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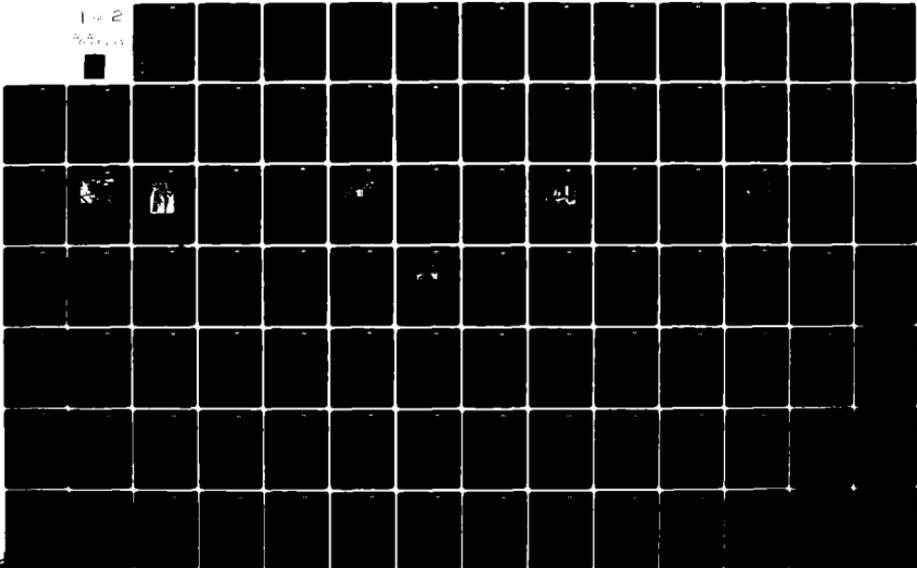
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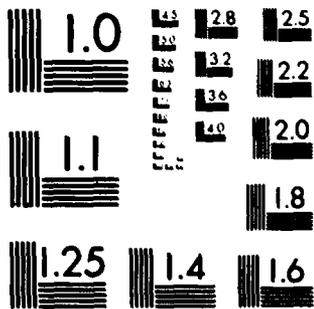
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Environmental Monitoring & Services Center  
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Report EMSC8313.1FR

Contract No. DAAG53-75-C-0271

12/15

**EXPERIMENTAL OILY WASTEWATER SEPARATION SYSTEM**

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28 November 1980

Final Report for Period 30 April 1975 - 15 October 1980

Approved for public release, distribution unlimited

Prepared for

U.S. ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT COMMAND  
Fort Belvoir, VA 22060

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A093 404	
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
EXPERIMENTAL OILY WASTEWATER SEPARATION SYSTEM.		Final Report 4/30/75 - 9/15/80
6. AUTHOR(s)		7. PERFORMING ORG. REPORT NUMBER
Steven Charles Gibson		EMSC8313.1FR
		8. CONTRACT OR GRANT NUMBER(s)
		DAAG53-75-C-0271
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Rockwell International Environmental Monitoring & Services Center 2421 West Hillcrest Drive Newbury Park, CA 91320		
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
U.S. Army Mobility Equipment Research and Development Command Fort Belvoir, VA 22060		28 November 1980
13. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		14. NUMBER OF PAGES
DCASMA 6230 Van Nuys Blvd. Van Nuys, CA 91408		131
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release, distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
Blank		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Ozone, Ultraviolet, Treatment, Oily Wastewater, Bilgewater, Ballast Water, Dissolved Organics, Suspended Organics		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The design, construction, testing, and delivery to the Army of an experimental system for total oil removal from oily bilge and ballast waters is described. The experimental system uses a two-stage treatment process. The first stage employs an oil-water separator using coalescence for the removal of suspended organics (oil). In the second treatment stage the dissolved organic compounds in the oily wastewater are oxidized by ozone in the presence of ultraviolet light in a well-stirred tank reactor. Laboratory testing with pure organic compounds in water, bilgewater simulants, and bilgewater demonstrated the		

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↙ enhancement of oxidation rates with increasing UV dosage. Both batch and flowthrough tests were conducted. Optimum treatment parameters depend on the goal of treatment (i.e., high throughput versus cost).

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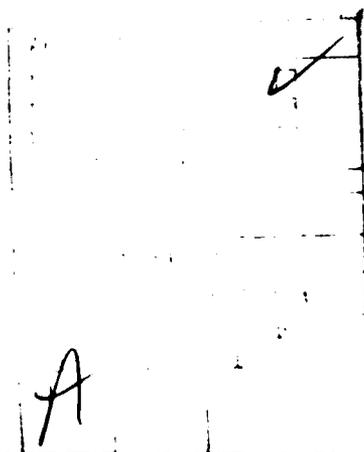
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### ACKNOWLEDGEMENTS

The author gratefully acknowledges the technical and management assistance provided by Mr. Edward C. Russell, Chief, Fuel and Water Quality Branch, Engineering Division, Energy and Water Resources Laboratory, U.S. Army, and Mr. Winfred Lindley, Army Project Officer. Special thanks are extended to Messrs. Lindley and James Christopher, Engineering Technician, U.S. Army, who installed the test system on board the Floating Machine Shop and who, along with Mr. Russell, were present during the on-board testing.

The assistance of Mr. Wen-Hsiung Tu and Mr. Larry F. Marx, EMSC, during the laboratory testing is also acknowledged.



## 1.0 SUMMARY

This final report describes a program to design, construct, test, and deliver a state-of-the-art experimental system using ozone in the presence of ultraviolet (UV) radiation for total oil removal from bilge and ballast oily wastewater.

During the design phase, a flow loop was constructed so that oil-water mixtures could be prepared. One such mixture was used for preliminary testing to determine the ozone and UV dosages required to destroy the compounds dissolved in the water phase of the oil-water mixture. Based on the results from these tests, a system was designed and constructed to treat oily wastewater utilizing a two-stage process.

The first stage uses an off-the-shelf oil-water separator employing the principle of coalescence to remove most of the free or undissolved oil from oily wastewater. The second process stage consists of a stainless steel reactor assembly where the dissolved components in the oily wastewater are oxidized with ozone in the presence of UV radiation.

During the laboratory testing phase of this program, both batch and flowthrough tests were conducted using: (1) solutions of pure compounds mixed with water which represented the types of compounds found dissolved in the water phase of oil-water mixtures, (2) prepared bilgewater mixtures synthesized by mixing various refined oils and fuels with water, and (3) actual bilgewater collected from Army watercraft.

The results of the laboratory tests established the optimum UV and ozone levels for removing pollutants from the test solutions and mixtures. Additionally, the effects of salt, stripping, reaction fluid concentration, and type of reaction fluid on treatment were evaluated.



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The laboratory test results indicate that the UV-ozone treatment process produces significantly improved oily wastewater effluent over that obtainable by currently employed treatment methods which do nothing to remove the dissolved oil component. The cost of treatment is attractive in light of the costs and problems associated with alternative treatment methods. For example, with only minor system modification, 1000 gallons of a simulated bilgewater can be effectively treated for approximately \$16. If a slightly higher organic content can be tolerated in the effluent, costs could be reduced to \$7.00. A program is recommended which would investigate ways of further reducing treatment costs.

Laboratory tests also established that the system produced no hazardous ozone, noise, or UV emissions. After the laboratory testing phase, the system was modified for shipboard installation. The modification involved changes in both the plumbing configuration and in the electrical system. Semi-automatic control of the system components was provided. The modified system was installed on board an Army watercraft and personnel were instructed in its use. An operations manual was prepared for the on-board system and is included as an appendix to this report. A 3-week laboratory testing program was conducted, funded under a separate but allied project (Contract No. DAAK70-78-C-0075). The results of the on-board tests appear in the final report of this allied project.



## 2.0 INTRODUCTION

### 2.1 BACKGROUND

This final report describes a program to design, construct, test, and deliver a state-of-the-art experimental system using ozone in the presence of ultraviolet (UV) radiation for total oil removal from bilge and ballast oily wastewater.

The United States Army recognized the need for such a program with the promulgation of the Federal Water Pollution Control Act. The Act, as amended, directs the Administrator of the Environmental Protection Agency to establish regulations for the discharge of bilge and ballast from ships. As a result, the EPA issued Regulations on Discharge of Oil (40CFR110; 25 November 1971), wherein Section 110.3 states that no discharges will take place which:

- (a) Violate applicable water quality standards
- (b) Cause a film or sheen upon or discoloration of the surface of the water or adjoining shoreline or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines

The regulations make it unlawful to discharge water containing insoluble or emulsified oil, but are silent on the discharge of water containing dissolved oil or other organic compounds. Thus, bilge and ballast waters treated for removal of insoluble oil to the 10-ppm level will usually satisfy today's EPA regulations.

The Act, however, does state, in Section 101:

"... it is the national goal that the discharge of pollutants into navigable waters be eliminated by 1985."

While contemporary regulations are addressed to insoluble oil, both the spirit and, by 1985, the letter of the act will require zero pollutant discharge.



### 2.1.1 Bilge and Ballast Water Composition

Bilge and ballast water, which constitute the major quantities of shipboard wastewater that require cleanup before discharge, are extremely variable in composition. Primarily, they consist of an aqueous phase in contact with a less dense and much less voluminous oily phase that floats on the water surface.

The aqueous phase of wastewaters generated on shipboard may be primarily fresh or marine, depending on their original source. They may, therefore, contain a considerable quantity of dissolved salts or may be nearly salt-free. In either event, they will contain the dissolved and suspended organic matter usually found in natural waters, as well as the inorganic suspended solids invariably present in such water. In principle, discharge of those components present in shipboard wastewaters that were originally present in their natural water source is permitted, but distinguishing and separating them from the contaminants introduced into bilge and ballast water is technically infeasible and economically unwarranted.

However, in addition to the naturally dissolved and suspended constituents, the wastewater will be contaminated by a variety of materials from a number of sources. Some may dissolve or disperse in water, some may remain suspended, and some may be formed as a result of biological and other processes acting on the otherwise insoluble oily phase. The magnitude of this contamination will depend on the nature of the oily layer in contact with the water, the temperature, the occurrence of mixing processes and the duration of contact before attempting to discharge the wastewater.

Despite its highly variable composition, treatment of the waste before discharge must include provision for removal of free, dispersed, and emulsified oil so that no visible sheen appears on the discharge water, and for removal of dissolved components that might otherwise damage the receiving water. To avoid the appearance of sheen, the undissolved oil content discharged must be at most 7 to 8 parts per million. To avoid ecological damage, the dissolved components must be reduced to a concentration that depends on their specific composition.



The solubility of hydrocarbons, even aromatic ones, in water is limited, but dispersion of oil globules by naturally occurring or artificially introduced emulsifying agents (e.g., detergents used to wash down decks) can greatly increase the total amount of nonfree oil that must be dealt with in wastewater. Further, it is well recognized that some oils (especially diesel fuel and used lubricating oil) may contain water-soluble components that will contribute to the total organic content of water with which they come in contact. The type of compounds and their concentrations found in dissolved oily bilge and ballast water depend on at least the following factors:

1. Source of water
2. Source and amount of oil in contact with water
3. Temperature
4. Duration of contact
5. Mixing of oil and water layers by ships' motion and vibration
6. Shipboard operations that contribute water-soluble compounds to wastewaters
7. Biological activity at oil-water interface
8. Exposure to air oxidation

The kinds of organic compounds dissolved in the water resulting from time-dependent effects will be determined predominantly by the original composition of the oil. For example, the order of hydrocarbon consumption by micro-organisms has been found to proceed according to the following progression (Ref. 1):

- Even carbon, linear  $C_6-C_{16}$  paraffins
- Odd carbon, linear  $C_5-C_{17}$
- Branched paraffins  $C_5-C_{17}$
- Low-molecular-weight aromatics with aliphatic side chains
- Aromatics with no side chains



- Linear hydrocarbons above C<sub>20</sub>
- Polynuclear aromatics

Hydrocarbons below about C<sub>12</sub> are lost by evaporation in the open ocean in about 24 hours, and even in the confines of bilge and ballast tanks, would be expected to evaporate more rapidly than higher homologs. Chemical oxidation should result in most rapid attack of low-molecular-weight, branched paraffins that contain large numbers of tertiary H-atoms and olefinic hydrocarbons (Ref. 1).

Hence, the hydrocarbons themselves may be expected to contribute oxygenated paraffinic compounds by oxidation of the C<sub>16</sub> and lower compounds to form products that dissolve in the aqueous layer. Water-soluble compounds derived from the aromatic hydrocarbons in the original oil may be present in smaller quantity. However, it is believed that compounds which possess aromatic structure tend to be more toxic to aquatic life than aliphatic compounds. Therefore, treatment methods should be able to remove aromatic compounds to a greater extent than the less toxic aliphatic compounds.

### 2.1.2 Ozone-UV Overview

Ozone is the triatomic form of oxygen and is a very powerful oxidizing agent, with over 1-1/2 times the oxidizing potential of chlorine. It is formed by the dissociation of diatomic oxygen according to the following assumed reactions:

1.  $O_2 \rightarrow O + O$
2.  $O + 2O_2 \rightarrow O_3 + O_2$

Ozone is a pale blue gas, with a strongly pungent odor that is detectable by human olfaction at about 0.1 ppm by volume, and is extremely toxic (see Fig. 2-1). However, even though ozone is extremely toxic and corrosive, it presents no safety or handling problems when the handling equipment is well designed and of the proper materials. Ozone can be formed by the following methods:

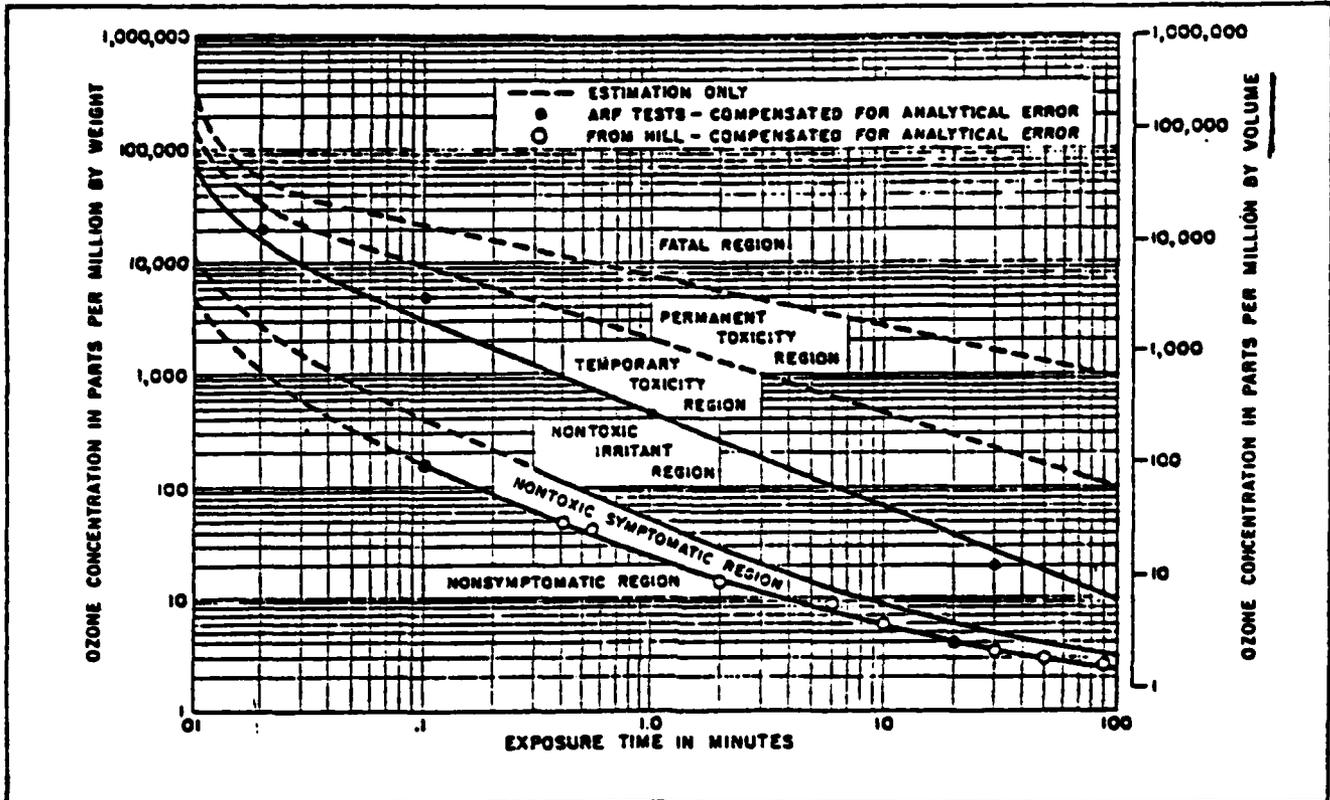


Figure 2-1. Ozone Toxicity  
(from Ref. 2)



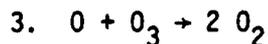
- A. Plasma jet
- B. Radiochemically
- C. Photochemically
- D. Silent electrical discharge

Almost all ozone is produced by the latter two methods and if large amounts are required, the silent electrical discharge is used exclusively. With this method, air, oxygen-enriched air (e.g., using a pressure swing device) or pure oxygen feed is passed between two electrodes separated by approximately 0.1 inch. The potential difference between the electrodes is on the order of 20,000 volts and ozone is formed as oxygen is passed through the electrical discharge occurring between the electrodes.

Production of ozone by the silent discharge method is directly related to the following factors:

- A. Dryness of gas fed to the ozone generator
- B. Rate of gas fed to the ozone generator
- C. The power applied to the electrodes

The concentration of ozone in the gas stream exiting from the discharge gap is inversely related to B, above. The higher the ozone concentration, the greater the auto decomposition rate of ozone back into molecular oxygen:



The maximum concentration of ozone that can be economically produced is between 1 and 1.5% by volume, in air.

#### 2.1.2.1 Ozone Treatment Applications

The highly reactive nature of ozone makes its use attractive in a variety of applications, such as:

- Wastewater treatment
- Odor abatement
- Bactericide for ultra-pure water



Fungicide in closed loop cooling systems  
Oxidation of stack gas  $SO_2$   
Preservation of food  
Manufacture of pharmaceuticals  
Bleaching of pulp  
Bleaching of ultra-white clays  
Regeneration of photographic ferrocyanide bleach  
Catalyst  
Organic synthesis reactions  
Swimming pool disinfection

The first major application of ozone was for the sterilization of drinking water for the City of Nice, France, in the early 1900s. Today, in Europe, there are over 500 water treatment plants using ozone, and at least 18 such installations in Canada. In the United States, ozone is used to treat the water supply of Whiting, Indiana.

Ozone is of great importance in many industrial applications, some of which are listed above, both in wastewater treatment and in manufacture. Ozonation is used extensively for treating such industrial wastewaters as cyanide and plating wastes (Ref. 3), phenol-laden wastewaters (Ref. 4), mine drainage discharges (primarily acids and iron complexes, Ref. 5), and is also used for color removal (Ref. 6), to name a few applications.

#### 2.1.2.2 UV-Enhanced Ozonation

As discussed in the previous section, ozone has been applied to many water quality problems, including municipal water supply treatment, and industrial wastewater treatment. However, only recently have investigations into the combined use of ozone and ultraviolet light for water treatment been undertaken.

The effectiveness of ozone destruction of many undesirable compounds found in wastewater is increased enormously under the influence of UV



radiation. For example, the effect of UV dosage on the oxidation of acetic acid is presented in Fig. 2-2 (from Ref. 7). Acetic acid oxidation was quantified by total organic carbon (TOC) measurement, and normalized on the y-axis. Significant improvement in the oxidation rate of acetic acid is achieved with increasing UV dosage.

The primary photochemical processes that appear to be operative in UV-induced oxidation with ozone are the formation of free radicals as well as neutral molecules such as  $\text{CO}_2$  and  $\text{CO}$ . Formation of these free radicals leads to more rapid subsequent oxidation reactions with ozone. The smaller neutral molecules are more easily oxidized and are further activated by UV. This reaction scheme is diagrammed in Fig. 2-3 (from Ref. 7).

Many molecules that are difficult to oxidize (i.e., refractory), even with ozone, can be easily oxidized using UV-ozone treatment. In fact, the oxidation of some of these compounds occurs so readily that the reaction is limited only by the rate of ozone mass transfer from the gas phase to the liquid phase.

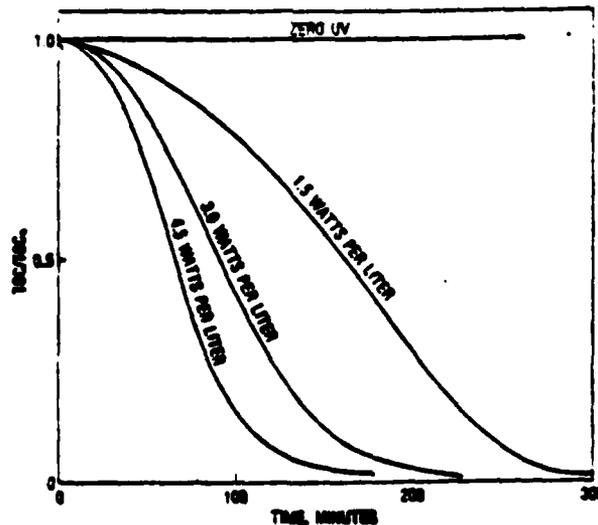


Figure 2-2. Ozone Oxidation of Acetic Acid, Effect of UV Near 30°C

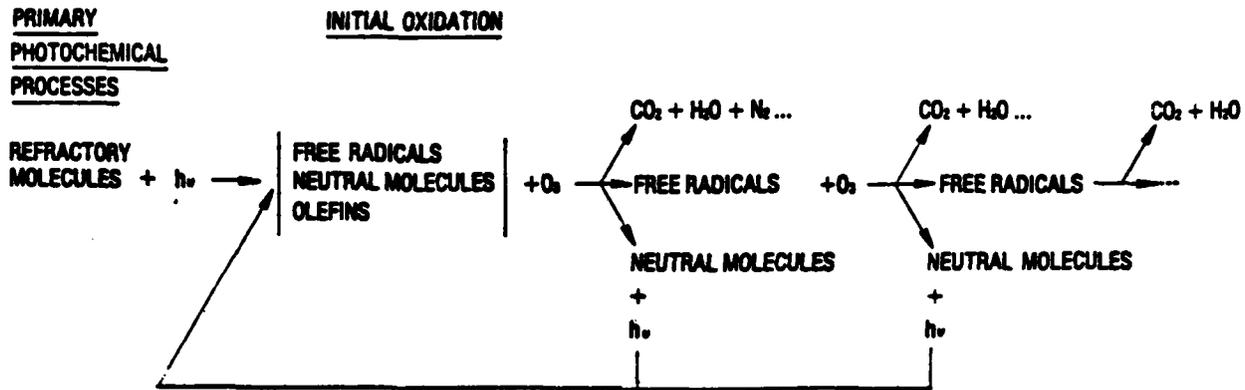


Figure 2-3. Overall Photochemical/Oxidation Process to Produce  $CO_2$ ,  $H_2O$ , etc.

## 2.2 PROJECT OBJECTIVES

The Army operates a sizable fleet of watercraft, consisting of tug boats, landing craft, barges, floating machine shops (FMS), supply ships, transports, and other specialized equipment. Consequently, the Army has investigated various treatment alternatives for the bilge and ballast waters from these watercraft, with an eye toward compliance with the future zero pollutant discharge requirement. One of these alternatives was the subject of this investigation, the design, construction, testing, and delivery of a state-of-the-art, integrated experimental system capable of separating and removing total oil (free, visible, dispersed, emulsified, soluble, dissolved, petroleum-derived organic materials) in oily wastewaters to a quantity of 5 parts per million or less, or to convert toxic substances to harmless compounds.

The system provides a two-stage treatment of the wastewater, and utilizes a new technology (ozone in the presence of ultraviolet [UV] light) for destruction of the petroleum-derived compounds dissolved in the water phase as the final treatment stage. The initial treatment step utilizes an off-the-shelf coalescence-type oil-water separator for removal of free or undissolved oil.



The Army recognized the advantages offered by the UV-ozone process for treatment of shipboard oily wastewater. One of the most important of these is that this process does not consume any material in limited supply. No quantities of replaceable items need be carried on shipboard. The source of ozone is dry compressed air fed through an ozonator in which an electric discharge converts some of the oxygen to ozone. The ozone-containing air is then allowed to contact the water to be treated under conditions to achieve the desired result. Ozone does not produce any undesirable products that create a disposal or regeneration problem.

The engineering and experimental efforts of this program were divided into three phases, as follows.

Phase I. Determine the engineering design parameters for the various components and unit processes for later fabrication of the experimental system, for removal of total oil from a flowing stream of oily wastewater. The design will be based on the constraints likely to be found on Army watercraft.

Phase II. Fabricate and assemble the commercial components and instruments procured as a result of the Phase I effort.

Phase III:

Task 1. Determine the composition of the effluent from the oil-water separator after passing an oil-water mixture through it.

Task 2. Determine experimentally the optimum conditions for rendering harmless by ozone-UV treatment under static conditions those toxic substances found to be prevalent in oily wastewater. Synthetic mixtures of the toxic substances in water will be exposed to the simultaneous effects of ozone and UV.



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Task 3. Optimize conditions for operation of the system with mixtures of toxic substances and other petroleum-derived compounds in water. The goal of this optimization will be to eliminate toxic substances at minimum expenditure of energy and cost. Nontoxic organic compounds will be permitted in the effluent up to 15 ppm.

Task 4. Conditions for operation of the system defined in the previous static batch tests will be applied to a flowthrough, steady-state operating mode to determine effectiveness in rendering harmless priority pollutants as identified in the Safe Drinking Water Act of 1974 and other regulatory sources. Tests will be conducted using mixtures of pure priority compounds in water, as well as actual oily bilge wastewaters collected from vessels belonging to the Army or others.

Task 5. The system will be modified to make it suitable for installation in the machinery space of a vessel. Safety shall be of primary concern, and such areas as ultraviolet leakage, ozone leakage, compatibility of electrical components with the shipboard environment, noise, and human factors engineering shall be addressed.

Task 6. Upon completion of all testing and system modifications, and prior to preparation for delivery, a demonstration test shall be conducted. The system will then be installed on board a selected Army watercraft, and a training course on the operation of the system will be conducted.

All phases of the program were completed. Tests of system performance were conducted both in the laboratory and in the field, on board an Army vessel. The results of the on-board testing program were funded under the program, "Technical Assistance: Mass Spectrometer Oil Monitoring System," Contract No. DAAK70-78-C-0075, and the results appear in the final report for this allied program. The sections that follow describe the design and fabrication of the system, the laboratory and field test configurations of the equipment, and the results of the laboratory investigation. Conclusions from the work described herein and recommendations for future work are also included.



### 3.0 SYSTEM DESIGN AND HARDWARE FABRICATION

The initial phase of this investigation was concerned with determining the various design parameters for treatment of the dissolved compounds in oily wastewater using UV-enhanced ozonation. With this information in hand, Phase II was executed, the fabrication and assembly of the total oil removal system. The following sections describe the Phase I and Phase II efforts.

#### 3.1 DETERMINATION OF DESIGN PARAMETERS

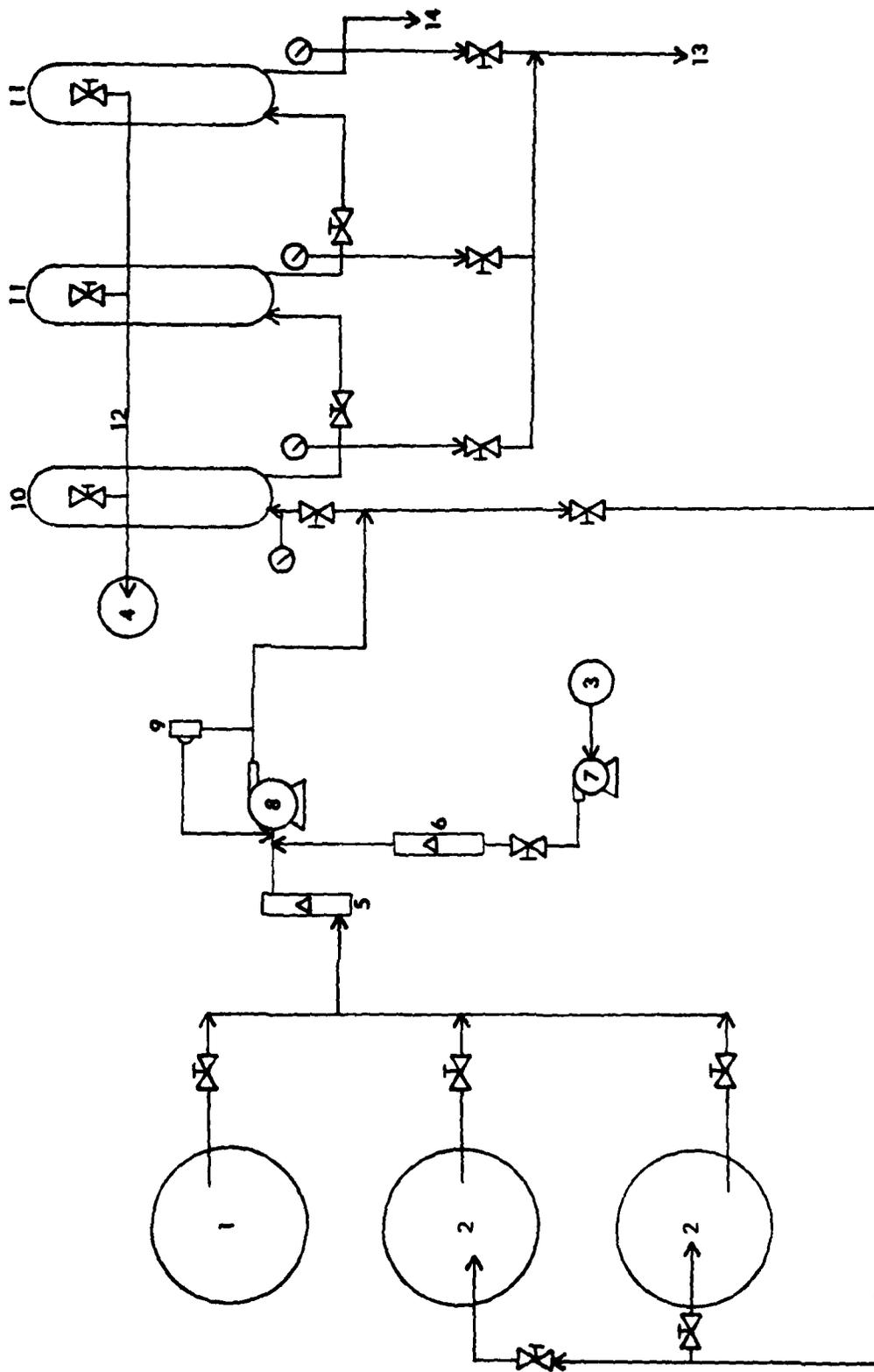
The first step of Phase I was to generate representative samples of oily wastewater which could be used to determine the ozone and UV dosages required for total oil removal. To this end, the flow loop schematically shown in Fig. 3-1 was constructed. Oil and water mixtures in any desired ratio could be prepared. This was accomplished by simultaneously metering water from the water storage drum and oil from the oil storage drum to the suction side of the main pump, in the desired ratio. The pump action effectively agitated the two fluids and the mixture was routed back to one of the oil-water storage drums. The mixture was then allowed to undergo separation for a predetermined period before being passed through the oil-water separator (made up of items 10 and 11 in Fig. 3-1) to remove the bulk of the free or undissolved oil. The water emerging from the oil-water separator, which contained primarily dissolved pollutants, was then collected from the sample line (item 14 in Fig. 3-1) and used for determining ozone and UV treatment levels.

A 55-gallon sample of an oil-water mixture prepared from tap water and used crankcase oil (with detergent additives) in a 9:1 ratio, by volume, was used for determining the ozone and UV treatment levels. The 55-gallon sample of oil-water mixture was sent to Houston Research, Inc., Houston, TX, for treatment with their bench-scale ozone-UV apparatus. Houston Research, Inc., conducted five experiments using three different ozone dosages, two different UV dosages, and with and without sea salt added to the oil-water



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- 1. Water storage drum
- 2. Oil-water storage drum
- 3. Oil storage drum
- 4. Recovered oil drum
- 5. Water flowmeter
- 6. Oil flowmeter
- 7. Oil pump
- 8. Main pump
- 9. Pressure relief valve
- 10. Prefilter stage
- 11. Coalescer stage
- 12. Recovered oil line
- 13. Drain
- 14. Sample line

Figure 3-1. Flow Loop for Preparing Oil-Water Mixtures



mixture in a 3% concentration. It was important to ascertain what effect, if any, salt had on the efficiency of UV-enhanced oxidation with ozone, since ultimately the equipment would be operated on ships that could contain salt water as the main component in their bilge and ballast oily wastewaters. The results of the tests conducted by Houston Research appear in Table 3-1. The results indicated that at higher ozone dosage rates the mass of ozone required per mass of TOC removed was increased. The lower ozone requirement at higher ozone dosages, however, was offset by a decrease in residence time required to reduce the TOC to 5 ppm.

As was expected, the addition of 3% sea salt lowered the overall oxidation rate. The interference from salts may have resulted from the oxidation of chloride which may have consumed some of the ozone and/or form hypochlorite that in turn absorbed some UV radiation. The effect of UV light on the ozone-TOC reaction in the presence of sea salt was substantial, as indicated by a comparison of the reaction times listed in Table 3-1 for experiments 4 and 5. Other than the single experiment without UV light, no experiments were conducted to determine the effect of UV intensity or the effect of the spectral distribution of the UV radiation on the reaction. Houston Research, Inc., was of the opinion that 4.2 watts/liter at wavelengths below 3600Å used in these experiments was probably excessive.

### 3.2 FABRICATION OF THE TOTAL OIL REMOVAL SYSTEM

The five experiments performed by Houston Research, Inc., and summarized in Table 3-1, provided the basic information on the ozone and UV dosages required to treat oily wastewater. Based on the results, the performance requirements of equipment to be delivered during this program, and the dimensional constraints placed on any equipment installed on board Army watercraft (e.g., equipment must be able to pass through watercraft hatchways), the following specifications were written up for the fabrication of the UV-ozone reaction portion of the total oil removal system:



TABLE 3-1. OXYPHOTOLYSIS OF OILY EFFLUENT RESULTING FROM THE  
MIXTURE OF WATER AND USED CRANKCASE OIL\*

Run No.	Ozone Dosage (mg/min)	Sea Salt Conc (%)	UV Intensity watts Titer < 3600A	Semibatch Reaction Time (min)**	Ozone Required O <sub>3</sub> /TOC
1	29.09	0	4.2	92	11.54
2	11.62	0	4.2	152	7.59
3	5.02	0	4.2	210	4.67
4	11.62	3	4.2	203	10.29
5	11.30	3	0	305	15.84

\* Results from tests conducted by Houston Research, Inc.  
\*\* Reaction time to reduce TOC from 16 ppm to 5 ppm.

1. The UV-ozone reactor shall include the following:
  - a. A Stainless steel reactor tank fitted with four baffles
  - b. A bolted removable lid for easy access to the tank interior
  - c. A stirring motor, shaft, and stirring impeller
  - d. An ozone-air sparger
  - e. UV lamps with electrical switches, power supplies and other components necessary for safe operation
  - f. Fittings or flanges and quartz, vycor, or Pyrex immersion wells for the UV lamps
  - g. A catalyst bed or thermal decomposition zone on the ozone-air exhaust line
  - h. A liquid sampling line
2. The reactor tank with all permanently attached parts shall be no larger than 18 inches in diameter.
3. The assembled unit (with support legs, stirring motor, and UV lamps mounted) shall be less than 5 feet in height.



4. The assembled unit will be constructed so that it is possible to remove the stirring motor, UV lamps, and stirring impeller with a maximum of 5 feet of head room.
5. The fluid inlet and exit lines shall be 1/2-inch standard pipe.
6. The ozone-air line to the sparger shall be constructed of stainless steel of a diameter to be specified by the supplier and will contain a check valve.
7. A pressure relief valve will be installed in the gas exhaust line.
8. The number, type, and power of the UV lamps required will be left up to the supplier.
9. The reactor must be equipped to accept one more UV lamp than the minimum required for the oxyphotolysis process to reduce the TOC content of the oily effluent to 5 ppm.

Houston Research, Inc., was contracted to fabricate the equipment and supply engineering drawings of the equipment. The drawings supplied by Houston Research utilized drawing numbers 13222E2643 through 13222E2690. These numbers were assigned by the U.S. Army Mobility Equipment Command, Mobility Equipment R&D Center. Once the equipment was received, inspected, and accepted, it was plumbed into the flow loop used to prepare the original oil-water mixtures (Fig. 3-1). The details of both the laboratory and field flow loop designs appear in the following section.



## 4.0 SYSTEM DESCRIPTION

During the course of this program, the experimental total oil removal system (or experimental oily wastewater separation system) was assembled in several different configurations so that specific kinds of tests could be performed. For the most part, the major system components remained unchanged and only the interconnecting plumbing was changed. Therefore, the first of the following subsections describes those major system components common to both the laboratory and field testing phases. Sections 4.2 and 4.3 describe the configuration of the components during the laboratory and field testing phases, respectively.

### 4.1 SYSTEM COMPONENT FUNCTIONS AND OPERATIONAL CHARACTERISTICS

The total oil removal system employs a two-stage process for the treatment of oily bilge and ballast wastewater. The first stage of treatment is for removing the free or undissolved oily component from the wastewater. This is accomplished by passing the wastewater stream through three fibrous bed filters plumbed in series. The first filter acts as a prefilter to remove particulate material from the wastewater stream. The second and third filters are coalescer filters which possess many tortuous paths through which the wastewater passes. The small oil droplets in the wastewater tend to combine or coalesce into larger drops during transit through the filter material. The larger drops then readily separate from the denser water phase and collect on the water surface where they are removed to an oil collection vessel or container.

#### 4.1.1 Coalescer

The filter-coalescer device used during this program was manufactured by Separation and Recovery Systems, Inc., of Irvine, CA, and had a maximum throughput of 5 gallons per minute (gpm). The device is shown in Fig. 4-1. The unit contained one Model 611-503 prefilter and two Model 611-621A coalescer filters. The fluid driving force was provided by a progressing cavity pump driven by a 1/2-hp, single-phase electric motor, located just upstream of the filter unit.



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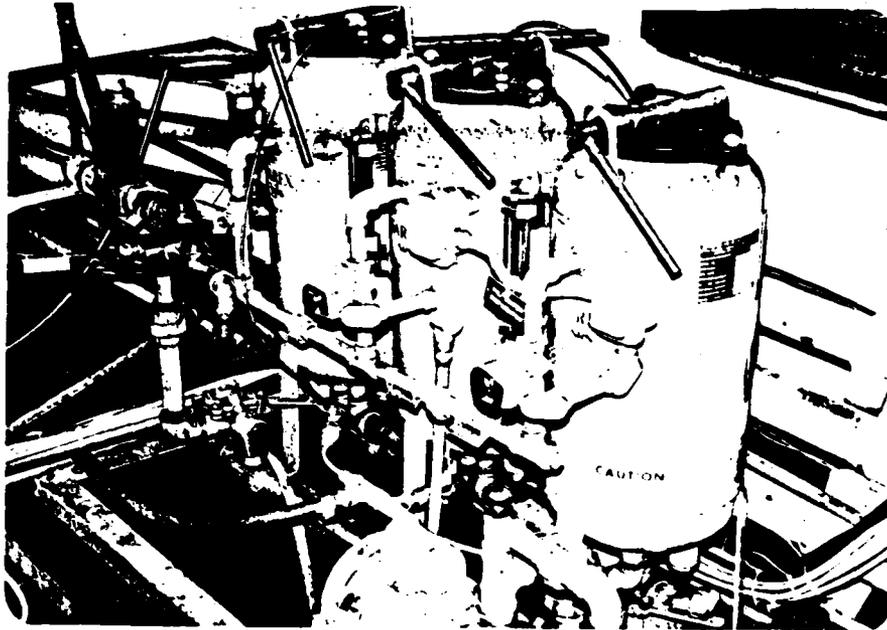


Figure 4-1. Filter-Coalescer Device for Removing Free or Undissolved Oil (From Shipboard Installation)

#### 4.1.2 Reactor

After treatment by the filter-coalescer device, the wastewater stream is directed to a well-stirred tank reactor called the oxyphotolysis reactor, where ozone in the presence of UV radiation is used to attack the remaining organics. The reactor is constructed of 316 stainless steel and is 39.4 centimeters (cm) in diameter (ID) and 71 cm high. The calculated volume of the reactor is 70.7 liters (L). The reactor fluid is stirred by a four-bladed impeller driven by a single-phase, 1/2-hp electric motor. The impeller rotates at a fixed speed of 421 revolutions per minute (rpm). The impeller shaft is stabilized on the top of the oxyphotolysis reactor by a water-cooled bearing and mechanical seal, and at the bottom of the reactor by a simple sleeve bearing constructed of Teflon. Three baffles are placed equidistant around the inside of the reactor to break up vortices formed by the impeller. The reactor and stirring motor are shown in Fig. 4-2.



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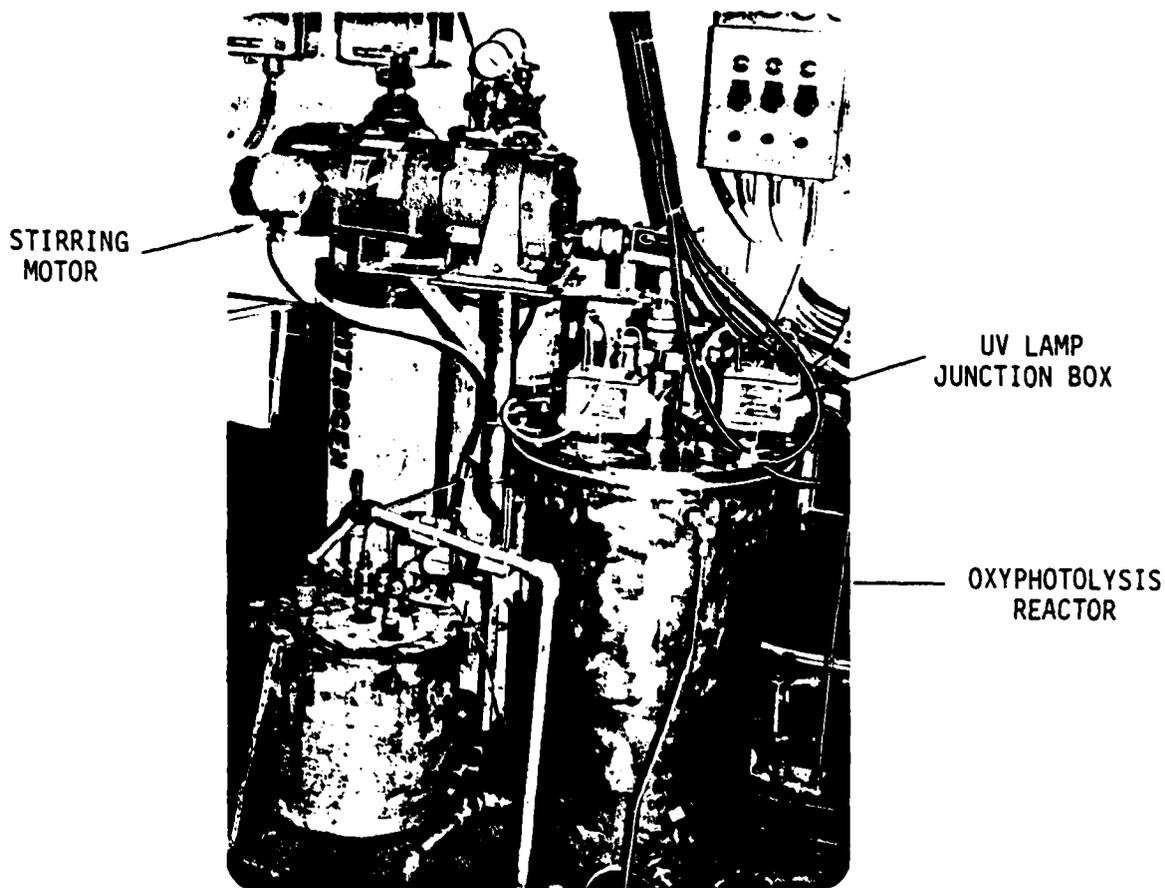


Figure 4-2. Oxyphotolysis Reactor Assembly (From Shipboard Installation)

Fluid exits the reactor by overflowing into a standpipe located inside the reactor. The fluid then passes through a gas-liquid separator (Anderson Model 81 XSS) which returns any gas entrained in the wastewater stream to the gas head space above the liquid in the reactor.

#### 4.1.3 UV Lamps

Within the reactor there are three Hanovia UV lamps housed in quartz sheaths located on a 14.6-cm radius from the cylindrical axis and set 120 degrees apart. The medium-pressure mercury UV lamps are rated at 550, 700,



and 1200 watts. The energy radiated by these lamps in the various spectral regions is given in Table 4-1 (Ref. 8).

The power supplies for the 550- and 700-watt lamps are housed in a single enclosure with externally mounted snap switches, one for each lamp. The power supplies are reactive-type transformers that supply the extra voltage and current required to initiate the arc and the reduced power for operation. Input voltage to these transformers is 115 volts.

The 1200-watt lamp is wired to an oil-immersed voltage stabilizer and transformer. The input voltage to the stabilizer is 230 volts. The power supplies to the UV lamps are shown in Fig. 4-3.

The void space between each lamp and its associated quartz sheath is purged with gaseous nitrogen during the operation of the lamps. This prevents the formation of unwanted ozone which would be created by the ionization of oxygen if air were allowed to fill this space. A schematic diagram of this purge system is shown in Fig. 4-4.

#### 4.1.4 Ozone Generator and Decomposer

Ozone was generated on-site for the destruction of the organics in the fluid contained in the oxyphotolysis reactor. A schematic diagram of the ozone gas feed system is presented in Fig. 4-5.

The ozone gas feed subsystem consists of (1) equipment to condition the compressed air, (2) an ozone generator to convert some of the oxygen in the compressed air into ozone, (3) the oxyphotolysis reactor where the air-ozone gas stream is allowed to react with the wastewater stream, (4) the ozone decomposition heater which destroys any unused ozone, (5) the cooling tube which lowers the temperature of the gas coming from the decomposition heater, and (6) the gas vent piping.



TABLE 4-1. SPECTRAL ENERGY DISTRIBUTION OF RADIATED MERCURY LINES IN  
HANOVIA MEDIUM-PRESSURE QUARTZ MERCURY-VAPOR LAMPS (Ref. 8)

Lamp watts	550	700	1200
Lamp volts	145	150	285
Current, amps	4.4	5.2	4.7
Arc-length (inch)	4.5	7.5	12
<u>Radiated Energy in Watts</u>			
Mercury lines (angstroms)			
13673 (infrared)	4.6	4.1	10.15
11287	3.8	5.0	6.93
10140	12.2	14.6	31.60
5780 (yellow)	23.0	32.1	69.35
5461 (green)	28.2	34.0	40.52
4358 (blue)	23.3	29.0	53.00
4045 (violet)	12.7	15.9	24.20
3660 (UV)	30.1	40.5	97.10
3341	2.8	3.8	6.93
3130	15.0	21.0	50.60
3025	8.2	11.3	32.90
2967	5.0	6.5	15.20
2894	1.8	2.3	4.41
2804	2.8	3.8	13.90
2753	0.8	1.0	4.20
2700	1.2	1.3	4.85
2652	4.6	6.6	27.80
2571	1.8	2.3	6.30
2537 (reversed)*	5.0	7.3	24.10
2482	2.6	3.2	10.15
2400	2.2	2.9	7.30
2380	2.6	3.2	8.40
2360	1.8	2.3	6.20
2320	2.4	3.1	7.65
2224	4.2	4.7	9.20
Watts in UV	94.9	127.1	337.20
Total Watts	202.7	261.8	572.90

\* 2537 line is reversed in medium-pressure lamps.



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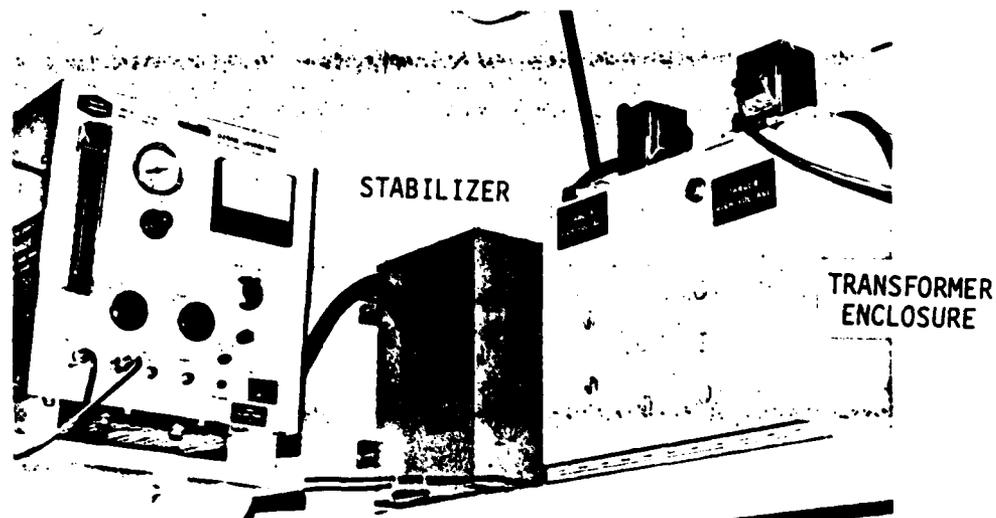


Figure 4-3. 1200-Watt UV Lamp Stabilizer, Enclosure for  
550-Watt and 700-Watt UV Lamp Transformers  
(From Shipboard Installation)

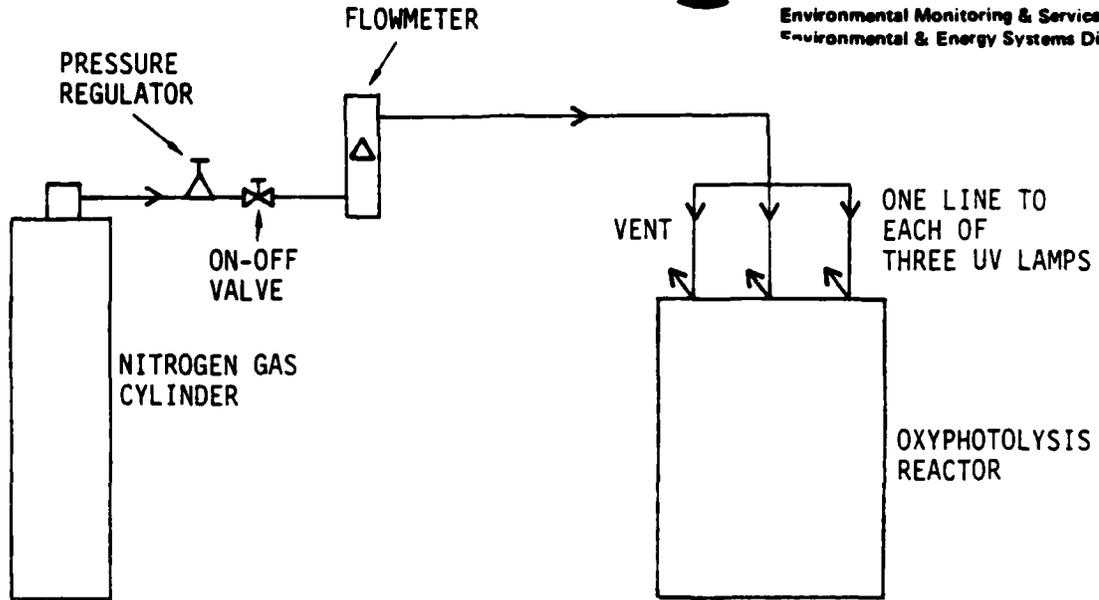


Figure 4-4. Nitrogen Purge System

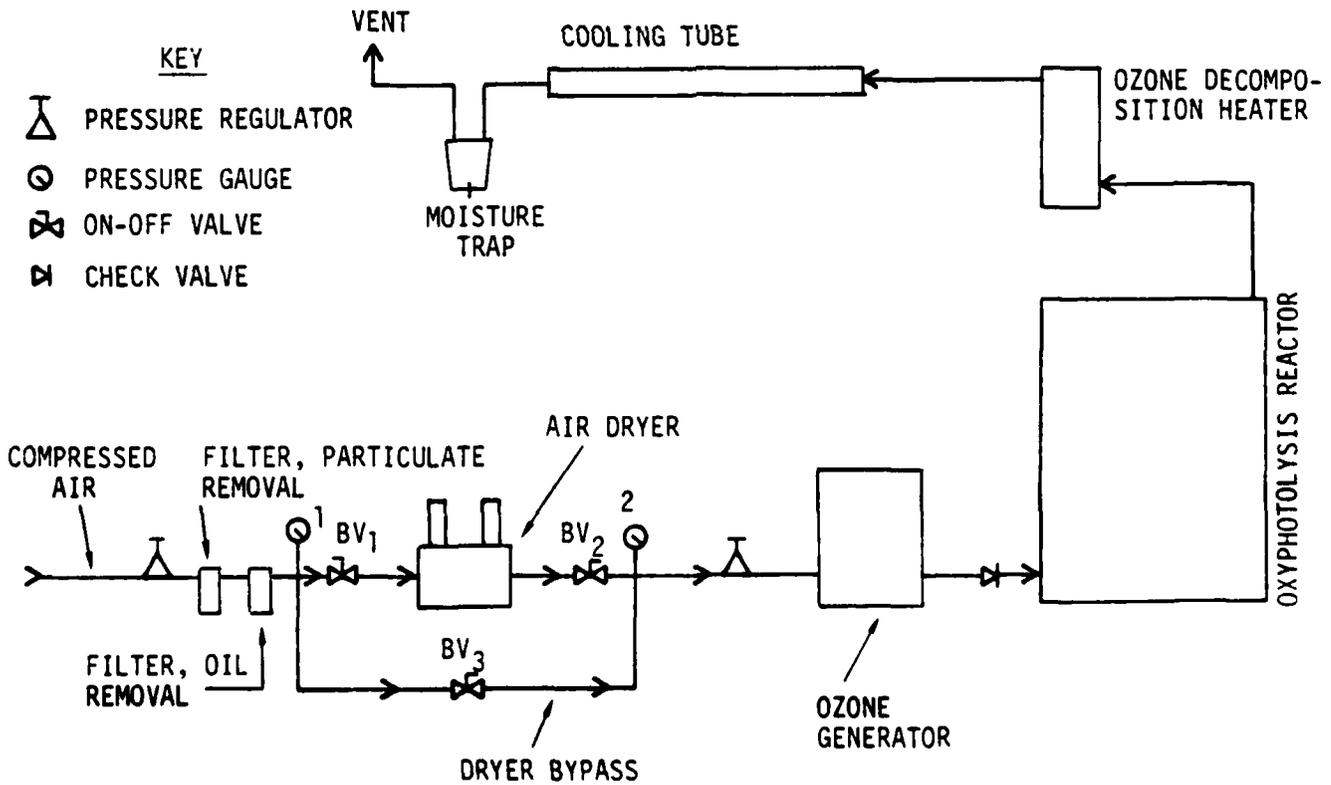


Figure 4-5. Ozone Gas Feed System



Compressed air of between 80 and 125 psig is first reduced in pressure with a pressure regulator (Norgren Model 11-002) to between 40 and 60 psig. The compressed air stream is then passed through a filter to remove particulate material (Norgren Model F07), and then through an oil removal filter (Norgren Model F45). The compressed and conditioned air is then dried to a dew point of at least  $-40^{\circ}\text{C}$  with a Puregas heatless dryer Model HF200-106-17. The apparatus to condition the compressed air is shown in Fig. 4-6.

The pressure of the compressed and conditioned air stream is further reduced with a pressure regulator (Norgren Model 11-044) to approximately 20 psig prior to being introduced into the ozone generator.

Three ozone generators were used during this investigation, two Scientific Industries Corporation models and a Linde Model SG 4060. The bulk of the experimental work was performed using the Linde instrument, which the manufacturer advertised as being able to produce one pound of ozone per day from an air feed. The actual performance in terms of ozone production and ozone concentration was determined at a number of power settings and gas flowrates using the standard iodometric technique. The performance is presented in Figs. 4-7 and 4-8. The instrument was easily able to produce the specified amount of ozone.

The ozone-air mixture produced by the ozone generator is introduced into the oxyphotolysis reactor through a sparger constructed of porous Teflon located about 25 cm below the impeller blades. Before the offgas from the reactor is discharged to the atmosphere, it is passed through a heater (designed and built by Gaumer Company, Inc.) operated at between  $425$  and  $650^{\circ}\text{C}$  to decompose any unused ozone and oxidize any volatilized organic compounds that may have been stripped from the fluid in the reactor, and then cooled by passage through a water-cooled stainless steel tube. The ozone generator and the ozone decomposition heater controller are shown in Fig. 4-9.



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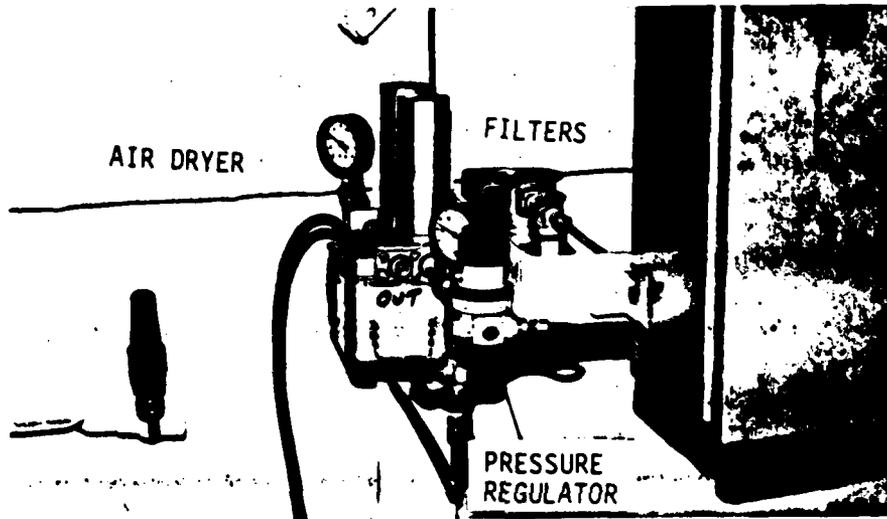
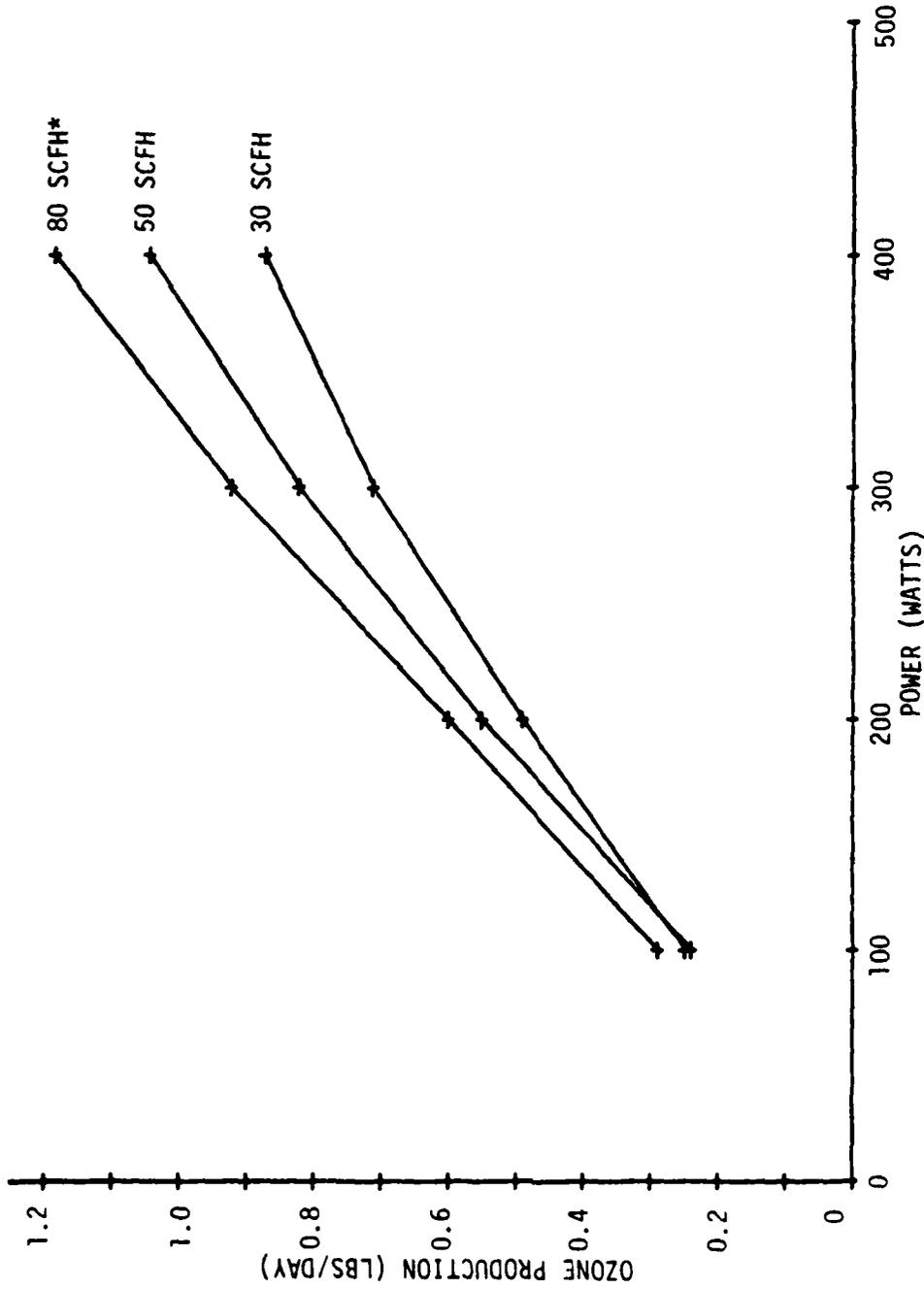
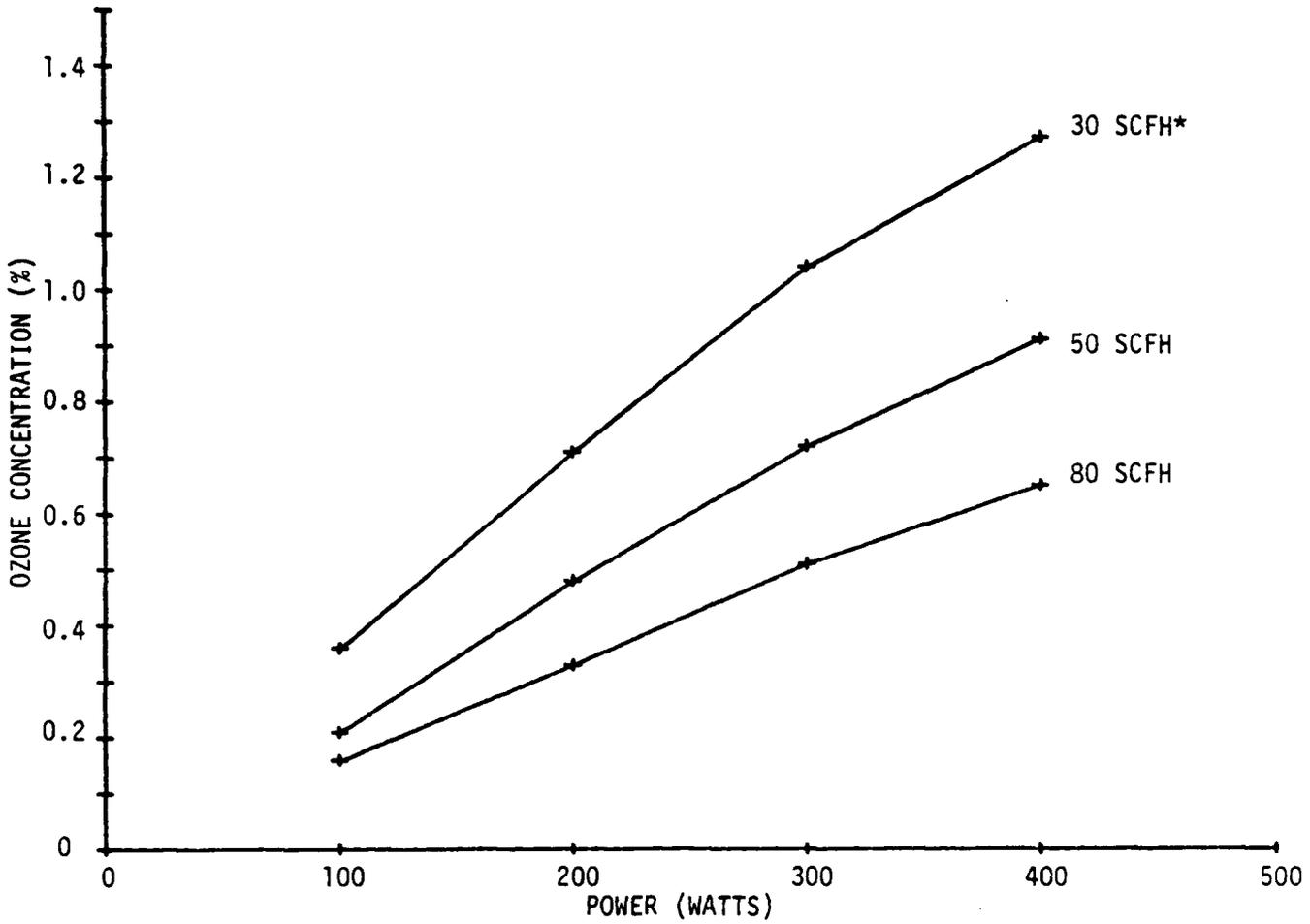


Figure 4-6. Compressed Air Conditioning Filters, Pressure Regulator, and Heatless Dryer (From Shipboard Installation)



\* Gas flowrate through ozone generator, standard cubic feet per hour.

Figure 4-7. Influence of Power and Gas Flowrate on Ozone Production, Linde Model SG 4060



\* Gas flowrate through ozone generator, standard cubic feet per hour.

Figure 4-8. Influence of Power and Gas Flowrate on  
Ozone Concentration in Exit Gas Stream,  
Linde Model SG 4060

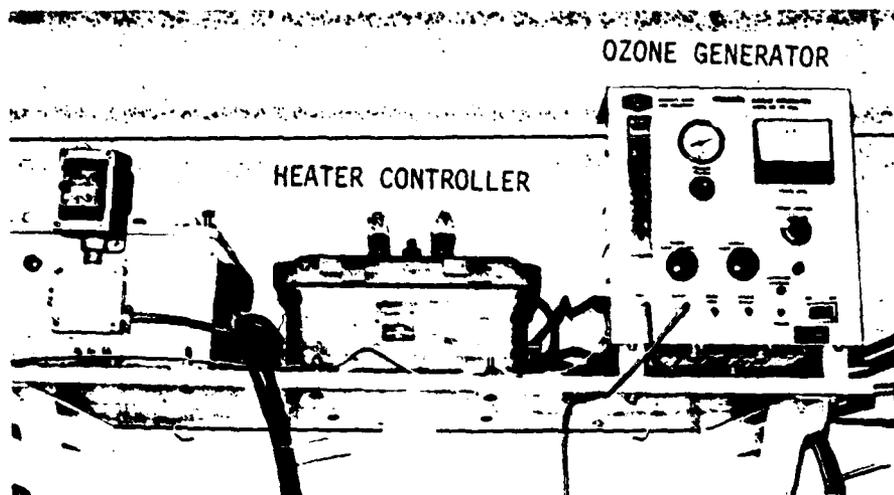


Figure 4-9. Ozone Generator and Ozone Decomposition Heater Controller (From Shipboard Installation)

#### 4.2 EQUIPMENT CONFIGURATION DURING LABORATORY TESTING

Figure 4-10 shows the liquid flow through the test apparatus used during the laboratory testing phase of this program. The gas flow systems for ozone and nitrogen were presented previously in Figs. 4-5 and 4-4, respectively. These remained the same for both laboratory and field testing.

The laboratory liquid flow loop design allowed preparation and testing of artificial bilgewater solutions (Phase III, Tasks 1, 2, 3, and 4), testing of actual bilgewater (Phase III, Task 3), and preparation and testing of pure organic compounds (Phase III, Tasks 2, 3, and 4).

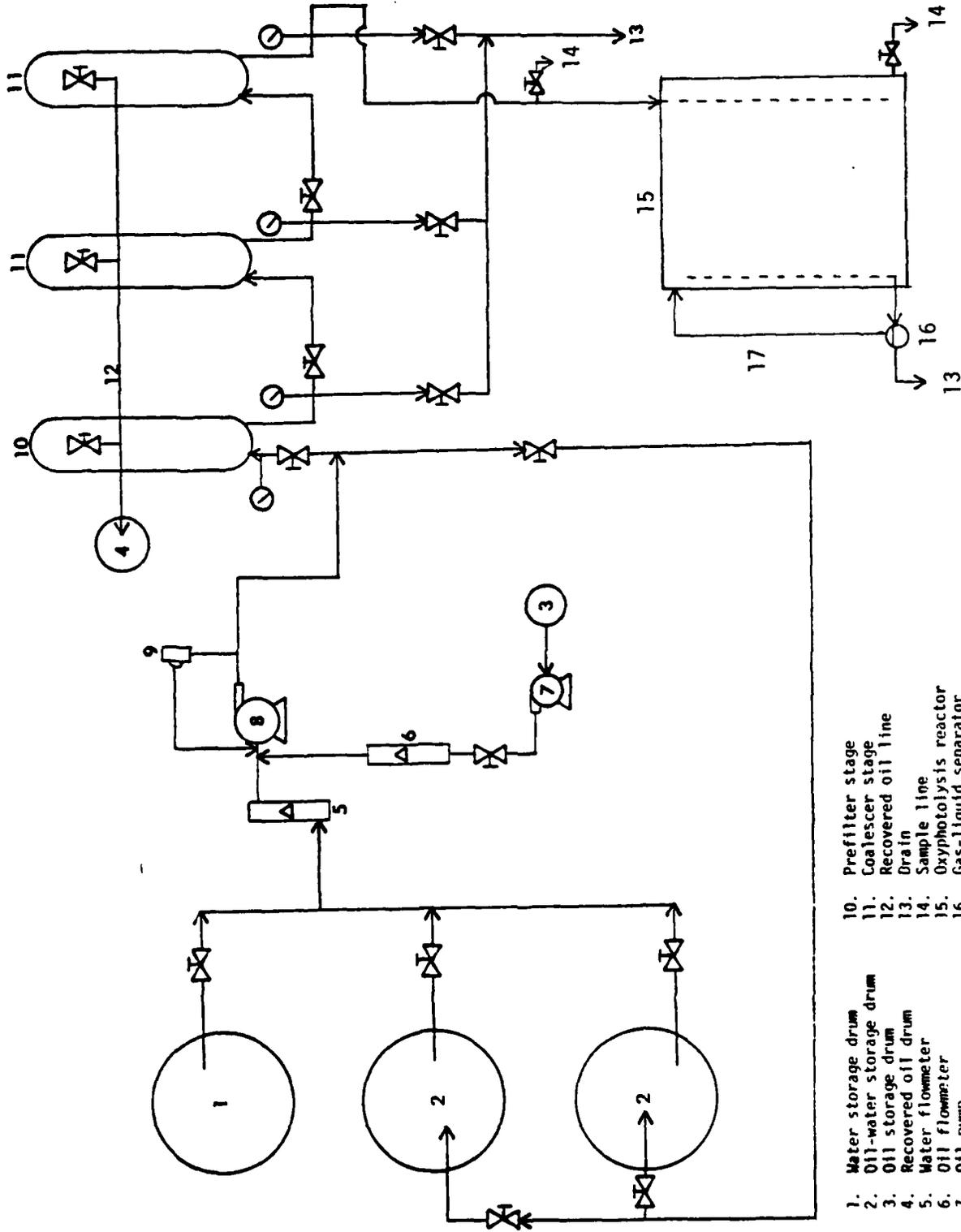
Artificial bilgewater solutions were prepared by mixing approximately 50 gallons of water in water storage drum with 5 gallons of the oil to be tested (#2 diesel fuel [DF2], used crankcase oil, hydraulic oil, or mixtures of the above). This was accomplished by passing the oil and water through



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- 10. Prefilter stage
- 11. Coalescer stage
- 12. Recovered oil line
- 13. Drain
- 14. Sample line
- 15. Oxyphotolysis reactor
- 16. Gas-liquid separator
- 17. Gas return line

- 1. Water storage drum
- 2. Oil-water storage drum
- 3. Oil storage drum
- 4. Recovered oil drum
- 5. Water flowmeter
- 6. Oil flowmeter
- 7. Oil pump
- 8. Main pump
- 9. Pressure relief valve

Figure 4-10. Laboratory Liquid Flow Loop Design



the main pump in a 1:10 ratio (by volume) and routing the mixture back to one of the oil-water storage drums. After a predetermined storage time, the oil-water mixture was passed through the oil-water separator and into the oxyphotolysis reactor.

When testing bilgewater, the substance was passed through the system by replacing one of the oil-water storage drums with the drum containing the bilgewater.

Pure organic compounds were prepared for testing in the static mode by mixing a known quantity of the substance directly in uncontaminated water contained in the oxyphotolysis reactor. Mixtures for flowthrough testing were prepared in the water storage drum and then passed through the oil-water separator and into the oxyphotolysis reactor.

The oil-water separator used during the laboratory test phase differed from that used during the field test phase only in that it was manually controlled rather than being under automatic control. All of the electrically powered equipment of the system ran off of the 115-volt power available in the laboratory. The 230-volt input to the stabilizer-transformer of the 1200-watt UV lamp was obtained by stepping up the house 115-volt power with a voltage transformer. Ordinary wall plugs were used and each piece of equipment was turned on by either plugging into the wall outlet or turning on the appropriate switch.

#### 4.3 EQUIPMENT CONFIGURATION DURING FIELD TESTING

Task 5 of Phase III required that the total oil removal system be modified to make it suitable for installation in the machinery space of an Army vessel. The test bed chosen for the field testing phase was a floating machine shop (FMS). This watercraft was not self-propelled, but required towing to its destination. The amount of space and power available on board the FMS made it ideal for checkout of the system under actual field conditions. Some of the specifications of the FMS appear in Table 4-2.



TABLE 4-2. PRINCIPAL CHARACTERISTICS OF FMS TEST BED (REF. 9)

---

Construction	Steel
Length, overall	210 feet 5 inches
Beam, molded	40 feet
Depth, molded	15 feet
Displacement:	
Light	1160 long tons
Loaded	1525 long tons
Draft:	
Light:	
Forward	5 feet 8 inches
Mean	5 feet 11 inches
Aft	6 feet 1 inch
Loaded:	
Forward	7 feet 5 inches
Mean	7 feet 7 inches
Aft	7 feet 9 inches
Freeboard, mean:	
Light	9 feet 1 inch
Loaded	7 feet 5 inches
Generators:	
Number	4
Current	ac
Output	100 kw
Volts	230
Engines, generator:	
Number	4
Type	diesel
Horsepower	150 bhp @ 1200 rpm
Fuel consumption	34 gallons per hour
Evaporator:	
Number	1
Type	thermocompression
Capacity	2000 gallons per day
Capacity:	
Fuel	52,000 gallons
Lube oil	600 gallons
Potable water	15,000 gallons
Fresh water	26,000 gallons

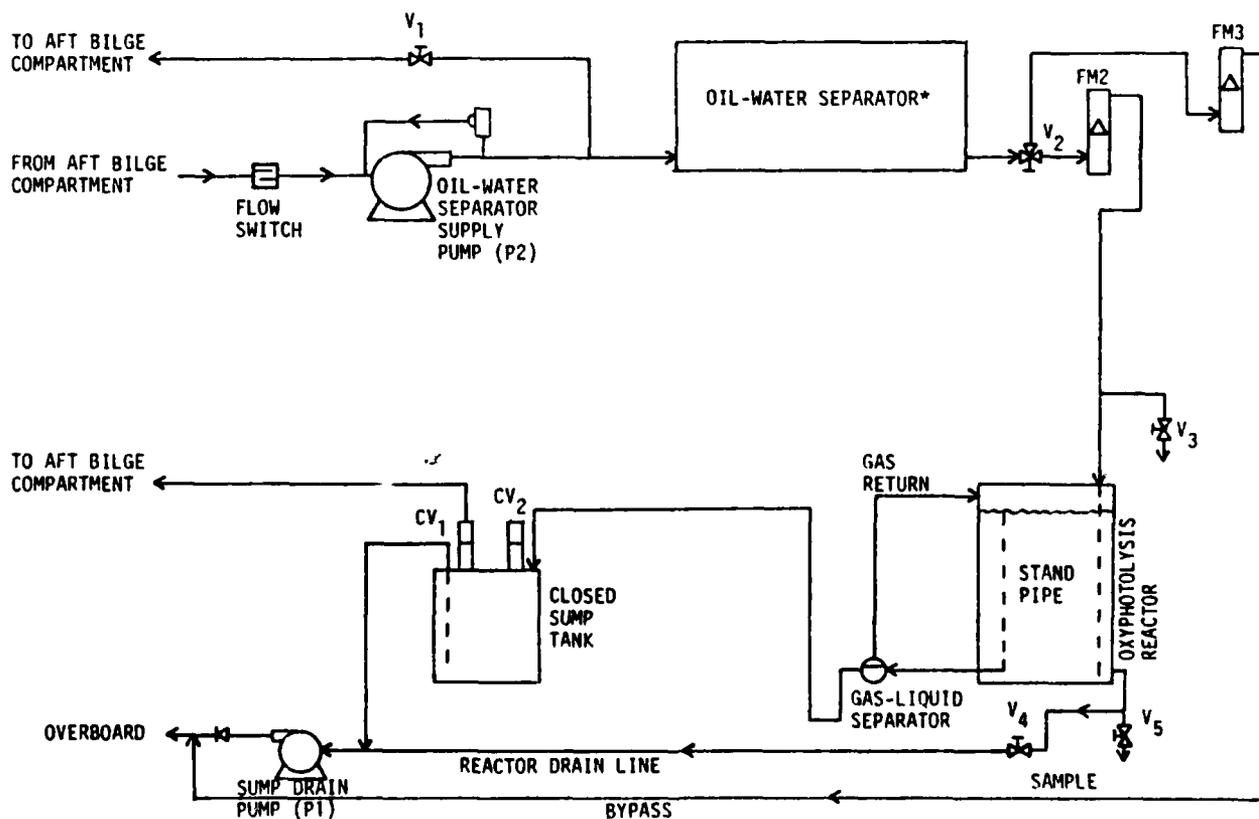
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The modifications required to make the total oil removal system compatible with the FMS fell into two classes: (1) plumbing modifications, and (2) electrical modifications. The types of modification that would be required were determined during a visit to the FMS during its refurbishment in Savannah, GA.

#### 4.3.1 Plumbing Modifications

Figure 4-11 shows the oily wastewater flow through the modified system on board the FMS. One of the principal challenges of the on-board



\* Valving associated with the oil-water separator is not shown in this generalized schematic.

Figure 4-11. Wastewater Flow Through the On-Board Total Oil Removal System



installation was that the discharge of the treated bilgewater effluent was from a point well above the location of the treatment system. This necessitated pumping the effluent from the oxyphotolysis reactor contained in a sump tank against this head. The pump used for this operation, the sump drain pump, was a diaphragm type with a stainless steel pumping chamber and Viton diaphragm (Gelber Model 77VAL). The closed sump contained two low-cracking-pressure check valves, one to vent makeup air into the tank and the other to allow drainage of the contents to the aft bilge compartment, should the sump pump fail.

The plumbing configuration also allowed for bypass operation whereby just the oil-water separator could be operated without ozone-UV treatment in the oxyphotolysis reactor. Provision was also made for draining the reactor of its fluid contents. Additionally, below maximum flowrates through the system could be achieved by adjustment of the valve labeled  $V_7$  in Fig. 4-11, which allowed a variable fraction of the 5-gpm flow generated by the oil-water separator supply pump to be routed back to the aft bilge compartment.

#### 4.3.2 Electrical Modifications

The FMS generated all of its own power from four 100-kilowatt (kw) alternating current (ac) generators supplying mostly 3-phase, 230-volt power. A limited amount of 110-volt power was available and was used primarily for the lighting circuits.

Much of the total oil treatment equipment was converted from 115-volt service to use the 230-volt service because of its availability. The stirring motor and the sump drain pump were rewired to operate from the 230-volt service. The 1200-watt UV lamp was wired directly to the 230-volt service rather than through a voltage transformer as during the laboratory tests (Section 4.2). The step-up transformer used with the 1200-watt UV lamp was rewired to step down the 230-volt power on the FMS to 115 volts. This transformer power was then used to run the ozone decomposition heater,



the air dryer, and the 700- and 550-watt UV lamps. Only two components of the system were operated off of the shipboard 115-volt service: the oil-water separator and the ozone generator. A very small additional amount of 115-volt power was used for the control circuitry, discussed below.

#### 4.3.2.1 System Control Modifications

The procedure used in the laboratory tests to activate the system components, plugging the components into wall-mounted electrical outlets, was a completely unacceptable practice on a vessel. Therefore, an electrical distribution system was designed and incorporated into the FMS installation which included protection against circuit overloads, on-off switching of individual components through the use of relays, and control of the relays with logic circuits that started up and shut down the system components in specific sequences.

Each of the following components were hard-wired to relays which were energized through a centralized control panel. Circuit breakers protected all of the circuitry.

1. UV lights
2. Ozone generator
3. Air dryer
4. Ozone decomposition heater
5. Stirring motor
6. Oil-water separator supply pump
7. Sump drain pump

The circuit-breaker panel contained eight circuit breakers. Two of these were service disconnect breakers for the 120-volt and 230-volt power supplies. Dedicated circuit breakers were provided for the ozone generator (120V), the 1200-watt UV lamp (230V), the stirring motor (230V), the oil-water separator supply pump (120V), the sump drain pump (230V), and one



breaker was supplied for the 550-watt and 700-watt UV lamps, the ozone decomposition heater, and the air dryer (all 120V, run off of a stepdown transformer from the 230-volt ship power).

The power was routed through the circuit breakers to seven contactors or relays. Three motor starter contactors (with overload protection) were housed in one box. These contactors provided power to the stirring motor, the oil-water separator pump motor, and the sump drain pump motor. The four remaining contactors were housed in another box. These controlled the power distribution to the ozone generator, the 1200-watt UV lamp, the 550-watt and 700-watt UV lamp together, and the ozone decomposition heater and air dryer together.

The contactors were selectively energized under control of a panel that contained the control logic. Switches on the front panel initiated logic sequences that controlled the various pieces of equipment by energizing or de-energizing the proper contactors. Figure 4-12 shows the control panel with its various switches and lights, and a photograph of the panel is shown in Fig. 4-13.

Also, several sensors were present (wired into the control panel circuitry) that continually monitored the vital functions of the system and relayed this information (in the form of switch closures or openings) to the control panel. These are:

<u>Sensor</u>	<u>Location</u>	<u>Function</u>	<u>Action</u>
Flow Switch	Oil-water separator pump suction line	Determine when bilge is dry (i.e., lack of flow)	Shut down entire system
Thermoswitch 1	Inside ozone decomposition heater	Determine when acceptable temperature is reached in heater	Hold startup sequence until correct temperature
Thermoswitch 2	Inside ozone decomposition heater	Sense overtemperature condition in heater	Shut down entire system
Delta Pressure Switch	Attached to blind tube inside closed sump tank	Sense sump overflow condition	Shut down entire system

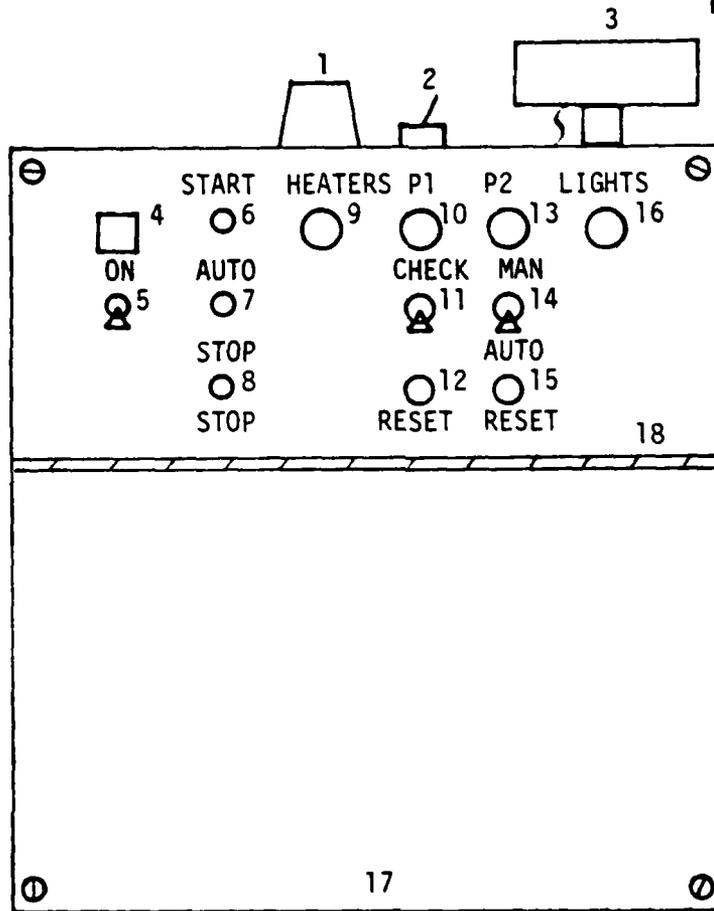


Figure 4-12. System Control Panel

An intermittent audible or visual (selectable) alarm was activated when the flow switch or thermoswitch 1 detected faults in the system. A continuous audible or visual (selectable) alarm was activated with thermoswitch 2 or the delta pressure switch detected faults.

Three operating modes were provided (initiated at the control panel): normal operation, bypass operation, and reactor drain. The system components operated during these modes are as follows:

<u>Mode</u>	<u>Component</u>
Normal	All components
Bypass	Oil-water separator supply pump only
Reactor Drain	Sump drain pump only

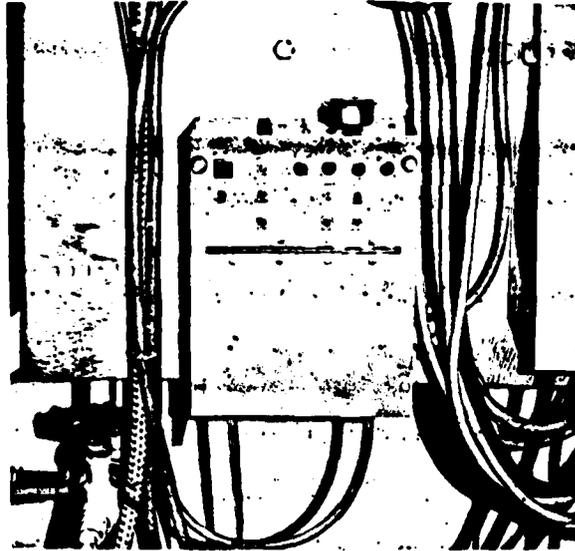


Figure 4-13. Photograph of System Control Panel

During the normal operation mode, a start pushbutton was provided which, when activated, brought the components and sensors on line in a predetermined sequence. If the operator wished to suspend treatment, an auto stop pushbutton shut down the system in the proper sequence. Some operator interaction was required.

Switches were also provided for both the bypass and reactor drain operation modes.

In all operating modes, total shutdown could be achieved by activating a stop button and following several shutdown steps.

A series of enunciator lights were provided on the control panel face that show the operator which system components were receiving power (see Fig. 4-12).



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Details of the semi-automatic operation of the system are given in the manual entitled, "Operation of the On-Board Oily Wastewater Treatment System," found as Appendix A. This manual was used during the instruction session to Army personnel under Task 6 of this program.



## 5.0 LABORATORY TESTING

Testing of the total oil removal system in the laboratory was initiated after receipt, assembly, and checkout of the equipment supplied by Houston Research, Inc. The controlled conditions of the laboratory were required for the types of tests performed during Phase III, Tasks 1-5 of the program.

### 5.1 OBJECTIVES

The primary objective of the laboratory testing was to optimize the treatment parameters using (1) pure organic compounds dissolved in water, (2) artificial oil-water mixtures, and (3) bilgewater obtained from Army watercraft. The optimization was to be performed under no-flow or static conditions. Tests would then be conducted using a flowthrough or steady-state flow regime to determine the system performance under simulated shipboard flow conditions.

Preparatory to shipboard installation, tests would be performed in the laboratory to measure ozone, ultraviolet, and noise emissions, and steps would then be taken to rectify any unsafe conditions.

### 5.2 METHODS

This section describes the methods used to prepare the test mixtures, to perform the static, flowthrough, and safety tests, and the analytical methods used to quantify the performance of the total oil removal system.

#### 5.2.1 Preparation of Test Solutions

Solutions of pure organic compounds in water to be used during static tests (i.e., no flow) were prepared by first filling the oxyphotolysis reactor approximately half full with distilled or deionized water. A known quantity of the pure compound was then added to the water in the oxyphotolysis reactor and stirred with the motorized impeller for several minutes



to several hours, depending on the ease with which the material was solubilized. Salt (NaCl) was added to the pure organic compound-water solution at this point, if the test was to be conducted using a salt water matrix. A sufficient volume of water was then added to the oxyphotolysis reactor to bring the liquid up to the level of the internal overflow standpipe. A final, brief agitation assured a homogeneous solution. The solution was then ready for testing.

A phenol-in-water solution was used for most of the flowthrough testing and a solution of sufficient volume for the protracted flowthrough tests was prepared as follows. First, a stock phenol solution was prepared in a 1-liter volumetric flask to approximately 50,000 ppm. The two drums labeled oil-water storage drums in Fig. 4-10 were lined with polyethylene bags and filled with 50 gallons of water each. Sufficient phenol stock solution was added to the 50 gallons of water and manually stirred to achieve the desired final concentration of phenol. Thus, 100 gallons of the phenol solution to be used during the flowthrough test could be prepared in advance of the test and new solution could be prepared during the test, if needed.

Artificial bilgewater solutions for both batch and flowthrough tests were prepared by mixing known quantities of the oil and water together and storing the mixture to allow the oil and water to separate prior to testing. The flow loop shown in Fig. 4-10 was used to prepare the artificial bilgewater solutions. Five gallons of the oil were placed in the oil storage drum and 50 gallons of tap water filled the water storage drum. Oil-water contact was achieved by metering the oil and water into the suction side of the main pump in a 1:10 volume ratio using the water and oil flowmeters. The pump action effectively mixed the two fluids together and the resulting suspension exiting the pump was routed back to one of the oil-water storage drums and allowed to stand for at least two days to permit some oil-water separation prior to testing. In experiments using salt water, NaCl was added to the tap water before mixing with the oil. For those batch tests using the artificial bilgewater solutions, the oxyphotolysis reactor was filled to the level of the internal standpipe with the



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separated oil-water mixture after first passing the mixture through the oil-water separator (items 10 and 11 in Fig. 4-10).

The batch tests utilizing bilgewater as the test fluid were conducted by pumping the bilgewater (contained in a 55-gallon drum) through the oil-water separator using the main pump (Fig. 4-10) and into the oxyphotolysis reactor.

### 5.2.2 Batch Testing

Once the oxyphotolysis reactor was filled with the fluid to be tested, the compressed air supply sufficiently dry, and the ozone decomposition heater at its control point, the batch test could commence. The UV lamps and the stirring motor were turned on. After allowing several minutes for the UV lamps to attain their rated power levels, the ozone generator was turned on and a timer was activated.

At intervals of 10 to 20 minutes, 75-milliliter (ml) samples of the test fluid were withdrawn from the oxyphotolysis reactor (from the reactor sample line, Fig. 4-10). Twenty-five ml of 2% (by weight) potassium iodide (KI) solution was added to each sample at the time of withdrawal to quench any further reaction. These samples were analyzed for total organic carbon (TOC). During several of the batch tests, larger samples of the test fluid were periodically collected and quenched with KI solution. These samples were analyzed using high-pressure liquid chromatography (HPLC).

### 5.2.3 Flowthrough Testing

The oxyphotolysis reactor was filled with the test fluid prepared previously and contained in the oil-water storage drums by using the main pump (Fig. 4-10). Once the oxyphotolysis reactor was full, flow was stopped and the test fluid treated in the batch mode for a period of time determined from previous batch tests. This batch treatment reduced the pollutant load to a level which theoretically could be maintained in the effluent from the



oxyphotolysis reactor when flowthrough treatment of the test fluid began. The flow of the test fluid through the oil-water separator and into the oxyphotolysis reactor was accurately metered through the flow loop shown in Fig. 4-10 by plumbing in a control valve between the main pump and the prefilter stage of the oil-water separator.

Samples of the effluent continually flowing out of the oxyphotolysis reactor were collected as described in the previous section, except that they were taken from the drain line (Fig. 4-10) rather than from the sample line.

#### 5.2.4 Safety Testing

Tests were conducted to determine ozone, noise and UV emissions from the total oil removal system. Ozone leakage was determined by operating the system continuously from 4 to 7 hours in a closed laboratory with ventilation kept to a minimum (i.e., no fume hoods on, no air conditioning, and doors kept closed as much as possible). The ozone level in the room was measured with an MEC 1100 ozone meter. Exterior ozone levels in the ambient air surrounding the building housing the test laboratory were obtained from an air monitoring station operated by the Ventura County Air Pollution Control District, since the exterior ozone could influence the interior ozone level.

Noise levels produced by the system were measured with a hand-held noise meter, Bruel and Kjaer Model 2205, from various locations around the equipment. A more detailed analysis of the noise emitted by the ozone generator was undertaken using an octave band analyzer, General Radio Model 1158-BP. Noise measurements were taken at the rear of the ozone generator, centerline of the fan exhaust, 6 inches away.

Leakage of ultraviolet radiation from the three UV lamps contained in the oxyphotolysis reactor was measured with an International Light 730A



radiometer. Background UV radiation emitted from the overhead fluorescent lamps in the laboratory was zeroed out prior to taking all UV leakage measurements.

#### 5.2.5 Analytical Methods

Samples were analyzed for TOC using either a Beckman 915A TOC analyzer, a Dohrmann DC 52 carbon analyzer, or an Oceanography International 0524B total carbon system. Prior to analysis, each sample was acidified with sufficient hydrochloric acid (HCl) to reduce the pH to 2 or less, which converted the carbon in the inorganic carbon compounds (e.g., carbonates and bicarbonates) to CO<sub>2</sub>. The CO<sub>2</sub> was stripped from solution by bubbling CO<sub>2</sub> free nitrogen or oxygen through the sample. Thus, the carbon measured during the TOC analysis was derived from organic compounds. For those samples that contained undissolved oil (e.g., the artificial bilgewater mixtures and the bilgewater), a filtration step utilizing Millipore filtration at 0.45 microns was performed prior to the TOC analysis to produce a sample free of undissolved oil (by definition).

The samples earmarked for analysis by HPLC were concentrated into a non-aqueous matrix prior to analysis, by one of two methods: liquid-liquid extraction of the sample with chloroform, or passage of the sample through an accumulator column packed with Amberlite macroreticular resin (the XAD series) and subsequent elution of the adsorbed compounds from the resin with methanol.

The concentrated sample was then used for HPLC analysis. The nominal conditions of the analysis are presented in Table 5-1.

The HPLC detector, which operated on the principle of UV absorption, is most sensitive to compounds that contain aromatic structure. This detector was used because the types of compounds most likely to be dissolved in oily wastewater and be most deleterious to aquatic life have aromatic structure.



TABLE 5-1. NOMINAL CONDITIONS OF HPLC ANALYSIS

---

Instrument:	Spectra Physics 3500B liquid chromatograph with UV absorption detector (254 nm)
Recorder:	1 mv, Hewlett Packard
Chart Speed:	7.5 inches/hour
Column:	Partisil PXS 10/25 ODS-2
Mobile Phase:	70% methanol, 30% water
Flow:	1.2 ml/min.
Pressure:	1660 psig
Sample Volume:	10 microliter
Peak Area Measurement:	Electronic integrator, Hewlett Packard, Model 3371B

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### 5.3 RESULTS AND DISCUSSION

In this section the results of 41 tests using the total oil removal system in the batch mode, and six tests in the flowthrough mode, are presented, as are the results of tests designed to determine the composition of the effluent from the oil-water separator after passing an oil-water mixture through it.

From the batch tests, the performance of the system was determined and the effects of UV and ozone dosage on the performance was quantified. These parameters could then be optimized. Additionally, the oxidation products resulting from the batch treatment of a phenol-water solution, a #2 diesel fuel - water mixture, and bilgewater were determined. Based on the data gathered during batch testing, the performance of the total oil removal system in the flowthrough mode was calculated. The accuracy of these calculations was verified by conducting actual flowthrough tests.



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In the last part of this section the results of the safety testing are presented and discussed.

### 5.3.1 Batch Testing

The 41 batch tests performed used pure organic compounds, artificial bilgewater mixtures, and bilgewater as test fluids. The pure compounds used in the batch tests were chosen after careful evaluation of the literature addressing the types of oil-derived compounds found dissolved in the aqueous phase of oil-water mixtures, and based on an experiment conducted under Phase III, Task 1 of this study.

The solubility of oily compounds in water is limited; however a relatively small fraction of the compounds making up crude and refined oils are polar enough to dissolve in water to a significant degree. Many of these possess aromatic structure, such as benzene, toluene, xylene, phenols, cresoles, and the nitrogenous heterocyclics (e.g., pyridine, quinoline) (Ref. 10).

In addition to the compounds that are highly water soluble, many compounds found in oils which normally possess limited solubility in water are made more soluble after attack by microorganisms. The concentration of dissolved organic carbon in the water phase of an oil-water mixture can increase dramatically over time because of metabolism of the oily compounds by microorganisms (Ref. 11). The classes of compounds produced by bacterial metabolism of oils can include aliphatic alcohols, acids, and esters.

An experiment was performed to determine the types of aromatic compounds present in the water phase resulting from the contact of #2 diesel fuel (DF2) with water. The oil-water mixture was prepared as outlined in Section 5.2.1, and allowed to separate for 60 hours before passing the mixture through the oil-water separator. A sample of the separator effluent was collected and extracted with chloroform (Section 5.2.5) under both basic and acidic conditions. The extract was then analyzed by HPLC.



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The results indicated the presence of 40 ppm of hydroxylated benzene compounds (e.g., phenols, hydroquinone), toluene (9 ppm), and traces of nitrogenous heterocyclic compounds (1.2 ppm).

Based on these results and the results of others, the following compounds were chosen for use during the batch testing with pure compounds:

Aromatics:	Phenol, hydroquinone, ortho cresol, toluene, mixed xylenes
Nitrogenous Heterocyclics:	Pyridine, quinoline
Alcohols:	Glycerol, normal amyl alcohol
Acid:	Heptanoic acid

Phenol and toluene are EPA priority pollutants.

The types of oils used to prepare the artificial bilgewater solutions used during batch testing represented the oils most likely to contaminate the water contained in the bilge compartments of Army watercraft. They were DF2, used crankcase oil, and hydraulic oil.

The bilgewater used for the batch tests was obtained from Army watercraft, primarily from a FMS stationed at Fort Eustis, VA. The bilgewater was collected in 55-gallon drums and shipped to the Rockwell laboratories in Southern California. The bilgewater was stabilized with either inorganic acid or bactericide (didecyl dimethyl ammonium chloride) against degradation by microorganisms.

The pure organic compounds in water, oil-water mixtures, and bilgewater were simultaneously exposed to UV radiation and ozone at various dosages in the oxyphotolysis reactor. During these batch tests, the removal of TOC from the test fluids was quantified over time. Thus, the influence of the UV and ozone dosages on the rate of TOC removal could be

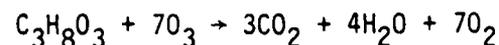


understood. Table 5-2 is a summary of the results from the batch tests with the pure organic compounds dissolved in water. Table 5-3 summarizes the results from the tests using artificial bilgewater solutions, and Table 5-4 is a summary of the results of batch treatment of bilgewater. Each experiment is referenced by a unique test number, used throughout this report. The three tables provide information on the composition of the reaction fluid, the ozone and UV dosages used, the initial concentration of TOC in the test fluid at the beginning of the experiment, the final concentration of TOC in the test fluid at the end of the experiment, the amount of TOC removed from the test fluid over the course of the experiment, the time required to reach the final TOC concentration, and the ozone required, defined as:

$$\text{Ozone required} = \frac{\text{Ozone dosage (mg/min)} \times \text{reaction time (min)}}{\text{TOC removed (mg)}}$$

In addition to this information, the minimum theoretical ozone requirement, calculated from the stoichiometry of the ozone reaction, is provided in Table 5-2 for the tests with pure compounds. This information is not given for the tests with artificial bilgewater mixtures and bilgewater (Tables 5-3 and 5-4, respectively) because the reaction stoichiometry is impossible to calculate with these fluids since their specific chemical compositions are unknown.

Table 5-5 summarizes the theoretical minimum ozone required for complete destruction in various units (moles ozone: moles compound, mass ozone: mass compound, and mass of ozone to mass of TOC in the compound). These figures represent the stoichiometric amount of ozone required to completely oxidize the pure compound, relative to the amount of compound present. For example, the stoichiometry of the reaction of ozone with glycerol is as follows:



Seven moles of ozone are required to completely oxidize one mole of glycerol. The mass ratio of ozone to compound is the product of the mole



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TABLE 5-2. SUMMARY OF BATCH EXPERIMENTS WITH PURE COMPOUNDS MIXED WITH WATER

Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Initial TOC (mg/L)	Final TOC (mg/L)	TOC Removed (gms)	Reaction Time Required to Final TOC (minutes)	Ozone Required <sup>c</sup> (mass O <sub>3</sub> : mass TOC)	Theoretical Min. Ozone Requirement (mass O <sub>3</sub> : mass TOC)
1	Glycerol	32.8	1.3	42.7	27.7	1.0605	175.0	5.4	9.3
2	Glycerol	32.8	7.9	40.7	5.1	2.5169	200.0	2.6	9.3
3	Glycerol	328.0 <sup>a</sup>	1.3	42.7	6.0	2.5947	100.0	12.6	9.3
4	Glycerol	328.0	3.1	42.0	5.0	2.6159	91.3	11.4	9.3
5	Glycerol	328.0	7.9	44.3	5.0	2.7785	83.7	9.9	9.3
6	Glycerol + salt <sup>b</sup>	328.0	7.9	42.9	5.0	2.6795	81.5	10.0	9.3
7	Hydroquinone	328.0	1.3	42.1	5.0	2.6230	54.4	6.8	8.7
8	Hydroquinone	328.0	7.9	40.8	5.0	2.5311	40.0	5.2	8.7
9	Hydroquinone + salt <sup>b</sup>	328.0	1.3	37.9	5.0	2.3260	54.0	7.6	8.7
10	o-cresol	328.0	1.3	40.3	5.0	2.4957	71.2	9.4	9.7
11	o-cresol	328.0	7.9	43.8	5.0	2.7432	61.6	7.4	9.7
12	Pyridine	328.0	7.9	58.0	15.5	3.0047	90.0	9.8	12.4
13	Quinoline	328.0	1.3	41.9	5.0	2.6088	76.8	9.7	10.9
14	Quinoline	328.0	7.9	41.5	5.0	2.5805	60.8	7.7	10.9
15	Phenol	328.0	1.3	37.4	5.0	2.2907	60.0	8.6	9.3
16	Phenol	328.0	1.3	51.0	5.0	3.2522	81.5	8.2	9.3
17	Phenol	328.0	3.1	40.8	5.0	2.5381	60.0	7.8	9.3
18	Phenol	328.0	7.9	42.3	5.0	2.6371	53.0	6.6	9.3
19 <sup>d</sup>	Phenol	328.0	7.9	40.8	5.0	2.5311	70.8	9.2	9.3
20	Phenol	372.0 <sup>e</sup>	7.9	46.0	2.3	3.0896	67.0	8.1	9.3
21	n-amyl alcohol	328.0	1.3	45.8	5.0	3.0967	109.6	11.6	12.0
22	n-amyl alcohol	328.0	7.9	48.0	5.0	3.0401	80.8	8.7	12.0
23	Heptanoic acid	328.0	1.3	38.4	5.0	2.3614	76.0	10.6	10.8
24	Heptanoic acid	328.0	7.9	42.3	5.0	2.6371	47.2	5.9	10.8

a. Ozone concentration was 0.92 weight % in the gas stream when the ozone dosage was 328 mg/min.

b. Specific gravity of reaction fluid = 1.0205

c. Ozone required = ozone dosage  $\frac{(\text{mg}/\text{min}) \times \text{reaction time (min)}}{\text{TOC removed (mg)}}$

d. Test conducted with interrupted stirring

e. Ozone concentration was 0.65 weight % in the gas stream



TABLE 5-3. SUMMARY OF BATCH EXPERIMENTS WITH ARTIFICIAL BILGEWATER MIXTURES

Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Initial TOC (mg/L)	Final TOC (mg/L)	TOC Removed (gms)	Reaction Time To Final TOC (min)	Ozone Required <sup>g</sup> (mass O <sub>3</sub> : mass TOC)
25	DF2 - water <sup>a</sup>	32.8	5.6	22.5	5.0	1.0598	180	5.6
26	DF2 - water	328 <sup>b</sup>	1.3	34.8	6.0	2.0362	120	19.3
27	DF2 - water	328	7.9	31.5	8.0	1.6615	84	16.6
28	DF2 - salt water <sup>b</sup>	328	7.9	21.5	5.0	1.1665	61.2	17.2
29	Hydraulic oil - water <sup>c</sup>	328	1.3	46.7	18.7	1.9796	180	29.8
30	Hydraulic oil - water	328	7.9	34.9	10.5	1.7251	130	24.7
31	Used crankcase oil - water <sup>d</sup>	328	1.3	36.5	15.3	1.4988	135	29.5
32	Used crankcase oil - water	328	7.9	37.4	5.0	2.2907	82	11.7
33	DF2 - used crankcase oil - salt water <sup>e, f</sup>	328	1.3	37.1	5.0	2.2695	178	25.7
34	DF2 - used crankcase oil - salt water	328	7.9	36.9	5.0	2.2553	63	9.2

a. No. 2 diesel fuel, federal specification V.V.F. 800a

b. Specific gravity of reaction fluid = 1.0175

c. 10-weight hydraulic oil non-detergent but with antioxidants and anticorrosives

d. Used detergent crankcase oil from service station

e. 5:1 volume ratio of DF2: used crankcase oil

f. Specific gravity of reaction fluid = 1.0300

g. Ozone required =  $\frac{\text{ozone dosage (mg/min)} \times \text{reaction time (minutes)}}{\text{TOC removed (mg)}}$

h. Ozone concentration was 0.92 wt % in gas stream



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TABLE 5-4. SUMMARY OF BATCH EXPERIMENTS WITH BILGEWATER

Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Initial TOC (mg/L)	Final TOC (mg/L)	TOC Removed (gms)	Reaction Time To Final TOC (minutes)	Ozone Required <sup>d</sup> (mass O <sub>3</sub> : mass TOC)
35	Bilgewater - dilute <sup>f</sup>	328 <sup>e</sup>	7.9	32.2	8.0	1.7109	140	26.8
36	Bilgewater - dilute	328	7.9	47.0	7.5	2.7926	150	17.6
37	Bilgewater - dilute	328	7.9	89.4	17.9	5.0550	225	14.6
38	Bilgewater - dilute	372 <sup>a</sup>	7.9	51.1	13.3	2.6725	165	23.0
39	Bilgewater - dilute	274 <sup>b</sup>	7.9	56.2	11.2	3.1815	150	12.9
40	Bilgewater	328	7.9	44.2	20.0	1.7322	90	17.1
41	Bilgewater	328	1.3	48.0	31.0	1.2019	150 <sup>c</sup>	40.9

a. Ozone concentration was 0.65 weight % in the gas stream

b. Ozone concentration was 1.26 weight % in the gas stream

c. TOC removal reached an asymptote at about 140 minutes of treatment

d. Ozone required =  $\frac{\text{ozone dosage (mg/min)} \times \text{reaction time (minutes)}}{\text{TOC removed (mg)}}$ 

e. Ozone concentration was 0.92 weight % in the gas stream

f. These samples of bilgewater contained extremely high TOC levels, possibly due to contamination with detergents. They were diluted with tap water to a concentration representative of uncontaminated bilgewater.



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Compound	Moles O <sub>3</sub> : Moles Compound	Mass O <sub>3</sub> : Mass Compound	Mass O <sub>3</sub> : Mass TOC
Glycerol	7.0	3.65	9.33
Phenol	14.0	7.14	9.33
o-Cresol	17.0	7.55	9.72
Hydroquinone	13.0	5.67	8.70
Quinoline	24.5	9.11	10.89
Normal amyl alcohol	15.0	8.17	12.00
Heptanoic acid	19.0	7.00	10.85
Pyridine	15.5	9.41	12.41

a. Based on a stoichiometry of one reactive oxygen atom per molecule of ozone.



ratio above and the ratio of molecular weights of ozone and glycerol:

$$7 \times (48 \text{ gms/mole}/92.1 \text{ gms/mole}) = 3.65$$

The mass ratio of ozone to TOC is obtained by dividing 3.65 by the fraction of the molecular weight of glycerol contributed by carbon:

$$3.65/(36 \text{ gms TOC/mole}/92.1 \text{ gms/mole}) = 9.33$$

These theoretical ozone requirements are based on a stoichiometry whereby only one reactive oxygen atom from each ozone molecule is utilized in the reaction with the pure compound.

#### 5.3.1.1 Effect of UV Dosage on Treatment

Tables 5-2, 5-3, and 5-4 show that with equal ozone dosages and initial TOCs, an increase in the UV dosage, in every case resulted in a lowered ozone requirement, except in test #19 with phenol. The increased UV radiation probably causes the formation of more free radicals, both from the ozone and from the oxidized species (Fig. 2-3) so that the destruction of the compounds is accelerated. During test #19, the stirring motor was shut off for the first 64 minutes of the experiment. The lack of stirring either interferes with the transfer of ozone from the gas to the liquid phase (perhaps because the ozone-air gas bubbles coalesce or become entrained into larger bubbles without stirring, thus reducing the surface area available for mass transfer), or reduces the average amount of time a molecule is being sufficiently irradiated by UV, or both.

Increased UV radiation also results in shorter reaction times because of the increased efficiency of the oxidation reactions. In some cases (see Tables 5-2, 5-3, and 5-4), for example with glycerol (test numbers 3-5) n-amyl alcohol (test #21 and 22), the artificial bilgewater mixtures (test #26-34), and bilgewater (test #40 and 41), the decrease in reaction times (and ozone requirements) with increasing UV dosage is dramatic.



These compounds and mixtures are apparently activated by the high UV dosage and the result is a much enhanced oxidation rate. In the case of test #40 and 41 with bilgewater, the higher UV dosage was necessary to remove TOC to below 31 mg/L. Further removal beyond this concentration was impossible with the lower UV dosage.

#### 5.3.1.2 Effect of Ozone Dosage on Treatment

The effect of ozone dosage on the removal of TOC from the reaction fluids is demonstrated by comparing test #1 and 3, 2 and 5, 18 and 20, 36 and 38, 38 and 39, and 36 and 39 in Tables 5-2 and 5-4. Between pairs of tests, the UV dosage was the same, and the initial TOCs were similar. In test #1, the ozone dosage was 10 times less than in test #3. The result was that the ozone required in test #1 was less than that required in test #3. However, the time to remove only 1.0605 grams of TOC from the reaction fluid during test #1 was 175 minutes compared with 100 minutes to remove 2.5947 grams of TOC during test #3.

The same result is true of test #2 and 5. These results indicate that a greater percentage of the ozone supplied at the lower dosage is being utilized to oxidize glycerol compared with the higher ozone dosage, but the amount of ozone available for oxidation is very much greater at the higher ozone dosage.

In test #18 and 20, the higher ozone dosage results in a slower reaction and the ozone requirement for complete oxidation is increased over the lower ozone dosage. Identical ozone dosages to those used for test #18 and 20 were used for test #36 and 38, respectively.

With bilgewater, both the reaction time and the ozone requirement are less at the lower ozone dosage, as seen with the phenol tests. This was also observed between test #38 and 39. The lower dosage used during test #39 compared with test #36 resulted in an equal amount of time (150 minutes) to remove slightly more TOC (3.1815 gms vs 2.7926 gms) than needed with the



higher ozone dosage used in test #36. The ozone requirement was less during test #39 compared with test #36, as observed with all of the ozone dosage tests.

These results indicate that the 32.8 mg/min ozone dosage used in test #1, 2, and 25 is well below the amount that can efficiently be used by the system. The high ozone dosage of 372 mg/min is less effective in removing TOC, both in terms of reaction time and the amount of ozone required, than ozone delivered at either 328 mg/min or 274 mg/min. The mass transfer of ozone from the gas phase to the liquid phase where the oxidation reactions occur must be less than with the lower ozone dosages. The low concentration of ozone in the gas phase at the higher dosage (0.65 wt %) probably results in a lowered "driving force" of ozone from the gas to the liquid phase. Additionally, if the gas to liquid interfacial area is reduced by virtue of the higher gas flows required to produce the higher ozone dosage (see Fig. 4-7), less ozone would be transferred into the liquid. The lowered interfacial area could result from coalescence of the gas bubbles at higher gas flowrates.

There is only slight difference in the effectiveness of the treatment when using either an ozone dosage of 328 mg/min or 247 mg/min. Only the flow of compressed air through the ozone generator was adjusted to deliver these two ozone dosages (Fig. 4-7); therefore the only savings in using the lower dosage would be due to the reduced requirement for compressed air.

#### 5.3.1.3 Effect of the Concentration of the Reaction Fluid on Treatment

Treatment of bilgewater at a high initial concentration (test #37) resulted in a lowered ozone requirement compared with tests at lower initial concentrations (e.g., test #36, Table 5-4). The large ozone demand of the high concentration reaction fluids may cause a lowered ozone concentration in the fluid. As a result, the mass transfer of ozone from the gas phase to liquid phase is increased, and less ozone is lost in the off-gas.



#### 5.3.1.4 Effect of Salt on Treatment

The effect of salt on the effectiveness of treatment was studied by performing test #6 and 9 and comparing the results with those of test #5 and 7, respectively. Salt did not degrade the treatment effectiveness with glycerol using the high UV dosage, as measured by treatment time or ozone requirement. Only a slight degradation was observed in the test with hydroquinone, conducted at a lower UV dosage. One possible explanation for these observations is that a greater percentage of the UV radiation may be absorbed by hypochlorite (formed by the oxidation of chloride ion) at the lower UV dosage than at the higher dosage and therefore the effect on treatment is greater. These results differ from those obtained by Houston Research, Inc., during the design phase of this program (Section 3.1); however, the design tests were conducted using a different reaction fluid and a higher salt concentration.

#### 5.3.1.5 Effect of Stripping on Treatment

Mixtures of water with toluene and with xylenes were treated with UV-ozone in the batch reactor. After 10 minutes of reaction, little of the organic compounds remained. Because of the high vapor pressure of these substances when dissolved in water, two experiments were conducted to determine how much toluene or xylenes could be removed by turning off the UV lamps and ozone generator and simply bubbling air through the water mixture. The results are shown in Fig. 5-1. The normalized TOC concentration is on the vertical axis, time is on the horizontal axis. Both toluene and the xylenes were substantially removed by air bubbling alone. These data indicate that volatile compounds will be rapidly removed from bilgewater by the combined actions of volatilization, or stripping, and UV-ozone treatment.

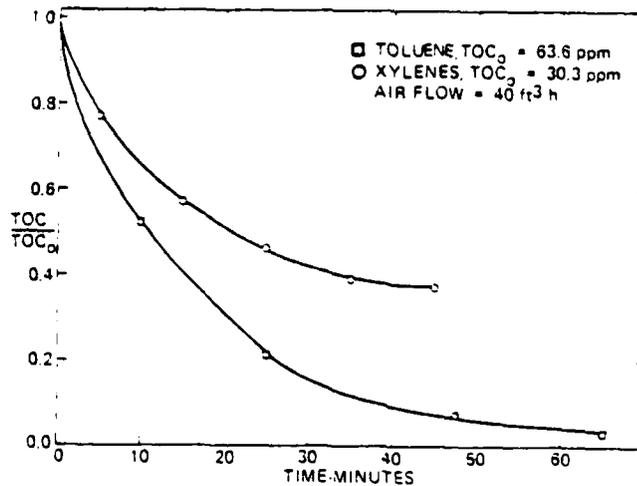


Figure 5-1. Effect of Stripping on the Removal of Xylene and Toluene from Water

#### 6.3.1.6 Effect of Reactor Fluid on Treatment

In all of the experiments using solutions of pure compounds, except for test #3-6 with glycerol, the ozone requirement was less than the theoretical minimum. That is, the amount of ozone used to completely oxidize the compounds was less than the stoichiometric amount. Several explanations may be offered to account for this. For example, more than one atom of oxygen per ozone molecule may participate in the oxidation reactions, or the UV radiation may render the organic molecules more susceptible to oxidation so that both dissolved ozone and oxygen transferred from the ozone-air gas feed to the liquid in the reactor participate in the oxidation reactions.

A measure of the difficulty in oxidizing the pure compounds is the ratio of the ozone requirement to the theoretical minimum requirement. This was done at a single UV dosage (1.3 watts/L) and ozone dosage (328 mg/min) and the order from most difficult to oxidize to least difficult is as follows:



Glycerol > heptanoic acid, n-amyl alcohol, o-cresol > phenol,  
quinoline > hydroquinone

A comparison of the difficulty of treatment of all of the compounds and mixtures tested can be made by arranging them in the order of their ozone requirements at single ozone (328 mg/min) and UV (7.9 watts/L) dosages:

Hydraulic oil-water > bilgewater > DF2-water > used crankcase oil-water > glycerol > Pyridine > DF2-used crankcase oil - salt water > n-amyl alcohol > quinoline > o-cresol > phenol > heptanoic acid > hydroquinone

Generally, the oil-water mixtures and bilgewater are more difficult to treat than most of the solutions of pure compounds in water. The mixtures either contained compounds that resist oxidation or the oxidation products which are formed are resistant. However, at maximum treatment levels, none of the mixtures was completely resistant to oxidation. All of these tests showed continued removal of TOC at the termination of the tests.

#### 5.3.1.7 Optimization

The optimum conditions of batch treatment depend to a large extent on whether the goal of the optimization is to minimize the treatment time or the energy costs. To evaluate the treatment parameters in terms of their effects on treatment time and energy costs, the results from the batch tests summarized in Tables 5-2, 5-3, and 5-4 were used.

The time required to remove TOC to one-half the initial concentration was first determined from each of the 41 batch tests. The power consumption of each piece of equipment in the total oil removal system was measured using a clamp-on amp meter. Power consumption is presented in Table 5-6. The treatment time to one-half TOC concentration and the power consumption



TABLE 5-6. POWER REQUIREMENTS FOR TOTAL OIL  
REMOVAL SYSTEM COMPONENTS

Equipment	Power (Watts)
O <sub>3</sub> Generator	840
O <sub>3</sub> Decomposition Heater	720
Air Dryer	60 (estimated)
700-watt UV	1200
1200-watt UV	1380
550-watt UV	2070
Stirring Motor	690
Oil-Water Separator Pump	<u>720</u>
Total	7680



were then used to calculate the time and energy required to treat 1000 gallons of reaction fluid. Treatment time was calculated as follows:

$$\text{Treatment time (hrs)} = 53.5 \text{ reactor volumes} \times t_{1/2} \text{ hrs/reactor volume} + 6.7 \text{ hrs}$$

53.5 reactor volumes would be required to treat 1000 gallons of fluid,  $t_{1/2}$  is the amount of time to reduce TOC by one-half in each reactor volume, and 6.7 hours of pumping time would be required to drain and fill the reactor 53.5 times, assuming a pumping rate of 5 gallons per minute.

The energy requirement in kilowatt hours (KWH) was calculated as follows:

$$\text{Energy Requirement (KWH)} = (53.5 \text{ reactor volumes} \times t_{1/2} \text{ hrs/} \\ \text{reaction volume} \times \text{power for treatment} \\ \text{in KW}) + (6.7 \text{ hrs} \times \text{power for pumping} \\ \text{in KW})$$

From Table 5-6 it can be seen that the power for pumping was 0.72 KW. The power for treatment varied only with the UV dosage since ozone dosage was determined by air flow through the ozone generator and not by power levels.

The treatment times and power requirements to treat 1000 gallons of reaction fluid are presented in Table 5-7 for the pure compounds in water. Tables 5-8 and 5-9 show the results for artificial bilgewater mixtures and bilgewater, respectively. The time required to remove 50% of the initial TOC, the amount of TOC removed from the 1000 gallons, and the energy required for treatment are presented for each test. The energy requirement is expressed in units of kilowatt hours per gram of TOC removed so that bias from the differences in the initial concentration of TOC between the tests could be eliminated. For test #1 and 41 the calculations were based on removal of 30% of the originally present TOC because 50% removal was never achieved during these tests.



TABLE 5-7. TIME AND ENERGY REQUIREMENTS FOR  
BATCH TREATMENT OF PURE COMPOUNDS MIXED WITH WATER

Test No.		Ozone Dosage (mg/min)	UV Dosage (watts/L)	Time <sup>a</sup> (hrs)	TOC Removed <sup>b</sup> (gms)	Energy Requirement <sup>c</sup> (KWH/gm TOC)
1	Glycerol	32.8	1.3	144.9 <sup>e</sup>	48.5	12.6
2	Glycerol	32.8	7.9	82.5	77.0	6.9
3	Glycerol	328	1.3	66.9	80.8	3.3
4	Glycerol	328	3.1	53.1	79.5	3.3
5	Glycerol	328	7.9	42.4	83.8	3.0
6	Glycerol + Salt	328	7.9	49.5	91.2	3.7
7	Hydroquinone	328	1.3	40.2	79.4	1.9
8	Hydroquinone	328	7.9	30.9	77.2	2.2
9	Hydroquinone + Salt	328	1.3	37.5	71.7	1.9
10	o-cresol	328	1.3	42.4	76.3	2.1
11	o-cresol	328	7.9	35.9	82.9	2.5
12	Pyridine	328	7.9	66.9	109.7	3.9
13	Quinoline	328	1.3	52.3	79.3	2.6
14	Quinoline	328	7.9	40.9	78.5	3.1
15	Phenol	328	1.3	42.4	70.8	2.3
16	Phenol	328	1.3	61.1	96.5	2.5
17	Phenol	328	3.1	42.4	77.4	2.6
18	Phenol	328	7.9	37.9	80.1	2.8
19	Phenol <sup>d</sup>	328	7.9	52.2	77.2	4.2
20	Phenol	372	7.9	50.4	87.1	3.5
21	n-Amyl alcohol	328	1.3	72.3	86.7	3.4
22	n-Amyl alcohol	328	7.9	41.6	90.8	2.7
23	Heptanoic acid	328	1.3	49.5	72.7	2.6
24	Heptanoic acid	328	7.9	25.7	80.1	1.8

- a. Time to reduce TOC by 50% in 1000 gallons of reaction fluid
- b. TOC removed in 1000 gallons
- c. Energy per gram of TOC removed, required to treat 1000 gallons
- d. Test conducted with interrupted stirring
- e. Time to reduce TOC by 30%



TABLE 5-8. TIME AND ENERGY REQUIREMENTS FOR BATCH  
TREATMENT OF ARTIFICIAL BILGEWATER MIXTURES

Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Time <sup>a</sup> (hours)	TOC Removed <sup>b</sup> (gms)	Energy Requirement <sup>c</sup> (KWH/gm TOC)
25	DF2 - water	32.8	5.6	102.1	42.6	15.7
26	DF2 - water	328	1.3	69.1	65.8	4.2
27	DF2 - water	328	7.9	61.1	59.6	6.4
28	DF2 - salt water	328	7.9	42.4	40.7	6.2
29	Hydraulic oil - water	328	1.3	153.8	88.4	7.3
30	Hydraulic oil - water	328	7.9	93.6	66.0	8.1
31	Used crankcase oil - water	328	1.3	91.4	69.1	5.4
32	Used crankcase oil - water	328	7.9	38.8	70.8	3.2
33	DF2 - used crankcase oil - salt water	328	1.3	63.8	70.2	3.6
34	DF2 - used crankcase oil - salt water	328	7.9	51.3	69.8	4.5

a. Time to reduce TOC by 50% in 1000 gallons of reactor fluid

b. TOC removed in 1000 gallons

c. Energy required per gram of TOC removed, required to treat 1000 gallons



TABLE 5-9. TIME AND ENERGY REQUIREMENTS FOR BATCH TREATMENT OF BILGEWATER

Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Time <sup>a</sup> (hours)	TOC Removed <sup>b</sup> (gms)	Energy Requirement <sup>c</sup> (KWH/gm TOC)
35	Bilgewater - dilute	328	7.9	106.6	60.9	11.5
36	Bilgewater - dilute	328	7.9	93.6	88.9	6.9
37	Bilgewater - dilute	328	7.9	131.1	169.2	5.1
38	Bilgewater - dilute	372	7.9	120.4	96.7	8.2
39	Bilgewater - dilute	274	7.9	96.3	106.4	5.9
40	Bilgewater	328	7.9	76.2	84.2	5.8
41	Bilgewater	328	1.3	86.9 <sup>d</sup>	54.5	6.5

a. Time to reduce TOC by 50% in 1000 gallons of reaction fluid

b. TOC removed in 1000 gallons

c. Energy required per gram of TOC removed, required to treat 1000 gallons

d. Time to reduce TOC by 30%. During this test TOC was never reduced by more than 30%.



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For all of the tests, increasing UV dosage results in less treatment time. For seven of the compounds and mixtures tested (hydroquinone, o-cresol, quinoline, phenol, DF2-water, hydraulic oil-water, and DF2-used crankcase oil-salt water) the lessening of treatment time with increasing UV dosage was insufficient to offset the increased power required for the higher UV dosages. Thus, energy requirements were greater at the high UV dosage. For the remaining five compounds and mixtures (glycerol, n-amy1 alcohol, heptanoic acid, used crankcase oil-water, and bilgewater) an energy savings was realized with the higher UV dosage. The optimum UV dosage to minimize treatment time is 7.9 watts/L; however the optimum UV dosage to minimize cost varies with the reaction fluid.

The ozone dosage of 32.8 mg/min used in test #1, 2 and 25 resulted in protracted treatment times and high energy requirements. The time to remove TOC to 50% of initial concentration with the high ozone dosage of 372 mg/min used in test #20 with phenol and #38 (bilgewater) was greater than at comparable tests at lower ozone dosages (test #18 with phenol and test #36 and 39 with bilgewater). The ozone dosage of 372 mg/min also resulted in higher energy requirements for treatment.

The ozone dosage of 274 mg/min used in test #39 appears to have slightly enhanced the treatment in terms of the energy requirement compared with test #36. The energy requirements were 5.9 and 6.9 KWH/gm TOC for the two tests, respectively. However, the two tests are not totally comparable because test #39 had an initial TOC concentration greater than the initial TOC concentration in test #36. This obviates a straightforward interpretation since the higher TOC concentration may have resulted in a greater utilization of the ozone supplied to the reactor. Based on these results, the optimum ozone dosage of those tested is between 274 and 328 mg/min. It would be expected that only slight performance variation would be experienced using ozone dosages within this range.

If the goal of treatment is to minimize treatment time the optimum UV dosage is 7.9 watts/L. If the goal of treatment is to minimize energy use,



the optimum UV dosage depends on the fluid to be treated. For either treatment goal, the ozone dosage which transfers the maximum quantity of ozone into the liquid phase is optimum, and this value is between 274 and 318 mg/min.

### 5.3.2 Flowthrough Testing

The batch tests provided an extensive data base which was used to predict the performance of the system in the continuous (flowthrough) mode of operation. The batch tests followed TOC removal as a function of time. These data were used to predict the amount of fluid per unit time which could be treated for any desired effluent concentration, based on a known, constant concentration of influent to the reactor.

At any one time the reactor contains compounds in solution which have unique reaction rates. This is even true when a pure compound is treated because of the immediate formation of oxidation products. These compounds have an average reaction rate, based on the combined unique reaction rates of the chemical species present.

The average rate of reaction for the fluid in the reactor is:

$$K_{ave} = \int_0^{\infty} K_t \left(\frac{F}{V}\right) e^{- (F/V)t} dt$$

where

$K_t$  = reaction rate for fluid of age  $t$

$F$  = flowrate to reactor

$V$  = fluid volume of reactor

$t$  = length of time in the reactor

$K_{ave}$  can be determined by calculating  $K_t$  at a number of points on the batch TOC curve separated by  $\Delta t$  and integrating numerically as follows:

$$K_{ave} = \sum_n \frac{K_{t_n} \left(\frac{F}{V}\right) e^{- (F/V)t_n} \Delta t}{n}$$



$K_{ave}$  is calculated for a number of different flowrates,  $F$ , and  $K_{ave} \cdot \frac{V}{F}$  is plotted versus  $F$ . Such a plot is shown in Fig. 5-2 for phenol, which was based on the results from test #16.

The change in TOC between the influent to the reactor and the effluent leaving the reactor is a function of the reactor volume, the flowrate,  $K_{ave}$ , and the effluent TOC concentration as follows:

$$[\Delta\text{TOC}] = \frac{V}{F} \cdot K_{ave} [\text{TOC}_{\text{effluent}}]$$

or,

$$\frac{[\text{TOC}_{\text{influent}}]}{[\text{TOC}_{\text{effluent}}]} - 1 = \frac{V}{F} K_{ave}$$

For example, if the TOC concentration in the influent to the reactor is 50 mg/L and the desired effluent concentration is 25 mg/L, the  $\frac{V}{F} \cdot K_{ave}$  value is:

$$\frac{V}{F} \cdot K_{ave} = \frac{50 \text{ mg/L}}{25 \text{ mg/L}} - 1 = 1$$

Therefore, from Fig. 5-2, a flowrate of approximately 1.3 L/min should produce the desired effluent concentration.

Flowthrough tests were performed to verify the accuracy of the above-described method of predicting flowthrough performance based on the batch tests. Another objective of the flowthrough tests was to determine how well the total oil removal system performed for long periods of continuous operation.

Six flowthrough tests were conducted, five using phenol and one using a DF2-water mixture. The reaction fluids were prepared as described in Section 5.2.1, and the tests were performed as described in Section 5.2.3.

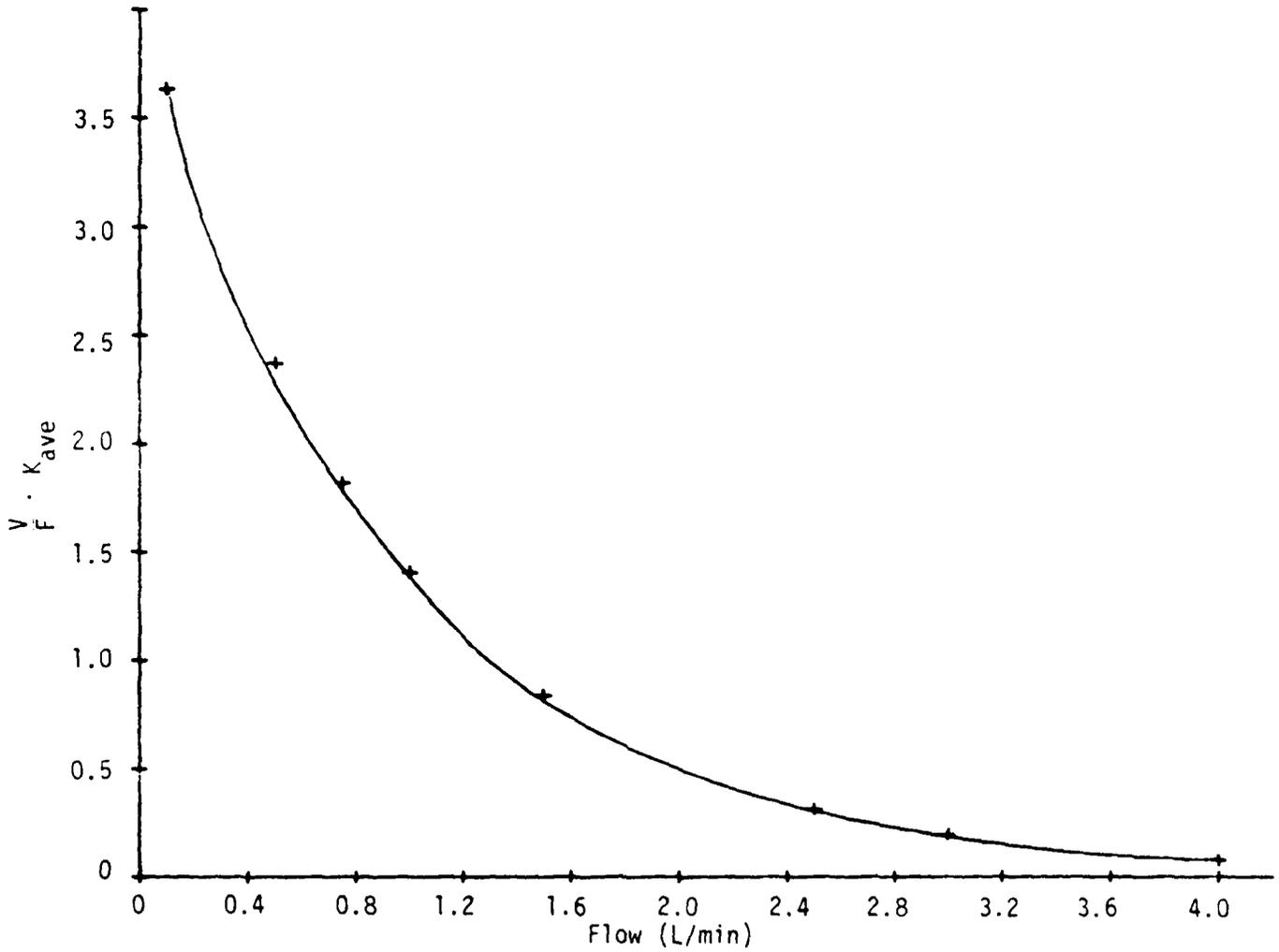


Figure 5-2.  $\frac{V}{F} \cdot K_{ave}$  for Various Flowrates Calculated  
From Test #16



Table 5-10 is a summary of the conditions and the results of the flow-through testing. The conditions of treatment, the calculated TOC in the effluent, the actual TOC in the effluent, the calculated energy requirement to treat 1000 gallons of reaction fluid, and the actual energy required are presented in Table 5-10. The calculated energy requirement was determined as follows:

Calculated energy required (KWH)/gm TOC) =

Time to treat 1000 gallons (hrs) x Power (KW)/TOC removed (gms)

where:

$$\text{Time to treat 1000 gallons} = \frac{1000 \text{ gal} \times 3.785 \text{ (L/gal)}}{\text{flowrate (L/min)} \times 60 \text{ (min/hr)}}$$

Power = from Table 5-6

$$\text{TOC removed} = [\text{TOC}_{\text{influent}} \text{ (mg/L)} - \text{calculated TOC}_{\text{effluent}} \text{ (mg/L)}] \times \\ 1000 \text{ gal} \times 3.785 \text{ (L/gal)} / 1000 \text{ (mg/gm)}$$

The actual energy requirement was obtained by substituting the actual  $\text{TOC}_{\text{effluent}}$  for the calculated  $\text{TOC}_{\text{effluent}}$  in the equation above.

From Table 5-10 it can be seen that the UV and ozone dosages were identical for each of the tests, and only the flowrate was varied. The greatest disparity between calculated and actual TOC values occurred in test #44 at the lowest flowrate tested of 0.5 L/min. The difference was 55%.

The low flowrate used in test #44 caused the reaction fluid in the oxyphotolysis reactor to heat up considerably because of the low throughput used during the test. This may have caused an increase in reaction rates and resulted in the low actual TOC compared with the calculated TOC effluent, since the calculated value was based on a batch test during which the temperature was considerably less.



TABLE 5-10. SUMMARY AND RESULTS OF FLOWTHROUGH TESTS<sup>e</sup>

Test No.	Conditions				Actual TOC <sup>b</sup> (mg/L)	Calculated TOC <sup>a</sup> (mg/L)	Calculated Energy Required <sup>c</sup> (KWH/gm TOC)	Actual Energy Required <sup>d</sup> (KWH/gm TOC)
	UV Dosage (Matts/L)	Ozone Dosage (mg/min)	Flow (L/min)	Duration (Hours)				
42	7.9	328	1.7	8	31.7	25.0	3.0	4.1
43	7.9	328	1.0	8	18.0	18.2	4.0	4.0
44	7.9	328	0.5	2	6.0	13.3	7.0	5.8
45	7.9	328	1.7	12	28.8	25.0	3.0	3.6
46	7.9	328	1.3	24	23.8	21.1	3.4	3.8
47	7.9	328	1.6	0.5	30.3	33.6	6.0	4.8

a. Based on calculations using batch test #18 or 27, TOC in reactor effluent

b. Average TOC in effluent from reactor

c. Based on calculations using batch test #18 or 27, energy per gram of TOC removed, required to treat 1000 gallons

d. Energy per gram of TOC removed, required to treat 1000 gallons

e. Tests #42-46 used phenol, test #47 used DF2-water mixture and was the final demonstration test. TOC in the influent to the reactor was 50 mg/L for the tests with phenol and 47 mg/L for the test with DF2.



The average disparity between calculated and actual TOC values, discounting the results from test #44, was 13%. This amount of error can be attributed to the accuracy of the analytical techniques and to temperature differences, as mentioned above. Therefore, the method for predicting the concentration of TOC exiting the reactor using calculations based on results from batch tests is reasonably accurate within a certain flowrate range.

Table 5-10 presents the calculated and actual energy requirements in the final two columns, respectively. Excepting the results from test #44, the calculated and actual energy requirements were, on the average, within 18% of each other.

During the flowthrough tests all of the equipment functioned as expected except for two malfunctions. During test #43, the feed pump used to supply the phenol feed stock to the reactor failed. This occurred after about 1 hour of flowthrough testing and the failure was manifested by a wildly fluctuating flowrate. The test was terminated and another pump was plumbed into the flow loop. The test was continued on the next day. It was later determined that the pump stator was worn and caused the failure. This replacement was considered to be routine maintenance.

While conducting test #44 the water-cooled impeller bearing became noisy, indicating an impending failure. The test was terminated after 2 hours of testing, rather than risk complete failure of the bearing. The bearing was rebuilt and the replaced part appeared to be poorly manufactured. The replacement part was of higher quality. This type of bearing and mechanical seal usually last many thousands of hours before rebuilding is required.

#### 5.3.2.1 Optimization

The agreement between the calculated and actual performance of the total oil removal system (in terms of the concentration of TOC effluent and the energy requirements) was sufficient to allow such calculations to be used



to determine the optimum conditions for flowthrough treatment based on the results of batch tests. Calculations were performed using the results from 16 batch tests to determine the time and the energy required to remove TOC from the reaction fluid during flowthrough treatment.

Table 5-11 shows the results of these calculations. The time to remove 50% of the concentration of TOC in the influent, and the energy required to remove TOC from the influent by three different amounts (25%, 50%, 75%) are presented.

In all of the tests, except for 26 and 27, an increase in UV dosage results in less time required for treatment to the 50% level. In tests 26 and 27, little difference in treatment time is observed between the two UV dosages.

For phenol and DF2-water, less energy is required for TOC removal to both the 25% and 50% levels when using the low UV dosage compared with the high UV dosage. With phenol, treatment to the 75% level requires less energy using the high UV dosage. For all of the other reaction fluids (hydraulic oil-water, used crankcase oil-water, DF2-used crankcase oil-saltwater, and bilgewater), the high UV dosage is the most energy-efficient treatment.

The experiments show that for phenol (both UV dosages), used crankcase oil-water (the high UV dosage), and DF2-used crankcase oil-saltwater (the high UV dosage) treatment to the 50% level requires slightly less energy per gram of TOC removed than treatment to the 25% level. This is because during the batch tests from which these values were calculated, the rate of TOC removal was greater from the 25% to 50% levels than from the beginning of the test to the 25% level.

The effect of ozone dosage on the calculated time and energy requirements is seen by comparing tests 36, 38, and 39 in Table 5-11. The ozone dosage of 328 mg/min produces the fastest and most economical treatment compared with dosages of 274 mg/min and 372 mg/min.



TABLE 5-11. CALCULATED TIME AND ENERGY REQUIRED FOR FLOWTHROUGH TREATMENT

Calculated From Test No.	Reaction Fluid	Ozone Dosage (mg/min)	UV Dosage (watts/L)	Time <sup>a</sup> (hours)	Energy Required <sup>b</sup> to Remove x % TOC <sup>c</sup> (KWH/gm TOC)		
					25%	50%	75%
16	Phenol	328	1.3	46.7	3.0	2.8	12.5
18	Phenol	328	7.9	37.5	3.1	3.0	9.0
26	DF2 - water	328	1.3	108.7	3.7	6.4	C
27	DF2 - water	328	7.9	112.6	5.4	9.1	C
29	Hydraulic oil - water	328	1.3	d	15.0	C	C
30	Hydraulic oil - water	328	7.9	371.0	8.1	30.1	C
31	Used crankcase oil - water	328	1.3	d	6.5	C	C
32	Used crankcase oil - water	328	7.9	39.4	3.3	3.2	6.6
33	DF2 - used crankcase oil - salt water	328	1.3	137.1	5.1	8.1	C
34	DF2 - used crankcase oil - salt water	328	7.9	38.5	3.3	3.1	7.3
36	Bilgewater - dilute	328	7.9	150.2	7.9	12.2	C
37	Bilgewater - dilute	328	7.9	371.1	11.6	30.1	C
38	Bilgewater - dilute	372	7.9	371.1	11.4	30.1	C
39	Bilgewater - dilute	274	7.9	197.1	8.3	16.0	C
40	Bilgewater	328	7.9	d	6.4	C	C
41	Bilgewater	328	1.3	d	C	C	C

- a. Time required to reduce TOC by 50% in 1000 gallons of reaction fluid from 50 mg TOC/L
- b. Energy per gram of TOC removed, required to treat 1000 gallons
- c. Energy requirement excessive, more than 35 KWH/gm TOC
- d. Time more than 500 hrs



Flowthrough treatment of hydraulic oil-water and used crankcase oil-water at the low UV dosage, and bilgewater at both UV dosages, to the 50% level and beyond would require excessive time and energy. For most of the reaction fluids, flowthrough treatment to the 75% level would also be prohibitive. This is because in a flowthrough system the fluid being treated is continually being supplemented by incoming fluid of higher concentration. To achieve an effluent of low concentration, therefore, requires quite low flowrates, so that the distribution of fluid residence times in the reactor is such that adequate treatment is rendered.

If low effluent concentrations are desired, batch treatment can be more energy-efficient than flowthrough treatment. This is true for treatment to the 50% level for all but the used crankcase oil-water mixture using 7.9 watts/L UV and the DF2-used crankcase oil-saltwater mixture at the same UV dosage. This can be seen by comparing the energy requirements shown in Tables 5-7, 5-8, and 5-9 for batch treatment with those calculated for flowthrough treatment shown in Table 5-11. For the two tests which are exceptions, the oxidation products that are formed during the ozone reaction with these fluids may inhibit continued reactions to the 50% level when treating in the batch mode. By continuously removing the accumulated oxidation products from the reactor, which occurs in flowthrough treatment, treatment to the 50% level becomes easier.

The optimum treatment conditions for flowthrough operation, as with batch testing, depends on the goal of optimization, i.e., reduced time or reduced energy requirements. The maximum UV dosage of 7.9 watts/L will produce the shortest treatment time and, with some reaction fluids, the most energy-efficient treatment. Other fluids can be treated more economically at a reduced UV dosage. The best ozone dosage is that which transfers the greatest amount of ozone from the gas to the liquid phase, and this appears to be between 274 and 328 mg/min.



### 5.3.3 Oxidation Products

Four tests in the batch mode were conducted to determine qualitatively and quantitatively the oxidation products resulting from the reactions of ozone with a phenol-water solution, a DF2-water mixture, and bilgewater. These tests were performed since TOC removal by oxyphotolysis, while ideal for determining the effects of changing treatment conditions on treatment time and energy efficiency, may not be the most important criteria for establishing an end point for treatment. When the toxic compounds in a reaction fluid are oxidized to less toxic compounds, this may be adequate treatment. Measuring TOC reveals nothing about the nature of the carbon that is measured. Therefore, during the tests for oxidation product determination, an analytical method that provides more information on compound specificity was employed. HPLC was used to separate and measure the most toxic compounds present in the reaction fluids.

As discussed in Section 5.2.5, the HPLC analysis utilized a method of detection (UV absorbance at 254 nm) which is sensitive to compounds containing aromatic structure. As oxidation of an aromatic molecule proceeds and the aromatic ring is cleaved, UV absorbance is dramatically decreased. It is generally true that as aromaticity decreases, so does toxicity. Therefore, the quantity of UV absorbing compounds in samples taken from the oxyphotolysis reactor is a measure of the toxicity of the fluid.

#### 5.3.3.1 Phenol

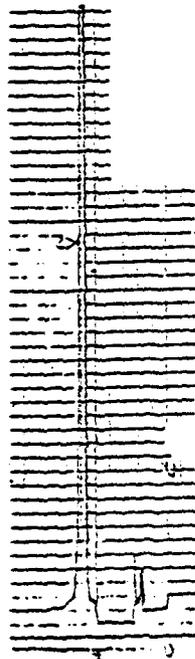
The test with phenol used an ozone dosage of 328 mg/min and a UV dosage of 7.9 watts/L. Seven samples were collected for HPLC analysis from 0 to 45 minutes after the initiation of treatment. The samples were concentrated using an accumulator column, described in Section 5.2.5, prior to analysis.

Figure 5-3 shows the HPLC chromatograms from each of the seven samples. The sample time is shown under each chromatogram. Initially ( $T = 0$ ), only

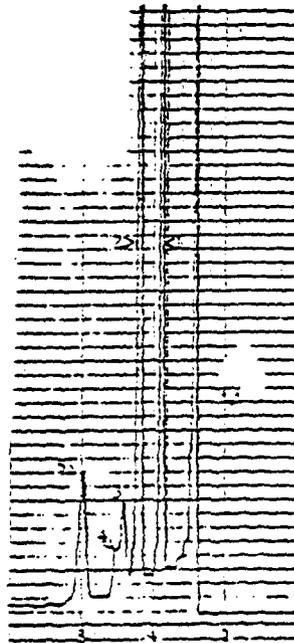


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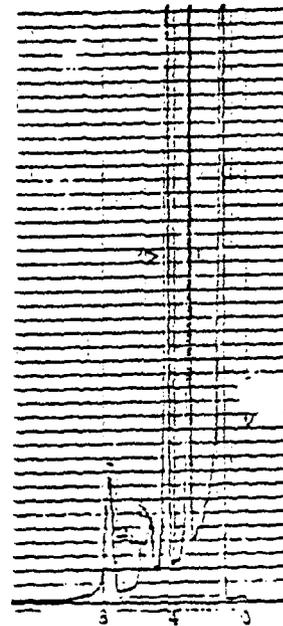
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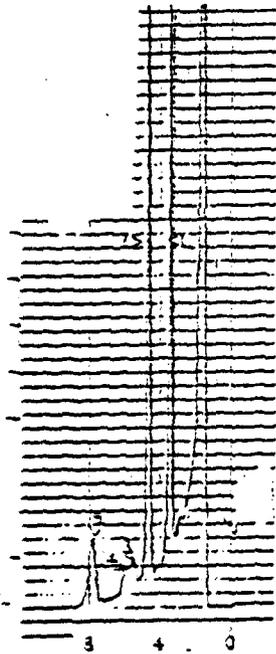
T = 0



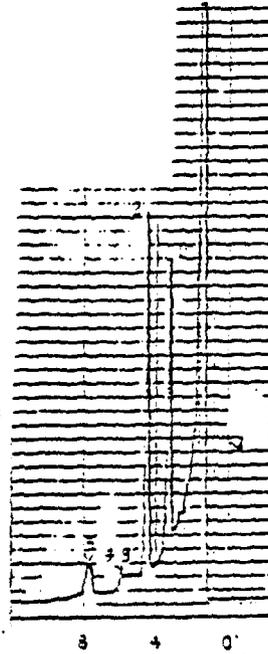
T = 5



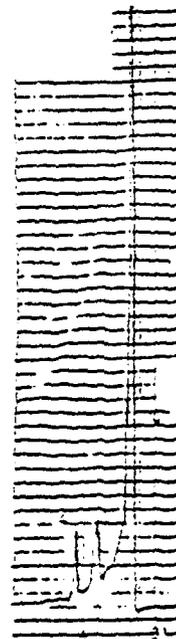
T = 10



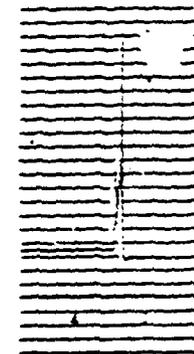
T = 15



T = 20



T = 30



T = 45

Figure 5-3. HPLC Chromatograms of Oxyphotolyzed Phenol Samples After Various Treatment Times (T = Minutes)  
abscissa = time (minutes), ordinate = detector response



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phenol is present, labeled #2 in Fig. 5-3. After just 5 minutes of treatment, four other compounds exhibiting UV absorbance at 254 nm were detected. The compound labeled #1 had an identical retention time as a standard of hydroquinone, a known oxidation product of phenol (Ref. 12). None of the other compounds detected in the samples (peak #3, 4, and 5) had retention times similar to the other standards used (catechol, o-quinone). No UV-absorbing compounds were detected in the sample taken after 45 minutes of treatment.

Other than compounds shown as peak #4, all of the compounds decrease in concentration or treatment proceeds past 5 minutes. The concentration of the compounds exhibited as peaks 3, 4, and 5 are unknown, since they were unidentified. The concentration of hydroquinone and phenol (peaks 1 and 2, respectively) in the reactor, as well as the percent removed, are tabulated in Table 5-12. Phenol is higher in concentration throughout the test; however, they decrease in concentration at similar rates.

TABLE 5-12. CONCENTRATIONS OF PHENOL AND HYDROQUINONE DURING PHENOL OXIDATION

Sample Time (Minutes)	Phenol Concentration (mg/L) $\pm$ Std.Dev.	% Phenol Removal	Hydroquinone Concentration (mg/L) $\pm$ Std.Dev.	% Hydroquinone Removal
0	57.7 $\pm$ 0.3	--	--	--
5	37.2 $\pm$ 2.5	35.5	20.3 $\pm$ 0.8	--
10	23.6 $\pm$ 0.0	59.1	11.5 $\pm$ 0.5	43.3
15	14.6 $\pm$ 0.2	74.4	6.3 $\pm$ 0.1	69.0
20	8.4 $\pm$ 0.5	85.4	3.7 $\pm$ 0.2	81.8
30	1.1 $\pm$ 0.3	98.1	0.7 $\pm$ 0.4	96.6
45	0	100.0	0	100.0



Table 5-13 shows the concentration of the oxidation products of phenol in the samples expressed as TOC. The TOC values are from an experiment in which treatment conditions and initial concentration of phenol were identical to those used during the present experiment to determine the phenol and hydroquinone concentrations. TOC contributed by compounds other than phenol, and TOC contributed by compounds other than phenol and hydroquinone are given. After about 7 minutes of oxyphotolysis treatment, 50% of the TOC present is contributed by compounds other than phenol. After slightly more than 10 minutes, half of the TOC present is made up of compounds other than phenol and hydroquinone.

TABLE 5-13. QUANTITY OF OXIDATION PRODUCTS OF PHENOL

Time (Minutes)	*TOC, All Compounds (mg/L)	Phenol (mg TOC/L)	TOC, Compounds Other Than Phenol		Phenol + Hydroquinone (mg TOC/L)	TOC, Compounds Other Than Phenol + Hydroquinone	
			mg/L	%		mg/L	%
0	50.2**	44.2**	0	0	44.2	-	-
5	49.0	28.5	20.5	41.8	41.8	7.2	14.7
10	48.0	18.1	29.9	62.3	25.6	22.4	46.7
15	46.8	11.2	35.6	76.1	15.3	31.5	67.3
20	45.0	6.4	38.6	85.8	8.9	36.1	80.2
30	41.1	0.8	40.3	98.1	1.3	39.8	96.8
45	31.7	0	31.7	100.0	0	31.7	100.0
60	14.9	0	14.9	100.0	0	14.9	100.0

\* These values are from a previous experiment.

\*\* The disparity between TOC values for all compounds and phenol at time = 0 is due to errors associated with analytical techniques.



Much more rapid and energy-efficient treatment could be realized if nontoxic compounds could be tolerated in the effluent from the oxyphotolysis reactor. For example, to remove TOC to 15 mg/L from 50 mg/L in 1000 gallons of reaction fluid would require 60 hours and 239 KWH of energy in the batch treatment mode and many times these amounts in the flowthrough treatment mode. However, if 41.1 mg/L of TOC could be tolerated in the effluent, 1.3 mg/L of which is contributed by phenol and hydroquinone and the remainder contributed by their less toxic oxidation products (Table 5-13), treatment becomes more time- and energy-efficient. Batch treatment would require 33.5 hours and 191.0 KWH of energy and flowthrough treatment would require 15.8 hours and 121.0 KWH of energy.

#### 5.3.3.2 DF2-Water

A DF2-water mixture was treated with an ozone dosage of 328 mg/min and a UV dosage of 7.9 watts/L. Five samples were collected, from time zero to 90 minutes after the initiation of treatment. The samples were prepared for HPLC analysis by extracting with chloroform, as described in Section 5.2.5.

Because of the complex nature of an oil-water mixture which can contain hundreds of compounds, the HPLC analysis employed a method of determining the classes of compounds present (phenolics, aromatics [BTX], and nitrogen heterocyclics). The compounds present as a class tend to elute from the HPLC column in specific time windows. The compounds eluting within a time window can be quantified by comparing their detector responses to the responses from standards in the same class.

Table 5-14 shows the results of the HPLC analysis. The removal of the originally present (at time zero) compounds or converted to non-UV-absorbing compounds through time is presented, as percent.

After 30 minutes of treatment, over 90% of the total phenolics and total aromatics present in the time zero sample are converted to compounds which are not detected, and over 60% of the total nitrogenous heterocyclics



TABLE 5-14. RESULTS OF HPLC ANALYSIS OF A DF2-WATER MIXTURE

Time (Min)	Removal or Conversion of Total Phenolics (%)	Removal or Conversion of Total Aromatics (%)	Removal or Conversion of Total Nitrogenous Heterocyclics (%)
0	0	0	0
15	75.2	92.6	a
30	90.9	93.6	62.5
60	94.1	98.2	50.0
90	95.8	98.6	68.7

a. No analysis performed.

are converted. The concentration of nitrogenous heterocyclic compounds was very small and their apparent increase from the 30-minute to the 60-minute sample was probably due to normal analytical error, since only a 0.2 mg/L change in concentration occurred between the two samples.

As discussed previously in reference to phenol, if relatively nontoxic compounds could be tolerated in the effluent from the reactor, treatment time and energy expenditure could be reduced. To remove TOC in 1000 gallons of DF2-water mixture from approximately 31 mg/L to 5 mg/L would require 90.5 hours and 588.2 KWH of energy using batch treatment, and many times this amount using flowthrough treatment. However, if 90% removal or conversion of total phenolics and total aromatics to less toxic species, and 60% removal or conversion of nitrogenous heterocyclics is acceptable, the time and energy requirements for batch treatment to this degree are 33.4 hours and 191.0 KWH, respectively. Flowthrough treatment to this same degree would require 30 hours and 230.7 KWH of energy.



### 5.3.3.3 Bilgewater

Two tests were performed using bilgewater; one used a UV dosage of 1.3 watts/L, the other used 7.9 watts/L. The ozone dosage was identical during the experiments at 328 mg/min. Fifteen samples were collected during these tests and prepared for HPLC analysis as described in Section 5.2.5, using an accumulator column to concentrate the sample.

Figures 5-4 and 5-5 show the HPLC chromatograms from the samples obtained during the two experiments conducted at 7.9 watts/L UV and 1.3 watts/L UV, respectively. Shown below each chromatogram is the elapsed time after initiation of treatment each sample was taken.

Three prominent compounds were detected by UV absorbance in the samples from each experiment. The peaks are labeled with numbers in the chromatograms presented in Figs. 5-4 and 5-5. In the initial sample ( $T = 0$ ) from the low UV dosage experiment, all three compounds are present. As treatment progresses, the compound represented as peak #2 decreases in concentration so that after 20 minutes of treatment it is barely detectable. The concentration of the compound represented as peak #1 decreases after 5 minutes of treatment but then increases in concentration in the  $T = 10$  minute sample. It is also barely detectable in the 20-minute sample. There is a general increase in the concentration of the compound represented as peak #3, except in the samples taken at  $T = 20$  and  $T = 90$ , where a decrease in concentration is observed from the  $T = 10$  and  $T = 60$  samples, respectively.

The compound represented as peak #2 was the only compound present in the initial sample ( $T = 0$ ) taken during the high UV dosage experiment. The compounds shown as peaks 1 and 3 appear in the  $T = 5$  sample, along with peak #2. After 15 minutes of treatment, the compounds shown as peaks 1 and 2 are undetected.

The compound shown as peak #3 is present in the initial sample from the low UV dosage experiment but not in the high UV dosage experiment. This



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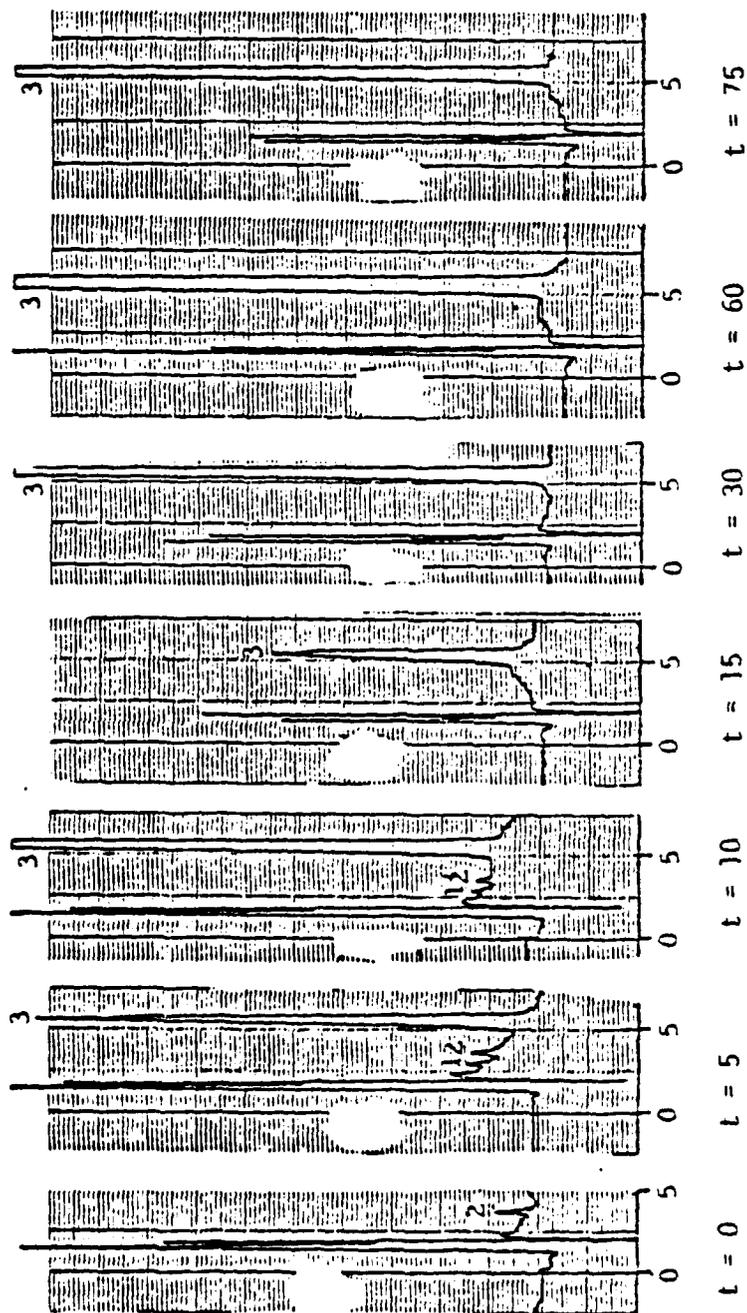


Figure 5-4. HPLC Chromatograms From Oxyphtolysis Samples, 7.9 Watts/L UV  
(abscissa = time [minutes], ordinate = detector response)

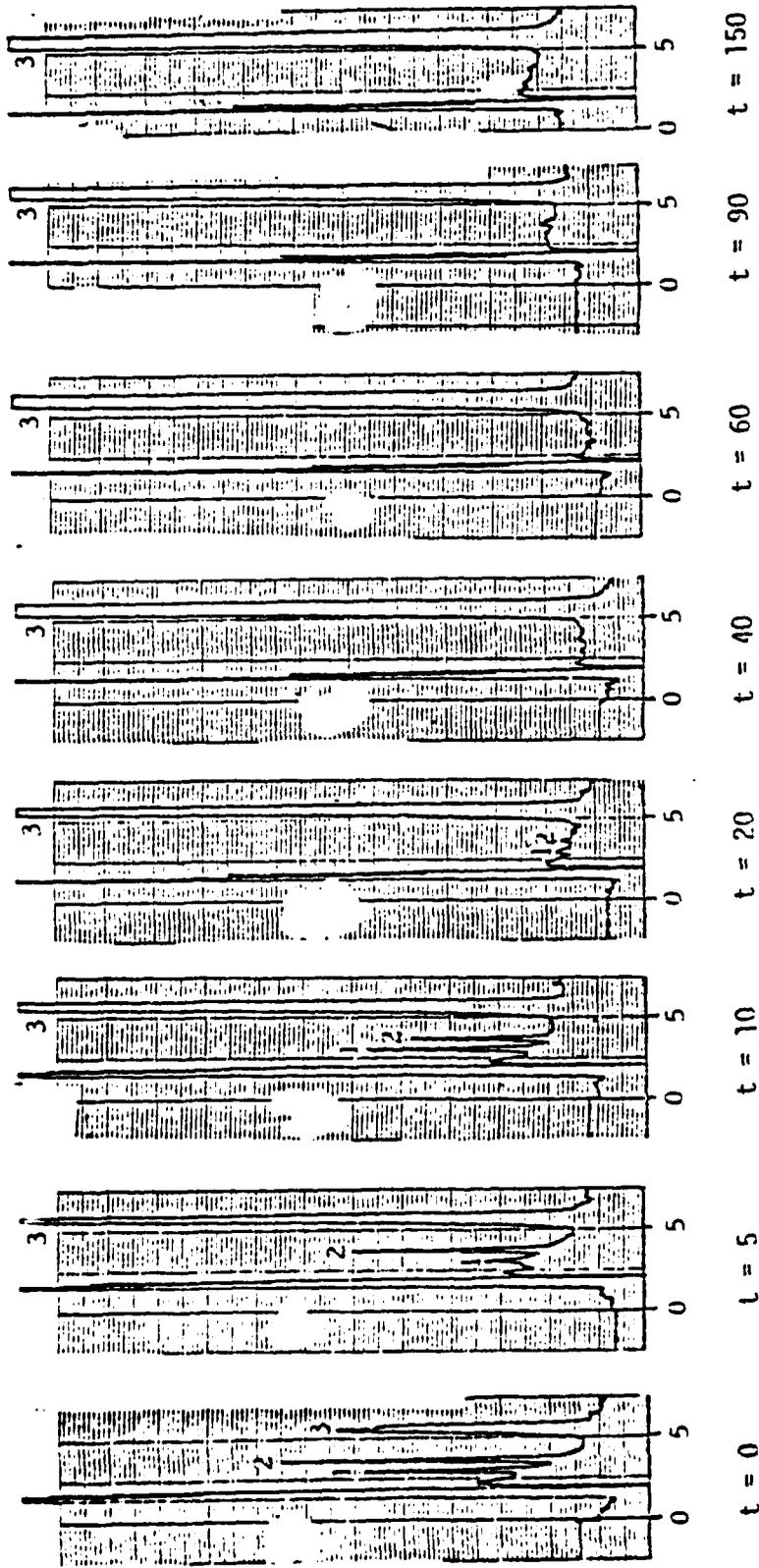


Figure 5-5. HPLC Chromatograms From Oxyphotolysis Samples, 1.3 Watts/L UV  
(abscissa = time [minutes], ordinate = detector response)



might be due to the way the experiments were conducted. The experiment using the high UV dosage was performed first, with the initial sample drawn before the air-ozone gas sparge was begun. Once sparging was started, a froth was noticed exiting from the ozone decomposition heater outlet. To prevent this occurrence during the subsequent experiment using the low UV dosage, air was sparged through the bilgewater in the oxyphotolysis reactor for 10 minutes prior to taking the initial sample. The froth was collected in a bucket as it left the reactor through the offgas line, upstream of the decomposition heater. The 10-minute air sparge undoubtedly saturated the bilgewater with oxygen, which may have caused some oxidation to occur, producing the compound shown as peak #3 in the initial sample of the low UV dosage test.

There is a striking similarity in the variation in concentration of the compound represented by peak #3 observed during the two experiments. A rise in concentration is observed in the 5- and 10-minute samples, followed by a drop in concentration. After 60 minutes of treatment, a sharp rise in its concentration occurs during both experiments, followed by another drop in concentration. The 150-minute sample of the low UV dosage experiment contained higher concentrations of the compound than the 60-minute sample.

The concurrent rise and fall of the concentration of the compound shown as peak #3 in the samples from both experiments suggests that these results represent actual conditions and not anomalous behavior or improper analytical techniques. The source of this compound is unknown. It could be an oxidation product of a compound which is undetected by the UV detector under the separation conditions used. A nonpolar molecule would have a strong affinity for the HPLC column packing material and would therefore have a long retention time. Another alternative source for this compound is from the undissolved oil component in the bilgewater. The stirring of the bilgewater while being subjected to UV and ozone could conceivably cause some compound or compounds of the undissolved oil to become more soluble and enter the water phase.



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The exact chemical nature of the compound represented as peak #3 was undiscovered, even after trying to match its retention time with a number of known standards. Therefore, the concentration of the compound is unknown. During the treatment using the low UV dosage, the rate of TOC removal was zero from  $T = 60$  to  $T = 150$ . The resistance to oxidation of the compound shown as peak #3 may account for the stable TOC concentrations.

The test using the high UV dosage showed a steady removal of TOC throughout the test. The compound represented as peak #3 was reduced in concentration after the 60-minute sample. Therefore, the compound was not resistant to oxidation at the high UV dosage. Continued treatment probably would have completely eliminated all UV-absorbing compounds from the reaction fluid.

#### 5.3.4 Safety Testing

The following subsections describe the results of the tests to measure ozone, noise, and UV levels in the environment around the total oil removal system. The methods employed while making these measurements are presented in Section 5.2.4.

##### 5.3.4.1 Ozone Levels

Three ozone leak tests were conducted on successive days (September 5, 6, and 7). On the 5th and part of the 7th, ozone was generated while the total oil removal system was operating. The background interior ozone level was measured on the 6th with the system off. For all three days, exterior ozone levels were obtained from the Air Pollution Control District of Ventura County. Their ozone monitoring station is located approximately 3.5 miles from the Rockwell laboratory in Newbury Park.

Figure 5-6 is a plot of the results. The mean interior and exterior hourly ozone value is plotted for each test day. The interior ozone level on September 5, with the system operating, never exceeded the Army ozone

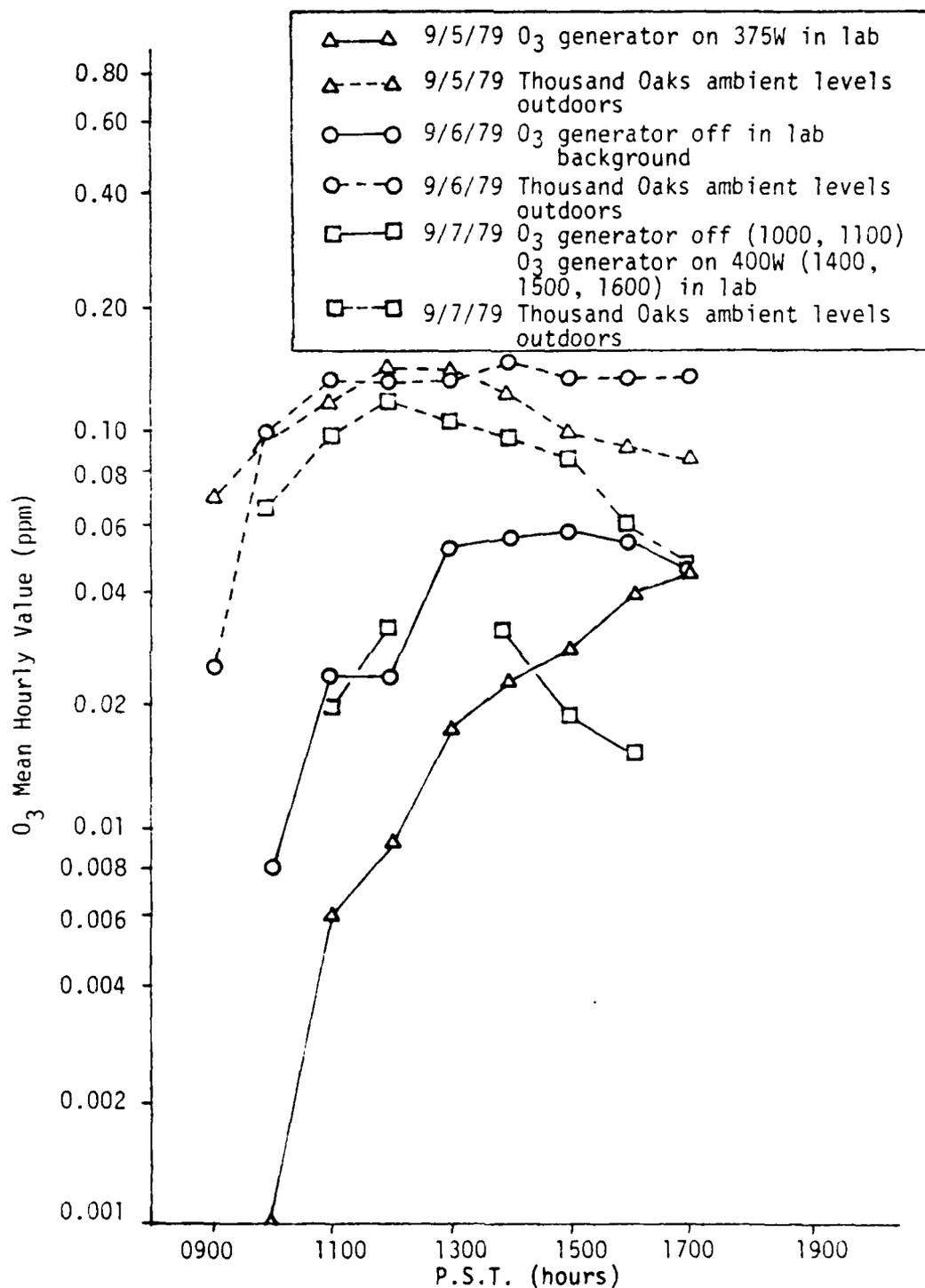


Figure 5-6. Mean Hourly Interior and Exterior Ozone Levels



limit of 0.05 ppm (Ref. 13). However, at 1700 hours the ozone level was 0.046 ppm and probably would have exceeded 0.05 ppm had the test continued. Exterior ozone levels exceeded 0.05 ppm for the entire test period on the 5th. Therefore, determining if the interior ozone level increased because of an ozone leak, because of infiltration of exterior ozone into the test room, or both, was difficult. On September 6, interior ozone levels increased as the day progressed in a similar manner as the interior levels measured on the 5th, even though no ozone was generated by the system. The interior ozone level on the 6th was greater for each hour than the interior level on the 5th, except for 1500 hours where a similar level was attained. Exterior ozone levels were similar for these two days from 1000 to 1300 hours, after which the ozone level was higher on the 6th. On the 7th, from 1400 to 1600 hours, while ozone was being generated by the system, the ozone level decreased in a similar fashion to the exterior ozone level of the same day.

These results suggest that the total oil removal system was leaktight. Ozone levels in the shipboard environment were measured during the on-board testing of the system and these results are presented in the final report for Contract DAAK70-78-C-0075.

#### 5.3.4.2 Noise Levels

The initial test measured the noise levels produced by the operating total oil removal system using a hand-held noise meter. The results indicated that most of the noise occurs at the high frequencies since very little difference was observed between measurements using the dBA scale (truncated lower frequencies) and the dBC scale (flat response over 20 to 20,000 Hz). Almost all of the high-frequency noise is produced by the ozone generator and more detailed measurements of this noise was undertaken using an octave band analyzer. Table 5-15 summarizes the results. Figure 5-7 is a plot of the dB levels at various frequency band centers for three ozone generator power levels as well as the upper limit, Category D of MIL-STD-1474A.

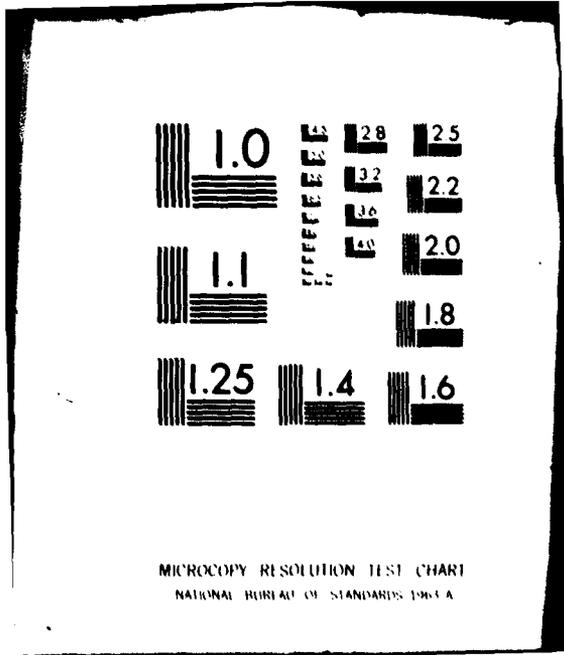


TABLE 5-15. OZONE GENERATOR NOISE LEVEL READINGS

Frequency	MIL-STD-1474 (dB)	dB at:						
		150W	200W	250W	300W	350W	400W	450W
A Scale	85	84	85,86*	87	96,92-96*	90	86,88*	85
31.5 Hz	--	84	83	84	83	83	83	84
63 Hz	106	84	83	84	83	83	83	84
125 Hz	96	89	89	89	89	88	88	88
250 Hz	89	83	83	83	84	83	83	83
500 Hz	83	79	79	79	80	79	79	80
1000 Hz	80	79	79	79	79	78	78	78
2000 Hz	79	77	82	86	94	84	78	77
4000 Hz	79	75	71	86	84	76	80	81
8000 Hz	81	69	65	81	72	67	76	75
16000 Hz	--	52	50	52	53	60	56	52

\* Noise level reading taken using a hand-held meter.





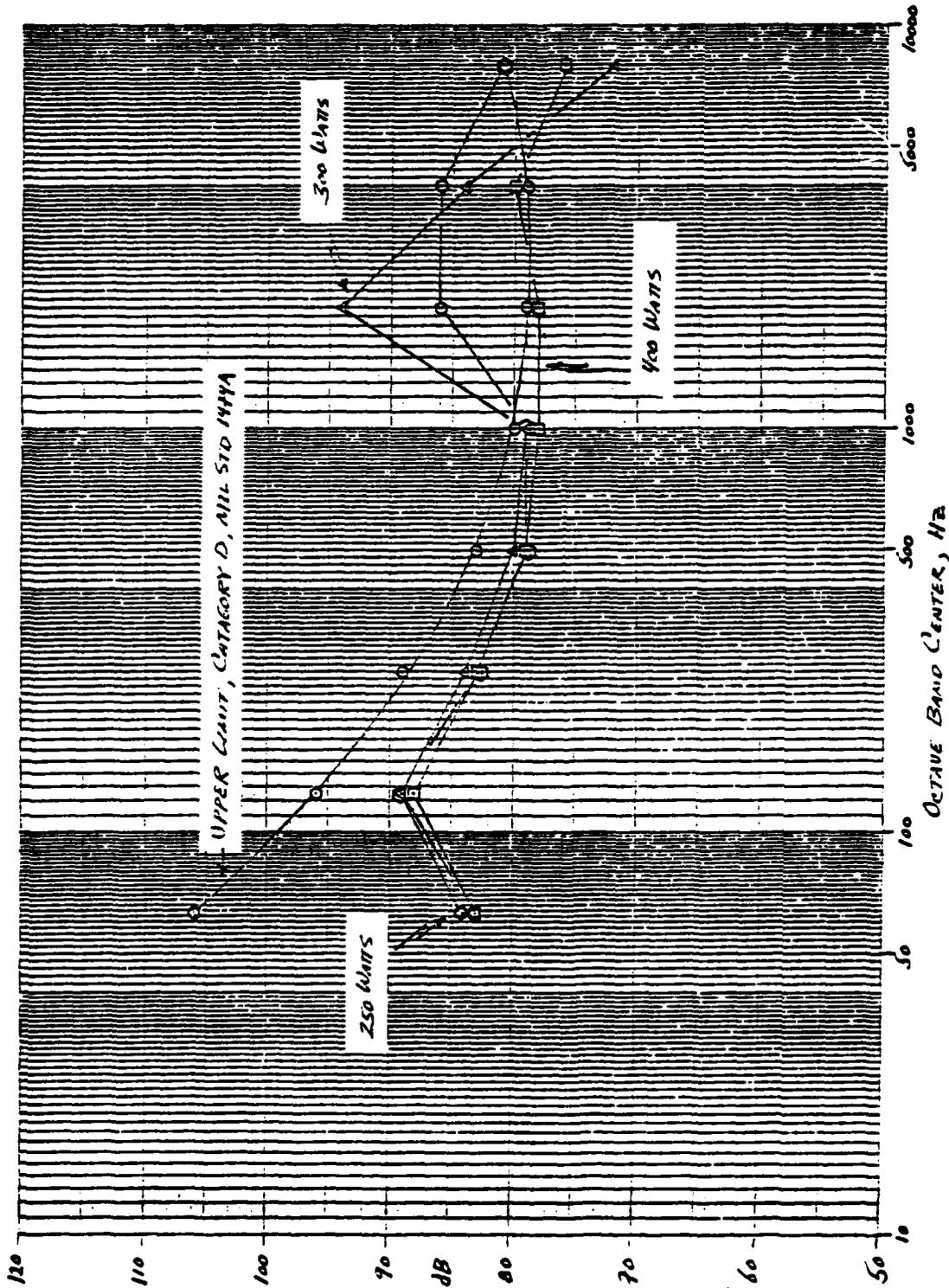


Figure 5-7. Ozone Generator Noise Levels Compared to Military Standards



At 400 watts, the normal operating power level, the ozone generator is below the Category D maximum levels, except at the octave band centered at 4000 Hz. At 4000 Hz, the ozone generator exceeds the standard by only one decibel. Since the measurements were taken at the rear of the ozone generator unit, these are worst-case levels. Actual noise levels experienced by operating personnel would probably be lower. Based on these results, no modification to the system equipment was necessary to deliver a noise-safe system for shipboard installation. Noise levels during on-board testing were made, and presented in the final report for Contract DAAK70-78-C-0075.

#### 5.3.4.3 UV Levels

Maximum permissible UV exposure levels to Army personnel are promulgated in AR 40-46 (Ref. 14) as follows:

1. For the near-UV spectral region (315 to 400 nano meters [nm]), total irradiance upon the unprotected skin or eye shall not exceed 1 milliwatt per square centimeter ( $\text{mW}/\text{cm}^2$ ) for periods greater than  $10^3$  seconds, and for exposure times less than  $10^3$  seconds should not exceed 1 joule per square centimeter ( $\text{J}/\text{cm}^2$ ).
2. For the actinic UV spectral region (200 to 315 nm), the radiant exposure incident upon the unprotected skin or eyes shall not exceed 0.1 microwatt per square centimeter ( $\mu\text{W}/\text{cm}^2$ ) for an 8-hour period.

UV leakage measurements were made from each of the three individual UV lamps, while the other two were off. Leakage from each lamp was measured at four locations shown in Fig. 5-8. The measurements were made in a horizontal plane out from the quartz lamp sheath which protruded from the top of the reactor and was topped by the lamp junction box. The amount of UV leakage from each position is given in Table 5-16.

UV leakage was also measured while all three UV lamps were on. The positions from which these measurements were taken are given in Fig. 5-9. Three measurements (A, B, and C) were taken from three different positions

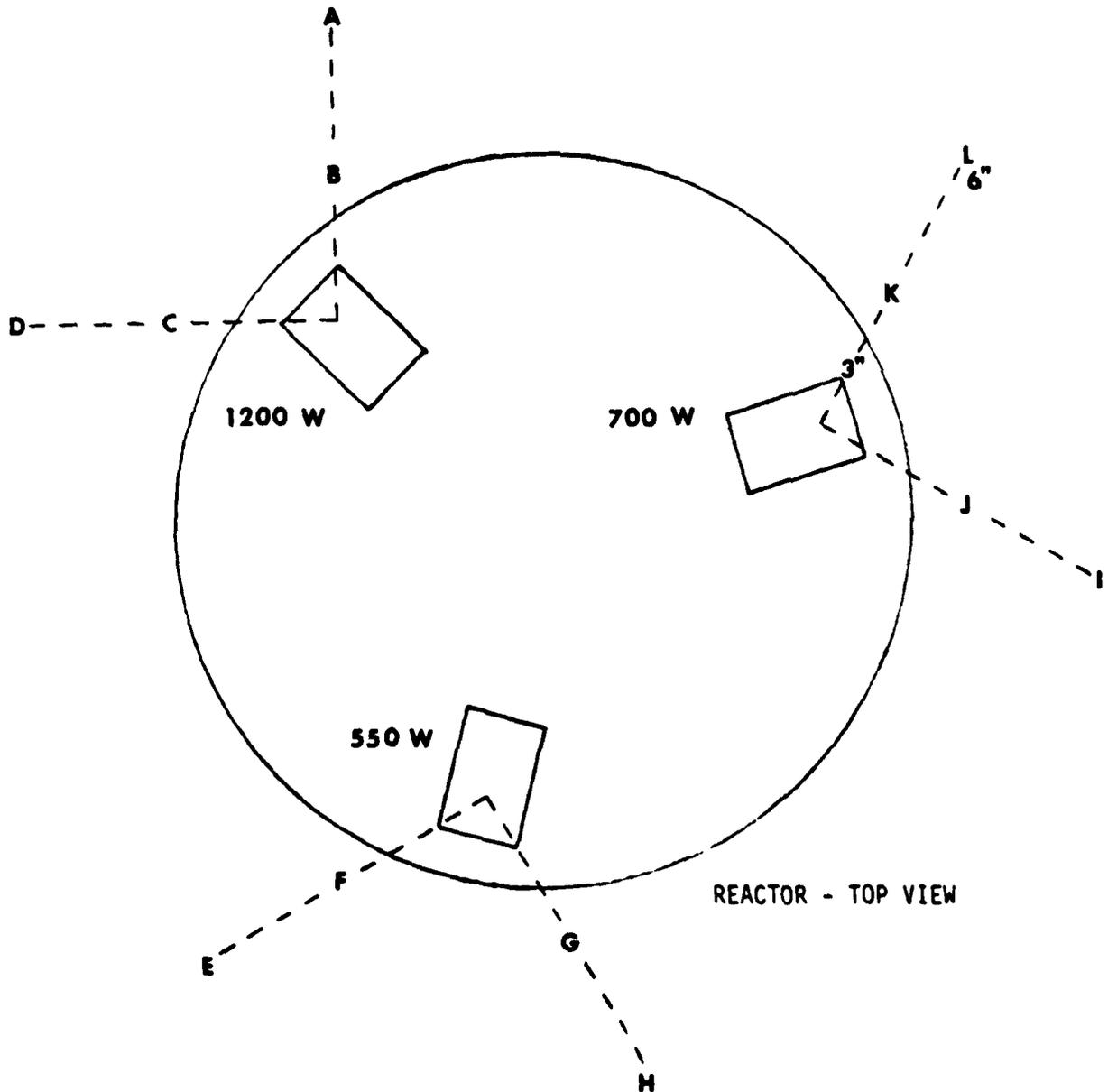


Figure 5-8. UV Exposure Measurement Positions,  
Exposure From Individual Lamps



TABLE 5-16. ULTRAVIOLET EXPOSURE FROM INDIVIDUAL LAMPS

Measurement Location (Fig. 5-8)	Distance From Lamp (inches)	$\lambda$ (nm)	Irradiance ( $\mu\text{W}/\text{cm}^2$ )	
A	6	 	0.004	
B	3		0.014	
C	3		0.008	
D	6		0.004	
E	6		0.006	
F	3		0.012	
G	3		0.020	
H	6		0.007	
I	6		0.002	
J	3		0.008	
K	3		0.004	
L	6		0.001	
Background*	-			0.058
Background**	-		<315	0.136
A	6	 	0.02	
B	3		0.05	
C	3		0.06	
D	6		0.03	
E	6		0.01	
F	3		0.03	
G	3		0.03	
H	6		0.01	
I	6		0.01	
J	3		0.02	
K	3		0.01	
L	6		0.00	
Background*	-			3.76
Background**	-		320-400	8.94

\* Detector 62 inches from a 4-tube fluorescent light fixture  
\*\* Detector 31 inches from a 4-tube fluorescent light fixture



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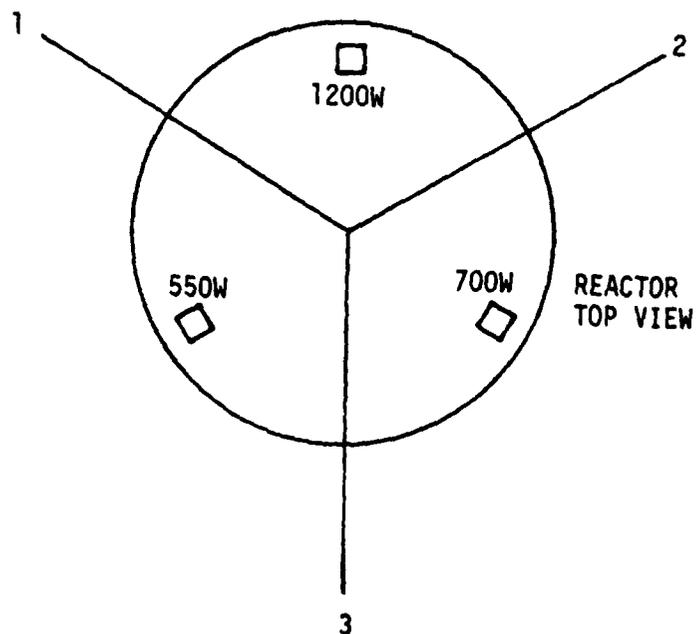
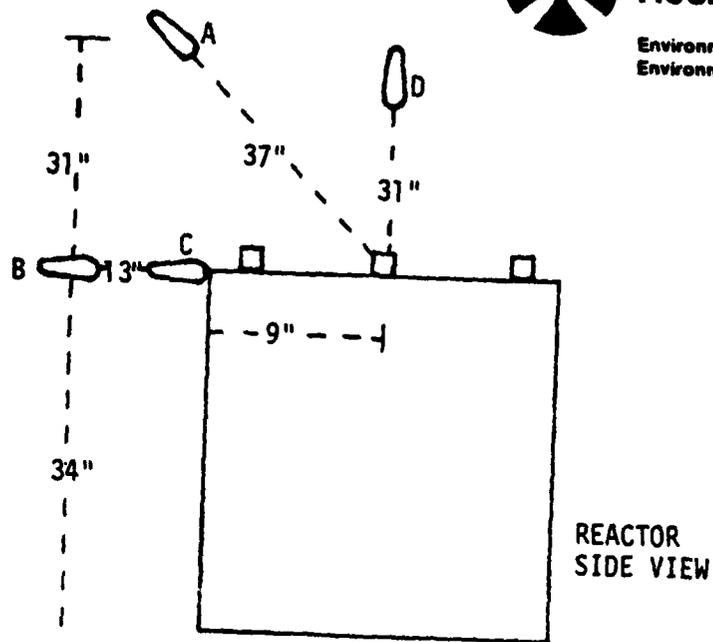


Figure 5-9. UV Exposure Measurement Positions, All Lamps On



(1, 2, and 3) around the vertical centerline of the reactor. A fourth measurement (D) was taken directly over the vertical centerline of the reactor. The values are presented in Table 5-17. These measurement positions were chosen because they are as close to the reactor as any operating personnel are likely to get. Position A, Fig. 5-9, is eye-level of a person 5 feet 9 inches tall, standing erect. Exposure at positions B and C would occur if the operator was bending down.

The greatest actinic exposure measured was 0.09 microwatts/cm<sup>2</sup> measured at position 2C, 9 inches from the reactor centerline with all of the lamps on. This is still below the protection standard of 0.1 microwatt/cm<sup>2</sup>. The greatest actinic exposure from any individual lamp was 0.020 microwatt/cm<sup>2</sup> measured at position G (Fig. 5-8).

The greatest near-UV leakage recorded was 0.06 microwatt/cm<sup>2</sup> at position C (Fig. 5-8) from the 1200-watt lamp. This is approximately 16,000 times below the maximum permissible exposure for periods exceeding 10<sup>3</sup> seconds, and corresponds to 0.06 mJ/cm<sup>2</sup> for a 10<sup>3</sup>-second exposure (w/cm<sup>2</sup> x seconds = J/cm<sup>2</sup>). This is also approximately 16,000 times below the maximum permissible exposure.

Based on these measurements, no shielding of the UV lamps was required to assure a safe system. It is interesting to note that UV exposure, both near and actinic, is higher from overhead fluorescent lamps than from the total oil removal system (Table 5-16). In fact, at 31 inches away from the fluorescent lamp fixture, the actinic UV exposure maximum is exceeded by 36%. Near-UV exposure at this distance is still 100 times below the maximum for the near-UV, however.



TABLE 5-17. ULTRAVIOLET EXPOSURE, ALL LAMPS ON

Measurement Location (Fig. 5-9)	Distance From Reactor Vertical Centerline (in.)	$\lambda$ (nm)	Irradiance ( $\mu\text{W}/\text{cm}^2$ )	
1A	37	<315	0.00	
1B	22		0.01	
1C	9		0.07	
2A	37		0.00	
2B	22		0.00	
2C	9		0.09	
3A	37		0.00	
3B	22		0.00	
3C	9		0.05	
D*	31		<315	0.01
1A	37		320-400	0.00
1B	22		0.01	
1C	9		0.03	
2A	37		0.01	
2B	22		0.01	
2C	9		0.03	
3A	37		0.00	
3B	22		0.01	
3C	9		0.02	
D*	31		320-400	0.02

\* Detector suspended directly above reactor vertical centerline



## 6.0 CONCLUSIONS AND RECOMMENDATIONS

This experimental program has provided basic information on the use of a new treatment process employing UV radiation and ozone to destroy the compounds prevalent in oily bilge and ballast wastewaters. The results of laboratory testing using reaction fluids consisting of pure compounds dissolved in water, artificial bilgewater mixtures prepared by mixing various oils with water, and bilgewater have led to the following conclusions:

1. Increasing UV dosage results in more efficient utilization of the ozone supplied to the reactor.
2. In many of the tests using pure compounds, the amount of ozone required for complete destruction was less than the stoichiometric quantity.
3. Stirring has a dramatic influence on reaction rate.
4. Salt had only a minimal effect on treatment.
5. Volatile compounds will be stripped from solution in addition to being destroyed by UV-ozone oxidation.
6. Generally, artificial bilgewater and bilgewater are more difficult to treat than the pure compounds dissolved in water.
7. If the goal of batch treatment is to minimize treatment time, the optimum UV dosage of those tested is 7.9 watts/L.
8. If the goal of batch treatment is to minimize the energy requirement, the optimum UV dosage depends on the fluid to be treated.
9. The optimum ozone dosage is that which transfers a maximum amount of ozone from the gas to the liquid phase, and is between 274 and 318 mg/min.
10. In the flowthrough treatment mode, a UV dosage of 7.9 watts/L will produce the shortest treatment time and, with some reaction fluids, the most energy-efficient treatment. Other fluids can be treated more energy-efficiently at a reduced UV dosage.



11. If low concentrations of pollutants are desired in the effluent, batch treatment can generally be more energy- and time-efficient than flowthrough treatment.
12. In a phenol-water solution and a DF2-water mixture, toxic substances possessing aromatic structure are rapidly converted to non-aromatic and generally less toxic compounds by UV-ozone treatment.
13. Treatment time and energy requirements can be greatly reduced if the conversion of toxic compounds to less toxic compounds is an acceptable end point to treatment.
14. The total oil removal system produces no ozone, noise, or UV emissions in excess of Army regulations.

The information generated during this experimental program allows additional conclusions to be drawn concerning the overall applicability of the UV-ozone treatment process to the treatment of oily bilge and ballast wastewaters.

Tests using the hardware assembled for this program have demonstrated that the combined effects of UV and ozone can indeed remove pollutants from a wide variety of solutions of pure compounds and oil-water mixtures, including bilgewater.

UV-ozone treatment produces a significantly improved oily wastewater effluent over that obtainable by currently employed treatment methods which do nothing to remove the dissolved oil component. The cost of treatment is attractive in light of alternative treatments.

For example, using the system without modification, the TOC in 1000 gallons of an artificial bilgewater solution of DF2-water could be reduced from 31 mg/L to 15 mg/L in 63.8 hours with an energy expenditure of 402 KWH, using maximum treatment levels in the batch mode. The generators on



board the FMS require approximately 0.08 gallon of DF2 to produce 1 KWH of energy. At an assumed diesel fuel cost of 75¢/gallon, the cost to generate 1 KWH of energy is 6¢. Therefore, the cost of treatment in this example would be about \$24.

With only slight modifications to the system, these costs could be significantly reduced. Approximately 61% of the power required by the system is used to produce the UV radiation. This could be dramatically reduced. For example, in order to achieve the 7.9 watts/L of UV radiation found to be optimum under some conditions, all three UV lamps were used. However, the lowest wattage UV lamp (550 watts) uses only 4.5% of the power it draws to produce UV energy. The intermediate sized lamp (700 watts) is 10.6% efficient, and the large lamp (1200 watts) is 25.4% efficient. By replacing the two smaller lamps with one 1200-watt lamp, the power required to produce the UV radiation would be reduced by 41%, and the overall power consumption would be reduced by 25%; this while increasing the effective UV dosage to 9.5 watts/L. Power requirements could be further reduced by substituting a catalytic ozone decomposer for the thermal unit currently used. These two measures would reduce overall power consumption by 34%. Costs would fall from \$24/1000 gallons in the above example to \$16/1000 gallons.

Additional savings in time and energy associated with treatment could be realized if relatively nontoxic compounds could be tolerated in the effluent. For example, again using DF2-water, if 25 mg/L of TOC could be tolerated in the effluent, a very small fraction of which is toxic, treatment becomes more time- and energy-efficient. Incorporating the savings provided by converting the three UV lamps to two 1200-watt UV lamps and replacing the thermal ozone decomposer with a catalytic unit, batch treatment of 1000 gallons of the DF2-water mixture would require 33.4 hours and 121 KWH. The cost would be \$7.26.

Reducing the concentration of pollutants in the reaction fluid would also lessen treatment time and costs. Oil-water mixtures such as bilge-water contain a wide variety of compounds, some of which are relatively



easy to oxidize, others difficult. Overall, the fluid is quite resistant to oxidation. By mandating consistent, standardized bilgewater handling procedures, the concentration of dissolved compounds could be minimized. The bilgewater would require less treatment and costs would be reduced.

There are many other measures which could lower the cost of treatment. A program should be undertaken with the goal of reducing the costs of UV-ozone treatment of oily bilge and ballast wastewaters. The investigation should:

1. Identify hardware components that are more energy-efficient than those used in the present system.
2. Use the data produced during this program in an engineering study of the effects of staging the UV-ozone treatment. As the oxidation reactions proceed, the optimum amount of UV radiation may change. By staging the process, treatment levels could be optimized for each stage and a net reduction in costs could result.
3. Investigate the effects of an oxygen feed to the ozone generator on treatment.
4. Investigate the effects of UV spectral intensity on treatment.

Based on the results, a decision could be made to retrofit the existing Army fleet to meet all forthcoming State and Federal watercraft discharge regulations.



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APPENDIX

OPERATION OF THE ON-BOARD  
OILY WASTEWATER TREATMENT SYSTEM

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## 1.0 PURPOSE

This instruction manual is intended to familiarize the operator with the oily wastewater treatment system. Section 2.0 provides brief background information on the development of the system and the principles employed to improve the quality of oily bilge wastewater prior to discharge. The third section describes the treatment system in detail and includes diagrams showing the gas and liquid plumbing configurations, and electrical systems. The next section addresses the actual operation of the system in its various modes, and includes stepwise instructions for each mode of operation.



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## 2.0 BACKGROUND

Over the last several years, the United States Army has recognized the need to minimize the discharge of oily wastewater from its sizeable fleet of watercraft and ships. To this end, the Army Mobility Equipment Research and Development Command contracted Rockwell International to design and test a system that employs a new technology for the treatment of oily wastewater. This treatment process, when combined with conventional, off-the-shelf treatment equipment, produces an effluent of significantly enhanced quality compared with past discharges.

All watercraft have bilge compartments, located between the lower deck plates and the hull, that collect the leaks which are inevitable on even the best-maintained vessels. Most of these are water leaks, and hence the term "bilgewater" is used to describe the contents of the bilge compartment. However, other materials also collect in the bilge compartment, including significant amounts of fuel oil, lubricating oil, and hydraulic oil. Therefore, "bilgewater" is more accurately described as oily wastewater, and discharge of this wastewater without treatment is undesirable because an oil sheen can result, which is strictly prohibited.

Conventional devices for reducing the amount of oil in the bilge discharge are available and many Army watercraft are equipped with such equipment. One type of device employs the principle of coalescence to remove the oil by passing the oily wastewater through one or more filters. These filters possess many circuitous routes through which the fluid passes. The droplets of oil in the oily wastewater tend to be retained on the external surface of the filter and as oil droplets accumulate, they form larger drops (i.e., coalesce) and eventually detach from the filters and float to the water surface where the oil is collected. These devices are effective in removing oil from water; however, oily wastewater also contains a variety of chemicals, some toxic, which are dissolved in the water, and such physical treatment methods do nothing to remove them.



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The oily wastewater treatment system is designed to remove and/or convert to less toxic compounds the undissolved and dissolved chemicals in oily wastewater. The system utilizes a conventional oil-water separation device (a coalescer) to remove the undissolved oily compounds. The next treatment step uses ozone (a gas at room temperature) which is a form of oxygen and ultraviolet light (which is invisible) in conjunction to treat the dissolved chemicals by oxidizing them. This process acts to change the complex dissolved chemicals to less complex and less toxic chemicals.



### 3.0 SYSTEM DESCRIPTION

The oily wastewater treatment system consists of three major subsystems: the gas feed subsystem, the bilgewater feed subsystem, and the electrical subsystem. The gas and bilgewater feeds come together in the oxyphotolysis reactor, the heart of the system, where the dissolved components of the bilgewater are treated. In addition to the major subsystems, two ancillary streams, one of cooling water and the other of nitrogen, are also required by certain system components. All of the equipment, with the exception of several manually operated valves and a manually operated electrical potentiometer, is operated under semi-automatic control from a centralized control box.

The following sections describe the function and the components contained in each subsystem and the ancillary streams. Diagrams of each are included.

#### 3.1 GAS FEED SUBSYSTEM

The gas feed subsystem consists of: (1) equipment to condition the compressed air supplied by the on-board compressors, (2) an ozone generator to convert some of the oxygen in the compressed air into ozone, (3) the oxyphotolysis reactor where the air-ozone gas stream is allowed to react with the bilgewater stream, (4) the ozone decomposition heater which destroys any unused ozone, (5) the cooling tube which lowers the temperature of the gas coming from the decomposition heater, and (6) the gas vent piping leading to the exterior of the ship.

Figure 3-1 shows the gas feed subsystem. As compressed air enters the subsystem (on the left-hand side of Fig. 3-1), its pressure is controlled by a pressure regulator. Flow is directed to the first of two filters, which removes small particulates from the gas stream. The second filter removes any entrained oil from the stream originating from the compressor. In the normal operation mode, the compressed air stream is directed to the air dryer (not bypassed) (i.e., BV1, BV2 open, BV3 closed), where excess moisture is removed before the gas enters the ozone generator through



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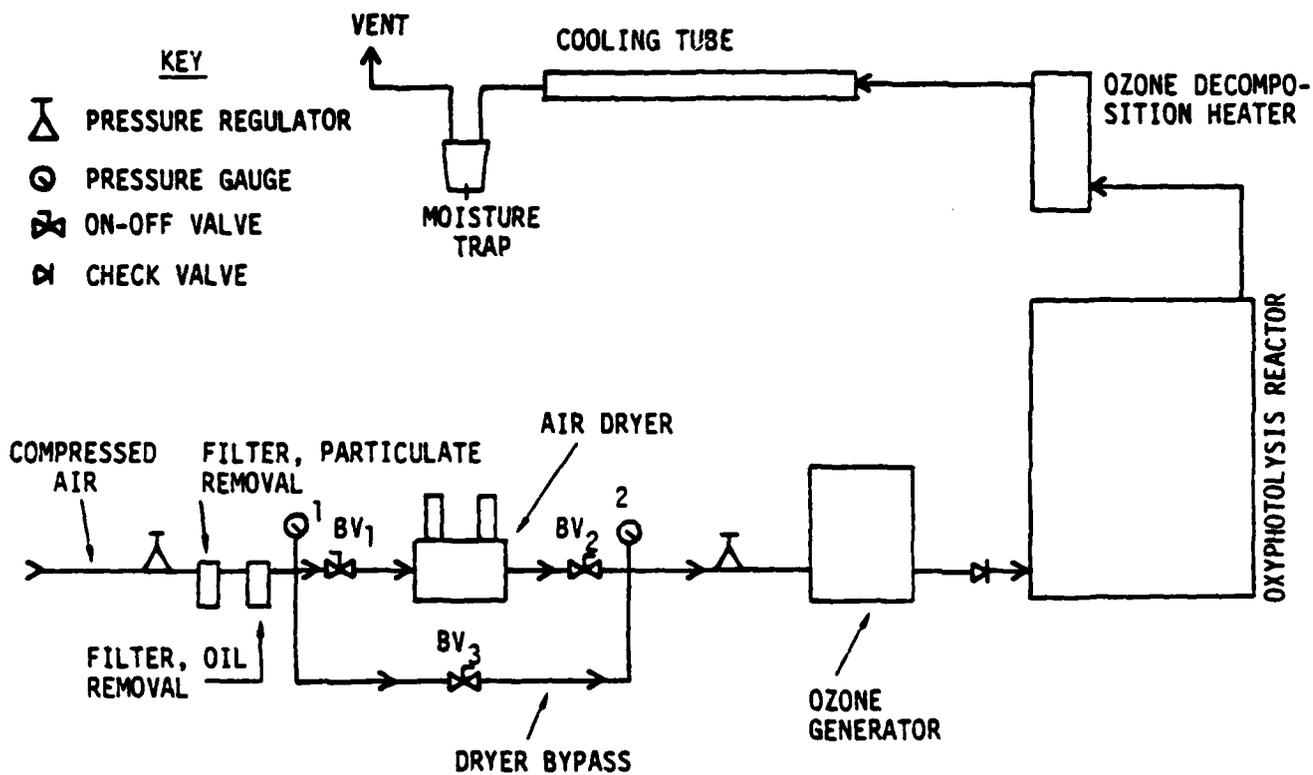


Figure 3-1. Gas Feed Subsystem



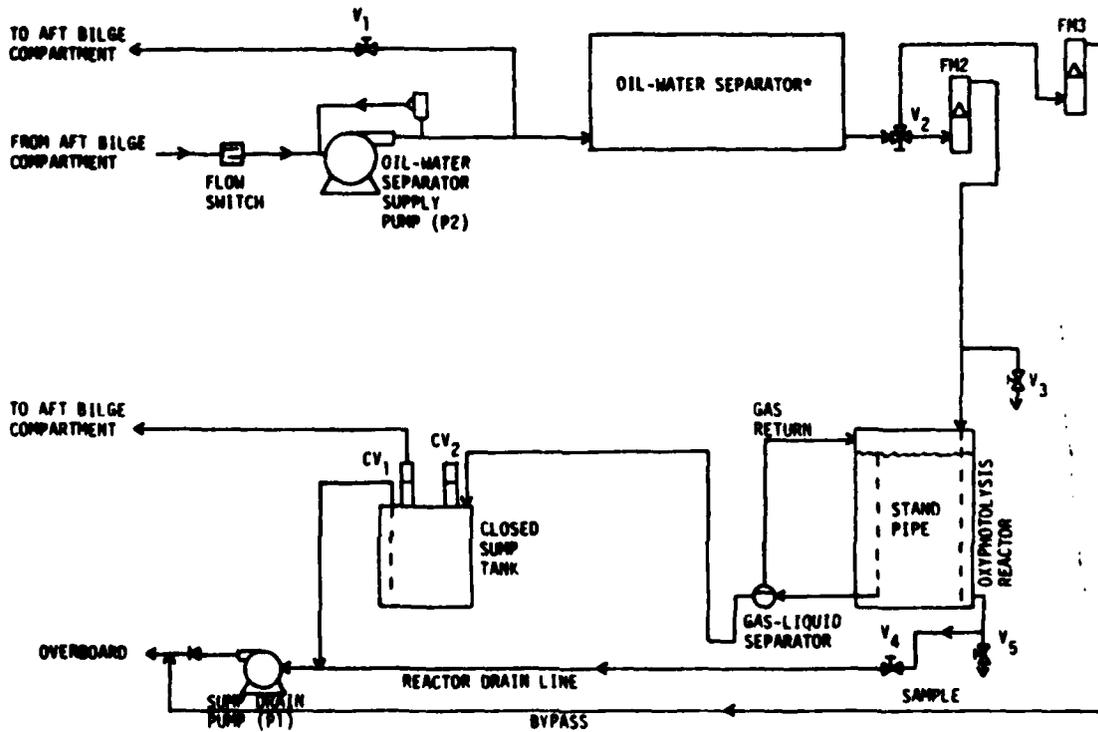
another pressure regulator. The exit gas stream from the ozone generator contains the reactive ozone-air mixture which proceeds to the oxyphotolysis reactor (through a check valve) where it is bubbled through the bilgewater. The offgas from the oxyphotolysis reactor, which still contains some ozone, is then routed to the ozone decomposition heater, which thermally decomposes any ozone that is present into oxygen. The hot exit gas from the heater is cooled in a cooling tube prior to venting to the exterior of the ship.

### 3.2 BILGEWATER FEED SUBSYSTEM

The bilgewater feed subsystem consists of (1) the plumbing to the oil-water separator supply pump, (2) the oil-water separator, (3) the plumbing between the oil-water separator and the oxyphotolysis reactor, (4) the closed sump tank and its drain pump and associated plumbing, and (5) the plumbing through which the treated bilgewater is discharged to the exterior of the vessel.

Figure 3-2 shows the bilgewater feed subsystem. Suction is taken from the aft bilge compartment by the oil-water separator supply pump (P2). The bilgewater proceeds to the oil-water separator. The flowrate can be varied by adjusting a valve ( $V_1$ ) on the bilge return line. After passing through the oil-water separator, the bilgewater flow can be routed either to the oxyphotolysis reactor or can be made to bypass the reactor to be discharged without any further treatment. This is accomplished with a three-way valve ( $V_2$ ). In either case, the bilgewater passes through one of two flowmeters (FM2 or FM3) so the flowrate can be monitored.

The liquid level in the reactor (the following discussion assumes the flow is directed to the reactor, not bypassed) is maintained by an internal standpipe, through which the overflow is routed to a gas-liquid separator. The liquid proceeds to a closed sump tank that is kept dry by the drain pump (P1). Pump discharge is to the same overboard line used for bypass discharge. If, for any reason, the sump overflows (e.g., failure of the drain pump and a safety override circuit -- discussed later) the excess liquid will be routed back to the aft bilge compartment after opening of



\* Valving associated with the oil-water separator is not shown in this generalized schematic.

Figure 3-2. Bilgewater Feed Subsystem



the low cracking pressure check valve (CV1). CV2 is for sump tank venting to allow makeup air for the sump drain pump.

Provisions also allow for the oxyphotolysis reactor to be drained by the simple turning of a valve ( $V_4$ ) which opens the reactor drain line to drain sump suction. Additionally, valve  $V_3$  allows sampling of fluid prior to treatment in the oxyphotolysis reactor, and valve  $V_5$  allows the treated fluid to be sampled.

### 3.3 ELECTRICAL SUBSYSTEM

Many of the components of the oily wastewater treatment system are electrically powered and control of their operation is semi-automatic. The electrical subsystem consists of the following components, all hard-wired to relays which are energized through a centralized control panel. Circuit breakers protect all of the circuitry.

1. UV lights
2. Ozone generator
3. Air dryer
4. Ozone decomposition heater
5. Stirring motor
6. Oil-water separator supply pump (P2)
7. Sump drain pump (P1)

The circuit-breaker panel contains eight circuit-breakers. Two of these are service disconnect breakers for the 120-volt and 230-volt power supplies. Dedicated circuit-breakers are provided for the ozone generator (120V), the 1200-watt UV lamp (230V), the stirring motor (230V), the oil-water separator supply pump (120V), the sump drain pump (230V), and one breaker is supplied for the 550-watt and 700-watt UV lamps, the ozone decomposition heater, and the air dryer (all 120V).

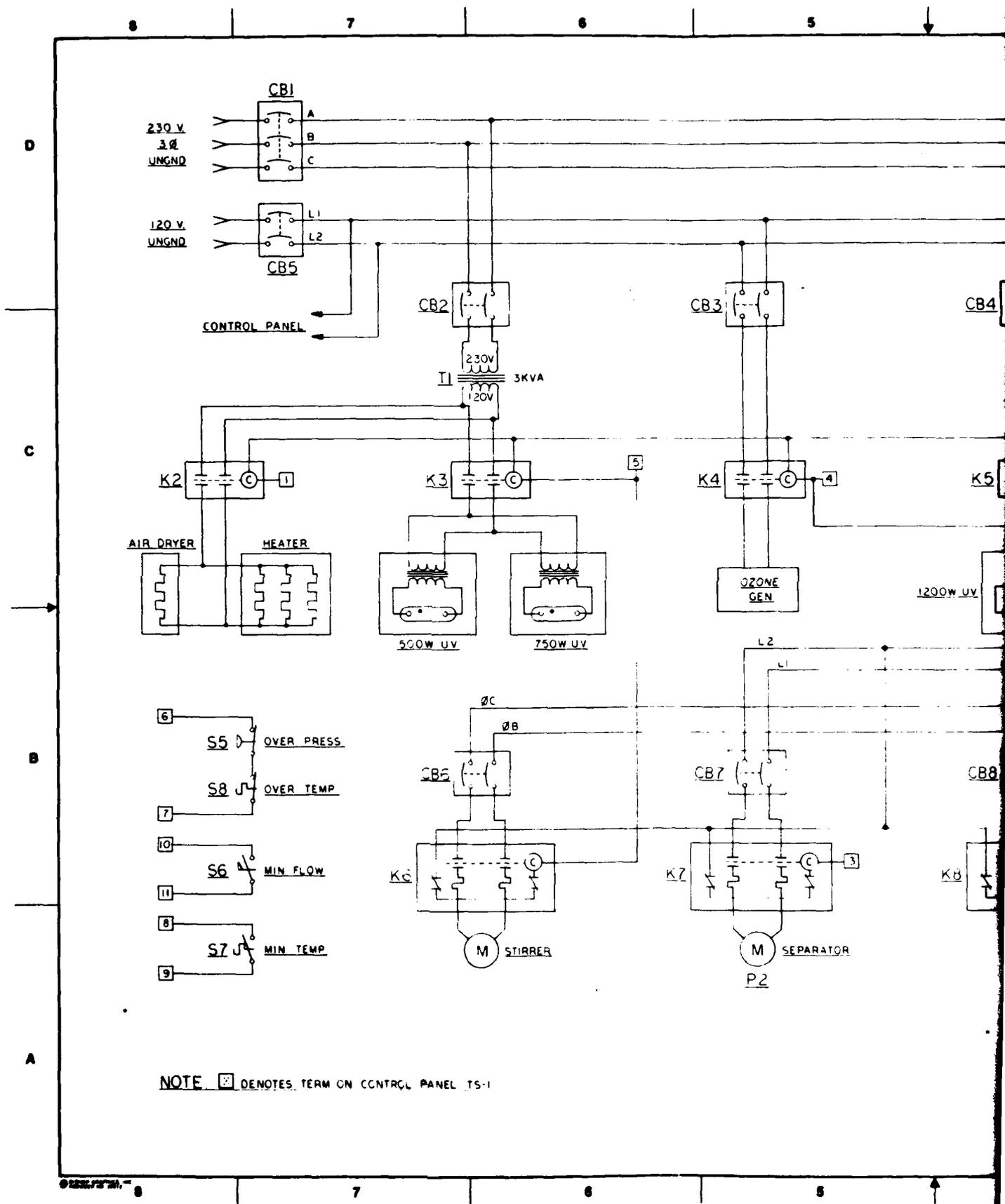


Power is routed through the circuit-breakers to seven contactors or relays. Three motor starter contactors (with overload protection) are housed in one box. These contactors provide power to the stirring motor, the oil-water separator pump motor, and the sump drain pump motor. The four remaining contactors are housed in another box. These control the power distribution to the ozone generator, the 1200-watt UV lamp, the 550-watt and 700-watt UV lamp together, and the ozone decomposition heater and air dryer together. Figure 3-3 is a schematic of the power wiring to the system. Table 3-1 lists the parts used for the power wiring.

The contactors are selectively energized under control of a panel that contains the control logic. Switches on the front panel initiate logic sequences that control the various pieces of equipment by energizing or de-energizing the proper contactors. Figure 3-4 shows the control panel with its various switches and lights. Figure 3-5 is a schematic of the control panel wiring. Table 3-1 lists the parts used in the control panel.

Also, several sensors are present (wired into the control panel circuitry) which continually monitor vital functions of the system and relay this information (in the form of switch closures or openings) to the control panel. These are:

<u>Sensor</u>	<u>Location</u>	<u>Function</u>	<u>Action</u>
Flow Switch	Oil-water separator pump suction line	Determine when bilge is dry (i.e., lack of flow)	Selectively shut down system
Thermoswitch 1	Inside ozone decomposition heater	Determine when acceptable temperature is reached in heater	Hold startup sequence until correct temperature, selectively shut down system
Thermoswitch 2	Inside ozone decomposition heater	Sense over-temperature condition in heater	Shut down entire system
Delta Pressure Switch	Attached to blind tube inside closed sump tank	Sense sump overflow condition	Shut down entire system



NOTE: □ DENOTES TERM ON CONTROL PANEL TS-1

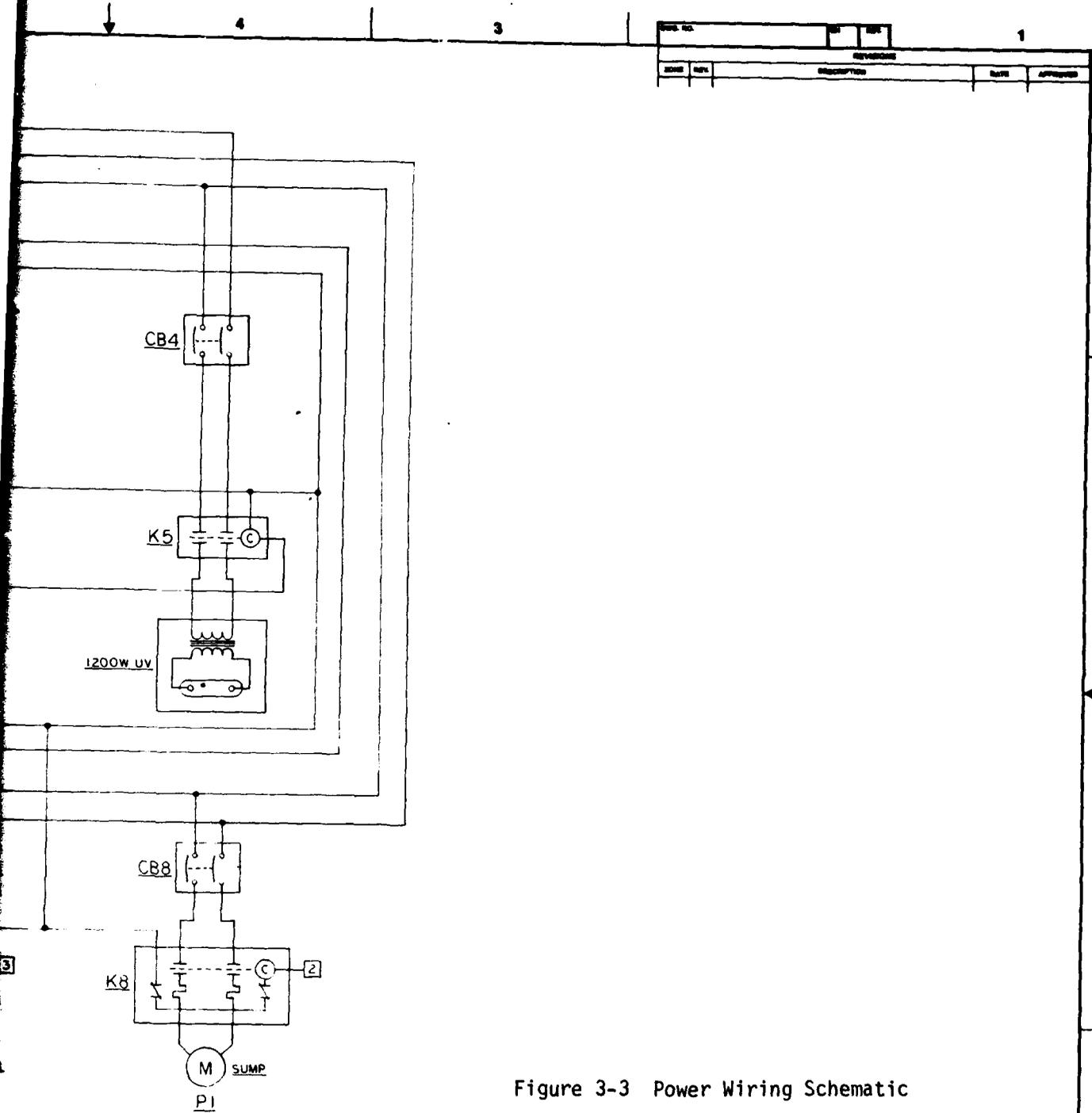


Figure 3-3 Power Wiring Schematic

SEE SHEET 3		CONTRACT NO.		DATE	
QTY	REQD	PART OR IDENTIFYING NO.	DESCRIPTION OF OPERATION		DELIVERY INSTRUCTIONS
PARTS LIST					
UNLESS OTHERWISE SPECIFIED TOLERANCES ARE FRACTIONS DECIMALS ANGLES DEG.			APPROVALS	DATE	<b>WIRING - POWER</b> <b>OILY WASTEWATER TREATMENT SYSTEM</b>
MATERIAL			DRAWN <i>F. HOWARD</i>	10 3 50	
FINISH			CHECKED <i>S. C. GIBSON</i>	10 8 50	
RELT ARRY	USG C		ISSUED		SHEET NO. <b>D</b>
APPLICATION	DO NOT SCALE DRAWING		SCALE		SHEET NO. 1

2



TABLE 3-1. PARTS LIST - TOTAL OIL REMOVAL SYSTEM - ELECTRICAL

<u>Reference Designation</u>	<u>Type No.</u>	<u>Description</u>	<u>Source</u>
550 W UV	673A	Ultraviolet UV lamp	Hanovia
700 W UV	674A	Ultraviolet UV lamp	Hanovia
1200 W UV	189A	Ultraviolet UV lamp	Hanovia
Ozone Generator	SG4060	1 lb/day ozone gen.	Union Carbide
Air Dryer	HF200-106-17	Compressed air dryer	Puregas
Heater	--	750 W ozone decomposition heater	Gaumer
Stirrer	C56E2590T-VB	1/2 HP motor	Reliance Electric
Separator	--	1/2 HP motor for pump	Dayton
Sump	77UAL	1/3 HP motor for pump	Gelber
AL1	273-051	Alarm buzzer - 12V	Archer
BR1	276-1146	Rectifier, bridge 4A, 50V	Archer
C1-C6, C9, C10, C13, C19		Capacitor, ceramic .001 $\mu$ f, 50V	
C7, C11, C14, C17		Capacitor, ceramic .01 $\mu$ f, 50V	
C8, C12, C15		Capacitor, tantalum 15 $\mu$ f, 15V	
C16		Capacitor, ceramic .005 $\mu$ f, 50V	
C18		Capacitor, electrolytic - 1 $\mu$ f, 15V	
C20		Capacitor, electrolytic - 2000 $\mu$ f, 30V	
C21-C32		Capacitor, ceramic .05 $\mu$ f, 25V	
CB1		Circuit breaker 3 pole, 60A	Murry, ITT
CB2-CB4		Circuit breaker 2 pole, 15A	Murry, ITT
CB5		Circuit breaker 2 pole, 50A	Murry, ITT
CB6-CB8		Circuit breaker 2 pole, 20A	Murry, ITT



TABLE 3-1 (Continued)

<u>Reference Designation</u>	<u>Type No.</u>	<u>Description</u>	<u>Source</u>
D1-D4, D10	1N4002	Diode, rectifier 1A, 100V	
D5-D9	1N914C	Diode, signal - silicon	
DS1-DS5	272-706	Lamp assy, neon	Archer
K1, K9-K11	275-206	Relay, DPDT - 12 VDC	Archer
K2-K5	SC0-1	Magnetic contactor 120V coil	Square D Co.
K6-K8	SBO-2	Magnetic contactor 120V coil	Square D Co.
Q1-Q4	MPS-A14	Transistor, NPN, silicon	Motorola
Q5	2N2222	Transistor, NPN, silicon	T.I.
Q6	MPS-A64	Transistor, PNP, silicon	Motorola
R1		Resistor, 680 ohm, 1/4 W, 5%	
R2, R5, R7, R9, R36		Resistor, 1000 ohm, 1/4 W, 5%	
R3, R33		Resistor, 10K ohm, 1/4 W, 5%	
R4, R6, R8, R10, R13, R14-R16, R19, R22, R24, R28, R32		Resistor, 33K ohm, 1/4 W, 5%	
R11		Resistor, 1800 ohm, 1/4 W, 5%	
R12		Resistor, 3000 ohm, 1/4 W, 5%	
R17, R31		Resistor, 22K ohm, 1/4 W, 5%	
R18		Resistor, 3300 ohm, 1/4 W, 5%	
R20, R23, R26		Resistor, 8.2M ohm, 1/4 W, 5%	
R21		Resistor, 56K ohm, 1/4 W, 5%	



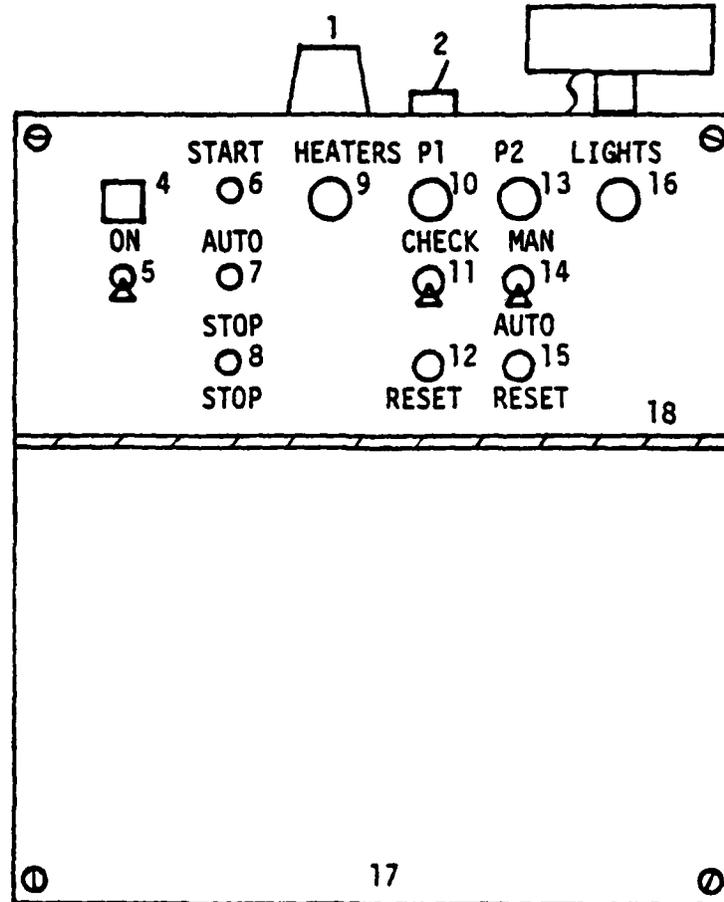
TABLE 3-1 (Continued)

<u>Reference Designation</u>	<u>Type No.</u>	<u>Description</u>	<u>Source</u>
R25		Resistor, 4.7M ohm, 1/4 W, 5%	
R27	271-229	Resistor, variable 1M, 1/4W	Archer
R29		Resistor, 200K, 1/4W, 5%	
R30		Resistor, 680K, 1/4W, 5%	
R34		Resistor, 1M, 1/4W, 5%	
R35		Resistor, 4700 ohm, 1/4W, 5%	
RV1	MOV750	Surge suppressor	GE
S1,S2,S4,S5, S6	275-1547	Switch, PB, SPST, NO	Archer
S3	275-1548	Switch, PB, SPST, NC	Archer
S7	275-614	Switch, toggle, DPDT	Archer
S9	275-701	Switch, toggle, SPST	Archer
T1		Transformer - 120/ 230V, 3 KVA	
T2	273-1514	Transformer - 18V @ 4.0 A	Archer
U1, U3	CD4044	I.C. - quad R-S latch	
U2,U4,U5,U9	CD4001	I.C. - quad NOR gate	
U6,U7	LM556	I.C. - dual timer	
U8	74C04	I.C. - hex inverter	
U10	CD4017	I.C. - decade counter	
U11	LM7812	I.C. - regulator, 12V	



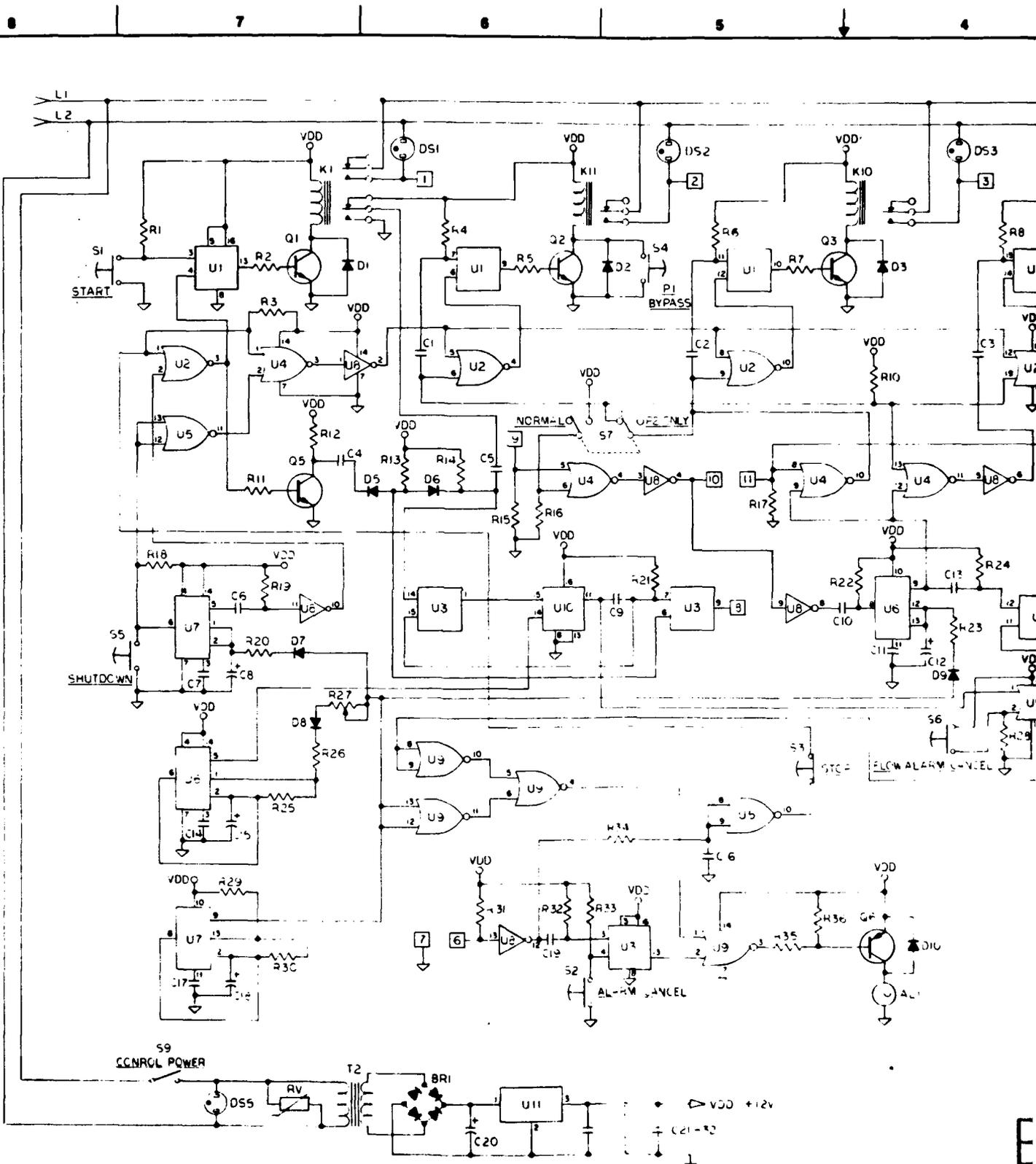
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- 1 Visual alarm
- 2 Visual - audible alarm selector toggle switch
- 3 Audible alarm
- 4 Power-on indicator light
- 5 Power on-off toggle switch
- 6 Auto start pushbutton
- 7 Auto stop pushbutton
- 8 Emergency stop pushbutton
- 9 Heaters enunciator light
- 10 P1 (sump) enunciator light
- 11 P1 on-off toggle switch
- 12 Alarm reset pushbutton (constant alarm)
- 13 P2 (oil-water separator) enunciator light
- 14 Manual-automatic operation mode selector toggle switch
- 15 Alarm reset pushbutton (intermittent alarm)
- 16 Lights, ozone generator, stirrer enunciator light
- 17 Electronics access panel
- 18 Switches - lights access panel

Figure 3-4. System Control Panel



NOTE: □ DENOTES TERM ON TEL.





An intermittent audible or visual (selectable) alarm is activated when the flow switch or thermoswtich 1 detect faults in the system. A continuous audible or visual (selectable) alarm is activated when either thermo-switch 2 or the delta pressure switch detect faults.

Three operating modes are provided (initiated at the control panel): normal operation, bypass operation, and reactor drain. The system components operated during these modes are as follows:

<u>Mode</u>	<u>Component</u>
Normal	All components
Bypass	Oil-water separator supply pump only (P2)
Reactor Drain	Sump drain pump only (P1)

During the normal operation mode, a start pushbutton is provided which, when activated, brings the components and sensors on line in a predetermined sequence. If the operator wishes to suspend treatment, an auto stop pushbutton will shut down the system in the proper sequence. Some operator interaction is required.

Switches are also provided for both the bypass and reactor drain operation modes.

In all operating modes, total shutdown can be achieved by activating a stop button and following several shutdown steps.

A series of enunciator lights are provided on the control panel face which show the operator which system components are receiving power (see Fig. 3-4).



### 3.4 ANCILLARY GAS AND LIQUID STREAMS

#### 3.4.1 Nitrogen Stream

The ultraviolet lamps used in the oily wastewater treatment system emit ultraviolet energy in wavelengths that could cause oxygen to be converted to unwanted ozone. To prevent this occurrence, the space between the lamps and their quartz sheaths (which is continuous with the shipboard atmosphere) is purged with harmless nitrogen. Figure 3-6 shows this nitrogen gas feed system.

The nitrogen is provided in compressed form from a gas bottle. The high-pressure nitrogen from the gas bottle is reduced in pressure with a pressure regulator and flow is controlled with a small valve located in the body of the flowmeter. From the flowmeter, the nitrogen is routed to the three UV lamps and is vented through the top of each lamp ballast.

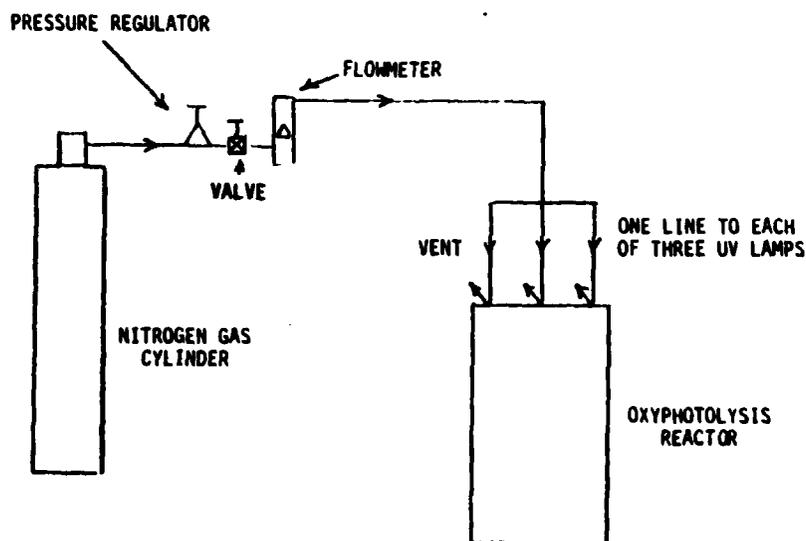


Figure 3-6. Nitrogen Stream



### 3.4.2 Cooling Water Stream

Two components of the oily wastewater treatment system require water to remove excess heat. These are the agitator bearing and seal located on top of the oxyphotolysis reactor, and the cooling tube through which the offgas flows prior to venting to the exterior of the ship (see Section 3.1). Figure 3-7 shows the cooling water feed system.

Water from the shipboard supply is controlled with a small valve located in the body of the flowmeter (FM1). The water is directed first to the cooling tube where it is used to cool the offgas from the oxyphotolysis reactor and then to the agitator bearing and seal assembly. The water from this assembly exits through a valve and into the closed sump tank and is discharged overboard along with the treated bilgewater (see Fig. 3-2) by the drain pump.

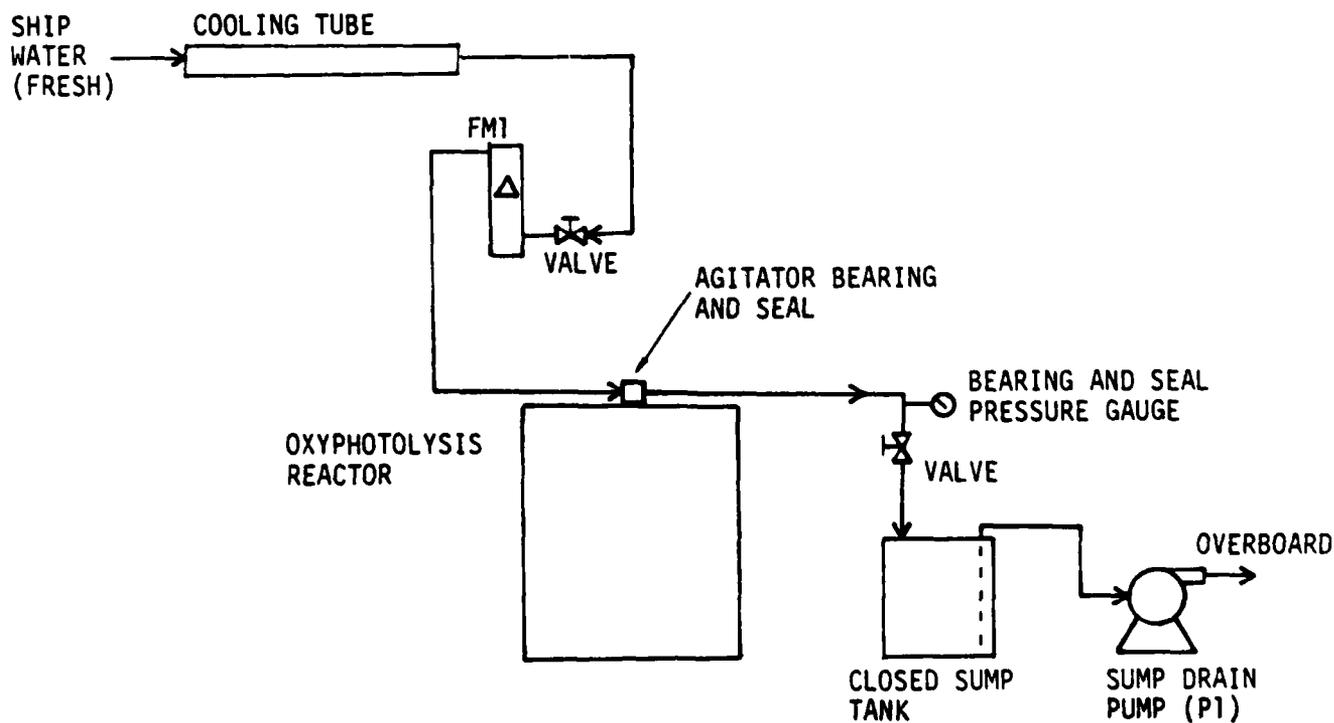


Figure 3-7. Cooling Water Stream



## 4.0 SYSTEM OPERATION

In each of the three operating modes of the oily wastewater treatment system -- normal, bypass, and reactor drain, a certain degree of operator interaction is required. The following sections describe the proper sequence of actions required by the operator to achieve successful operation of the system in each mode.

### 4.1 NORMAL OPERATION

#### CAUTION

Prior to startup, confirm that the oxy-photolysis reactor contains fluid to the standpipe level.

#### CAUTION

If an emergency arises during the following startup sequence, immediate system shutdown can be achieved by depressing the stop button (#8, Fig. 3-4) on the control panel.

The following steps must be performed in the sequence outlined below in order to start up the system in its normal operating mode:

<u>Step</u>	<u>Required Action</u>
1	Circuit breakers on and pressure control (regulator) on face of ozone generator fully counterclockwise (CCW)
2	Pressure regulator upstream of dryer fully CCW, BV1, BV2, BV3 closed (Fig. 3-1)



- | <u>Step</u>  | <u>Required Action</u>  |
|--|---|
| 3  | Adjust valves as follows (Fig. 3-2):<br>V <sub>2</sub> flow to oxyphotolysis reactor<br>V <sub>3</sub> closed<br>V <sub>4</sub> closed<br>V <sub>5</sub> closed   |
| 4  | Place switch #5 in ON position, observe illumination of light #4 (Fig. 3-4), power-on light   |
| 5  | Place switch #14 in auto position, push button 6, the start button (Fig. 3-4). This energizes the ozone decomposition heater and air dryer. Observe illumination of "Heaters" enunciator light on control panel (#9).   |
| 6  | Adjust pressure control (regulator) upstream of air dryer (Fig. 3-1) so that pressure gauge 1 registers between 40 and 60 lbs/sq.in.  |
| 7  | Slowly open BV1 and then BV2.   |
| 8  | Open the ozone flow control valve on face of ozone generator slightly and open pressure regulator (same location) so that a flow of 50 SCFM (read on flowmeter on front face of ozone generator) and a pressure of 12 psig (gauge on front face of ozone generator) are achieved. |
| <p>A 30-minute period will elapse to allow the ozone decomposition heater to come up to temperature and the compressed air to dry sufficiently. After 30 minutes, thermostwitch 1 must close before the auto startup sequence will continue. Upon closure of thermostwitch 1 and 30 minutes elapsed time, the oil-water separator pump and sump drain pump will be energized, indicated by illumination of the "P1" and "P2" enunciator lights on the control panel. When these lights come on, proceed with step 9.</p> |   |
| 9  | Adjust V <sub>1</sub> to achieve desired flowrate (0.25-0.75 gpm) on FM2 (Fig. 3-2).  |
| 10   | Adjust cooling water to 0.25 gpm and 20 psig as indicated on FM1 and the bearing and seal pressure gauge (PG1) (Fig. 3-7), respectively.  |



<u>Step</u>	<u>Required Action</u>
11	Turn on nitrogen and adjust flow to 120 cc/hr (Fig. 3-6).

Five minutes will elapse before the UV lamps, the ozone generator, and the stirring motor will be energized. However, the flow switch must be closed (i.e., bilgewater flow through the system) prior to the startup sequence proceeding after the 5-minute delay. After closure of the flow switch and the 5-minute delay, the remaining equipment will be energized, indicated by the illumination of the "lamps" enunciator light on the control panel. When this light comes on, proceed to step 12.

<u>Step</u>	<u>Required Action</u>
12	Adjust the power control potentiometer on the ozone generator front panel to the desired level (do not exceed 400 watts).

The system is fully operational at this point.

#### CAUTION

Ozone is now being generated. An ozone monitor must be used to detect ozone leakage during operation in this mode.

If, during operation, the alarm is activated, this indicates that one of the safety sensors has detected a system fault. Turn off the flow of cooling water immediately and place the power control on the ozone generator to its 0 setting. If the alarm is intermittent, this indicates that either flow has stopped (flowswitch) or that the ozone decomposition heater has dropped below minimum temperature for maximal ozone destruction (thermoswitch 1). If this occurs, power to the pumps, lamps, stirring motor, and the ozone generator will be cut off and the "P1," "P2," and "Lamps" enunciator lights on the control panel will be extinguished. However, power to the ozone decomposition heater and the air dryer will remain, indicated by



the continued illumination of the "heaters" enunciator light on the control panel. Therefore, caution should be exercised when troubleshooting the ozone decomposition heater. If the problem with the flow or heater temperature can be rectified, the operator need only depress the start button (button 6, Fig. 3-4) on the control panel to reinitiate the automatic start-up sequence and proceed from step 10. Reset button #15 (Fig. 3-4) will turn off the alarm. The 30-minute time delay will not be in effect; however, thermoswitch 1 must be closed in order for sequencing to proceed.

If, during operation, the alarm is activated in a continuous manner, this indicates that either the delta pressure switch or thermoswitch 2 have been activated. If this happens, power to all of the system components will be terminated, indicated by all of the enunciator lights being extinguished. The problem must be rectified before the system will restart. Depressing the reset button #12 (Fig. 3-4) will turn off the alarm. Restart must proceed from step #1.

The following steps must be performed in the sequence outlined below to automatically shut down the system in its normal operating mode:

<u>Step</u>	<u>Required Action</u>
1	Depress auto stop button (#7, Fig. 3-4). Turn off cooling water and nitrogen.

Power will be terminated to all components but the ozone decomposition heater and the air dryer, so that ozone can be purged from the system. These components will remain on for 5 minutes. Once these two components are also de-energized (indicated by extinguishment of the "heaters" enunciator light #9, Fig. 3-4), proceed with the shutdown sequence:

- |   |   |
|---|---|
| 2 | Turn the power control potentiometer on the front panel of the ozone generator to 0. Turn fully CCW the pressure regulator on the same front panel. Turn fully clockwise the ozone control valve. |
| 3 | Close BV1 and BV2, turn fully CCW the pressure regulator upstream of the air dryer (Fig. 3-1).  |



<u>Step</u>	<u>Required Action</u>
4	Place switch #5 in off position, observe extinguishment of power-on light (#4, Fig. 3-4) on control panel.

#### 4.2 BYPASS OPERATION

At times, it may be desirable to utilize only the oil-water separator for bilgewater treatment. This can be accomplished by operating in the bypass mode. The following steps performed in proper sequence by the operator will result in bypass operation:

<u>Step</u>	<u>Required Action</u>
1	Adjust valves as follows (Fig. 3-2): $V_1$ fully closed $V_2$ flow to bypass line
2	Place switch #5 in ON position, observe illumination of light #4 (Fig. 3-4), power-on light.
3	Place switch 14 in the manual position and observe illumination of "P2" enunciator light on control panel (Fig. 3-4).

The system will now operate in the bypass mode. As in the normal operating mode, the operator is allowed 5 minutes to establish bilgewater flow through the system. If after 5 minutes flow is not established or flow is terminated after 5 minutes, then power to the oil-water separator supply pump will be terminated, and the intermittent alarm activated.

In order to terminate bypass operation, simply depress the stop button (#8) on the control panel (Fig. 3-4).



### 4.3 REACTOR DRAIN OPERATION

Should draining of the oxyphotolysis reactor become necessary (for maintenance), operation in the reactor drain mode is required. The following steps will drain the reactor:

<u>Step</u>	<u>Required Action</u>
1	Open valve $V_4$ (Fig. 3-2).
2	Place switch #5 in ON position, observe illumination of light #4 (Fig. 3-4), power-on light.
3	Place switch #11 in CHECK position and observe illumination of "P1" enunciator light (Fig. 3-4).

Approximately 10 minutes are required to completely drain the reactor. At the end of this time, turn switches #11 and #5 to the OFF position (Fig. 3-4) and close valve  $V_4$  (Fig. 3-2).