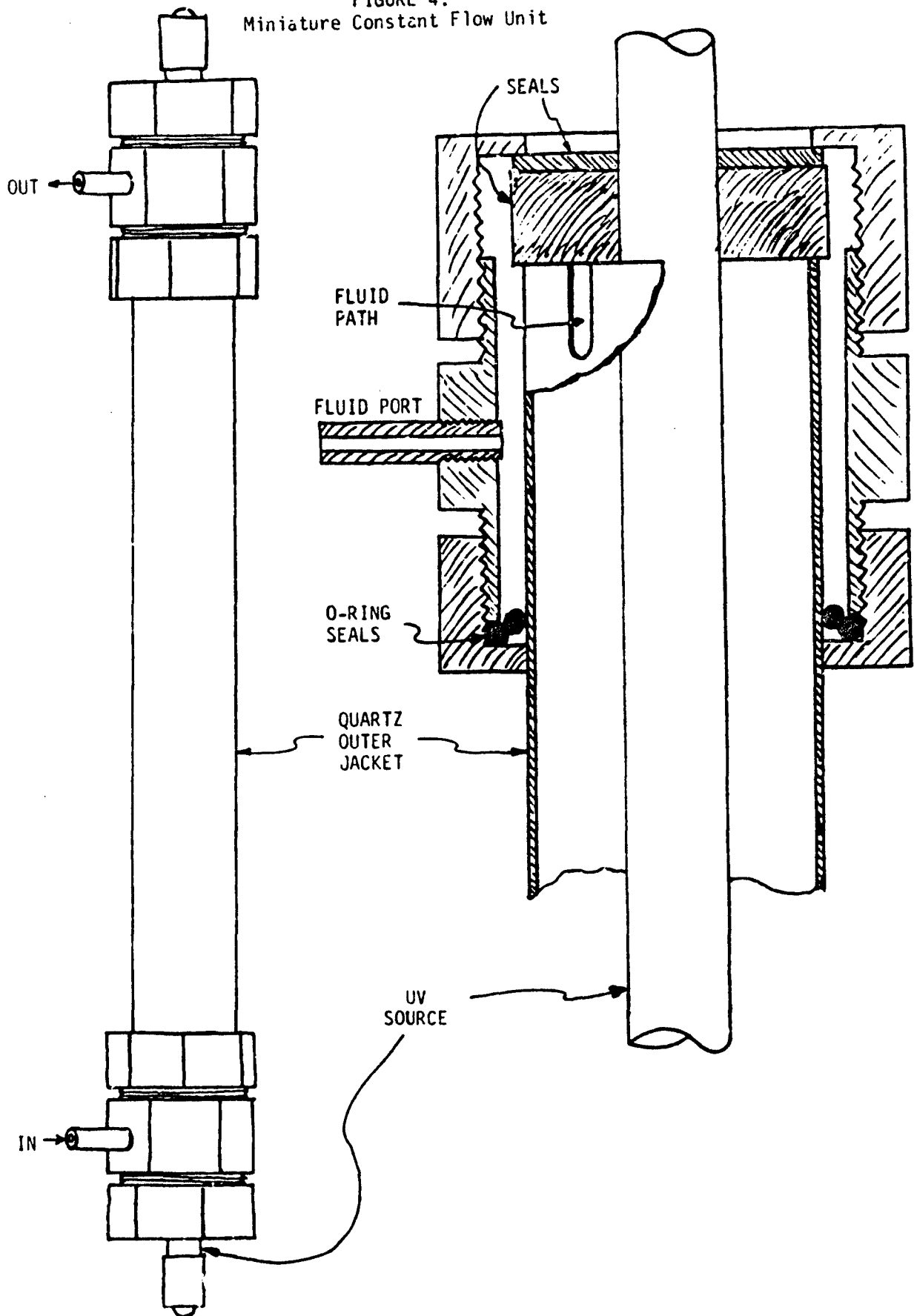


FIGURE 4.
Miniature Constant Flow Unit



The output of the lamp was determined by comparing its output with that of a known source, using a Gamma Scientific Model 700-31 Monochrometer. Through its 68.6 cm working length the bulb produced 4.8 watts of ultraviolet light at 254 nm.

METHODOLOGY: Chemical

Feed waters for use in the reactors were prepared in one of the following three ways:

a saturated stock solution was prepared by allowing an excess of explosive crystals to stand in distilled water in the dark for several days. This stock solution was filtered, diluted to the approximate desired concentration and analysed as described below; or

hot (ca. 70°C) tap water was passed through a cartridge containing crystalline explosive. After cooling the water was analysed for actual explosive concentration; or

wastewater was collected from the steamout plant at NWS Yorktown, packaged in 55 gallon drums and shipped to this Center. It was filtered before use, but received no other treatment.

Explosive analyses were conducted by liquid chromatography. Aliquots of the water samples were extracted with equal volumes of 1,2-dichloroethane in separatory funnels. Portions of the solvent extract were injected automatically into a liquid chromatograph fitted with a 250 mm long, 4.6 mm diameter column packed with DuPont Zorbax Sil. The developing solvent was 1,2-dichloroethane. Detection was by means of a 254 nm UV detector. Standards were aqueous samples containing known amounts of the explosives.

The hydrogen peroxide content of the water samples was measured by titration of acidified samples with potassium permanganate.

Measurements of pH, BOD, Total Organic Carbon and ammonium content were by standard methods (9).

Nitrate and nitrite concentrations were measured using high pressure liquid chromatography through an Alltech CN analytical column 4.6 mm diameter and 250 mm long. The solvent system is phosphate buffer-methanol supplemented with hexadecyl trimethyl ammonium bromide. Detection is with a 215 nm UV detector.

Samples for measurement of volatile organic acids were neutralized, concentrated 100 times in a vacuum and reacidified. Aliquots were injected into a gas chromatograph with a 3 foot Poropak Q column at 150 C and a flame ionization detector. The carrier gas was helium. Authentic samples of formic, acetic, and propionic acids were injected as standards.

Analyses utilizing the gas chromatograph-mass spectrometer were conducted on 4 ml aliquots of the reaction liquor which had been dried under flowing nitrogen on an aluminum coupon, desorbed at 160°C, reconcentrated, then purged at 200°C with helium into the gas chromatograph fitted with a six foot long Tenax-GC column. Peaks were analysed in a mass spectrometer having a range of 35 to 350 atomic mass units.

Gas samples from the reactor were collected over water in an inverted separatory funnel and transferred to an evacuated sample bottle containing desiccant to dry the gases. One ml aliquots were injected into a gas chromatograph fitted with a CTR column and a thermal conductivity detector. The carrier gas was helium. Commercial gas standards were injected for standardization.

Qualitative tests for mono-, di-, and triaromatic phenols and for nitrosoamines were conducted normally on 4 ml aliquots which had been evaporated to near dryness under flowing nitrogen. Five hundred ml samples from the 24 hour experiment were adjusted to pH 7 and evaporated under vacuum in a rotary evaporator to near dryness. Spot tests for nitrosoamines (12,13) and phenols (14) were done according to accepted practice.

RESULTS AND DISCUSSION

Although we have previously amassed considerable amounts of information concerning the degradation of TNT and other explosives under the influence of hydrogen peroxide and UV light, data which can be used for the design and construction of an operating system has not been available. This report is intended to provide this information which includes the rates and natures of the reaction, the factors which bear on it and the nature of any reaction products.

It had previously been determined that the reaction proceeds most rapidly at 0.1% (0.03 M) hydrogen peroxide. This represents approximately a 66:1 molar ratio of peroxide to TNT, or approximately 3.5 times as much peroxide as required to stoichiometrically oxidize TNT to carbon dioxide, nitric acid and water.

TNT absorbs relatively strongly at 254 nm, the principle wavelength of the UV light involved in the reaction. A 1 milliMolar (mM) aqueous solution at 254 nm through a 1 mm path length has an absorbancy of 1.97 (transmits less than 0.1% of incident light). Conversely, a similar solution of hydrogen peroxide under similar conditions has an absorbancy of only 0.001 (transmits more than 97%). At the nominal concentrations of TNT and peroxide to be utilized in this system (100 mg/l TNT, 1000 mg/l peroxide), the TNT:peroxide absorbance ratio is approximately 3:1.

Both peroxide and TNT are degraded by UV light alone. TNT is very slowly (0.028 milliMoles per liter per hour--mM/l/hr) converted to pigmented aromatic compounds in the absence of peroxide. During the period of irradiation of TNT in the absence of peroxide there is no change in acidity, indicating that complete oxidation of TNT with the concomitant liberation of nitric acid has not occurred. Upon addition of peroxide, TNT oxidation proceeds immediately (0.19 mM/l/hr). Figure 5 is a graphical depiction of this process. Peroxide, conversely, reacts much more vigorously. Under conditions similar to those for the TNT reaction, the rate of reaction for hydrogen peroxide, which is similar in either the presence or absence of TNT, is approximately 5 to 7 mM/l/hr. At nominal peroxide concentration, 0.1% TNT concentrations had minimal effect on the rate of peroxide utilization (Table 3).

Since the rate of peroxide loss does not change significantly as the TNT concentration changes, it can be readily understood that the molecules of peroxide utilized per molecule of TNT destroyed increases significantly as the reaction proceeds (Table 4 and Figure 6). It can be seen (Figure 6) that during the early stages of the reaction, the peroxide:TNT usage approaches the theoretical stoichiometric amount (18 Moles/Mole). As the TNT level drops below 15 mg/l, the efficiency of the conversion decreases. A much larger percentage of the peroxide is converted to oxygen.

In view of the molar TNT:peroxide ratios and the independence of the peroxide decomposition rate on TNT concentration, it was assumed that the bimolecular reaction could be viewed kinetically as a pseudo-unimolecular reaction.

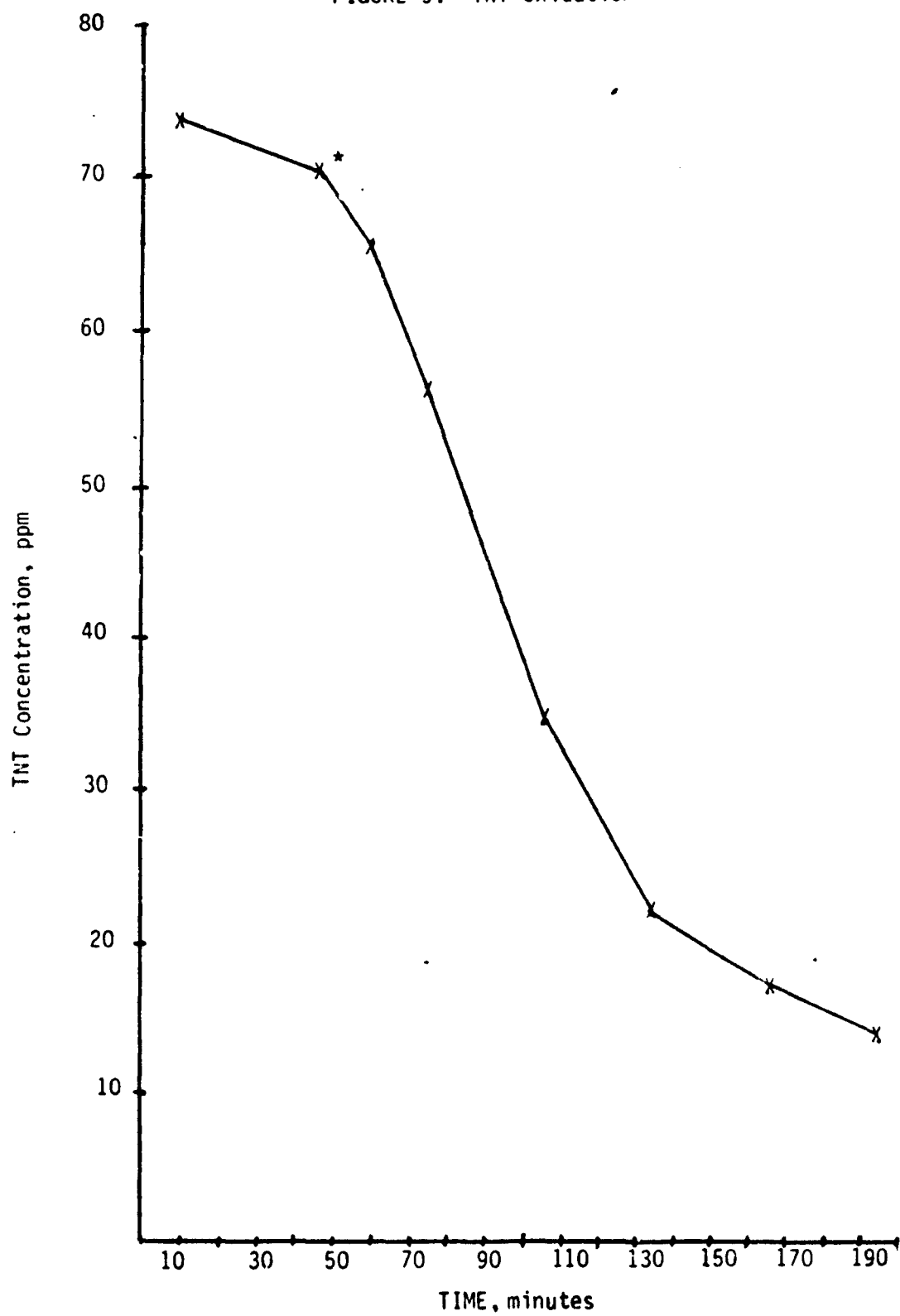
Previous data from our laboratories, as well as preliminary data generated in these studies, were reviewed for a possible kinetic model. Since the concentration-time data for explosive decomposition in these studies is a non-linear decay function, a first order model with respect to TNT destruction was evaluated and found to fit. A simple computer program was devised to treat all data generated in this study and calculate reaction rates based on this first order model. The reaction rates (k) are derived from the equation:

$$kt = -\ln c/C$$

in which t = time (minutes), c = concentration of reactant at the end of t, and C is the concentration when t = 0.

With calculation of the reaction rate for the decomposition of TNT available, a variety of experiments were conducted to compare the effects of the variance of different parameters on the rate. The parameters monitored included pH, flow rate, peroxide concentration, power (UV light) provided, and temperature.

FIGURE 5. TNT Oxidation



* Peroxide added.

TABLE 3.
EFFECT OF TNT CONCENTRATION
ON
RATE OF PEROXIDE UTILIZATION

TNT Concentration (mM/L)	Peroxide Utilization Rate (mM/L/hr)*	
	TD-5 Unit	UV-500 Unit
0.03	5.6	
0.13		0.25
0.30		0.20
0.32	7.6	
0.33	5.3	

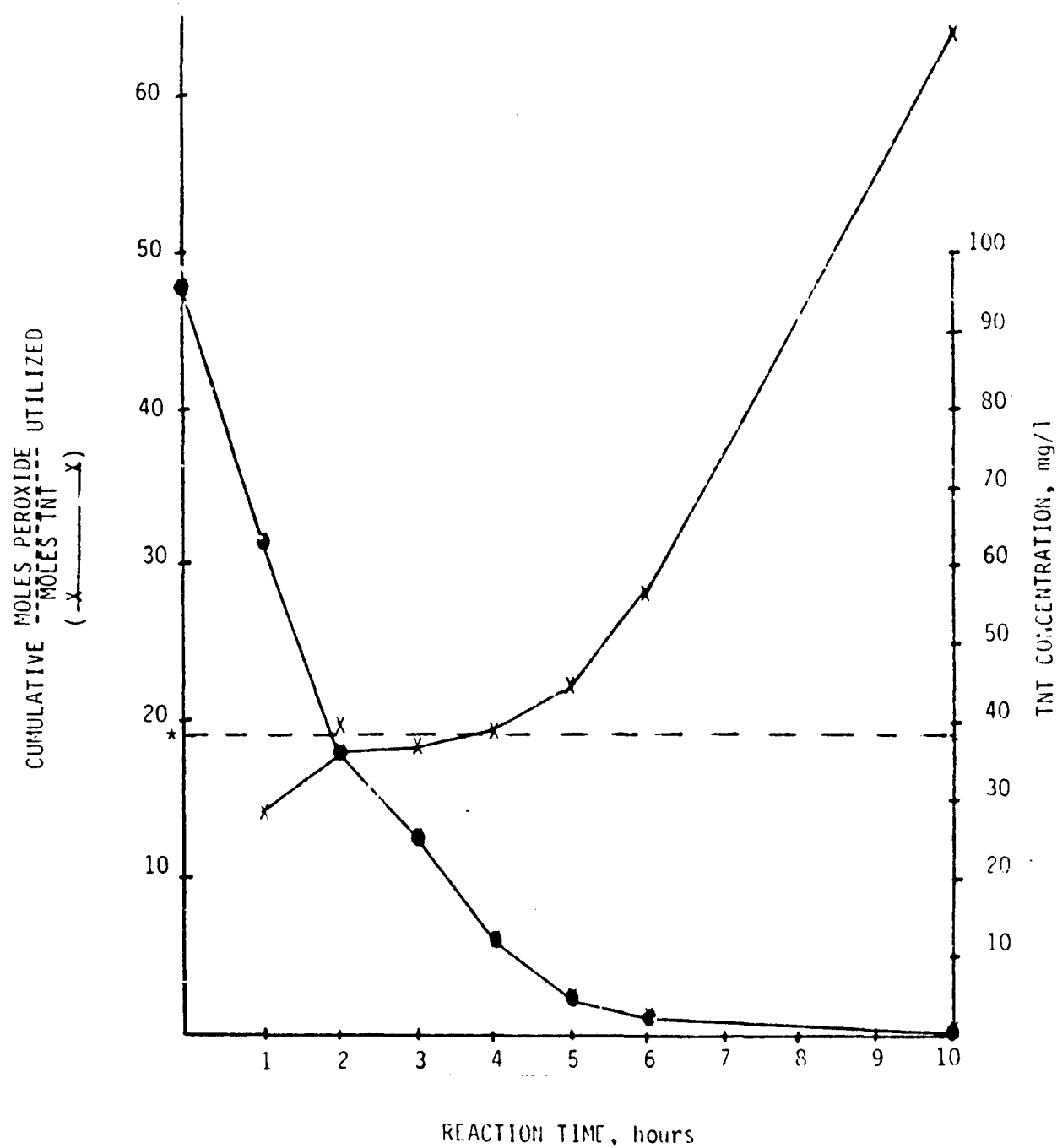
* Measured during first hour of reaction when initial concentration of TNT was as shown.

TABLE 4.
RATIO OF MOLECULES OF PEROXIDE UTILIZED
PER MOLECULE OF TNT DESTROYED
DURING THE COURSE OF REACTION

Hour of Reaction	mM/liter TNT lost	mM/liter peroxide used	Ratio mM peroxide: mM TNT
1 st	0.15	2.06	13.73
2 nd	0.11	3.09	28.09
3 rd	0.06	1.03	17.17
4 th	0.04	0.76	19.00
5 th	0.04	1.81	45.25
6 th	0.01	2.81	281
7 th thru 10th	0.01	15.30	1530

FIGURE 6.

TNT and Peroxide Utilization During Reaction



* Theoretical H_2O_2 :TNT

The effect of pH was measured in two separate experiments: one conducted at values of 3, 4, and 5, the other at pH levels of 5, 6 and 7. Although the results between the two experiments are not strictly reproducible, the indication is that pH levels between 3 and 7 do not have any significant effect on the rate of TNT decomposition (Figure 7). When pH is not controlled, solutions decrease in pH value to approximately 3 and remain stable. This verifies previous studies which indicated that pre-acidification to pH 3 or above was ineffectual and maintenance of pH was of little consequence. The earlier study had indicated that, at artificially induced pH levels of 1 or 2, TNT degradation proceeded very slowly. This is attributed to the fact that extremely acidic pH levels stabilize hydrogen peroxide.

The effect of hydrogen peroxide concentration variance on reaction rate had been explored in previous research and current experiments confirmed that TNT oxidation slowed as peroxide concentrations exceeded 0.1% (Table 5).

The most dramatic reduction in TNT reaction rates was observed with changes in the amount of UV light input. When the amount of light available was curtailed by disconnecting a portion of the UV bulbs, the reaction rate decreases linearly with the decrease in available UV light (Figure 8).

The rate of chemical reactions usually increases with temperature increases. A common rule of thumb is that reaction rates double for each ten degree C increase in temperature. This rule does not seem to apply in this system. In general, reaction rate is independent of temperature (Figure 9). This incongruity apparently can be explained if one examines the output of the UV bulbs at various temperatures. The maximum 254 nm output of the bulb is at a temperature of 37 to 40°C. At temperatures both above and below this temperature the output decreases dramatically (Figure 10). The spectral distribution of the light does not change with changes in temperature. It is relatively important, therefore, that for maximum efficiency the reactor run at minimum temperature of 35°C. The diminished light output at temperatures above 40°C will normally be compensated for by the increased rate of reaction.

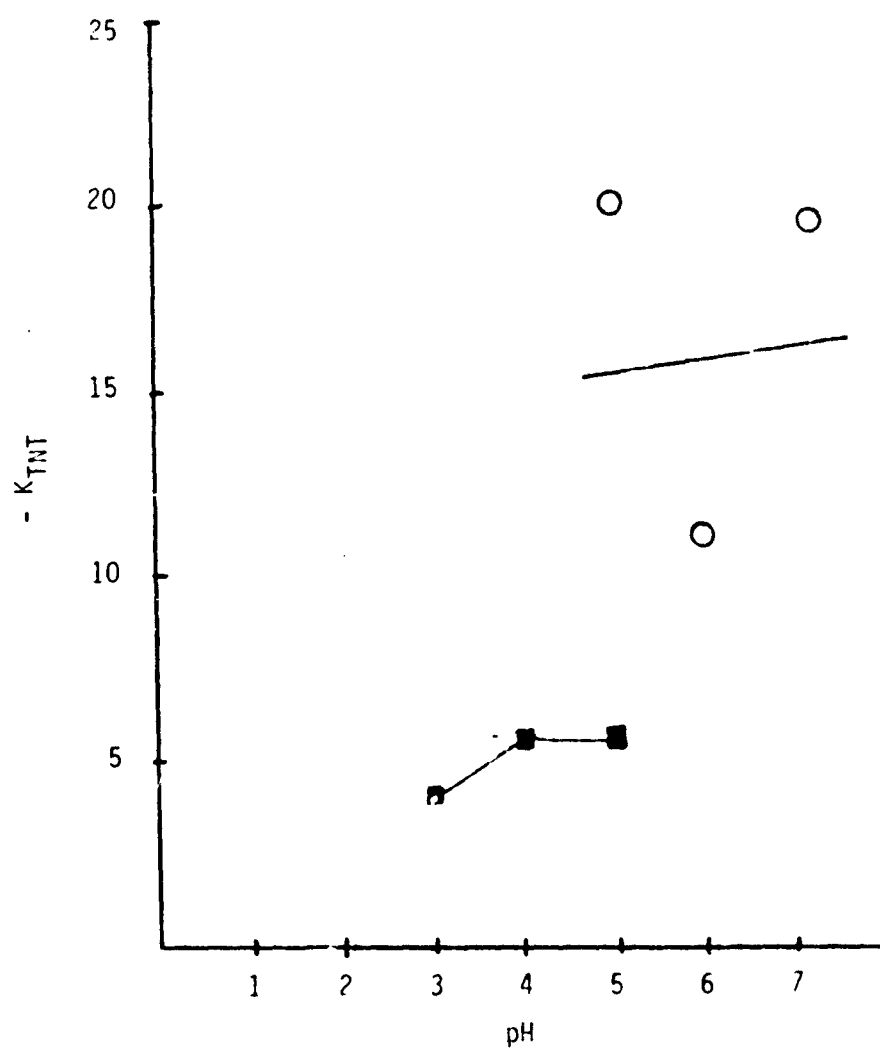
In a recirculating system in which the flow rate has no influence on the total illumination to which the waste is exposed, the rate of flow has no bearing on TNT destruction rate.

Reaction rates for RDX were in the same range, although usually slightly higher, as those for TNT (Table 6). The rate of HMX oxidation is similar. However, the sparing solubility of HMX makes accurate measurements difficult.

In studies using actual wastewater rather than synthetic wastes made from recrystallized explosives the reaction rates for TNT, RDX and HMX did not vary significantly from those of the synthetic feeds.

FIGURE 7.

Effect of pH on K_{TNT}



o Run #1

■ Run #2

TABLE 5.
EFFECT OF PEROXIDE CONCENTRATION
ON
RATE OF TNT OXIDATION

<u>Peroxide Concentration</u>	<u>- K_{TNT}</u>
0.1 %	.048 min ⁻¹
0.4 %	.014 min ⁻¹
0.6 %	.023 min ⁻¹

FIGURE 8.

Effect of Illumination
on Reaction Rates

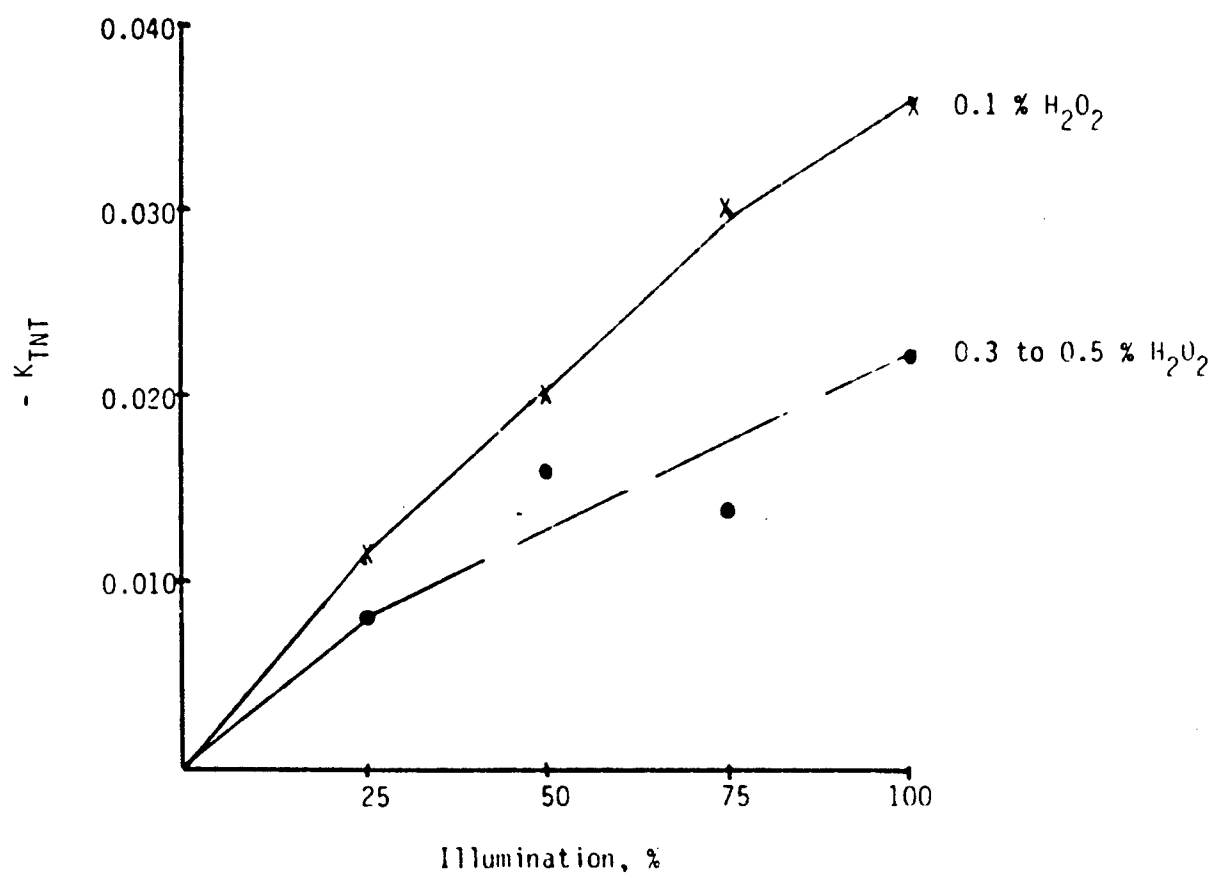


FIGURE 9.
Effect of Temperature
on
Reaction Rate

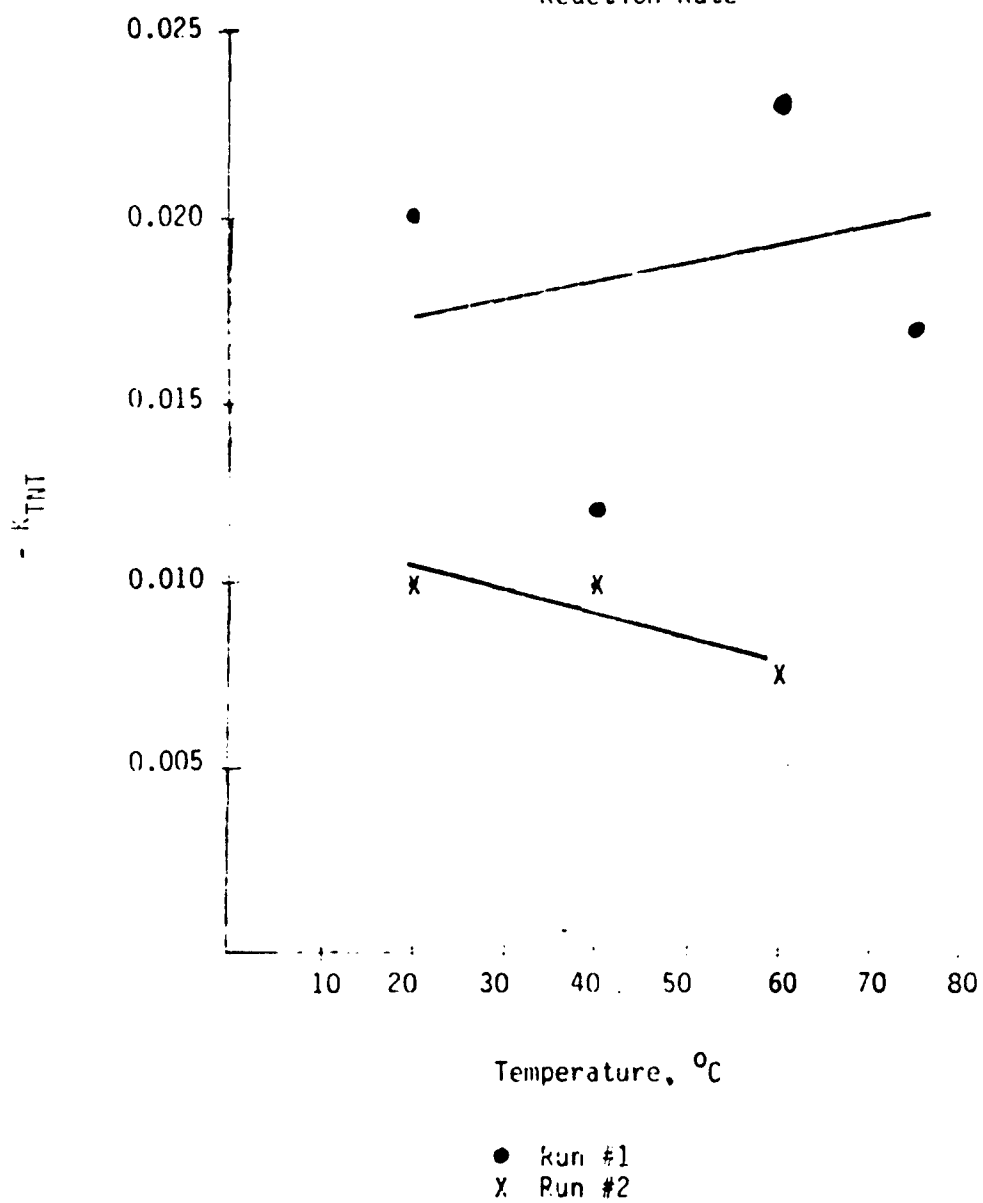


FIGURE 10.

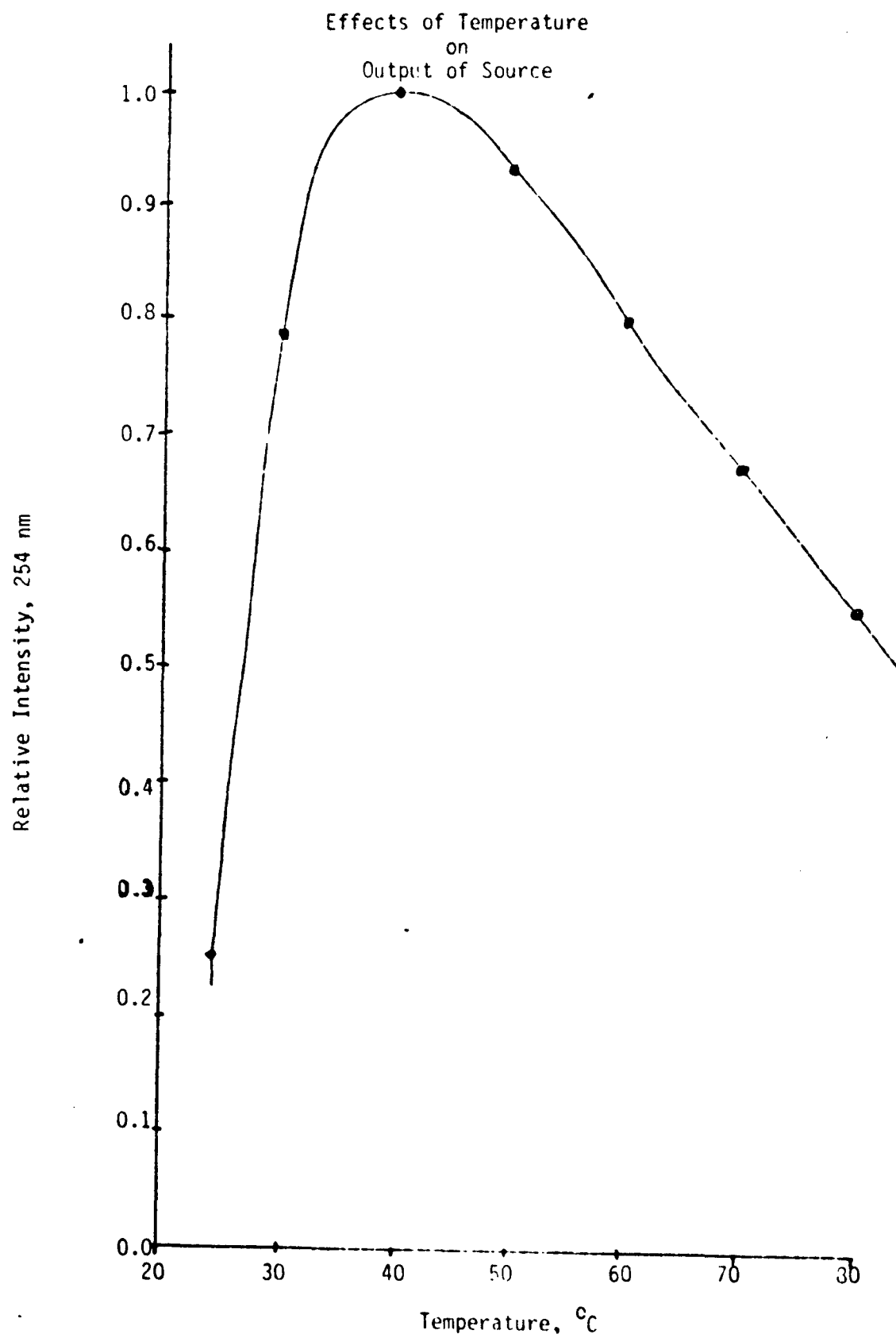


TABLE 6.
COMPARISON OF TNT AND RDX REACTION RATES

<u>Concentration, ppm</u>		<u>Reaction Rate, -K</u>	
<u>TNT</u>	<u>RDX</u>	<u>TNT</u>	<u>RDX</u>
63	52	0.045	0.059
41	51	0.080	0.104
29	53	0.057	0.117
0	53	----	0.097

Discussion thus far has been limited to the "rate" of reaction given the available variables. The reaction itself, the breakdown of TNT or RDX, to innocuous by-products is also an item of concern. The final effluent must be environmentally safe or a conversion of hazardous forms will be all that is accomplished.

Extensive analysis of the wastewater to be processed has been conducted and the results discussed previously.

During the course of the studies described above various analyses for explosive content, peroxide concentration, pH, and presence of various reaction products have been performed from time to time. However, no systematic examination of the reaction liquor has been carried out. Therefore, a simple system of experiments was devised in which synthesized TNT waste water is reacted for 2, 4, 6, 8 or 24 hours. The reaction liquor at the end of each time period is analysed exhaustively. The course of the reaction is described chemically in Table 7. As can be seen, almost all of the TNT nitrogen is recovered as inorganic ammonium or nitrate ion. Nitrite did not appear as a reactant product at any time studied.

Because of the nature of the reaction system it was impossible to quantitatively measure the gas released during the reaction. Gas collection was difficult. The solubility of the gases was influenced by the temperature and pH of the reaction fluid. At the end of the 24 hr reaction, however, a one liter aliquot of the liberated gases was found to contain 5.05 per cent carbon dioxide. No evidence of cyanide or other noxious volatile products was found.

It should be noted that as TNT disappears there is a concomitant reduction in the Total Organic Carbon (TOC) content of the reaction liquor until the TOC level approaches that of the tap water with which it is made. The rate of reduction of TNT is faster than the rate of disappearance of TOC. However, by the end of the reaction both the explosive and TNT-related TOC have disappeared.

Inasmuch as it is not possible to do a mass balance on the carbon fraction of the TNT reaction, the treated liquors were analysed exhaustively for evidence of any undesirable chemicals. Nitrosoamines, known carcinogens, would have been detected had they been present at concentrations as low as 0.05 micrograms(ug) per 4 ml of reaction fluid in the 2, 4, 6 or 8 hour samples, or as low as 0.05 ug in 500 ml of the 24 hour sample. Mono-, di- or triaromatic phenols or amines would have been detected at concentrations of approximately 1 ug per 4 ml in the early samples, or in 500 ml of the final sample. No volatile organic compounds other than acetic acid were detected, nor were any nitroaromatic compounds other than those listed in Table 7 present in concentrations greater than 1 ug per ml. Further, gas chromatography-mass spectrography detected no organic residues in concentrates

TABLE 7.
CHEMICAL ANALYSES OF REACTION LIQUOR AFTER VARIOUS
PERIODS OF REACTION

Component	0 Hrs	2 Hrs	4 Hrs	6 Hrs	8 Hrs	24 Hrs
Trinitro- toluene, ppm	98.0	11.8	0.7	2.4	0.1	0.1
Trinitro- benzene, ppm			1.3	1.8	1.8	0.2
Acetic Acid, ppm		1.2	1.2	1.0	1.4	0.1
Total Organic Carbon, ppm	40.0	25.0	19.5	11.7	7.4	4.2
Hydrogen Peroxide, %	0.10	0.08	0.08	0.07	0.05	0.00
Ammonia, ppm		21.9	17.6	11.7	7.4	4.7
Nitrate, ppm		4	13	19	26	52

of 4 ml of reaction fluids. Based on these analyses it is considered that no noxious materials were present in the wastewater at the end of the reaction.

The miniature reactor was utilized to establish more precise data concerning continuous flow reactions (i.e., one pass through the reactor). Preliminary data indicated that the amount of light energy necessary to degrade equivalent amounts of TNT in the large TD-5 system when operated in a recirculating mode or in the miniature system used as a continuous flow system are essentially identical (Table 8).

Analysis of the effluent wastewater from the continuous flow system, when operated at various flow rates, indicate the same reaction patterns as seen during studies with the TD-5 system operating in a recirculating mode. Greater exposure to UV causes the greatest amount of decontamination (Table 9). At a flow rate of 23 ml/min (approximately 6 minutes in the reactor) all the TNT has been destroyed. There still is residual TOC, and the trinitrobenzene (TNB) reaction product has appeared. If the exposure time is prolonged to 140 minutes in the reactor (flow rate is 1 ml/min) all organic residues have disappeared. These data are graphically presented in Figure 11. In the figure energy input is presented as megawatt-minutes of ultraviolet light at 254 nm per mole (MW/Mole) of TNT. To eliminate small differences between composition of input waste stream the data in the figure are normalized as percent of input concentration. The TNB data are normalized as 80% of maximum observed during the studies. It can be seen that at an energy input of 10 MW/Mole all traces of TNT and its reaction products have been eliminated.

Similar data have been developed for RDX. See Table 10 and Figure 12. Although RDX disappears more rapidly than TNT it appears a safe energy level to cause complete removal of all organic residues is 10 MW/Mole. The data in Table 11 illustrate that mixtures of explosives also can be destroyed during continuous flow reactions.

During the course of the experimentation several material problems which could effect system design and operation were noted. These included: actinic degradation of some polymeric materials; absorption of explosives from solution into some plastics; effect of some metals on hydrogen peroxide stability; and effect of some materials on explosives.

Polyolefins are known to be particularly susceptible to deterioration by ultraviolet light, and were scrupulously avoided in these studies.

During early studies it was noted that plasticised polyvinyl tubing which was in contact with the explosive solutions became discolored and embrittled. This discolorization was discovered to be caused by absorption of TNT and/or colored degradation products of TNT into the polymer matrix. Subsequently it was

TABLE 8.

ENERGY* REQUIRED TO EFFECT
99% REDUCTION OF EXPLOSIVE COMPOUND

EXPLOSIVE	TD-5	<u>REACTOR</u>
		Continuous Flow
TNT	0.4	0.55
RDX	----	0.5

* Energy is expressed in Mw-min/mole.

TABLE 9.
EFFECT OF FLOW RATE ON TNT OXIDATION IN THE CONTINUOUS FLOW SYSTEM

CONCENTRATIONS	FLOW RATE, ml/min					
	100	80	60	40	23	10 4 1
Original TNT, ppm	87.39	82.31	68.18	70.04	54.11	74.57 65.17 65.53
Terminal TNT, ppm	47.35	33.59	13.39	7.36	0.01	0.01 0.01 0.01
Original Peroxide, %	0.13	0.13	0.11	0.13	0.13	0.12 0.13 0.13
Terminal Peroxide, %	0.12	0.12	0.09	0.09	0.03	0.01 0.00 0.00
Original TOC, ppm	31.20	29.48	26.69	26.56	20.30	27.10 22.91 23.93
Terminal TOC, ppm	28.64	26.20	21.45	17.52	5.07	1.67 0.44 1.30
Terminal TNB, ppm	0.23	0.35	1.33	2.68	3.50	0.37 0.04 <0.01

FIGURE 11.

Effect of Exposure Time on Concentration

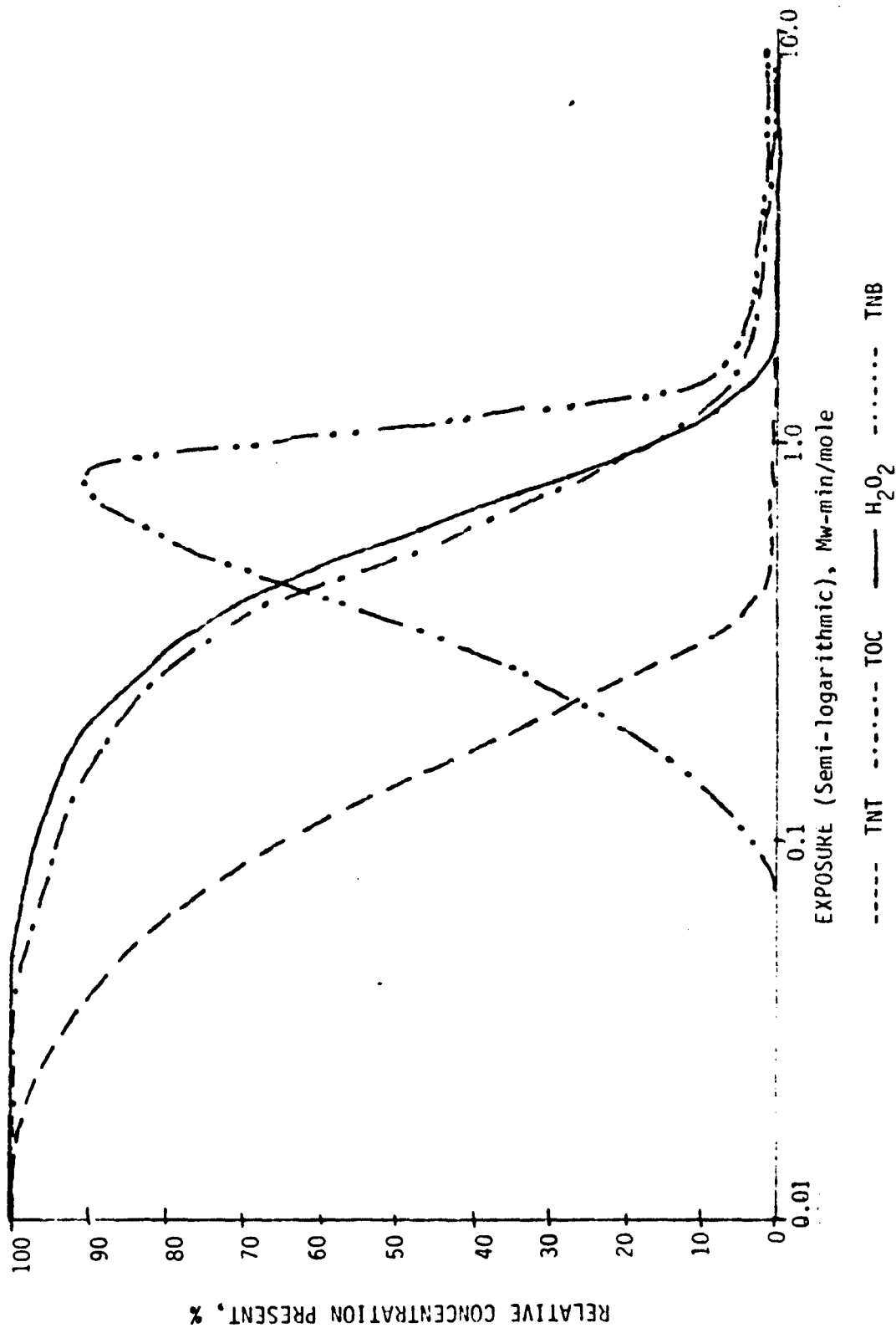


TABLE 10.
EFFECT OF FLOW RATE
ON RDX OXIDATION
IN THE CONTINUOUS FLOW SYSTEM

Concentration	Flow Rate, ml/min		
	500	250	23
Original RDX, ppm	33.33	29.68	30.32
Terminal RDX, ppm	6.05	1.75	<0.01
Original Peroxide, %	0.13	0.13	0.13
Terminal Peroxide, %	0.12	0.12	0.03
Original TOC, ppm	7.16	8.57	8.40
Terminal TOC, ppm	6.80	7.92	2.90

FIGURE 12.
Effect of Exposure Time on Concentration, RDX

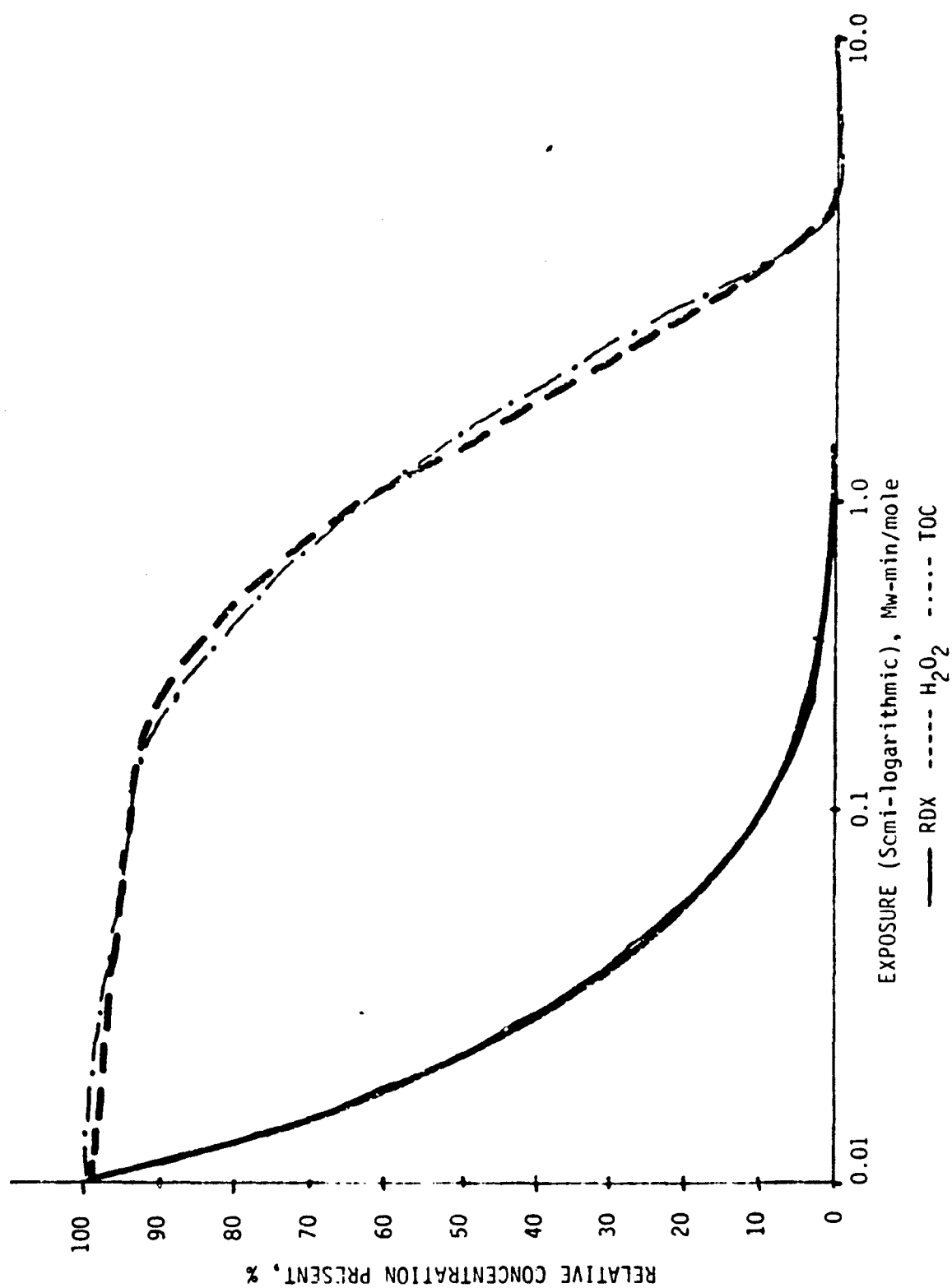


TABLE 11.
MIXED TNT AND RDX OXIDATION AT 4 mL/min FLOW RATE

<u>Concentration</u>	<u>Original</u>	<u>Terminal</u>
TNT, ppm	65.09	1.99
RDX, ppm	47.74	0.01
Peroxide, %	0.13	0.00
TOC, ppm	35.41	2.59

determined that if various polymers were immersed into TNT solutions overnight the solutions lost from 3 to 40 per cent of the explosive in solution. The polymers included some grades of teflon, some nylon fixtures, various rubber hoses, and some rigid (unplasticized?) PVC piping. It appears probable that plastic fittings, fixtures and plumbing should be avoided in the design and installation of such a system unless significant testing is done to insure that the polymeric material is completely compatible with system operation.

It is known that hydrogen peroxide reacts rapidly with some metals, particularly if the metal is in the finely divided state. We have found that the use of black iron or brass fixtures cause almost instantaneous decomposition of peroxide, making it unavailable for the photochemical reaction. Glass, quartz and at least two types of stainless steel (304 or 316) were used without apparent adverse effect during these studies.

Previous research has indicated that photooxidative treatment of wastewater was effective in reducing the explosive content of contaminated water from demilitarization facilities. Current research has confirmed these findings while expanding the concept in order to determine what operating parameters would make the process economically feasible. This expansion has included:

- complete characterization of the influent waste stream;

- determination of physical and chemical requirements for the destruction of the explosive contaminant;

- complete characterization of the effluent waste stream and any post-processing requirements.

From each of these points the basic design criteria for a working system can be determined. By looking at the characterization of the influent waste stream it becomes apparent that some sort of pretreatment of the solution is necessary before introduction to the reaction chamber.

The presence of insoluble waxes or explosive crystals that recrystallize from the hot solution on cooling will interfere with transmission of ultraviolet light. Further, simple mechanical pretreatment is the more efficient method of removing these solids from suspension. The pretreatment should include a holding tank or reservoir where the solution can equilibrate both in temperature and concentration. This will allow for settling of insoluble materials, and for crystallization of excess explosive. Residence in the holding tank should be followed by a series of filters or a continuous flow centrifuge to remove particles larger than 0.5 microns in diameter.

Various physical and chemical parameters were examined to determine their impacts on the rates and overall success of the reaction. Those determined to be crucial to the destruction of the explosives included:

peroxide concentration, optimized at 0.05 to 0.10 percent, although concentrations up to 0.15% are acceptable;

a minimum of 10 megawatt-minutes of ultraviolet light at 254 nm for each mole of explosive to be destroyed. Ideally the light level should be higher;

compatibility of reactor and plumbing materials with the waste stream and with the peroxide oxidant.

The determination of the UV light required to affect destruction of the explosives allows the calculation of the light requirements for the system. This will have bearing on the total size and flow rate of the system.

In general, stainless steel, glass and quartz are the ideal materials for construction of the parts of the reactor system which will come into contact with the waste stream. The use of polymeric materials, on the other hand, are contraindicated.

Finally, characterization of the wastewater after treatment indicates that no noxious products remain. The chief indicator of residual organic contaminants, TOC, is essentially eliminated. The only post-treatment processing required could be adjustment of pH. For wastewaters having high contaminant load the post-UV pH may be below pH 3. Water with this degree of acidity should be adjusted to near neutrality prior to release.

ACKNOWLEDGEMENTS

Appreciation is expressed to the following personnel of the Explosive Sciences Branch for their laboratory and technical assistance. These personnel include: Anita Allen, Dan Burch, Bob Coyle, Bill Emily, Kim Fleming, Richard Goff, Dr. Robert Klausmeier, Larry Kovach, Nancey Kristler, Stephen Maegerlein, Becky Patton, Dave Phillips, Steve Wharton and John Wiegand.

REFERENCES

1. Andrews, C. C. and Osmon, J. L., "The Effects of Ultraviolet Light on TNT in Aqueous Solutions," WQEC/C 75-197, NWSC Crane, IN, 1975.
2. Andrews, C. C. and Osmon, J. L., "The Effects of UV Light on TNT and Other Explosives in Aqueous Solutions," WQEC/C 77-32, NWSC Crane, IN, 1977.
3. Andrews, C. C., Klausmeier, R. E. and Osmon, J. L., "Method for Degrading Aromatic Explosive Solutions," U. S. Patent 4,038,116, 1977.
4. Andrews, C. C., "Photooxidative Treatment of TNT Contaminated Waste Water," WQEC/C 80-137, NWSC Crane, IN, 1980.
5. Burlinson, N. E., Kaplan, L. A. and Adams, C. E., "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NOLTR 73-172, Naval Ordnance Laboratory, Silver Springs, MD, 1973.
6. Andren, Nystrom and Erikson, "Treatment of TNT Munitions Wastewater Using Polymeric Absorption Resins," U. S. Army Natick Laboratories, Natick, MA, 1975.
7. Farrell, F. C., Zeff, J. D., Crase, T. C. and Boylan, D. T., "Development Effort to Design and Describe Pink Water Abatement Processes--Final Technical Report," Westgate Research Corp., West Los Angeles, CA, 1977.
8. Okamoto, Y., Chou, E. J., Cocle, M. and Roth, M., "Application of Foam Separation to Aqueous Solutions of Trinitrotoluene (TNT)--Part II. Removal of Organic Explosives with Surfactants," Report ARLCD-CR-78020, US AARDCOM, Dover, NJ, 1978.
9. Standard Methods for the Examination of Water and Wastewater, 15th Edition, American Public Health Association, 1980.
10. Chandler, C. D., Journal of Chromatography, Vol. 64 (1972), pp. 123-128.
11. Hoffsommer, J. C., Journal of Chromatography, Vol. 51 (1970).
12. Feigl, F., Spot Tests in Organic Analysis, 6th Edition, Elsevier Publishing Co., New York, NY, 1960, pp. 170-171.
13. Zweig, G. and Sherma, J., Handbook of Chromatography--Vol. I, CRC Press, Cleveland, OH, 1972, p. 146.

14. Feigl, F., Spot Tests in Organic Analysis, 6th Edition,
Elsevier Publishing Co., New York, NY, 1960, p. 141.