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**ENGINEERING AND DEVELOPMENT SUPPORT OF GENERAL DECON  
TECHNOLOGY FOR THE DARCOM INSTALLATION RESTORATION PROGRAM**

**Final report**

**Task 2. Treatment of Explosives Contaminated Lagoon Sediment -  
Phase I. Literature Review and Evaluation**

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**July 1981**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents a technical and economic evaluation of 8 processes for removal of high concentrations of explosives from contaminated lagoon sediments. The processes evaluated were set-air oxidation, incineration, molten salts incineration, microwave plasma, high energy electrons, gamma radiation, UV-ozone, UV-peroxide, and chemical degradation. Each process was evaluated for its technical effectiveness, costs, mobility, advantages and disadvantages in application to lagoon decontamination and ability to meet air and water quality standards.		

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## SUMMARY

The purpose of this study was to evaluate the technical feasibility, costs and problems associated with potential processes for decontamination of high concentrations of explosives in lagoon sediments. Eight processes were evaluated during the study : 1) wet-air oxidation, 2) incineration, 3) molten salts incineration, 4) microwave plasma, 5) electron beam processing, 6) gamma irradiation, 7) ultraviolet-ozone and ultraviolet-peroxide and 8) chemical degradation of nitrocellulose. All the processes were compared on the basis of treating 11 standard lagoons within 1 year. A standard lagoon was defined as a 30.5 m x 47.5 m x 2.7 m deep lagoon containing 447,500 liters of sediment. The sediment is approximately 50% solids containing 10% TNT and 5% RDX.

The reactors for molten salts incineration and microwave plasma have not been developed to the sizes required for processing the lagoons. Thus, these processes do not appear to be viable alternatives for treating explosives contaminated lagoon sediment. The equipment for electron beam, gamma irradiation and UV-oxidation is developed, however, no data bases are available on which to judge the effectiveness of these processes on high concentrations of explosives. Wet-air oxidation, incineration, chemical degradation of nitrocellulose and composting of TNT (examined in a parallel report) are all proven technologies for degradation of explosives in high concentration. Each process has its own advantages and disadvantages. It is difficult to place a dollar value on these advantages and disadvantages without more information on the actual sediment, therefore these processes were evaluated on the basis of their capital and operating costs. Of the four basic processes, wet-air oxidation has a capital cost of greater than three times the other processes. Operating costs for wet-air oxidation are slightly higher than those for the competing processes. Based on the high costs and technical factors associated with the process, it is not recommended for further evaluation for decontamination of lagoon sediment.

Incineration appears to be the most cost effective process for near term treatment of explosives contaminated lagoon sediment. Rotary kiln, fluidized bed, and electric furnace are recommended for near term study. Composting and chemical degradation are less expensive solutions than incineration. However, approximately 12 months of further developmental efforts are needed to answer technical questions before either of these processes could be used in the field.



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## I. INTRODUCTION

### A. Objective

The objective of this study was to identify and evaluate viable processes to treat explosives contaminated lagoon sediment. Eight treatment areas were considered in this evaluation: 1) wet-air oxidation, 2) incineration, 3) molten salts, 4) microwave plasma, 5) high-energy electrons, 6) gamma radiation, 7) UV-ozone and UV-peroxide, and 8) chemical degradation. Each process was evaluated for its projected effectiveness, cost, mobility, advantages and disadvantages, and ability to meet water and air quality standards.

### B. Background

The Army has been involved in the manufacture and loading of explosives since the 1930's. During this time, the Army has operated Ammunition Plants located throughout the United States. These operations have resulted in the generation of significant amounts of solid and liquid wastes. At many installations, the explosives contaminated liquid wastes were lagooned. Over the years, the sediments in these lagoons have become highly contaminated with explosives. Problems of explosives leaching into ground water and other environmental problems have necessitated the treatment of these sediments. Two types of explosives contaminated sediments which require treatment have been identified: 1) sediment contaminated with 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and 2) sediment contaminated with nitrocellulose.

### C. Standard Lagoon

The explosives wastewater lagoons, located at the various Army Ammunition Plants, vary widely in their physical and chemical characteristics. To compare different processes, it was necessary to establish a typical lagoon. This typical lagoon has the following characteristics:

Size	30.5 m x 45.7 m x 2.7 m deep
Depth of sediment to be treated	0.3 m
Volume of sediment to be treated (wet)	447.5 m <sup>3</sup>
Weight of sediment to be treated (wet)	499,400 - 544,800 kg

#### Sediment characteristics

Moisture content 50-80%

#### Composition (dry basis)

TNT 10%

RDX 5%

other organics 10%

ash 75%

DNT 100 µg/g

Tetryl 100 µg/g

#### Heat Content

dry 1028 Kcal/kg (1850 Btu/lb)

60% moisture 102 Kcal/kg (184 Btu/lb)

80% moisture -244 Kcal/kg (-439 Btu/lb)

For some treatment methodologies, it is desirable to be able to slurry the explosives containing sediment. Approximately 894,650-2,236,630 liters of a slurry containing 5-10% solids could be formulated from the standard lagoon.

#### D. Economics and Effectiveness Criteria

The various units were sized on the basis of treating 11 standard lagoons/year or one lagoon in 25 days. The capital costs include the process units and all ancillary equipment, i.e. dredge, tanks pumps, air and water pollution abatement equipment, etc. The operating costs include installation, maintenance, electrical and water, fuel, etc.

Criteria used to select the most promising technologies for immediate development were:

- state-of-the-art of explosives degradation with the process
- costs
- mobility
- ability to meet the operational parameters of the standard lagoon scenario
- ability to meet air emission and water effluent standards.

## II. WET-AIR OXIDATION

### A. Process Description

Wet-air oxidation is a liquid phase, high pressure oxidation process for aqueous organic wastes. The basic flow scheme for the current commercially available wet-air oxidation process is presented in Figure 1. The waste slurry is pumped by means of a high pressure pump through a heat exchanger where it is heated to temperatures near that required for the reaction. It then passes into a high pressure reactor along with compressed air. The reactor vessel is carbon steel lined with titanium. Temperatures in the reaction vessel range from 177 to 320°C. Pressures of 6.9 - 20.7 MPa (1000-1800 psia) are employed. Specific catalysts may also be added. Retention time of the waste in the reactor is on the order of 40-60 minutes. After leaving the reactor, the slurry is passed through the heat exchanger where it is cooled. The cooled slurry then goes to a gas-liquid separator where gaseous products are removed. Depending on the type of wastes being treated, the gaseous or liquid products from the wet-air oxidation unit may require further treatment before they can be released into the environment, i.e. biological degradation for the liquid and specific scrubbers for the gases.

### B. Review and Evaluation of Literature

#### L. Treatment of Organic Wastes

This wet-air oxidation process has been widely used to condition sewage sludge. This pretreatment destroys pathogens, reduces odor and increases dewatering rates (Wilhelmi and Knopp, 1979). A sewage plant in England used the wet-air oxidation process to reduce the insoluble organics by 90% and eliminate odors. The resultant product was a non-hygroscopic ash (McDonald et al., 1974).

The initial work on wet-air oxidation for industrial wastes was conducted about 30 years ago. Since that time, numerous types of industrial and hazardous wastes have been subjected to wet-air oxidation treatment. For example, in the pulp and paper process industry, the wet-air oxidation process has been used to treat black liquor and recover sodium carbonate and energy (Flynn, 1976). Wet-air oxidation for steam generation from low grade fuels, wastes and liquids was discussed by Pradt (1979). The advantages of the system included no SO<sub>x</sub>, NO<sub>x</sub>, metal or particulate emissions.

Sommers and Curtis (1977) conducted studies to determine the forms of nitrogen, phosphorus, copper, zinc, nickel, cadmium and lead in sludges treated by wet-air oxidation. Concentrations of soluble phosphorus and soluble and particulate forms of nitrogen were reduced by the wet-air oxidation treatment. The fate of metals in the sludges after treatment with wet-air oxidation were variable. In one wastewater plant, soluble and total metal levels remained the same. At a second plant, increased metal levels were found in the sludge after treatment. However, high sulfate and bicarbonate levels in the latter plant could have aided in the precipitation of the metals.

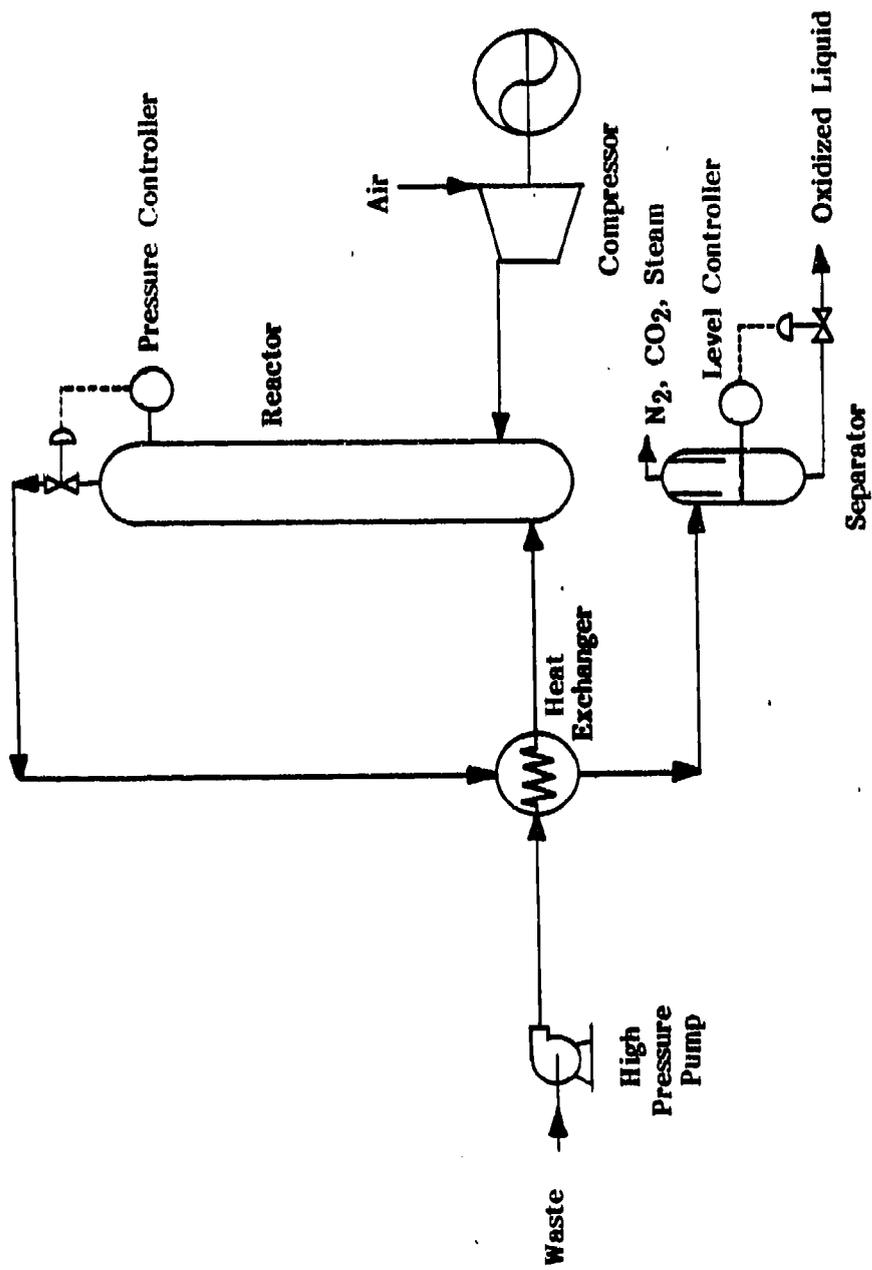


Figure 1. Basic Wet-Air Oxidation Flow Scheme (Flynn, 1979)

The effectiveness of wet-air oxidation for degradation of several hazardous chemicals was evaluated by Wilhelmi and Knopp (1979). The results of their investigations are presented in Table 1. Generally, wet-air oxidation was successful in reducing the concentration of the chemicals. However, significant amounts of 2-chlorophenol and pentachlorophenol remained in the effluent after oxidation at the lower temperature (275°C). The presence of an oxidation catalyst,  $\text{Cu}^{++}$ , improved the degradation at 275°C.

Wet-air oxidation of Amiben (a herbicide) wastes and wastewaters from a coke plant was evaluated by Adams *et al.* (1976). The results of the wet-air oxidation of the coke plant wastewater are presented in Table 2. The cyanide, phenol and cresol levels were substantially reduced. However, the quinoline was not completely destroyed and  $\text{NH}_3$  levels in the effluent, as N, were 2410 mg/l. High levels of carbon monoxide, 1050 ppm, were also released into the air. The results of the wet-air oxidation of Amiben wastes are presented in Table 3. The two chemicals of concern, 2,5-dichloro-6-nitrobenzoic acid and 2,5-dichloro-3-nitrobenzoic acid, were effectively treated by wet-air oxidation. However, 2,5-dichloronitrobenzene, formed by decarboxylation of the initial chemicals, was present in the effluent. In addition, 3210 ppm of carbon monoxide and 750 ppm of hydrocarbons were released into the air during the treatment.

Katzer (1975) calculated degradation rate constants for yeast and glucose solutions treated by wet-air oxidation. The effects of variations in temperature and pressure on the rate of removal were also evaluated. The data on the effects of temperature and pressure on total organic carbon (TOC) reduction for the glucose solutions are presented in Table 4. The percent TOC reduction was greatest under high temperatures and pressure conditions. As shown in Table 5, the highest rate of removal of yeast from the solutions occurred at a process temperature of 225°C and a pressure of 0.65 MPa.

## 2. Treatment of Explosives Containing Wastes

Zimpro (1971) treated waste propellants, containing primarily nitrocellulose and nitroglycerine, by wet-air oxidation. The compositions of the solid propellants for each of the two runs are presented in Table 6. The propellant formulations were slurried in water containing 27% nitric acid in run 1 and 12% nitric acid in run 2 to give the concentrations shown in Table 6. In run 1, a 9.2% slurry was fed into the reactor at 19 liters per minute (5 gpm). For run 2, an 11.4% slurry was fed in at 18.7 liters per minute (4.4 gpm). Water and compressed air were fed separately at 8.3 liters per minute (2.2 gpm) in this run so that the final slurry contained 7.8% propellant. The slurries were subjected to wet-air oxidation treatment at 204°C (400°F) and 5.4 MPa (800 psig) for at least three hours.

The chemical analyses for the aqueous effluents from both runs are presented in Table 7. Effluent COD (chemical oxygen demand) levels were over 1300 mg/l in both cases. The effluent from the reactor was very acidic, with a pH between 1.4-1.6, and had a high solids content. Filtration and neutralization of the effluent were required before disposal. The high lead and aluminum levels in the effluent were reduced by the filtration and neutralization process.

Table 1. Wet-Air Oxidation of Some Hazardous Chemicals  
(Wilhelmi and Knopp, 1979)

Compound	Starting Concentration, mg/l	Final Concentration, mg/l*	
		320°C	275°C/Cu <sup>++</sup>
Acenaphthene	7,000	2.8	0.7
Acrolein	8,410	23.4	79.9
Acrylonitrile	8,060	7.3	81.0
2-Chlorophenol	12,410	17.4	625.0
2,4-Dimethylphenol	8,220	0.8	0.8
4-Nitrophenol	10,000	4.0	40.0
Pentachlorophenol	5,000	6.0	902.0
Phenol	10,000	3.0	23.0
2,4-Diphenylhydrazine	5,000	1.0	1.0

\* After one hour treatment

Table 2. Wet-Air Oxidation of Coke Plant Waste (Adams et al., 1977)

Waste Component	Concentration, mg/liter		
	Feed	Effluent	% Destruction
Cyanide	309	3	99
Phenol	743	1.05	99.9
Cresol	188	.2	99.9
Quinoline	38	13	65.7
BOD5	2083	23	98.9
COD	5520	481	91.3

Operating Conditions: 279°C (535°F)  
10.7 MPa

1.15 Hour Residence Time

17

Table 3. Wet-Air Oxidation of Amiben Waste (Adams et al., 1976)

Waste Component	Concentration, mg/liter		
	Feed	Effluent	% Destruction
2,5-Dichloro-6-nitrobenzoic Acid plus	19,100	<0.1	>99.9
2,5-Dichloro-3-nitrobenzoic Acid	5,280	900	90
BOD5	30,500	2,920	82
COD			

Operating Conditions: 281°C (538°F)  
10.7 MPa

1 Hour Residence Time

Table 4. Dependence of Total Organic Carbon Removal (Glucose Solutions) on Temperature and Oxygen Partial Pressure<sup>†</sup> (Katzner, 1975)

Oxygen Pressure, MPa (psia)	Temperature, °C	Total Pressure, MPa (psia)	% TOC* Reduction	Treatment Time, min.
0	175	1.10 (160)	7	—
.20	175	1.10 (160)	47.8	50-66
.55	175	1.45 (210)	55.3; 40	28-38
.90	175	1.79 (260)	43	35-45
1.31	175	2.21 (320)	60	27-38
1.86	175	2.76 (400)	64.3	23-26
3.24	175	4.14 (600)	60.1	32-35
1.86	175	2.76 (400)	65.7	23-26
1.86	200	3.42 (496)	72.6	7-12
1.86	215	4.11 (596)	75.3	6-9
1.86	230	4.76 (691)	78.0	4

<sup>†</sup> glucose concentration 4%

\* % removed after one-hour time at reactor condition

Table 5. Wet-Air Oxidation of Yeast Solutions Under Various Conditions (Katzner, 1975)

Summary of First-Order Rate Constants for Yeast Solubilization *					
Atmosphere	O <sub>2</sub> Pressure, MPa (psia)	Initial Solids Concentration, Weight %	Temperature, °C	k <sub>1</sub> Phase I, min <sup>-1</sup>	
O <sub>2</sub>	.69 (100)	0.5	170	+0.070	
O <sub>2</sub>	.69 (100)	1.5	170	+0.070	
O <sub>2</sub>	.69 (100)	2.0	170	+0.10	
O <sub>2</sub>	.63 (91)	2.0	200	+0.47	
O <sub>2</sub>	.65 (95)	2.0	225	+0.90	
He	0 (0)	2.0	180	+0.04	

\* Defined by  $\frac{dC_s}{dt} = -k_1 C_s$

C<sub>s</sub> = yeast concentration

t = time, min

k<sub>1</sub> = rate constant, min<sup>-1</sup>

Table 6. Approximate Composition of Solid Propellant Slurries  
Treated by Wet-Air Oxidation Runs 1 and 2  
(Zimpro, 1971 and Schaefer, 1980a)

	Run 1 Composition %		Run 2 Composition %	
	Solid Propellant	Slurry	Solid Propellant	Slurry
Nitrocellulose (13.5% N)	51.0	4.7	48.5	3.7
Nitroglycerine (18.5% N)	38.5	3.5	36.5	2.8
Triacetin	7.5	0.7	7.1	0.5
Lead Salts	2.0	0.2	1.9	0.1
Carbon (Graphite)	1.0	0.1	1.0	0.1
Aluminum	0.0	0	5.0	0.4
Water	<u>0.0</u>	<u>90.8</u>	<u>0.0</u>	<u>92.4</u>
<b>Total</b>	<b>100.0%</b>	<b>100.0%</b>	<b>100.0%</b>	<b>100.0%</b>

Table 7. Analyses of Liquid Effluent Samples from Wet-Air Oxidation of Propellants (Zimpro, 1971)

Analysis	Run No. 1	Run No. 2
pH	1.4	1.6
COD, g/l	1.32	1.34
Volatile Acids, as Acetic Acid, g/l	0.24	0.36
Ammonia-Nitrogen, g/l	0.011	0.035
Total Kjeldahl Nitrogen, g/l	0.014	0.045
Total Solids, g/l	7.27	11.6
Total Ash, g/l	3.31	8.0
Volatile Solids, g/l	3.96	3.6
Suspended Solids, g/l	0.14	6.8
Suspended Ash, g/l	0.10	5.4
Volatile Suspended Solids, g/l	0.04	1.4
*Acidity as g/l CaCO <sub>3</sub>	5.950 (pH 7.0) *	2.70 (pH 4.6)
	6.275 (pH 8.3)**	4.10 (pH 7.0)
		4.50 (pH 8.3)
Turbidity, JTU	190	4600
Nitrite-Nitrogen, g/l	-	-
Nitrate-Nitrogen, g/l	-	-
BOD <sub>5</sub> , g/l	0.297	-
Aluminum, mg/l	-	9818
Iron, mg/l	26.5	0.1
Chromium, mg/l	0.6	0.3
Nickel, mg/l	1.9	16.4
Lead, mg/l	1400	1880

\*Acidity measured as g/l CaCO<sub>3</sub> which precipitates when solution adjusted to pH shown.

Mass balances calculated for runs 1 and 2 are presented in Table 8. While these balances indicate that most nitrogen and carbon which enter the system as propellants are released in gaseous form, the liquid effluent had high levels of nitrate and total organic carbon. Based on the carbon levels, Zimpro (1971) reported a minimum degree of propellant destruction in runs 1 and 2 of 97.6% and 97.9%, respectively. While the mass balance is a useful tool in understanding a chemical process, it is unlikely that a measured mass balance in a practical situation would show such good agreement between what enters and what leaves the system. Zimpro's data are therefore somewhat suspect.

The analytical results from the propellant destruction by wet-air oxidation are questionable. The percent degradation appears to have been obtained by comparing the total organic carbon in the aqueous effluent to the theoretical total organic carbon (TOC) of the propellant slurry since no analyses were presented on the influent slurry. This procedure is highly risky since the TOC and COD analyses of these types of compounds do not always yield theoretical values. If this procedure was used to calculate the destruction of the propellant, the percent destruction should have been 97.0% and 96.9%, for runs 1 and 2, respectively, instead of the values reported. No specific chemical analyses were performed for nitroglycerine, nitrocellulose or any other chemical in the effluent. Yet the author states that the remaining organic carbon "was probably due to small quantities of aldehyde, ketones, organic acids and short chain alcohols as well as unoxidized graphite, rather than nitroglycerine or nitrocellulose." No analytical evidence for the statement is presented in the report and indeed, the TOC analysis should be able to separate graphite from truly organic carbon.

In conclusion, it appears that wet-air oxidation of propellant ingredients can be a viable process. However, due to the low quality analytical data, it is impossible to make claims on process efficiency or the nature of the resulting aqueous effluent.

Schaefer (1980b) reported that Zimpro has also conducted wet-air oxidation studies for the U.S. Navy on TNT, red water, and double base propellants with removal rates between 96-99%. These studies are listed below, however, experimental details were not available.

<u>Report Date</u>	<u>Type of Waste</u>	<u>Percent Oxidation</u>
April 9, 1973	Modified Double Base Propellant	99%
March 16, 1973	Double Base Propellant	95%
March 17, 1972	Otto Rocket Fuel	98.3%
June 28, 1971	Casting Powder	98+%
July 3, 1957	TNT Red Water	96%
April 19, 1956	TNT Red Water	97%

Table 8. Mass Balances for Wet-Air Oxidation of Propellants (Zimpro, 1971)

	Run No. 1				Run No. 2			
	Nitrogen, kg (lb)	Carbon, kg (lb)	Oxygen, kg (lb)		Nitrogen, kg (lb)	Carbon, kg (lb)	Oxygen, kg (lb)	
<b>IN</b>								
Air	1225.8 (2700)	-	325 (718)		819 (1806)	-	248.1 (547)	
Nitrocellulose	32.8 (72.3)	60.8 (134.8)	148.5 (327)		39.5 (87.2)	73.0 (161.8)	178.3 (393)	
Nitroglycerine	34.8 (74.8)	29.2 (64.3)	115.8 (255)		48.7 (107.8)	34.9 (77.0)	139.2 (307)	
Triacetin	-	17.7 (39.0)	15.9 (35)		-	21.3 (47.0)	19.1 (42)	
Graphite	-	4.8 (10.5)	-		-	6.1 (13.5)	-	
<b>TOTAL IN</b>	<b>1292.6 (2847.1)</b>	<b>112.5 (247.8)</b>	<b>606.2 (1335)</b>		<b>899.5 (1983.0)</b>	<b>135.4 (298.5)</b>	<b>584.7 (1289)</b>	
<b>OUT</b>								
Vapors								
- O <sub>2</sub>	-	-	318.5 (684)		-	-	172.4 (380)	
N <sub>2</sub>	1265.1 (2789.1)	-	-		877.2 (1933.8)	-	-	
CO	-	38.9 (85.7)	51.8 (114.2)		-	51.9 (114.5)	69.2 (152.5)	
CO <sub>2</sub>	-	69.9 (154.2)	186.8 (411.5)		-	56.6 (124.8)	151.0 (333.0)	
N <sub>2</sub> O	8.3 (18.2)	-	5.2 (11.4)		9.8 (21.7)	-	5.5 (12.4)	
CH <sub>4</sub>	-	1.2 (2.7)	-		-	1.9 (4.1)	-	
HO <sub>2</sub>	0.1 (0.3)	-	0.32 (0.7)		negligible	-	negligible	
- NO <sub>2</sub> -N	0.02 (0.045)	-	0.82 (1.8)		0.05 (0.1)	-	0.1 (0.3)	
NO <sub>2</sub> -N	17.8 (39.15)	-	61.8 (134.3)		12.0 (26.5)	-	41.2 (90.8)	
Total Organic Carbon	-	3.4 (7.4)	-		-	4.2 (9.3)	-	
Volatile Acids	-	-	0.8 (1.7)		-	-	1.9 (4.1)	
Kjeldahl N	0.1 (0.235)	-	-		0.4 (0.9)	-	-	
Pb(OH) <sub>2</sub>	-	-	1.7 (3.8)		-	-	23.4 (51.6)	
H <sub>2</sub> O Formed	-	-	98.1 (216)		-	-	1.95 (4.3)	
<b>TOTAL OUT</b>	<b>1291.4 (2847.1)</b>	<b>113.4 (250.8)</b>	<b>655.2 (1452.4)</b>		<b>899.5 (1983.0)</b>	<b>114.6 (252.7)</b>	<b>584.7 (1289.0)</b>	

- not present

C. Application of Wet-Air Oxidation to Decontamination of Explosives Contaminated Lagoon Sediments

As envisioned, the treatment of contaminated lagoon sediments with wet-air oxidation will require the following equipment:

- dredge to remove the sediment from the lagoon
- holding tank for the sediment
- mixing tank for dilution of the sediment to 5-10% solids
- two 39 liter/min wet-air oxidation units
- neutralization tank
- final liquid effluent treatment system
- air pollution abatement system

Zimpro (Schaefer, 1980c) has recommended the treatment scheme shown in Figure 2 for decontamination of the lagoons. In this scheme, the sediment and a small amount of the supernatant are dredged and placed in a sediment mix tank. The sediment slurry is pumped into the wet-air oxidation units. The oxidized liquid effluent from the wet-air oxidation units is sent to a supernatant mix tank where it is combined with the lagoon supernatant. The combined liquids are then subjected to Zimpro's biophysical treatment process. This process combines aerobic biological degradation with powdered activated carbon. The biomass and spent carbon are sent to the wet-air oxidation units where the carbon is reactivated and the biomass degraded.

An alternative treatment scheme is shown in Figure 3. This scheme differs from that proposed by Zimpro in several ways. First, the sediment and supernatant of the lagoon are mixed or water from another source is added to produce a 5-10% slurry. In contrast with the scheme proposed by Zimpro, this process flow routes all of the explosives contaminated material through the wet-air oxidation unit. Secondly, there is a wet-air effluent recycle to the mixing tank not present in Zimpro's scheme. Thirdly, a neutralization process has been added in the alternative scheme to neutralize the acidic wet-air oxidation effluent to a pH of approximately 7.5. Finally, this alternative scheme differs from that of Zimpro in that the wet-air oxidation effluent will be subjected to biological degradation in aerobic and anaerobic rotating biological contactors (RBC). For comparison purposes, both treatment schemes will be costed in Section D. The equipment to be used in each treatment scheme is described below.

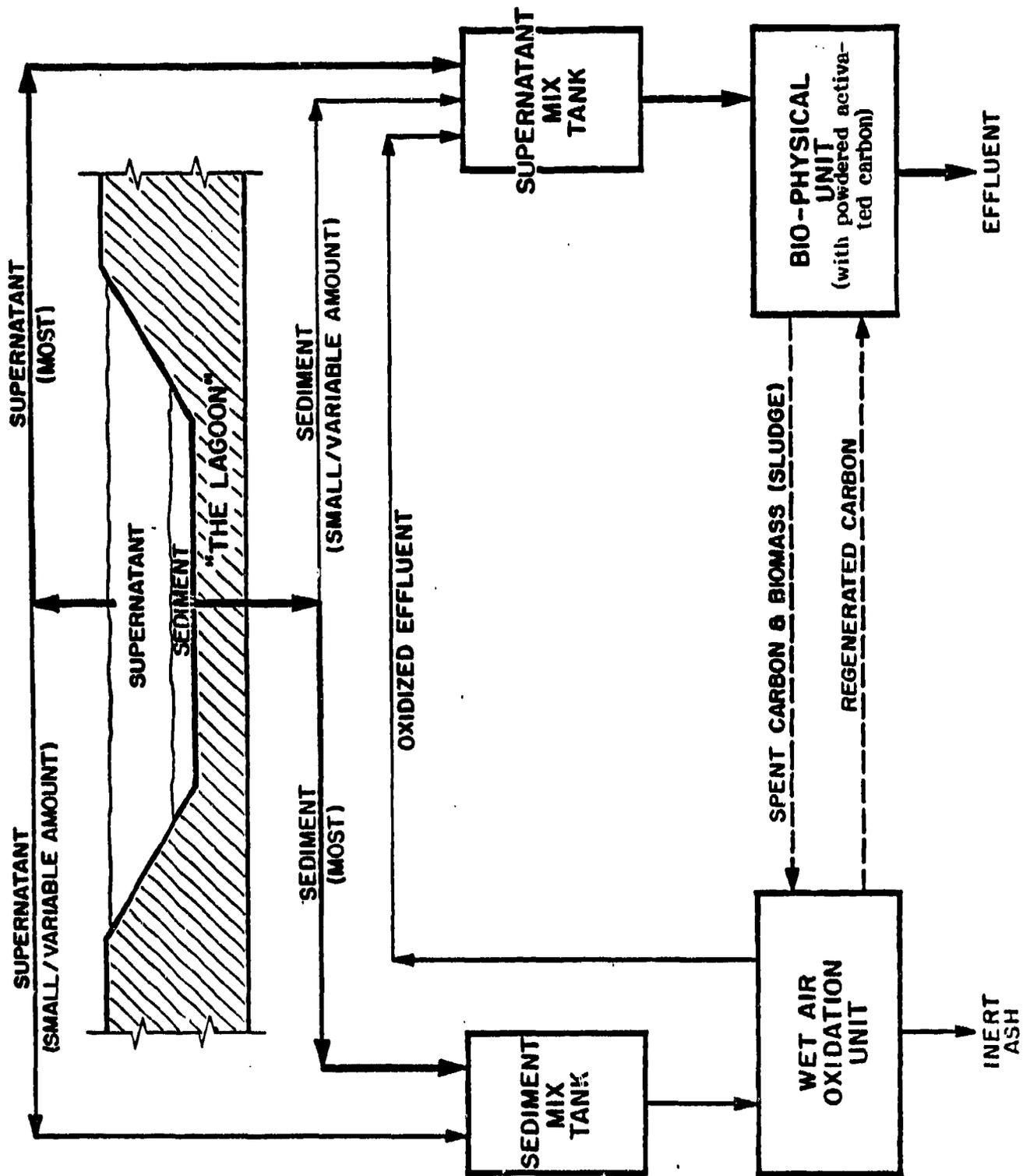


Figure 2. Zimpro's Flow Scheme for Wet-Air Oxidation of Explosives Contaminated Lagoon Sediment (Schaefer, 1980c)

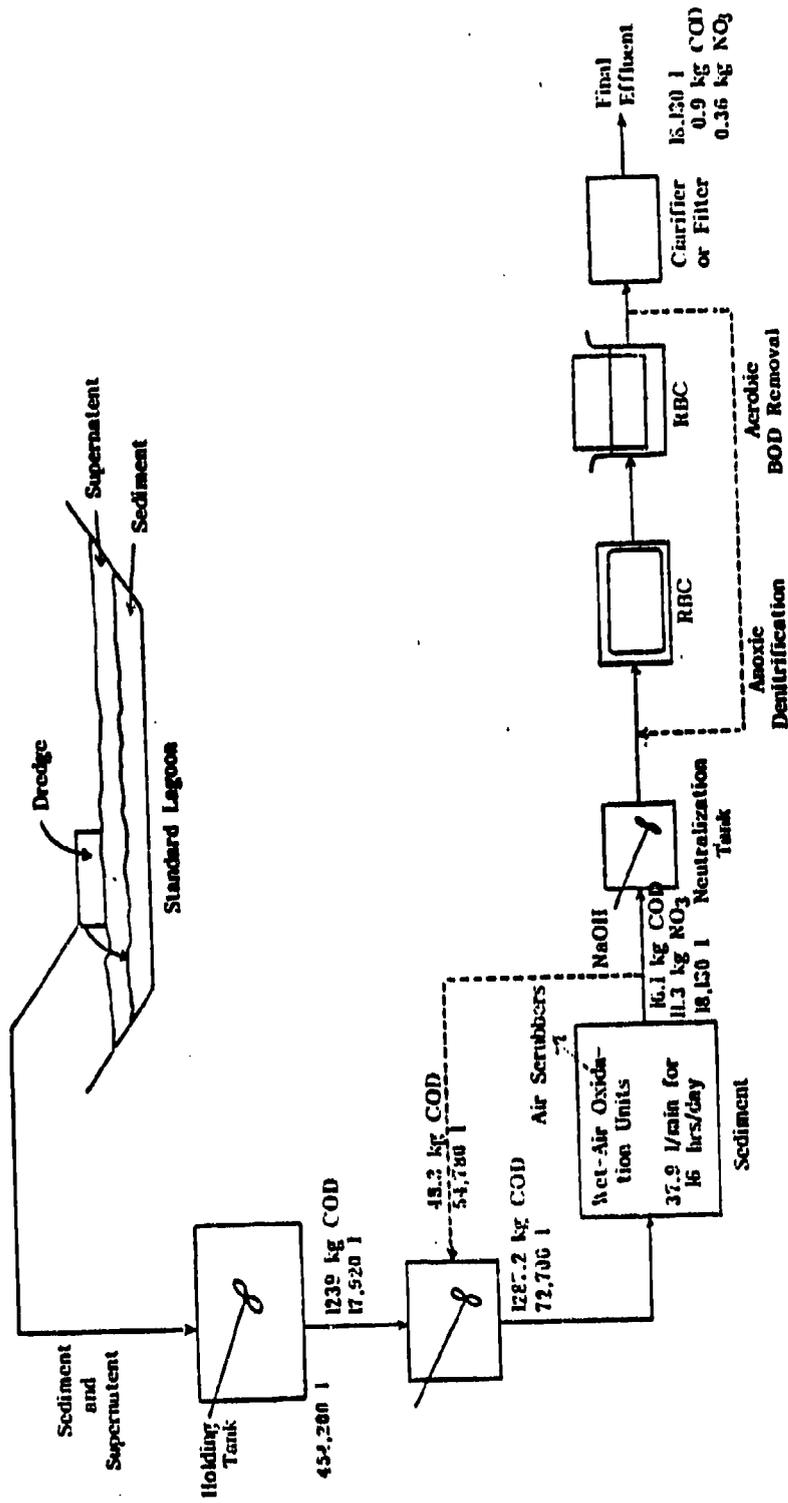


Figure 3. Alternative Wet-Air Oxidation Flow Scheme for Explosives Contaminated Lagoon Sediments

## L. Dredge, Holding and Mixing Tanks

Before treatment by wet-air oxidation and many of the other treatment alternatives, the sediment will have to be dredged from the lagoon. The high level of explosives in some of the lagoon sediments may present a potential hazard during the dredging operation. This problem will have to be addressed in detail when the final selection of the dredge system is made. For the purposes of this report, a small dredge similar to that manufactured by Assemblers, Inc. will be used. This dredge, the PD-4 Porta-Dredge, has the following general characteristics (Salemink, 1980):

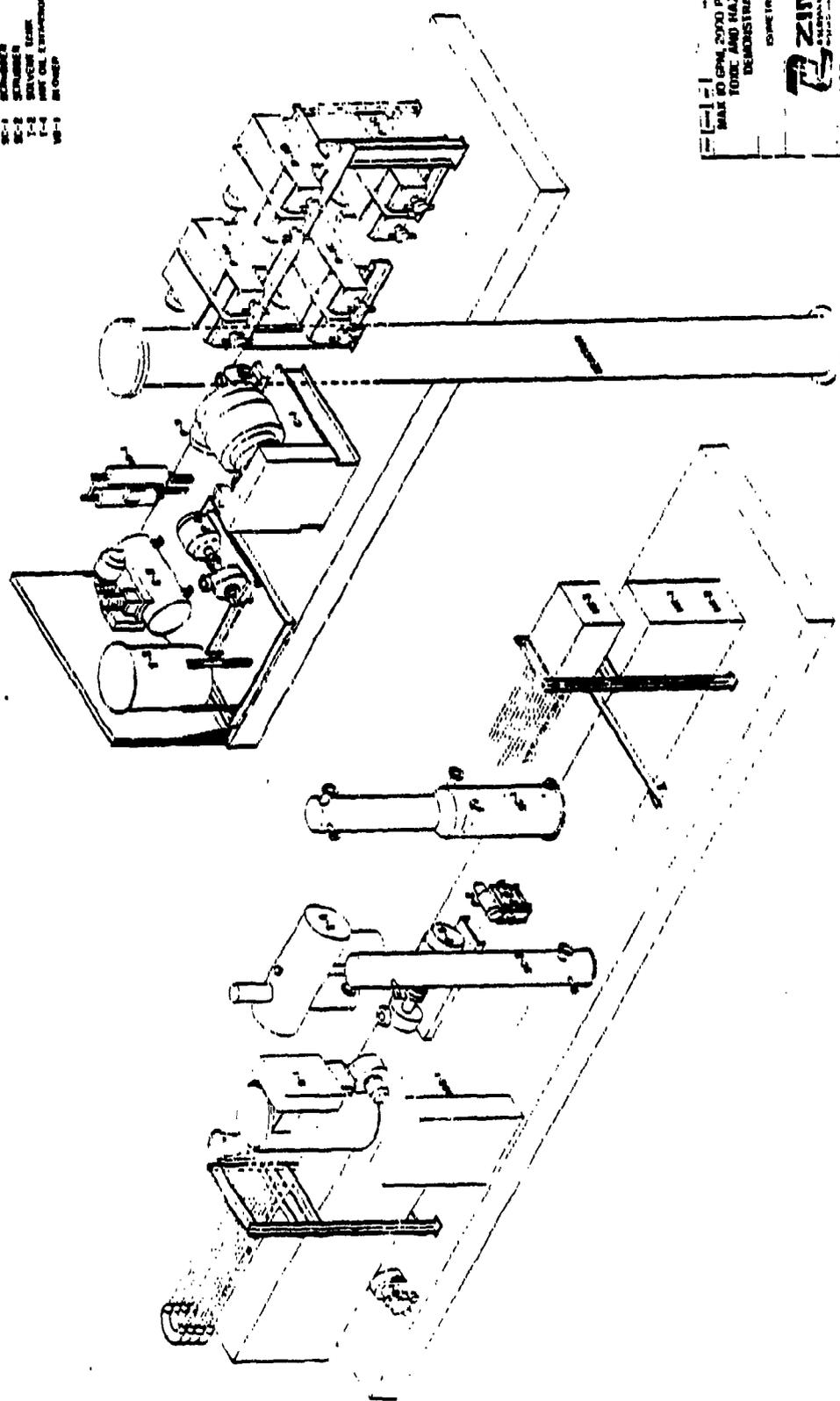
- length 8.5 m (28 ft.)
- width 2.44 m (8 ft.)
- overall height 2.74 (9 ft.)
- weight 5448 kg (12,000 lb)
- pump rate 1136 liter/min at 24.4 m of discharge pressure (300 gpm at 80 ft. of discharge pressure)

The dredge will pump 545,040 liter/8 hr day (144,000 gal/8 hr day). Thus, the dredge will completely remove all the sediment from one lagoon (447,375 liter) in one 8-hour working day. Since smaller dredges are not available, draining a lagoon in one day is the most cost effective use of dredging equipment and personnel. The sediment slurry (50% solids) will be pumped into a 454,200 liter (120,000 gal) holding tank. This tank should be made of carbon steel to withstand the abrasion of the sediment. The sediment will be maintained in suspension by means of a 75 hp side entry turbine mixer. For wet-air oxidation, the solids concentration in the slurry must be in the 5-10% range. Thus, the slurry will have to be diluted with water. This dilution will be accomplished in a 15,140 liter (4000 gal) mixing tank made of tar epoxy coated carbon steel and stirred with a 30 hp side entry turbine mixer. Dilution water will be obtained from the lagoon, if sufficient quantity is available. Since most of the lagoons to be treated are dry, it is anticipated that dilution water will have to be obtained from another source. This source could be surface or well water or recycle of the effluent from the wet-air oxidation unit. Recycle would provide the most economical alternative due to the reduced load on the potentially expensive biotreatment process.

## 2. Wet-Air Oxidation Units

Two 38 liter/min (10 gal/min) wet-air oxidation units will be used. Each wet-air unit is in three separable pieces as shown in Figure 4. Each skid can be transported on a standard low boy trailer. The reactor is 7.62 m (25 ft.) long and weighs 7719 kg (17,000 lb). The other skids contain the ancillary pumps, compressors, heat exchangers, etc. The smaller of the skids is 9.75 m (32 ft.) long, 2.44 m (8 ft.) wide and 2.74 m (9 ft.) high and weighs 10,900 kg (24,000 lb). The larger skid weighs

- EQUIPMENT LIST**
- MB-1 INSTRUMENTS AND TUBES
  - MB-2 CARBON ADSORPTION TANK
  - MB-3 AIR HEATER
  - C-1 PROCESS AIR COMPRESSOR
  - C-2 INSTRUMENTS AND COMPRESSOR
  - MB-4 AIR EXHAUSTER
  - MB-5 AIR EXHAUSTER
  - P-1 AIR PRESSURE PUMP
  - P-2 SPRING LOADED LUBRICATION PUMP
  - P-3 WATER PUMP
  - P-4 SOLVENT PUMP
  - SC-1 EXHAUSTER
  - SC-2 EXHAUSTER
  - T-1 SOLVENT TANK
  - T-2 AIR OIL EXTRACTION TANK
  - MB-3 IN OIL



MAX 60 GPM, 2000 PSI, 41 AIR COMPRESSOR  
 TOXIC AND HAZARDOUS WASTE  
 DEMONSTRATION UNIT  
 ZIMPRO  
 10000 1/2 INCH W x 9

Figure 4. Zimpro's Mobile 38 1/min Wet-Air Oxidation Unit (Schaefer, 1980d)

11,350 kg (25,000 lb) and is 10.7 m (35 ft.) long, 2.44 m (8 ft.) wide and 2.74 m (9 ft.) high. Once at the site, the individual pieces must be bolted to a concrete pad, the piping connected and electrical and cooling water supplies hooked-up. Each wet-air unit requires 215 hp of electricity and 284 liters/min (75 gal/min) of cooling water (Schaefer, 1980d). A shelter, approximately 17.1 m (56 ft.) by 26.8 m (88 ft.), is provided to protect the equipment from the weather. All of the above equipment is included in the capital cost estimate.

Delivery time for two transportable wet-air oxidation units is approximately 18 months from time of order. Installation at the site takes about three weeks. The down time for a move to a new location is three to six weeks depending on travel distance. This time includes installation of a cement pad, set-up and hook-up of utilities (Schaefer, 1980e).

In a 16-hour working day, the two wet-air units will be capable of treating 72,700 liter/day (19,200 gal/day) of a 10% solids slurry. This treatment rate will be adequate to process the sediment from one lagoon in approximately 25 days. Influent to the wet-air units will be 72,700 liter/day containing an estimated 1239 kg (2790 lb) of COD. It is anticipated that temperatures of approximately 204°C and pressures of 5.4 MPa (800 psig) will be needed to degrade the explosives. Degradation of approximately 95% of the COD should be accomplished in these units. However, reactor conditions need to be further optimized during laboratory and pilot tests.

Typical down time of the wet-air oxidation units is 10-15% (Schaefer, 1980e). However, the units will be operated under very adverse conditions. A high sand content in the sediments will cause increased wear on the pumps and heat exchangers. Clay sediments will tend to block pump and heat exchange lines and build up in the reactor. Scale and clay build up in the reactor could mandate periodic cleaning procedures in addition to periodic blowdown.

The wet-air units are equipped with wet scrubbers to remove air emissions. Air emissions are expected to contain at a minimum CO, CO<sub>2</sub>, N<sub>2</sub>, NO<sub>x</sub> and particulates. Other air pollutants could be released depending on their presence or the presence of their precursors in the sediment. Details on these scrubbers are not available, however, if they are properly designed, no additional air pollution control equipment should be necessary.

Significant amounts of solids build-up are expected in the reactors due to the large volume of dirt to be processed. These solids will have to be blown out of the reactor at least once every 8 hours. The solids should be free of organic contaminants and could be disposed of in the lagoon. These solids will be sterile and could provide a haven for wild-type microorganisms. Thus, to regain a representative microbial population, this sterile soil should be mixed with native soils before disposal.

The liquid effluent from the wet-air units will be approximately 72,700 liter (19,200 gal) per day containing approximately 62.0 kg (136.5 lb) COD (886 mg/l) and approximately 45.2 kg (99.5 lb) nitrates (661.7 mg/l). The pH of this effluent should be 1-2. These effluent values were calculated based on 95% reduction of the theoretical COD of the explosives and the steady-state formation of 15% nitrates from the explosives nitrogen. The formation of 15% nitrates was based on the results of wet-air oxidation of nitroglycerine and nitrocellulose (Zimpro, 1971). The percentage nitrate formation highly impacts the biological treatment plant design. Thus, reactor conditions must be optimized to obtain minimum nitrate levels. If 75% of the wet-air oxidation effluent is recycled to the mixing tank, then approximately 18,130 liters/day (4790 gal/day) will have to be further treated. This 18,130 liter/day will contain 16.1 kg/day (35.4 lb/day) of COD and 11.3 kg/day (24.9 lb/day) of nitrate at a pH of approximately 1.

### 3. Final Effluent Treatment

The effluent from the wet-air unit must be neutralized before biological treatment. This neutralization process will be accomplished in a 15,140 liter (400 gal) coal tar epoxy coated carbon steel tank and will require the addition of approximately 72 kg (159 lb) of sodium hydroxide per day. Precipitation of metals may also be required. However, sufficient information on metal concentrations in the lagoons is not available to make a judgement on treatment processes. Therefore, metal precipitation and removal have not been included in the treatment scheme or the cost analysis.

Removal of nitrates and COD from the effluent will be accomplished with biological treatment. These units will operate 24 hours/day. Zimpro has proposed the use of their biophysical process using powdered activated carbon to accomplish this treatment. This system can be employed with either activated sludge or rotating biological contactors (Bauer et al., 1980). Since the data on the effluents are estimates only, the time and costs required for two types of plant design and economic analysis are not warranted. Therefore, the comparison between the RBC and Zimpro's biophysical process with powdered activated carbon will be made on the RBC system. Rotating biological contactors were chosen for the biological treatment processes because of the portability of these units. Alternative treatment schemes would be to lagoon or land spray the neutralized wastes or pump them into an existing biotreatment plant. The lagooning and land spraying alternatives could produce significant environmental pollution depending on the chemicals present and the ability of the chemicals to reach ground or surface waters.

The RBC system must consist of an aerobic COD removal process and an anoxic denitrification for nitrate removal. Treatment could be affected with the aerobic units first or last. Both placement schemes have their advantages and disadvantages which must be weighed on the basis of the particular waste stream to be treated. For a system very high in nitrates, the placement of the anoxic RBC units first with a high recycle from the aerobic units is probably the most satisfactory alternative. Typical loading parameters for the anoxic RBC units and the aerobic RBC units are 1.0 lb.  $\text{NO}_3/1000 \text{ ft}^2/\text{day}$  and 2.0-2.5 lb.  $\text{COD}/1000 \text{ ft}^2/\text{day}$ ,

respectively (Autotrol Corporation, 1979). Based on the calculated wastewater parameters of 99.5 lb nitrate and 136.5 lb COD, the area of the anoxic discs should be 9290 m<sup>2</sup> (100,000 ft<sup>2</sup>) and that of the aerobic disc 5110-6317 m<sup>2</sup> (55,000-68,000 ft<sup>2</sup>). These RBC media area requirements could be met with a variety of RBC products with one each (aerobic and anoxic) 7.6 m (25 ft.) x 3.7 m (12 ft.) commercial scale units (100,000 ft<sup>2</sup>) which require concrete tubs or 5.2 m (17 ft.) x 2.4 m (8 ft.) steel tank portable units (24,000 ft<sup>2</sup>). Four anoxic and three aerobic portable units would be required to obtain the necessary disc area.

Final treatment of the RBC effluent will include clarification in a 15,140 liters (4000 gal) carbon steel tank and possibly filtration depending on the ultimate disposal of the effluent. Effluents containing 20-50 mg/l COD and 10-20 mg/l NO<sub>3</sub> should be attainable with this system.

For the Zimpro biophysical process with RBCs, the potential process difference is in the loading of the RBCs. In the presence of activated carbon, the loading per 92.9 m<sup>2</sup> (1000 ft<sup>2</sup>) of disc area is claimed to increase to approximately .02 kg COD/m<sup>2</sup>/day (4 lb/1000 ft<sup>2</sup>/day) or by approximately 60% (Bauer et al., 1980). If this increase in loading can be achieved in both the anoxic and aerobic RBC units, the disc area necessary would decrease to 3159 to 3995 m<sup>2</sup> (34,000 to 43,000 ft<sup>2</sup>) for the aerobic unit and 5760 m<sup>2</sup> (62,000 ft<sup>2</sup>) for the anoxic unit. This increase in loading would require only three anoxic and two aerobic portable units. Thus, a significant reduction in capital costs could be achieved. Powdered activated carbon utilization is approximately 0.175 g/g COD or 10.8 kg powdered activated carbon/day. A loss of carbon of approximately 10% can be expected per day. Thus, 1.08 kg of powdered activated carbon must be replaced each day or approximately 405 kg per year.

#### D. Economic Analysis for Wet-Air Oxidation of Lagoon Sediment

The capital and yearly operating costs for wet-air oxidation of lagoon sediment are presented in Tables 9 and 10. The capital costs for the wet-air oxidation are \$3,722,580. The additional capital costs for the biological post treatment processes are \$236,300 for the Zimpro biophysical treatment and \$317,300 for the RBC process. Operating costs are \$657,263/yr for the Zimpro wet-air/biophysical process and \$664,131/yr for the Zimpro wet-air/RBC process. Greater than 90% of the operating costs are associated with the wet-air units.

#### E. Advantages and Disadvantages of Wet-Air Oxidation of Explosives in Sediments

For all of the treatment processes considered, including wet-air oxidation, the explosives contaminated sediment is a unique degradation problem. Wet-air oxidation has been shown to be effective on slurries of solid propellants and explosives in solution. Degradation of the propellants and explosives in the 96-99% removal range has been achieved based on COD reductions. Thus, wet-air oxidation has the advantage of "proven technology" for handling high levels of explosives. Processing capability of transportable units is within the standard lagoon in the 25 day range. However, there are also many problems associated with treatment of the explosives containing lagoon sediment by this method. The disadvantages include:

Table 9. Capital Costs for Wet-Air Oxidation for Decontamination of Lagoon Sediment

Quantity	Equipment	Price	Reference
1	Dredge: Porta-Dredge PD-42S-1136 liter/min	\$ 53,200	Sakovich, 1968
1	Holding Tank: 454,200 liter (120,000 gal) carbon steel with 75 hp side entry turbine mixer	132,000	Peters and Timmerhaus, 1968
1	Slurry pump: 1/2 hp	800	Peters and Timmerhaus, 1968
2	Mixing tanks: 15,140 liter (4000 gal) each for epoxy coated carbon steel with 20 hp side entry turbine mixer	43,400	Peters and Timmerhaus, 1968
3	Pumps: 0-12 liter/min for feeding RINC unit	400	Gaigher Co., 1968
2	Wet air oxidation units: transportable, 30 liter/min (10 gal/min) capacity - Zimpro	3,300,000	Schaefer, 1968a
1	Metering pump: 0-75 liter/hr for NaOH	2,400	Milton Roy Co., 1968
1	Pump: 0-40 liter/min for recycle	240	Gaigher Co., 1968
1	Building	100,000	Peters and Timmerhaus, 1968
	TOTAL (Wet-air oxidation)	\$3,772,500	
<b>Biological Post Treatment</b>			
Zimpro biophysical process with RINC			
3	Aerobic RINC: 24,000 ft <sup>2</sup> media area each, steel tank	129,000	Gierhardt, 1968
2	Anaerobic RINC: 24,000 ft <sup>2</sup> media area each, steel tank	16,000	Gierhardt, 1968
1	Clarifier Tank: 15,140 liter (4000 gal) carbon steel	3,300	Peters and Timmerhaus, 1968
1	Sand Filter	25,000	
	TOTAL Zimpro biophysical process	\$ 236,300	
	TOTAL (Wet-air oxidation plus Zimpro biophysical process)	\$3,958,800	
<b>RINC</b>			
4	Aerobic RINC: 24,000 ft <sup>2</sup> media area each, steel tank	172,000	Gierhardt, 1968
3	Anaerobic RINC: 24,000 ft <sup>2</sup> media area each, steel tank	114,000	Gierhardt, 1968
1	Clarifier Tank: 15,140 liter (4000 gal) carbon steel	3,300	Peters and Timmerhaus, 1968
1	Sand Filter	25,000	
	TOTAL (RINC post treatment)	\$317,300	
	TOTAL (Wet air oxidation plus	\$4,039,800	

Table 10. Yearly Costs for Wet-Air Oxidation of Lagoon Sediments

Zimpro Wet-Air/Biophysical Process

Installation Costs (5% of capital)	\$ 197,944
Electricity ( $1.72 \times 10^6$ KWH @ \$0.07/KWH)*	120,400
Labor (3 operators @ \$45,000/man year; 1 supervisor @ \$75,000/man year)	135,000 75,000
Maintenance (3% of total capital)	118,766
Cooling water ( $11.4 \times 10^6$ liter/yr @ \$0.0264/1000 liters)	301
Carbon (405 kg/yr @ \$0.77 kg)†	312
NaOH and other chemicals	<u>9,540</u>
<b>TOTAL YEARLY COSTS</b>	<b>\$ 657,263</b>

Zimpro Wet-Air/RBC Process

Installation Costs (5% of capital)	\$ 201,994
Electricity ( $1.73 \times 10^6$ KWH @ \$0.07/KWH)	121,100
Labor (3 operators @ \$45,000/man year; 1 supervisor @ \$75,000/man year)	135,000 75,000
Maintenance (3% of total capital)	121,196
Cooling water ( $11.4 \times 10^6$ liter @ \$0.0264/1000 liters)	301
NaOH and other chemicals	<u>9,540</u>
<b>TOTAL YEARLY COSTS</b>	<b>\$ 664,131</b>

\* Schaefer, 1980d; Gerhardt, 1980

† Based on 0.175 carbon/g COD (Baur et al., 1980)

- required dilution of the sediment to a 5-10% solids content slurry
- wear and tear on the pumps and heat exchangers from the sediment resulting in high down-time and maintenance costs
- build-up of grit, dirt and ash in the reactors which will require blowdown at least once every 8 hours and possibly shutdown to scrape out the scale
- dependence of optimum reaction conditions on a relatively constant COD input
- incomplete degradation with high levels of nitrate and COD output requiring additional treatment
- if effluent recycle is not used, large amounts of wastewater with high COD and nitrate levels will have to be biotreated or treated by some other method
- high capital costs of the wet-air oxidation units
- long delay time in obtaining the units, and
- bulky transportation of the units (8 standard trailers are required for the wet-air units alone).

The advantages and disadvantages of all the treatment methods investigated are weighed against each other in Section XI.

F. Laboratory and Pilot Scale Demonstrations for Wet-Air Oxidation of Explosives Containing Lagoon Sediment

Laboratory scale studies for feasibility of wet-air oxidation on a waste stream consist of autoclave tests. Cost estimates for an autoclave test for samples of lagoon sediment slurries range between \$6,000 and \$15,000. Analysis of air emissions should be performed for N<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, CO, CO<sub>2</sub> and hydrocarbons. For the analysis of the aqueous influent and effluent, the following tests should be performed: nitrate, nitrite, COD, BOD<sub>5</sub> (biochemical oxygen demand, 5 day), TOC, TSS (total suspended solids), TVS (total volatile solids), TS (total solids), explosives, sulfate, pH, and gas chromatography-mass spectrometry to identify COD components. These test results should allow a material balance to be made. Temperature and pressure conditions and explosives/solids content of the slurry can be improved on the basis of these tests.

A typical pilot-scale test in Zimpro's 19 liter/min pilot reactor costs between \$5000 and \$20,000 although costs of \$100,000 have been incurred with munitions testing (Schaefer, 1980 ). Air and water emission analyses similar to that described for the laboratory tests will require \$10,000-15,000 in analytical support depending on the number of samples taken. Thus, pilot-scale testing could cost between \$15,000 and \$115,000 per test.

### III. INCINERATION

#### A. Introduction

Incineration has long been recognized as one of the most effective methods of destroying hazardous wastes. Complete oxidation of organic compounds at high temperatures releases only carbon dioxide, NO<sub>x</sub>, SO<sub>x</sub> and water to the atmosphere and leaves a small amount of inert ash to be disposed of in some other way. Some of the primary advantages offered by incineration are maximum volume reduction of a given waste, decomposition of organic materials, and the possibility of energy recovery from the waste material (EPA, 1979). In addition, incineration technology is well-developed and widely available for a broad range of applications (Scurlock, et al., 1975).

Some of the more important drawbacks of incineration as a method of hazardous waste disposal are the high costs of equipment, maintenance and fuel for incineration systems, and the requirements of many systems for additional treatment of discharge streams before release into the environment (EPA, 1979). No incinerator achieves complete combustion, and all carry some level of particulate loading in the effluent gas stream. In this discussion, the required air pollution control measures will be included as part of each incinerator system for cost and effectiveness comparisons.

Factors which affect incineration performance include heating value of the waste material, residence time of the waste in contact with high temperature air, mixing of oxygen and waste material, and incineration temperature (Conway and Ross, 1980). In cases where the heating value of the waste is not sufficient to maintain autogenous combustion, it is desirable to conserve fuel by introducing the minimum amount of excess air which will produce adequate combustion. The formation of nitrogen oxides can be minimized by reducing the amount of excess air and by keeping the temperature as low as possible (Conway and Ross, 1980). Additional performance improvements can be achieved by reducing the moisture content of the waste and by assuring that the waste is as finely divided as possible (Conway and Ross, 1980). Since inorganic compounds are not destroyed during incineration, toxic heavy metals should not be burned unless vaporization of the metal components can be controlled (Shen et al., 1979).

Pyrolysis is the thermal degradation of a substance in the absence of oxygen. Pyrolysis products are typically combustible gases. Starved air combustion is a closely related process in which less than the theoretical amount of air is supplied to the incinerator. The terms "pyrolysis" and "starved air combustion" are often used interchangeably. In commercial pyrolysis units, the combustible gases are burned to completion in an afterburner, sometimes with energy recovery, or are compressed and stored for later use as fuel (Conway and Ross, 1980). Most incinerators can be run under starved air conditions, however, an afterburner must be provided to complete combustion.

There are several advantages to pyrolysis which should be considered in designing an incineration system. Mixing excess air with the combustible off gas is much easier than mixing with the original solid, so combustion in the afterburner requires less excess air and is therefore more efficient. In addition, lower gas flow through the primary combustion chamber produces less entrainment of particulates. Finally, since there is no need to heat the large volumes of excess air required for conventional incineration, control of the reactor temperature is easier because the system responds more rapidly to adjustment of process parameters. The net result is a more stable operation. Disadvantages of starved air combustion are that the process requires more instrumentation than conventional incineration, the exhaust gases from the primary combustion chamber may be highly corrosive, and there may be significant amounts of combustible material and fixed carbon remaining in the ash (Sittig, 1979).

## B. Process Descriptions

Several types of incinerator designs are available. A description of each incinerator type, its operational parameters and its advantages and disadvantages are presented in the following sections. The manufacturers of the various incinerator designs and the size ranges available are summarized in Table 11.

### 1. Air Curtain Incinerator

The air curtain incinerator or pit incinerator was developed by DuPont to burn nitrocellulose and packing material (Carpenter *et al.*, 1978). The incinerator consists of a 1 to 3 m deep pit blanketed by a curtain of air blown through nozzles on one side of the pit against the opposite wall (Conway and Ross, 1980). The air curtain provides primary and excess air to the flame, produces turbulent mixing patterns to maintain good contact between waste and oxygen, and helps to contain particulates. While this method is an improvement over open air burning, it suffers some serious drawbacks. There is little possibility of confining effluent gas for further treatment, and while particulate emissions are less than for open burning, they are somewhat greater than for more conventional incinerators (Sittig, 1979). The pit incinerator was designed for solids with high heating values or materials which tend to detonate and cause damage to enclosed incinerators (Sittig, 1979). It provides high burning rates, long residence times, and high flame temperatures, and is particularly well-suited for materials of less than 1-2% ash. The most attractive features of the air curtain incinerator are its simplicity of design and its low cost compared with other incineration systems. Air curtain incinerators have successfully been used for disposal of heavy timbers, cable reels, construction wastes, plastics (Sittig, 1979), and explosives contaminated packaging (Carpenter *et al.*, 1978).

### 2. Cyclone Furnace

The cyclone furnace or rotary hearth furnace, shown in Figure 5, is a refractory-lined steel cylinder with a single rotating hearth. Wastes are introduced at the outer edge of the hearth and are gradually moved inward by a fixed plow toward an ash discharge chute at the center of the hearth. Combustion air is injected above the hearth at high tangential velocity in the opposite direction to

Table 11. Manufacturers of Incineration Equipment

1. Cyclone/Rotary Hearth Furnace

Nichols Engineering and Research Corporation  
Neptune International Corporation  
Homestead and Willow Roads  
Belle Mead, NJ 08502

Rotary Hearth Furnace

Roto-Hearth Corporation  
10 Walnut Place  
Thornwood, NY 10594

Annular Rotary Hearth Thermal Processor  
Sizes: 4.6 - 2.30 m<sup>3</sup>  
Loading: 2.4 - 73 kg/m<sup>2</sup>/hr

2. Multiple Hearth Furnace

Bethlehem Corporation  
33 Rector Street  
New York, NY 10006

Multiple Hearth Furnace  
Sizes: 15.8 - 548 m<sup>2</sup>

Elmco BSP Division  
Envirotech Corporation  
1 Davis Drive  
Belmont, CA 90220

BSP Multiple Hearth Furnace

Nichols Engineering and Research Corporation  
Neptune International Corporation  
Homestead and Willow Roads  
Bell Mead, NJ 08502

Multiple Hearth Furnace  
Sizes: up to 46 m<sup>2</sup>

3. Electric Furnace

Shirco, Incorporated  
2451 Stemmons Freeway  
Dallas, TX 75207

Shirco Infrared Furnace  
Capacities: 14 - 181,600 kg/day

Table 11. (cont.)

4. Fluid Bed Incinerator

BSP  
1 Davis Drive  
Belmont, CA 94002

BSP Fluidized Bed Energy Systems  
Capacities: 15,400 - 310,500 kg/day

Dorr-Oliver, Incorporated  
77 Havemayer Lane  
Stamford, CT 06904

FluoSolids Reactor  
Sizes: 1.5 - 7.6 m

Nichols Engineering and Research Corporation  
Neptune International Corporation  
Homestead and Willow Roads  
Belle Mead, NJ 08502

Fluid Bed Reactor

5. Rotary Kiln

C-E Raymond  
Combustion Engineering Inc.  
200 West Monroe Street  
Chicago, IL 60606

Bartlett-Snow Tumble Burner  
Capacities: 13.6 - 1421 kg/hr  
Cylinder Lengths: 1.2 - 3.0 m

Bartlett-Snow Rotary Kiln  
Cylinder Lengths: 4.6 - 33.5 m  
Inside Diameters: 2.8 - 4.0 m

C&H Combustion  
1985 West Big Beaver Road  
Troy, MI 48084

Rotary Kiln

Met-Pro Corporation  
Systems Division  
160 Cassell Road  
Box 144  
Harleysville, PA 19438

Reac-O-Therm  
Capacities: 190 - 1135 l/hr

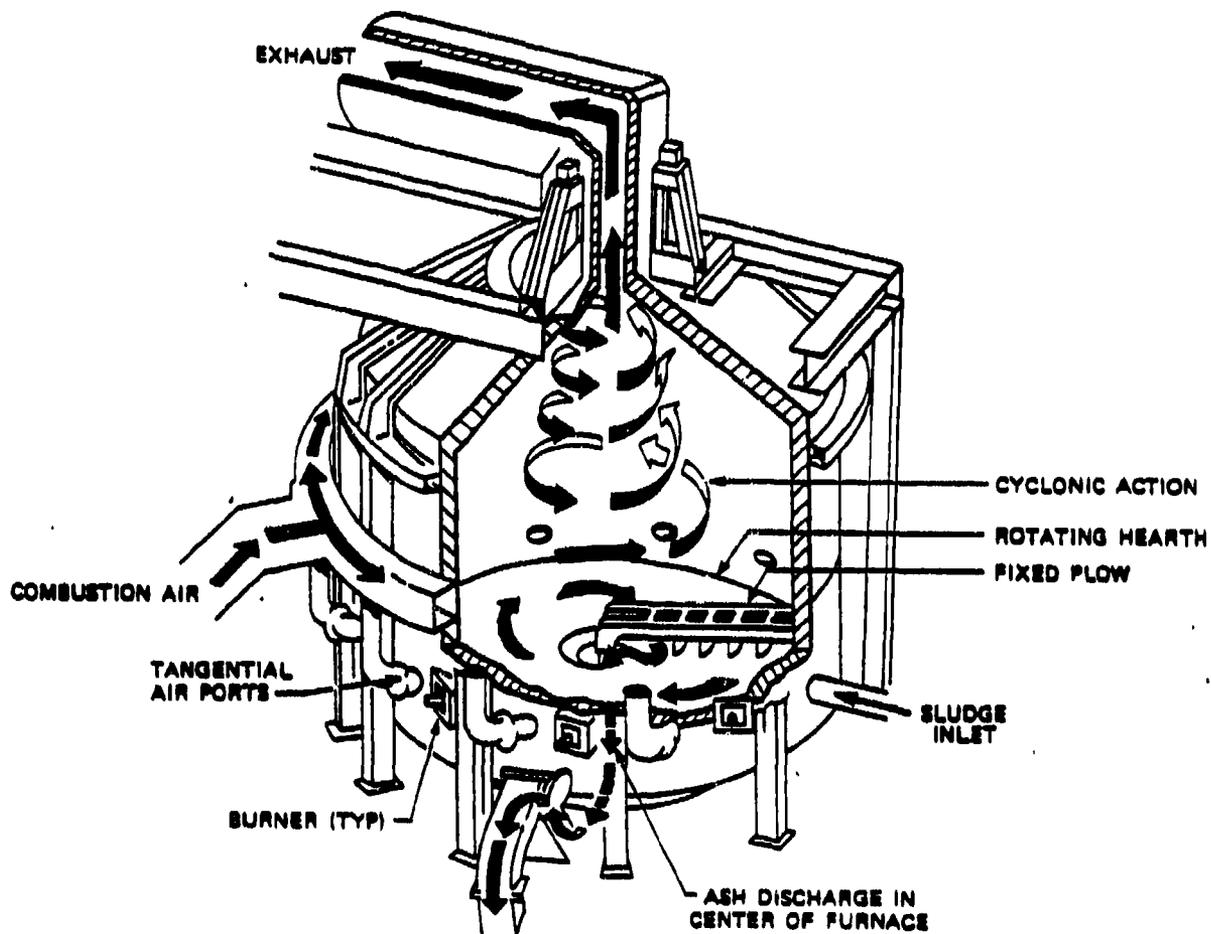


Figure 5. Cross Sectional View of a Cyclonic Furnace (EPA, 1979)

hearth rotation. The air sweeps over the burning waste, then spirals upward toward the exhaust. The cyclone is operated at high temperatures with exit gases leaving the system at around 820°C (1500°F) (EPA, 1979). Combustion products must pass through this high temperature central vortex before leaving the furnace, and this passage essentially completes combustion of all organics without any need for an afterburner (Stribling, 1972).

Cyclone furnaces typically require 30-80% excess air (EPA, 1979), although some units have been operated with as little as 10-20% excess air using computer control (Stribling, 1972). Units are currently available with diameters up to 9 m, but larger units are possible (EPA, 1979). Cyclone furnaces have been used to incinerate sewage sludge, oil and chemical sludges, aqueous organic suspensions, solvents and chlorinated hydrocarbons (Stribling, 1972).

Some of the advantages of cyclone incineration stem from the fact that combustion air passes over rather than through the waste material - the furnace temperature is less susceptible to upsets caused by uneven bed conditions and there is less particulate entrainment (Stribling, 1972). Additional advantages result from the cyclonic air motion - oxygen remains longer in contact with the burning material; the cyclone acts as a dust collector to prevent carry over of fine grit; the spiral action "spins out" cold, oxygen-rich air to the furnace walls, protecting them from high temperatures (Stribling, 1972).

### 3. Multiple Hearth Furnace

A schematic drawing of a multiple hearth incinerator is presented in Figure 6. The furnace is a refractory-lined steel cylinder containing a number of horizontal refractory hearths stacked vertically. Internally air cooled rabble arms pivot about the center, raking burning material spirally towards the center or towards the edge on alternating hearths. Waste material enters the top of the furnace, dropping from hearth to hearth through the drying zone (310 to 540°C), the combustion zone (760°C to 980°C), and the ash cooling zone (200°C to 315°C) (EPA, 1979). Combustion air is introduced at the bottom of the incinerator, and may be preheated by first circulating as cooling air through the rabble arms.

The multiple hearth furnace is the most widely used sludge incinerator in the United States (EPA, 1979). It was originally designed to incinerate sewage sludge in 1934, but has also been used to process a variety of metal ores (Conway and Ross, 1980). Multiple hearth furnaces range in diameter from 1.4 m to 7.6 m with 3-17 hearths (Nichols Engineering and Research Corporation, 1972). Capacities vary from 90 kg/hr to 3630 kg/hr (Schroeder, 1977) with retention times up to several hours for some wastes. Excess air requirements are normally in the 75-100% range. Typical multiple hearth furnace design parameters reported by Niessen are given in Table 12.

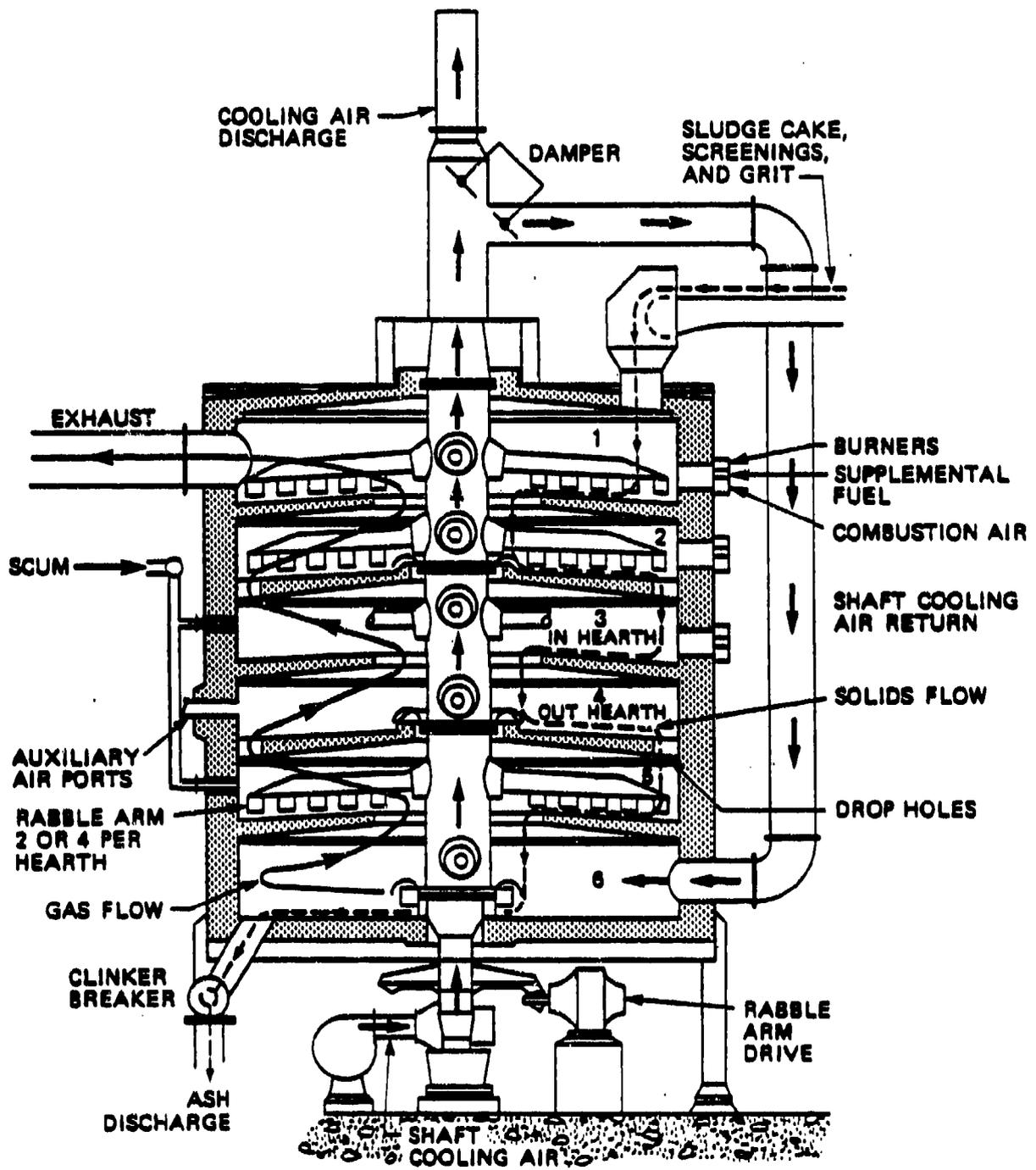


Figure 6. Cross Sectional View of a Multiple Hearth Furnace (EPA, 1979)

Table 12. Typical Design Parameters for Multiple-Hearth Incinerators  
(Niessen, 1978)

<u>Parameter</u>	<u>Units</u>	<u>Low</u>	<u>Mean</u>	<u>High</u>
Hearth area burning rate	kg dry solids hr <sup>-1</sup> m <sup>-2</sup>	7.2	9.8	16.2
Excess air	percent overall	20	50	80
Cooling air exit temperature	°C	95	150	195
Discharge ash temperature	°C	38	160	400
Off-gas temperature	°C	360	445	740
<b>Sludge properties</b>				
heat content	Kcal/kg volatiles	5300	5550	7760
volatile content	% of dry solids	43.4	54.2	71.8
Total energy input (fuel plus sludge)	Kcal/kg wet sludges	810	-	-
	(for 25% solids sludges)	1595	1100	1355
	(for 48% solids sludges)		1730	1922
Volumetric heat release (fuel plus sludge)	Kcal hr <sup>-1</sup> m <sup>-3</sup>		67,600	

In addition to its long history of successful sludge incineration, the multiple hearth furnace has other advantages over other incineration systems. The furnace can accommodate wide fluctuations in loading rates and feed quality (EPA, 1979; Schroeder, 1977). Sludge is constantly turned and broken by the rabble arms, providing good contact between air and the waste material. Burners on all or selected hearths permit incineration of low heating value materials which could not otherwise be burned.

Multiple hearth incineration also suffers from some disadvantages. Since low heating value wastes are often burned, large amounts of auxiliary fuel are required (Conway and Ross, 1980). The furnace system has high maintenance requirements due to mechanical motion in a high temperature region (Conway and Ross, 1980). There is a high incidence of rabble arm failure and refractory failure resulting from too rapid heating or cooling (Niessen, 1978). The unit must be run continuously, since start-up and shut-down each require 24 to 30 hours to prevent damage to incinerator internals (Niessen, 1978). Slagging and clinkering caused by local high temperatures can interfere with rabble arms and block drop holes. This problem is particularly likely when a high level of inorganic salts is present in the waste material (Niessen, 1978). Finally, warm air and unburned solids come into contact at the top of the furnace just before the air exits. This feature can drive off volatile organics from the waste, requiring the use of an afterburner to ensure that organics are completely destroyed before release to the atmosphere.

#### 4. Electric Furnace

A relatively new type of sludge incinerator, the electric furnace, was introduced in 1975 (EPA, 1979). The electric or infrared furnace consists of a horizontal metal mesh conveyor belt which passes under a series of electrical heating elements as seen in Figure 7. The shell is steel lined with ceramic fiber insulation. Sludge feed and combustion air enter the furnace at opposite ends. As in the multiple hearth furnace, this contact of warm air with cold sludge will probably require the use of an afterburner for the gas to reduce organic emissions (EPA, 1979). Furnace sizes range from 1.2 m x 6.1 m to 2.9 m x 29.3 m with capacities up to 540 kg/hr. The electric furnace requires 20-70% excess air for sludge combustion, but does not require any primary air for burner operation (EPA, 1979). While this feature results in an overall reduction in energy requirements, any savings is probably offset by the higher cost of electricity relative to natural gas or fuel oil (EPA, 1979). Ceramic fiber insulation can be heated and cooled very rapidly without adverse effects, making this furnace ideally suited to intermittent operation; this will however, result in increased energy expenditure (EPA, 1979).

The electric furnace is relatively inexpensive compared to other incinerators, however, certain major components have a very short lifetime which should be taken into account at the time of incinerator selection. The infrared heaters can be expected to last for three years while woven wire belts usually last for three to five years (EPA, 1979).

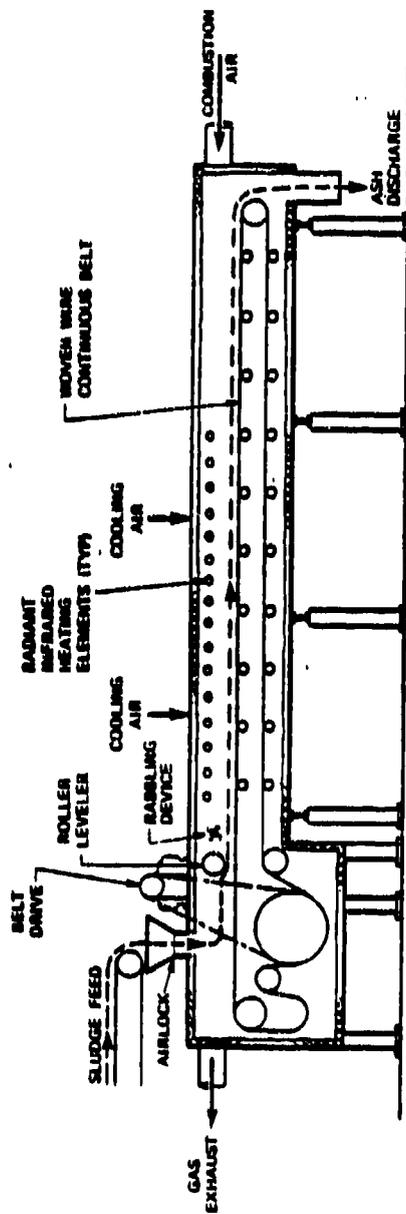


Figure 7. Cross Sectional View of an Electric Furnace (EPA, 1979)

## 5. Fluid Bed Incinerator

The fluid bed was originally designed to contact finely divided catalysts with high molecular weight petroleum feedstocks in a cracking process (Niessen, 1978). It was first used for incineration in 1962 (EPA, 1979). A fluid bed incinerator is a vertical refractory-lined cylinder with a bed of sand or some other particulate suspended by air flowing up through the bottom of the incinerator, as shown in Figure 8. Burners above the fluidized bed and at the air inlet provide heat to raise the bed temperature and to provide combustion heat to low heating value wastes (EPA, 1979). Sludge is fed either into the fluidized sand or into the freeboard space above the sand bed (EPA, 1979). Bed temperature is maintained at 750° to 850°C (Dawson et al., 1978) with excess air requirements in the range of 20-30% (Ferrel, 1973). Bed diameters up to 15 m are possible (Scurlock et al., 1975), but size is limited by the self-supporting reactor roof (Cheremisinoff et al., 1976). When fluidized, bed depths range from 40 cm to several meters (Scurlock et al., 1975). Since bed depth is controlled by air flow rates as well as by the amount of sand, variations will affect system pressure drop and particle residence time (Sittig, 1979). Air velocities must be high enough to fluidize the bed material but not so high as to carry it out of the incinerator, usually 1.5-2.1 m/sec (EPA, 1979). Increasing air velocity causes higher bed attrition and higher particulate loading of exit gases as well as higher power requirements for the compressor (EPA, 1979). Waste solids are retained in the bed until combustion reduces them to the point where the fluidizing air carries them out of the bed (EPA, 1979). This method of ash removal requires a particulate scrubber for the flue gas, however, an afterburner is not usually needed for a fluidized bed because of the high uniform bed temperatures (EPA, 1979).

Major advantages of the fluid bed incinerator include the excellent mixing properties in the fluid bed which reduce excess air requirements and the lack of moving parts in the high temperature region which greatly reduces maintenance requirements (Ferrel, 1973). The lower air requirements and lack of localized very high temperature areas reduces nitrogen oxide formation (Conway and Ross, 1980). When the unit is shut down, the sand bed acts as a heat sink, maintaining a nearly constant temperature overnight (EPA, 1979). This greatly reduces startup fuel requirements and makes the fluid bed incinerator very attractive for intermittent use (EPA, 1979). The fluid bed incinerator is highly versatile and can be used for liquid, solid, or gaseous combustible wastes (Sittig, 1979). In the past, it has been successfully applied to the incineration of petroleum wastes, paper, nuclear wastes and sanitary sludges (EPA, 1979).

Some of the problems associated with fluid bed incineration are the result of sand and ash carry over in the exit gas stream. A particulate scrubber is always required to remove ash and sand from the effluent gas, and serious erosion problems in the scrubber have resulted from sand impingement (EPA, 1979). In addition, screw and pump feeds have had difficulty with sludge drying out and plugging the point of injection to the bed (EPA, 1979). Ash removal can pose problems for those materials which do not break down into particles which can be carried out of the bed by the fluidizing gases (Scurlock et al., 1975; Dawson et al., 1978). Materials which melt or slag can upset fluidization by binding sand particles and by forming large heavy masses which can not be supported by the air flow (Niessen, 1978).

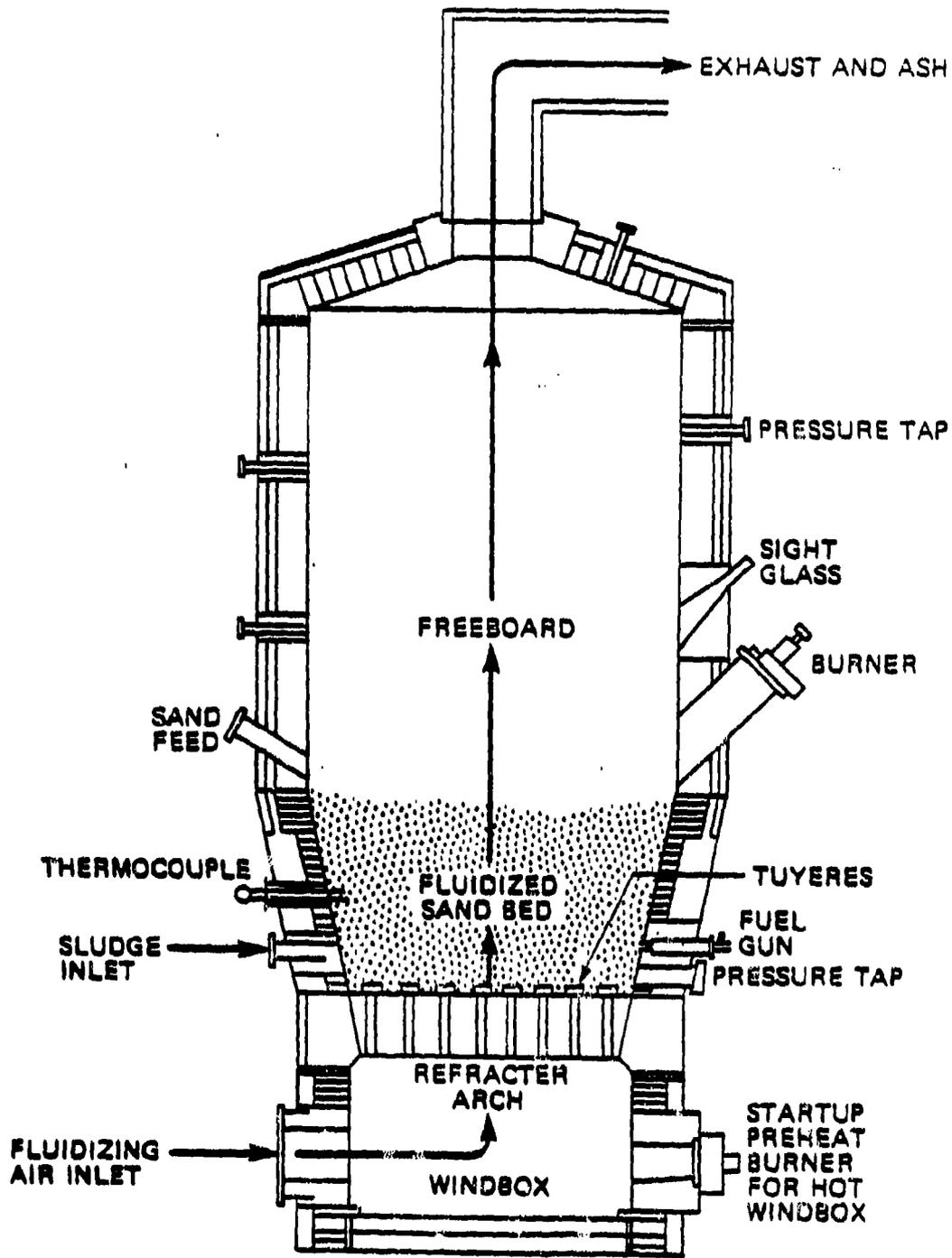


Figure 8. Cross Sectional View of a Fluid Bed Furnace (EPA, 1979)

## 6. Rotary Kiln

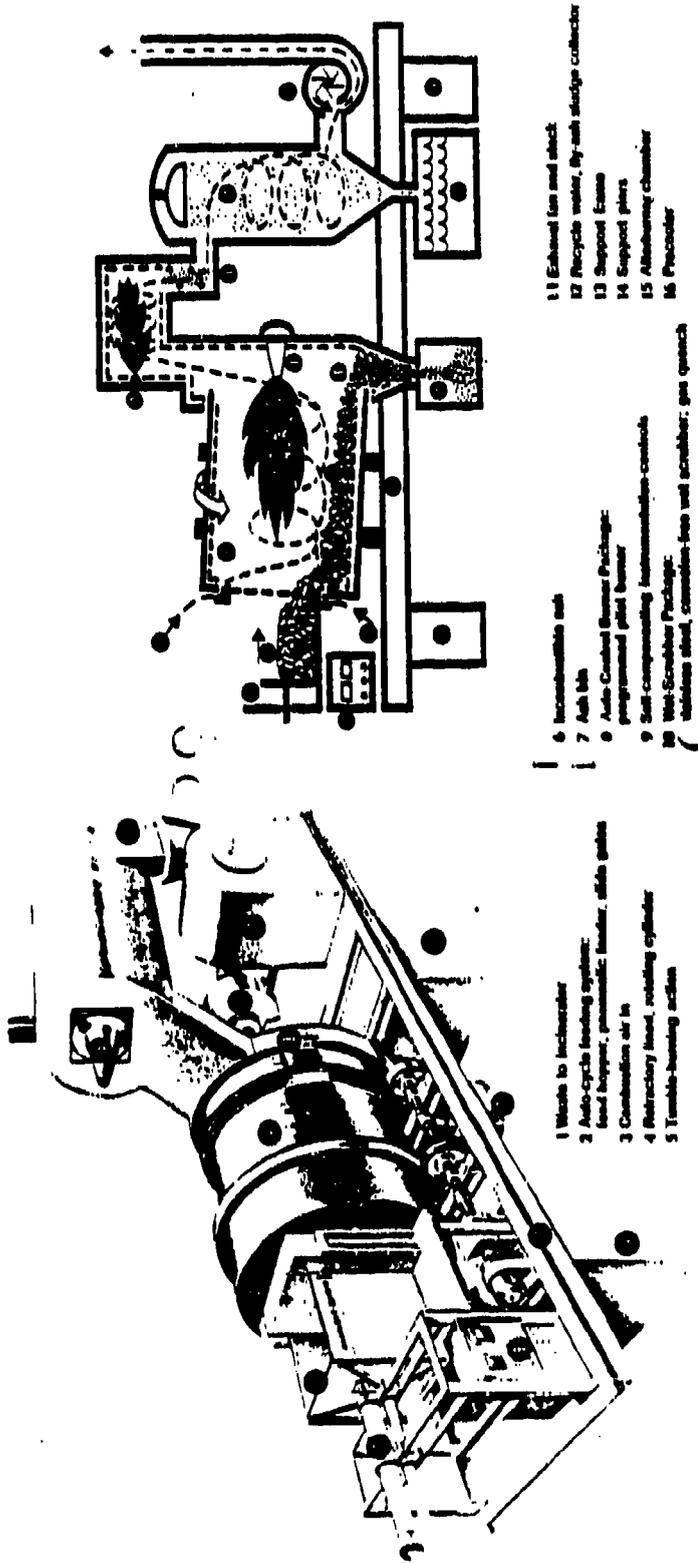
A rotary kiln, shown in Figure 9, is a horizontal refractory-lined cylinder which rotates on a pair of steel tires. The kiln is sloped downward from inlet to exit, with combustion air inlet and the burner usually located at the lower end (Conway and Ross, 1980). The rotational speed and angle of incline determine the residence time of waste material in the kiln (Conway and Ross, 1980) which varies from several seconds to several hours (Scurlock et al., 1975). Combustion temperatures can range from 810-1650°C (Dawson et al., 1978). Excess air requirements are usually around 40% (Hathaway, 1977).

Rotary kilns are versatile enough to handle solid, liquid and gaseous waste (Dawson et al., 1978). Designed for high throughput on a continuous basis (Ferrel, 1973), the rotary kiln provides a brute force method which can be used to incinerate almost any waste (Conway and Ross, 1980). The rotary kiln has low maintenance requirements because of its simplicity of design and rugged internal structures (Conway and Ross, 1980). Since it has no moving parts, the rotating hearth is not likely to be damaged by high temperatures.

Particulate loading of the exit gas is generally high, so some form of scrubber is usually required (Conway and Ross, 1980). An afterburner is often included to complete combustion and reduce emissions (Conway and Ross, 1980).

### C. Air Pollution Control Equipment

In view of recent and anticipated air pollution regulations, few incineration systems can be operated without additional pollution abatement measures. First, many incinerators cannot achieve complete combustion, emitting unburned or partially burned organics in the vapor effluent. When incomplete combustion occurs, a secondary combustion chamber is needed to reheat the gases and provide additional oxygen to assure complete combustion. Thus, additional auxiliary fuel and additional capital investment to purchase a secondary burner and combustion chamber are required. In addition, the effluent gases from many combustion processes carry a high level of particulates which must be removed before release to the atmosphere. Such materials can be removed by cyclone separators, fabric filters or baghouses, electrostatic precipitators, and by wet scrubbers. Cyclone separators are relatively inexpensive to purchase and operate. They remove 95% of all particles greater than 25 $\mu$ , but are not very efficient for smaller particles (Chalmers, 1981). Baghouses are more effective but have high pressure drops and therefore require fairly high power consumption to move the gases through (Hathaway, 1977). Electrostatic precipitators are also very effective, but have comparable power requirements (Hathaway, 1977). Wet scrubbers are reasonably effective at removing particulates and water soluble pollutants, however, they produce contaminated water which must be treated before release (Hathaway, 1977). Each method has its merits and its drawbacks and the appropriate method for a particular situation should receive careful consideration. The previously discussed incineration methods and the pollution control measures recommended for each are listed in Table 13.



- 1 Waste to Incinerator
- 2 Auto-cycle feeding system: load hopper, pneumatic transfer, slide gates
- 3 Combustion air in
- 4 Refractory lined, rotating cylinder
- 5 Turbine-driving acton

- 6 Incineration ash
- 7 Ash bin
- 8 Auto-Cycled Burner Package: programmed pilot burner
- 9 Self-compressing instantaneous-control
- 10 Wet-Scrubber Package: tubular shell, corrosion-free wet scrubber; gas quench
- 11 Exhaust fan and stack
- 12 Recycle water, fly-ash sludge collector
- 13 Support frame
- 14 Support plate
- 15 Allowing chamber
- 16 Precipitator

Figure 9. Cross Sectional View of a Rotary Kiln Furnace (C.E. Raymond, 1979)

**Table 13. Recommended Pollution Control Measures  
for Various Incinerator Types**

<b>Air Curtain Incinerator</b>	<b>No additional measures possible</b>
<b>Cyclone/Rotary Hearth Furnace</b>	<b>Particulate Scrubber</b>
<b>Multiple Hearth Furnace</b>	<b>Afterburner and particulate scrubber</b>
<b>Electric Furnace</b>	<b>Afterburner and particulate scrubber</b>
<b>Fluid Bed Incinerator</b>	<b>Particulate scrubber</b>
<b>Rotary Kiln</b>	<b>Afterburner and particulate scrubber</b>

D. Application to Treatment of Explosives Contaminated Lagoon Sediment

The most important considerations in handling explosives contaminated materials are personnel and equipment safety. The possibility of detonation must be anticipated and either be prevented or be contained. Studies done by Rolison and Dickenson at Radford AAP indicated that slurries which are 3 parts water to 1 part explosive waste by weight can be ground, pumped, and incinerated without difficulty (Rolison and Dickenson, 1975). Impact sensitivity for dry TNT fines is  $6.43 \times 10^4$  J/m<sup>2</sup> and for damp fines more than  $1.5 \times 10^5$  J/m<sup>2</sup>. Friction sensitivity is approximately  $1.63 \times 10^5$  N/m<sup>2</sup> @ 2.4 m/sec for both dry and damp fines (Rolison and Dickenson, 1975).

In view of the sensitivity of sediment which contains 15% explosives on a dry basis, it is judged wise to avoid incinerator systems which have moving mechanical parts in the incineration region. Rabble arms and fixed plows in the multiple hearth and cyclone furnaces could suffer continual damage from minor detonations. Fluid bed incinerators may run into difficulties because of the extremely high ash content of the sediment. Ash may not be carried out of the bed by the effluent stream, so some other provisions would have to be made. No particular problems are expected for the electric furnace, and a large body of data documents the success of the rotary kiln in incinerating explosives and explosives contaminated wastes. The open pit incinerator is an unacceptable alternative because of high pollutant emission levels. While pyrolysis may be an acceptable alternative to conventional incineration, experiments would be required to determine whether complete destruction of the explosives of interest can be accomplished by this technique.

Table 14 lists bench and pilot scale data for incineration of hazardous chemical wastes and explosives. When supplied with appropriate afterburner and/or scrubber systems, most of the furnaces discussed are shown to effect complete destruction of the hazardous materials with reasonable emission levels. Acceptable destruction of TNT and RDX was observed in the Radford rotary kiln with a main chamber temperature of 870°C and an afterburner temperature of 927°C (Rolison and Dickerson, 1975). Data for the rotary hearth and electric furnace incinerators were not available for this type of material.

For the standard lagoon described earlier, the following equipment will be needed to decontaminate lagoon sediment by incineration:

- dredge
- holding tank
- incineration unit
- air pollution abatement system

To keep the heating value of the sediment as high as possible, contaminated sediment is not diluted, but is fed as is from the holding tank to the incineration system. Contaminated sediment, as described in the standard lagoon scenario, is incinerated at a rate of 900 kg/hr.

Table 14. Incineration of Hazardous Wastes

Hazardous Chemical Incineration	Material	Equipment	Performance	Reference
2,4,5-T, DDT, sewage sludge	multiple hearth furnace	99.9% destruction	Dawson et al., 1978	
2,5% DDT in sewage sludge	multiple hearth furnace	99.9% destruction	Scurlock et al., 1975	
PCBs in sewage sludge	multiple hearth furnace	>99.9% destruction	Scurlock et al., 1975	
herbicide orange	fluid bed incinerator	>99.99% destruction	Ackerman et al., 1978	
phenol	fluid bed incinerator	>99.999% destruction	Ackerman et al., 1978	
methyl methacrylate	fluid bed incinerator	>99.996% destruction	Ackerman et al., 1978	
PVC	rotary kiln	>99.999% destruction	Ackerman et al., 1978	
PCBs in capacitors	rotary kiln			

RAAP Rotary Kiln	pH	Water Analysis (Itolisa and Itorson, 1975)			Suspended Solids
		Sulfates	Nitrates	Chlorides	
TNT	5.9	88 ppm	19 ppm	19.0 ppm	194 ppm
TNT	6.5	60	23	8.7	232
TNT	6.6	85	46	8.0	207
A-5	6.0	71	13	0	152
A-5	6.0	76	14	0	161
A-5	6.1	87	16	0	185
A-5	6.1	86	16	0	187
A-5	6.2	70	11	0	180
A-5	6.0	86	19	0	187
A-5	5.3	100	18	0	197
A-5	6.5	84	19	0	190
A-5	6.3	93	22	0	210
B	6.0	88	23	0	0
B	5.7	90	23	0	0
B	6.1	74	12	11.3	219
B	5.8	92	12	8.9	166

Composition A-5 - 98.5% RDX, 1.5% wax  
 Composition B - 60% RDX, 39% TNT, 1% wax

Table 14. (cont.)

Small Scale Open Burn - RAAP Prototype Rotary Kilo  
(w/afterburner, wet scrubber) (Robison and Dickerson, 1975)

Material	N <sub>2</sub>	O <sub>2</sub>	CO	CO <sub>2</sub>	Hydrocarbons	H <sub>2</sub> S	NO	NO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	CO	Soot	Particulates (corrected 12%, CO <sub>2</sub> )
TNT	-	-	-	3.2	49 ppm	39 ppm	148 ppm	5 ppm	-	0 ppm	-	-	-
TNT	80.19	12.44	-	5.92	0	17	196	33	-	0	-	-	-
TNT	78.96	12.17	-	7.14	0	75	189	83	-	73	-	-	-
A-5	78.29	11.63	-	7.58	0	33	383	4	-	51	-	-	-
A-5	78.01	11.15	-	7.58	0	62	151	1	-	19	-	-	-
A-5	77.30	12.05	-	7.18	0	79	81	0	-	22	-	-	-
A-5	81.44	13.12	-	7.14	0	5	160	32	-	0	-	-	-
B	-	-	-	6.28	30	13	145	14	-	0	-	-	-
B	-	-	-	7.60	0	15	120	0 ppm	-	0	-	-	-

Fluid Bed Incinerator  
(w/cyclone scrubber) (Carroll, 1979)

5% B Slurry (w/water)	80.47	15.31	NA	4.83	-	-	-	-	173 ppm	-	-	-	1.945 R/SCAI
15% B Slurry	79.84	14.78	NA	5.28	-	-	-	-	360	-	-	-	0.1522
15% B Slurry	83.59	14.75	NA	3.17	-	-	-	-	187	-	-	-	3.5245
25% B Slurry	79.34	15.38	NA	5.28	-	-	-	-	388	-	-	-	0.1183
5% TNT Slurry	80.73	15.99	NA	3.48	-	-	-	-	280	-	-	-	2.0758
15% TNT Slurry	80.63	15.59	NA	3.92	-	-	-	-	295	-	-	-	4.4524
25% TNT Slurry	80.08	15.73	NA	4.19	-	-	-	-	336	-	-	-	2.7931

In order to decontaminate lagoons at various locations with a minimum of equipment, it is important that the equipment be easily moved from site to site. Ideally, the incineration equipment and all auxiliary equipment can be built onto a 12.2 m x 2.7 m flat bed trailer. Such a scheme is clearly not feasible for an open pit incinerator. At a hearth loading rate of 147 kg/m<sup>2</sup> hr (EPA, 1979), a cyclone furnace with a 34-99 kg/m<sup>2</sup> hr diameter is required for 900 kg/hr of lagoon sediment. Loading rates for multiple hearth furnaces are usually around 54-68 kg/m<sup>2</sup> hr (EPA, 1979). Treatment at the desired rate requires an 2.4 m diameter unit with five hearths. An electric furnace loaded at a rate of 220-270 kg/m<sup>2</sup> hr (EPA, 1979) would be 2.7 m wide by 6.1 m long. Because of the relatively large volume of high temperature region per unit of surface area, fluid beds are typically loaded at 220-270 kg/m<sup>2</sup> (EPA, 1979). A unit to process 900 kg/hr would have to be 2.1 m in diameter. A portable rotary kiln system including afterburner and scrubber for the desired incineration rate could be 4 m wide by 7.9 m long by 4.3 m high (CE Raymond, 1979) or 4 m wide by 7.9 m by 11.6 m high (Met-Pro, 1977). Of all of the systems discussed, only the rotary kiln is advertised as an easily movable unit.

#### E. Economics

Capital costs for various incineration systems for a 900 kg/hr incineration rate are presented in Table 15. These costs include dredging equipment, flat bed trailer and afterburners and venturi scrubbers where needed. Operating costs are listed in Table 16. Fuel requirements for each system are based on heat available in the incoming sediment and the excess air requirements for the system. Fluid bed incineration costs may be somewhat deceptive. With the figures presented, air velocity through the bed is only approximately 0.4 m/sec instead of the recommended 1.5-2.1 m/sec. The incinerator will not operate at this air flow. Either air throughput must be greatly increased, requiring significantly higher fuel and electrical costs, or bed diameter must be reduced. While this would decrease capital costs, it would also increase loading rates. Pilot scale experimental work would be required to determine whether it is feasible to burn sediment with such a low heating value in a fluid bed incinerator. Overall, the rotary kiln appears to be the most economical approach over the entire expected range of sediment characteristics.

#### F. Advantages and Disadvantages of Incineration of Explosives Contaminated Lagoon Sediment

Incineration is also a "proven technology" for disposal of high concentrations of explosives and propellants. Additional advantages of the incineration technique in general include low capital and operating costs, no need to dilute the sediment, no post treatment of aqueous effluents from the incineration process itself and transportability. A major disadvantage of incineration is the need for air pollution abatement devices. Air pollution will be a major problem if the sediment is high in metals, however, a scrubber can be found that will remove metals from the air at additional capital costs. Another disadvantage is the large amount of down-time and maintenance required.

#### G. Laboratory and Pilot Studies

Prior to any experimental incineration, it would be desirable to perform various tests to determine safe methods of handling explosive contaminated

Table 15. Capital Incineration Costs to Decontaminate Lagoon Sediment

Capital Costs

<u>Quantity</u>	<u>Equipment</u>	<u>Installed Cost</u>	<u>Reference</u>
1	Dredge: Porta-Dredge PD-4LS-1136 1/min	\$ 53,260	Salemink, 1980
1	Holding Tank 454,200 l (120,000 gal) w/75 hp side entry turbine	132,000	Peters and Timmerhaus, 1968
1	Slurry Pump, 1/2 hp	800	" "
1	Flat Bed Trailer	10,000	
1	Incineration System (includes feed system, incinerator, afterburner and/or scrubber)		
	Cyclone/Rotary Hearth Furnace	482,000	EPA, 1979
	Multiple Hearth Furnace	503,000	EPA, 1979
	Electric Furnace	330,000	EPA, 1979
	Fluid Bed Incinerator	630,000	EPA, 1979
	Rotary Kiln Incinerator	272,000	Met-Pro, 1980

System

	<u>Total Cost</u>
Multiple Hearth Furnace	\$699,000
Electric Furnace	526,000
Fluid Bed Incinerator	826,000
Rotary Kiln Incinerator	488,000
Cyclone/Rotary Hearth Furnace	658,000

Table 16. Incineration Annual Operating Costs

	<u>Cyclone/Rotary Hearth Furnace</u>	<u>Multiple Hearth Furnace</u>	<u>Electric Furnace</u>	<u>Fluid Bed Incinerator</u>	<u>Rotary Kiln</u>
Installation (2% of capital)	13,200	14,000	10,500	16,500	9,400
Labor (3 operators @ \$45,000/man year 1 supervisor @ \$75,000/man year)	210,000	210,000	210,000	210,000	210,000
Maintenance (5%/yr. 10% for multiple hearth)	32,900	68,800	26,300	41,300	23,400
Fuel Oil No. 2 (Q \$8.269/l)	122,400-171,000	152,600-188,000	-	108,300-167,500	125,000-176,000
Electricity	-	-	52,500-246,500	-	-
Electric Furnace Elements	200	200	200	200	200
Slurry Pump	5,000	17,500	2,300	8,800	8,900
Additional Power (Fan or compressor, furnace or internal motion)	\$112,300-443,000	\$462,400-500,500	\$383,300-517,300	\$429,300-485,500	\$372,900-424,500
<b>TOTAL</b>					

sediments. In addition, laboratory analysis of actual sediment samples is required to determine their compositions and combustion characteristics. Costs of these tasks are estimated at \$8,000. Finally, pilot scale experiments with various incineration systems are needed to determine how well they can handle the sediment. Table 17 lists available pilot scale equipment and approximate costs. Most of these facilities do not have extensive analytical support. Therefore, an additional \$5,000 in analytical support will be required.

On the basis of this report, several of the incineration methods discussed can be eliminated from laboratory and pilot scale tests since they do not appear to be feasible for this application. The air pit incinerator suffers from high particulate emission with no possibility of additional treatment and is therefore an unacceptable choice. The multiple hearth and cyclone furnaces drag rabble arms and plows across the burning waste. Since this is a high friction process, danger of detonation is expected to be greater than for the other types of incinerators discussed. In addition, high levels of inorganic material in the sediment and uneven heating in the furnace could lead to severe clinkering problems. High ash levels may present some difficulties for the fluid bed incinerator, however, experimental work with actual contaminated lagoon sediment is needed to determine whether or not this is the case. No serious problems are foreseen for the electric furnace. Rotary kiln incineration is expected to work very well, although experimental work will be needed to determine unit size requirements and optimal operating conditions. In short, additional experimental work is recommended for the electric furnace, the fluid bed incinerator, and the rotary kiln.

Table 17. Pilot Scale Incinerator Test Facilities and Costs for Tests

1. **BSP Division**  
Envirotech Corporation (Lurgi Corporation)  
1 Davis Drive  
Belmont, CA 94002

**Pilot Scale Tests  
Facilities:**

Fluid Bed Reactor (0.6 m diameter, 4.7 m height)  
Fluid Bed Reactor (1.8 diameter, 2.4 m height)  
Multiple Hearth Furnace (0.33 m)  
Analytical Laboratory (well-equipped)

**Cost:**

approximately \$3,000/day

2. **C-E Raymond**  
Combustion Engineering, Inc.  
200 West Monroe Street  
Chicago, IL 60606

**Pilot Scale Tests  
Facilities:**

Bartlett-Snow Tumble Burner

**Cost:**

\$600/8 hrs

3. **Dorr Oliver, Inc.**  
77 Havermeyer Lane  
Stamford, CT 06904

**Pilot Scale Tests  
Facilities:**

Fluid Bed Incinerator (3.7 m diameter)

**Material Required:**

approximately 380 liters

**Cost:**

approximately \$10,000

Table 17 (cont.)

4. **Met-Pro Corporation**  
**Systems Division**  
**160 Cassell Road**  
**Box 144**  
**Harleysville, PA 19438**

**Pilot Scale Tests**

**Facilities:**

**React-O-Therm**

**Cost:**

**approximately \$3,000 (for 2 days)**

5. **Midland Ross Corporation**  
**Surface Division**  
**2375 Dora Street**  
**Toledo, OH 43607**

**Bench Scale Tests**

**Characterization for time, temperature, quantitative and qualitative analysis**

**Cost:**

**\$5,000-\$15,000 (usually \$8,000-\$10,000)**

**Pilot Scale Tests**

**Facilities:**

**Batch Furnace**  
**Rotary Hearth**

**Cost:**

**\$15,000-\$100,000 (usually \$25,000-\$40,000)**

6. **Nichols Engineering and Research Corporation**  
**Homestead and Willow Roads**  
**Belle Mead, NJ 08502**

**Pilot Scale Tests**

**Facilities:**

**Multiple Hearth Furnace (5.5 m diameter)**  
**Multiple Hearth Furnace (4.9 m diameter)**  
**Shaft Kiln**  
**Fluidized Bed**

**Cost:**

**approximately \$1500/day**

Table 17 (cont.)

7. **Shirco, Inc.**  
2451 Stemmons Freeway  
Dallas, TX 75207  
Bench Scale Tests  
Facilities:  
Thermogravimetric Analyzer (simulates electric furnace)  
Cost:  
Rental \$1500/month
  
8. **Trane Thermal**  
250 Brook Road  
Conshohocken, PA 19428  
Pilot Scale Tests  
Facilities:  
300 Kw  
Costs:  
approximately \$10,000/day
  
9. **Tooele Army Depot**  
Pilot Scale Tests  
Facilities:  
Rotary Kiln  
Cost:  
approximately \$5,000 to set up tests  
approximately \$1,000/day to run tests

## IV. MOLTEN SALT INCINERATION

### A. Process Description

Molten salt incineration is a process for burning hazardous chemicals which combines simultaneous combustion of the material and scrubbing of the effluent gas stream. This system has been mainly developed by Atomics International although Anti-Pollution Systems, Inc. also has a molten salts incinerator. The incineration is accomplished by injecting the hazardous material and air beneath the surface of a pool of molten salts. Typically sodium carbonate with a small amount (1-10%) of sodium sulfate is used as the molten salt, however, other alkali metal carbonates or mixtures of alkali metal carbonates can be employed. Sodium carbonate is used because it reacts instantly with acidic gases to form sodium salts. The small amount of sodium sulfate is used to catalyze the combustion of carbon. Temperatures of the molten salts are usually in the 700-1000°C range (Yosim et al., 1974).

A schematic diagram of the molten salt incineration process is shown in Figure 10. The wastes to be burned are pulverized. The pulverized wastes are normally blown into the bottom of the furnace with air. The air supplies the oxygen for combustion (Wilkinson et al., 1978). The gases produced from the burned wastes are oxidized and scrubbed as they pass up through the pool of molten salts. This scrubbing action converts the gases into mainly CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and O<sub>2</sub> and particulates (Wilkinson et al., 1978; Yosim et al., 1973; Yosim et al., 1974). The off-gases are passed through a baffle assembly to trap salt particles and a high energy venturi to remove fine particulates (Wilkinson et al., 1978).

As the waste material is oxidized, sodium chloride, sodium phosphate, sodium sulfates and inorganic ash are accumulated in the molten salt medium. When the dissolved impurities reach 20% by weight of the salt medium, the spent molten salt must be replaced (Yosim et al., 1978; Wilkinson et al., 1978). The salt can either be disposed of or it can be regenerated. A regeneration scheme is shown in Figure 11. Regeneration consists of quenching in water followed by filtration to remove ash. Carbon dioxide is bubbled through the quench solution to precipitate sodium bicarbonate. The solid sodium bicarbonate is filtered and returned to the molten salt furnace. The bicarbonate is converted to carbonate upon heating in the furnace (Berk, 1973).

### B. Review and Evaluation of the Literature

#### 1. Degradation of Hazardous Materials

A variety of materials has been subjected to decomposition by the molten salts incineration process. These materials include pesticides (Yosim et al., 1974; Yosim et al., 1978; Atomics International, 1975), chemical warfare agents (Dustin et al., 1977), nitrogen and arsenic containing compounds (Atomics International, 1975), photographic films (Atomics International, 1973), solid wastes (Hammond and Mudge, 1975), explosives and propellants (Yosim et al., 1973; Knight and Elston, 1978; 1979) and removal of SO<sub>2</sub> from power plant stack gases (Atomics International, 1968; Greenburg, 1972).

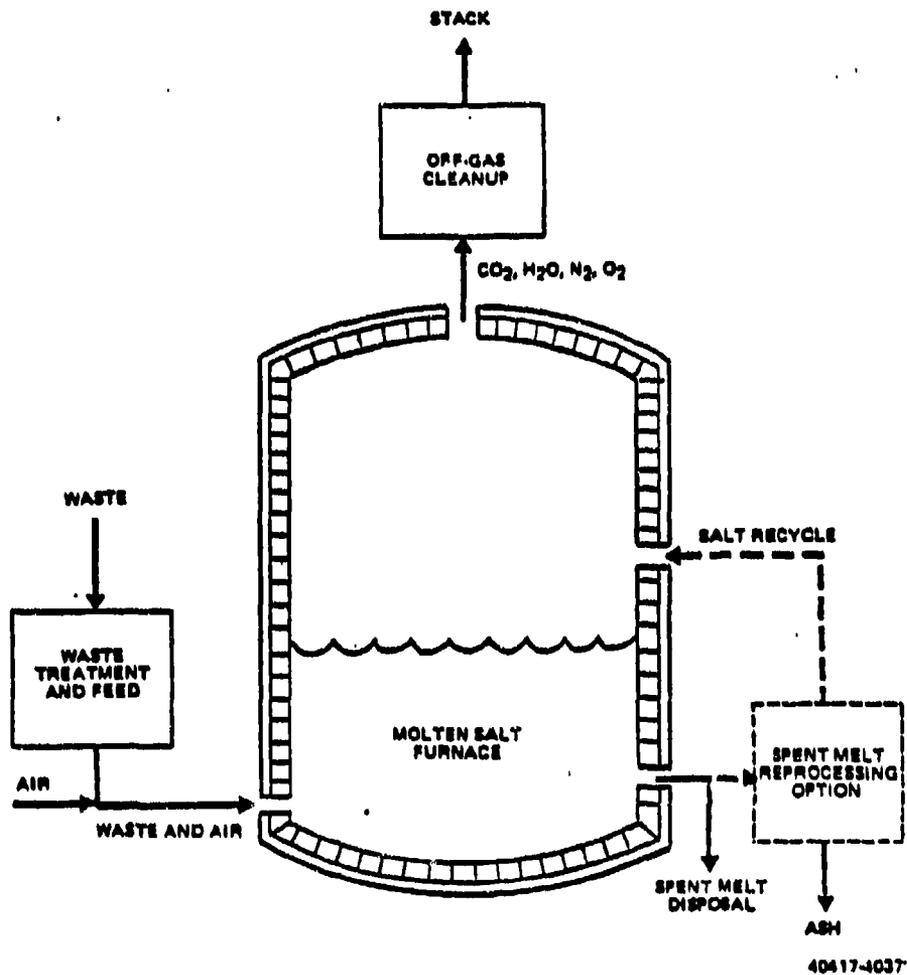


Figure 10. Molten Salt Combustion Process Concept  
 (Yosim et al., 1978, Disposal and Decontamination of Pesticides)

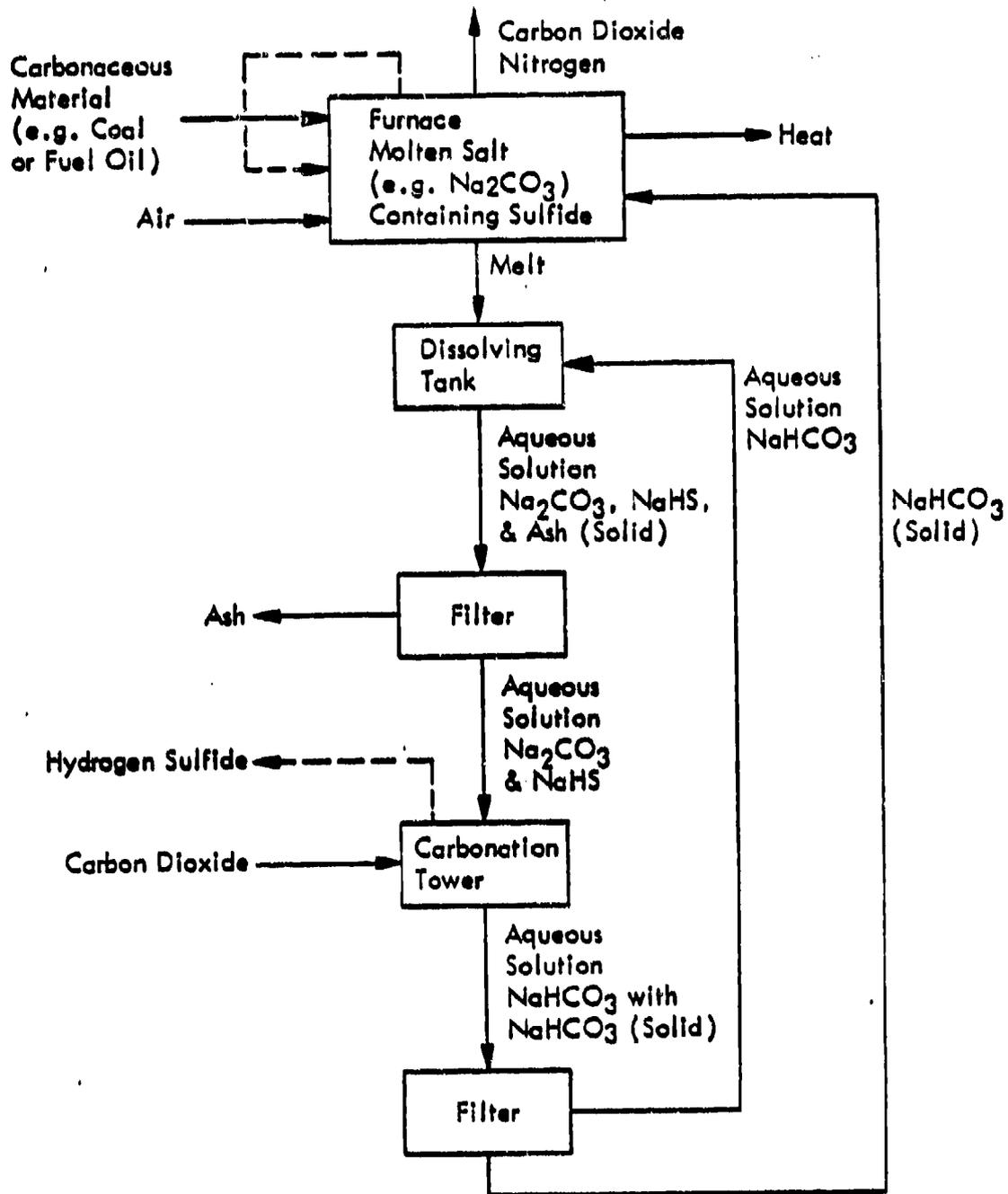


Figure 11. Schematic Flow Diagram for Recycling Carbonate Melt (Wilkinson et al., 1978)

The combustion of pesticides by molten salts has been studied by Yosim and coworkers at Atomics International (Yosim et al., 1978; Atomics International, 1975; Yosim et al., 1974). The results of these studies are summarized in Table 18. In general, greater than 99.9% destruction of the pesticides was obtained with pesticide residuals in the melt of less than the analytical detection limits. However, small amounts of the pesticides were detected in the exhaust gases from the reactor.

Molten salt incineration of various neat chemical agents was investigated by Dustin et al., (1977). They found the following destruction efficiencies:

- distilled mustard - 99.999997%
- VX ( $C_{11}H_{26}PO_2S$ ) - 99.999988%
- GB ( $C_4H_{10}FO_2P$ ) - 99.999985%

Concentrations of agents in the air emissions were below detection limits.

## 2. Degradation of Explosives and Propellants

Yosim and Darnell (1980) examined the disposal of composite and double based propellants by molten salt combustion. The compositions of the propellant materials were not analyzed, but were presumed to be within production formulation specifications. Effluent gases from the molten salt reactor were analyzed for  $NO_x$  by a chemiluminescent gas analyzer and for CO and unburned hydrocarbons by a non-dispersive infrared analyzer. Their results indicated that submerged combustion was best for halogen containing propellants because it allowed acidic waste gases to be scrubbed by the caustic salt. For  $NO_2$  and  $NO_3$  containing propellants, however, lack of sufficient air contact in submerged combustion produced higher levels of  $NO_x$  and CO. Surface combustion with forced air at high temperatures produced the lowest pollutant emission levels with the  $NO_2$  and NO containing propellants. Yosim and Darnell's experimental results for surface combustion of propellants and explosives at 800°C are listed in Table 19.

### C. Application to Explosives Contaminated Lagoon Sediment

Molten salt incineration represents a safe, convenient way to dispose of explosives. Good heat transfer and good contact with combustion air are provided without mechanical friction or impact which might cause detonation. The heat sink effect of the bed stabilizes combustion temperatures, preventing local hot spots which could also cause explosions.

For the standard lagoon, molten salt combustion of contaminated lagoon sediment will require the following equipment items:

- dredge
- holding tank
- molten salt combustion unit

Table 18. Summary of Results of Molten Salt Incineration of Pesticides and Other Hazardous Materials

Chemical	Salt	Temperature °C	% Chemical Destroyed	Concn of Pesticide in Melt (ppm)	Quantity in Effluent (as mg/m <sup>2</sup> )	Type of Reaction	Reference
50% Chloroac, 31% octachloro- 4,7-methano-1,2,3,4,5,6,7,8,9,10,11,12- dodecahydroindane and 28% related compounds	85% Na <sub>2</sub> CO <sub>3</sub> 15% Na <sub>2</sub> SO <sub>4</sub>	900	>99.9	ND*	ND	Batch	Yosim et al., 1974
Methilene	90% Na <sub>2</sub> CO <sub>3</sub> 10% Na <sub>2</sub> SO <sub>4</sub>	850-1000	ND	ND	ND	Batch	Yosim et al., 1974
Weed B (as [71.8% isooctyl ester of 2,4-D, 8.4% monoethyl ester of silver, 11.8% Lercosene])	90% Na <sub>2</sub> CO <sub>3</sub> 10% Na <sub>2</sub> SO <sub>4</sub>	850-1000	99.96	ND	ND	Batch	Yosim et al., 1974
Servia (1-naphthyl-N-methyl) carbamate	90% Na <sub>2</sub> CO <sub>3</sub> 10% Na <sub>2</sub> SO <sub>4</sub>	850-1000	>99.99	ND	ND	Batch	Yosim et al., 1974
Liquid chloroac (72% emulsifiable concentrate)	90% Na <sub>2</sub> CO <sub>3</sub> 10% Na <sub>2</sub> SO <sub>4</sub>	868	99.96	ND	ND	Continuous at a feed rate of 1.6 kg/hr	Yosim et al., 1974
DIT	Na <sub>2</sub> CO <sub>3</sub>	832	99.997	ND - 0.05	1.4	Continuous	Yosim et al., 1974
DIT	K <sub>2</sub> CO <sub>3</sub>	854	99.998	ND - 0.2	0.5	Continuous	Yosim et al., 1974
Machlucos	Na <sub>2</sub> CO <sub>3</sub>	822	99.996	ND < 0.01	1.1	Continuous	Yosim et al., 1974
Machlucos	K <sub>2</sub> CO <sub>3</sub>	856	99.999	ND - 0.005	ND - 0.4	Continuous	Yosim et al., 1974
Chloroform	NG	818	>99.999	< 0.1	< 0.5	NG	Atomics International, 1975; Wilkinson et al., 1978
Diphenylamine, HCl	NG	822	99.992	0.1	0.4	NG	Atomics International, 1975; Wilkinson et al., 1978
Nitrocellulose	NG	892	99.993	1	4.4	NG	Atomics International, 1975; Wilkinson et al., 1978
Peroxyacetic acid	NG	924	99.9994	0.1	0.8	NG	Atomics International, 1975; Wilkinson et al., 1978
NG - not given							
ND - not determined							

Table 19. Surface Combustion Tests of Composition B and Propellants in Molten Carbonate at 800°C (Yosim and Darnell, 1980)

Composition	Sample Size		Combustion Interval (sec)	NO <sub>x</sub> (lb/ton)	C/O (lb/ton)	H/C	Plume Opacity (%)
	WT (gm)						
Composition B RDX 60%, TNT 40%	25		41	10	28	nm <sup>a</sup>	12
	25		40	8	28	nm	12
	50		53	11	22	nm	10
	50		50	12	30	nm	11
	100		62	11	30	nm	9
	100		63	9	35	nm	11
	50 <sup>a</sup>		121	4.6	17.1	5.9	8
	500		125	5.2	15.10	6.6	9
	1000		140	5.2	17.2	5.3	10
	1000 <sup>b</sup>		49	4.9	19.3	6.3	10
		125	.3	3.2	4.9	7	
Propellant P Nitrocellulose 50% Nitroglycerine 35% Diethylphthalate 10%	500		35	3.2	19.3	1.3	10
	500		33	2.9	17.2	1.0	12
	1000		35	3.0	8.2	0.6	15
	1000		37	3.4	8.2	0.0	18
Propellant E Nitrocellulose 46% Dinitrotrinitrate 4% TEGDN 10%	25		14	16	117	1	5
	25		14	21	129	1	5
	100		28	35	108	3	9
	100		26	32	119	4	9
Propellant F RDX 75% SDNP/F 19% Polyethylene glycol 5% 2,4-toluenedisocyanate 1%	500		215	0.6	17.1	3.4	7
	500		225	0.5	19.3	3.2	8
	1000		265	0.2	5.4	4.3	9
	1000		275	0.2	10.3	4.5	9
Propellant C Ammonia perchlorate 5% HMN 26% Nitroglycerine 32% Nitrocellulose 15% Aluminum 15%	100		25	26	11	3	10
	100		29	26	11	3	10
	100		55	63	11	3	10
	500		69	57	11	2	12
	500		69	57	11	3	12
	1000		69	57	11	2	25

<sup>a</sup>Not measured

<sup>b</sup>Consists of two 500 gram samples

- air pollution abatement system
- spent salt recovery system (optional)

Contaminated sediment from the standard lagoon will be treated at a rate of 900 kg/hr without dilution. A mobile molten salt unit designed to process 230 kg/hr of pesticides is shown in Figure 12. Since the desired treatment rate for lagoon sediment is 900 kg/hr a larger unit will be required and truck mounting may be a problem.

In the current scenario, the sediment on a dry basis is 75% inorganic which would be deposited as ash in the reactor. Since fluidization is impaired when the level of ash reaches 20% by weight, spent salt would have to be recycled or discarded at a high rate to keep the ash level down. For 50% solids slurry and a waste feed rate of 900 kg/hr, make-up or recycled salt must be added at a rate of 2250 kg/hr to maintain the bed ash level at 15%. This is a serious drawback for this method, since a recycling process of this magnitude could mean large energy losses. A recycle system has been proposed by Atomic International (McKenzie et al., 1975) to remove the ash from the spent salt. In this process, the spent salt is cooled and dissolved in water. The ash is filtered from the solution. The salt is then recrystallized, removed from the solution, and returned to the molten salt bath. No attempt is made to recover the energy lost in removing molten salt from the bath. Operation without recycle results in the same energy loss plus the additional problem of disposing of large quantities of salt/ash mixture.

#### D. Economics

Molten salt incineration is an expensive way to dispose of contaminated lagoon sediment because of the low heating value and high ash content of the waste. Capital costs are approximately \$2,000,000 (see Table 20), while annual operating costs are around \$2,500,000 for a molten salt system without salt recycle (Table 21). A recycle system for the required 2250 kg/hr of spent salt would cost over \$7,000,000. Make-up salt costs would drop to around \$90,000/yr, and fuel costs would remain about the same. Cooling water would be required for melt crystallization, adding another \$89,000 to the annual operating costs. Total annual operating costs for a molten salt incineration system with recycle would be approximately \$1,300,000/yr. If all the heat lost in the recycling could be recovered, annual operating costs with recycle would only drop to \$1,116,000/yr. With so much non-combustible material in the contaminated sediment, it is not economically feasible to decontaminate the material by the molten salt process.

A word of caution must be inserted here concerning the validity of the cost figures presented. To date, there are no operating commercial scale molten salt incinerators. Costs presented were scaled up from cost estimates by Atomic International (McKenzie et al., 1975; Yosim and Darnell, 1980) for two 90 kg/hr units, a capacity only one tenth that required in the current discussion. Costs for the salts recovery system are even more likely to be in error, having been scaled from estimates for a 22 kg/hr unit to a 2250 kg/hr unit. However, even if the costs presented were wrong by a factor of two, treatment of the sediment by molten salt combustion would still cost \$558,000 - \$650,000/yr.

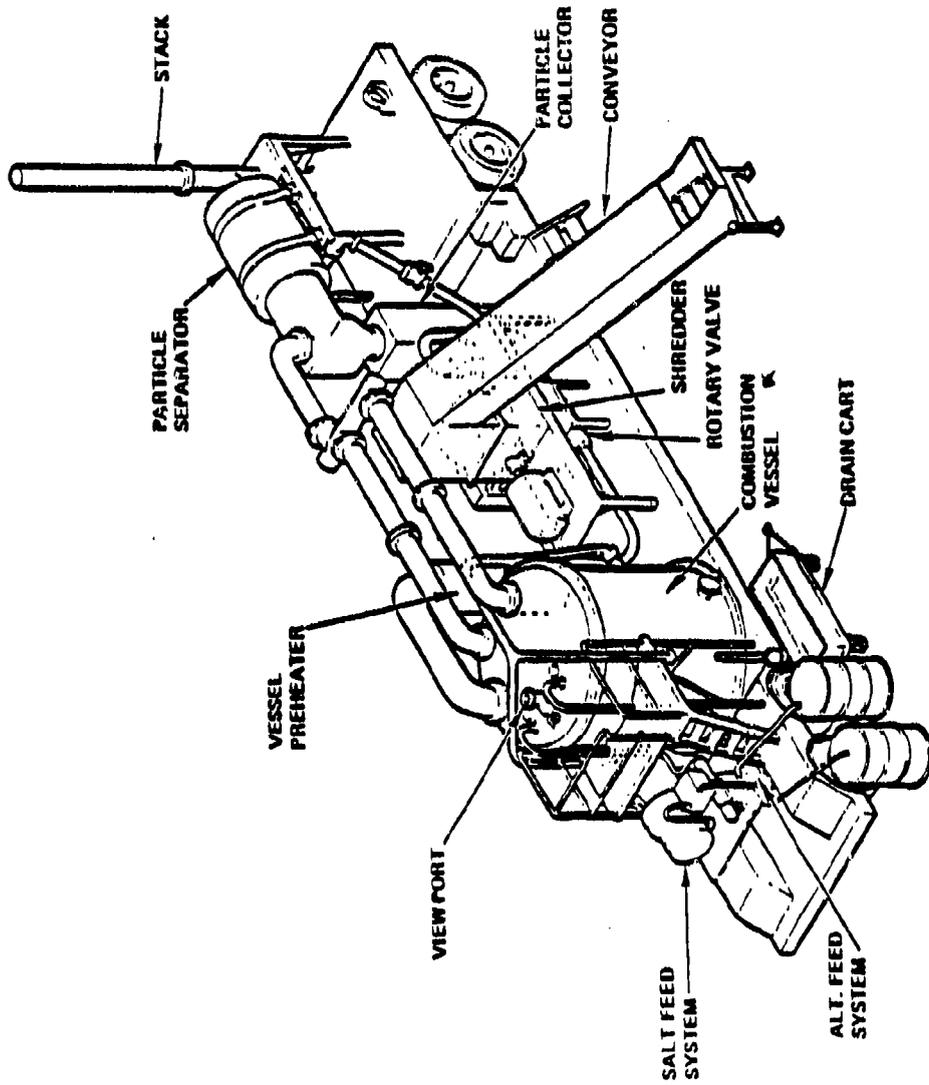


Figure 12. Mobile Molten Salt Incineration System (Wilkinson et al., 1978)

Table 20. Capital Costs for Molten Salts Combustion

<u>Quantity</u>	<u>Equipment</u>	<u>Price</u>	<u>Reference</u>
1	Dredge: Porta Dredge, 1136 l/min	\$ 53,260	Salemink, 1980
1	Holding Tank: 454,200 l, carbon steel	132,000	Peters and Timmerhaus, 1968
1	Slurry Pump: 1/2 hp	800	Peters and Timmerhaus, 1968
1	Flat Bed Trailer	10,000	Peterbilt, 1980
1	Molten salt incineration system: 2.75 m inside diameter, 7.6 m height (includes venturi scrubber)	<u>1,441,200 (2,061,000)</u>	Yosim and Darnell, 1980
	TOTAL	\$ 1,747,260 (2,257,060)	McKenzie et al., 1975

Table 21. Annual Operating Costs for Molten Salt Combustion

	<u>Price</u>
Maintenance (5% of capital)	\$ 87,400 (112,900)
Labor (3 operators @ \$45,000/man year) 1 supervisor @ \$75,000/may year)	210,000
Fuel Oil No. 2 (@ \$0.269/l)	315,000 (3.53x10 <sup>6</sup> Btu/hr for combustion 2.5x10 <sup>6</sup> Btu/hr in extracted salt)
Electricity (@ \$0.07/KWH) compressor, exhaust fan, 300 KW)	150,000
Makeup Salt (Sodium carbonate @ \$0.11/kg)	<u>1,792,900 (4950 lb/hr)</u>
TOTAL	\$ 2,525,300 (2,580,800)

E. Advantages and Disadvantages of Molten Salt Combustion

The main advantages of molten salt combustion are the excellent thermal contact provided by the molten salts, the retention of acidic gases by the caustic salt, and the scrubbing of most particulates from the off gases by the molten salt bed. For high heating value and low ash wastes, molten salt incineration appears to be an economically feasible alternative to conventional incineration.

In the standard lagoon scenario, the heating value of the sediment is low, thereby requiring fairly high expenditures for supplementary fuel. More serious, however, is the large volume of ash deposited in the molten salt bed by the treated sediment. Since 75% of the dry sediment is expected to be retained in the bed as inorganic ash, clean salt must be added and spent salt withdrawn at a high rate to maintain bed fluidity. Since salt replacement costs and salt recycle costs are very high for the amount of sediment treated, molten salt combustion is an economically unattractive treatment method for this scenario.

## V. MICROWAVE PLASMA

### A. Process Description

A microwave plasma is ionized gas produced by reactions of electrons with neutral gas molecules. The reaction is induced by the action of the microwaves on the electrons. The electrons are accelerated by the microwave electromagnetic field and undergo inelastic collisions with gas molecules, which produce more electrons and charged ions. When the production rate of electrons and ions is greater than the loss rate, plasma generation occurs (Bailin *et al.*, 1975). This plasma can react to break down chemicals and thus provides a means of decomposition of hazardous materials.

A microwave plasma can only break down materials when they are in the gaseous state. Since vaporization is a surface phenomena, the rate of vaporization of liquid and solid hazardous chemicals is directly related to the microwave power density and the heat of vaporization of the reactant. The microwave power density influences the rate of vaporization by supplying heat to the reactant and supplying free electrons and positive ions which recombine on the reactant surface and supply energy to the particle. As the reactant burns on the particle surface, it supplies the heat to the inner particle which also increases its rate of vaporization.

The degradation rate of the chemical in the microwave plasma is related to the pressure in the reactor, the free electrons per cubic centimeter, and the temperature of the electrons. The electron density and temperature are related to microwave power density. Typically, an increase in the microwave power density will increase the electron density and temperature.

A block diagram of a microwave plasma system designed by Lockheed is presented in Figure 13. The microwave power supply is normally a variable power source. This source delivers microwave radiation of 2540 MHz through the rectangular trough wave guides to the microwave power applicator which supplies the radiation to the plasma. The power applicator length defines both the volume of the plasma and the residence time of the gases within the plasma. Hazardous chemicals are delivered into the system as a pure organic liquid, as a slurry, or in a water or methanol solution. The material to be treated is then mixed with a carrier gas, (oxygen, or oxygen-argon mixture, or steam) and fed into the plasma reactor. The microwave unit operates at a reduced pressure, so the chemical to be treated is forced by gravity and the carrier gas through the reactor. The residence time of the of the chemical in the plasma is increased with quartz wool or quartz raschig ring packing. The increased residence time results in a more complete treatment of the chemical (Wilkinson *et al.*, 1978). The hot gases from the reactor effluent are cooled in a radiative heat exchanger followed by cooling to room temperature by a water-cooled shell and tube heat exchanger. Next the gases are passed through a packed-section caustic scrubber to remove any acid products (Hertzler *et al.*, 1979). Solid chemicals have been treated by placing a pellet of the material on a quartz ring in the plasma. However, a feed system for solids has yet to be developed (Hertzler *et al.*, 1979).

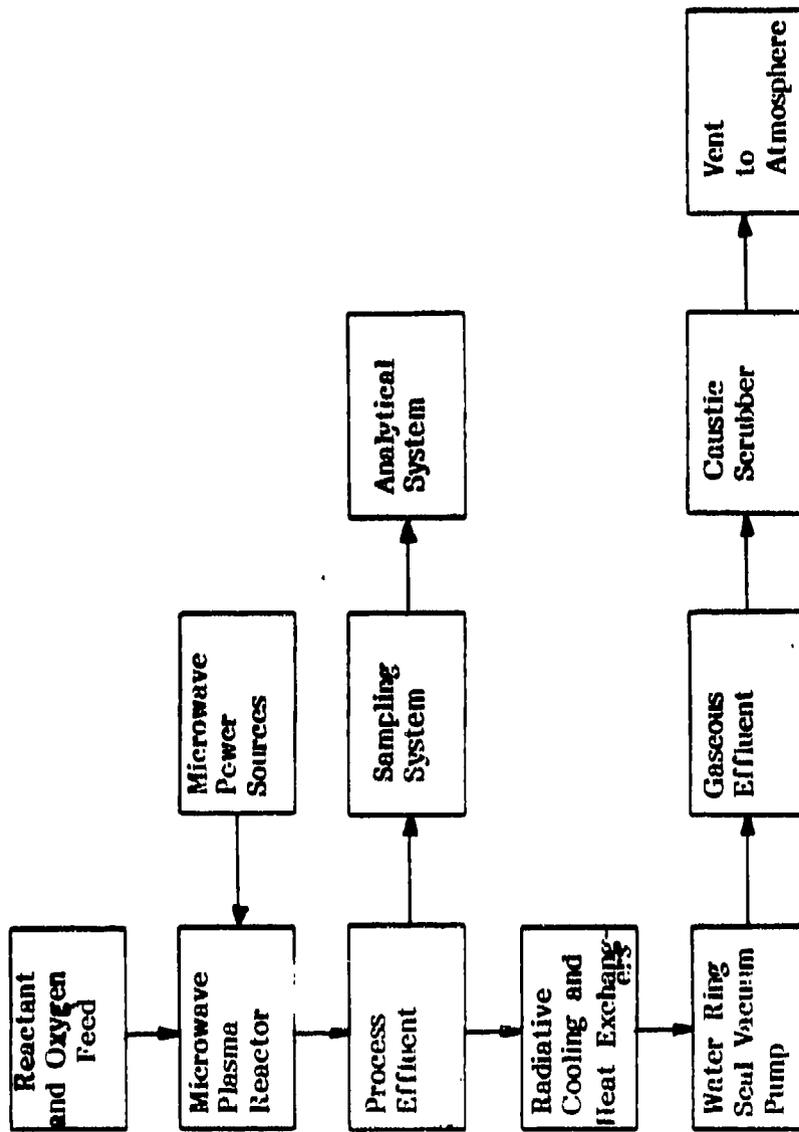


Figure 13. Block Diagram of 15-kW Microwave Plasma Reactor System (Hertzler et al., 1979)

## B. Review and Evaluation of Literature

Bailin et al. (1975) examined the use of microwave plasma to degrade dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate (DIMP). The plasma reactions were carried out in the presence of helium or air in a 2.5 kW unit. The experimental conditions and percent decomposition of DMMP in helium and air are presented in Tables 22 and 23, respectively. The breakdown of DMMP was higher in helium than in air. The optimum conditions for degradation of DMMP were relatively high power, high plasma volume and long residence times. The products of DMMP decomposition in helium were trimethylphosphite  $[(CH_3O)_3P]$  and methanol. In air, the decomposition products of DMMP were methylphosphonic acid, phosphoric acid and either methylphosphoric acid or methylphosphorus acid.

The results and experimental conditions for the decomposition of DIMP in helium and air are presented in Tables 24 and 25, respectively. The reduction of DIMP differed from DMMP in that the air plasma reactions produced higher decomposition of DIMP than helium plasma tests. Up to 99.5% DIMP removal was obtained in the air plasma. The decomposition products of DIMP in the helium and air plasmas were phosphoric acid and methylphosphoric acid.

In another study, Bailin et al. (1978) evaluated the effects of microwave plasma on several hazardous compounds. For this study, they used a larger 5 kW unit, which could handle about 2 kg per hour. The results are presented in Table 26. The microwave plasma treatment of malathion was essentially complete with residues containing 12 and 1 ppm malathion. The main products of the reaction were  $SO_2$ ,  $CO_2$ ,  $CO$ , and  $H_2O$ . The percent destruction of phenylmercuric acetate was estimated to be greater than 99.99%. The products were reported to be  $CO_2$ ,  $CO$ ,  $H_2O$ , and metallic mercury. Bailin et al. (1978) also tested kepone in solid, aqueous, and methanol solution forms. No kepone was detected in the solid residues and the reported products were  $CO_2$ ,  $CO$ ,  $HCl$ , and  $H_2O$ . A red dye mixture in an aqueous slurry was also treated by microwave plasma. After treatment, the solid residue contained no more than 5 ppm of the original mixture.

Hertzler et al., (1979) developed and tested a 15 kW microwave plasma reactor. This unit can process 2.3-9.1 kg/hr (5-10 lb/hr). Vinyl bromide was subjected to the microwave plasma in this unit at feed rates of 2.1-6.4 kg/hr (4.7-14.1 lb/hr) in the presence of oxygen. Power densities ranged from 6.5 kW/liter to 10.1 kW/liter. Degradation efficiency was 99.98% or greater in all cases. Reaction products were  $CO_2$ ,  $HBr$ ,  $NO$ , and vinyl bromide.

In another set of experiments, aniline, toluene and 1,1,1-trichloroethane were all destroyed with greater than 99.99% efficiency. Carbon tetrachloride was destroyed with greater than 99.7% efficiency. These results are presented in Table 27. Reaction products were not reported.

Table 22. DMMP-He Decomposition - Microwave Plasma (Bailin et al., 1975)

Power	Pressure (Torr)	DMMP flow (g/hr)	DMMP Con. (g/L He)	Plasma vol. (cm <sup>3</sup> )	Residence time (sec)	Conversion (%)
50	55	2.95	0.25	4.8	1.5	95.4
100	44	2.80	0.21	6.5	1.8	96.5
100	55	2.00	0.15	6.5	1.8	97.5
150	44	0.80	0.06	7.0	1.9	99.1
150	55	1.40	0.10	7.0	1.8	98.8
150	55	4.20	0.31	7.3	1.9	96.2
200	33	2.40	0.18	8.8	2.4	99.1
200	88	1.20	0.09	8.8	2.4	99.5
180	10	1.40	0.10	8.5	2.2	99.2
200	10	1.75	0.13	8.6	2.3	98.0

Table 23. DMMP-Air Decomposition - Microwave Plasma (Bailin et al., 1975)

Power	Pressure (Torr)	DMMP flow (g/hr)	DMMP Con. (g/L Air)	Plasma vol. (cm <sup>3</sup> )	Residence time (sec)	Conversion (%)
140	30	1.28	0.0128	3.7	0.14	72.1
160	36	0.919	0.0108	3.5	0.15	76.7
150	62	0.919	0.0108	2.8	0.12	82.9
250	29	1.28	0.0128	4.0	0.13	84.4
370	30	1.28	0.0128	3.1	0.12	87.8
390	34	0.92	0.0108	2.8	0.12	78.1
510	36	0.92	0.0108	3.1	0.13	97.9

Table 24. DIMMP-He Decomposition - Microwave Plasma (Bailin et al., 1975)

Power	Pressure (Torr)	DIMP flow (g/hr)	DIMP Con. (g/L He)	Plasma vol. (gm <sup>3</sup> )	Residence Time (sec)	Conversion (%)
135	17	1.27	0.017	5.6	0.27	76.5
130	14	1.27	0.017	5.5	0.26	62.4
140	9	1.30	0.086	3.6	0.86	94.7
140	9	1.30	0.085	3.6	0.85	92.7
150	10	1.75	0.15	3.6	0.85	80.4
200	11	1.28	0.084	4.5	1.1	92.8
210	9	1.50	0.132	3.8	1.2	87.6
210	9	1.50	0.137	3.8	1.3	91.7

Table 25. DIMMP-Air Decomposition - Microwave Plasma (Bailin et al., 1975)

Power	Pressure (Torr)	DIMP flow (g/hr)	DIMP Con. (g/l Air)	Plasma vol. (cm <sup>3</sup> )	Residence Time (sec)	Conversion (%)
125	82	0.44	0.0052	3.0	0.13	94.0
130	50	1.04	0.0245	3.1	0.26	93.9
145	70	0.84	0.0158	3.6	0.24	99.5
150	16	1.34	0.048	3.8	0.49	90.7
150	25	1.47	0.026	4.1	0.26	97.4
160	11	1.25	0.025	3.6	0.13	99.5
160	22	1.41	0.033	3.4	0.29	91.1

Table 26. Summary of Expanded-Scale Oxygen Reactions of Hazardous Material (Bailin et al., 1978)

Table XXVI. Summary of Expanded-Scale Oxygen Reactions of Hazardous Material (Bailin et al., 1978)

Product/Mixt	Microwave power (kW)	Feed Rate g/hr (lb/hr)	Pressure Range (atm)	Oxygen gas Flow (L/hr)	Reactor Packing	Conversion %
Methalbon "Cylindar" U1Y	3.7	504 (1.1)	28-66	361	Wool Plug	99.9986
Methalbon "Cylindar" U1Y	4.7	488 (1.1)	28-38	488	Wool Plug	99.9995
PCB Aroclor 1242	4.6	278 (0.6)	17-25	323	Wool Plug	99
PCB Aroclor 1242	4.2	492 (1.1)	19-36	395	Wool Plug	99
PCB Aroclor 1254	4.5	286 (0.4)	13-25	368	Solid Rings	99
Trolyson PMA-38	4.6	1078 (2.25)	128-148	968	Racclag Rings	Complete, cooled 99.99
Trolyson PMA-38	4.8	2188 (5.25)	108-128	792	Racclag Rings	Complete, cooled 99.99
Trolyson PMS-38	4.3	2958 (6.5)	108-128	792	Racclag Rings	Complete, cooled 99.99
Kryone 88/28 28% methanol solution	4.6	ND	45-68	728	Racclag Rings	99
Kryone 88/28 87% solids, aqueous slurry	4.2	---	35-58	None	Racclag Rings	99
Kryone 88/28 2-to-3% solid discs	4.6	---	38-78	888	Racclag Rings	99
Red dye mixture 15.5% solids aqueous slurry	4.6	128-488 (2.6-1.06)	35-68	388	Racclag Rings	99.999

ND - not determined  
PMA - phenylmercuric acetate

Table 27. Microwave Plasma Conversion Efficiencies for Selected Chemicals (Hertzler et al., 1979)

Run	Reactant	Reactant Feed Rate (g/sec)	Reactant Feed Rate (cc/min)	Oxygen/Reactant Ratio Actual	Oxygen/Reactant Ratio Stoichiometric	Pressure (Pa)	Pressure (mm)	Reactor Packing	Conversion Efficiency (%)	Fraction Reactant Unreacted (ppm)
1	Aniline	0.068	0.54	0.6	0.75	0.000	60	YES	99.999931	0.069
2	Aniline	0.102	0.81	0.1	0.75	0.200	62	YES	99.999800	0.20
3	Aniline	0.140	1.00	0.1	0.75	0.400	71	YES	99.9985	1.1
4	Toluene	0.057	0.45	0.35	0.8	0.000	52	YES	99.99924	7.6
5	Toluene	0.104	0.90	0.8	0.8	0.000	72	YES	99.99969	3.1
6	1,1,1-trichloroethane	0.100	1.43	2.75	2.75	0.500	52	YES	99.9988	12
7	1,1,1-trichloroethane	0.224	1.78	0.5	2.75	0.000	51	NO	99.9916	84
8	1,1,1-trichloroethane	0.45	3.57	7.8	2.75	0.500	49	NO	99.9978	22
9	Carbon tetrachloride	0.085	1.47	7.8	1.0	0.700	50	NO	99.72	2000
10	Carbon tetrachloride	0.205	2.10	5.3	1.0	0.700	50	NO	99.73	2700
11	Carbon tetrachloride	0.520	4.20	2.7	1.0	0.700	50	NO	99.88	1200
12	Carbon tetrachloride	0.794	6.30	2.6	1.0	0.700	50	NO	99.348	520

\* For experimental uncertainty on these numbers is about 75 percent of the values shown.

C. Applicability of Microwave Plasmas to the Degradation of Explosives Contaminated Sediments

The microwave plasma process has not been used to treat non-volatile sediments. The feed systems now in use to deliver materials into the reactor are not applicable to sediment slurries. The design of the microwave reactor also restricts the applicability of this process. The geometric requirement necessary to contain and distribute the microwaves places constraints on the size and design of the reactor. The reactor tube can have an outside diameter no greater than 5 cm and a length no greater than 1.37 m. An additional problem encountered in the microwave reactor is the deterioration of the vacuum O-ring seals when exposed to the heated effluent gases. A new technology for seals will have to be developed before large volumes of material can be treated by the microwave plasma process.

The current status of the microwave plasma process is uncertain. Hertzler (1980) at Lockheed, stated that the process was between funding. He estimated that it would take a year to develop a unit to treat 22.7-45.4 kg/hr (50-100 lb/hr) and another year to produce a marketable microwave process. Thus, although the microwave plasma process could potentially be a good technique for degradation of hazardous chemicals, it does not appear applicable to the current problem of treating explosives contaminated lagoon sediment.

D. Economics Analysis for Microwave Plasma Degradation of Explosives in Lagoon Sediments

Bailin et al. (1978) made conservative cost estimates for a microwave plasma process to treat 45.4 kg/hr (100 lb/hr) of toxic chemicals. Scaling up these costs to meet the 1247-1362 kg/hr (2747-3000 lb/hr) for the model lagoon was not feasible due to the developmental stage of the process. The cost analysis would require a scaling factor of 30 with many parts of the process to be developed.

E. Advantages and Disadvantages of Microwave Plasma for Treatment of Explosives Contaminated Sediments

There are several major problems in the use of the microwave plasma process on explosives contaminated sediments. First, no technique has been developed to deliver a 5-10% solid slurry into the reactor. The two systems which can deliver liquids into the reactor are not applicable to treatment of explosives contaminated sediment. It is unknown how long it would take to develop a sediment slurry delivery system.

The second major problem with the microwave plasma process is scale-up of the process. Restrictions on the size of the reactor limit the volume of material that can be treated. The deterioration problems with vacuum O-ring seals will increase as the volume of material increases. If, as Hertzler (1980) estimated, it will take 2 years to develop a marketable 22.7-45.8 kg/hr (50-100 lb/hr) unit, then development of the process to treat 1247 kg/hr (2750 lb/hr) required by the lagoon criteria will require a much longer time period.

The presence of solids and inorganic particles in the sediment will interfere with the formation of the plasma. This could lead to incomplete treatment of the explosives. Since explosives have never been submitted to microwave plasma destruction, the hazards associated with degradation processes, the degradation products and the reaction rates are unknown. In spite of demonstrated degradation of toxic liquids, the large number of uncertainties associated with the microwave plasma process and reactor as well as those associated with the treatment of explosives by the method, limit the usefulness of this process to the contaminated sediment problem. Many years of research and development would be needed to produce a microwave plasma unit capable of meeting the lagoon decontamination scenario requirements. Thus, microwave plasma should not be further considered for this scenario.

## VI. ELECTRON BEAM PROCESSING

### A. Process Description

The bombardment of a material with high velocity electrons liberates orbital electrons in the material with the concurrent production of free radicals, ions or excited species. These free radicals, ions or excited species can react with other molecules in the material to form new chemical species. Thus, the overall effect of the interaction of electron beams with molecules is the breaking of chemical bonds and the attendant recombinations. Control of the bond breaking/recombination process to obtain the desired results depends on the dose of the electrons, their penetration in the material, their absorption efficiency and the chemical environment.

The dose is a measure of the total energy which must be delivered to a unit mass of the material to cause the desired reaction. Dose is measured in rads (100 ergs/g). The necessary dose varies significantly depending on the desired reaction, e.g., disinfection of water and sludge requires doses of 0.05 to 0.5 Mrads while doses of 1 to >15 Mrads are required to crosslink polyethylene (High Voltage Engineering Corp., 1980). The penetration of the material by the electron beam is a function of the energy of the beam and the thickness of the material. Penetration is usually expressed as the weight of material treated per unit area. With commercial electron beam instruments covering the range of 0.3 to 300 MeV energy regions, penetration can vary from  $<0.1 \text{ g/cm}^2$  to  $>1.0 \text{ g/cm}^2$  for a single one-sided treatment. The effective penetration can be more than doubled if a simultaneous double-sided treatment is used, since the doses obtained from opposing beams are additive.

The electrons must not only penetrate the material but must have sufficient energy to cause the desired reaction throughout the material. Thus, the absorption efficiency of a material being irradiated by an electron beam is dependent on the energy of the electrons necessary to cause the desired reaction, the shape of the electron beam, the geometry of the material and the variation of dose with thickness of the material. These parameters must be experimentally optimized to provide consistent results at the lowest energy costs.

High energy electron generation equipment is available from several companies, however, only one firm has equipment in actual operation for processing sludge. This unit is in the 850 kV research facility located at Boston's Deer Island Sewage Facility. The Deer Island Unit was designed by Dr. J.G. Trump at the Massachusetts Institute of Technology and was constructed by High Voltage Engineering Corporation. The Electron Beam unit consists of a patented Insulating Core Transformer (ICT) power supply. The monoenergetic electron beam produced is scanned at a high frequency (~200 Hz) to provide a product beam. This product beam has a uniform lateral intensity distribution. This unit is shown in Figure 14. A larger 1500 kV unit is being installed at the Miami, Florida, wastewater treatment plant (Bryan, 1980).

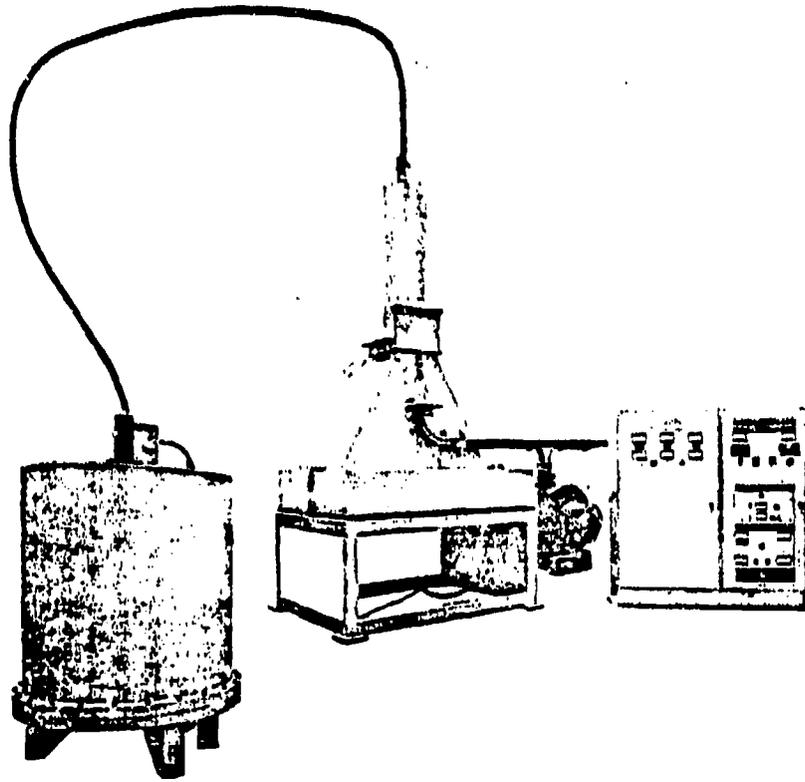


Figure 14. Cable Connected 300 kV to 800 kV Electric Beam Unit (High Voltage Electron Corporation, 1980a)

The 850 kV Deer Island Electron Beam Facility has a treatment capacity of 100,000 gallons of sludge containing up to 8% solids per day. The layout of this facility is shown in Figure 15. The scanner head is located in a concrete shielded vault. The sludge is continuously fed onto a spreader to reduce the sludge to a thin layer. The thin layer of sludge is irradiated by the scanner at a sweep rate of 400 times per second.

#### B. Review and Evaluation of Literature

The majority of the research work on disinfection of water and sludge with high energy electrons has been conducted by Dr. Trump at MIT. Trump and coworkers (Massachusetts Institute of Technology, 1977) studied the effects of high energy electrons on bacteria, fungi and viruses. The microorganisms were suspended in a 0.067 M phosphate buffer solution. Irradiation was accomplished in thin liquid layers on Petri dishes or a rotating cylinder which uniformly distributed the microbial sample in a 1 mm layer on the walls of the container. The effectiveness of the radiation treatments was measured using the  $D_{10}$  value. A  $D_{10}$  value is the dose needed to reduce the population by a factor of 10. It is calculated by the following formula:

$$D_{10} = \frac{D}{\log_{10}N_i - \log_{10}N_g}$$

- D - Dose in rads  
 $N_i$  - initial number of microorganisms  
 $N_g$  - final number of microorganisms

The results from this study are presented in Table 28. They found that the *Micrococcus*, *Citrobacter*, *Klebsiella* and *Escherichia* bacteria were the most susceptible to the high-energy electron. The virus particles were generally the most resistant.

The disinfection effectiveness of high energy electrons on microorganisms and viruses in sludge was also studied by Trump and coworkers (Massachusetts Institute of Technology, 1977). The results of this experiment are presented in Table 29. Once again, the bacteria were found to be the most sensitive to the high-energy electrons, with up to eight  $\log_{10}$  reductions at a 40 Krad dose. However, the *Clostridia* in sludge was found to be very resistant. Viruses also were relatively resistant with slightly greater than a ten fold reduction in numbers at a dose of 400 Krad.

Electron beams have also been used to degrade toxic organic compounds (Massachusetts Institute of Technology, 1977; 1979; Trump et al., 1979). Three chemicals were evaluated - monuron (a herbicide), and two chlorinated biphenyls (3,4,2'-trichlorobiphenyl and 4-chlorobiphenyl). The samples were irradiated in glass Petri dishes with a sample depth of 6 mm. The results from the irradiation of monuron are presented in Table 30. The monuron was 98% degraded at a dose of 30 Krads.

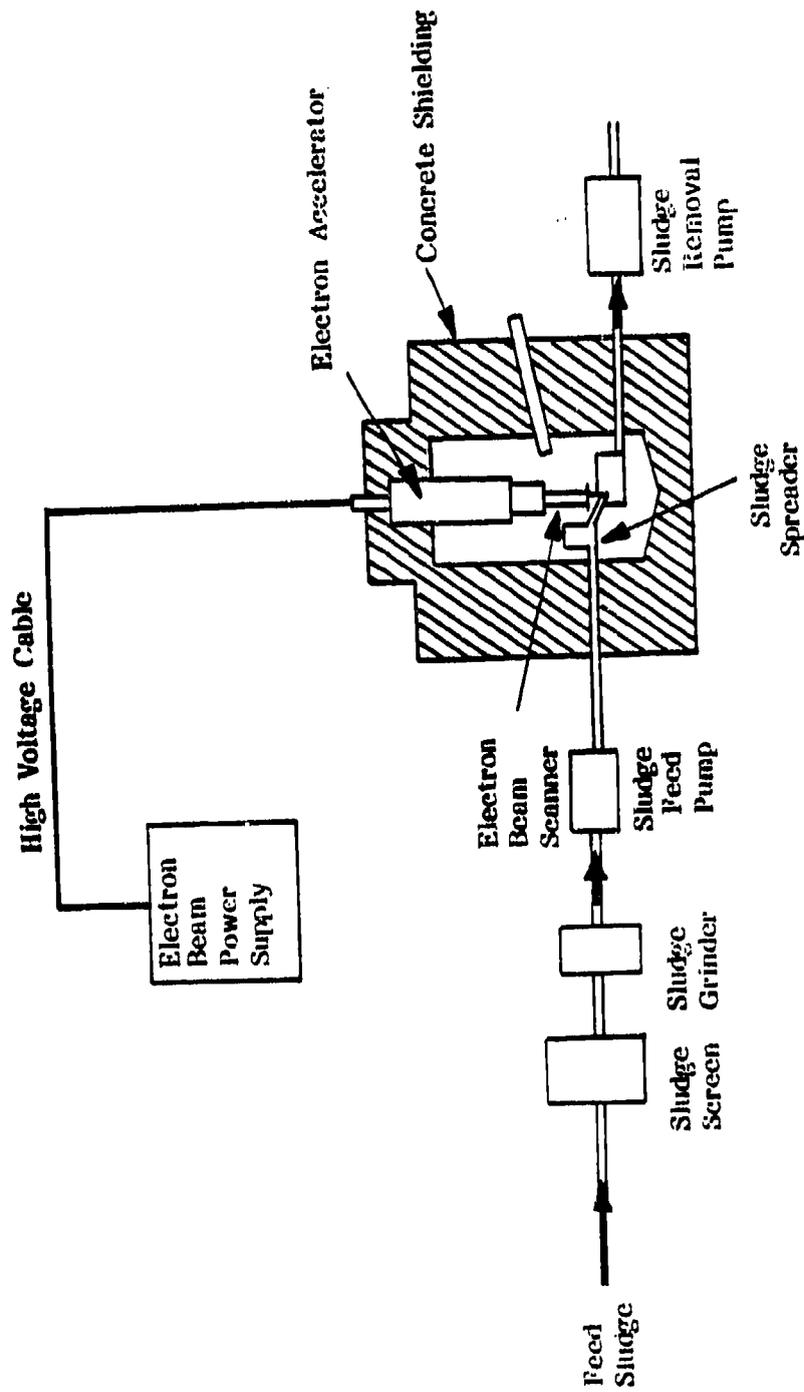


Figure 15. Layout of Electron Beam Sludge Treatment Facility (EPA, 1979)

Table 28.  $D_{90}$  (90 Percent) Inactivation Electron Dose for Various Microorganisms in Pure Cultures (Trump *et al.*, 1979)

	$D_{90}$ Dose (kilorads)	Calculated $\text{Log}_{10}$ Reduction for 400 kilorad Electron Dose
<i>Escherichia coli</i> strain KI2	27	15.0
Micrococcus species	14	28.0
<i>Citrobacter freundii</i>	5	80.0
<i>Klebsiella pneumoniae</i>	12	33.3
<i>Salmonella enteritidis</i>	15	26.6
<i>Salmonella typhimurium</i> strain LT2	16	25.0
<i>Salmonella typhimurium</i> strain R6008	105	3.8
<i>Salmonella typhimurium</i> strain 24	30	13.0
<i>Streptococcus faecalis</i>	125	3.2
<i>Clostridium perfringenes</i> spores strain 8798	200	2.0
<i>Clostridium perfringenes</i> vegetative cells strain 8798	75	5.3
<i>Aspergillus niger</i> spores	31	13.0
Polliovirus type 2	185	2.2
Corsackievirus type B3	200	2.0
Echovirus type 7	170	2.3
Reovirus type 1	165	2.4
Adenovirus type 5	150	2.6
Bacteriophage P22	60	6.6

Table 29. D<sub>10</sub> (90 Percent) Inactivation Electron Dose for Various Bacterial Groups in Sludge (Trump et al., 1979)

	D <sub>10</sub> Dose (kilorads)	Calculated Log <sub>10</sub> Reduction for 400 Kilorad Electron Dose
Total bacteria in raw primary sludge	103	4.6
Total bacteria in anaerobically digested sludge	133	3.6
Total bacteria in secondary waste-activated sludge	62	5.6
Total coliforms in raw primary sludge	25	7.6
Total coliforms in anaerobically digested sludge	28	7.2
Total coliforms in secondary waste-activated sludge	36	6.4
Fecal coliforms in raw primary sludge	28	8.0
Fecal coliforms in anaerobically digested sludge	29	8.0
Fecal streptococci in raw primary sludge	157	2.5
Fecal streptococci in anaerobically digested sludge	110	3.6
Clostridia in raw primary sludge	600	0.6
Clostridia in anaerobically digested sludge	500	0.8
Salmonellae in raw primary sludge	26	8.0
Poliovirus type 2 in anaerobically digested sludge	365	1.1
Coxsackievirus type B3 in anaerobically digested sludge	400	1.0
Echovirus type 7 in anaerobically digested sludge	335	1.2
Reovirus type 1 in anaerobically digested sludge	330	1.2
Adenovirus type 5 in anaerobically digested sludge	300	1.3

**Table 30. High Energy Electron Treatment of Monuron in Water  
(Massachusetts Institute of Technology, 1977)**

<u>Dose</u>	<u>Peak Height Before Irradiation, mm</u>	<u>Peak Height After Irradiation, mm</u>	<u>Percent Degradation</u>
30 Kilorads	163	3	98.0
25 Kilorads	163	7	95.8
20 Kilorads	163	11	93.4
15 Kilorads	163	29	82.6
10 Kilorads	163	45	73.1
8 Kilorads	163	62	62.8
6 Kilorads	163	87	52.1
4 Kilorads	163	106	36.5
2 Kilorads	163	141	15.6
0 (control)	163	167	0

The data on the degradation of the chlorinated biphenyls are presented in Table 31. 3,4,2'-Trichlorobiphenyl was dissolved in water at concentrations of 70 ppb (although the paper refers to ppm) and exposed to various high energy electron doses. At doses of greater than 1 Krad the 3,4,2'-trichlorobiphenyl compound was not detected by HPLC. Irradiation of 3,4,2'-trichlorobiphenyl was also carried out in various organic solvents and soap solutions. As can be observed in Table 31, increased doses were required to degrade this compound in organic solvents and in soap solutions. The authors attribute the difference in dosage requirement to secondary reactions of hydrogen and hydroxyl radicals formed during irradiation of water. Thus, the dosage required for 50% degradation of 3,4,2'-trichlorobiphenyl in water is less than that required for the same amount of degradation in soap solutions or non-aqueous solvents. Complete degradation of 4-chlorobiphenyl at 800 ppb in water required a dose of 10 Krads. The dose is 10 times higher than that required for complete degradation of 3,4,2'-trichlorobiphenyl. However, the concentration of 4-chlorobiphenyl was 10 times that of 3,4,2'-trichlorobiphenyl.

Kawakami *et al.* (1978) studied the effects of high-energy electrons on decoloration of wastewater from a dye process. They found that water soluble dyes were decolorated at low doses, but that disperse dyes required higher doses of electrons.

C. Application of High Energy Electrons to Degradation of Explosives in Lagoon Sediment

To date, only a few toxic chemicals have been subjected to electron beam degradation. The degradation products, pathways and mechanisms have not been fully characterized. However, it is highly probable that products and pathways of aqueous solutions of toxic chemicals will somewhat approximate those of ultraviolet photolysis. TNT and RDX are both known to undergo ultraviolet degradation. Thus although no data are available, electron beam degradation of these compounds would also be expected to occur. The degradation pathway may be very similar to UV-ozonolysis since ozone is formed by the interaction of the beam and oxygen in the system. However, the concentration - electron beam dose relationship is unknown as is the effect of sediment and particulate TNT and RDX on the degradation.

The electron beam system anticipated for on-site treatment of contaminated lagoon sediment is shown schematically in Figure 16. This system would consist of a dredge, sediment holding tank and a slurry mixing tank to provide a 10% slurry using water recycled from the electron beam treatment. This equipment was described in the wet-air oxidation section. The slurry will be pumped from the mixing tank onto a spreader to form a thin film (approximately 6 mm) to obtain optimum beam penetration. This spreader could be of several different designs depending on the physical characteristics of the sediment and will have to be evaluated when more information on the sediment is available. The thin layer of sediment will be passed under the electron beam. It is recommended that a double

**Table 31. Degradation of 3,4,2'-Trichlorobiphenyl by High-Energy Electrons (Massachusetts Institute of Technology, 1977)**

<u>System</u>	<u>Conc. mg/liter</u>	<u>Dose in kilorads for 50% degradation</u>
Hexane	4.0	1350
Hexanol	4.3	1000
Hexanol + 6% H <sub>2</sub> O	4.1	800
0.5% Na Stearate	0.7	350
0.1% Na Stearate	0.7	250
Water	0.07	<1

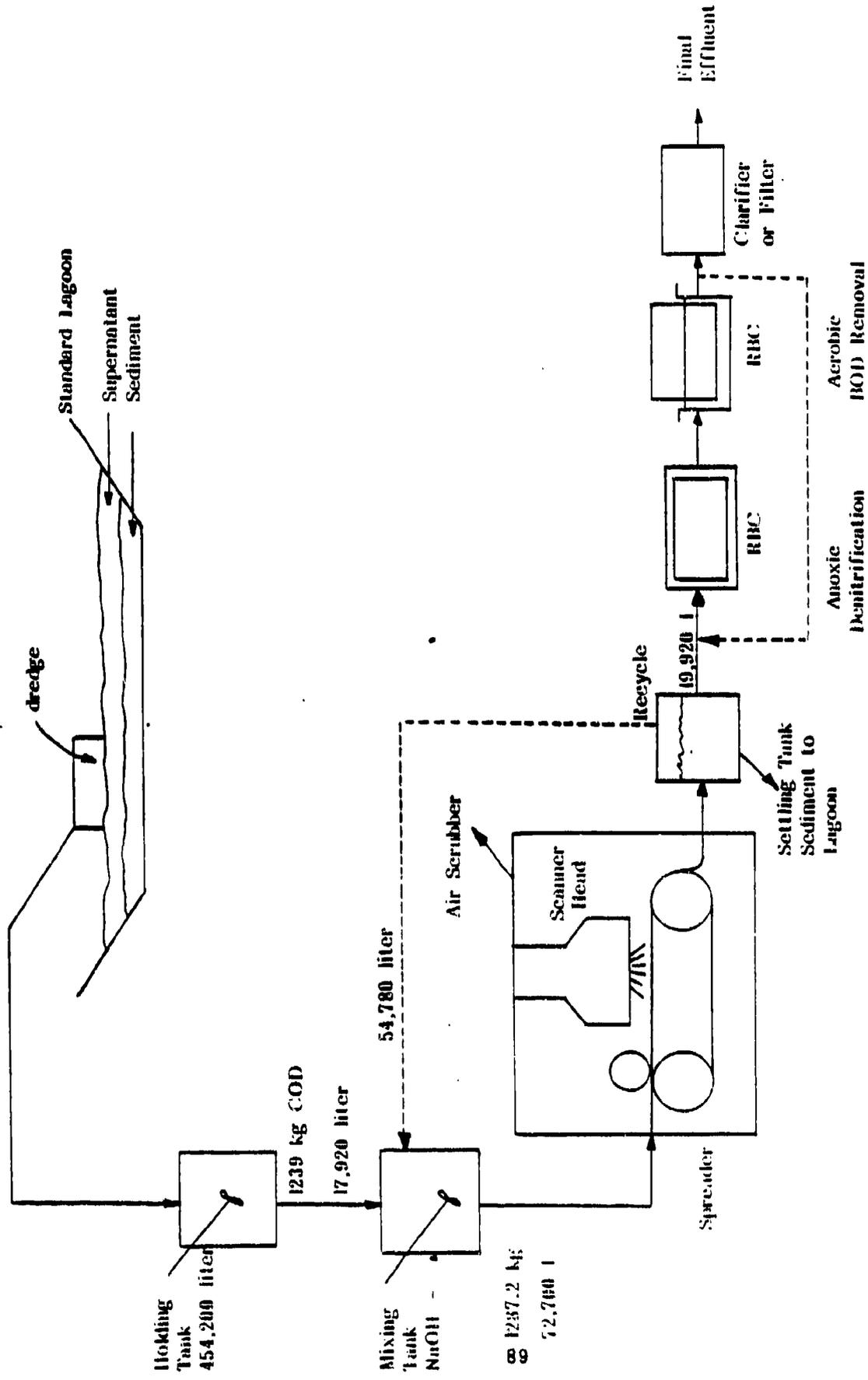


Figure 16. Electron Beam Flow Scheme for Treatment of Contaminated Lagoon Sediment

beam approach, be used. The rate of passage will have to be determined experimentally. Several passes may also be necessary for complete degradation. However, it is expected that the treatment rate of 72,700 liter/day can be easily met. The resulting sediment slurry will probably contain some low molecular weight acids (such as nitric acid) or organics. Thus, neutralization and biological degradation may be required as the final step in the treatment chain.

The electron beam equipment recommended for treatment of the lagoon sediment is a 1000 KV unit. This unit can be placed on a 12.2 m (40 ft.) heavy duty trailer for transport. The power supply and control electronics will remain on the trailer. The scanner head must be mounted in a concrete block radiation shelter. An underground explosive storage bunker could be used in place of the block shelter and would eliminate the need for a second truck to transport the blocks. The electronics truck will be backed up to the shelter and power supply and electronics connected to the scanner via a cable. Set-up time for the unit is approximately three months. Delivery time is 18 months. The unit requires cooling water at a maximum temperature of 70°F. Power requirements are 100 KW. Downtime for the electron beam equipment is 2-5%.

D. Economic Analysis of Electron Beam Degradation of Explosives Contaminated Lagoon Sediment

The capital and operating costs for electron beam treatment of explosives contaminated sediment are presented in Tables 32 and 33. These costs have been based on the processing of a 10% solid slurry at a rate of 72,700 liters in a 24-hour day with a 1000 kV unit and a reduction in COD of approximately 95%. This unit is capable of much higher handling rates (based on sewage sludge) which could cut costs significantly. However, actual degradation rates (and thus through-put) must still be determined experimentally. These accelerators are relatively utility efficient and maintenance free, thus yearly operating costs are relatively low.

E. Advantages and Disadvantages of Electron Beam Processing

Electron beam processing for destruction of hazardous materials is a relatively new field. Only limited information is available on the chemical reactions induced by the beam. For this process to be viable for destruction of explosives in sediment, a significant amount of research will have to be conducted. Process unknowns which must be determined include:

- the degradation pathway and reaction products,
- the degradation rate,
- the potential for explosion hazards, and
- the effects of the solids in the sediment on the degradation.

The air emissions will potentially include CO<sub>2</sub>, CO, NO<sub>x</sub>, ozone, etc. The aqueous effluent may contain nitric acid and possibly small carbon compounds. A process train similar to that used for the wet-air oxidation will follow the electron beam treatment. There are three important differences in the treatment of the aqueous effluent.

Table 32. Capital Costs for Electron Beam Processing of Lagoon Sediments

<u>Quantity</u>	<u>Equipment</u>	<u>Total</u>	<u>Reference</u>
1	Dredge: Porta-Dredge PD-4LS-1136 liter/min	\$ 53,260	Salemink, 1980
1	Holding Tank: 454,200 liter (120,000 gal) carbon steel with 75 h.p. side entry turbine mixer	132,000	Peters and Timmerhaus 1968
1	Slurry pump: 1/2 hp	800	Peters and Timmerhaus, 1968
2	Mixing Tanks: 15,140 liter (4000 gal) coal tar epoxy coated carbon steel with 20 hp side entry turbine mixer	21,700	Peters and Timmerhaus, 1968
1	Settling Tank: 113,550 liter (30,000 gal) carbon steel	12,500	Peters and Timmerhaus, 1968
1	Electron Beam Processing Unit: 1000 KV with cooler, truck mounted	1,500,000	High Voltage Electron Corp, 1980b
1	Pump: 0-40 liter/min for recycle	240	Galigher Co., 1980
1	Settling Tank	3,300	Peters and Timmerhaus, 1968
1	Metering Pump: 0-76 liter/hr NaOH	2,400	Milton Roy Co., 1978
1	Shielding and Ancillary Equipment	300,000	High Voltage Electron Corp., 1980a
1	Slurry Spreader	<u>5,000</u>	
Total for Basic Electron Beam Processing		\$2,031,200	
<u>Biological Treatment with RBC</u>			
4	Anoxic RBC: 24,000 ft <sup>2</sup> media area each, steel tank	\$ 172,000	Gerhardt, 1980
3	Aerobic RBC: 24,000 ft <sup>2</sup> media area each, steel tank	114,000	Gerhardt, 1980
1	Clarifier Tank: 15,140 liters (4000 gal) coal tar epoxy coated carbon steel	3,300	Peters and Timmerhaus, 1968
1	Sand Filter	<u>28,000</u>	
TOTAL CAPITAL COST		\$2,345,500	

Table 33. Yearly Costs for Electron Beam Processing

Installation (5% of capital)	\$ 117,275
Electricity and Cooling Water (\$7.00/hr of operation x 7200 hrs)* + RBC (\$.5/hr x 8448)	54,624
Labor (3 operators @ \$45,000/man year 1 supervisor @ \$75,000/man year)	135,000 75,000
Maintenance (\$2/operational hour* + (\$.25/operational hour for RBC)	16,512
NaOH and other chemicals (est)	<u>15,000</u>
TOTAL YEARLY COST	\$ 413,411

\*High Voltage Electron Corp., 1980a; Gerhardt, 1980

1) The sediment will have to be removed from the recycled water. This step will be accomplished in a 113,550 liter (30,000 gal) settling tank.

2) Based on UV-ozonolysis work, it is expected that electron beam degradation will occur most rapidly in basic solution thus, the addition of base to a pH of 9-10 will be required. This addition of base will be accomplished in the mixing tank. The effluent to the RBCs will probably be in the 7-8 range and not require acid or base treatment.

3) Air emissions control may be necessary to treat  $\text{NO}_x$ , CO and ozone, however, no selection of such a device can be made on the limited data available.

The sediment from the electron beam treatment will be sterile, therefore, it should be mixed with normal soil before disposal to prevent infestation of disease carrying organisms. If significant air emissions occur, the addition of costs for treatment of the air or a cost trade off with the aqueous effluent treatment will have to be made.

The drawbacks of electron beam processing for degradation of explosives and the hazardous chemicals are based on the insufficient data base in this area. In contrast, the equipment itself is highly developed, reliable, and relatively energy and water efficient. Radiation risks are minimal if proper shielding is provided and radiation is non-existent when the power is turned off. Another advantage of this system in treating sediments is the non-existence of particulate and metal air emissions. Thus, only CO, ozone,  $\text{NO}_x$  and possibly  $\text{SO}_x$  will have to be treated.

In summary, electron beam processing offers a potential cost effective method for decontamination for the future. The equipment is highly developed. However, significant amounts of research are necessary to improve the data base on degradation of hazardous materials by this method.

F. Laboratory and Pilot Scale Demonstrations for Electron Beam Treatment of Explosives Containing Lagoon Sediment

Laboratory scale demonstrations of electron beam processing for degradation of explosives contaminated sediment will require consideration of two objectives. The first objective is to establish the safety of electron beam interaction with explosives. The second is to optimize beam conditions and degradation rates. The following experimental methodology is proposed to meet these objectives.

The initial run should be carried out with a 200 mg/l aqueous explosive mixture. This mixture is slightly above the solubility limits and should give an early indication of any safety problems. This experiment should be run under several beam conditions. The entire solution from each exposure should be extracted and analyzed

for COD,  $\text{NO}_3^-$  and the explosives. This procedure will result in the optimization of beam conditions and will yield percentage degradation under the conditions as well as the expected products. Depending on the results of these tests, higher concentrations of (approximately 10%) explosives in an aqueous slurry should be run and optimized. If the results of these tasks are good, sediment should be added and the conditions reoptimized.

Costs for the laboratory experiments would be \$500/hr and would require 20-30 hours of machine time (\$10,000-\$15,000) (High Voltage Corp., 1980). Analytical back-up would require an additional \$10,000, for a total of \$20,00-\$25,000.

Pilot-scale tests should be relatively simple. All the beam parameters will be known from the laboratory tests since all the tests will be performed on the 1000 KV machine. These pilot runs will demonstrate through-put and operational characteristics. The pilot runs are estimated to cost \$700-\$1000. Analytical back-up will cost approximately \$5000 for a total of \$5700-\$6000.

## VII. GAMMA IRRADIATION

### A. Process Description

Gamma irradiation is produced during the decay of selected radioactive isotopes. The two isotopes most often used in controlled irradiation with gamma radiation are Cesium-137 and Cobalt-60. Cesium-137 has a half life of 30 years and emits a 0.66 MeV gamma ray. Cobalt-60 has a half life of five years and emits two gamma rays with an average energy of 1.2 MeV.

Gamma irradiation differs from high-energy electrons in two ways. First, gamma rays are very penetrating. A 64 cm (25 inches) thick layer of water is needed to absorb 90 percent of the rays from a Cobalt-60 source while electrons from a 1-MeV accelerator can only penetrate 1 cm of water. Second, gamma rays are continuously emitted thus, the exposure can only be varied with time.

### B. Review and Evaluation of Literature

#### L. Treatment of Sludge with Gamma Irradiation

Two types of sludge disinfection processes, liquid and dry sludge, are currently being evaluated. The liquid sludge facility is located in West Germany and was designed to treat 152,000 liters (40,000 gallons) per day. However, the initial Cobalt-60 source can only treat 30,800 liters (8,000 gallons) per day (EPA, 1979). The sludge is exposed to the radiation in batches by pumping it into the source cavity as shown in Figure 17. The effectiveness of the process was measured by the reduction in bacterial levels in the sludge. At a dose of 260 Krads for 210 minutes, total bacteria levels were reduced by two to four logs. Bacteria enclosed in plastic capsules were also irradiated. Nine *E. coli* strains were exposed to a dose of 260 Krads. Three strains were inactivated, four strains were reduced by six to eight logs, and two strains were relatively resistant and were reduced by five to six logs. *Salmonella* and *Klebsiella* strains were also exposed to radiation of 260 Krads. The *Salmonella* populations were reduced by four to seven logs and the *Klebsiella* populations were reduced by six to eight logs (EPA, 1979).

A facility to treat dry sludge has recently been completed by Sandia Laboratories in New Mexico. The facility can treat eight tons of dry sludge per day and uses a one million curie, Cesium-137 source. A diagram of the facility is presented in Figure 18. Morris *et al.* (1979) estimated  $D_{10}$  values for bacteria in dried sludge exposed to gamma rays. The results of the study were variable due, perhaps to the variation in the moisture content of the sludge. Morris *et al.* (1979) also examined the reduction and embryonation of *Ascaris* ova when exposed to gamma rays. They found that a dose of 150 Krads reduced the embryonation by greater than 99.9 percent. This group also studied the inactivation of polio virus by gamma irradiation. The results of this study are presented in Figure 19. As can be observed from the figure, relatively high doses were required for inactivation of this virus.

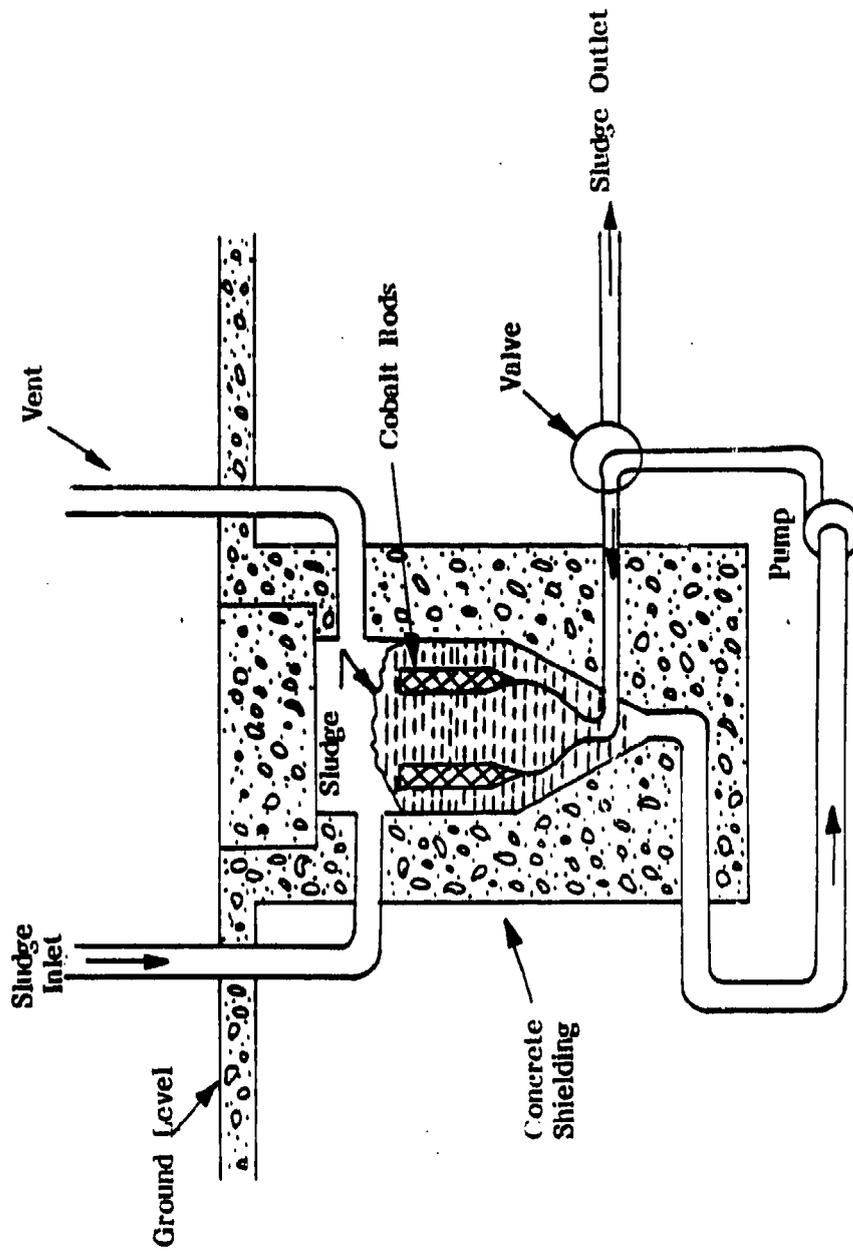


Figure 17. Liquid Sludge Gamma Irradiation Facility at Gusebullach, West Germany (EPA, 1979)

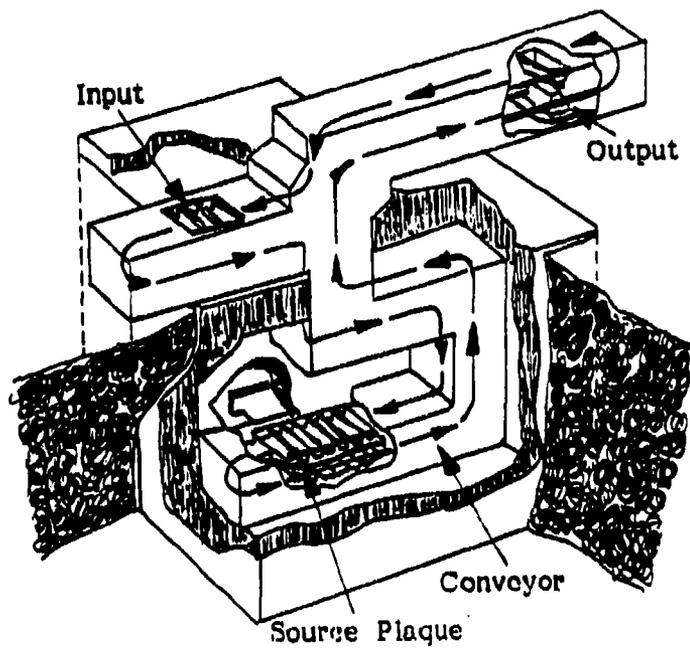


Figure 18. Gamma Irradiation Treatment System for Dried Sewage Sludge (Morris et al., 1979)

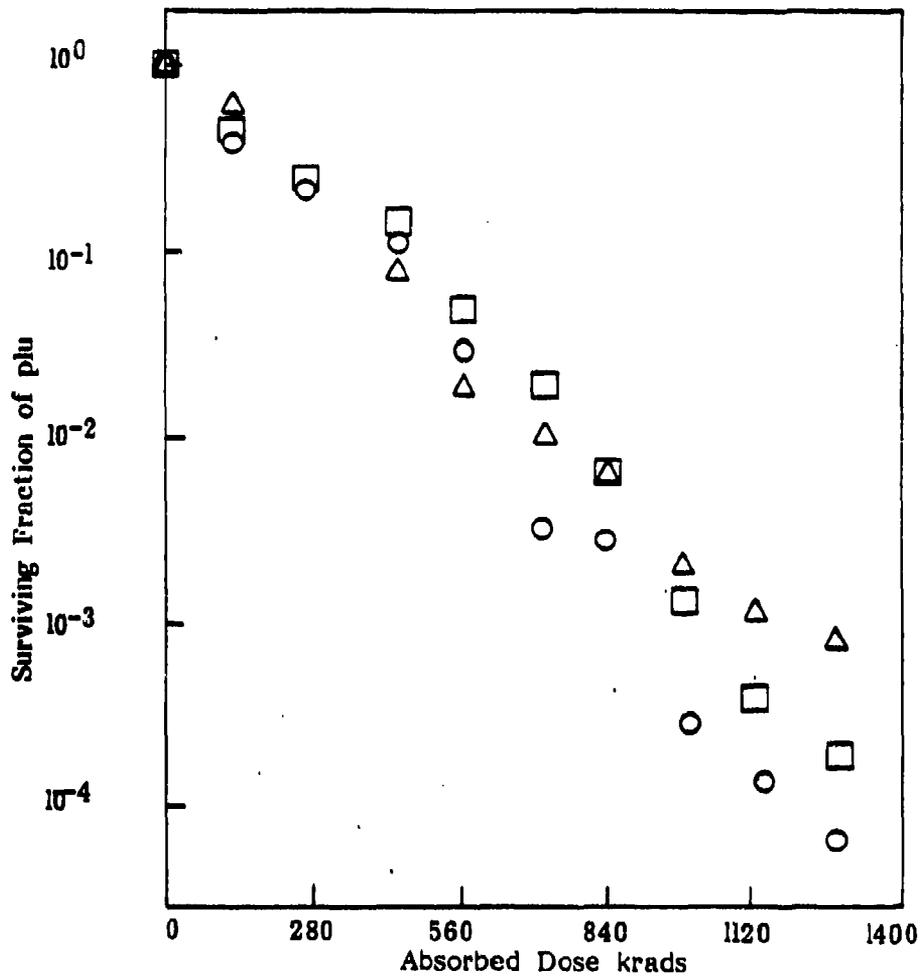


Figure 19. Rates of Poliovirus Inactivation by Cesium-137 in Raw Sludge Containing 5 Percent ( $\Delta$ ) or 80 Percent ( $\square$ ) Solids or in Composted Sludge Containing 80 Percent Solids ( $\circ$ ) (Morris et al., 1979)

Brandon (1979) compared bacteria  $D_{10}$  values in three types of sludge-digested, composted and dried. The results of this study are presented in Table 34. He found that the dosage requirement for a 90% reduction in bacterial populations was higher in the dried sludge. However, bacterial populations are initially lower in dried sludge versus digested sludge.

The reduction in COD levels in wastewater exposed to gamma radiation was examined by Condron and Etzel (1967). They irradiated the wastewater under three different conditions, non-aerated, aerated/mixed and aerated/settled. The results of the experiment are presented in Figure 20. At an exposure of 1 Mrads, only 20-30% of the COD in the non-aerated sample was removed. The aerated and mixed wastewater had COD destruction levels of about 70% and over 80% COD removal was observed in the aerated and settled wastewater.

## 2. Application of Gamma Radiation to Destruction of Hazardous Chemicals

Treatment of PCBs by gamma radiation has yielded mixed results. PCBs in a 15% ethanol/85% water mixture were exposed to gamma radiation at doses up to 15 megarads (Kroft *et al.*, 1975). A maximum of 20% destruction of the PCBs was found. In contrast, PCBs dissolved in an alkaline/2-propanol solution at a dose of 500 rads were dechlorinated (Sawai *et al.*, 1974). The same type of solvent dependence of PCB destruction with ultraviolet light has been noted in our laboratories. Thus, there is a preliminary indication that gamma radiation induced chemical degradation proceeds by mechanisms similar to ultraviolet light induced degradation.

Pink water has also been exposed to gamma radiation using a Cobalt-60 source (Helms, 1980). The TNT levels in the pink water were reduced from 89 mg/liter to 2  $\mu$ g/liter (no irradiation time given). The pink color disappeared during the irradiation and did not return. However, no analysis was performed on the effluent.

### C. Applicability of Gamma Radiation to Decontamination of Explosives Containing Sediment

A gamma radiation facility to degrade explosives in contaminated lagoon sediment will contain the following processes:

- dredge to remove the sediment from the lagoon
- holding tank for the sediment slurry and a mixer to maintain it in suspension
- underground batch gamma radiation unit with recirculation and aeration capabilities
- air pollution control devices
- biological post treatment, if necessary

Table 34. D10 Values for Bacteria in Sludges (kilorads) (Brandon, 1979)

Genus	Digested (2-10% Solids)	Composted (40% Solids)	Dried (90% Solids)
<i>Pseudomonas</i>	10	-	-
<i>Proteus</i>	11	-	-
<i>Salmonellas</i>	25-30	30	35-80
<i>Fecal Streptococci</i>	100-150	120-150	70-36
<i>Mycobacteria</i>	160-300	-	-
Coliforms	20-30	120-150	15-350
Total Bacteria	100-200	-	-

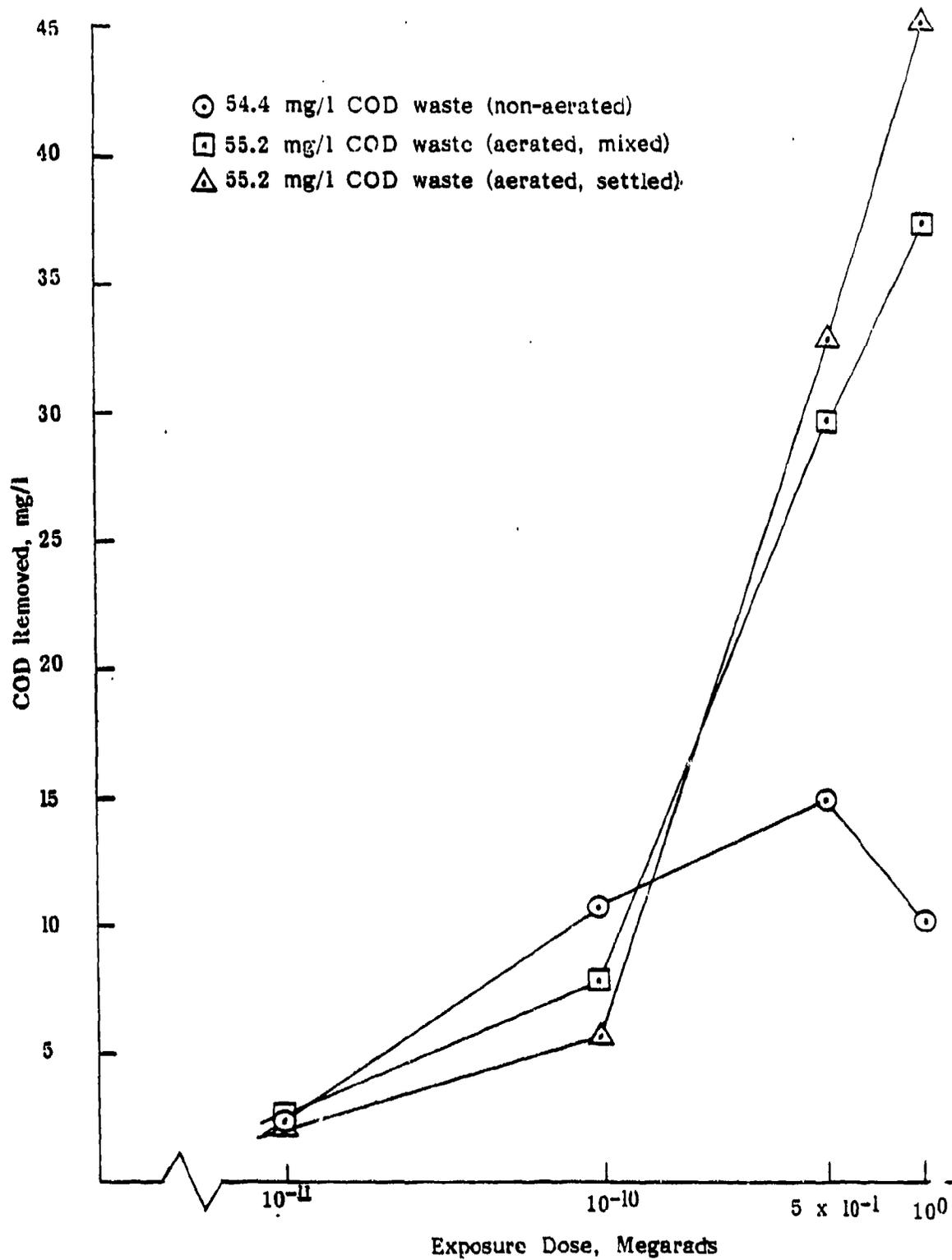


Figure 20. Effect of Air Diffusion During Irradiation of a 50 mg/l COD Synthetic Wastewater (Condon and Etzel, 1967)

The removal of the sediment from the lagoon will use the same equipment and procedures described for wet-air oxidation. The sediment in the mixing tank should be directly usable by this system, thus there will be no need for dilution. Based on the little information available on destruction of hazardous chemicals by gamma radiation, it appears that effective degradation requires conditions similar to ultraviolet degradation. Therefore, it is anticipated that optimum reaction conditions will be obtained at a pH of approximately 10. Thus, addition of sodium hydroxide to the holding tank to raise the pH will be necessary.

The 50% solids sediment slurry will be gravity fed into the underground gamma radiation unit. This unit will be buried or placed in an explosives bunker to provide adequate shielding. The unit will preferably operate in a batch mode similar to the West German facility. Constant recirculation of the material in the reactor will be necessary to prevent the solids from settling. Aeration of the material during the recirculation will help the degradation rate.

Air emissions will contain  $\text{NO}_x$ ,  $\text{CO}_2$ ,  $\text{CO}$  and possibly  $\text{SO}_x$ . No particulate air emissions are anticipated. The liquid effluent should be free of COD and explosives if sufficient residence time is allowed in the reactor. Since only 17,900 liters/day must be treated, the holding times in a 4400 liter reactor could be as long as six hours. If short holding times are used, a biological post treatment may be necessary. As with the other treatment systems, the sediment will be sterile and should be mixed with soil before disposal.

D. Economic Analysis of Gamma Radiation for Treatment of Explosives Contaminated Sediment

The costs for a gamma radiation liquid sludge facility to treat 113,562 liter (30,000 gal) of sewage sludge per day were given by EPA (1979). This liquid facility includes the following components:

- insulated concrete building with 7.6 m (25-foot) ceiling
- equalization sludge storage tank
- emergency water dump tank (for source shielding water)
- irradiating capsules (radiation source)
- steel-lined source handling pool
- deionizer
- data acquisition and control system
- oxygen injection facility
- pumps, piping and flow meters

- radiation alarm
- fire suppression system

The capital and operating costs for this facility, escalated to 1980 dollars, are presented in Tables 35 and 36.

E. Advantages and Disadvantages of Gamma Radiation for Treatment of Contaminated Lagoon Sediment

Gamma radiation offers what appears to be a relatively low cost method of decontamination of explosives in lagoon sediment. Degradation of explosives by this method has been shown to be effective, however, there are many unknowns associated with this process for treating high concentrations of explosives. Research will have to be conducted to determine the following parameters:

- safety factors associated with exposure of high concentrations of explosives to gamma radiation
- optimum conditions for degradation
- degradation rates

It appears that explosive-degradation by gamma radiation and electron beam processing in the presence of air and ultraviolet ozonolysis (to be discussed in a later section) all proceed via similar degradation pathways. The gamma radiation has the advantage in this situation in that it is not significantly hindered by the presence of sediment or explosive crystals. This penetration ability is also a disadvantage due to the high shielding requirements. Unlike electron-beam and ultraviolet, gamma radiation can not be turned off with a flick of a switch.

The major disadvantage associated with gamma radiation is negative public opinion. This problem will be present at the site and could be of particular importance during transport of the source.

F. Laboratory and Pilot-Scale Tests with Gamma Radiation

The laboratory evaluation of gamma irradiation of the explosive contaminated sediment will be conducted at Sandia Laboratories in Albuquerque, New Mexico. The levels of explosives in the sediment will be determined before and after treatment at Atlantic Research Corporation. TNT, RDX, DNT and tetryl levels will be determined.

Table 35. Capital Costs for Gamma Radiation Facility

<u>Quantity</u>	<u>Equipment</u>	<u>Total</u>	<u>Reference</u>
1	Dredge: Porta-Dredge PD-4LS-1136 liter/min	\$ 53,260	Salemink, 1980
1	Gamma Radiation facility	\$798,840	EPA, 1979
COSTS FOR GAMMA RADIATION		<hr/>	
		\$852,100	
<u>Biological Treatment with RBC</u>			
4	Anoxic RBC: 24,000 ft <sup>2</sup> media area each, steel tank	172,000	Gerhardt, 1980
3	Aerobic RBC: 24,000 ft <sup>2</sup> media area each, steel tank	114,000	Gerhardt, 1980
1	Clarifier tank: 15,140 liter (4000 gal) coal tar epoxy coated carbon steel	3,300	Peters and Timmerhaus, 1968
1	Sand Filter	<hr/> 28,000	
		\$317,300	
	TOTAL CAPITAL COSTS	\$1,169,400	

Table 36. Yearly Costs for Gamma Radiation Facility

Electricity (100,000 KWH/yr @ \$0.07/KWH) *	\$ 7,000
Maintenance (3% of capital)	35,082
Labor (3 technicians @ \$45,000/man year 1 supervisor @ \$75,000/may year)	135,000 75,000
Installation (5% of capital)	<u>58,470</u>
TOTAL YEARLY COSTS	<u>\$310,552</u>

\*EPA, 1979

The sediment will be exposed to gamma radiation as a 10-15% slurry in 100 ml plastic bottles. The samples will be subjected to a variety of process conditions. The parameters which will be varied are the radiation dose, the percent solids in the slurry and aeration of the slurry. The effects of these variables on explosives degradation will be evaluated, and this information will be used to generate revised cost estimates. Total costs for the laboratory scale evaluation, including both sample irradiation and analysis, are estimated at \$750.

## VIII. ULTRAVIOLET-OXIDATION

### A. Process Description

Photochemistry has long been utilized as a cool method for initiating synthetic chemical reactions such as chlorination, polymerization, etc. In the last decade, the ability of photochemistry to initiate degradation reactions to destroy environmentally hazardous materials has been recognized. Several researchers have evaluated photochemical degradative techniques for this purpose. Usually shortwave ultraviolet light (2537 Å) is used to initiate the desired reaction and the conditions are optimized to favor the desired product(s). Other agents which have a synergistic effect with the ultraviolet light may be added to the reactant media to increase the degradation rate. Several oxidizing agents have been investigated for this purpose including ozone, Oxone and hydrogen peroxide.

Essentially the photochemical reaction is initiated by the absorption of ultraviolet light to promote a ground state electron in the molecule to a higher energy "excited" state. The energy in this excited state can be dissipated in several competing pathways - 1) internal conversion to the ground state, 2) fluorescence, 3) intersystem crossing to a triple excited state, 4) phosphorescence or 5) chemical reaction (i.e., dissociation, rearrangement, etc.) To minimize the non-desired reactions the conditions of the reaction medium must be optimized to favor the desired chemical reaction. Since the excited states are normally highly reactive, optimization can be accomplished by providing a suitable oxidizing, reducing, polymerization reagent, etc., in the medium.

There are several conditions which must be met to maximize photochemical degradation:

- The chemical to be degraded must absorb the incident light. Thus, the absorption spectrum of the compound should normally overlap with the emission spectrum of the lamp. There are ways to get around this requirement, (such as employing an energy transfer agent); however, the photochemical efficiency is greatly reduced.
- If possible, it is normally more efficient to irradiate the hazardous material with a wavelength of light that corresponds in energy with the particular excited state at which the photochemical reaction occurs.
- The light must reach the hazardous molecule in solution before it can be absorbed. As the ultraviolet light passes through the solution, it is attenuated by absorption and scattering processes. This requirement places restrictions on the pathlength (distance between the lamps) to that distance the light can penetrate. Thus a short pathlength must be used and the solvent should be relatively optically clear at the irradiation wavelength. Alternatively, turbulent flow can be employed to ensure that all of the hazardous material comes within the pathlength of the ultraviolet light.

- If a reactant is employed, it must come into contact with the photochemically excited molecule. Therefore, the reactant must be well dispersed throughout the solution.

If the above conditions are met, the photochemical reaction will occur. The next problem then becomes one of optimizing the reactor conditions, e.g. pH, lamp spacing, flowpath of liquid, concentrations of hazardous chemical and reactant, residence time, temperature, etc. These parameters will normally be different for different chemical/solvent systems, however, optimization can be accomplished rapidly by extrapolating from results of similar hazardous material/solvent systems.

Several reactor systems have been designed for UV photochemical degradation. These systems are shown in Figures 21-24. The reactors shown in Figures 21 and 22 are ultraviolet-ozonolysis systems. Both of these units employ long pathlengths and rely on stirring action (from ozone bubbling or mechanical stirrer) to provide contact of the hazardous material with the light. The ULTROX<sup>®</sup> P801 pilot plant (Figure 21) is manufactured by Westgate Research Corporation. The 316 stainless steel reactor has a capacity of 2555 liters (675 gal). The liquid to be treated is pumped at a rate of 1.9-37.9 liters/min (0.5-10 gal/min) through a series of six stages. Each stage has twenty-four 65 watt shortwave (low pressure) mercury lamps which emit ultraviolet light ( $\approx 95\%$  at 2537 Å). Spacing between lamps is approximately 7.5 cm (3 in) center-to-center and approximately 7.5 cm (3 in) lamp center to wall. Each lamp is jacketed with a quartz or Vicor sleeve for protection. Ozone is produced by a PCI Ozone Corporation Model G-14 ozone generator. This unit is capable of producing 18 kg/day of ozone at a 2% concentration using oxygen feed. The ozone is fed into the reaction solution via six spargers, one located along the bottom of each chamber. The gases are collected at the tops of the chambers and routed through a heated exhaust tube to decompose any residual ozone (Zeff, 1980; Westgate Research Corporation, 1979).

The second ultraviolet ozonolysis system was made by Houston Research, Inc. (now presumably defunct). This system utilizes the tank arrangement shown in Figure 22. The ultraviolet lights are placed in quartz wells which are equally spaced in the tank. Low, medium or high pressure lamps can be used to provide different irradiation spectra. Contact of the hazardous material with the light is accomplished by stirring the solution with a mechanical stirrer. The ozone is fed into the solution through spargers located in the bottom of the tank (Garrison et al., 1975; Schneider et al., 1979).

The Navy has a pilot reactor very similar in design to Westgate's Ultrox unit except that a liquid oxidant is used in place of ozone. This reactor, shown in Figure 23, is a 1325 liter (350 gal) 316 stainless steel tank with 908 liters (240 gal) of the liquid exposed to the light at any one time (Andrews, 1980). The reactor contains eight chambers, each housing fourteen 163 cm (64 in), 65 watt low pressure mercury lamps (2537 Å). Each lamp is surrounded by a quartz jacket. The lamps are placed at 7.6 cm (3 in) centers with 3.2 cm (1 1/4 in) from the lamp center to the wall of the chamber. Maximum liquid film depth for this reactor is 2.5 cm (1 in) which is slightly less than that used by Westgate. The liquid oxidant is mixed with the hazardous chemical in the influent line.

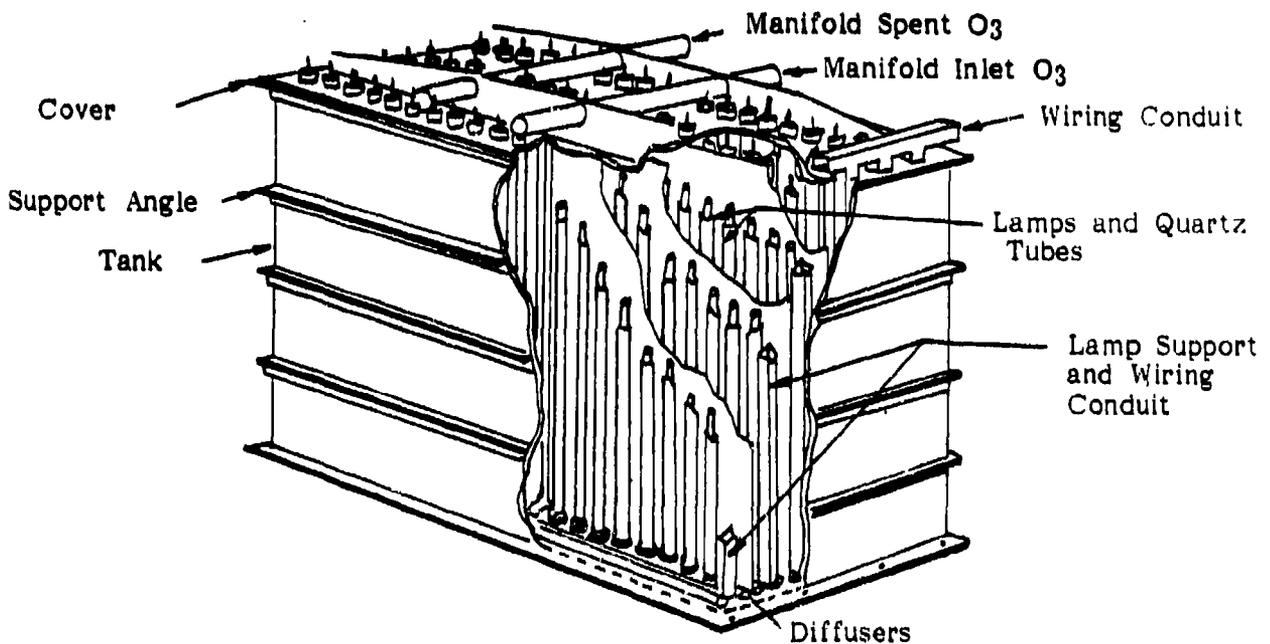
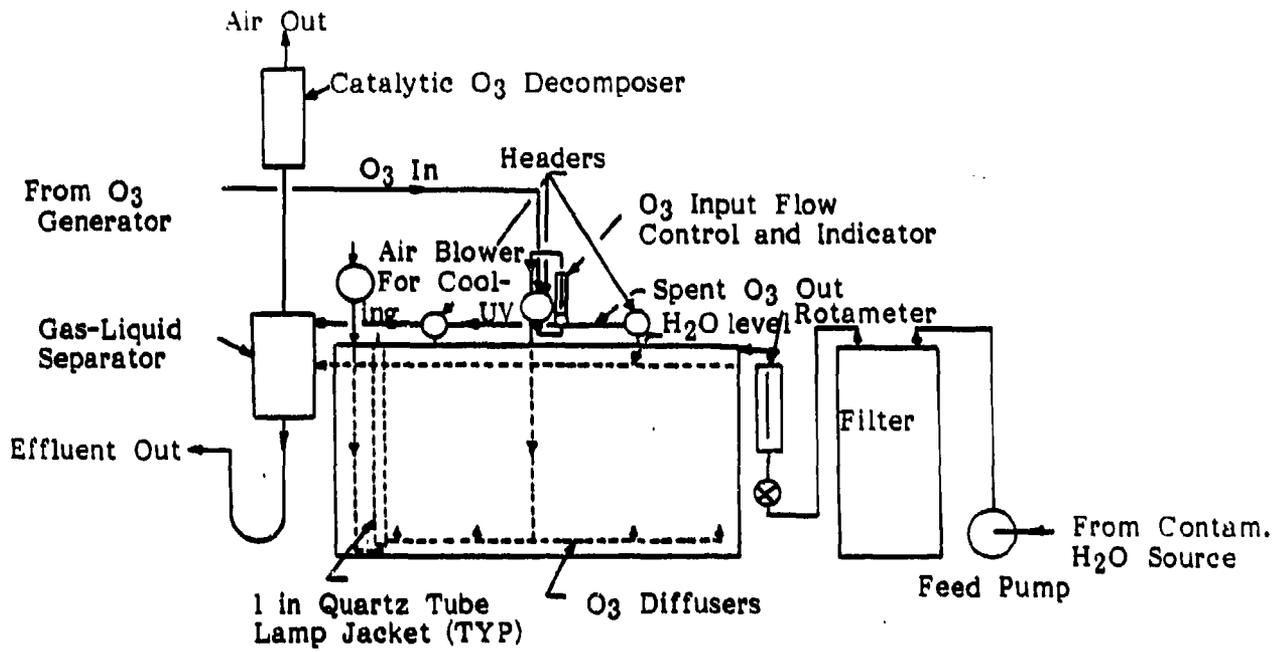


Figure 21. Westgate's Model P801 ULTRON<sup>®</sup> Pilot Plant (Westgate Research Corp., 1979)

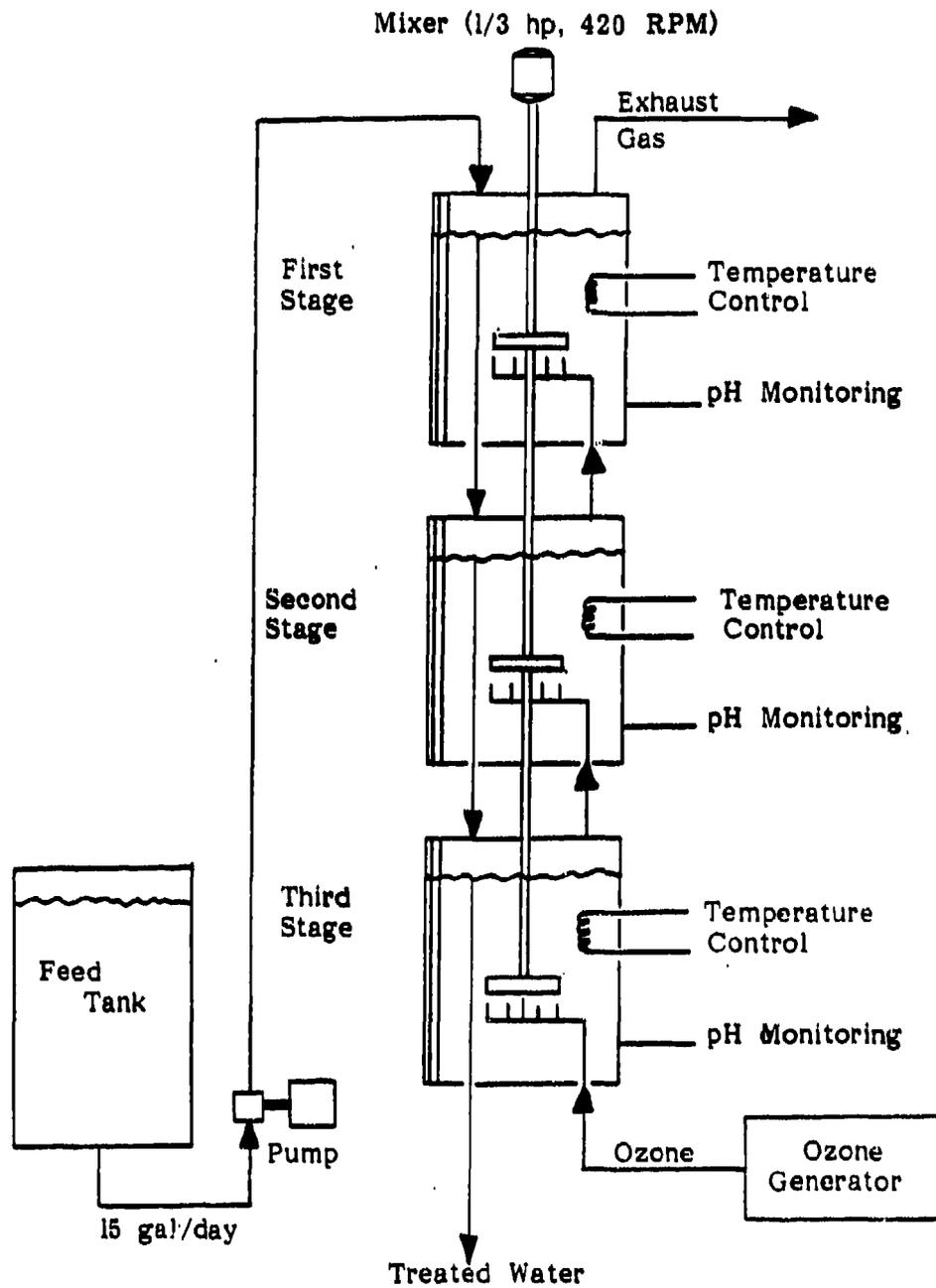


Figure 22. Houston Research's Prototype UV-ozone Reactor for Cyanide Degradation (Garrison, 1973)

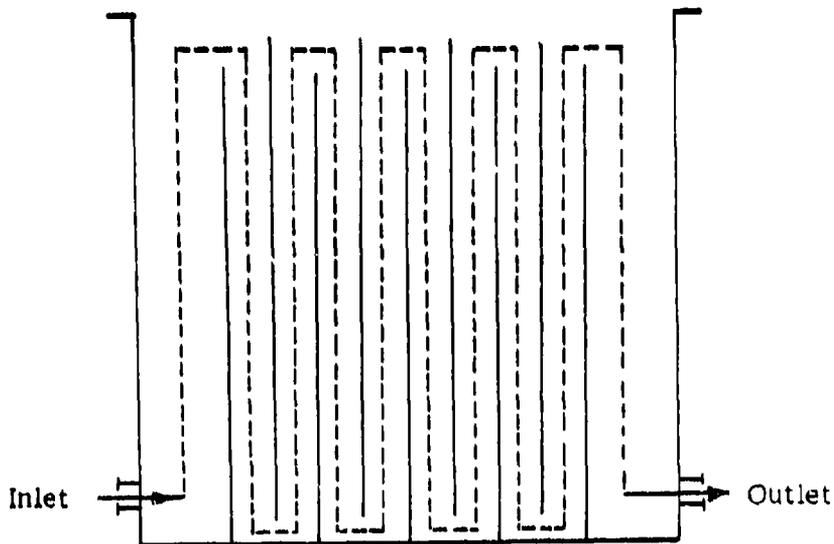
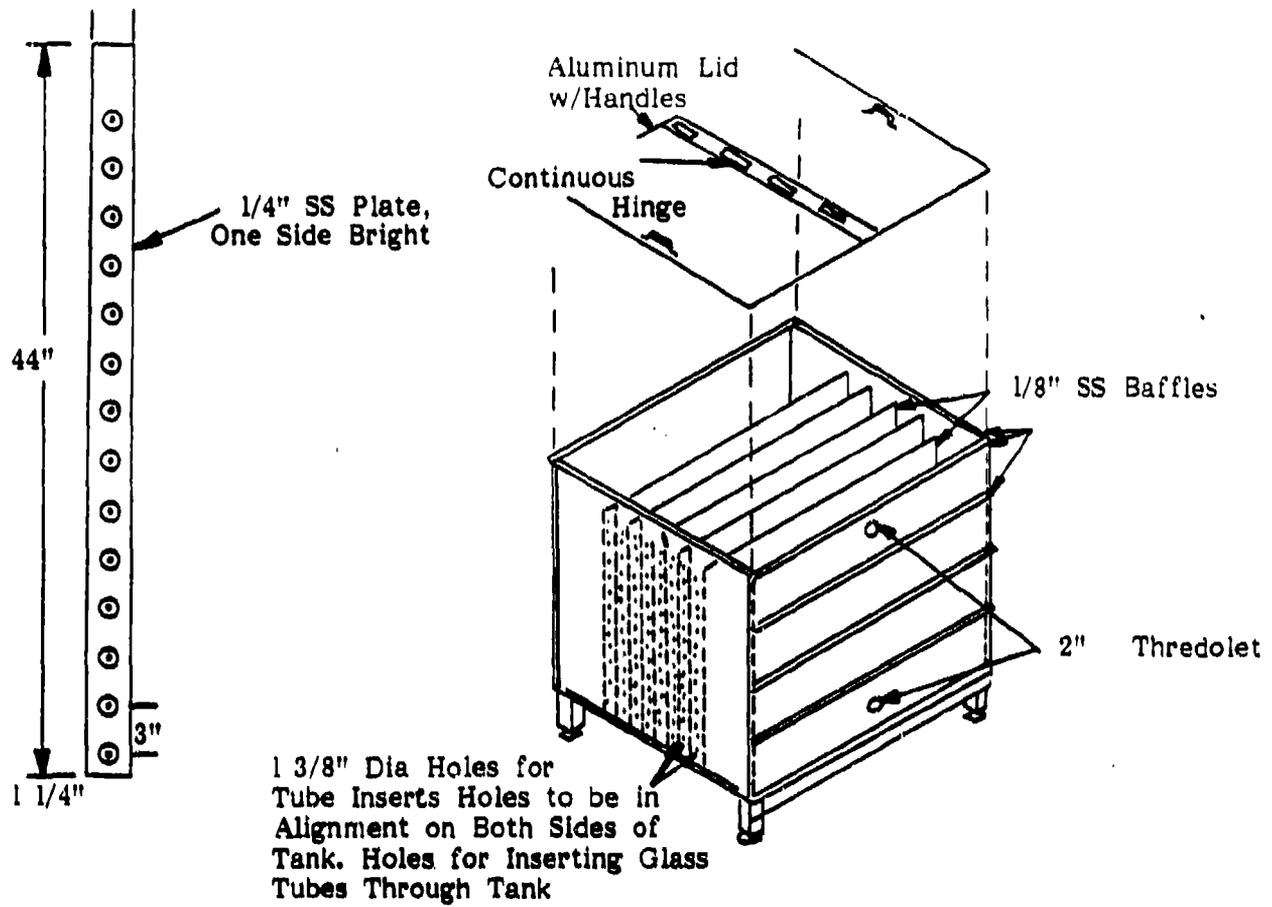


Figure 23. Navy's Pilot Ultraviolet-Peroxide Reactor (Andrews, 1980)

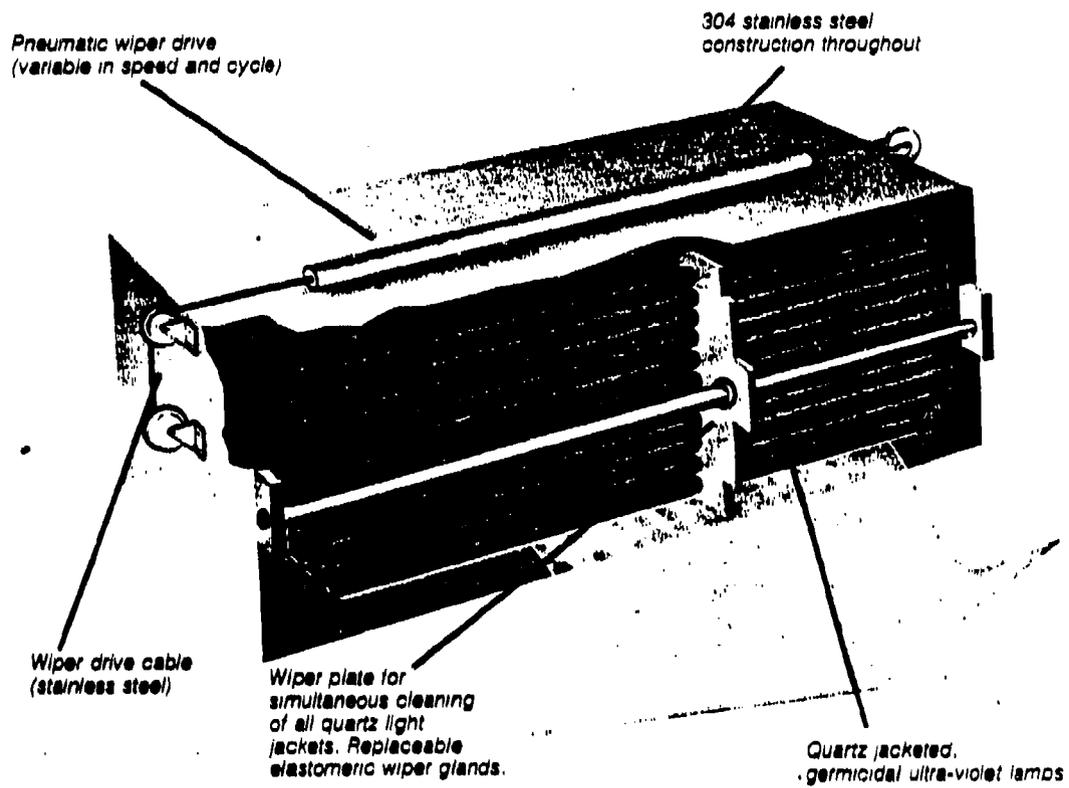


Figure 24. Pure Water Systems, Inc. Ultraviolet Reactor  
(Pure Water Systems, Inc., undated)

The fourth reactor design available is that produced commercially by Pure Water Systems, Inc. This reactor, shown in Figure 24, differs from the reactors previously described in that it employs very short liquid film depth. The commercial scale unit, SE-15B, is a 1.05 m (42 in) x 1.05 m (42 in) x 1.52m (60 in) 304 stainless steel reactor. It has 676 quartz jacketed 152 cm (60 in) low pressure ultraviolet lamps. Distance between the quartz jackets is 1 cm yielding an average film depth of 0.5 cm. Hydraulically, the unit can handle a liquid flow rate of 56.8 million liters/day (15.0 MGD). The unit is equipped with an automatic wiper system which periodically wipes any deposits from the quartz tubes. Theoretically, this unit can be modified to handle liquid oxidants or ozone.

## B. Literature Review and Evaluation

### L. Ultraviolet-Oxidation Systems for Treatment of Wastewaters

Many of the early ultraviolet-oxidant studies were aimed at sterilization of water. Zeff et al. (1974;1975) investigated the effects of ultraviolet light and a combination of ultraviolet light and ozone on the survival of bacteria in water. They found that the combination of UV and ozone was more effective in destroying *Escherichia coli*, *Streptococcus faecalis*, *Klebsiella pneumoniae* and *Acanthamoeba castellanii* than either UV or ozone alone. Effective disinfection was obtained with an ozone concentration of 0.3 mg/l in the presence of ultraviolet light and a contact time of two minutes. Ozone concentrations of 0.5 to 1.5 mg/l were necessary for disinfection in the absence of the light. An increase in temperature to 40°C did not significantly improve the disinfection effectiveness.

Ultraviolet disinfection of the effluent from an activated sludge sewage treatment was demonstrated by Wren (1979) using a Pure Water Systems Model SE-8B reactor. This reactor measures 76.2 cm (30 in) x 76.2 cm (30 in) x 152.4 cm (60 in) and contains 400 quartz jacketed 85 watt low pressure ultraviolet lamps. The liquid film thickness was ~0.5 cm (1/2 in). A pos-a-wipe cleaning system was used to remove deposits from the quartz jackets. Fecal coliforms in the influent and effluent from the reactor were measured. This data are presented in Table 37. Disinfection effectiveness was 99.8% at flow rates of 27.7-28.4 million liters per day (6.0-7.5 MGD).

Early work on the synergistic effects of ultraviolet light and ozone on the destruction of cyanides in water was performed by Houston Research, Inc. (Garrison et al., 1973; Mauk et al., 1976; Garrison et al., 1975). The apparatus used for these studies is shown in Figure 22. The initial studies were an evaluation of the ozonation of cyanides. In these studies, iron cyanides were found to be very resistant to ozonolysis. However, upon heating the iron cyanide solution and/or irradiating it with ultraviolet light (2537 Å), the destruction of iron cyanides was accomplished. A comparison of the effects of heat, light and ozone concentration on the degradation of photobleach containing iron cyanide is shown in Figure 25. The most rapid degradation was obtained with high temperatures (66°C, 150°F), 16 watts of ultraviolet light and 5% ozone. The authors stress caution in design of a reactor for destruction of cyanides. The heat and/or the ultraviolet light should only be used when necessary since both heat and ultraviolet light accelerate the rate of ozone decomposition.

Table 37. Fecal Coliform Counts\* Before and After Ultraviolet Sterilization (Wren, 1979)

<u>INFLUENT</u>	<u>EFFLUENT</u>	<u>INFLUENT S/S mg/l</u>
<b>6.0 MGD FLOW RATE</b>		
99,000	28	17
147,000	67	9
298,000	53	7
190,000	17	25
100,000	11	17
93,000	14	24
136,000	11	10
57,000	13	15
<b>6.5 MGD FLOW RATE</b>		
239,000	79	6
307,000	36	7
22,000	40	3
<b>7.0 MGD FLOW RATE</b>		
76,500	17	7
560,000	90	18
25,000	14	8
<b>7.5 MGD FLOW RATE</b>		
155,000	6	20
46,000	28	15
11,000	26	10
15,000	13	9
48,000	35	17

\*Membrane Filter Technique

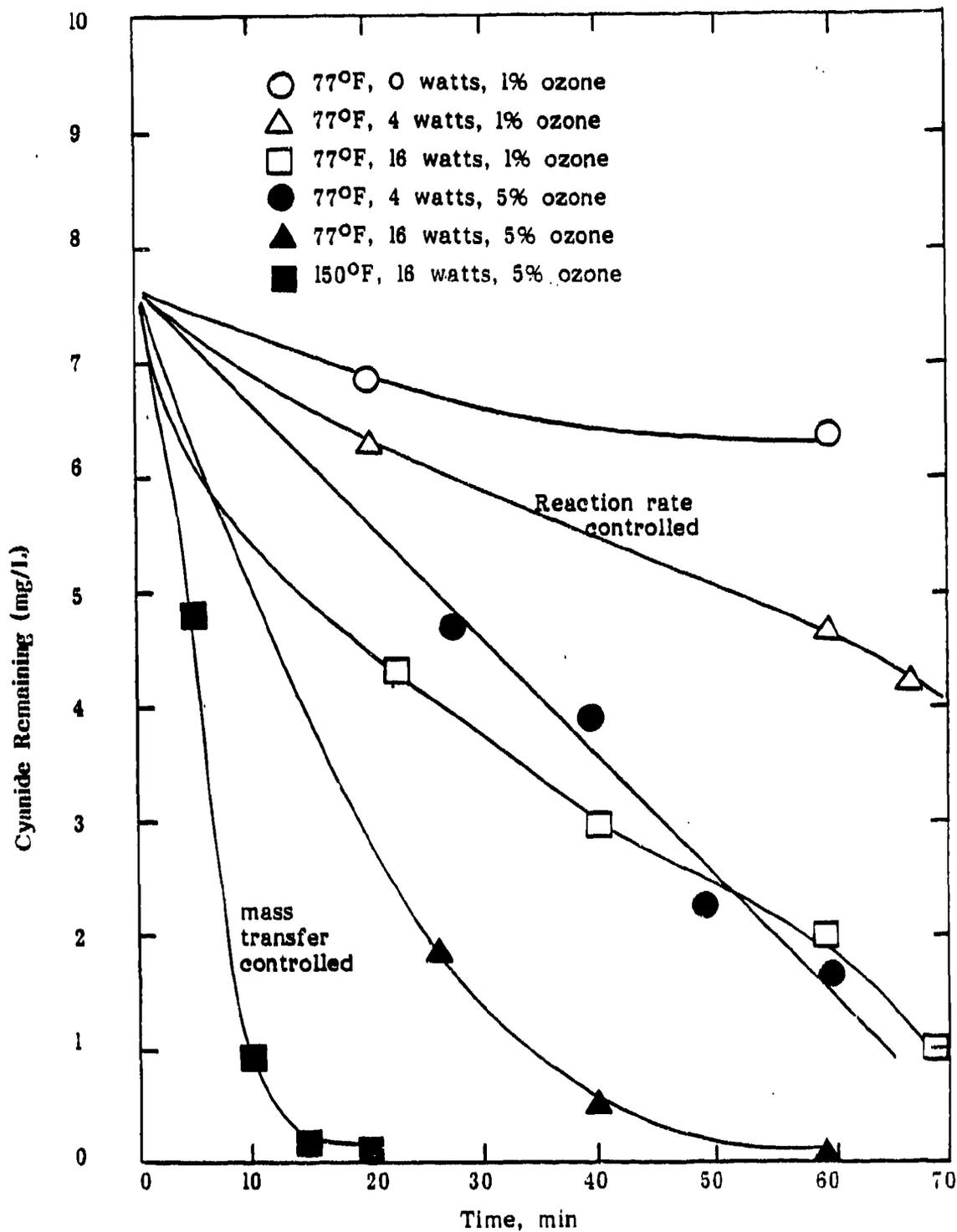


Figure 25. Effect of UV Wattage, Ozone Concentration and Temperature on the Decomposition of Photo Bleach (Garrison et al., 1970)

The UV-ozonolysis of "refractory" organic compounds was investigated by Hewes et al. (1974). For the study, they used a single stage reactor similar to that shown in Figure 22. Their reactor was 27.5 cm (10 13/16 in) tall, 22.9 (9 in) in diameter with a volume of 9.92 liters (2.62 gal). A 15 watt low pressure mercury lamp was 2/3 immersed in the solution to give a useful ultraviolet dosage of 0.44 watts/liter. This number was calculated on the following basis - 2/3 of the light reached the solution, 60% electric conversion efficiency, 74% jacket transmission efficiency and 9.92 liters of liquid.

$$\frac{2/3(15 \text{ watts}) \times 0.60 \times 0.74}{9.92 \text{ liters}} = 0.44 \text{ watts/liter}$$

The lamp efficiency (0.60 x 0.74 x 100% = 44%) is high. Normal efficiency for these lamps is approximately 35% at 2537Å. Using these numbers, the input into the solution would be 0.35 watts/liter. Ozone concentration and flow rates were varied throughout the tests. The "refractory" compounds chosen for this study were glycine (an amino acid, NH<sub>2</sub>CH<sub>2</sub>COOH), acetic acid, ethanol and glycerol (CH<sub>2</sub>OHCH-OHCH<sub>2</sub>OH).

Oxidation of 106 mg/l of acetic acid without UV was not accomplished after 10 hours of ozonation at a flow of 45.6 mg/l min. The addition of ultraviolet light resulted in complete oxidation in approximately four hours. An increase in temperature from 30°C to 50°C improved the oxidation rate. The general effects of UV and temperature on the ozonation of the other compounds were similar to that observed with acetic acid. However, the degree to which UV and temperature increased the degradation rate varied with the compound tested. The results of these experiments are summarized in Table 38.

The results of UV ozonolysis on these compounds were compared to those obtained on the same concentrations of these chemicals by Westgate (Zeff et al., 1975). Westgate used a 15.2 cm (6 in) diameter 91.4 cm (36 in) high reactor with a liquid volume of 12 liters. One 43 watt 2537Å UV lamp was completely submerged in the reactor. Effective output wattage was calculated to be 15 watts (assuming 35% efficiency). In comparison of the reactant conditions, Zeff et al., (1975) state the following differences in operating variables.

	<u>Houston</u>	<u>Westgate</u>
$\frac{\text{O}_3 \text{ mass flow}}{\text{vol of H}_2\text{O}}$	$\frac{4.5 \text{ mg O}_3/\text{min}}{\text{liter H}_2\text{O}}$	$\frac{3.95 \text{ mg O}_3/\text{min}}{\text{liter H}_2\text{O}}$
$\frac{\text{UV Power}}{\text{Vol of H}_2\text{O}}$	$\frac{1.5 \text{ watts}}{\text{liter H}_2\text{O}}$	$\frac{3.58 \text{ watts}}{\text{liter H}_2\text{O}}$

Table 38. Ultraviolet-Ozonolysis of "Refractory" Organic Compounds (Hewes et al., 1974)

Chemical	Concentration at To (µg/l)	Concentration 360 min (µg/l)	TOC at To (mg/l)	TOC at 360 min (mg/l)	Effective UV Input Wattage	Ozone Flow Rate (mg/min)	Temperature (°C)	Stirring Rate (RPM)
acetic acid	105.70	50	41	4.3	0	45.64	27-31	708
acetic acid	104.85	16	48	1	3.5	45.64	27-31	704
acetic acid	105.78	0	50	0	3.5	45.84	50	703
ethanol	115.82	0	54.2	38.2	0	43.26	26-28	703
ethanol	115.15	0	54	3	3.5	45.5	28-31	703
ethanol	115.15	0	48	1	3.5	45.5	50	703
glycine	117.38	44*	39	0	0	45.84	26-30	698
glycine	117.28	52*	39	0	3.5	45.84	26-33	701
glycine	117.28	55*	42	0	3.5	45.84	50	707
glycerol	105.56	NG	44	13	3.5	49.58	31	700
glycerol	105.56	NG	44	0	3.5	45.84	27-36	695
glycerol	105.56	NG	44	0	3.5	45.84	50	695

NG: - not given

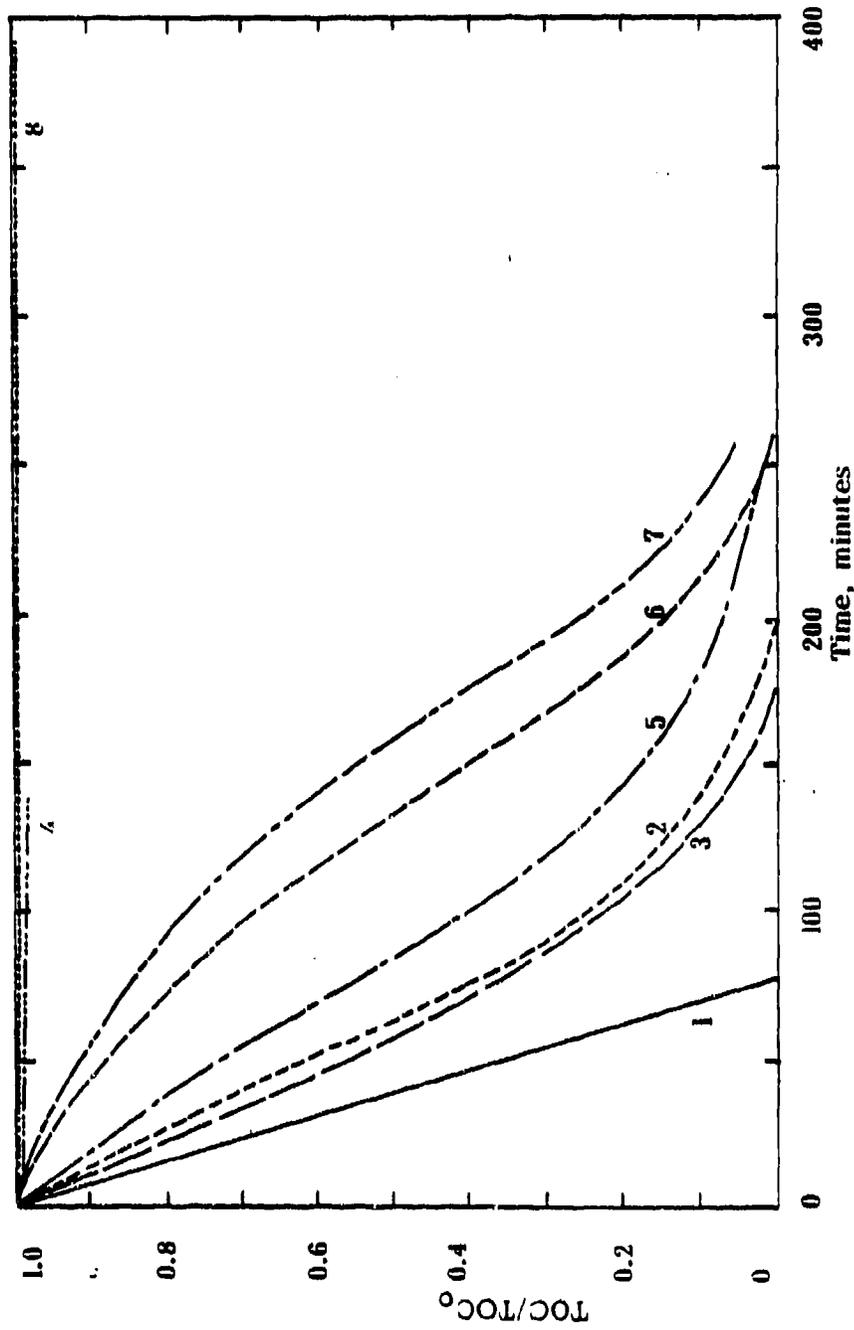
\* - analysis procedures gave glycine concentrations of greater than 0 when no TOC was present in the solution.

After examination of the data in both reports and calculation of actual UV input into the system, the following variables were obtained

	<u>Houston</u>	<u>Westgate</u>
<u>O<sub>3</sub> mass flow</u> vol of H <sub>2</sub> O	<u>4.5 mg O<sub>3</sub>/min</u> liter H <sub>2</sub> O	<u>6.04 mg O<sub>3</sub>/min</u> liter H <sub>2</sub> O
<u>UV power</u> vol H <sub>2</sub> O	<u>0.35 watts</u> liter H <sub>2</sub> O	<u>1.25 watts</u> liter H <sub>2</sub> O

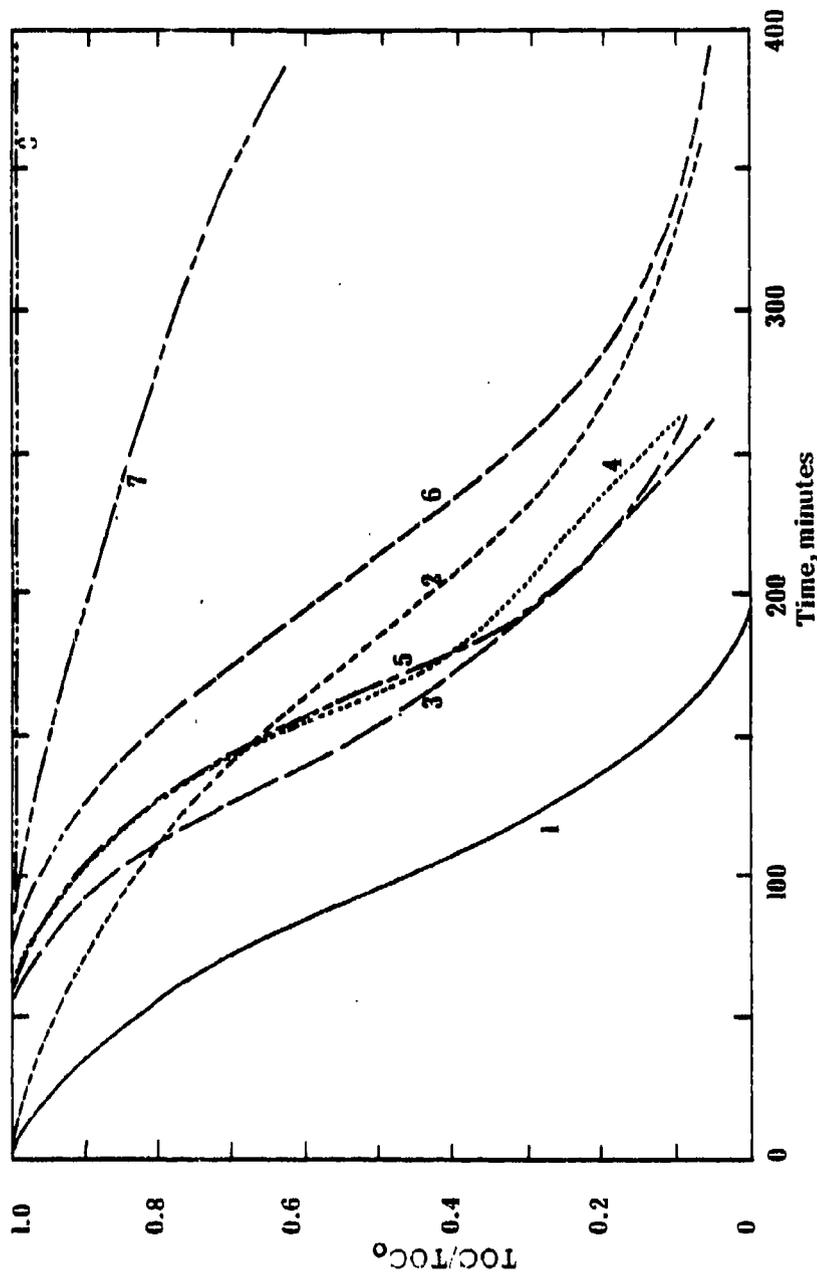
The results of the UV-ozonolysis of acetic acid, ethanol and glycerol by Houston and Westgate (Zeff et al., 1975) are presented in Figures 26-28. A comparison of the results obtained in the two geometry reactors lead to some interesting observations. For example, in Figure 27, Houston observed degradation (up to 40%) of ethanol with ozone alone while Westgate did not (compare lines 7 and 8). Thus, high mass flow of ozone was not effective, however, stirring probably broke up the bubbles and improved mass transfer. Comparison of the room temperature reactions (lines 2, 3, 5 and 6 in Figure 27) yielded interesting information on the stirring effects. Houston's (Figure 27) reaction rate (line 2) was slightly better than Westgate's (line 6) at approximately the same optimum placement of the stirrer in Houston's system. At higher ozone mass flow rates, stirring in Westgate's reactor was obtained by the large volume of gas flowing through the reactor (line 4). The turbulence was so great that mechanical mixing did not improve the degradation rate (compare lines 3 and 5). The turbulence caused by the higher gas volume and greater ozone mass flow resulted in an increase in the degradation rate over that of Houston's system. Increase in temperature in Westgate's system did not increase reaction rate (compare line 4 with line 5) probably due to the wide temperature ranges over which the reactor was run. In conclusion, the data appeared to refute Westgate's observations that stirring and increased temperature have little effect on the degradation rate. In essence, Westgate's provided the stirring by a huge gas flow through the system at the cost of ozone and oxygen expenditures. Temperature effects on the reaction rate were controlled by the reaction mechanism. These effects varied from compound to compound and under different experimental conditions. Thus, temperature effects must be determined on an individual basis.

Schneider et al. (1979) compared Houston Research's and Westgate's data on ultraviolet ozonolysis of glycerol. They used a reactor very similar in design to Houston Research's reactor except that three medium pressure mercury lamps were used (550, 700 and 1200 total watts) and the reactor was larger (total volume ~ 67.3 liters). The ozone feed rate was varied from 33-328 mg/min or an ozone mass flow of 0.49-4.87 mg/min/liter of H<sub>2</sub>O. UV dosages were varied from 1.41 to 8.31 watts/liter. Their results are shown in Figure 29 along with those from Houston and Westgate. They found that both ozone feed rate and UV dosage controlled the rate of the reaction, however, at an ozone feed rate of 328 mg/min (4.87 mg/min/liter of H<sub>2</sub>O) and a UV dosage of 8.31 watts/liter, the degradation reaction became mass transfer limited. The differences between the results of Schneider et al. (1979) and of Hewes et al. (1974) are due to the high input UV dosage and the broader spectrum of UV light used by Schneider et al. (1979).



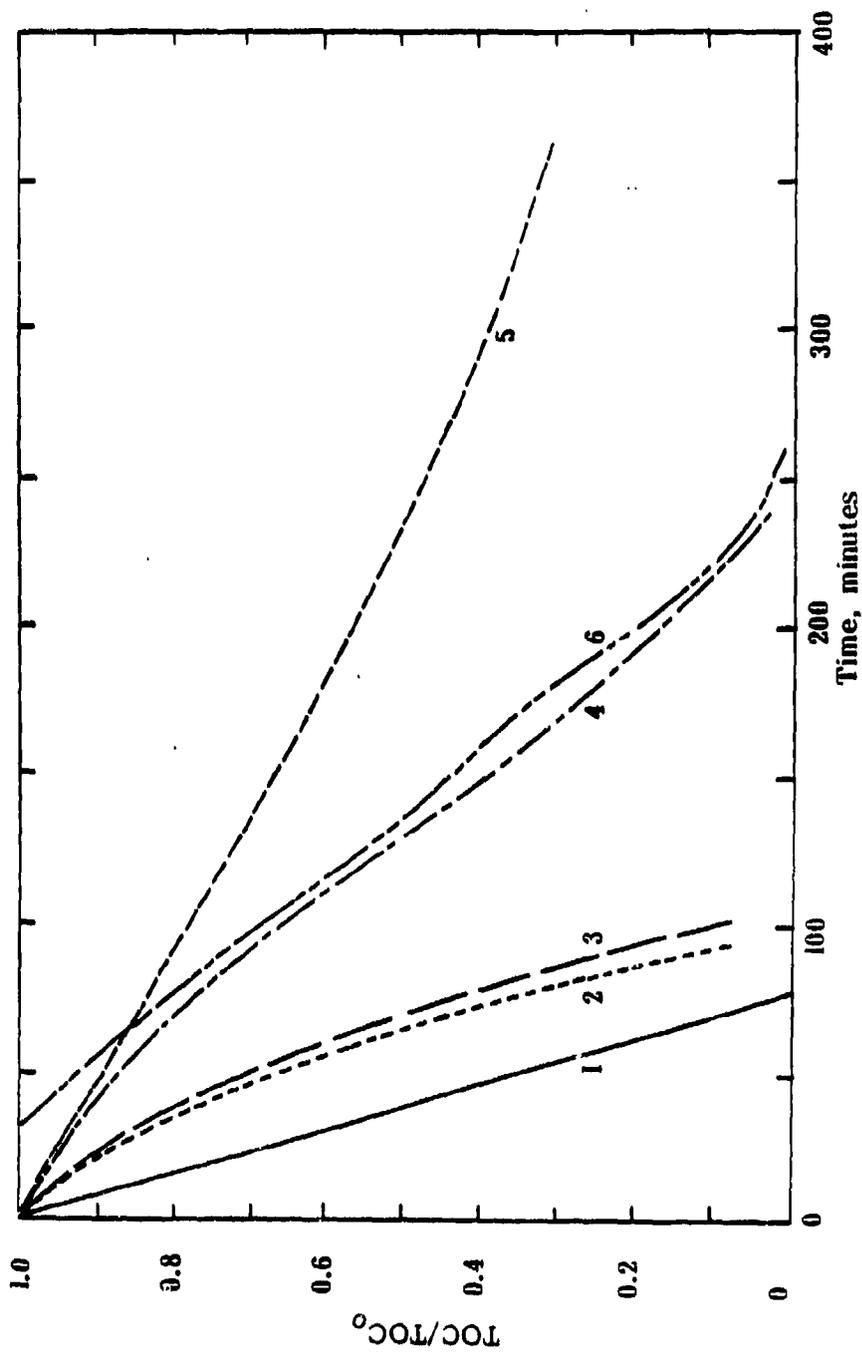
- 1 ——— Limiting line
- 2 - - - - - WG V302 - 74.5 mg O<sub>3</sub> min, @ 2.7% no mech mix
- 3 ——— WG V300 - 72.5 mg O<sub>3</sub>/min @ 2.7% O<sub>3</sub>-mech mix
- 4 - - - - - Houston 27°C, no UV
- 5 ——— WG V303 - 47.4 mg O<sub>3</sub>/min @ 2.55% O<sub>3</sub> mechanical mix Houston 50°C, UV
- 6 - - - - - Houston 30°C
- 7 ——— WG V301 - 72.5 mg O<sub>3</sub>/min @ 2.7%. No UV mech mix
- 8 - - - - - Limiting line

Figure 26. Effects of Ultraviolet Light on Ozonation of Acetic Acid (Zeff et al., 1975)



- |   |       |  |   |       |  |
|---|-------|--|---|-------|--|
| 1 | —     | Houston 50°C, UV   | 5 | - - - | WG Et 302 - 72.5 mg O <sub>3</sub> /min @ 2.7%, mech mix         |
| 2 | - - - | Houston 30°C, UV   | 6 | - - - | WG Et 304 - 47.4 mg O <sub>3</sub> /min @ 2.55% mech mix         |
| 3 | —     | WG Et 300 - 72.5 mg O <sub>3</sub> /min @ 2.5% no mech mix       | 7 | - - - | Houston 27°C no UV   |
| 4 | · · · | WG Et 300 - 72.5 mg O <sub>3</sub> /min @ 2.7%, mech mix 37-48°C | 8 | - - - | WG Et 301 - 72.5 mg O <sub>3</sub> /min @ 2.7% No UV or mech mix |

Figure 27. Effects of Ultraviolet Light on Ozonation of Ethanol (Zeff et al., 1975)



- 1 ——— Limiting Line
- 2 - - - - Houston, 30°C
- 3 - · - · Houston 50°C, UV
- 4 - - - - WG G301 - 49.4 mg O<sub>3</sub>/min @ 2.55% O<sub>3</sub> 29°C, No UV
- 5 - - - - Houston, 27°C, No UV
- 6 - - - - WG G300 - 47.4 mg O<sub>3</sub>/min @ 2.55% O<sub>3</sub>, 28°C mech mix

Figure 28. Effects of Ultraviolet Light on Ozonation of Glycerol (Zeff et al., 1975)

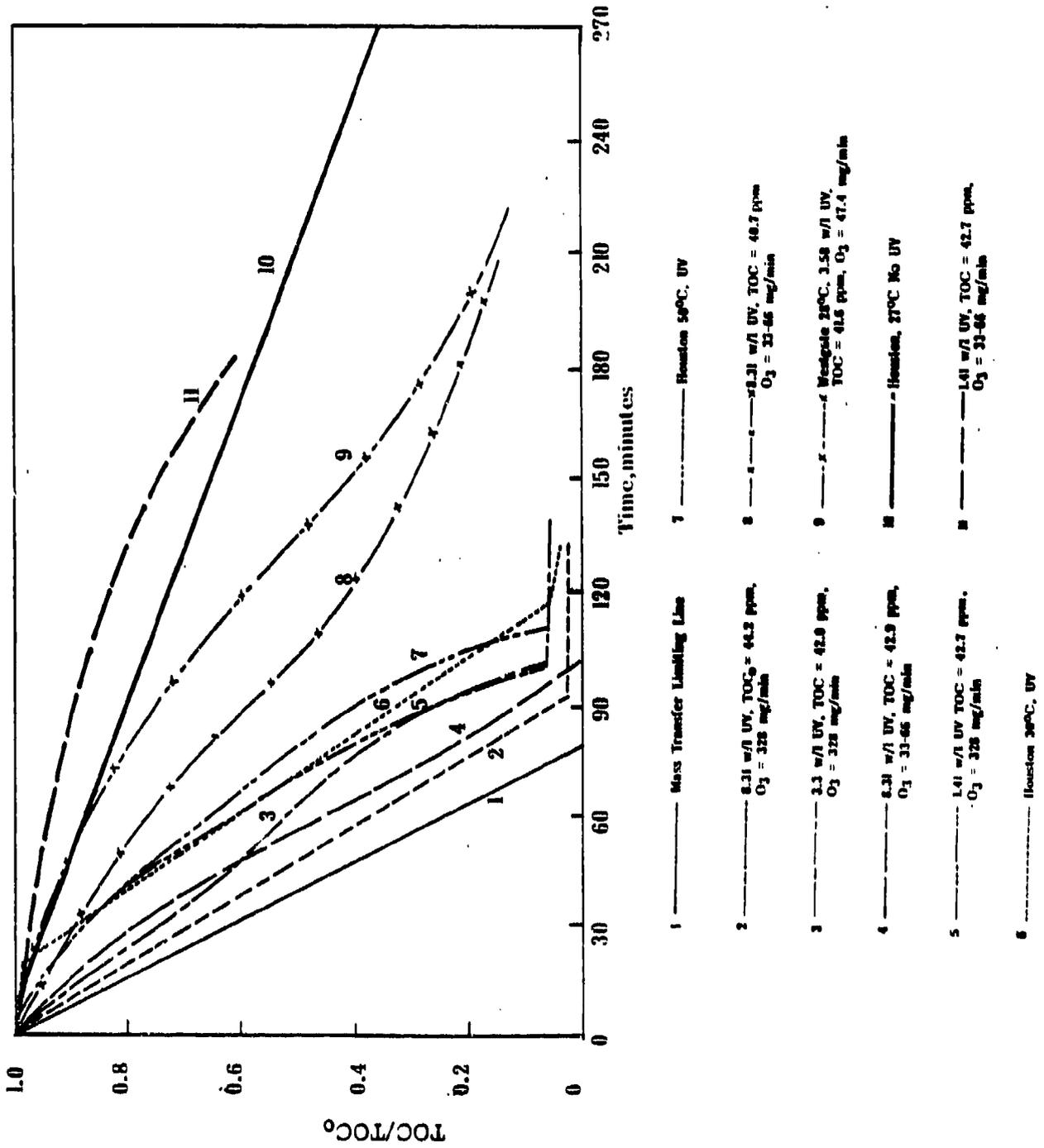


Figure 29. Effects of Ultraviolet Light and Ozone Mass Flow on Glycerol Oxidation (Schneider et al., 1979)

Schneider et al. (1979) also studied the ability of UV-ozonolysis to remove organic contaminants from bilge water. They found that the TOC could be reduced by this method. Those organics with high vapor pressures were stripped from the solution during the ozonolysis.

Westgate (Zeff, 1978) investigated the UV-ozonolysis of kepone in sediment. This system was run with a sediment concentration of 20% by volume. The analytical results (performed by Battelle Northwest) are presented in Table 39. The supernatant showed 21-29% degradation with monohydrokepone as the degradation product. The sediment showed what appeared to be 81% destruction of kepone after 2 hours. Westgate concluded that the kepone on the sediment was dissolving as the kepone in the supernatant was destroyed. This assumption is quite logical and we have observed the same phenomenon in our laboratories. However, the sediment data appears somewhat suspicious for the following reasons: 1) the second extraction of the feed sample is way out of line, 2) the formation of monohydrokepone (a known photolytic degradation product of kepone) does not increase in concentration, and 3) no other degradation products are mentioned (several lower chlorinated "kepones" should have shown up in the GC traces). The apparent discrepancies could be due to the pH of the solutions during the UV-ozonolysis and analysis since the solubility of kepone in aqueous and organic solutions is highly pH dependent.

Leitis (1979; Leitis et al., 1979) studied the oxidation of mononitrobenzene and monochlorobenzenes by ozone, UV-ozone and Fenton's Reagent. A 7.5 cm (3 in) diameter x 76 cm (30 in) high reactor was used in these tests. A short wave 40 watt (138 watts out) UV lamp was employed with an ozone mass flow rate of 0.055 mmoles O<sub>3</sub>/liter soln/min. The initial degradation rates were first order with respect to the substituted benzene when the oxidizing agent was present in excess. No differences in the initial rates were observed for ozone and UV-ozone, indicating that UV does not play an important role in the initial degradation reaction. The degradation of nitrobenzene in the presence of ozone or UV-ozone proceeds via formation of o, m and p-nitrophenols. Nitroresorcinols are then formed, after which oxidation proceeds until stable intermediates such as oxalic acid, formic acid and glyoxal are formed. In contrast to the initial degradation rates, the presence of UV enhances the complete oxidation of these intermediates.

One of the major objectives of Leitis' (1979) study was to determine the nature of the oxygenating species in UV-ozonolysis. For this study, he compared the formation of the o, m and p-nitrophenols with using ozone, UV-ozone and Fenton's Reagents from 0.8 mM nitrobenzene in water. It is generally believed that Fenton's Reagent oxidizes via the hydroxyl radical and results in electrophilic substitution of the benzene ring. The data showed the following ratios of o:m:p isomers after 2 minute reactions time under the various conditions:

	<u>o</u>	<u>m</u>	<u>p</u>
UV-ozone	1.0	3.2±0.2	7.0±0.2
Ozone	1.0	2.5±0.2	6.9±0.2
Fenton's Reagent	1.0	0.67±0.1	0.67±0.1
NaOCl/H <sub>2</sub> O <sub>2</sub>	1.0	1.0±0.1	0.77±0.1

Table 39. Kepone Analyses of Westgate Samples (Zeff, 1978)

Sample	Separable Only (µg/l)		4d Extraction		2nd Extraction		Mixed Samples (µg/kg)		406 Extraction	
	Monohydroxycopone	Kepone	Monohydroxycopone	Kepone	Monohydroxycopone	Kepone	Monohydroxycopone	Kepone	Monohydroxycopone	Kepone
Hayley Hay-Feed	0.12	2.29	3.89	95.69	0.77	31.83	1.54	51.44	1.84	45.69
Effluent--30 min	0.52	1.62	1.95	30.61	1.64	26.51	--	11.88	--	4.87
Effluent--60 min	0.59	1.82	1.27	26.44	0.78	21.34	--	7.54	--	2.60
Effluent--90 min	1.44	1.81	1.24	25.73	0.44	21.81	--	5.68	--	1.78
Effluent--120 min	1.08	1.73	1.20	21.29	0.38	13.35	0.86	2.93	--	0.60

Daily Hay-Feed	Summation of Mixed Sample (µg/kg)		% Kepone Destroyed
	Monohydroxycopone	Kepone	
	7.38	728.14	0.0
Effluent -- 30 min	3.51	81.81	63.8
Effluent -- 60 min	2.64	66.74	73.6
Effluent -- 90 min	3.12	56.01	75.2
Effluent -- 120 min	2.65	48.88	81.9

Thus with UV-ozone and ozone the para position is respectively, 14 and 13.4 times more reactive than the ortho position (number of available positions taken into account). With Fenton's Reagent, the para position is only 1.3 times more reactive than the ortho position. Singlet oxygen generated from  $\text{NaOCl} + \text{H}_2\text{O}_2$  shows a para to ortho reactivity of 1.54. From these data and the rate constants for anisole, and benzoic acid, the author concluded that the mechanism of oxidation of these compounds by ozone or UV-ozone is probably not due to the hydroxyl radical but to ozone itself.

Creeden (1979) investigated ultraviolet/peroxide oxidation of several organic compounds using a bench scale thin film reactor with a low pressure mercury lamp (2537 Å). No lamp wattage or film thickness was given. Presumably film thickness was approximately 0.64 cm (1/4 in) since most of Pure Water's reactions are in this range. The amounts of hydrogen peroxide added to the solutions were chosen based on a cost of \$0.06/liter (\$0.4/gal) (up to 16,000 the theoretical stoichiometric value) except for phenol which required higher  $\text{H}_2\text{O}_2$  concentrations. Dwell time in the reactor was five minutes. Analyses were performed by GC-EC for substituted phenols and GC-FID for phenol. These analyses were performed by Princeton Testing Laboratory. The results of these tests are presented in Table 40. Degradation efficiency appears to be very good in a short residence time. However, no mention was made of degradation products or TOC concentrations.

## 2. Ultraviolet Oxidation Systems for Treatment of Explosives

For ultraviolet light to be effective in UV-ozonolysis, the compound being degraded must absorb the incident light. The absorption spectra of TNT in cyclohexane shows a shoulder at 3150 Å with a molar absorptivity coefficient of 650 liters/mole-cm. This excitation probably is an  $n \rightarrow \pi^*$  transition. The major transition occurs at 2245 Å with an  $\epsilon = 23,000$  liters/mole cm (Sandus and Stagg, 1972). In methanol, this transition exhibits a bathochromic shift to 2270 Å and  $\epsilon$  of 19,200 liter/mole-cm (Kamlet et al., 1962). Thus, significant absorption of TNT occurs at the emission wavelength of the low pressure mercury lamp (2537 Å). RDX also absorbs in the 2537 Å region. This absorption band has a maximum 2380 Å (Smetana and Bulusu, 1977).

The photolysis of RDX in presence and absence of ozone was studied by Smetana and Bulusu (1977). These authors compared photolysis of a 20 mg/l aqueous RDX solution at various wavelength with ozonation. As shown in Figure 30, photolysis was most rapid at a wavelength of 2537 Å. Photolysis at 3500 Å, ozonolysis and UV-ozonolysis ( $\lambda = 3500 \text{ Å}$ ) of a 20 mg/l aqueous RDX solution are presented in Figure 31. As can be observed from the Figure, a synergistic effect on the degradation rate was observed with the combination of UV and ozone. Photolysis of aqueous RDX and crystalline RDX resulted in the evolution of  $\text{N}_2$ , NO,  $\text{N}_2\text{O}$ , CO and  $\text{CO}_2$ .

Table 40. UV-Peroxide Degradation of Phenol Derivatives  
(Creeden, 1979)

RESULTS:

Compound	Initial Conc. (ppm)	Con. After Treatment (ppm)	ml H <sub>2</sub> O <sub>2</sub> added per 100 ml	Percent Removal
Phenol	65,000	8300.0	5	87
Phenol	3,000	0.39	6	99+
Phenol	1,000	0.17	6	99+
Trichlorophenol	800	120	6	85
Trichlorophenol	50	3	6	94
Trichlorophenol	10	0.2	6	98
2,4-Dinitrophenol	5,600	140	6	96
2,4-Dinitrophenol	1,000	ND	6	99+
2,4-Dinitrophenol	100	ND	6	99+
4-Chloro-3-methyl phenol	3,600	1200	6	67
pentachlorophenol	80	ND	6	99+
pentachlorophenol	10	ND	6	98+
pentachlorophenol	1	ND	6	90+

ND - Not Detected

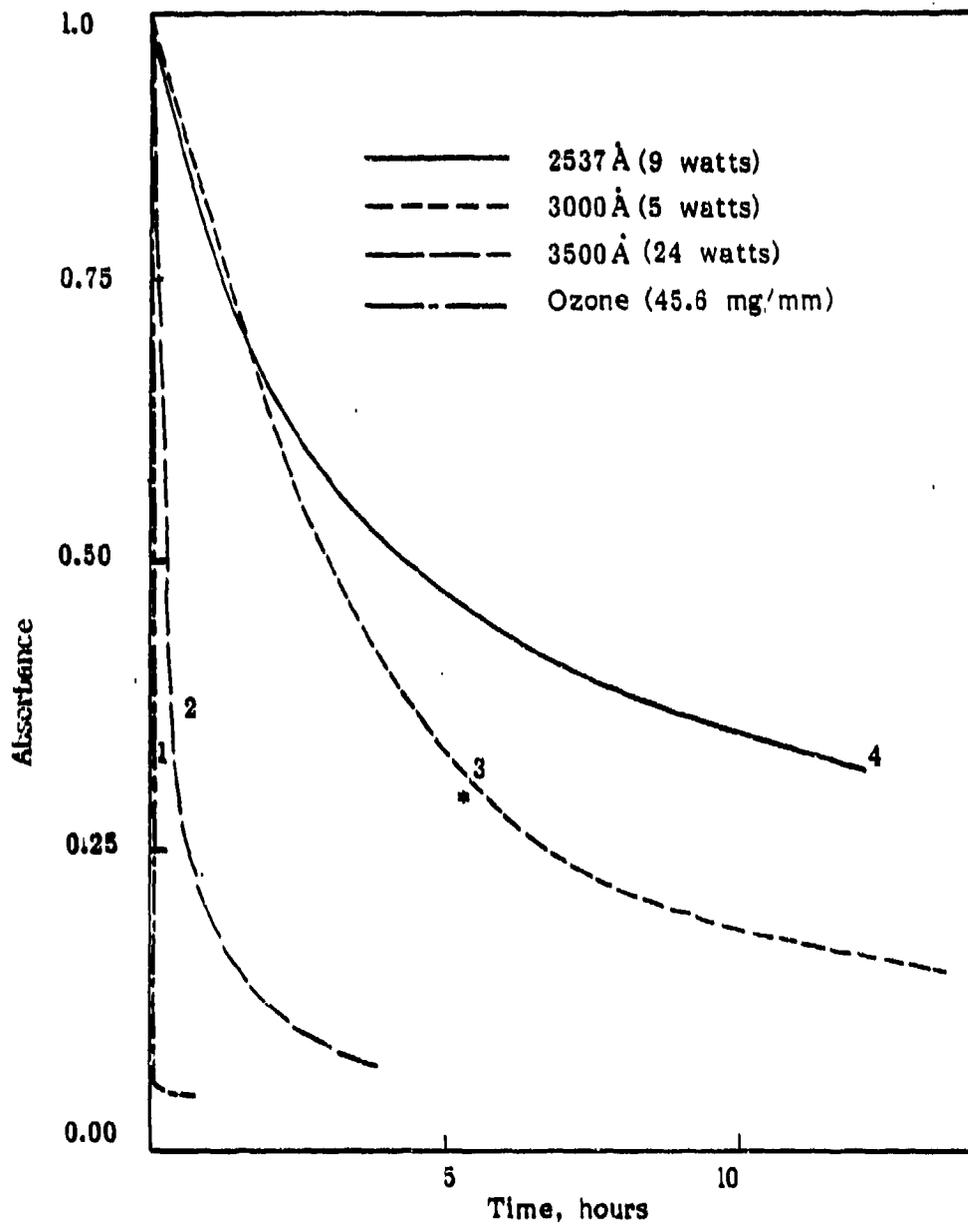


Figure 30. Change in Absorbance of Aqueous RDX Solutions with Time of Photolysis or Ozonolysis (Smetana and Bulusu, 1977)

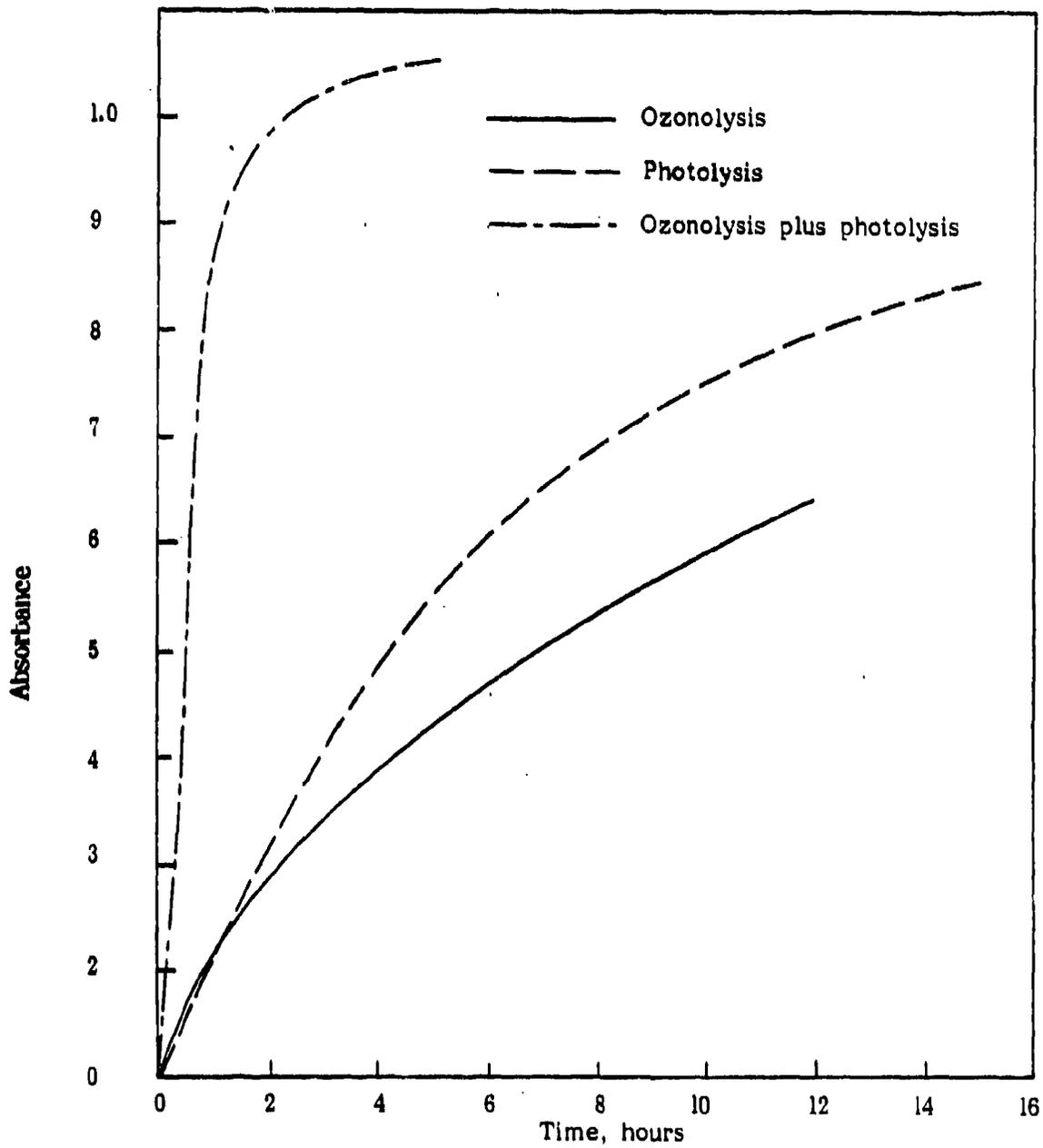


Figure 31. Ozonolysis, Photolysis and Their Combined Action on the Degradation of RDX (Smetana and Bulusu, 1977)

In a more recent study, Day and Zimmermann (1980) investigated UV-ozonolysis of Composition A-5 (95% RDX) wastewater. The objectives of this study were to determine the treatment effectiveness, the optimum operating parameters, and the costs of the UV-ozonolysis system. A Westgate P602 ULTROX<sup>®</sup> pilot unit was used in this study (284 liters, 6 stages, thirty 40 watt low pressure UV lamps). The RDX concentration in the influent ranged from 0.8 mg/l to 20.9 mg/l with an average of 9.7 mg/l. The concentration of RDX in the effluent ranged from 0.1 to 0.3 mg/l with an average of 0.2 mg/l (detection limit 0.1 mg/l). Ozone concentration was varied and 2.1% ozone was determined to be the optimum concentration. From their data on the effluent, the authors concluded that the UV-ozonolysis system was effective for degradation of RDX, was pH independent over the range of 7.15 to 7.85 and was temperature independent over the range of 0°C to 25°C. Since the wastewater treated was from a production system, the parameters of the influent varied widely. Not enough data were presented for a thorough evaluation of the findings, but it does appear that UV-ozonolysis can be readily adapted to a production line situation.

The results of a UV-ozonolysis investigation of the degradation of synthetic and real pink water were reported by Roth and Murphy (1978). A Westgate P602 ULTROX<sup>®</sup> pilot plant was used in this study. The pink water samples contained 140 mg/l TNT, 22 mg/l RDX and 10 mg/l wax resulting in approximately 58 mg/l TOC. Synthetic samples were made to approximately the same concentrations. The treatment parameters were optimized on the synthetic solution, however, actual pink water required a high UV power/carbon input to achieve the same degradation as shown below:

Sample	O <sub>3</sub> /TOC (mg/mg)		UV Input (w/mg)		TOC (mg/l)		
	Stages 1-3	Stages 4-6	Stages 1-3	Stages 4-6	Influent	Stage 3	Stage 6
1024 (synthetic)	15	198	7	60	66	5	1.2
1029 (real)	13	180	11	140	70	5	3

The ozone efficiency was 89.3% in these studies.

The effectiveness of UV-ozone treatment of pink water was studied at Iowa AAP (Layne *et al.*, 1980). An ULTROX<sup>®</sup> P-801 pilot reactor was used in this study. These authors studied the effects of the following parameters on the process efficiency: 1) reaction time, 2) flow rate, 3) number and location of UV lamps, 4) ozone flow rate and 5) pH. In a non-flowing system, the rate of decomposition was shown to be dependent on ozone flow rate. At an ozone flow rate of 4.7 mg/l the slope of the TNT decomposition line was -0.67 mg/l/min. With an ozone flow rate of 26-30, a decomposition rate of approximately 1.7-2.1 mg/l/min was obtained.

UV, ozone and synergistic effects of these reactants on TNT destruction were studied by Layne *et al.* (1980). The results of these experiments are presented in Figure 32. At the onset, only UV light was employed. UV light resulted in a slow decrease in total TOC and TOC due to TNT and pH. At six hours, the UV was turned off and the ozone turned on. A dramatic decrease in the TOC due to

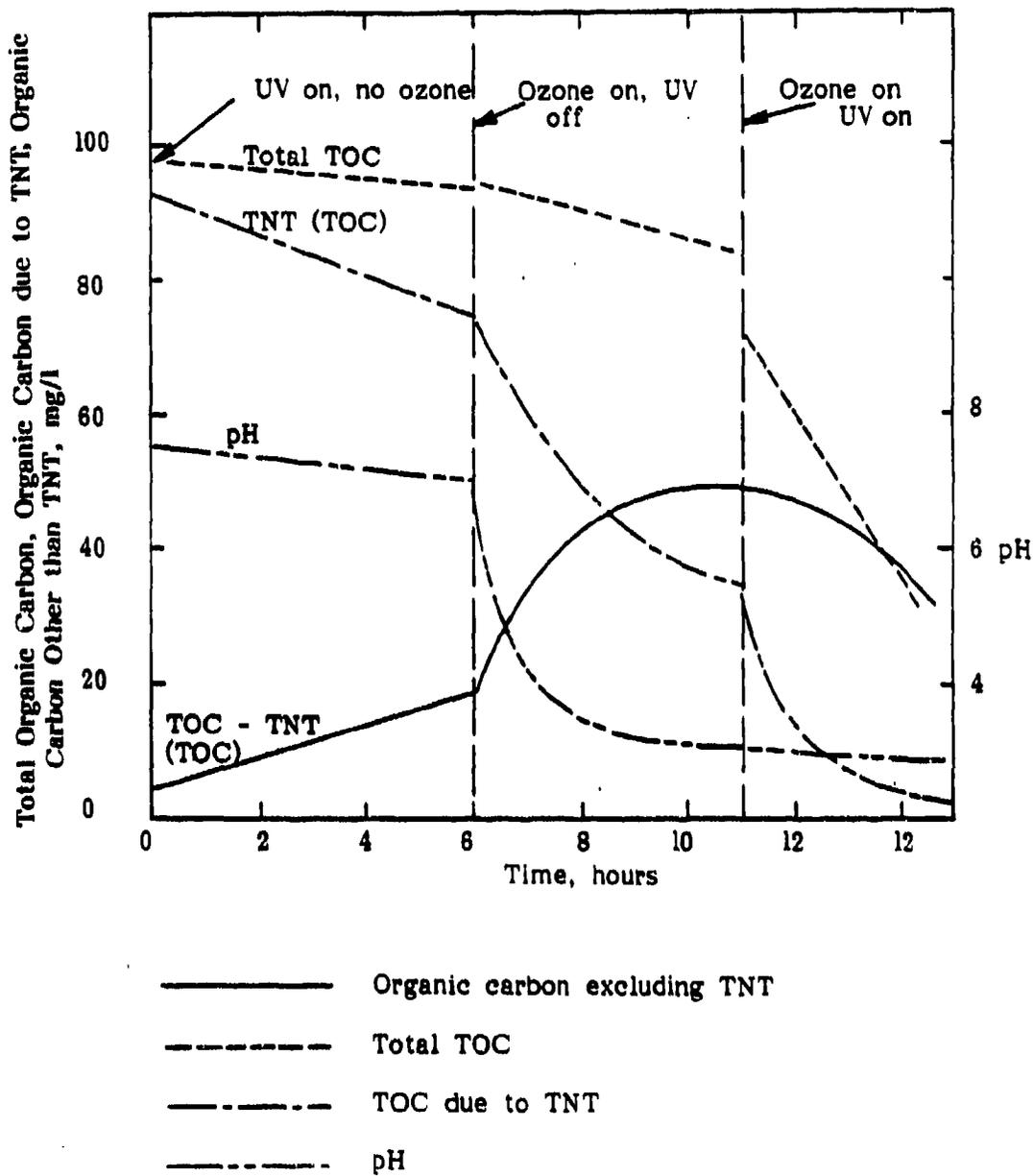


Figure 32. Effects of UV, Ozone and UV-ozone on the Degradation of Pink Water at Zero Flow\* (Layne et al., 1980)

\*This figure represents a combination of Figures 5 and 7 in the report.

TNT was observed. The pH also decreased dramatically. A small increase in the rate of decrease in total TOC was observed. When the UV and ozone were both turned on at 11 hours, an increase in the rate of decrease in the TOC due to TNT was observed while the pH remained almost constant. A dramatic increase in the rate of disappearance of total TOC was also observed. These results agree with those of Leitis (1979) in that ozone plays the major role in the initial degradation of nitroaromatics. However, the combination of UV and ozone is more effective than ozone in the complete degradation of the intermediate compounds. The pH of the solution is not a good measure of degradation.

Nitrate ion is produced in the UV-ozonolysis of TNT and is one of the final products. The rate of nitrate production is shown in Figure 33. This figure has been corrected and data on TNT concentrations (obtained from other figures of the same runs) added when available. The authors (Layne et al., 1980) claim that the high initial nitrate concentration observed in runs 7-12 was due to the stripping of the nitro groups off the TNT in basic media. If this is true, then the ratio of nitrate given off TNT degradation should change dramatically. If one compares the data for run 7-12 (pH adjusted to 9.7) and 7-5 (no pH adjustment), the following results are obtained:

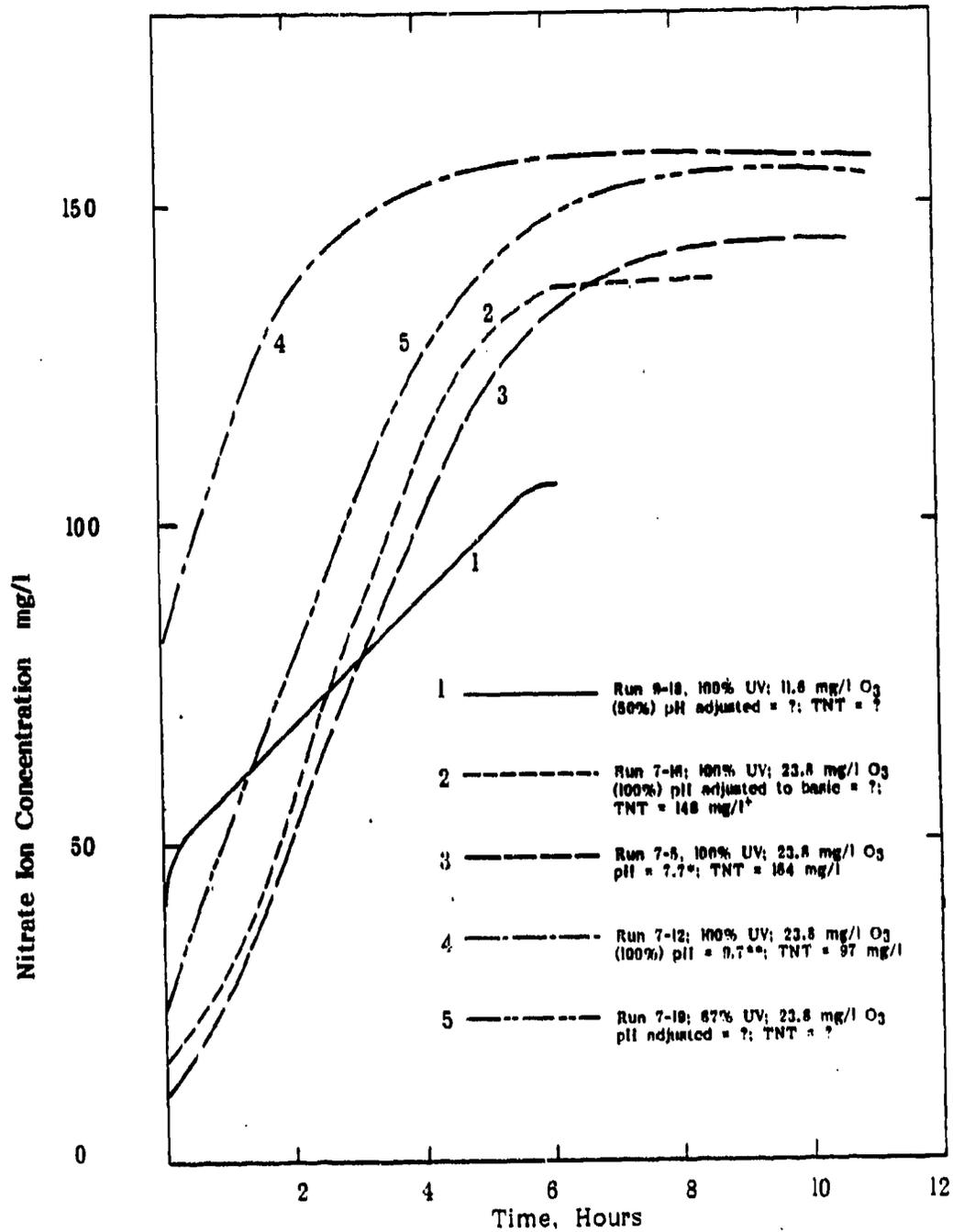
$$7-12 \quad \frac{(\text{NO}_3)}{(\text{TNT})} = \frac{77}{97} = 0.794$$

$$7-5 \quad \frac{(\text{NO}_3)}{(\text{TNT})} = \frac{134}{164} = 0.819$$

Thus, the ratios are approximately constant and no nitrate stripping occurred in basic media. This conclusion is upheld by run 7-16 which showed no high initial nitrate concentration although base was also added. The most likely cause of the shift in the initial 7-12 nitrate concentration was an analytical error which was carried through the experiments.

Runs 7-5 (no pH adjustment) and 7-12 (pH adjusted to 9.7) are further compared in Figures 34 and 35. A comparison of the figures shows that the addition of base increased the rate of disappearance of TNT, and increased the rate of formation of the organic intermediates and disappearance of these intermediates. Since the nitrate ion concentration did not reach its maximum until the "organic carbon other than TNT" began to decline, some of this "organic carbon other than TNT" must be nitrated intermediates. The pH of the reaction media fell until the nitrate ion concentration reached its maximum and the "organic carbon other than TNT" was depleted and then began to level out or increase if the reaction medium was near neutral. This fact would tend to lend support to some of the intermediate products in the degradation reaction proposed by the authors, e.g. oxalic acid.

Layne et al. (1980) also evaluated the degradation of pink water in the ULTROX® P-801 pilot plant in a flow through mode. The liquid flow rate was 0.25 liters/sec which yielded a turnover in 2.6 hours. The ozone flow rates were normally 0.17 m<sup>3</sup>/min, however, the flows were varied. The reactor was initially filled with water and the pink water flow started. Approximately four hours were required



\* ref Figure 11  
 † ref Figure 4  
 \*\*ref text p26  
 \*\*\*ref Figure 7

Figure 33. Formation of Nitrate Ion During UV-Ozonolysis of TNT in Zero Flow Mode (Layne et al., 1980)

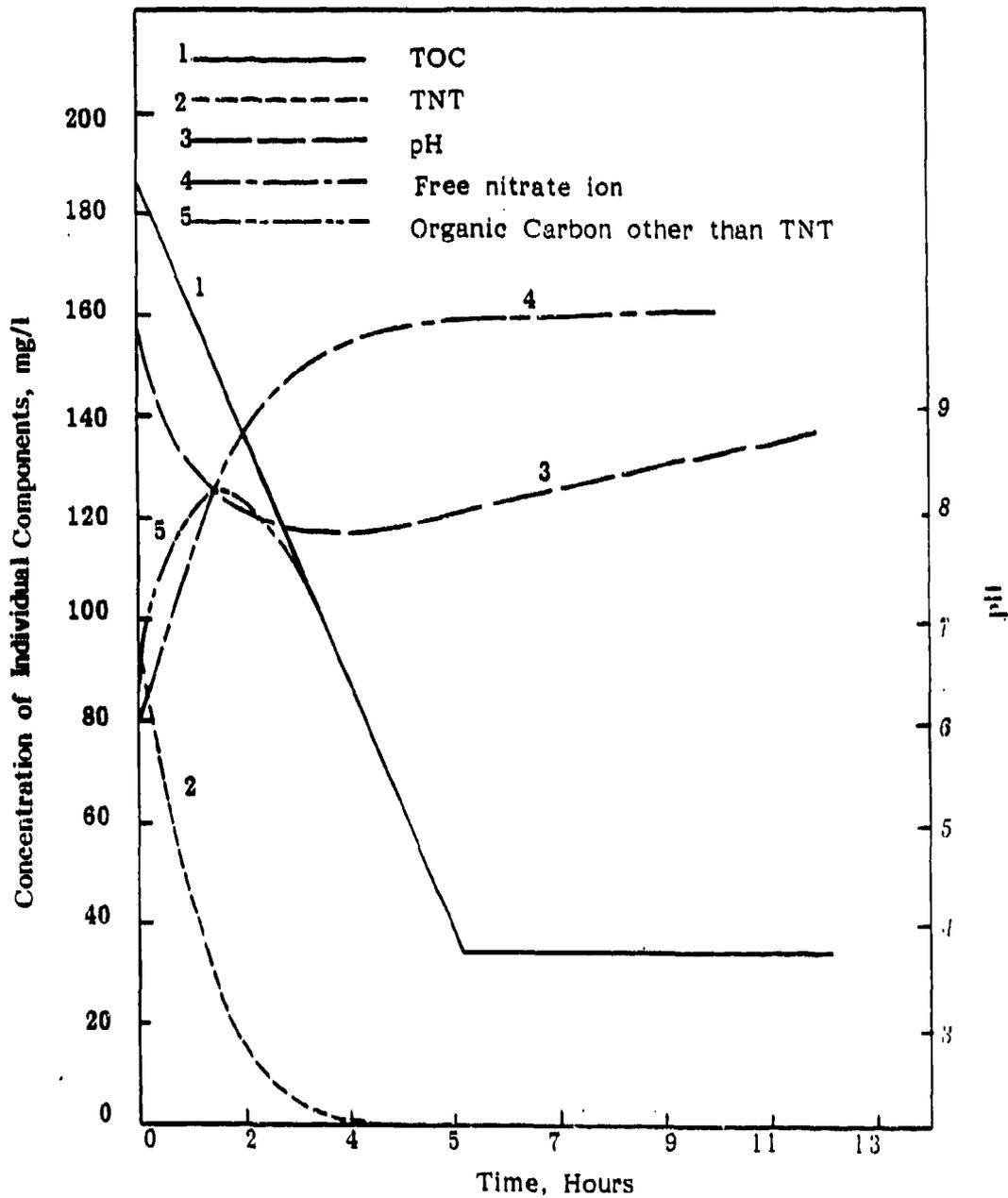


Figure 34. Detailed Analysis of Run 7-12: 100% UV, 23.8 mg/l O<sub>3</sub>, pH = 9.7, Zero Flow (compiled, Layne et al., 1980)

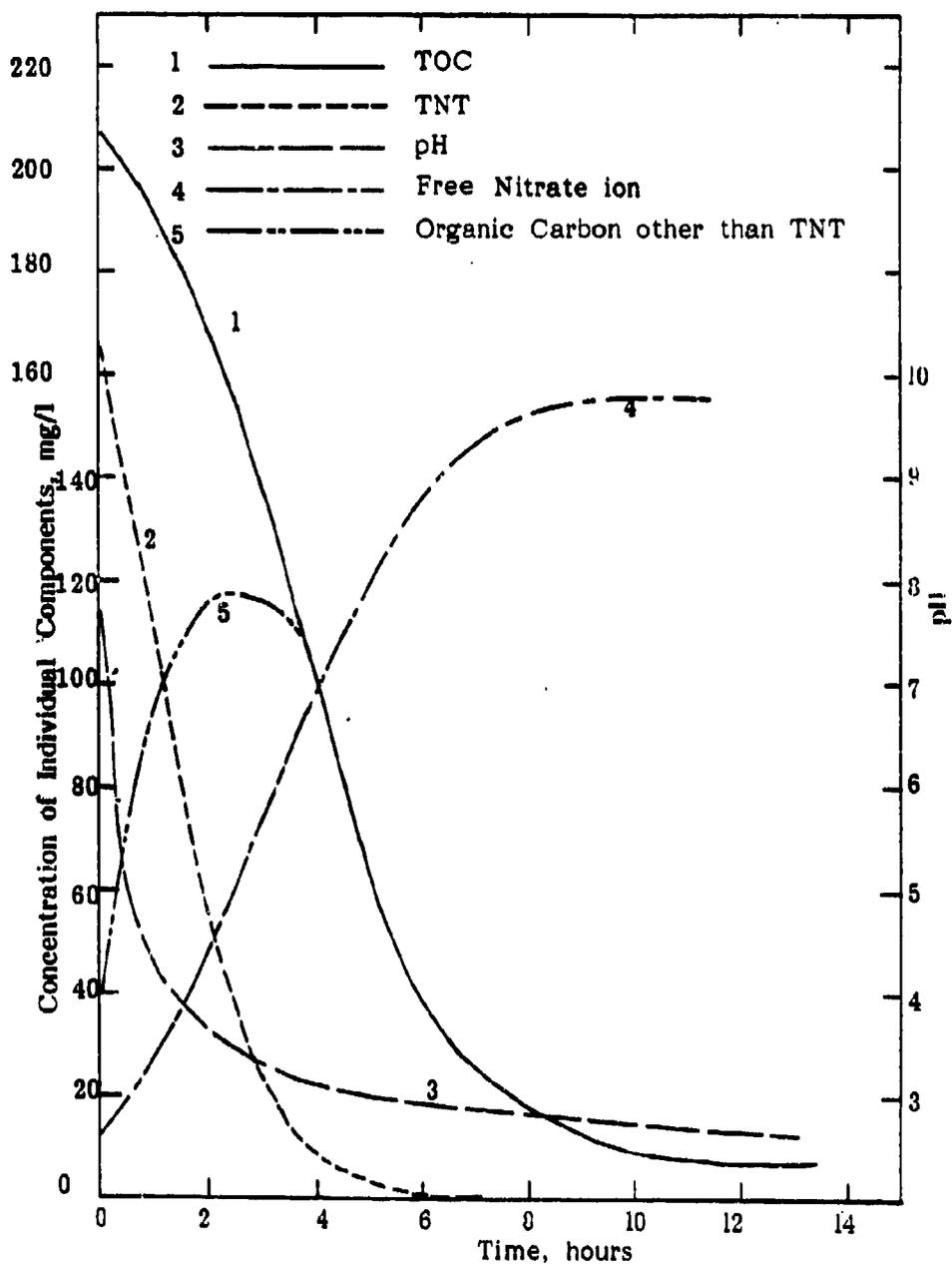


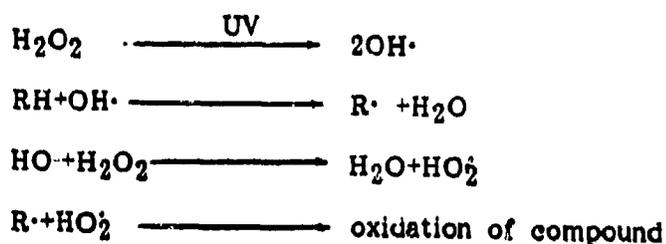
Figure 35. Detailed Analysis of Run 7-8:100% UV, 23.8 mg/l O<sub>3</sub> from Air, Zero Flow, No pH Adjustment (compiled, Layne et al., 1980)

for steady state operation. Leakages around the partitions in the reactor were thought to be the cause of some of the anomalies in the data. The ozone concentration in the gas stream and the number of lamps used were varied. Ozone uptake was greatest when the percentage of ozone in the gas was low (when air was used as the source). For higher ozone concentrations (made from oxygen), the ozone uptake appeared to be a function of the number of lamps in operation. Ozone efficiency was calculated to be between 33 and 45%. Sufficient data were not presented to evaluate the ozone lamp interactions or ozone efficiency any further.

In summary, as a result of all the years of study of the UV-ozonolysis conditions for degradation of TNT, very little is known about the optimum conditions and the degradation mechanism. There is evidence that under neutral conditions, the following are true: 1) the mechanism is initially controlled by the ozone, 2) ozone itself is the reacting agent, and 3) ultraviolet light promotes the degradation of the intermediates formed. However, there is also evidence that UV-ozonolysis of TNT occurs more rapidly under basic conditions. The mechanism, effect of ozone and/or UV under these conditions have received very little attention. Layne et al. (1980) may possess the data to shed some light on the subject. Their experimental plan appears to have obtained a wide variety of data. However, the data are not presented in the report.

Initial studies on the effectiveness of ultraviolet/peroxide degradation of explosives were conducted by the Navy (Andrews and Osmon, 1977; Andrews et al., 1977). In these studies, 100 mg/l TNT solutions were exposed to various concentrations of hydrogen peroxide (0.01-2.0%) in static and flow through photolysis systems. The best results were obtained in the static system shown in Figure 36. This reactor contained a 30 watt short wave mercury lamp with a maximum film depth of 5 mm.

The ultraviolet peroxide degradation mechanism was proposed as follows:



The UV light thus initiates the decomposition of the hydrogen peroxide yielding two hydroxyl radicals. Once formed, these radicals can react in a variety of ways to yield the oxidized products. The concentration studies with peroxide showed an initial peroxide concentration of 0.1% to be optimum. At this concentration, the TNT was oxidized within one hour of irradiation and the TOC was reduced to 2-3 mg/l after 5 hours. The peroxide appears to be completely used up after 1-2 hours of reaction time. Brief studies of the products showed that <sup>14</sup>C-TNT was at least

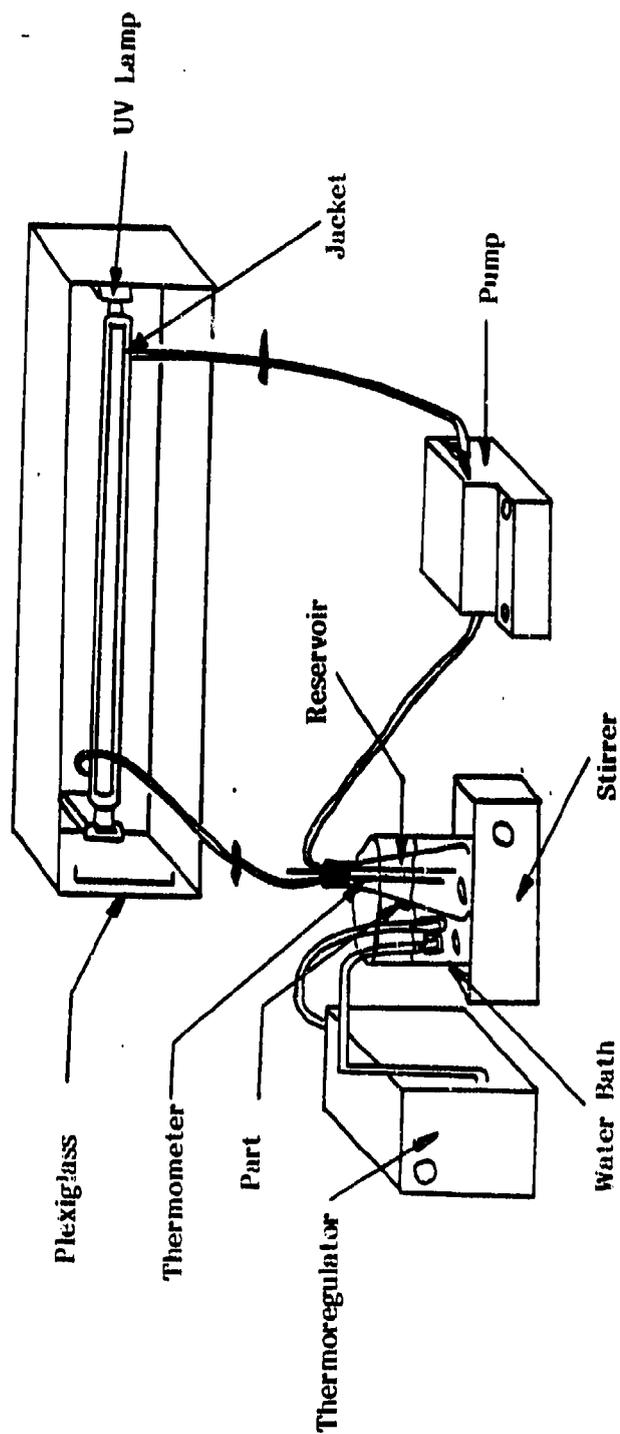


Figure 36. Navy's Bench-Scale UV Reactor (Andrews, 1980)

partially decomposed to  $^{14}\text{CO}_2$ . 1,3,5-Trinitrobenzene was isolated as an intermediate in the reaction after one hour but not at later times. Other reaction products include high levels of nitrate (0.1%  $\text{H}_2\text{O}$ ) with a concurrent pH drop and high levels of ammonia at peroxide concentrations of 2%. Adjustment of the initial pH of the solution to acid decreased the rate of TNT degradation. Adjustment of the initial pH to basic (8-10) did not appear to increase the TNT degradation rate although the data are very scattered (Andrews, 1980).

Other explosives were also subject to the static UV-peroxide system. The reductions obtained are presented in Table 41.

An extension of this work was reported by Roth and Murphy (1978) and Andrews (1980). Both reports present the exact same data but neither refers to the other. Therefore, the person or persons doing the original work are unknown. They used ultraviolet units manufactured by Ultradynamics Corporation for these tests. Two units were used - Model 2000 and Model 500. The Model 2000 unit is a series of 4 chambers each with a capacity of 22.8 liters (6 gal), one 40-watt low pressure UV lamp and a film depth of 5.72 cm (2 1/2 in). The Model 500 is a 2.84 liter (3/4 gal) chamber with one 40 watt low pressure UV lamp and a film depth of 2.54 cm (1 in). The solution in the reactor was recirculated through a reservoir. Recirculation rate in the Model 2000 was 2730 liters/hr and 400 liter/hr in the Model 500. The effects of 0.1%  $\text{H}_2\text{O}_2$  and Oxone (potassium monopersulfate mixture with potassium sulfate and potassium hydrogen sulfate) on pink water degradation were studied in these reactors. The data are compiled in Table 42. The Oxone appeared to be more efficient than the  $\text{H}_2\text{O}_2$  in removing the explosives. Trinitrobenzene also did not appear to be a significant product. The shorter pathlength of the Model 500 reactor also improved the degradation rate. However, the major problem associated with the use of Oxone for degradation of explosives was the potassium sulfate salts formed and their effect on the environment.

The Navy designed and built a pilot scale UV-peroxide reactor. The design of this reactor was discussed earlier (see Section VIIIA and Figure 23). The unit was tested at one of the Army's Load, Assembly and Pack plants by Navy personnel. The explosives content of the water was variable during this study due to backwashing of the carbon columns at the plant. The pilot unit was operated at flow rates of 3.8-15 liters/min (1-4 gpm). Typical results of the 7.6 liters/min (2 gpm) flow rates are presented in Table 43. The RDX and TNT were effectively eliminated, however, residual TOC remained. At 15 liters/min (4 gpm), the treatment was not effective for TNT concentrations of greater than 25 mg/l. A problem was also encountered in silicone grease build up on the lamps which blocked the UV output. For further work on the UV-peroxide process, Andrews (1980) recommends the use of wipers to clean the lamps and a maximum film depth of 5 mm.

Table 41. Summary of Data from the UV-0.1% Static System Treatment Aqueous Solutions of Explosive D, HMX, RDX, 2,4-DNT and 2,6-DNT (Andrews and Osmon, 1977)

<u>Compound</u>	<u>Exposure (hr.)</u>	<u>ppm H<sub>2</sub>O<sub>2</sub></u>	<u>ppm TOC</u>
Explosive D	0	1000	168
Explosive D	1	-12	15.6
Explosive D	2	0	2.2
Explosive D	5	0	-
HMX	0	1000	-*
HMX	0.5	-100	-
HMX	1	>12<50	-
HMX	5	0	-
RDX	0	1000	12.8
RDX	0.5	>5<100	2.37
RDX	2.5	-3	-
RDX	3.0	0	-
2,4-DNT	0	1000	38.4
2,4-DNT	1	>12<50	2.4
2,4-DNT	2	-1	-
2,4-DNT	5	0	-
2,6-DNT	0	1000	45.3
2,6-DNT	1	>12<50	3.15
2,6-DNT	2	1	-
2,6-DNT	5	0	-

\*Sensitivity of TOC analyzer insufficient to determine the concentration.

Table 42. Oxidation in the UV-2000 and UV-500 Systems with Oxone of H<sub>2</sub>O<sub>2</sub> (Andrews, 1980)

System	Oxidizing Agent	Total UV Exposure (hr)	Decolorization Time (hr)	Explosives Concentration (ppm)			TNB** Concentration (ppm)	TOC (ppm)	PNA*** (number present)
				TNT	RDX	HMX			
UV-2000	0.1% H <sub>2</sub> O <sub>2</sub>	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 <sub>2</sub> O <sub>2</sub>	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 43. Results of UV-Peroxide Pilot Study on Pink Water (Andrews, 1980)

Sample	TNT (mg/L)	RDX (mg/L)	TOC (mg/L)
O-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
O-Time	8.6	6.6	14.5
Baffle 4	≤0.02	≤0.08	6.9
O-Time	28.0	17.4	25.5
Baffle 4	≤0.02	≤0.08	8.3

\*Flow rate 7.6 liters/min (2 gpm)

C. Advantages and Disadvantages of UV-Oxidation for Decontamination of Explosives Contaminated Lagoon Sediment

UV-ozonolysis and UV-peroxide have both been shown to be effective for decomposition of dilute solutions of explosives (up to 140 mg/l TNT; 50 g/l RDX). Reaction time required for complete degradation of these concentrations to CO<sub>2</sub>, H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> is on the order of 2-3 hours. The reactor time can be cut by approximately two thirds, if degradation to the biodegradable stage is utilized. The concentrations on which these rates were based are much lower than those found in explosives contaminated lagoon sediments. Thus, either dilution or significantly longer reaction time is necessary to affect the degradation. The slow degradation rate is a major economic disadvantage.

D. Application of UV-Oxidation to Decontamination of Lagoon Sediment

To use UV-oxidation to decontaminate lagoon sediment which contains explosives, sediment will be mixed with enough water to allow complete solution of all explosive contaminants. Assuming 50% solids for the standard lagoon, water will have to be added to produce 12,450 l/min of solution with less than 100 mg/l TNT and 30 mg/l RDX. Equipment required for the UV-ozonolysis process is listed below:

- dredge
- holding tank
- mixing tanks
- UV-ozonolysis reactors
- RBC biological treatment system

Explosives in solution can be degraded to a biologically treatable stage in the ultraviolet reactor. The reactor is a portable unit which contains 28,160 lamps which is used in conjunction with a 7-ton ozone generator. Effects of sediment on reactor internals and performance are not known and will have to be determined by experiment.

E. Economics of UV-Ozonolysis

Capital and operating costs for UV-ozonolysis of contaminated lagoon sediment are presented in Tables 44 and 45. These costs are based on the minimum residence time, ozone and radiation requirements which have been demonstrated for degradation of saturated solutions of explosives to biologically treatable levels. Overall, UV-ozonolysis appears to be a very expensive treatment method for contaminated lagoon sediment. Costs for the UV-peroxide system should be within 10% of the UV-ozonolysis system.

Table 44. Capital Costs for UV-Ozonolysis to Decontaminate Lagoon Sediment

Quantity	Equipment	Cost	Reference
1	Dredge: Porta-Dredge PD-42S, 1136 l/min.	\$ 53,260	Salemink, 1980
1	Holding Tank: 454,200 l, carbon steel with 75 hp side-entry turbine mixer	132,000	Peters & Timmerhaus, 1968
1	Slurry Pump: 1/2 hp	800	Peters & Timmerhaus, 1968
2	Mixing Tanks: 15,140 l coal tar epoxy-coated carbon steel with 30 hp side-entry turbine mixer	43,400	Peters & Timmerhaus, 1968
3	Pumps: 0-12 l/min. for feeding RBC unit	480	Galigher Co., 1980
1	UV-Ozonolysis Reactor and Ozone Generator	8,947,290	Zeff, 1981
4	Anoxic RBC: 2230 m <sup>2</sup> media area each, steel tank	172,000	Gerhardt, 1980
3	Aerobic RBC: 2230 m <sup>2</sup> media area each, steel tank	114,000	Gerhardt, 1980
1	Clarifier Tank: 15,140 l carbon steel	3,300	Peters & Timmerhaus, 1968
1	Sand Filter	28,000	
	Total	\$9,494,480	

Table 45. Operating Costs for UV-Ozonolysis

Installation (5% of capital)	\$	474,400
Electricity (@ \$0.07/KWH)		922,500
UV lamps (28,160 lamps, 65 watts each)		1,630,000
Ozone generation (10 KWH/lb, 37.5 lb/day-unit)		62,200
Other power requirements		210,000
Labor (3 operators @ \$45,000/man-yr, 1 supervisor @ \$75,000/man-yr)		284,800
Maintenance (3% of capital)		234,000
Oxygen		<u>12,000</u>
Oxygen tank rental (34,800 l, \$1,000/month)		
Total monthly cost	\$	3,830,200

F. Laboratory and Pilot Scale Tests

The laboratory tests must be aimed at obtaining degradation reaction rates of explosives in the sediment. These tests must show that the degradation is rapid enough to provide a competitive cost picture. Both UV-ozonolysis and UV peroxide should be investigated. For UV-ozonolysis, the following experiments should be run:

- 1) 10% sediment slurry in Westgate's reactor with ozone flow of approximately 72 mg/min,
- 2) 10% slurry with pH adjusted to 10-11 in Westgate's reactor with ozone flow of approximately 72 mg/min,
- 3) 10% sediment slurry in thin film reactor with ozone flow of approximately 72 mg/min,
- 4) 10% sediment slurry in thin film reactor with pH adjusted to 10-11 with ozone flow of approximately 72 mg/min, and
- 5) ozone flow optimization tests on the best process.

Westgate's costs are estimated at approximately \$15,000 for lab scale tests. The thin film reactor work would cost about \$5,000. Analysis of all samples will cost an additional \$10,000. Costs for pilot scale tests are unavailable.

Several variables should be investigated with the UV-peroxide system including: 1) the effect of the addition of a solvent such as isopropanol to the system to improve the solubility of the explosives and improve the degradation rate, 2) the effect of pH on the system, and 3) the effect of peroxide concentration. These reactions should be carried out in a thin film reactor. Costs for the tests are estimated at \$5,000. Analytical costs will require an additional \$5,000. Pilot scale cost should run about the same price.

## IX. CHEMICAL DEGRADATION

### A. Background

The data on chemical degradation of RDX, TNT or nitrocellulose were evaluated for application to the explosive contaminated sediments. The degradation of nitrocellulose with aqueous ammonia was determined to be a viable chemical treatment which could be applied to the scenario.

### B. Review and Evaluation of the Literature

Dogliotti et al. (1974) conducted several tests to determine if nitrocellulose could be degraded with a weak base such as ammonium hydroxide and to compare the degradation with that obtained with sodium hydroxide. With a 3% aqueous sodium hydroxide solution, 100% of a 5% slurry of nitrocellulose can be decomposed in less than one hour at 98°C.

In a series of experiments, Dogliotti et al. (1974) reacted nitrocellulose with ammonium hydroxide under various conditions at temperatures of 73°C. The results of these studies are presented in Table 46. They found that the degradation of nitrocellulose by ammonia in water could be optimized for reaction time or economics. A 10% slurry of nitrocellulose could be degraded completely when exposed to a 10% solution of ammonia in water for 10 hours at 73°C. A more economical reaction is the degradation of a 20% slurry of nitrocellulose by a 10% solution of ammonia in water for 24 hours at 73°C. Products were amorphous in structure when viewed under the microscope and gave negative Modisch tests for carbohydrates indicating breakdown of the polymer.

Bissett and Levasseur (1976) studied the chemical degradation of nitrocellulose for fertilizer. By using ammonium hydroxide, they hoped to form ammonium nitrate and nitrite. A closed system with elevated temperature and pressure was used to degrade the nitrocellulose. The results are presented in Table 47. They found that a 5% nitrocellulose suspension can be degraded by a 5% ammonium hydroxide solution in three hours at 90°C in a closed system. Similar results could be obtained for a 5% nitrocellulose slurry in an open system using 10% ammonium hydroxide at 33°C for eight hours or 29% ammonium hydroxide at room temperature for 120 hours.

### C. Application of Chemical Treatment to Nitrocellulose in Lagoon Sediment

For the chemical treatment of nitrocellulose-containing lagoon sediment to be practical, the sediment will have to be dredged from the lagoon. The dredged sediment will be placed in a stirred holding tank (described in the wet-air oxidation section). The sediment is expected to contain approximately 5% nitrocellulose, therefore, no dilution will be necessary. Aqueous ammonia (30% by weight) will be added to the sediment slurry in a continuous stirred tank reactor to bring the ammonia concentration of the mixture to 10%. A recycle loop with temperature

**Table 46. Degradation of Nitrocellulose with Ammonium Hydroxide at 73°C**  
(Dogliotti et al., 1974)

Ammonium Hydroxide (%)	Nitrocellulose (%)	Time (hrs)	Recovered Solid (%)	Unreacted Nitrocellulose (%)
5	5	4	58	39
5	10	12	12.9	4
10	5	4	9.9	*
10	5	8	3	<1
10	10	7	3.3	<1
10	10	8	5.8	1.6
10	10	12	0.9	<1
10	20	24	3.4	<1
15	5	4	6.5	*
15	5	12	0.9	<1
15	10	4	12	5
15	15	7	4.9	<1

Table 47. Degradation of Nitrocellulose with Ammonium Hydroxide  
(Bissett and Levasseur, 1976)

Nitrocellulose (%)	NH <sub>4</sub> OH (%)	Time (hrs)	Temp. °C	Type of System	Unreacted Nitrocellulose (%)
5	1	19	90	closed	60
5	3	4	90	closed	9
5	5	3	90	closed	0
5	10	16	room temp	open	100
5	29	120	room temp	open	3
5	10	104	50	open	7
5	10	1	98	open	50
5	10	4	75	open	57
5	10	8	75	open	0

controller and heat exchanger will maintain the reactor temperature at 73°C. Residence time in the reactor will be approximately eight hours. After processing, the mixture will be returned to the lagoon for biological degradation of any remaining ammonia and TOC. A neutralization step may be included if necessary. Major equipment items for the chemical treatment process are listed below and are depicted in Figure 37.

- Dredge
- Holding Tank
- Ammonia Storage Tank
- Reactor

D. Economics of Chemical Treatment for Nitrocellulose Contaminated Lagoon Sediment

The capital investment costs and annual operating costs for a plant to chemically treat nitrocellulose in lagoon sediment are listed in Tables 48 and 49. Additional capital and operating costs will be incurred if it is deemed necessary to remove ammonia from the effluent stream. Ammonia removal could be done most easily by vacuum evaporation of the ammonia and water from the treated sediment mixture. Equipment and operating costs would depend on the concentration of unreacted ammonia and on the desired purity of the distilled streams.

E. Advantages and Disadvantages of Ammonium Hydroxide Treatment of Nitrocellulose Contaminated Lagoon Sediment

Ammonium hydroxide chemical degradation of nitrocellulose appears to be a relatively inexpensive process for decomposition of nitrocellulose. The major unknowns are the effect of sediment on the chemical reaction and the ultimate process efficiency. There are other unknown factors such as the amount of ammonia remaining in the processed sediment and the biodegradability or treatability of the remaining carbon products. In essence, laboratory scale studies will have to be performed with the actual sediment before a reliable equipment design and cost analysis can be undertaken.

F. Laboratory and Pilot Scale Studies

The decomposition of nitrocellulose in a 5-10% slurry with ammonium hydroxide has been shown to be effective. However, the reaction rates in the presence of sediment need to be defined, the products need further identification, and more information is needed on the biological degradation of the products. Laboratory testing to determine the reaction rates, identify the products and determine their biodegradability should be conducted. Costs for the laboratory scale tests are estimated at \$20,000 for a four month effort. Pilot-scale studies to determine the basic process parameters for design and construction of a large scale plant should then be undertaken. The pilot-scale studies should be run in a continuous flow made at a rate of 15 liters/hr. Construction of the pilot-scale reactor and testing will require eight months to complete at a cost of \$50,000.

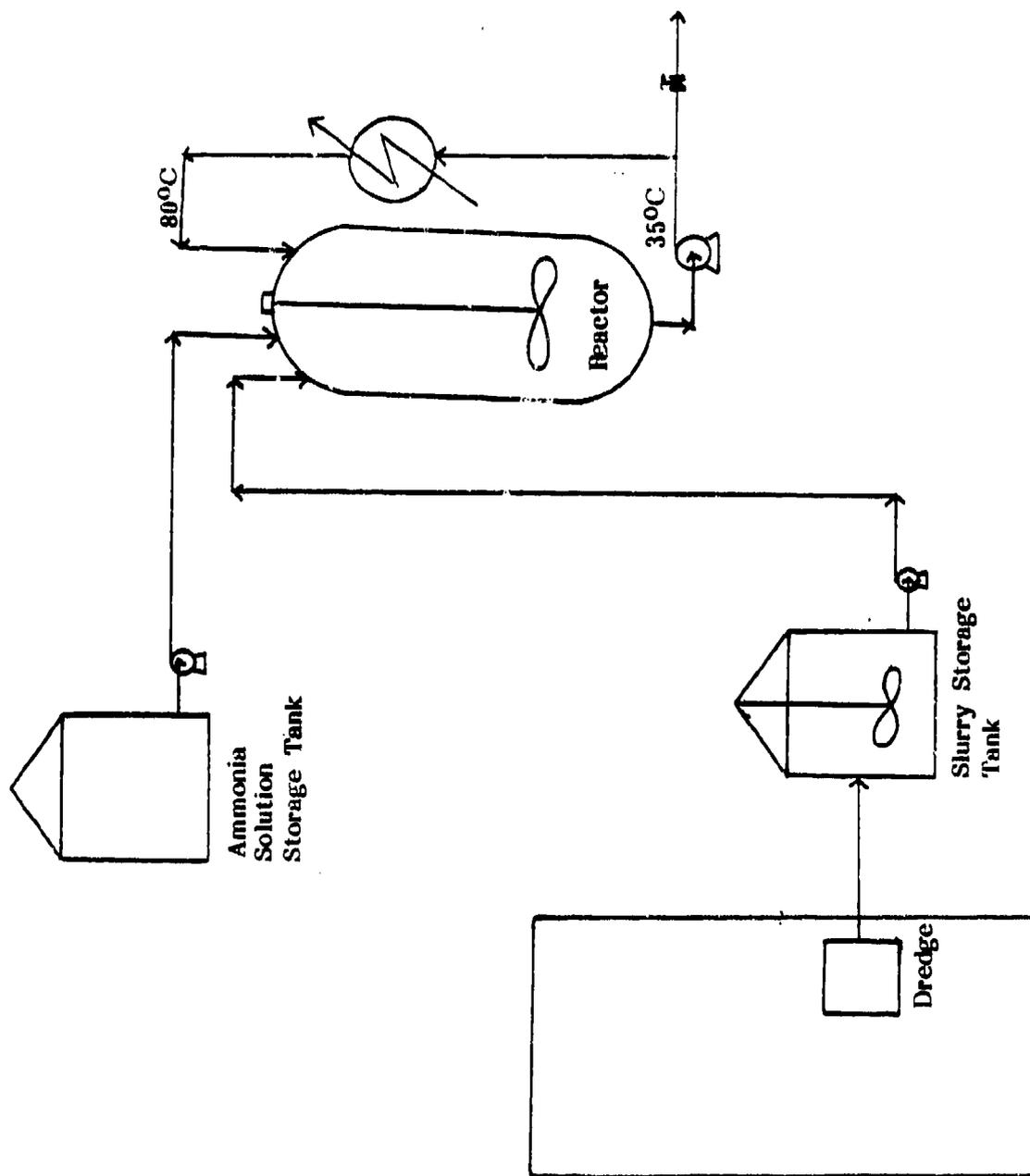


Figure 37. Flow Diagram for Nitrocellulose Degradation

Table 48. Capital Costs for Ammonium Hydroxide Degradation of Contaminated Lagoon Sediment

Quantity	Equipment	Cost	Reference
1	Dredge: Porta-Dredge PD-42S, 1136 l/min.	\$53,260	Salemink, 1980
1	Holding Tank: 454,200 l, carbon steel with 75 hp side-entry turbine wiper	132,000	Peters & Timmerhaus, 1968
1	Slurry Pump: 1/2 hp	800	Peters & Timmerhaus, 1968
1	Metering Pump: 0-540 l/hr.	7,800	Milton Roy, 1980
1	Pump (for recirculation): 30 GPM	800	Peters & Timmerhaus, 1968
1	Heat Exchanger: 0.9m <sup>2</sup> surface area	880	Guthrie, 1970
1	Stirred Tank Reactor: carbon steel, 10,280 l	12,300	Peters & Timmerhaus, 1968
	Instrumentation: temperature controller, 5% capital	10,000	
	Total	<u>\$217,500</u>	

**Table 49. Annual Operating Costs for Ammonium Hydroxide Degradation of Contaminated Lagoon Sediment**

Installation (5% of capital	\$ 10,900
Electricity (@ \$0.07/KWH)	34,000
Labor (3 operators @ \$45,000/man yr, 1 supervisor @ \$75,000/man yr)	210,000
Maintenance (3% of capital)	6,500
Steam (@ \$2.75/10 <sup>6</sup> Kcal)	1,100
Ammonia (144.3 kg/hr NH <sub>3</sub> @ \$0.269/kg. as 30% solution)	<u>279,500</u>
<b>Total</b>	<b>\$542,000</b>

## X. ENVIRONMENTAL EVALUATION OF TREATMENT PROCESSES

The lagoons contaminated with explosives were separated into two scenarios. Lagoon sediment in Scenario A was contaminated primarily with TNT, RDX and DNT and Tetryl. Small amounts of lead chromate, ammonium nitrate and sodium dichromate may also be found in the sediment and were listed as potential process interference contaminants. The potential sites for Scenario A lagoons are:

<u>Potential Site</u>	<u>State</u>
Milan AAP	Tennessee
Cornhusker AAP	Nebraska
Tooele AD	Utah
Lone Star AAP	Texas
Hawthorne AAP	Nevada
Joliet AAP	Illinois
Alabama AAP	Alabama
Radford AAP	Virginia
Navajo Depot	Arizona
Volunteer AAP	Tennessee
Umatilla Depot	Oregon
Louisiana AAP	Louisiana
Fort Wingate Depot	New Mexico
Iowa AAP	Iowa
Savanna Depot	Illinois

Nitrocellulose contaminated lagoon sediments were considered in Scenario B. The potential sites for Scenario B lagoons are:

<u>Potential Site</u>	<u>State</u>
Sunflower AAP	Kansas
Badger AAP	Wisconsin

### A. Anticipated Air Emissions and Aqueous Effluents

The conditions and contaminants in Scenario A were primarily used to estimate air and water pollutants from the treatment processes considered. All of the treatment scenarios can also be applied to nitrocellulose contaminated lagoon sediment, however, the data bases for decontamination of nitrocellulose with these processes are not well developed. In general, the air emissions and water effluents estimates made for the TNT/RDX lagoons are also applicable to the nitrocellulose lagoons. Estimated air emissions and water effluent constituents are compared for the different treatment processes in Table 50 and 51. Microwave, molten salt incineration, and multiple hearth and cyclone incinerators are not included since they do not appear to be feasible processes for these scenario. All data shown are with air pollution control equipment.

Table 50. Estimated Air Emissions from the Treatment of Explosive Contaminated Lagoons by the Candidate Processes

Process	NO <sub>x</sub>	CO	HC	Particulates	Pb	Cr	O <sub>3</sub>	NH <sub>3</sub>
Wet-Air Oxidation	L	L-M	L	L	L	L	NA	?
Incineration								
1. Rotary Kiln	M	L	L	L	H	M-H	NA	NA
2. Fluidized Bed	L	L	L	L	M	M	NA	NA
3. Electric Furnace	L	L	L	L	L	L	NA	NA
High Energy Electrons	NA	NA	NA	NA	NA	NA	H	?
Gamma Radiation	NA	NA	NA	NA	NA	NA	H	?
UV-ozone	NA	NA	NA	NA	NA	NA	H	NA
UV-peroxide	NA	NA	NA	NA	NA	NA	NA	L
Chemical Degradation	NA	NA	NA	NA	NA	NA	NA	H

H = High release - treatment necessary

M = Moderate release - treatment probable

L = Low release - some treatment probable

NA= Not applicable - no emission

Table 51. Estimated Water Pollutants From Treatment of Explosives Contaminated Lagoon Sediment by the Candidate Processes

Process	COD	BOD	Pb	Cr	Suspended Solids	pH	Ammonia
Wet-Air Oxidation	H	H	M-H	M	H	H	?
Incineration							
1. Rotary Kiln	NA	NA	L-M	L-M	M	L	NA
2. Fluidized Bed	NA	NA	L-M	L-M	H	L	NA
3. Electric Furnace	NA	NA	L-M	L-M	M	L	NA
High Energy Electrons	H	H	M-H	M	H	M	L
Gamma Radiation	H	H	M-H	M	H	M	L
UV-ozonolysis	H	H	L	L	H	L-M	NA
UV-peroxide	H	H	L	L	H	L-M	L
Chemical Degradation	H	H	NA	HA	H	H	H

H = High release - treatment necessary

M = Moderate release - treatment probable

L = Low release - some treatment probable

NA = Not applicable - no emission

When secondary treatment equipment such as afterburners and scrubbers is included, most of the processes are relatively free of air emissions. Of major concern are the emissions of lead and chromium from incineration when sediments containing these metals are burned. At temperatures above 800°C, vaporization of lead occurs to some extent. Temperatures around or above this range occur in both the rotary kiln and fluidized bed incinerators. The electric furnace operates at a much lower temperature, (approximately 550°C), and thus lead emissions should not be a problem with this incineration method.

Wet-air oxidation, high energy electrons, gamma radiation, UV-oxidation and chemical degradation of nitrocellulose are all expected to produce large quantities of aqueous effluents which will require some type of treatment. In most cases, this treatment will consist of neutralization, possibly precipitation and biological degradation. The degree of the post-treatment needed to meet effluent criteria has not been established for many of these treatment processes because data are not available on process efficiency for explosives degradation. For costing purposes, one biological treatment system has been designed and applied to all the treatment processes. If the size of this system is compatible with the COD, BOD, NH<sub>3</sub> and NO<sub>3</sub> levels in the process effluent, the biological system should yield the following final effluent parameters:

COD	50 mg/l
BOD	10-50 mg/l
TSS	15-30 mg/l
NO <sub>3</sub>	20 mg/l
NH <sub>3</sub>	5 mg/l

The solid from most of the main treatment processes will be sterile soil. This soil can be put back into the lagoon; however, to prevent rapid growth of wild organisms, it is recommended that the sterile soil be mixed with equal amounts of native soil before returning it to the lagoon.

#### B. Air and Water Emissions Regulations for the Specific Army Sites

Air quality criteria are primarily from three regulations, the Clean Air Act Amendments of 1970, the Energy Supply and Environmental Coordination Act of 1974, and the Clean Air Act Amendments of 1977 (EPA, 1979a). The National Ambient Air Quality Standards for the pollutants of concern to the Army are presented in Table 52. Air quality standards for the individual states in which the Ammunition Plants having explosives contaminated lagoons are located are presented in Table 53. Most of the states have air criteria standards which are similar to the Federal standards.

Natural water quality criteria are presented in Table 54. Only the possible pollutants of concern to the Army were included. The EPA recommends for maximum protection of human health that no 2,4-DNT be released into the water (EPA, 1979c). The water quality criteria from the states of concern are presented in Table 55. The state regulations are either the same as or slightly less stringent than the Federal standards. In addition, the states usually do not have specific regulations for DNT and phenols.

Table 52. Federal Ambient Air Quality Standards for Certain Chemicals (CFR, 1979)

Chemical	National Standard
Sulfur Oxides (Sulfur dioxide)	(A) 80 micrograms per cubic meter (0.03 ppm) - annual arithmetic mean. (B) 365 micrograms per cubic meter (0.14 ppm) - maximum 24 hour concentration not to exceed more than once per year.
Particulate Matter	(A) 75 micrograms per cubic meter annual geometric mean. (B) 260 micrograms per cubic meter - maximum 24 hour concentration not to exceed more than once per year.
Carbon Monoxide	(A) 10 milligrams per cubic meter (9 ppm) - maximum 8 hour concentration not to exceed more than once per year. (B) 40 milligrams per cubic meter (35 ppm) maximum 1-hour concentration not to be exceeded more than once per year.
Ozone	0.12 parts per million ( $235 \mu\text{g}/\text{m}^3$ ). The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 parts per million ( $235 \mu\text{g}/\text{m}^3$ ) is equal to or less than 1.
Hydrocarbons	160 micrograms per cubic meter (0.24 ppm) maximum 3 hour concentration (6-9 a.m.) not to be exceeded more than once per year.
Nitrogen Dioxide	100 micrograms per cubic meter (0.05 ppm) - annual arithmetic mean.
Lead	1.5 micrograms per cubic meter, maximum arithmetic mean averaged over a calendar quarter.

Table 53. State Ambient Air Quality Standards for Certain Chemicals

State	Chemical	Standards
Alabama BNA, 1980a		Same as Federal
Arizona BNA, 1980b		Same as Federal
Illinois BNA, 1980c		Same as Federal
Iowa BNA, 1980d	Sulfur dioxide	80 micrograms per cubic meter (0.03 ppm) 24-hour average
	Sulfur dioxide and Particulate Matter combined	3.0 COH (coefficient of haze/1000 linear ft) or 355 micrograms per cubic meter 24-hour average
	Carbon monoxide	17 milligrams per cubic meter (15 ppm) 8-hour average
	Oxidants (Ozone)	200 micrograms per cubic meter (0.1 ppm) 1-hour average
	Nitrogen dioxide	130 micrograms per cubic meter (0.6 ppm) 1-hour average or 282 micro- grams per cubic meter (0.15 ppm) 24-hour average
	Lead	1.5 $\mu\text{g}/\text{m}^3$
Kansas BNA, 1980e		Same as Federal
Louisiana BNA, 1980f		Same as Federal
Nebraska BNA, 1980g		Same as Federal
Nevada BNA, 1980h	Carbon monoxide	6 ppm maximum 8-hour exposure above 5,000 ft.
	Others	Same as Federal

Table 53 continued.

New Mexico BNA, 1980i	Beryllium in total suspended particulates	0.01 $\mu\text{g}/\text{m}^3$ maximum concentration
	Asbestos in total suspended particulates	0.01 $\mu\text{g}/\text{m}^3$ maximum concentration
	Heavy metals (total combined) in total suspended particulates	10 $\mu\text{g}/\text{m}^3$ maximum concentration
	Sulfur dioxide	0.02 ppm annual arithmetic mean at maximum concentration
	Hydrogen sulfide	For the state, except Pecos-Permian Basin Intra-State Air Quality Control Region (1-hr average, not to exceed more than once per year) 0.010 ppm maximum concentration
	Total reduced sulfur	For the state, except the Pecos-Permian Basin Intra-State Air Quality Control Region including hydrogen sulfide-0.003ppm maximum 1-hour concentration
	Carbon monoxide	8.7 ppm maximum concentration on an 8-hour average. 13.1 ppm on a 1-hour average
	Nitrogen dioxide	0.10 ppm maximum concentration on a 24-hour average. 0.05 ppm on an annual arithmetic mean
	Photochemical oxidants	1-hour average 0.06 ppm maximum concentration
	Non-methane hydrocarbons	3-hour average 0.19 ppm maximum concentration
Oregon BNA, 1980j	Particulate fallout	10 $\text{g}/\text{m}^2/\text{mo.}$ in an industrial area
	Suspended particulate matter	60 $\mu\text{g}/\text{m}^3$ annual geometric mean for year, 150 $\mu\text{g}/\text{m}^3$ 24-hour concentration not more than once per year
	Sulfur dioxide	60 $\mu\text{g}/\text{m}^3$ annual mean for year 260 $\mu\text{g}/\text{m}^3$ maximum 24-hour average
	Carbon monoxide	10 $\text{mg}/\text{m}^3$ or 8.7 ppm maximum 8-hour average
	Photochemical oxidants	160 $\mu\text{g}/\text{m}^3$ maximum 1-hour average, once per year
	Hydrocarbons	160 $\mu\text{g}/\text{m}^3$ maximum 3-hour average, once per year

Table 53 continued

	Nitrogen dioxide	100 $\mu\text{g}/\text{m}^3$ , annual mean
	Ammonia	2 $\text{mg}/\text{m}^3$ , 30-day average, once per year 5 $\text{mg}/\text{m}^3$ , 8-hour average, once per 24 hours
Tennessee BNA, 1980k		Same as Federal
Texas BNA, 1980l		Same as Federal
Utah BNA, 1980m	Photochemical oxidants	0.08 ppm maximum 1-hour concentration not to exceed more than once a year
	Others	Same as Federal
Virginia BNA, 1980n		Same as Federal
Wisconsin BNA, 1980o		Same as Federal

**Table 54.**  
**Federal Water Criteria for Certain Pollutants**

Chemical	Criteria for Aquatic Life
Chromium (EPAa) Trivalent chromium	The criterion to protect freshwater aquatic life as derived using the guidelines is (e)(0.83·ln (hardness)+ 2.94) as a 24-hour average, and the concentration should not exceed (e)(0.83·ln (hardness) +3.72) at any time.
Hexavalent chromium	The criterion to protect freshwater aquatic life as derived using the guidelines is 10 µg/l as a 24-hour average concentration and the concentration should not exceed 110 µg/l at any time.
NOTE:	For saltwater aquatic life no criterion for trivalent chromium can be derived using the guidelines, and there are insufficient data to estimate a criterion using other procedures.
Chromium (EPA, 1976)	Criteria for Human Health
	For the protection of human health from the toxic properties of chromium (except hexavalent chromium) ingested through water and contaminated aquatic organisms, the recommended water quality criterion is 50 µg/l.
DNT (EPAc)	Criteria for Aquatic Life
	The criterion to protect freshwater aquatic life for 2,3-dinitrotoluene as derived using procedures other than the guidelines is 6.20 µg/l as a 24-hour average and the concentration should not exceed 1,400 µg/l at any time.

Table 54 Continued

	Criteria for Human Health
DNT (EPAc)	For the maximum protection of human health from the potential carcinogenic effects of exposure to 2,4-dinitrotoluene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero.
	Criteria for Aquatic Life
Lead (Federal Register, 1979)	[1.51 ln (hardness) - 3.37] on a 24-hour average. [1.51 ln (hardness) - 1.39] not to exceed at any time
Benzene (EPAb)	For benzene, the criterion to protect freshwater aquatic life, as derived using the guidelines, is 3,100 µg/l as a 24-hour average and the concentration should not exceed 7,000 µg/l at any time. The criteria for saltwater aquatic life as derived using procedures other than the guidelines, is 920 µg/l as a 24-hour average and the concentration should not exceed 2,100 µg/l at any time. For human health the potential carcinogenic effects of exposure to benzene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero.
Phenols (EPA, 1976)	The criterion for phenols is 1 µg/l for domestic water supply and to protect against fish flesh tainting.
Solids (dissolved) and salinity (EPA, 1976)	The criterion for solids is 250 mg/l for chlorides and sulfates in domestic water supplies (welfare).
Ammonia (EPA, 1976)	The criterion for ammonia is 1.02 mg/l (as un-ionized ammonia) for freshwater aquatic life.

Table 55. State Water Criteria for Certain Pollutants

<u>State</u>	<u>Pollutant</u>	<u>Criteria</u>
Alabama BNA, 1980p	Toxic substances	0.1 of 96-hour TLM value
Arizona BNA, 1980q	Toxic substances	Shall not be present in concentrations which are deleterious to human, animal, plant or aquatic life.
Illinois BNA, 1980r	Chromium (total)	0.05 maximum concentration mg/l
	Lead	0.05 maximum concentration mg/l
Iowa BNA, 1980s	Nitrogen - nitrate	10.0 maximum concentration mg/l
	Chromium (total)	0.05 mg/l
	Nitrate, as (NO <sub>3</sub> )	45 mg/l
	Ammonia Nitrogen	2.5 mg/l
	Phenol - includes all phenolic compounds	0.05 mg/l
Kansas BNA, 1980t	Ammonia	Undissociated ammonium hydroxide concentration of waters of the state shall not exceed 0.15 mg/l as nitrogen
	Toxic substances	Limited to concentrations in the receiving water that will not be harmful.
Louisiana BNA, 1980u	Toxic substances	Not exceed 1/10 96-hour median tolerance limit bioassay
	Toxic substances	None alone or in combination with other substances or wastes in concentrations rendering the receiving water unsafe.

Table 55 continued

Nevada BNA, 1980w	Chromium	Not more than 0.1 mg/l
	Lead	Not more than 0.05 mg/l
	Ammonia nitrogen	Not more than 0.02 mg/l
	Phenols	Not more than 0.001 mg/l
New Mexico BNA, 1980x	Chromium	0.05 mg/l, .05 96-hour median tolerance limit
	Lead	0.05 mg/l
	Nitrate	10.0 mg/l
	Phenols	0.005 mg/l
	Ammonia	0.02 m/l
Oregon BNA, 1980y	Chromium	0.02 ppm
	Lead	0.05 ppm (50 ug/l)
	Phenols	0.001 ppm
	Total Dissolved Solids	100 ppm
	Nitrate Plus Nitrate	0.30 mg/l
	Chromium (total)	3.0 ppm daily maximum concentration
	Lead	10.0 ppm daily maximum concentration
Tennessee BNA, 1980z	Phenols	1.0 ppm daily maximum concentration
	Suspended solids	40 ppm daily maximum concentration
	Average	Daily con posite
	0.5 ppm	1.0 ppm
Texas BNA, 1980aa	Lead	0.5 ppm
	Chromium	1.0 ppm

Table 55 continued

	Standard for raw Water source for domestic use:	Standard for Protection of aquatic wildlife:
Utah BNA, 1980ab	Chromium, dissolved Lead, dissolved NH <sub>3</sub> as N	<hr/> .10 mg/l .05 mg/l .02 mg/l
Virginia BNA, 1980ac	Chromium (total) Lead	Public water supply standard in mg/l: 0.05 mg/l 0.05 mg/l
Wisconsin BNA, 1980ad	Toxic substances	Unauthorized concentrations of substances are not permitted that, alone or in combination with other materials present, are toxic to fish or other aquatic life.

The NPDES discharge limits for the AAP's are presented in Table 56 through 64. No data were presented for Badger AAP or Savanna AAP because no useful limitations were established. Also no NPDES limits were evaluated for Alabama AAP or Cornhusker AAP because they are inactive (Asselin, 1980).

Several AAP's have sewage treatment plants on-site. Because of the plants, they are allowed to release relatively high amounts of COD, nitrates and suspended solids. Radford AAP can release up to 7470 kg/day of COD and 3976 kg/day of nitrates at their sewage treatment plant outfall. Joliet AAP can release up to 1376 kg/day of COD and 1376 kg/day of nitrate from certain outfalls. The AAP's which do not have sewage treatment plants typically have release limitations on COD, nitrates and suspended solids of less than 200 kg/day. The release of explosives as nitrocompounds has usually been limited to less than 1.0 ppm. However, Iowa AAP was permitted to release a maximum of 25 ppm of RDX. Lead limitations ranged from 0.1-1.0 ppm, when they were specified. Total chromium limitations range from 0.05-1.0 ppm.

Piercy (1978) stated that current NPDES effluent limitations for TNT ranged from 0.3-0.5 ppm for a seven day average, RDX average values were 15 ppm and nitrocompounds ranged from 0.3-1.0 ppm. Piercy (1978) predicted that new NPDES permits would have limitations of 0.01 ppm on TNT, 0.03 ppm on RDX and 0.03 ppm on HMX.

Table 56. Range of Discharge Limitations for Outfalls at Joliet AAP, Illinois (Ulrich, 1979)

Effluent Parameter	Daily Average (kg/day)	Daily Max. (kg/day)	Daily Max. (mg/l)
COD	1.71 - 1194	2.62 - 1376	30
Iron, dissolved	0.028 - 20	0.13 - 23	.5
Nitrates, as "N"	716 - 1194	512 - 1376	30
Sulfates	150.6 - 23880	187.6 - 27520	600
Suspended Solids	0.85 - 597	1.31 - 688	15
Mercury	0.000028 - 0.02	0.0004 - 0.023	.0005
Lead	0.0057 - 0.022	0.0086 - 0.34	0.1
Sulfite	3.01	3.75	-
Nitrite	48	34 - 55	2.0
TNT			0.14

Table 57. Discharge Limitations for Outfalls at Indiana AAP, Indiana (Donald, 1978)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
Ammonia Nitrogen	0.3 - 6.0	0.7 - 10.0
Nitrate, as "N"	0.3 - 3.2	1.0 - 10.3
Phosphorus, as "P"	0.2 - 4.4	0.5 - 9.8
COD	14 - 70	30 - 153
TSS	6 - 10.2	10 - 45
Flow	18.9 - 6048 m <sup>3</sup> /day	26.5 - 6048 m <sup>3</sup> /day

Table 58.. Discharge Limitations for Iowa AAP, Iowa  
(Snow, 1980)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
TNT	0.05	1.0
RDX	15	25
Phosphate, total	5	10
Chromium, total	0.1	0.15
Copper	1.0	2.0
Zinc	1.0	2.0
Lead	0.1	0.15
Iron, dissolved	1.0	2.0
Ammonia	2.0	
Flow	20 - 2794 m <sup>3</sup> /day	40 - 4750 m <sup>3</sup> /day

Table 59. Discharge Limitations for Sunflower AAP, Kansas (Svore, 1974)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
Aluminum, dissolved	1.0	2.0
Iron, dissolved	1.0	2.0
Sulfate	215	275
Suspended Solids	30	-

Table 60. Discharge Limitations for Louisiana AAP, Louisiana  
(Dutton, 1979a)

Effluent Parameter	Daily Average (kg/day)	Daily Maximum (kg/day)
Zinc	.9	1.6
Total Phosphorus	0.49 - 0.67	0.57 - 1.68
Iron	1.34 - 2.2	1.64 - 3.3
Chromium, Total	1.1	1.6
Chromium, III	0.23	0.26
Chromium, VI	0.15 - 0.49	0.22 - 0.33
Nickel	1.2	2.4
Copper	1.3	2.4
Total Suspended Solids	49.0 - 65.3	96.0 - 192.9
Flow	143.6 m <sup>3</sup> /day	1701.0 m <sup>3</sup> /day

Table 61. Discharge Limitations for Milan AAP, Tennessee  
(Ravan, 1974)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
Chromium		1.0
Zinc	0.5	1.0
Copper	0.5	1.0
Phenol	1.0	2.0
Nitro bodies, total (TNT, RDX, Tetryl)	1.0	1.5
Suspended Solids	25.0 - 30	40.0 - 50

Table 62. Discharge Limitations for Volunteer AAP, Tennessee  
(Harvey, 1980)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
Ammonia Nitrogen		1.5
Dissolved Solids	750	1800
Suspended Solids	30	60
Nitrate	-	10
TNT and Nitrobenzenes	0.3	0.5
Chromium	-	0.05
Iron	-	1.0
Manganese	-	1.0
Phosphorus	-	1.0
Sulfate	-	0.1
Weekly Average Flow	19.0 - 567 m <sup>3</sup> /day	

Table 63. Discharge Limitations for Lone Star AAP, Texas  
(Dutton, 1979b)

Effluent Parameter	Daily Average (mg/l)	Daily Maximum (mg/l)
Lead, total	0.5	1.0
COD	-	200

Table #4. Discharge Limitations for Radford AAP, Virginia  
(Lawson, 1979)

Effluent Parameter	Daily Average (kg/day)	Daily Maximum (kg/day)
COD	90 - 3995	406 - 7470
Oxidized Nitrogen	50 - 2471	148 - 3976
Sulfates	2442 - 37093	1353 - 37490
TNT and Nitrobenzenes	0.87	1.31
Total Suspended Solids	29 - 7491	58 - 11912

## XI. CONCLUSIONS AND RECOMMENDATIONS

A comparison of the various technologies considered for decontamination of lagoon sediments is presented in Table 65. In essence, the molten salts incineration and the microwave plasma methods are not developed (either equipment or data on explosives degradation) to the point where they can be considered for decontamination of explosives in lagoon sediment. The equipment for electron beam processing, gamma irradiation and UV-oxidation is relatively well developed. However, a data base for decontamination of high concentrations of explosives in sediment by these methods has not been established. Incineration and wet-air oxidation are both proven technologies for degrading high concentrations of all explosives. Explosives degradation with incineration and wet-air oxidation has been demonstrated on a scale similar to that required for decontamination of lagoon sediment. Chemical degradation of high concentrations of nitrocellulose has also been demonstrated but on a laboratory scale. Another process which has also been demonstrated on a large scale for degrading TNT is composting (Osmon and Andrews, 1978). Thus, based on the available technical information, incineration, wet-air oxidation, chemical degradation of nitrocellulose, and composting for TNT appear to be the most viable processes.

Even though wet-air oxidation, incineration and composting have been demonstrated for explosives degradation at the pilot or commercial scale, these processes could not be placed in the field without testing on actual lagoon sediment samples. Each process has advantages and disadvantages and pollutant effluents associated with it which must be ascertained on the actual material. In most instances, secondary pollution control techniques can remove the pollutants in the effluent to discharge levels. These pollution control devices must be selected and sized to meet the particular needs. A major pollution problem of high metal air emissions could occur if sediments containing high levels of metals are incinerated. However, the significance of metallic air pollution can not be ascertained until adequate analytical data are available on metal levels in the various lagoons to be treated.

It is difficult to put a dollar value on the various advantages and disadvantages of the treatment processes in this preliminary study. Therefore only the capital and operating costs of the processes will be used. In comparison of capital costs, chemical degradation (\$217,500) and composting (\$307,010) are the least expensive. Incineration capital costs range from \$468,000-\$826,000 while capital costs of wet-air oxidation are \$3,722,600. Operating costs are \$542,000 for chemical degradation, \$379,600 for composting, \$312,300-\$547,300 for incineration and \$657,000-\$664,000 for wet-air oxidation. Based on cost comparisons, wet-air oxidation appears to be by far the most expensive of the "proven technologies." The high costs associated with this process, the bulkiness of the reactors and the long lead time associated with obtaining the equipment make wet-air oxidation an unattractive alternative for lagoon sediment decontamination.

Table 65. Summary of Potential Lagoon Sediment Treatment Methods

Technology	Capital Costs w/o post Treatment	Capital Costs w/ post Treatment	Operating Costs w/post treatment	Major Advantages	Major Disadvantages
Wet-air Oxidation	\$3,722,600	\$3,958,900-4,839,900	\$657,000-\$664,000	Proven technology for degradation of high concentrations of propellants. No metallic air emissions.	High capital costs. Potential problems with dirt build up in the reactor. High down-time and maintenance costs. Requires post treatment. Difficult to transport. Dilution of the sediment is required.
Incineration	\$468,000-826,000		\$312,300-547,300	Proven technology for degradation of high concentrations of propellants and explosives. Lower capital and operating costs. No sediment dilution is necessary. Easily transported. No aqueous post treatment necessary.	Air pollution abatement devices are necessary. Metals in the sediment result in air pollution problems in all incinerators except the electric furnace. High down-time and maintenance costs.
Blitten Salts	\$1,747,300-2,257,000		\$2,525,300-2,500,000	Soluble acidic off gases	Low heating value of sediment requires high fuel expenditures. High ash content of sediment requires frequent change in the salt bed leading to high salt and fuel costs. High capital costs. Large quantities of salt must be disposed of. Not easily transported. No full scale unit operational.
Microwave	costs unavailable		costs unavailable		Reactor not suited for use with sediments. Process not sufficiently developed. No data on degradation of explosives by this process.
Electron Beam Processing	\$2,031,200	\$2,345,000	\$413,000	Equipment high developed. Downtime low. Energy and water costs low. No metal air emissions.	Data base for destruction of toxic materials is limited. Hazards associated with handling explosives is unknown. Degradation products and degradation rates unknown. Requires dilution of the sediment.

Table 65 continued

Chemical Reduction	\$452,000	\$1,059,000	\$310,600	<p>Data on degradation of high concentration of explosives not available. Degradation products and reaction rates unknown. Safety aspects of handling high concentrations of explosives is unknown. Public reaction.</p>
UV Oxidant	\$9,491,500	?	\$3,820,200	<p>Capital and operating costs are very high. No data exists on UV-oxidant degradation of explosives in more concentrated forms. System would not be transportable. Very high dilution of sediment required. Potential problems with sediment clogging reactors.</p>
Chemical Degradation of Nitrocellulose	\$217,500	?	\$542,000	<p>Data suggests that degradation of nitrocellulose to readily biodegradable products can be accomplished. Low capital costs. No dilution of sediment required.</p>
Composting	\$307,000	?	\$375,600*	<p>Data available on 80% TNT degradation. Low capital and operating costs. No dilution of sediment required. No down-time.</p>

\*Baker et al., 1988

Composting and chemical degradation of nitrocellulose require significant laboratory and pilot studies to optimize conditions and identify the degradation products. For composting to be of value, it must also be applicable to RDX. The applicability of composting to the degradation of this explosive has not been shown. Thus, approximately one year would be required to develop composting into a usable process. To prove the reliability and identify the degradation products of the ammonium hydroxide-nitrocellulose reaction will take approximately four months of effort. Pilot scale studies will also have to be conducted to obtain the necessary process parameters for design of a full scale unit. Pilot studies will require eight months to build the plant and obtain process parameters. Thus, both of these processes are at least a year away from the point where they could be implemented. However, their low capital and operating costs make them attractive candidates for further study. Thus, it is recommended that the Army undertake further work to more thoroughly investigate these technologies.

Of the processes, incineration is the most readily implementable method for decontamination of lagoon sediments. Therefore, further investigation into incineration of explosives contaminated lagoon sediments should be undertaken. Three incineration processes appear to be applicable to the lagoon sediment problem - rotary kiln, fluid bed and electric furnace. Tooele is also developing a "car bottom" incinerator which is supposed to handle 1000 lb/hr and will be at all explosives plants (Crist, 1980). At least two of these processes should be tested. The initial work on incineration of lagoon sediment should be laboratory testing of the sediment to determine the heat content of the material. These tests should take approximately one month. Pilot-scale testing of at least two types of incinerators should be performed to determine air emission levels. At least one of the samples for each incineration type should intentionally be spiked with lead oxide to determine lead air emissions.

There are many problems associated with pilot scale tests on explosives incineration by commercial firms which must be evaluated. First many of the firms have no explosive handling capabilities and thus knowledgeable personnel will have to be present throughout the tests. Second, the equipment must be insured against damage. Thus, a special insurance policy will have to be purchased for the tests. Third, EPA permits may have to be obtained before the tests can be conducted. Utilization of this site would eliminate the insurance and handling problems associated with the explosives. It is also recommended that the electric furnace be further investigated if satisfactory arrangements can be made with the manufacturer.

In summary, microwave plasma and molten salts approaches are not developed sufficiently to be considered as viable processes for the lagoon sediment decontamination problem. Insufficient data are available on the UV-oxidation, electron beam and gamma radiation processes for inclusion as viable alternatives. However, since Sandia has offered to run a laboratory scale test for no fee, it might be worthwhile to obtain preliminary data on the applicability of this technique. Of the demonstrated explosives degradation processes, wet-air oxidation is considerably more expensive than the other processes and it is recommended that this method not be further considered. Composting and chemical degradation of nitrocellulose each require approximately one year of developmental effort. The further development of these processes for future use should be undertaken. Of all the processes, incineration is the only short lead time cost effective method. It is recommended that at least two incinerators be evaluated at the pilot scale level.

The cost of decontamination of the lagoon sediments may appear to be high. It must be remembered that the yearly operating costs are for treatment of 11 lagoons. In comparison, it would cost from \$162,000 to \$294,000 to completely bottom seal one of these standard lagoons (Kitchens, 1980). Thus, it is more cost effective to decontaminate the source than to prevent its escape into the ground water.

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LIST OF SYMBOLS AND ABBREVIATIONS

AAP	-	Army Ammunition Plant
AD	-	Army Depot
Å	-	angstrom ( $10^{-8}$ cm)
A - 5	-	propellant composition
B	-	propellant composition
BNA	-	Bureau of National Affairs
BOD <sub>5</sub>	-	biochemical oxygen demand, 5 day
BTU	-	British Thermal Unit
CaCO <sub>3</sub>	-	calcium carbonate
cal	-	calorie
C <sub>4</sub> H <sub>10</sub> FO <sub>2</sub> P	-	GB chemical agent
(CH <sub>3</sub> O) <sub>3</sub> P	-	trimethylphosphite
C <sub>11</sub> H <sub>26</sub> PO <sub>2</sub> S	-	VX chemical agent
cm	-	centimeter
CO	-	carbon monoxide
COD	-	chemical oxygen demand
CO <sub>2</sub>	-	carbon dioxide
Cr	-	chromium
Cs	-	cesium
Cu <sup>++</sup>	-	copper ion
curie	-	unit of radioactivity
D <sub>10</sub>	-	dose necessary to reduce the population of microorganisms by ten.
DDT	-	dichlorodiphenyltrichloroethane
°C	-	degrees Celsius
°F	-	degrees Fahrenheit
DIMP	-	diisopropyl methylphosphonate
DMMP	-	dimethyl methylphosphonate
DNT	-	2,4- dinitrotoluene
ε	-	epsilon
EIS	-	Environmental Impact Statement
EPA	-	Environmental Protection Agency
ergs	-	measure of work
ft	-	feet
g	-	gram
gal	-	gallon
GB	-	C <sub>4</sub> H <sub>10</sub> FO <sub>2</sub> P

GC	-	gas chromatography
gpm	-	gallons per minute
HBr	-	hydrogen bromide
HC	-	hydrocarbon
He	-	helium
HMX	-	cyclotetramethylene tetranitramine
H <sub>2</sub> O	-	water
H <sub>2</sub> O <sub>2</sub>	-	hydrogen peroxide
hp	-	horsepower
HPLC	-	high pressure liquid chromatography
hr	-	hour
HZ	-	Hertz (measure of frequency)
ICT	-	Insulating Core Transformer
JTU	-	Jackson Turbidity Unit
k	-	kilo- (10 <sup>3</sup> )
k <sub>1</sub>	-	rate constant for chemical reaction
K <sub>2</sub> CO <sub>3</sub>	-	potassium carbonate
kg	-	kilogram
kV	-	kilovolt
kW	-	kilowatt
l	-	liter
lb	-	pound
log <sub>10</sub>	-	logarithm to base 10
M	-	mega- (10 <sup>6</sup> )
M	-	molar
m	-	milli- (10 <sup>-3</sup> )
μ	-	micro- (10 <sup>-6</sup> )
μ	-	micron (10 <sup>-6</sup> meter)
MeV	-	mega electron volts
mg	-	milligram
M̄GD	-	million gallons per day
min	-	minute
min <sup>-1</sup>	-	inverse minute
Molar	-	(measure of concentration)
N	-	atomic nitrogen
N <sub>2</sub>	-	molecular nitrogen
Na <sub>2</sub> CO <sub>3</sub>	-	sodium carbonate

NaHCO <sub>3</sub>	-	sodium carbonate hydrogen
NaHS	-	sodium sulfide
NaOCL	-	sodium hypochlorite
NH <sub>4</sub> OH	-	ammonium hydroxide
NH <sub>3</sub>	-	ammonia
NO <sub>x</sub>	-	nitrogen oxides
NO <sub>3</sub>	-	nitrate ion
NPDES	-	National Pollutant Discharge Elimination Systems
o	-	ortho
O <sub>2</sub>	-	molecular oxygen
O <sub>3</sub>	-	ozone
P	-	para
Pa	-	Pascal (unit of pressure)
Pb	-	lead
PCB	-	polychloro biphenyl
%	-	percent
pfu	-	plaque forming units
pH	-	potential of hydrogen (measure of hydrogen ion concentration)
PNA	-	polynitroaromatic compounds
ppb	-	parts per billion
ppm	-	parts per million
psia	-	pounds per square inch absolute (unit of pressure)
PVC	-	polyvinyl chloride
RAAP	-	Radford Army Ammunition Plant
rads	-	unit of energy absorbed from ionizing radiation
RBC	-	rotating biological contractors
RDX	-	hexahydro-1,3,5-trinitro-1,3,5-triazine
rpm	-	revolutions per minute
sec	-	second
SO <sub>2</sub>	-	sulfur dioxide
SS	-	stainless steel
SO <sub>x</sub>	-	sulfur oxides
t	-	time
TNB	-	trinitrobenzene
TNT	-	2,4,6-trinitrotoluene
TOC	-	total organic carbon
Torr	-	unit of pressure
TS	-	total solids

TSS - total suspended solids  
TVS - total volatile solids  
UV - ultraviolet  
VX -  $C_{11}H_{26}PO_2S$