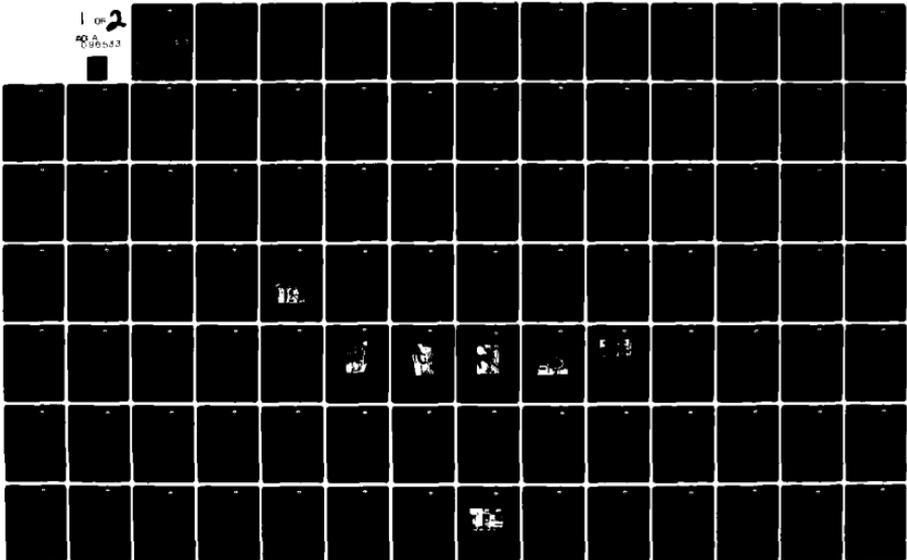


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Report EMSC8314.1FR

Contract No. DAAK70-78-C-0075

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TECHNICAL ASSISTANCE: MASS SPECTROMETER OIL MONITORING SYSTEM

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SUMMARY

This final report describes the results from two separate field studies. Part I describes the effectiveness of state-of-the-art on-board oil-water separation equipment. Part II describes the effectiveness of the on-board Experimental Oily Wastewater Separation System.

PART I

Samples of untreated bilgewater and treated bilgewater processed through off-the-shelf oil-water separators (coalescers) were collected from 10 different Army watercraft including large ships, landing craft, tugs, and barges. The samples were analyzed for suspended and dissolved pollutants.

The following conclusions were reached based on the results from the testing of on-board oil-water separators.

- Generally, the larger ships show a lower concentration of suspended pollutants in their bilgewater influents to their oil-water separators than the smaller vessels. This could be due to greater ease of maintenance on the larger ships and to the fact that the volume of water in the bilge compartments in the larger ships is much greater than in the small watercraft, and therefore any fuel or lube oil leaks fall into a much larger volume of bilgewater and are diluted to a greater extent.
- The low concentration of suspended pollutants in the influents to the oil-water separators on the large ships does not appear to result in enhanced performance of the oil-water separators.
- The on-board oil-water separators were effective in reducing suspended pollutant levels in bilgewater. On the average, 77.8% of the suspended pollutants were removed by the process.



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- There exists a wide disparity in the performance of the oil-water separators from watercraft to watercraft.
- Several of the watercraft showed signs of bilgewater contamination by nonpetroleum fluids.
- Several of the watercraft possessed high dissolved pollutant concentrations in their bilgewater, indicative of prolonged oil-water contact.
- On the average, the large ships had a higher quality influent and effluent, in terms of total pollutants, than any other vessel class. The LCUs had the highest influent total pollutant concentrations, while the crane barge had the highest effluent total pollutant concentration.
- Few volatile compounds were found in the bilgewater samples.

The exemplary performance of several of the on-board oil-water separators in removing suspended pollutants from bilgewater proves that these devices can be effective in producing a bilgewater effluent that meets current regulations. The large disparity in performance of the on-board oil-water separators from vessel to vessel suggests that the problem lies with procedural variations between watercraft or because of faulty oil-water separator elements. It is believed that by cataloging the procedures used on board vessels with oil-water separators and correlating these with the performance of their systems, those procedures that interfere with optimum performance can be identified. Once these faulty procedures are identified, they can be modified and the proper procedures standardized so that all of the on-board oil-water separator systems can be made to perform as some now do. Additionally, to assure the quality of oil-water separator elements, test hardware and procedures should be developed that will allow the Army to formulate a qualified products list.



PART II

Field tests were conducted on board a floating machine shop (FMS) using experimental hardware employing a conventional oil-water separator as a first stage to remove suspended pollutants, and a reactor as the second stage where ozone in the presence of ultraviolet radiation is used to oxidize the dissolved pollutants.

The on-board testing of the experimental system has led to the following conclusions:

- The system is capable of removing a high percentage of suspended pollutants from bilgewater.
- The UV-ozone process participates in the removal of suspended pollutants.
- The UV-ozone process produced a significantly cleaner bilgewater effluent than oil-water separation alone.
- The UV-ozone process is capable of removing dissolved pollutants, in the form of TOC, from bilgewater.
- The UV-ozone process is effective in destroying dissolved aromatic compounds in bilgewater.
- The Experimental Oily Wastewater Separation System is a safe system. It produces no noise, ozone, or UV radiation in excess of the maximum promulgated in military standards.
- The energy consumption costs associated with this treatment process could be reduced with minor equipment modifications.



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Oil-water separation and UV-ozone appears to be a viable process for the treatment of oily bilgewater. Components and designs with greater energy efficiencies could significantly reduce treatment costs. Additionally, procedures for minimizing the contamination of bilgewater would greatly increase the throughput for such a system. A program is recommended that would lead to an operational total pollutant removal system for treatment of the bilgewater of Army watercraft.



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PREFACE

The amended Federal Water Pollution Control Act directed the administrator of the Environmental Protection Agency (EPA) to establish regulations addressing the discharge of bilge and ballast water from ships. As a result, the EPA issued Regulations on Discharge of Oil (40CFR110; 25 November 1971), wherein Section 110.3 states that no discharge shall take place which:

- a) Violates applicable water quality standards
- b) Causes a film or sheen upon or discoloration of the surface of the water or adjoining shoreline or causes a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.

The United States Army has investigated a number of oily wastewater treatment technologies with the goal of bringing its sizable flotilla of watercraft into compliance with the federal discharge standards. One such technology, the separation of oily wastewater into discrete oil and water phases using the principle of coalescence, was employed in a shore-based bilgewater treatment facility. The effectiveness of this facility has been investigated and reported (Refs. 1, 2).

In the past several years, selected Army watercraft have been fitted with on-board bilgewater treatment systems also employing the principle of coalescence. The effectiveness of these on-board units is the subject of Part I of this report.

In addition to restricting the discharge of free or undissolved oil into receiving waters, the federal Regulations on Discharge of Oil (Section 101) states that:

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

Therefore, in the future, soluble pollutants present in bilge and ballast water must be removed, along with free or undissolved oil.



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With an eye toward the 1985 zero pollutant discharge standard, the Army funded the design, construction, and testing of an experimental oily wastewater treatment system employing the new technology of ultraviolet (UV) enhanced oxidation using ozone. The system uses an off-the-shelf oil-water separator (coalescer) for removal of the free or undissolved oil from the oily wastewater, and ozone in the presence of UV radiation to oxidize the pollutants dissolved in the water phase of the wastewater.

The design, construction, and laboratory testing of this system was funded under Army Contract DAAG53-75-C-0271, and described in the final report entitled "Experimental Oily Wastewater Separation System." Contract DAAG53-75-C-0271 also provided for the installation of the system on board an Army watercraft for testing its effectiveness in the field. The field testing of the unit was funded under the present contract and the results of the testing is the subject of Part II of this report.



1.0 PART I

EFFECTIVENESS OF STATE-OF-THE-ART ON-BOARD

OIL-WATER SEPARATION EQUIPMENT

1.1 INTRODUCTION

The U.S. Army fabricated a shore-based centralized bilgewater treatment facility on a floating barge. This treatment facility was designed to accept and treat the oily bilge wastewater from the sizable flotilla of Army watercraft based at the Third Port at Fort Eustis, VA.

The facility consisted of four pontoon sections welded to the barge deck, three of which were interconnected by pipe and acted as holding tanks, and the fourth as an oil storage tank. A 100-gpm oil-water separation device employing the filter-coalescence principle was the heart of the facility.

The oily bilge wastewater was pumped from the watercraft to the three holding tanks, where some gravity separation of the oil-water phases took place, and then to the oil-water separator for final treatment. The water-free oil was stored in a dedicated pontoon for ultimate transfer to the post steam plant, where it was used to fire the boilers. The treated bilgewater was discharged to the James River estuary.

The effectiveness of this centralized bilgewater treatment facility was the subject of a study conducted during the Spring and Winter of 1976, and the results of the study were published (Refs. 1, 2).

The primary limitation of centralized bilgewater treatment is that the ship's engineer cannot discharge his watercraft's bilgewater at leisure, but rather must wait to do so until he has access to the centralized treatment facility. Thus, the mobility of the ship is restricted, particularly when the bilges are full. For this reason, the Army chose to install oil-water separators on many of its watercraft, which allows the craft to be unencumbered by the shore-based discharge requirement.



The effectiveness of these on-board oil-water separators is the subject of Part I of this report. The following section describes the objectives of this effectiveness study (Section 1.2); Section 1.3 is a description of the coalescer device and the watercraft on which the devices were installed; Section 1.4 describes the methods used during the effectiveness evaluation; the results and a discussion are presented in Sections 1.5 and 1.6, respectively; Section 1.7 contains the conclusions resulting from this study; and Section 1.8 contains recommendations for improving the performance of the units and for future work.

1.2 OBJECTIVES

The primary objective of this study was to determine the effectiveness of on-board oil-water separators in removing free or undissolved oil from bilgewater under actual field use conditions. This included not only taking bilgewater samples before and after treatment and analyzing for pollutants, but also observing bilgewater handling procedures on the various watercraft and correlating these with the effectiveness of the on-board treatment units.

Additionally, the dissolved components of the bilgewater were analyzed with an eye toward the 1985 zero discharge standard. Such information will be useful for designing second-generation pollution control equipment, such as that described in Part II of this report.

1.3 EQUIPMENT DESCRIPTION

1.3.1 Coalescer

The oil-water separators installed on board selected Army watercraft are based on the principle of coalescence to remove free or undissolved oil from oily bilgewater. This involves the process whereby small oil droplets suspended in the water phase combine or coalesce into larger drops which readily separate from the water phase due to density differences. The



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coalescing action occurs as the bilgewater flows from the inside to the outside of a coalescer filter cartridge. Small oil droplets accumulate on the outside filter surface. As more fluid is processed, the drops grow in size (coalesce) until they are forced off of the filter surface by the fluid flow. The detached oil drops rise and accumulate at the top of the filter housing, and form an oil layer that can then be collected.

While some variation existed between the oil-water separator hardware installed on board the watercraft, the following description applies to the majority of the units tested. Three separate pressure vessels are plumbed in series; the first vessel contains a prefilter and the other two vessels contain coalescer filters. The prefilter protects the following two coalescer filters by removing particulate material and air from the bilgewater process fluid. Primary oil-water separation also occurs in the prefilter stage. As the prefilter stage fills with fluid, air is discharged through an air elimination valve located on top of the prefilter stage. The particulate-free bilgewater exits the prefilter stage and enters the second stage, which removes any oil that may not have been removed by the prefilter stage. The oil collected at the top of this stage and the prefilter stage is automatically discharged to a waste oil storage tank when a capacitance-type level detector probe senses the accumulated oil and electronically signals the simultaneous opening of a solenoid-operated oil discharge valve and closing of the main water discharge valve. The water discharge valve is closed during the oil discharge operation to provide the water pressure necessary to drive the oil into the waste oil storage tank. The valves remain in this position until the capacitance probe is uncovered, which then causes the valves to switch to their normal positions.

Effluent leaves the second stage and enters the bottom of the third and final stage. The third stage is identical to the second stage except that it is with a manual oil discharge valve instead of a solenoid-operated valve. This stage functions as a final refinement or polishing stage.

The three stages are constructed of carbon steel and each stage is equipped with a cover secured by a cam bar to provide access to the filter



cartridges. In each cover is an automatic air elimination valve, and each stage has a sight glass through which to view water clarity and the oil level. Each stage also contains an oil discharge valve, a drain valve, and pressure gauges for indicating inlet and outlet pressures so that the pressure drop across the filter can be determined. The fluid driving force is provided by a 5-gallon-per-minute (gpm), progressing cavity pump, driven by a 1/2-horsepower electric motor.

1.3.2 Watercraft

The performance of oil-water separators on four different classes of watercraft was evaluated. These included large ships or transports, landing craft - utility (LCU), tug boats, and crane barges. The specific vessels sampled are shown in Table 1-1, along with some of their principal characteristics (from Ref. 3). The bilge compartments in these watercraft varied in capacity from an estimated several hundred gallons in the LCUs to many thousands of gallons in the large ships.

1.4 METHODS

The following sections describe the sampling and analytical methods used during this study.

1.4.1 Sampling

Three sampling trips were made to Fort Eustis, VA, in the Winter and Fall of 1979, and in the Spring of 1980. A total of 14 sets of bilgewater samples were collected from 10 different vessels operating out of the Third Port at Fort Eustis, representing four different classes of vessels. Often the bilgewater of ships was unable to be sampled for a variety of reasons. For example, during the October 1979 sampling trip, a total of nine ships were inspected, but only three were found to be satisfactory for sampling.

Samples of both untreated (prior to oil-water separation) and treated (after oil-water separation) bilgewater were collected during this study.

TABLE 1-1. PRINCIPAL CHARACTERISTICS OF SAMPLED ARMY WATERCRAFT (REF. 3)

Vessel Class	Vessel Designation	Length, Overall (ft)	Beam, Molded (ft)	Depth, Molded (ft)	Displacement (Long tons)	Engine Data		Generator Engines		Capacity (gallons)				
						No.	Type	No.	Type	Fuel	Lube Oil	Fresh Water	Potable Water	
Large Ship - Transport	FMS	210.5	40	15	1160	1525.0	None	4	Diesel	150	52,000	600	26,000	15,000
	Page	223.0	38	19	1068	2037.5	2 Diesel	2	Diesel	800	54,100	450	15,896	10,000
	Sutton	177.5	32	14	465	935.4	2 Diesel	2	Diesel	500	20,042	292	11,624	2,042
LCU	1672, 1579, 1571	115.0	34	6	58.8	116.1	3 Diesel	2	Diesel	165	870	-	-	-
Tug	2088, 1972	107.0	26.5	15	295.0	390.0	1 Diesel	2	Diesel	1200	21,146	450	-	2,756
	1989	70.0	19.5	9.5	100.0	122.0	1 Diesel	2	Diesel	600	18.8 or 25 or 34	5,844	150	900
Crane Barge	6701	140.0	70	12.5	-	1630.0	None	2	Diesel	200	15,000	110	200	-



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Collection of the untreated samples was accomplished by either (1) disconnecting the pressure monitor line leading from just upstream of the first stage of the oil-water separator to the oil-water separator monitor-control panel, or (2) using a small hand-held pump to collect bilgewater directly from the bilge compartment. Samples of the treated bilgewater effluent were collected via the pressure monitor line downstream of the final stage of the oil-water separator.

The sample containers were 1-liter (L) glass or plastic jars and 100-milliliter (ml) glass jars, depending on the type of analysis to be performed. Degradation of the samples prior to analysis was suppressed by the addition of either hydrochloric or sulfuric acid. All analyses were performed in Newbury Park, CA, within 10 days of sample collection.

1.4.2 Analysis

All of the samples were analyzed for total, suspended, and dissolved pollutants (total = suspended + dissolved). Analysis for dissolved pollutants involved filtering a small portion of the sample through a previously washed, 0.45-micron Millipore filter to remove the bulk of the "free," or undissolved oil and particulates. The filtrate was then analyzed for total organic carbon (TOC) on an Oceanography International 052413 total carbon system. The units are milligrams of TOC per liter (mg TOC/L). While the quantity of dissolved pollutants in bilgewater effluent is not currently regulated, it was an important component to determine because second-generation treatment equipment (such as that described in Part II of this report) will have to reduce the level of both suspended and dissolved pollutants.

The quantity of suspended pollutants was determined by using the standard method AP4A 502A (Ref. 4). This method involves a liquid-liquid extraction of the sample with Freon 113, followed by evaporation of the solvent and a gravimetric determination of the residue. It is believed that the bulk of the residue is free or undissolved oil; however, the Freon



undoubtedly also extracts a small amount of the compounds dissolved in the water phase. The units of this analysis are in mg/L.

The total pollutant value was determined by summation of the dissolved pollutant and suspended pollutant values, in units of mg TOC/L. The suspended pollutant values were converted from mg/L to mg TOC/L prior to summation with the dissolved pollutant values by multiplying by 0.85; the approximate weight fraction of carbon in a saturated aliphatic hydrocarbon molecule.

In addition to the gross chemical profiling of the treated and untreated bilgewater samples, selected samples were subjected to detailed analyses to reveal information on the specific types of compounds present. Selected samples collected before and after on-board treatment were analyzed for their volatile organic content and for the presence of dissolved polar, ultraviolet (UV) absorbing compounds. Volatile organics were determined by sparging a 500-ml bilgewater sample with purified nitrogen and collecting the stripped, volatile organics by adsorption on activated carbon. The adsorbed compounds were removed by soaking the carbon in 1 ml of carbon disulfide (CS_2). Aliquots of the CS_2 -volatile organic mixture were then separated by gas chromatography (GC) and identified and quantified by mass spectrometry (MS).

The dissolved polar, UV-absorbing compounds were analyzed using high-pressure liquid chromatography (HPLC). The samples were first filtered through a 0.45 micron Millipore filter and the dissolved compounds were then adsorbed onto Amberlite macroreticular resin from the water matrix and finally desorbed from the resin with methanol (CH_3OH). The methanol concentrate was then injected into an HPLC, using the nominal conditions presented in Table 1-2.



TABLE 1-2. NOMINAL CONDITIONS OF HPLC ANALYSIS

Instrument:	Spectra Physics HPLC Model 3500B
Column:	Partisil PXS/10/25, ODS-2, 25 cm long, Whatman Corp.
Detector:	uv at 254 nm
Mobile Phase:	30% water, 70% methanol, isocratic
Flowrate:	1.2 ml/min.
Pressure:	2224 kg/cm ²
Sample Size:	10 microliter
Recorder Speed:	0.5 in./min.

1.5 RESULTS

Table 1-3 shows the suspended, dissolved, and total pollutant values for the 10 different vessels which were sampled during the three sampling trips to Fort Eustis, VA.

1.5.1 Suspended Pollutants

In Table 1-3, the first column of figures under the "Suspended Pollutants" heading shows the concentration of suspended pollutants contained in the samples of influent to the on-board oil-water separators. At the bottom of this column is the average influent suspended pollutant concentration for all of the watercraft, excluding the values from the crane barge and the Page. The average value for the suspended pollutants was 275.9 mg/L. This average value does not include the samples collected from the crane barge or the Page, since these samples contained very high amounts of suspended oil because the bilge levels were quite low, so that the oil-water interface coincided with the oil-water separator pump suction port level. Two of the larger ships had significantly lower suspended pollutant levels



TABLE 1-3. GROSS CHEMICAL CHARACTERISTICS OF UNTREATED AND TREATED
BILGEWATER FROM ARMY WATERCRAFT, ON-BOARD TREATMENT

Vessel Class	Designation	Date Sampled	Suspended Pollutants ^a		% Removal	Dissolved Pollutants (mg TOC/L)		Total Pollutants ^e	
			Influent (mg/L)	Effluent		Influent	Effluent	Influent	Effluent
Large Ship - Transport	FMS	1/79	141.6	53.9	61.9	46.0	1130.8	166.4	1176.6
	FMS	4/80	15.6	7.5	51.9	77.0	86.0	90.3	92.4
	Page	1/79	2274	25	96.7	123.3	55.3	2056.2	76.5
	Sutton	11/79	60.7	10.2	83.2	26.5	20.5	78.1	29.2
LCU	1672	1/79	343.0	214.0	37.6	901.4	543.5	1192.9	725.4
	1579	1/79	539.0	35.0	93.5	1027.0	12278.7	1485.1	12308.5
	1571	10/79	286.5	106.9	62.7	5288.0	3340.0	5531.5	3430.9
Tug	2088	1/79	123.0	22.0	82.1	189.6	317.2	294.1	335.9
	2088	10/79	169.5	26.6	84.3	49.7	106.2	193.8	128.8
	2088	4/80	658.0	38.7	94.1	671.0	965.0	1230.3	997.9
	1972	1/79	132.0	11.0	91.7	301.6	284.8	413.2	294.1
	1989 (65')	10/79	566.2	31.5	94.4	703.0	74.1	1184.3	100.9
Crane Barge	6701	4/17/80	3.7% ^b	168.3	99.5	12700.0	13500.0	44150.0	13643.0
	6701	4/23/80	9% ^b	87.7	99.9	13522.0	10525.0	90022.0	10599.5
AVERAGES ± STANDARD DEVIATION			275.9 ^f ±211.4	59.8 ±60.8	77.8 ^c ±18.7	374.2 ^d ±359.9	See Note	762.3 ^d ±654.9	See Note

^a Freon extraction, gravimetric procedure (502A).

^b Percent, by volume. Because the oil-water suction line was near the oil-water interface in the bilge compartment, these influent samples contained large amounts of oil.

^c Excludes crane barge values in average.

^d Excludes crane barge and LCU 1571 values in average.

^e These values combined mg/L suspended pollutants with mg TOC/L dissolved pollutants. The suspended pollutants are multiplied by 0.85 (see text).

^f Excludes crane barge and Page values in average.

NOTE: These averages are not computed since the effluent dissolved pollutant values are in question.



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in their influent than the other vessels sampled, the FMS sampled in April 1980 and the Sutton. However, the low level measured in the FMS sample (15.6 mg/L) is probably artificially low, since the vessel had just returned from an extensive modification and refitting, during which the bilges were cleaned. Additionally, influent samples from the FMS taken previously (January 1979) showed a much higher suspended pollutant level (141.6 mg/L).

Generally, the larger ships show a lower concentration of suspended pollutants in their influents than two smaller vessel classes, the LCUs and the tugs. This is shown in Table 1-4. The average influent suspended pollutant concentration for the large transport ships was 72.6 mg/L (excluding the Page), compared with 389.5 mg/L for the LCUs and 329.7 mg/L for the tugs (the crane barge was not evaluated in this respect because of the atypically high and unrepresentative suspended pollutant levels). Several reasons could account for this trend. First, the decking above the bilge compartments in the larger ships is less crowded with machinery than in the small watercraft. The machinery is therefore easier to maintain and fewer fuel and oil leaks to the bilge compartment probably occur. Secondly, the volume of water in the bilge compartments in the larger ships is much greater than in the small watercraft, and therefore any fuel or lube oil leaks fall into a much larger volume of bilgewater and are diluted to a greater extent.

The low influent suspended pollutant concentrations found in the larger ships does not appear to result in enhanced performance of their on-board oil-water separators above that achieved by the separators on some of the small watercraft. For example, all of the tugs produced an effluent of similar suspended pollutant concentrations as the larger ships (Tables 1-3 and 1-4), even though the influent concentrations on these watercraft were significantly higher. The correlation coefficient, r , between the influent and effluent suspended pollutant concentrations for all 14 samples was only 0.31, indicating only slight positive correlation between influent and effluent values.

TABLE 1-4. AVERAGE GROSS CHEMICAL CHARACTERISTICS OF UNTREATED AND TREATED BILGEWATER FROM ARMY WATERCRAFT, BY VESSEL CLASS, ON-BOARD TREATMENT

Vessel Class (Number of Samples Averaged)	Average Suspended Pollutants (mg/L)		Average % Removed	Average Dissolved Pollutants (mg TOC/L)		Average Total Pollutants ^b (mg TOC/L)	
	Influent	Effluent		Influent	Effluent	Influent	Effluent
Large Ship - Transports (4)	72.6 ±52.1 ^c	24.2 ±18.4	73.4 ±17.6	68.2 ±36.5	323.2 ±467.9	597.7 ±842.7	343.7 ±481.4
LCUs (3)	389.5 ±108.2	118.6 ±73.5	64.6 ±22.9	2405.4 ±2038.9	5387.4 ±5004.8	2736.5 ±1979.9	5488.3 ±4947.5
Tugs (5)	329.7 ±232.9	26.0 ±9.3	89.3 ±5.1	383.0 ±260.9	349.5 ±322.2	663.1 ±449.9	371.5 ±326.1
Crane Barge (2)	a	128.0 ±40.3	a	13111.0 ±111.0	12012.5 ±1487.5	a	12121.2 ±1521.7

a Averages not given because influent suspended pollutant concentrations were atypically high (see text).

b These values are the additive value of suspended pollutants in mg/L and dissolved pollutants in mg TOC/L. Suspended pollutants were multiplied by 0.85 (see text).

c Average does not include value from the Page (see text).



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The suspended pollutants present in the influent to the oil-water separator were removed to a large extent by the treatment process. The efficiency of the process is shown as the percent removal in Table 1-3. The lowest removal efficiency was 37.6% from LCU 1672. Seven influent-effluent sample pairs showed removal efficiencies exceeding 90%. The average removal efficiency for all of the influent-effluent sample pairs was 77.8%.

There exists wide disparity in the performance of the oil-water separators from watercraft to watercraft. Three of the watercraft, LCUs 1672 and 1571, and the crane barge produced an effluent containing significantly greater concentrations of suspended pollutants than the other watercraft sampled. Three watercraft produced quite low suspended pollutant concentrations in their effluents, the FMS (4-80), the Sutton and tug 1972. The remaining vessels produced effluents of intermediate quality between these two extremes.

The variation in suspended pollutant removal efficiencies of the on-board oil-water separators suggests that either poor-quality filter elements or procedural idiosyncrasies operating on each watercraft might be the causal factor. The following examples of improper procedures would negatively impact the effectiveness of an on-board oil-water separator.

1. Improper deck cleaning procedures
 - Contamination of bilge with detergents
 - Use of bilge cleaners

If surface-active agents used for deck or bilge cleaning are allowed to contaminate the bilge fluid, the coalescing action of the filters in the oil-water separator is rendered impotent.

2. Lax maintenance procedures
 - Many fuel oil and/or lube oil leaks to the bilge increase the amount of oil to be removed by the oil-water separator and increase the concentration of naturally occurring (in the oils) emulsifying agents.



- Improper handling of replacement oil-water separation filter cartridges. Skin oils on the external surface of these filters reduces the effectiveness of the coalescing action.
 - Improper installation of replacement oil-water separator filter cartridges. Improper seating of the filter within the housing, omission of the O-ring in the filter hold-down assembly, or improper tightening of the wing nut holding the filter in place can result in oil bypassing the filter.
3. Incorrect oil-water separator operation
- Faulty valve positioning by operator
 - No observation of the visual quality of the oil-water separator effluent. By not carefully noting the performance of the unit, the need for unscheduled maintenance will go unnoticed.
 - No schedule for filter cartridge replacement. Degradation in the performance of the oil-water separator can begin before large pressure drops across the filters indicate the need for replacement, the usual criterion used for deciding to replace a filter.
4. Non-optimum bilge handling procedures
- Allowing the bilge to accumulate to an excessive degree before processing
 - Excessive elapsed time between processing. Large amounts of oil contacting water for protracted periods results in more difficult oil-water separation because of increased emulsification and large oil concentrations.

Eliminating these types of procedural deficiencies would probably dramatically improve the performance of the oil-water separators shown to be discharging bilgewater with relatively high levels of suspended pollutants, to a level which several of the units tested are now achieving.



1.5.2 Dissolved Pollutants

The dissolved pollutant concentrations (Table 1-3) found in the influents ranged from a low of 26.5 mg TOC/L to a high of 13,522 mg TOC/L (1.35%). The very high dissolved pollutant values (e.g., LCUs 1571, 1579, crane barge) are indicative of bilge contamination. The bilgewater from LUC 1579 possessed a greenish cast which could have been caused by an antifreeze (primarily ethylene glycol) leak into the bilge. The engineer on board the crane barge said that Lysol was used to clean up oil and fuel spills and some undoubtedly was washed into the bilge.

The influent to the oil-water separators on board the FMS, Sutton, and tug 2088 (10/79) contained dissolved pollutant concentrations which are similar to those observed in unaged mixtures of diesel fuel and used oil with water prepared in the laboratory. The remaining vessels (Page, LCU 1672, Tug 2088 [1/79, 4/80], Tug 1972 and tug 1989) contained dissolved pollutant concentrations in their influents similar to the levels observed in water that had been contacted with fuel oils (JP-5, DF-2, Navy distillate) and gasolines for protracted periods (42 days) during a laboratory study (Ref. 5). These moderately high levels (roughly 100-900 mg TOC/L) result from a degradation of the free oil film by bacteria that use the oil as a food source and produce metabolites with a high solubility in water. Thus the concentration of dissolved organic carbon increases as the bilge fluid ages.

On the average (see Table 1-4), the large ships had a lower concentration of dissolved pollutants in their influents (68.2 mg TOC/L) than either the LCUs (2405.4 mg TOC/L), the tugs (383.0 mg TOC/L), or the crane barge (13111.0 mg/L). This is similar to the trend observed for the concentrations of suspended pollutants in the influents and the reasons may be the same, i.e., less contamination probably reaches the bilge compartment in the larger ships because maintenance of machinery is easier, the volume of bilgewater is greater in these large craft compared with the LCUs, tugs, and crane barges, and therefore contamination is diluted to a greater extent.



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For many of the vessels, the dissolved pollutant concentration in the effluent does not correspond to the concentration in the influent samples. In many of these cases (e.g., the LCUs) there was insufficient fluid in the bilges to adequately flush the oil-water separators prior to sampling the effluent. As a result, the effluent samples may have been in contact with a large volume of separated oil contained in the upper parts of the oil-water separator filter stacks. Therefore, the water had an opportunity to attain large concentrations of water-soluble components from this large oil source. The effluent values for dissolved pollutants can largely be ignored since they should be identical to the influent samples. A physical separation step, such as that which occurs in the oil-water separator, should cause no change in the dissolved pollutant concentration.

The concentration of compounds found dissolved in oily bilgewater depends 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 ship's 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 concentration can be minimized by reducing the amount of oil in contact with the water layer (i.e., repairing fuel oil and lube oil leaks quickly), reducing the duration the oil and water are in contact, and preventing contributions of water-soluble compounds to the bilgewater (e.g., antifreeze). By altering faulty operational procedures which encourage high concentrations of dissolved pollutants, a cleaner bilgewater would result, one more amenable to further cleanup by secondary treatment methods.



1.5.3 Total Pollutants

The total pollutant concentration is the sum of the suspended and dissolved pollutant concentrations. The units of suspended (mg/L) and dissolved (mg TOC/L) pollutants are different; therefore the suspended pollutant concentrations in Table 1-3 were multiplied by 0.85 in order to convert the units to mg TOC/L so that they could be added to the dissolved pollutant values. The 0.85 multiplier is based on the fact that saturated hydrocarbons found in fuel and lube oils are approximately 85% carbon, by weight.

The influent total pollutant concentrations are all rather high (except for the FMS [4/80] and the Sutton) owing to the large influent concentrations of suspended and dissolved pollutants. The effluent values have much less meaning because of the problems associated with sampling the dissolved pollutants in the effluents, as discussed in the previous section.

On the average (Table 1-4), the large ships had a higher quality influent and effluent, in terms of total pollutants, than any other vessel class. The LCUs had the poorest influent total pollutant concentrations, while the crane barge had the lowest quality effluent.

1.5.4 Detailed Analyses

Samples of influent and effluent from tugs 2088 (1/79) and 1972, LCUs 1579 and 1672, and the Page and FMS (1/79) were analyzed for their volatile organic content using the method described in Section 1.4.2. Only the Page contained 0.15 mg/L of volatile aliphatic compounds in its influent, the FMS contained 0.36 mg/L in its effluent, and LCU 1672 contained 0.43 mg/L in its effluent.

Fuel oils and lubricating oils contain few volatile compounds and therefore it was expected to find little dissolved in the water phase. These analyses confirmed this expectation.



The effluent samples from Tugs 2088 (10/79) and 1989, and from LCU 1571 were analyzed by HPLC for their dissolved, polar, UV-absorbing compounds using the method described in Section 1.4.2. The Partisil HPLC column retains compounds to a degree relating directly to compound polarity. The phenolic materials elute from the column in about 1 to 3.5 minutes, nitrogenous heterocyclics in about 3.5 to 7 minutes, and BTX in about 7 to 14 minutes (Ref. 2). During the analysis the peaks caused by compounds that eluted in each time window were integrated and related to an average integrator response per mg/L for compounds in that time window, established in earlier work (Ref. 2). Some of these response factors were confirmed during analysis. None of the samples contained compounds (principally benzene, toluene, and xylenes) that eluted in the 7- to 14-minute time window. This was in accord with analyses for volatile fraction performed by GC, which also disclosed the absence of volatile aromatic hydrocarbons in the samples. This type of analysis is only sensitive to polar compounds that exhibit UV absorbance, primarily compounds containing aromatic structures. Such compounds are generally more toxic than aliphatic compounds and are generally more soluble than the aliphatic compounds found in oil (especially straight chain aliphatics). The results are presented in Table 1-5. The concentrations of the UV-absorbing, polar compounds listed in Table 1-5 are only approximate, since class factors were used to arrive at the concentrations. However, these concentrations provide some insight into the composition of the dissolved component of the effluent samples.

TABLE 1-5. RESULTS OF HPLC ANALYSIS FOR DISSOLVED,
POLAR, UV-ABSORBING COMPOUNDS

Watercraft Type	Designation	Dissolved Component (Effluent, mg/L)	
		1 - 3.5 Mins.	3.5 - 7 Mins.
Tug	2088 (10/79)	290.5 ±2.0	7.9 ±1.4
Tug (65 foot)	1989	59.0 ±4.5	5.6 ±2.2
LCU	1571	25.6 ±9.0	0.0



The dissolved component of the effluent samples from tug 2088 and tug 1989 contain significant amounts of UV-absorbing, polar compounds. Both effluents contained compounds that eluted in the phenolic and nitrogenous heterocyclic time windows, with the phenolics in higher concentration. The higher phenolic concentration is to be expected based on the composition of refined oils and fuels. The high approximate concentration of compounds eluting from 1 to 3.5 minutes found in the effluent from tug 2088 (290.5 mg/L) relative to the dissolved TOC level (106.2 mg/L) (Table 1-3) has two possible explanations. First, the compounds detected by HPLC may have a high percentage of noncarbon atoms in their molecules. A high concentration of these molecules would result in a low dissolved TOC level relative to the actual concentration of these compounds. Tri-hydroxy benzenes and organic acids containing an aromatic ring are examples of such compounds. Secondly, if a compound exhibiting high UV absorptance happened to elute during the 1- to 3.5-minute time window, the computed concentration would be in error.

The LCU effluent had relatively little polar aromatic material, comprising approximately 1% of the dissolved TOC. This suggests that the material that caused the high dissolved TOC level (3340 mg TOC/L) was of nonpetroleum origin.

1.6 DISCUSSION

The results from this study on the performance of on-board oil-water separators can be compared with those from a study of a shore-based, centralized treatment facility (Refs. 1, 2). Table 1-6 shows a comparison of the average values of total, suspended, and dissolved pollutants in the bilgewater samples collected before and after centralized treatment (average of spring and winter samples), and before and after on-board treatment.

The average influent to the on-board oil-water separators contained greater amounts of total, suspended, and dissolved pollutants than the average influent to the centralized treatment facility. This suggests that either the on-board units are variable in quality, or the operating procedures



TABLE 1-6. COMPARISON OF CENTRALIZED AND ON-BOARD TREATMENT OF BILGEWATER

		On-Board	Centralized ^d (mg TOC/L)
Influent	Total	762.3 ±654.9 (mg TOC/L) ^b	167.3 ±153.6
	Suspended	275.9 ±211.4 (mg/L) ^c	113.0 ±105.1
	Dissolved	374.2 ±359.9 (mg TOC/L) ^b	53.7 ±47.6
Effluent	Total	a	1671.0 ±902.0
	Suspended	59.8 ±60.8 (mg/L)	655.5 ±655.5
	Dissolved	a	1015.5 ±246.5

a - Averages not given because the dissolved pollutants in the effluents are in question (see text).

b - Excludes crane barge and LCU 1571 values in average.

c - Excludes crane barge and Page values in average.

d - Average of spring and winter samples. Influent samples were from a tug boat, an LCU, and a transport ship.

in effect on those vessels with facility for on-board treatment have a negative impact on the quality of the bilgewater influent, compared with those craft that utilize the centralized facility for disposal of their bilge wastes.

Apparently the ability to discharge bilgewater regardless of time or place offered by the on-board treatment systems is not being taken advantage of on some of the watercraft. Rather, it appears that the operating personnel wait until the bilges are full before they begin on-board treatment. The longer treatment is postponed, the longer the oil and water remain in contact and dissolved pollutant levels can become quite high. This is apparently what has happened on some vessels with on-board oil-water separators.

In contrast, those vessels dependent on centralized treatment may discharge their bilgewater to the facility before the bilges are full in order



to avoid having their bilges full when sailing orders arrive. Therefore, dissolved pollutant levels would be lower with such operational procedures because oil-water contact time would be minimized.

The on-board oil-water separators appear to produce a higher quality effluent with respect to suspended pollutants compared with that discharged from the centralized treatment facility, based on the results summarized in Table 1-6. The average effluent from the on-board treatment systems contained 59.8 mg/L suspended pollutants, while the average for centralized treatment facility effluent was 655.5 mg TOC/L. This high average for centralized treatment is entirely due to the discharge sampled in the winter which contained 1311 mg TOC/L of suspended pollutants. The spring sample contained no suspended pollutants. In contrast, the effluent quality from the on-board treatment systems appears to be independent of season (Table 1-3).

The average dissolved and total pollutants in the effluents produced by the on-board treatment systems are not presented because the values from certain watercraft are in question, as discussed previously.

From Table 1-3 it can be seen that certain vessels had on-board oil-water separators that performed very well, much better, in fact, than the performance of the oil-water separator used in the centralized treatment facility during winter. Most notably of these, the Sutton, produced an effluent of low suspended, dissolved, and total pollutants. The oil-water separators on board the FMS (4/80) and tug 1972 also produced effluents with quite acceptable levels of suspended pollutants. However, many of the vessels produced effluents with excessive amounts of suspended, dissolved, and total pollutants.



1.7 CONCLUSIONS

The following conclusions were reached based on the results from the testing of on-board oil-water separators.

- Generally, the larger ships show a lower concentration of suspended pollutants in their bilgewater influents to their oil-water separators than the smaller vessels. This could be due to greater ease of maintenance on the larger ships and to the fact that the volume of water in the bilge compartments in the larger ships is much greater than in the small watercraft, and therefore any fuel or lube oil leaks fall into a much larger volume of bilgewater and are diluted to a greater extent.
- The low concentration of suspended pollutants in the influents to the oil-water separators on the large ships does not appear to result in enhanced performance of the oil-water separators.
- The on-board oil-water separators were effective in reducing suspended pollutant levels in bilgewater. On the average, 77.8% of the suspended pollutants were removed by the process.
- There exists a wide disparity in the performance of the oil-water separators from watercraft to watercraft.
- Several of the watercraft showed signs of bilgewater contamination by nonpetroleum fluids.
- Several of the watercraft possessed high dissolved pollutant concentrations in their bilgewater, indicative of protracted oil-water contact.
- On the average, the large ships had a higher quality influent and effluent, in terms of total pollutants, than any other vessel



class. The LCUs had the poorest influent total pollutant concentrations, while the crane barge had the lowest quality effluent.

- Few volatile compounds were found in the bilgewater samples.

The exemplary performance of several of the on-board oil-water separators in removing suspended pollutants from bilgewater proves that these devices can be effective in producing a bilgewater effluent that meets current regulations. The large disparity in performance of the on-board oil-water separators from vessel to vessel suggests that the problem lies with procedural variations between watercraft or because of faulty oil-water separator elements. It is believed that by cataloging the procedures used on board vessels with oil-water separators and correlating these with the performance of their systems, those procedures that interfere with optimum performance can be identified. Once these faulty procedures are identified, they can be modified and the proper procedures standardized so that all of the on-board oil-water separator systems can be made to perform as some now do.

To assure the quality of oil-water separator elements, test hardware and procedures should be developed that will allow the Army to formulate a qualified products list.

1.8 RECOMMENDATIONS

A study to catalog and observe the activities and procedures that could possibly influence the quality of bilgewater should be undertaken. Procedures such as the following would be studied:

1. Maintenance of oil-water separator
2. Frequency of oil-water separator operation
3. Fuel and lubricating oil spill cleanup procedures (including types of detergents used in cleanup)



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4. Leak rates of oil and fuel to the bilge compartment

Samples of the bilgewater from the study craft would be analyzed for pollutant levels to correlate these with maintenance procedures. In this way, maintenance procedures that result in satisfactory oil-water separator performance could be identified.

The proper maintenance procedures could then be standardized, in the form of a manual. Care would be taken to recommend procedures that would in no way impair the preparedness of watercraft for movement.

Such a study would result in the improvement of the performance of the on-board oil-water separators to a level equal to that claimed by the manufacturer and observed in a few present-day watercraft.

Additionally, a study designed to develop hardware and procedures for oil-water separator element quality conformance testing should be undertaken so that a minimum number of faulty elements will be installed in the oil-water separators.



2.0 PART II

EFFECTIVENESS OF ON-BOARD EXPERIMENTAL OILY WASTEWATER SEPARATION SYSTEM

2.1 INTRODUCTION

Contemporary regulations on the discharge of bilge and ballast waters from ships address free or insoluble oil; however, both the sprit and, by 1985, the letter of the Clean Water Act will require zero discharge of pollutants.

Hardware must be developed that can remove both the free or undissolved oil and dissolved pollutants from bilge and ballast water. To this end, the Army funded the design, construction, testing, and delivery of an experimental system to remove both undissolved and dissolved pollutants from bilgewater under Contract DAAG53-75-C-0271. During this contract, the Experimental Oily Wastewater Separation System was tested under laboratory conditions, after which the system was modified and installed on board an Army Floating Machine Shop (FMS) for determining its effectiveness under field conditions. A description of and the results of these phases can be found in Ref. 11. The field testing phase was funded under the present contract and the details of the work are reported in this section of the final report.

The Experimental Oily Wastewater Separation System uses a two-stage process to clean up oily bilgewater. The initial stage removes the bulk of the free or undissolved oil from the bilgewater with an oil-water separator identical to those whose effectiveness was evaluated in one part of this program (see Section 1.0). The second stage removes dissolved compounds from the bilgewater by oxidizing them with ozone in the presence of UV radiation.

2.1.1 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. 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:

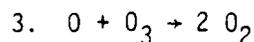
- A. Plasma jet
- B. Radiochemically
- C. Photochemically
- D. Silent electrical discharge

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:





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

2.1.1.1 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 system
- 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 more than 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. 6), phenol-laden wastewaters (Ref. 7), mine drainage discharges (primarily acids and iron complexes, Ref. 8), and is also used for color removal (Ref. 9), to name a few applications.



2.1.1.2 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. 2-1 (from Ref. 10). 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.

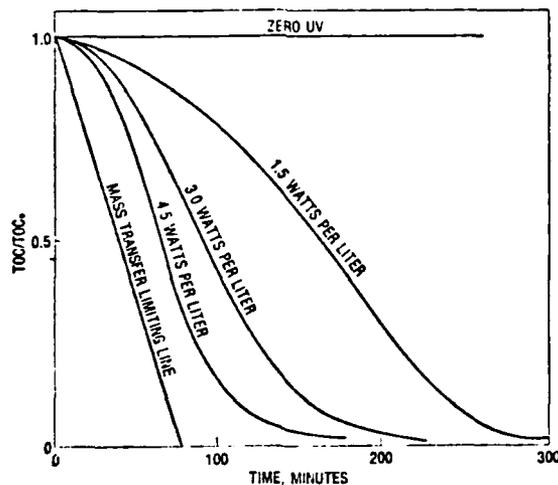


Figure 2-1. Ozone Oxidation of Acetic Acid, Effect of UV Near 30°C



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 CO_2 and 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. 2-2 (from Ref. 10).

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.

The sections that follow present the objectives of the on-board field testing of the Experimental Oily Wastewater Separation System, a detailed description of the system equipment and operation, the methods used to conduct the field tests, a presentation and discussion of the results, and the conclusions and recommendations formulated based on the results.

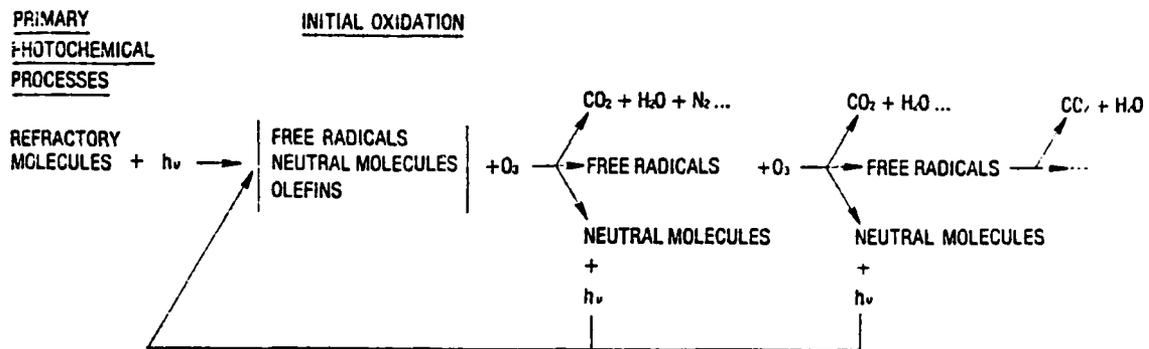


Figure 2-2. Overall Photochemical/Oxidation Process to Produce CO_2 , H_2O , etc.



2.2 OBJECTIVES

The purpose of the field testing was to evaluate the effectiveness of the Oily Wastewater Separation System under real-life conditions. Previous testing had been under controlled laboratory conditions using artificial bilgewater solutions of pure organic compounds in water and mixtures of refined oils and fuels with water, as well as with actual bilgewater obtained from Fort Eustis-based watercraft. However, none of the laboratory tests could exactly simulate actual field conditions.

The field tests were conducted with the following objectives in mind:

1. Quantify bilgewater pollutant concentrations prior to oil-water separation, after oil-water separation, and after UV-ozone treatment.
2. Determine the effects of various combinations of treatment parameters on final effluent quality.
3. Evaluate the system in terms of human factors engineering.
4. Determine noise and ozone emissions into the operational environment.
5. Evaluate the potential of UV-ozone treatment in meeting present and future bilgewater discharge standards.

2.3 EQUIPMENT DESCRIPTION AND OPERATION

The Experimental Oily Wastewater Separation System was installed on board an Army Floating Machine Shop (FMS) based at the Third Port, Fort Eustis, VA. The principal operating characteristics of this vessel are presented in Table 2-1.

The Experimental Oily Wastewater Separation System employs a two-stage process for the treatment of oily bilgewater. The first stage of treatment is for removing the free or undissolved component from the wastewater. This



TABLE 2-1. PRINCIPAL CHARACTERISTICS OF FMS TEST BED (REF. 3)

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



is accomplished by passing the wastewater through three fibrous bed filters plumbed in series. A complete description of this type of oil-water separator appears in Section 1.3.1 of this report. The oil-water separator is shown in Fig. 2-3, which is a photograph of the major components of the Experimental Oily Wastewater Separation System shipboard installation.

From the oil-water separator, the bilgewater flows into the oxyphotolysis reactor assembly, where ozone and UV radiation are used to destroy the dissolved components in the fluid. Figure 2-3 shows the features of the second-stage reactor assembly. The following section describes in detail the second-stage components. Section 2.3.2 describes the functions and operation of the various gas, liquid, and electrical subsystems of the two-stage treatment system.

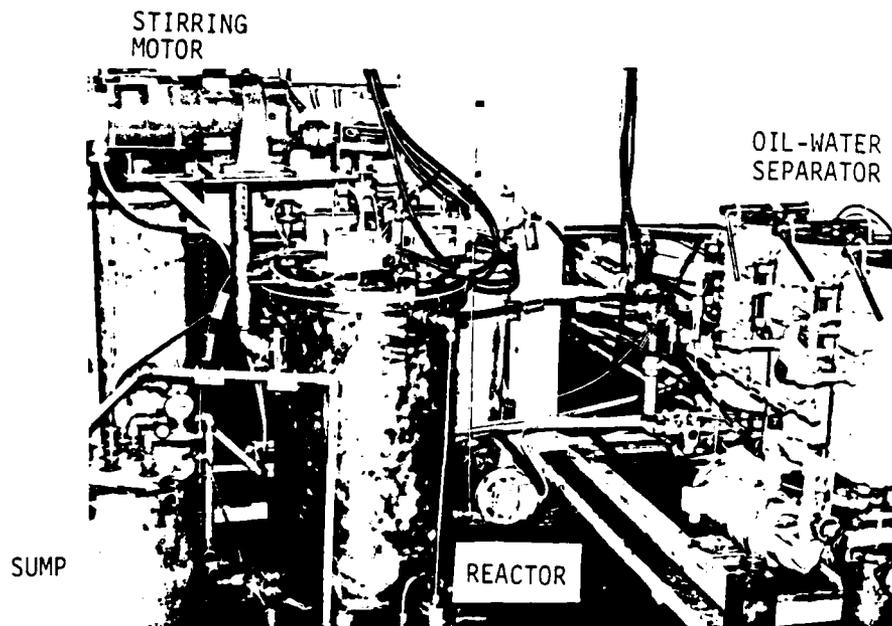


Figure 2-3. Experimental Oily Wastewater Separation System - On-Board Installation



2.3.1 Second-Stage System Component Description

2.3.1.1 Oxyphotolysis Reactor

The oxyphotolysis 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.

2.3.1.2 UV Lamps

Within the oxyphotolysis reactor 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 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.

2.3.1.3 Ozone Generator and Decomposer

Ozone is generated on-site for the destruction of the organics in the fluid contained in the reactor.



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The ozone generator is a Linde Model SG 4060, which produces one pound of ozone per day from an air feed. The ozone output of the unit was calibrated against various power levels and air flowrates in the laboratory.

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°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.

2.3.2 System Gas, Liquid, and Electrical Subsystem Operation

The Oily Wastewater Separation 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 semiautomatic control from a centralized control box.

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

2.3.2.1 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 oxy-photolysis reactor where the air-ozone gas stream is allowed to react with the bilgewater stream in the presence of UV radiation, (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 2-4 shows the gas feed subsystem. As compressed air enters the subsystem (on the left-hand side of Fig. 2-3), 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

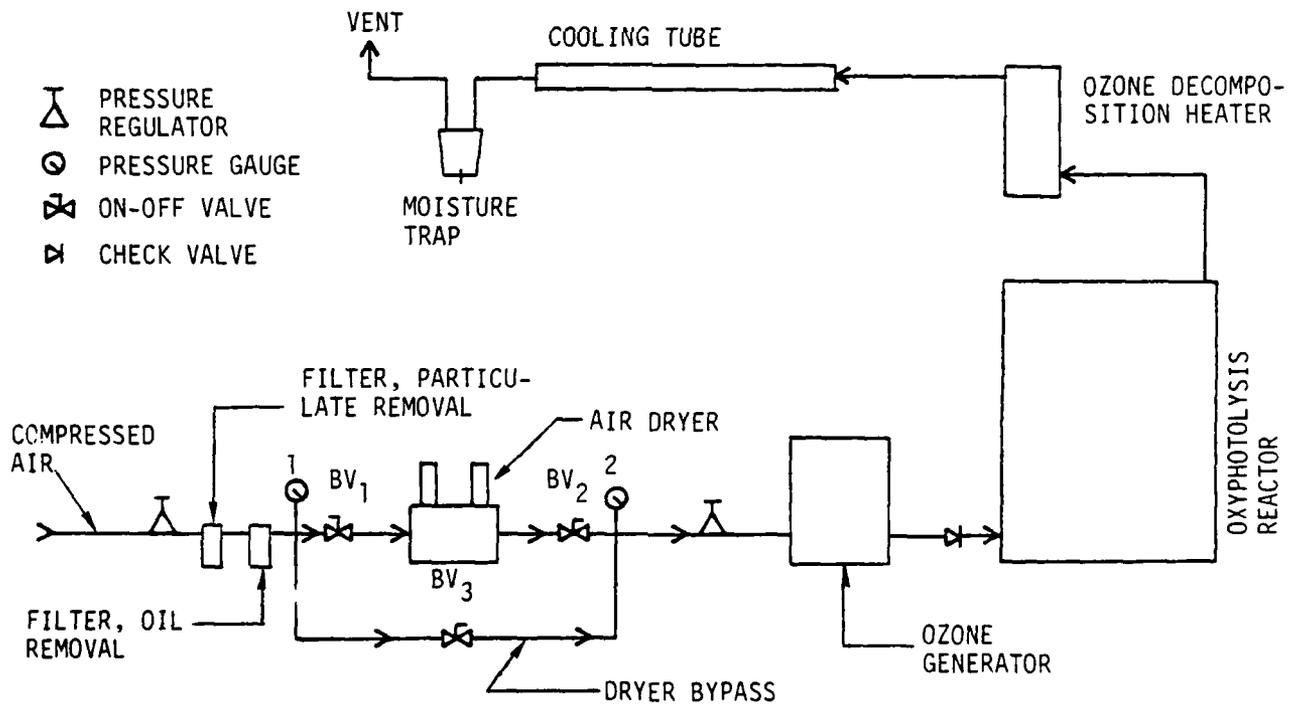


Figure 2-4. Gas Feed Subsystem



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 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.

2.3.2.2 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 2-5 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.

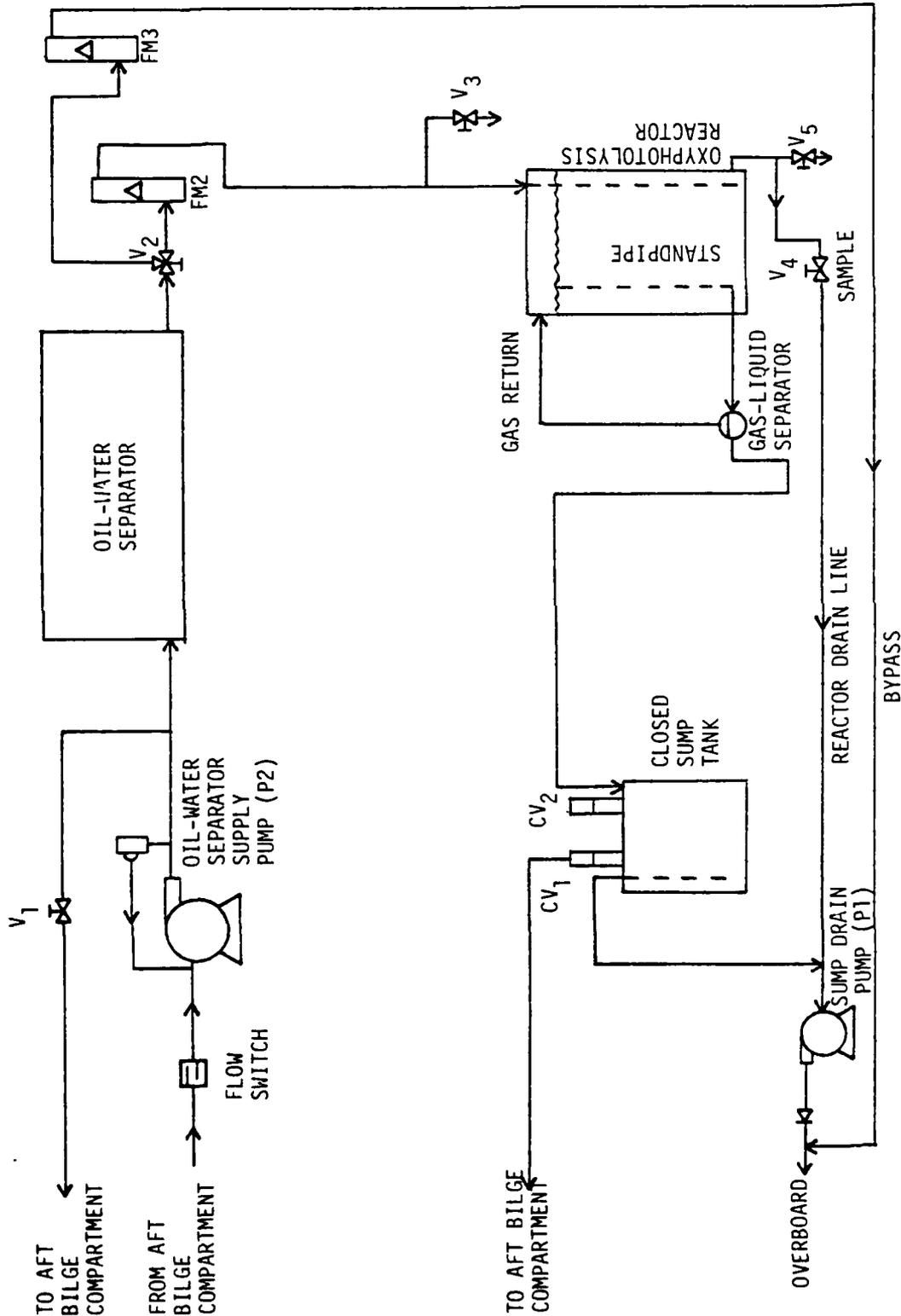


Figure 2-5. Bilgewater Feed Subsystem



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 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.

2.3.2.3 Electrical Subsystem

Many of the components of the oily wastewater treatment system are electrically powered and control of their operation is semiautomatic. 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- 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- and 700-watt UV lamp together, and the ozone decomposition heater and air dryer together.

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 2-6 shows the control panel with its various switches and lights.

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:

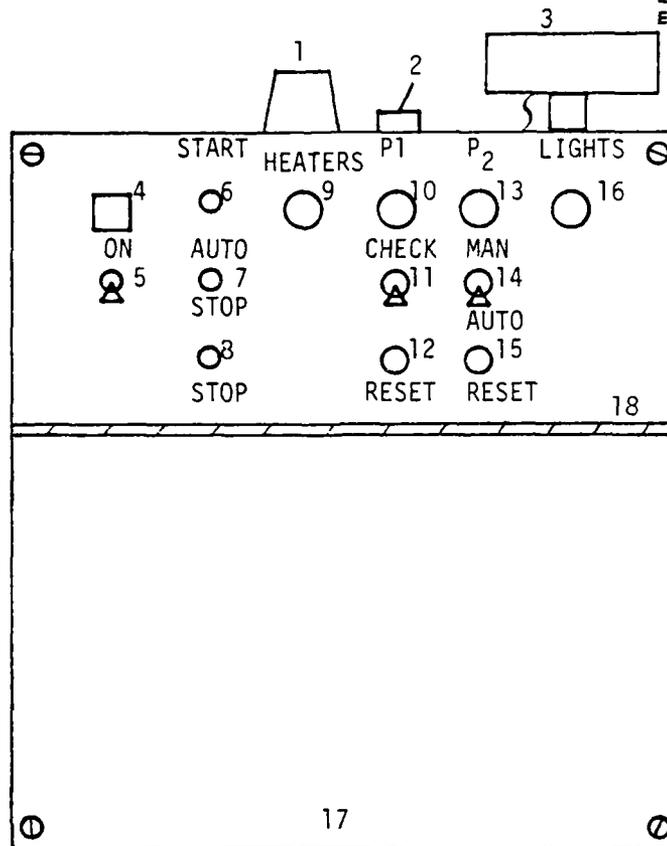
<u>Sensor</u>	<u>Location</u>	<u>Function</u>	<u>Fault Action</u>
Flow Switch	Oil-water separator pump suction line	Determine when bilge is dry (i.e., lack of flow)	Selectively shut down system
Thermoswitch 1	Inside ozone decomposition heater	Determine when acceptable temperature is reached in heater for maximum ozone destruction	Hold startup sequence until correct temperature, selectively shut down system



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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 2-6. System Control Panel



<u>Sensor</u>	<u>Location</u>	<u>Function</u>	<u>Fault Action</u>
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

An intermittent audible or visual (selectable) alarm is activated when the flow switch or thermoswitch 1 detect faults in the system. A continuous audible or visual (selectable) alarm is activated when either thermoswitch 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. 2-6).

2.3.2.4 Ancillary Gas and Liquid Streams

2.3.2.4.1 Nitrogen Stream. The ultraviolet lamps used in the Oily Wastewater Separation 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 2-7 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

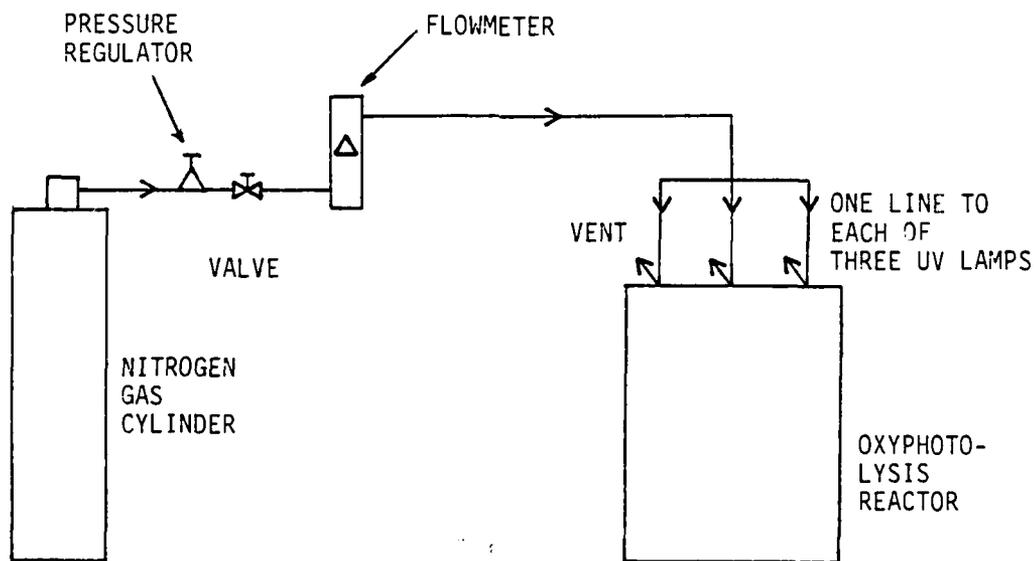


Figure 2-7. Nitrogen Stream



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.

2.3.2.4.2 Cooling Water Stream. Two components of the oily waste-water 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.

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 pressure across this assembly is controlled by a downstream valve. The water then

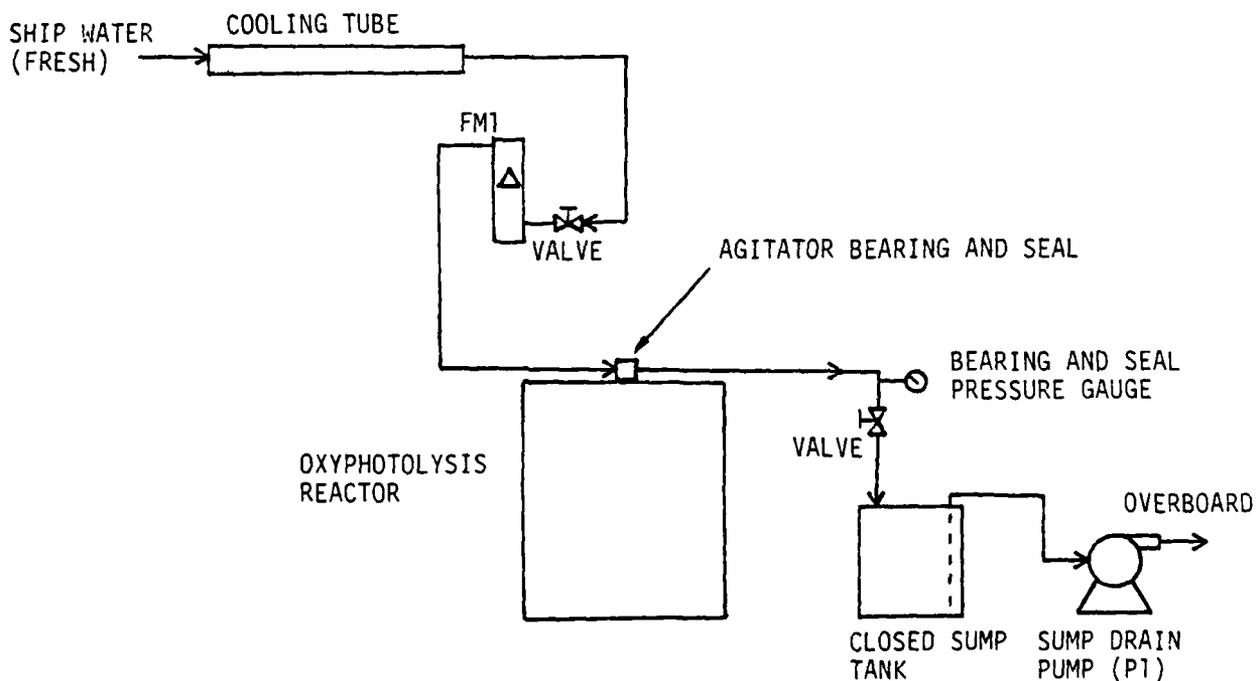


Figure 2-8. Cooling Water Stream



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exits into the closed sump tank and is discharged overboard along with the treated bilgewater (see Fig. 2-5) by the sump drain pump.



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2.4 METHODS

The following sections describe the methods used for the collection, preparation, and analysis of samples from the on-board testing of the experimental oily wastewater treatment system. Additionally, the test methods employed for determining the ozone and noise levels produced by the operating system are described.

2.4.1 Sampling

During each experiment, bilgewater samples at various stages in the treatment process were collected so that analyses could be performed to determine the following:

1. Suspended pollutants (SP)
2. Dissolved nonspecific pollutants (DN)
3. Dissolved aromatic pollutants (DA)

Figure 2-9 shows the three sampling points and which of the three analyses were performed on the samples collected from these locations. Sample point number 1 was upstream of the oil-water separator (i.e., untreated bilgewater). Samples from this point were analyzed for suspended pollutants. The second sampling point was downstream of the oil-water separator but upstream of the UV-ozone reactor, and the third sampling point was downstream of the reactor. Samples collected from these two sampling points downstream from the oil-water separator were subjected to the three types of analyses: suspended pollutants, dissolved nonspecific pollutants, and dissolved aromatic pollutants. This sampling scheme provided information on the effectiveness of each stage of treatment. Samples from sample location #1 were not analyzed for dissolved pollutants since physical separation of the oil and water would not be expected to alter the amount or type of dissolved pollutants.

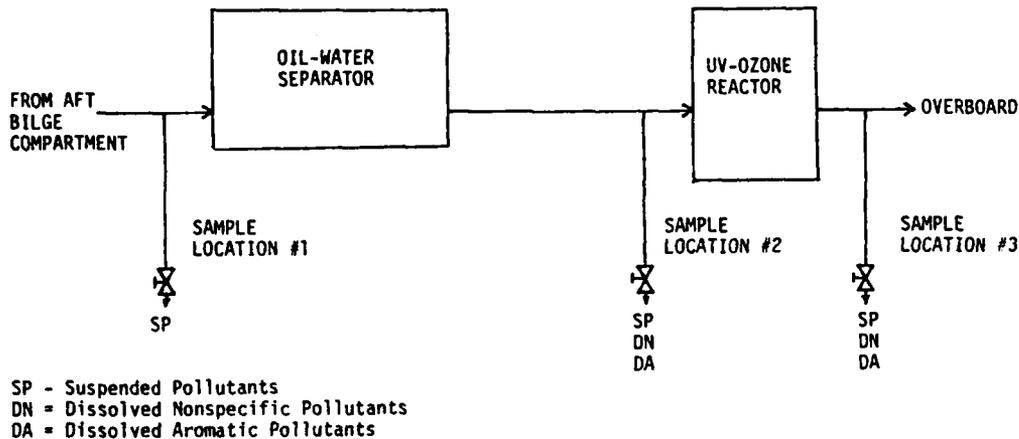


Figure 2-9. Sampling Locations and Types of Analyses Performed on Samples From These Locations

Figures 2-10 through 2-12 are photographs of samples being collected from sample locations #1, #2, and #3, respectively. Samples from sample location #1 (Fig. 2-10) were obtained from the pressure monitor line leading to the oil-water separator control panel. Samples from sample location #2 and #3 were collected by activating valves plumbed into tees in the process line.

Each experiment lasted for 245 minutes, during which nine samples were collected for suspended pollutant analysis, four samples for dissolved aromatics pollutant analysis, and 17 samples for dissolved nonspecific pollutant analysis.

Samples were collected in either 1-liter jars or 100-milliliter (ml) vials, depending on the type of analysis to be performed. A potassium iodide (KI) solution (prepared in distilled water) was added to those samples to be analyzed for dissolved aromatics and dissolved nonspecific



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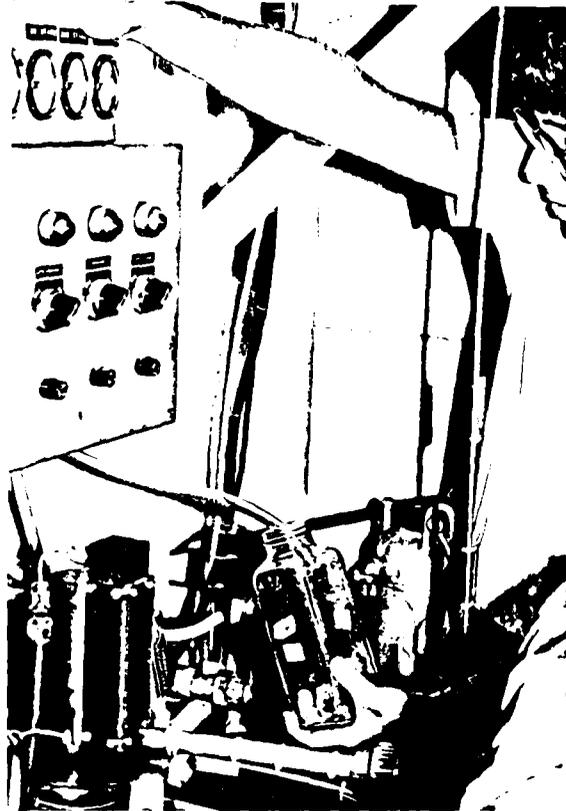


Figure 2-10. Sample Location #1



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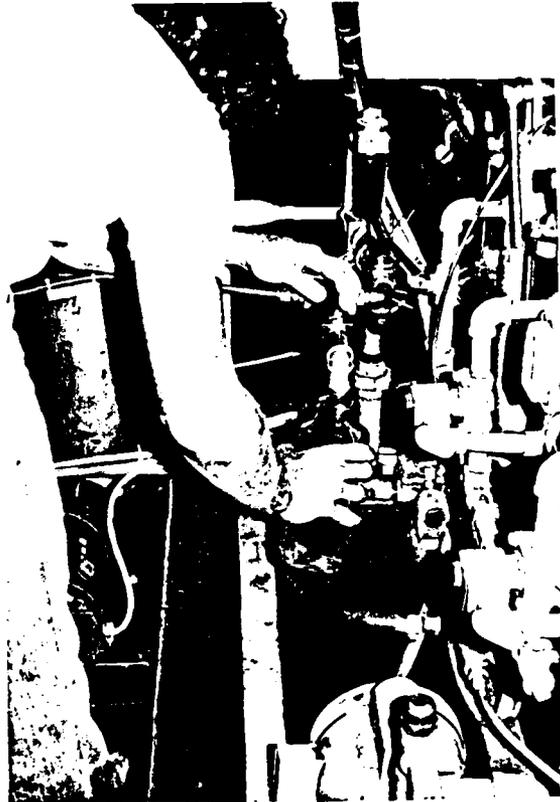


Figure 2-11. Sample Location #2



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Figure 2-12. Sample Location #3



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pollutants to quench the ozone reaction. All samples were acidified to a pH of 2 or less by adding concentrated hydrochloric acid (HCl).

2.4.2 Sample Preparation and Analysis

A temporary laboratory was set up in a vacant quarters area on board the FMS so that rapid sample preparation and analysis could be carried out. Figures 2-13 and 2-14 are photographs of some of the laboratory apparatus used for sample preparation in the on-board laboratory.

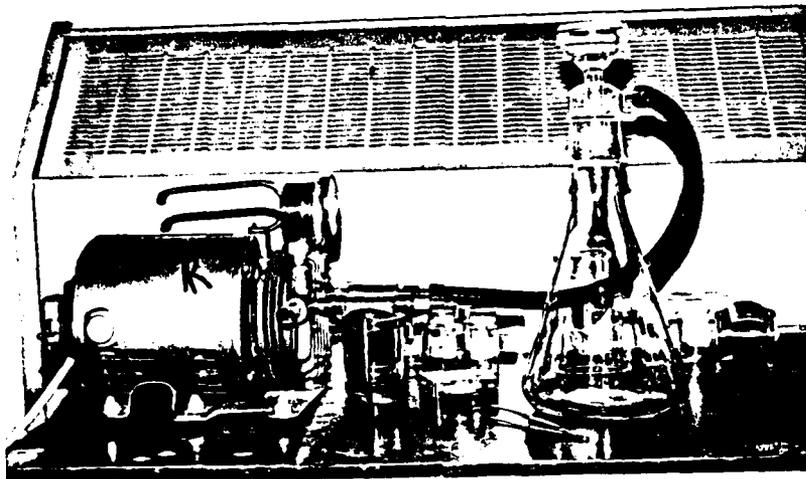


Figure 2-13. Millipore Filtration Apparatus

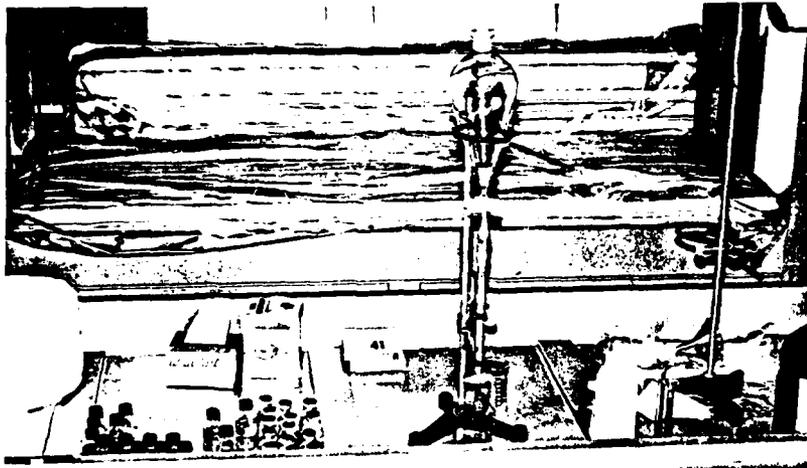


Figure 2-14. Adsorption Column for Concentrating Samples

2.4.2.1 Suspended Pollutants

Standard Method 502A (Ref. 4) was used to determine the quantity of suspended pollutants in the bilgewater samples. Briefly, the sample was placed in a 1-liter separatory funnel and extracted successively with three volumes of Freon 113. The Freon containing those compounds extracted from the sample (primarily free or undissolved oil) was placed in a previously weighed beaker. The Freon was evaporated and the residue weighed to the nearest 0.1 milligram on a Voland Model 640-D analytical balance set up on shore, away from the ship's vibration.

2.4.2.2 Dissolved Nonspecific Pollutants

The samples to be analyzed for dissolved nonspecific pollutants were first filtered through a 0.45-micron Millipore filter (Fig. 2-13) to remove the suspended pollutants. A 20-ml aliquot of the filtrate was placed in a



glass vial with a tight-fitting cap lined with aluminum foil. The vials were hand-carried back to the Rockwell International laboratory in Newbury Park, CA, for analysis. Each sample was analyzed for total organic carbon (TOC) on an Oceanography International 0524B total carbon system.

2.4.2.3 Dissolved Aromatic Pollutants

Samples for dissolved aromatic pollutant analysis were first filtered as described in the previous section. Four hundred milliliters of the sample was then passed through a packed column of Amberlite XAD-7 macroreticular resin (Fig. 2-14) until the sample level just reached the top of the resin bed. Polar organic compounds have an affinity for the resin and adsorb onto the high surface area resin beads (Ref. 12).

Twenty-five ml of distilled water was then passed through the column to remove salt and acidity from the resin. Twenty-five ml of spectrograde methanol was used to elute the adsorbed compounds from the resin.

The methanol eluate obtained during the preparation of each sample was placed in vials and transported to Newbury Park for analysis by high-pressure liquid chromatography (HPLC). The conditions of the analysis are shown in Table 2-2.

TABLE 2-2. CONDITIONS OF HPLC ANALYSIS

Instrument:	Spectra Physics 3500B liquid chromatograph with UV absorption detector (254 nm)
Chart Speed:	0.5 cm/min.
Column:	Partisil PXS 10/25 ODS-2
Mobile Phase:	70% methanol, 30% water
Flow:	1.6 ml/min.
Pressure:	2080 psig
Sample Volume:	100 microliters
Peak Area Measurement:	Electronic integrator, Hewlett Packard Model 3380A with recorder



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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.

During this analysis, the quantity of aromatic compounds in the samples was determined by comparing the detector response of a sample (determined by summing the areas of all peaks resulting from the compounds detected), to the response of standards composed of the following: naphthalene, pyridine, naphthoic acid, resorcinol, pyrocatechol, and phenol. This method of quantifying the aromatic compounds in the samples was necessary because the specific compounds present were not known, thus precluding a comparison of sample compounds with standards prepared using the same compounds. However, the fact that the compounds used as standards are known constituents of bilgewater (Ref. 2) and the concentration values of dissolved aromatic pollutants in the samples (presented in later sections) are similar to those observed previously (Ref. 2) lends validity to this quantitative method.

2.4.3 Safety Tests - Ozone and Noise Level Testing

During each experiment the amount of ozone in the ambient environment surrounding the oily wastewater treatment system was monitored. A Mast Development Company oxidant monitor Model 724-4 was used. The monitor sampled air from a point where an operator would normally be positioned.

During one of the tests, the steady-state noise emitted by the operating system was measured using a hand-held noise meter, Bruel and Kjaer Model 2205. Measurements were made on both the dBA (truncated lower frequencies) and the dBC (flat response over 20 to 20,000 Hz) scales. Noise measurements were taken from a variety of locations around the equipment.



2.5 RESULTS

The testing was carried out during a 3-week period in July 1980 at Fort Eustis, VA. Five tests were performed, each approximately 4 hours in duration. The conditions of each test are presented in Table 2-3.

TABLE 2-3. TEST CONDITIONS

Test No.	UV Dosage (watts/L)	Ozone Dosage (lbs/day)	Flow (L/min)	Average Residence Time (min)
1	6.6	1.04	1.00	70.7
2	1.8	1.04	1.00	70.7
3	6.6	1.04	2.45	28.9
4	1.8	1.04	2.45	28.9
5	0	1.04	1.00	70.7

The effects of UV dosage and flowrate on bilgewater quality were tested as defined by the quantity of suspended and dissolved pollutants. Ozone dosage was held constant at 1.04 lbs/day, which produced maximum ozone mass transfer from the gas to the liquid phase (Ref. 11). Two UV dosages were tested: 1.8 and 6.6 watts/liter (watts/L). These dosage values represent the amount of UV radiation between 222.4 and 366.0 nanometers (nm) available per liter of liquid contained in the reactor (Ref. 13). The 1.8-watts/L dosage was produced by using the 700-watt UV lamp (Section 2.3.1.2), and the 6.6-watts/L dosage by using the 1200-watt and 700-watt lamps together. The highest UV dosage obtainable (7.9 watts/L, produced by using the 1200- and 700-watt, and 550-watt UV lamps together) could not be tested because of fear that the additional lamp would overload the power transformer. Test #5 was performed without UV radiation.

Two bilgewater flowrates were tested: 1.00 and 2.45 liters/minute (L/min). These flowrates produced average fluid residence times in the



oxyphotolysis reactor (average residence time = reactor volume/flow) of 70.7 and 28.9 minutes, respectively.

The following sections describe the results of each test in terms of the suspended, dissolved nonspecific, and dissolved aromatic pollutants in the bilgewater before and after each stage of treatment. Section 2.5.4 presents the results of the safety tests.

2.5.1 Suspended Pollutants

Table 2-4 shows the quantity of suspended pollutants in the bilgewater before oil-water separation, after oil-water separation (i.e., before UV-ozone), and after treatment with UV-ozone, for each of the five tests. The values of suspended pollutants measured throughout each test are provided, as well as the values averaged over the duration of each test. Distilled water blanks prepared in the same manner as the samples (Section 2.4.2.1) yielded suspended pollutant blank values of 0.5 mg/L and 0.0 mg/L.

The suspended pollutants in the influent to the oil-water separator (i.e., pre-oil-water separation) decreased throughout each test. The reason for this is unknown. Prior to collecting the time 0 sample, the oil-water separator was operated for 5-10 minutes and the sample line flushed by collecting and discarding approximately 1 liter of the untreated bilgewater. The credibility of the data is enhanced by the close correlation of the influent and effluent suspended pollutant values. The quantity of suspended pollutants in the initial oil-water separator effluent samples (i.e., post-oil-water separation) tended to be the highest compared with the latter samples, as were the influent values.

In each test, the oil-water separator effectively removed suspended pollutants from the bilgewater. The highest value of suspended pollutants in the effluent from the oil-water separator was 7.3 mg/L (test #4) and the lowest value was 0.0 mg/L (test #3). The oil-water separator effluent would



TABLE 2-4. EFFECT OF TREATMENT ON THE REMOVAL OF SUSPENDED POLLUTANTS

Test No.	Test Conditions	Sample Time (Minutes)	Suspended Pollutants				% Removal ^c	% Removal ^d
			Pre-Oil-Water Separation (mg/L)	Post-Oil-Water Separation (mg/L)	% Removal ^b	Post-UV-Ozone (mg/L)		
1	High UV, ozone, low flow	0	52.3	4.2	-	-	-	-
		35	-	-	-	0.2	-	-
		125	6.5	-	-	-	-	-
		130	-	2.8	-	-	-	-
		140	-	-	-	0.0	-	-
		230	33.7	-	-	-	-	-
		240	-	5.1	-	-	-	-
		245	-	-	-	2.9	-	-
	Average	30.8	4.0	87.0	1.0	75.0	96.8	
2	Low UV, ozone, low flow	0	36.9	5.6	-	-	-	-
		35	-	-	-	6.2	-	-
		125	15.8	-	-	-	-	-
		130	-	1.7	-	-	-	-
		140	-	-	-	8.1	-	-
		230	5.6	-	-	-	-	-
		240	-	3.4	-	-	-	-
		245	-	-	-	5.2	-	-
	Average	19.4	3.6	81.4	6.3	+80.6	66.5	
3	High UV, ozone, high flow	0	101.1	1.1	-	-	-	-
		35	-	-	-	0.5	-	-
		125	11.8	-	-	-	-	-
		130	-	0.0	-	-	-	-
		140	-	-	-	0.0	-	-
		230	5.0	-	-	-	-	-
		240	-	1.1	-	-	-	-
		245	-	-	-	0.0	-	-
	Average	39.3	0.7	98.2	0.2	71.4	99.5	
4	Low UV, ozone, high flow	0	45.8	7.3	-	-	-	-
		35	-	-	-	4.7	-	-
		125	9.2	-	-	-	-	-
		130	-	6.4	-	-	-	-
		140	-	-	-	3.3	-	-
		230	8.7	-	-	-	-	-
		240	-	6.6	-	-	-	-
		245	-	-	-	3.5	-	-
	Average	21.2	6.8	67.9	3.8	44.1	82.1	
5	No UV, ozone,	0	31.8	5.5	-	-	-	-
		35	-	-	-	1.8	-	-
		125	8.3	-	-	-	-	-
		130	-	3.8	-	-	-	-
		140	-	-	-	2.0	-	-
		230	2.2	-	-	-	-	-
		240	-	a	-	-	-	-
		245	-	-	-	1.8	-	-
	Average	14.1	4.7	66.7	1.9	59.6	86.5	
Average, All Tests			25.0	4.0	80.2	2.7	33.9	86.3

a - Anomalous value
 b - Average percent removal by first stage (oil-water separator)
 c - Average percent removal by second stage (UV-ozone reactor)
 d - Average percent removal by both stages



probably not have produced a sheen if discharged directly overboard without proceeding to the UV-ozone reactor, since it is generally agreed that bilge or ballast wastewater with a concentration of suspended pollutants less than about 8-10 mg/L will not produce a sheen on the receiving water. The average suspended pollutant removal efficiencies ranged from 66.7% (test #5) to 98.2% (test #3). The average removal efficiency for all five tests was 80.2%.

Prior to the start of the tests, new prefilter and coalescer elements were installed in the oil-water separator. The results demonstrate the ability of these types of oil-water separators to produce high-quality effluents when they are properly operated. The tests were run at flowrates of 1.00 and 2.45 L/min. The nominal flowrate through the oil-water separator is 15 to 19 L/min. It is not known if the low flowrates used during the tests contributed to the excellent performance of the oil-water separator.

Further removal of suspended pollutants resulted from treatment by UV-ozone (test #1, #3, and #4) and from ozone alone (test #5). On the average, 33.9% of the suspended pollutants present in the influent to the UV-ozone reactor (i.e., the oil-water separator effluent) were removed. The process by which the suspended pollutants are removed in the reactor is probably oxidation of the suspended pollutants, which increases their polarity and causes them to dissolve in the water. The dissolved species would be much less likely to be extracted by the Freon solvent and therefore the suspended pollutant value would be less.

During test #2 the concentration of suspended pollutants increased as a result of UV-ozone treatment. The conditions used during test #2 (low UV, ozone, low flow) may have resulted in creating oxidation products more soluble in the Freon than their parent compounds (either dissolved or suspended). The result would be a higher concentration of suspended pollutants in the effluent from the UV-ozone reactor compared with the influent. It is unlikely that the suspended pollutant values in the effluent are anomalous, since the sample collection and analytical procedures were consistent throughout the tests.



2.5.2 Dissolved Nonspecific Pollutants

The amount of dissolved pollutants measured as TOC in both the UV-ozone reactor influent and effluent throughout each test is presented in Figs. 2-15 through 2-19 for test #1 through #5, respectively. The sample times for the reactor effluents are adjusted to reflect the average residence time of fluid in the reactor at the particular flowrates used (Table 2-3). For example, during test #1 the flowrate was 1.00 L/min and the average residence time was 70.7 minutes. Fluid entering the reactor at time 0 will spend an average of 70.7 minutes in the reactor, with some fluid exiting prior to this and some after 70.7 minutes. The 70.7 minutes was subtracted from the time at which each effluent sample was collected to simplify the comparison of the influent and effluent TOC values.

There was significant variability in the concentration of TOC throughout the tests in both the reactor influent and effluent. The TOC variation may have resulted from artificial agitation of the bilgewater (which is vertically heterogeneous with respect to TOC) in the aft bilge compartment, which occurred during the tests. The low flowrates used during the tests necessitated routing approximately 4 GPM of bilgewater back to the aft bilge compartment (see Fig. 2-5) through valve V1, to avoid starving the oil-water separator pump. This created a top-to-bottom and side-to-side mixing pattern within the bilge compartment and probably contributed to the variation in TOC.

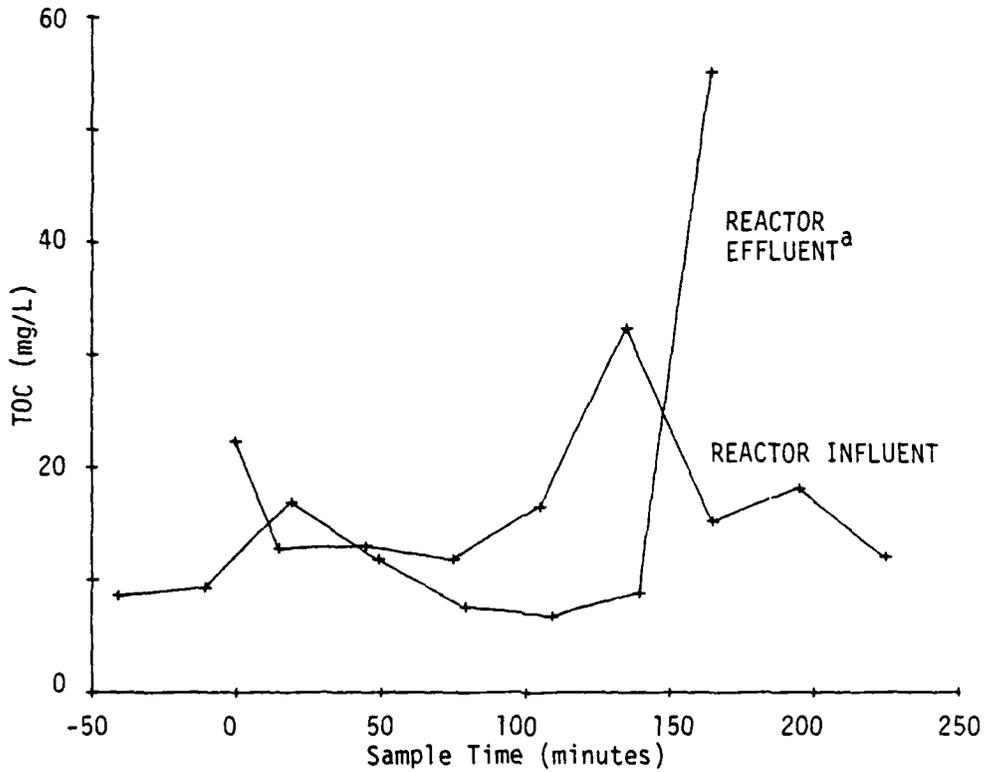
Generally, there is close correlation in TOC variation between the reactor influent and effluent. During test #1 these TOC maxima for both the reactor influent and effluent occurred at approximately 0-20 minutes and 130-150 minutes. During test #2 a coincidental TOC maximum occurred at 0-40 minutes. During test #3, coincidental TOC maxima occurred at 60-80 minutes and 210-225 minutes. A TOC maximum occurred at approximately 120-135 minutes during test #4 and TOC maxima for the reactor influent and effluent during the first part of the test differed by approximately 45 minutes. There was less correlation in TOC maxima during test #5.



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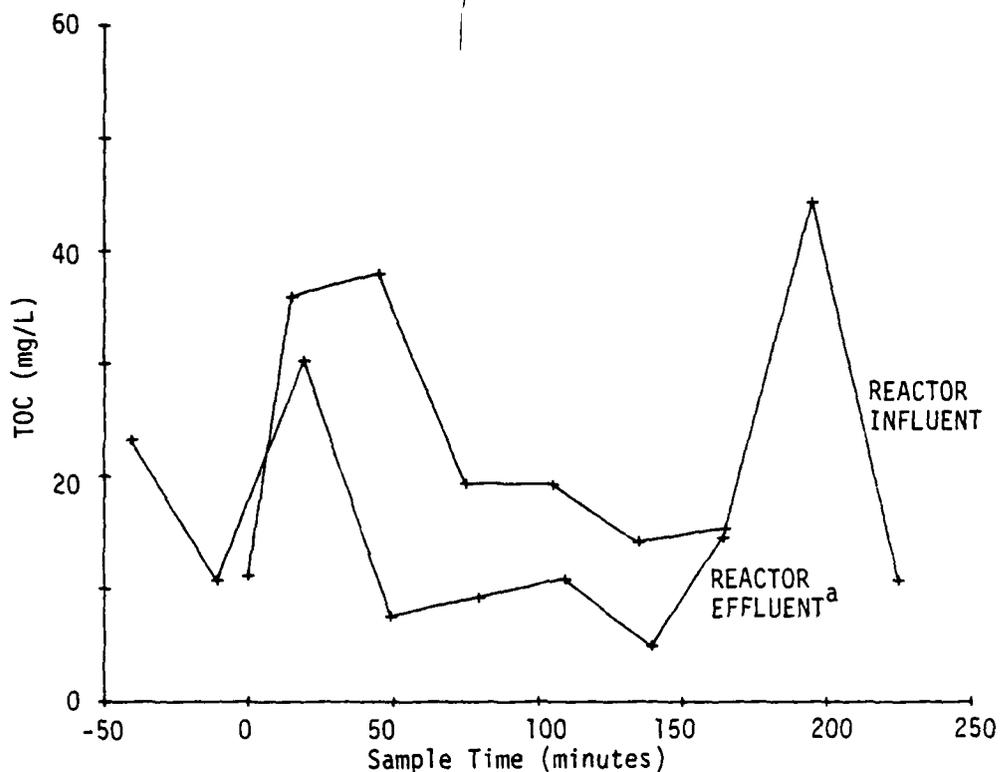
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a. Sample times corrected for fluid residence time in reactor.

Test No. 1 - High UV, Ozone, Low Flow

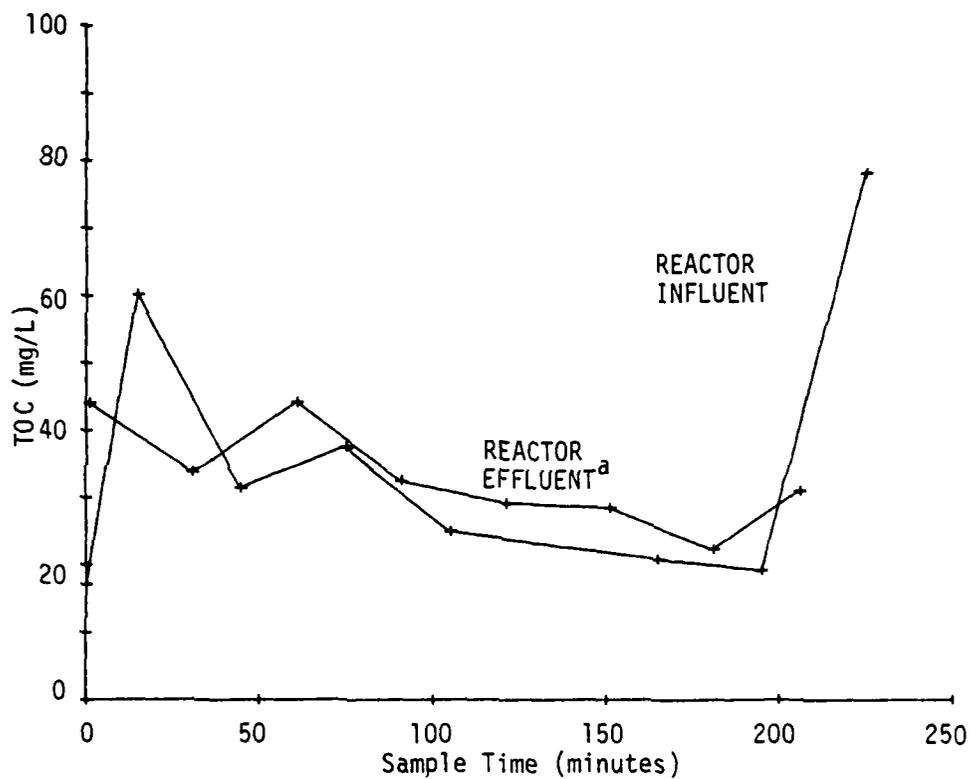
Figure 2-15. Dissolved Nonspecific Pollutants, Test No. 1



a. Sample times corrected for fluid residence time in reactor.

Test No. 2 - Low UV, Ozone, Low Flow

Figure 2-16. Dissolved Nonspecific Pollutants, Test No. 2



a. Sample times corrected for fluid residence time in reactor.

Test No. 3 - High UV, Ozone, High Flow

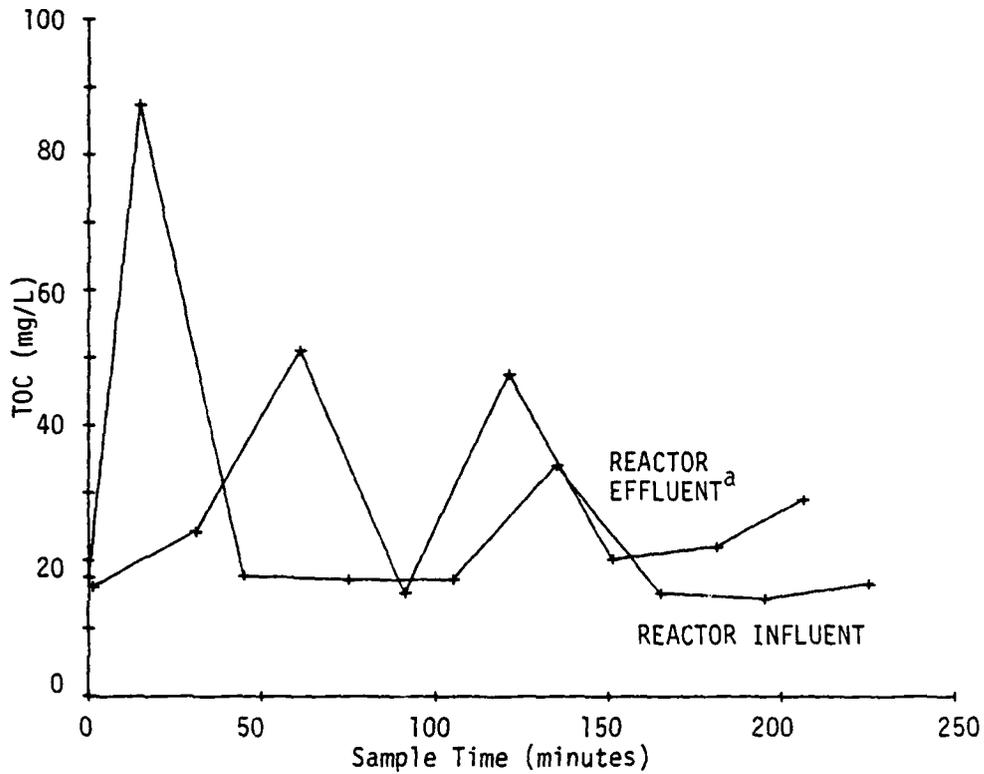
Figure 2-17. Dissolved Nonspecific Pollutants, Test No. 3



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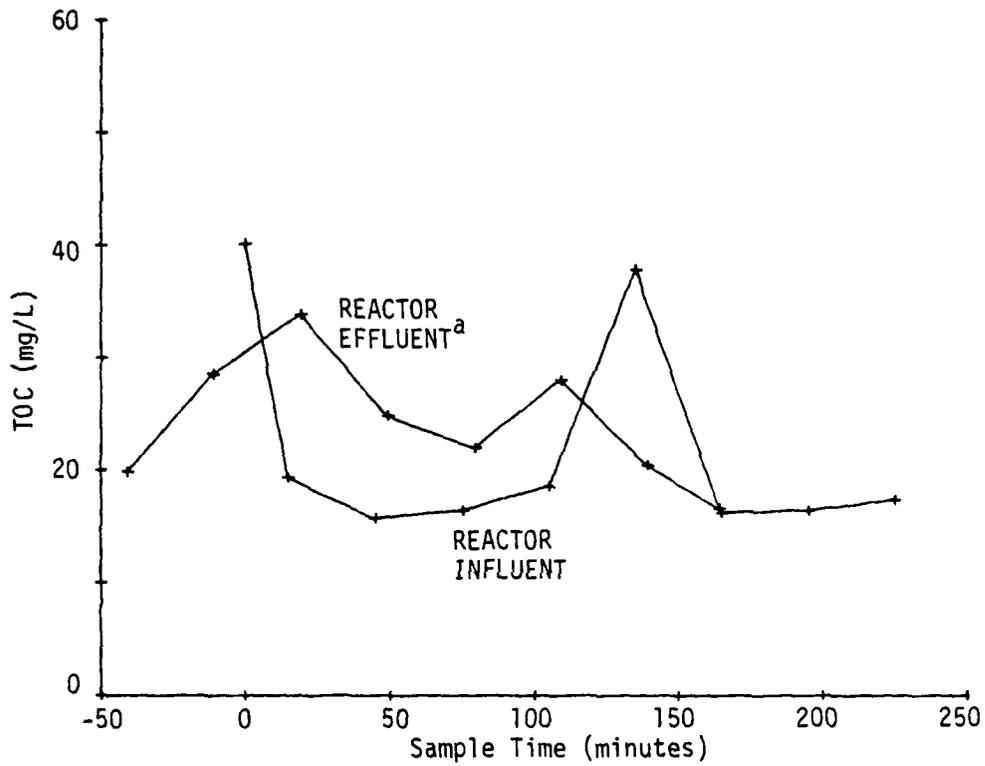
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a. Sample times corrected for fluid residence time in reactor.

Test No. 4 - Low UV, Ozone, High Flow

Figure 2-18. Dissolved Nonspecific Pollutants, Test No. 4



a. Sample times corrected for fluid residence time in reactor.

Test No. 5 - No UV, Ozone, Low Flow

Figure 2-19. Dissolved Nonspecific Pollutants, Test No. 5



There was generally less TOC in the reactor effluent than in the reactor influent during test #1 and #2, and a similar TOC concentration in reactor influent and effluent during test #3. The results from tests #4 and #5 show that during parts of these tests the TOC in the reactor effluent was in greater concentration than in the influent, but in lower concentration during other times.

An explanation that would account for a higher concentration of TOC in the reactor effluent than in the reactor influent is that some of the suspended pollutants may be rendered more soluble in the water by oxidation in the reactor, thus increasing the dissolved TOC level in the reactor effluent. This apparently occurred, since the suspended pollutant concentration was lower in the reactor effluent than in the reactor influent during four of the five tests (Table 2-4).

2.5.3 Dissolved Aromatic Pollutants

Figures 2-20 through 2-24 show the HPLC chromatograms from test #1 through test #5, respectively. Each figure shows four chromatograms, two from reactor influent samples collected at 105 and 225 minutes into the test, and two from reactor effluent samples collected at 120 and 235 minutes. Figure 2-25 shows the HPLC chromatograms for blank samples of James River water and distilled water. Each blank sample was prepared in an identical manner as the samples. Table 2-5 shows the concentration of dissolved aromatic pollutants in the samples whose chromatograms are shown in the preceding figures. The method used to quantify the aromatics is described in Section 2.4.2.3.

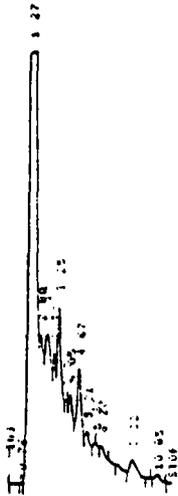
In all of the tests, UV-ozone together (test #1 through #4) or ozone alone (test #5) caused a reduction in the amount of dissolved aromatic pollutants. This can be seen by comparing the reactor influent and effluent chromatograms and from Table 2-5. There is good agreement between the concentration of dissolved aromatic pollutants in both reactor influent samples (105 and 225 minutes) and effluent samples (120 and 235 minutes) from each test, except for test #1, where the 120-minute effluent sample



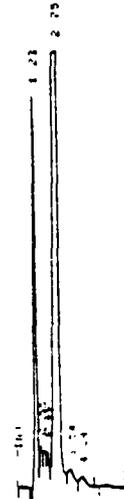
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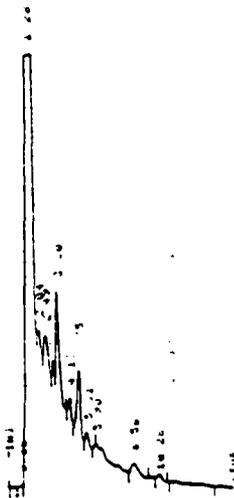
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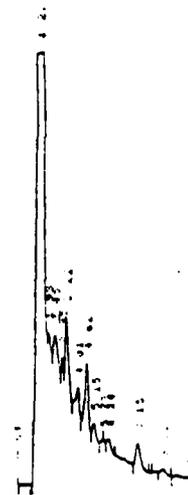
T = 105, Reactor Influent



T = 120, Reactor Effluent

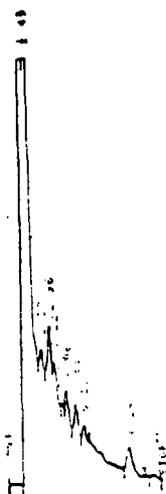


T = 225, Reactor Influent



T = 235, Reactor Effluent

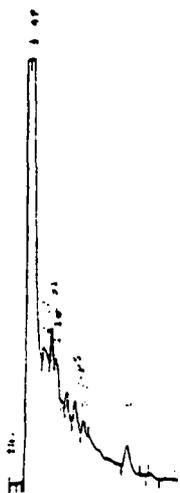
Figure 2-20. HPLC Chromatograms, Test #1



T = 105, Reactor Influent



T = 120, Reactor Effluent

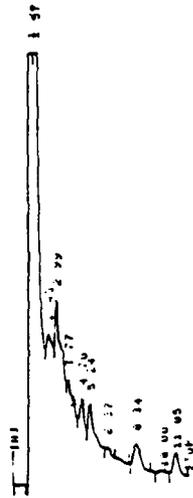


T = 225, Reactor Influent



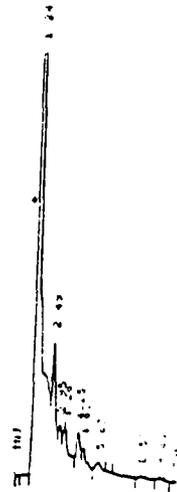
T = 235, Reactor Effluent

Figure 2-22. HPLC Chromatograms, Test #3

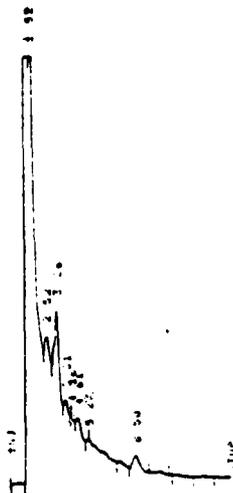




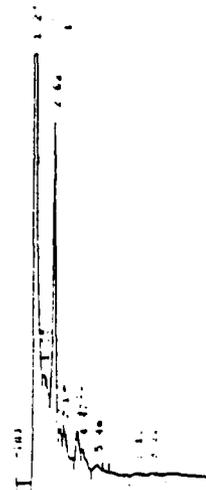
T = 105, Reactor Influent



T = 120, Reactor Effluent

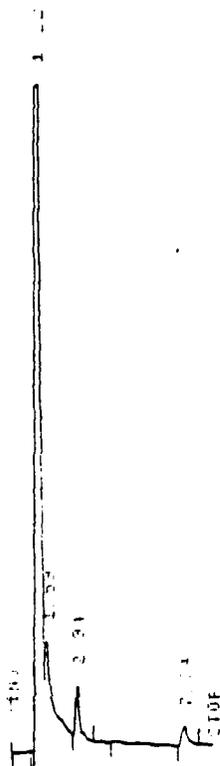


T = 225, Reactor Influent

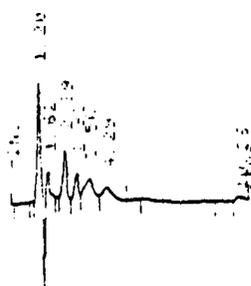


T = 235, Reactor Effluent

Figure 2-24. HPLC Chromatograms, Test #5



James River Water



Distilled Water

Figure 2-25. HPLC Chromatograms, Water Blanks



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TABLE 2-5. DISSOLVED AROMATIC POLLUTANT REMOVAL

Test No.	Test Conditions	Sample Time (Minutes)	Dissolved Aromatic Pollutants (mg/L)	
			Reactor Influent	Reactor Effluent
1	High UV, ozone, low flow	105	16.7	-
		120	-	10.5
		225	17.0	-
		235	-	17.0
		Average	16.8	13.7
2	Low UV, ozone, low flow	105	14.9	-
		120	-	8.0
		225	14.0	-
		235	-	8.1
		Average	14.5	8.1
3	High UV, ozone, high flow	105	16.7	-
		120	-	3.3
		225	17.0	-
		235	-	2.8
		Average	16.9	3.1
4	Low UV, ozone, high flow	105	18.2	-
		120	-	4.4
		225	17.9	-
		235	-	4.6
		Average	18.1	4.5
5	No UV, ozone, low flow	105	17.3	-
		120	-	7.1
		225	16.2	-
		235	-	7.4
		Average	16.8	7.3



contained 10.5 mg/L aromatics and the 235-minute effluent sample contained 17.0 mg/L aromatics. The relatively large amount of aromatics in this sample corresponds to a high level of dissolved nonspecific pollutants also found in this sample (approximately 55 mg TOC/L). However, in other samples there was no clear correlation between dissolved nonspecific and dissolved aromatic pollutant concentrations. In fact, the concentration of dissolved aromatics in the reactor influent remained quite stable (average, 10 samples = 16.6 \pm 1.2 mg/L) throughout the five tests. This evidence suggests that the fluctuations in concentration of dissolved pollutants observed during the five tests was caused by a variation in the concentration of compounds other than aromatics.

In test #1 and #2, a major oxidation product is formed (except in the 235-minute reactor effluent sample from test #1) with an HPLC retention time of approximately 2.80 minutes. This oxidation product does not appear in the other chromatograms. The oxidation product could be from a parent compound dissolved in the bilgewater or from a parent compound which was undissolved (i.e., a suspended pollutant) in the bilgewater when present in the reactor influent but which became more water-soluble as a result of oxidation.

All of the chromatograms show the presence of a polar, UV-absorbing compound with a retention time of approximately 1.2 to 1.3 minutes. This compound or one with a similar retention time was present in the James River water blank sample (Fig. 2-25), although apparently in lower concentration judging by the area underneath the peak. The concentration of compounds detected in the James River water and distilled water blank samples was 3.5 and 0.9 mg/L, respectively.



2.5.4 Safety Tests - Ozone and Noise Levels

The amount of ozone in the ambient environment surrounding the Oily Wastewater Separation System was measured during each test. The background ozone level was recorded prior to each test and the ozone level was periodically noted throughout each test. The results are presented in Table 2-6.

TABLE 2-6. AMBIENT OZONE CONCENTRATION

<u>Test No.</u>	<u>Ambient Ozone Level (ppm-Volume)</u>	
	<u>Ozone Concentration, Pre-Test</u>	<u>Maximum Ozone Concentration During Test</u>
1	0.020	0.030
2	-	0.001
3	0.015	0.020
4	0.005	0.030
5	0.005	0.005

An increase in the ambient ozone level occurred during test #1, #3, and #4. During test #2 the pre-test ozone level was not noted; therefore it is not known if an increase occurred. No increase in the ozone level occurred during test #5. The increase in the level of ambient ozone noted during three of the tests may have been from sources other than the experimental system, either exterior sources or on-board sources such as electric motors. This view is supported by the data from test #5 which showed no increase in the ozone level.

At no time during the five tests did the ozone level exceed the maximum allowable level of 0.05 ppm set forth by the Army (Ref. 14). The highest concentration recorded (0.03 ppm during test #1 and #4) was still 40% below the Army maximum. These results show that the experimental system meets the ozone safety standard of the Army.



Noise level measurements were taken at a number of locations around the test equipment. The measurement locations and the noise levels at these locations (in dBA and dBC) are presented in Table 2-7.

The noise measurements made on the dBA scale (truncated lower frequencies) were consistently lower than those made on the dBC scale (flat response over 20-20,000 Hz). This indicates that much of the noise was produced at the lower frequencies, for example by the on-board generators and machining equipment.

The highest continuous noise level was recorded 1.5 feet away from the bottom front of the ozone generator (79 dBA). This was still well below the 85 dBA limit for exposure to continuous noise during an 8-hour period set forth in MIL-STD-1474A (Noise Limits for Army Materiel), Category D (no hearing protection required). The intermittent noise produced by the cycling of the air dryer was 88 dBA, also well below the 140 dBA limit set forth in MIL-STD-1474A for impulse noise for unprotected personnel. Therefore, personnel would not require hearing protection when operating the experimental system. If other equipment is installed in the vicinity of the experimental system it is conceivable that the noise standard could be exceeded, in which case hearing protection would need to be used.



TABLE 2-7. EQUIPMENT NOISE LEVELS^a

Location	dBA	dBC
Front of reactor, 2 feet away, chest high	76	80
Same as above, 10 feet away	72	77
Same as above, 25 feet away	71	75
Side of reactor, 10 feet away, chest high	74	78.5
Center of installation area, chest high	69	76
1.5 feet away from bottom - front of ozone generator	79	81
1.5 feet to the side of air dryer when solenoid valves changed, meter on fast response (intermittent noise)	88	88
Standing at system control panel, facing equipment, chest high	72.5	76

a. Measured during test #2.



2.6 DISCUSSION

Both stages of the Experimental Oily Wastewater Separation System, the oil-water separator and the UV-ozone reactor, were effective in reducing the amount of pollutants in the bilgewater effluent. On the average, for the five tests conducted, the oil-water separator removed 80.2% of the suspended pollutants from the influent bilgewater. Somewhat surprisingly, the UV-ozone treatment (or just ozone in test #5) reduced the amount of suspended pollutants on the average by an additional 6.1%. This probably resulted from the oxidation and subsequent dissolution of the suspended pollutants by ozone.

In all of the tests the bilgewater effluent from the UV-ozone reactor was remarkably clear, much more so than the reactor influent. Figure 2-26 is a photograph of the three bilgewater samples collected during test #3. The left-hand sample is untreated bilgewater, the middle sample shows the bilgewater after treatment by the oil-water separator, and the right-hand sample shows the clear effluent from the UV-ozone reactor. The improved appearance of the bilgewater after oil-water separation is due to the removal of suspended pollutants and particulates. The clarity of the final effluent is probably due to the solubilization of suspended pollutants and/or the coagulation of colloidal sized material by the action of the ozone. This could happen by a change in the surface charge of the colloid particles brought about by the addition of ozone to the bilgewater (Ref. 15.)

In addition to removing suspended pollutants from the bilgewater, the UV-ozone treatment was effective in removing dissolved nonspecific pollutants (i.e., dissolved TOC) and reducing the quantity of dissolved aromatic pollutants in the bilgewater. A summary of the effects of UV-ozone (test #1 through #4), ozone (test #5) and flowrate on suspended pollutants, dissolved nonspecific pollutants, dissolved aromatic pollutants, and total pollutants (suspended + dissolved nonspecific) is presented in Table 2-8. The values that appear in the body of the table are average values, computed over the course of the tests.



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Figure 2-26. Samples From Test #3 (left to right, pre-oil-water separation, post-oil-water separation, post-UV-ozone)



TABLE 2-8. EFFECT OF UV-OZONE, OZONE AND FLOWRATE ON BILGEWATER EFFLUENT QUALITY

Test No.	Bilgewater Component ^a					
	Suspended Pollutants			Dissolved Nonspecific Pollutants		
	Reactor Influent (mg/L)	Reactor Effluent (mg/L)	% Removal	Reactor Influent (mg TOC/L)	Reactor Effluent (mg TOC/L)	% Removal
1	4.0	1.0	75.0	17.1	15.6	8.8
2	3.6	6.5	+80.6	23.2	14.0	40.0
3	0.7	0.2	71.4	36.2	33.3	8.0
4	6.8	3.8	44.1	26.4	28.3	+7.2
5	4.7	1.9	59.6	22.1	24.3	+10.0
Average, all tests	4.0	2.7	33.9	25.0	23.1	7.9
	Dissolved Aromatic Pollutants			Total Pollutants ^b		
1	16.8	13.7	3.1	18.4	20.5	19.5
2	14.5	8.1	6.4	44.1	26.3	26.0
3	16.9	3.1	13.8	81.7	36.8	33.5
4	18.1	4.5	13.6	75.1	32.2	31.5
5	16.8	7.3	9.5	56.5	26.1	25.9
Average, all tests	16.6	7.3	9.3	55.2	28.4	25.4

a. Values averaged over the course of each test.

b. Total Pollutants - (suspended pollutants x 0.85) + Dissolved Nonspecific Pollutants.



The summary data presented in Table 2-8 provide information about the effects of the two independent treatment variables, UV dosage and flowrate, on the bilgewater components. To facilitate comparisons of tests, the percent removal values from Table 2-8 were used to formulate Table 2-9. In Table 2-9 the effect of UV dosage and flowrate on each bilgewater component is shown by a + if there was enhanced removal with either increased UV dosage or flowrate, by a - if there was lessened removal with either increased UV dosage or flowrate, or by a 0 if little difference was noted. The effect of UV dosage was determined by comparing the results from tests with the same flowrates, tests 1:2, 1:5, 2:5, and 3:4. The effect of flowrate was determined by comparing the results from tests with identical UV dosages, tests 3:1, and 4:2.

While not entirely consistent, Table 2-9 shows that generally, a high UV dosage enhanced the percentage removal of suspended, dissolved nonspecific, and total pollutants, but caused a decreased percent removal of dissolved aromatic pollutants. A high flowrate enhanced the percent removal of suspended and dissolved aromatic pollutants, but resulted in decreased percent removal of dissolved nonspecific and total pollutants.

The results for suspended pollutant removal shown in Table 2-9 must be tempered with the knowledge that the quantity of suspended pollutants removed during the tests was quite small and subject to an error in the range of approximately 0-0.5 mg/L. Such errors would drastically alter the removal percentages shown in Table 2-8, and therefore also alter the results for suspended pollutants shown in Table 2-9.

The fact that the dissolved nonspecific and total pollutants are best removed by the high UV dosage and low flowrate is not surprising. This combination of treatment parameters represents the highest degree of treatment used. The high UV dosage and lengthy reactor residence time afforded by the low flowrate causes maximum oxidation of the pollutants in the bilgewater. These results are consistent with those obtained using solutions of pure organic compounds dissolved in water, artificial bilgewater solutions, and bilgewater during tests conducted in the laboratory (Ref. 11).



TABLE 2-9. EFFECT OF UV DOSAGE AND FLOWRATE
ON BILGEWATER COMPONENTS

Bilgewater Component	Experimental Pair ^a						Best Conditions for Maximum Removal
	Effect of UV				Effect of Flowrate		
	1:2	1:5	2:5	3:4	3:1	4:2	
Suspended Pollutants	+	+	-	+	0	+	High UV, high flowrate
Dissolved Non- specific Pollutants	-	+	+	+	0	-	High UV, low flowrate
Dissolved Aromatic Pollutants	-	-	-	0	+	+	Low UV, high flowrate
Total Pollutants	0	+	+	+	-	-	High UV, low flowrate

+: Enhanced removal with either increased UV dosage or flowrate.

-: Lessened removal with either increased UV dosage or flowrate.

0: Little difference in removal with either increased UV dosage or flowrate.

a. For each experiment pair, the first experiment utilized a higher UV dosage or flowrate than the second experiment.



The combination of low UV dosage and high flowrate, which produced the greatest reduction in the concentration of dissolved aromatic pollutants, is pleasantly surprising, since this combination of treatment parameters represents the lowest level of UV-ozone treatment. At first these results appear to be unusual because the destruction of dissolved aromatics by oxidation would seem to occur most readily at a high UV dosage and with a long reactor residence time. However, an explanation can be offered for the results. The oxidation products formed during maximum treatment (high UV and low flowrate) may, in some way, inhibit attack by ozone of the aromatic compounds (for example due to preferential oxidation of these compounds over the aromatics), thus their concentration remains high. However, at a lower UV dosage and higher flowrate less oxidation products are formed and inhibition of oxidation of the aromatics is lessened. The concentration of dissolved aromatics in the reactor effluent would therefore be less under the lowered treatment conditions.

The destruction of dissolved aromatic compounds is desirable since these compounds are in high concentrations in oily bilge and ballast wastewaters (Ref. 2, Ref. 11) and they are generally regarded as the most toxic constituents of the dissolved fraction of such wastewaters. Removal or conversion to less toxic compounds of dissolved aromatics is preferable to oxidative destruction of nontoxic or mildly toxic compounds that are present as dissolved pollutants in bilgewater. The oxidation products resulting from ozonation of aromatic compounds are generally regarded as less toxic than the parent compounds (Ref. 16).

The final effluent from the experimental oily wastewater separation system was in full conformance with existing regulations which address the discharge of bilgewater. The quantity of suspended pollutants in the effluent during each test was below the level usually considered to cause a sheen or discoloration upon receiving water. In fact, as mentioned previously, the effluent was quite clear and pure in appearance (Fig. 2-26).



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The system was also capable of removing dissolved pollutants from the influent. Up to 40% of the dissolved pollutants (as measured by TOC) were removed during the tests. The effluent produced during test #1 and #2 was in full conformity with the zero pollutant discharge standard to be in force in 1985. It is generally agreed that the 1985 standard will be interpreted to mean that discharges shall not contain more pollutants than present in the receiving water. James River water contained approximately 18 to 20 mg/L of dissolved TOC. Therefore, the effluents produced during test #1 and #2 were cleaner, in terms of TOC, than the receiving water.

Perhaps even more important than this, the on-board tests have demonstrated that the UV-ozone treatment process is able to significantly reduce the concentration of aromatic compounds in bilgewater. Such compounds are generally regarded as the most toxic constituents in bilgewater and their destruction is important in rendering bilgewater effluents harmless.

The data generated during the field testing of the Experimental Oily Wastewater Separation System permits calculation of the costs associated with treatment. This was done and the results are shown in Table 2-10. The power required for treatment was determined during the laboratory study phase (Ref. 11). The total energy required was calculated by multiplying the time (in hours) required to treat 1000 gallons of bilgewater at the particular flowrate used (either 1.00 or 2.45 L/min) by the power requirement. The values for the amounts of energy used per gram of pollutant removed (or converted to nonaromatic species) were calculated for both total pollutants and dissolved aromatics by dividing the total energy required by the quantity of pollutant removed from the 1000 gallons. For example, for test #3 the quantity of dissolved aromatics removed (or converted) in 1000 gallons was:

$$\frac{13.8 \text{ mg/L (from Table 2.8)} \times 3.785 \text{ L/gal} \times 1000 \text{ gal}}{1000 \text{ mg/gm}} = 52.2 \text{ gms}$$



TABLE 2-10. TREATMENT COSTS^c

Test No.	Power Required (KW)	Total Energy Required ^a (KWH)	Energy Used per Gram of Pollutant Removed (or Converted)		Cost (\$) ^b
			KWH/gm Total Pollutants	KWH/gm Dissolved Aromatics	
1	6.07	382.9	25.3	32.6	23.0
2	4.69	295.9	11.5	12.2	17.7
3	6.07	156.3	12.5	3.0	9.4
4	4.69	120.6	45.5	2.3	7.2
5	3.49	220.2	290.9	6.1	13.2

a - Energy required to treat 1000 gallons.

b - Cost to treat 1000 gallons to the levels shown in Table 2-8, assuming an energy generation cost of \$0.06/KWH.

c - Costs associated with power consumption only.

Therefore, the energy used per gram was:

$$156.3 \text{ KWH}/52.2 \text{ gms} = 3.0 \text{ KWH/gm}$$

The final column in Table 2-10 shows the cost of treatment. The generators on board the FMS require approximately 0.08 gallon of DF2 to produce 1 KWH of energy. At an assumed DF2 cost of 75¢/gallon, the cost to generate 1 KWH of energy is 6¢. The cost figures were calculated by taking the product of the total energy requirement and the energy cost. The costs are for power consumption only.

The lowest treatment cost was during test #4, the highest during test #1. These two tests represented the lowest and highest levels of treatment, respectively. Even though test #5 was performed without UV, the low flowrate used during this test produced a higher treatment cost than either test #3 or #4.

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On an energy per gram of total pollutants removed basis, the lowest values occurred during test #2 and #3, even though the conditions used during test #3 resulted in much less removal of total pollutants (see Table 2-8). The energy usage was similar for the two tests because of the higher flowrate used during test #3 which resulted in a lower total energy requirement than in test #2. Test #1 used 25.3 KWH/gm total pollutants. This value is very similar to the values calculated for bilgewater based on batch testing in the laboratory (Ref. 11). The lowest energy usage per gram of dissolved aromatics removed (or converted) occurred in test #3 and #4.

The figures in Table 2-10, along with those in Table 2-8, show that the composition of the effluent will decide the cost of treatment. For example, if the effluent is required to have the lowest possible total pollutant content, then conditions of high UV and low flowrate should be used (Table 2-9). From Table 2-10 it can be seen that costs would range from approximately \$17 to \$23 per 1000 gallons. On the other hand, if conversion of the toxic components of the bilgewater (dissolved aromatic pollutants) to less toxic compounds is desirable and less emphasis is placed on total pollutants, then conditions of low UV and high flowrate should be used. Costs would range from approximately \$7 to \$9.50 per 1000 gallons.

Simple modifications to the experimental system would significantly reduce the treatment costs associated with energy usage. For example, with minor design changes the sump system with its associated pump (Fig. 2-5) could be eliminated. Additionally, the ozone decomposition heater (Fig. 2-4) could be replaced by a catalytic unit. These two measures would reduce power consumption by 1.18 KW. The cost of bilgewater treatment would fall to \$18.50, \$13.30, \$7.60, \$5.40, and \$8.70 per 1000 gallons for the treatment conditions used during test #1 through #5, respectively.



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Further cost reductions could probably be realized by staging the UV-ozone treatment process. As the oxidation reactions proceed, the optimum amount of UV radiation and/or ozone may change. By staging the process, treatment levels could be optimized for each stage and a net reduction in costs could result. More energy-efficient components could be substituted for those currently supplied with the experimental system for lower cost. Additionally, an oxygen feed or an oxygen-enriched air feed (e.g., by pressure swing) to the ozone generator might produce more cost-efficient treatment, as would utilization of that part of the UV spectrum that results in maximum treatment.

The on-board testing of the Experimental Oily Wastewater Separation System showed that the equipment does not produce unsafe noise or ozone levels. The system can be operated for extended periods by personnel without the need for hearing protection. During laboratory testing (Ref. 11) UV leakage from the system was measured. It was concluded from these measurements that UV leakage from the system does not exceed the maximum permissible levels promulgated in AR40-46 (Ref. 17). Thus, it has been shown that a treatment system based on UV-ozone technology can be safely operated in an on-board environment. Noise levels and UV radiation leakage would not be expected to increase over the life of the system. Safe ozone levels in the area of operation could be assured by periodic maintenance procedures (e.g., maintaining tight connector seals on all piping containing ozone). However, as with any installation using ozone, an ozone monitor with audible and visual alarms and with system shut-down capability upon unacceptable ozone level should be used and maintained to assure personnel safety.

In addition to a minor system startup problem experienced with the pulley on the sump pump motor, two system malfunctions occurred during the on-board testing, both in the electronic control systems. The first occurred in the oil-water separator control electronics. Upon startup, a solenoid valve on the effluent line closes for a predetermined time delay to allow the separator to fill with bilgewater. After the time delay the solenoid valve



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is supposed to open to allow processing through the unit. However, during the second test the time delay lengthened far beyond the nominal period. The commencement of this and subsequent tests had to wait until proper valve positioning was achieved. The second electronic malfunction occurred in the control panel (Fig. 2-6) logic circuitry during test #3. One of the integrated circuits (ICs) failed which prevented the automatic startup of the system to proceed past an initial stage. To continue testing, the relays that are controlled by the control panel (see Section 2.3.2.3) were bypassed and the system components were brought on line by using the circuitbreakers as switches. The faulty IC was replaced for test #5.

It is believed that the extreme environmental conditions experienced during the on-board testing may have caused the electronic malfunction in the oil-water separator control circuitry described above. During the period of these tests, the east coast of the United States was experiencing high temperature and humidity. The location of the experimental system, below decks of the steel-hulled FMS in a closed area without air conditioning, resulted in temperatures above 100°F and humidities ranging from 90 to 100% (estimated) during the tests. Such harsh conditions necessitate rugged and well-designed electronics packages to minimize malfunctioning. It should be noted that neither the oil-water separator control box nor the experimental oily wastewater separation control panel were fan-cooled or otherwise well-ventillated.

Other than the malfunctions described above, the experimental equipment performed as intended. The on-board testing showed that the system is compatible with the shipboard environment and systems. The automatic control proved to be enormously helpful in controlling the functioning of what is a fairly complex system. Total automation could be easily built in, including control of all valves. By providing 100% automation of a relatively complex system, operator mistakes would be eliminated and minimum operator training would be required.



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2.7 CONCLUSIONS

The on-board testing of the Experimental Oily Wastewater Separation System has led to the following conclusions:

- The system is capable of removing a high percentage of suspended pollutants from bilgewater.
- The UV-ozone process participates in the removal of suspended pollutants.
- The UV-ozone process produced a significantly cleaner bilgewater effluent than oil-water separation alone.
- The UV-ozone process is capable of removing dissolved pollutants, in the form of TOC, from bilgewater.
- The UV-ozone process is effective in destroying dissolved aromatic compounds in bilgewater.
- The Experimental Oily Wastewater Separation System is a safe system. It produces no noise, ozone, or UV radiation in excess of the maximum promulgated in military standards.
- The energy consumption costs associated with this treatment process could be reduced with minor equipment modifications.

Oil-water separation and UV-ozone appears to be a viable process for the treatment of oily bilgewater. Components and designs with greater energy efficiencies could significantly reduce treatment costs. Additionally, procedures for minimizing the contamination of bilgewater would greatly increase the throughput for such a system.

2.8 RECOMMENDATIONS

The following multiphase program would lead to an operational total pollutant removal system for use on board Army watercraft.



Phase I - Research

Task A. Investigate methods to reduce the concentration of pollutants in bilgewater which would also lessen treatment time and costs. Oil-water mixtures such as bilgewater contain a wide variety of compounds, some of which are relatively easy to oxidize, others difficult. Overall, bilge 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.

Task B. Determine the effects of staging, UV spectral intensity, and oxygen feed to the ozone generator on destruction of pollutants in bilgewater by UV-ozone.

Phase II - Design, Construction, and Testing

Task A. From the information gathered from Ref. 11, from this on-board investigation, and from Phase I, Task B, above, design an automated, ruggedized UV-ozone treatment system using the most energy-efficient components available.

Task B. Construct a prototype of the system designed in Task A.

Task C. Test the prototype system.

Task D. Based on the test results, make necessary design modifications that will result in the final hardware design.



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3.0 REFERENCES

1. Lysyj, I., and E.C. Russell, "Effectiveness of Centralized Bilge Water Treatment - a Field Study," Environment International, Vol. 2, pp. 177-182, 1979.
2. Lysyj, I., "Pyrolysis/Mass Spectrometer Oil-in-Water Analytical System: Analytical Scheme for the Characterization of Bilgewater," final report, Army Contract DAAK02-74-C-0311, 1978.
3. Department of the Army Technical Manual 55-500, "Marine Equipment Characteristics and Data," February 1968.
4. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th Edition, 1975.
5. Lysyj, I., and E.C. Russell, "Transfer of Organics From an Oil Film Into Water," presented before the Division of Environmental Chemistry, American Chemical Society, Philadelphia, PA, 1975.
6. Bollyky, L.J., "Ozone Treatment of Cyanide and Plating Wastes," First International Symposium on Ozone for Water and Wastewater Treatment, December 2-5, 1973, Washington, DC.
7. Kroop, R.H., "Ozonation of Phenolic Aircraft Paint Stripping Wastewater," First International Symposium on Ozone for Water and Wastewater Treatment, December 2-5, 1973, Washington, DC.
8. Swain, H.A., and R.B. Royelle, "Use of Ozone for Treatment of Mine Drainage Discharges," First International Symposium on Ozone for Water and Wastewater Treatment, December 2-5, 1973, Washington, DC.
9. Skelrata, A., "Dye Works Wastewater Decolorization Treatment Using Ozone," First International Symposium on Ozone for Water and Wastewater Treatment, December 2-5, 1973, Washington, DC.
10. Prengle, H.W., C.E. Mauk, R.W. Legan, and C.G. Hewes, III, "Ozone/UV Process Effective Wastewater Treatment," Hydrocarbon Processing, October 1975.
11. Gibson, S.C., "Experimental Oily Wastewater Separation System," final report, Army Contract DAAG53-75-C-0271, 1980.
12. "Preliminary Technical Notes - Amberlite XAD-7," Rohm and Haas product literature.
13. Hanovia product literature.



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14. Personal communication, Mr. Jack Dixon, acting chief, Safety Office, MERADCOM, Fort Belvoir, VA, 28 November 1978.
15. Nemerow, N.L., Liquid Waste of Industry, Addison-Wesley Publishing Co., 1971.
16. Jollez, R.L., and R.B. Cumining, "Oxidant Effects on Complex Mixtures of Nonvolatile Organics in Polluted Waters: Examination by HPLC and Bioscreening," Ozone: Science and Engineering, Vol. 1, No. 1, pp 31-37, 1979.
17. Army Regulation AR-40-46, Protection Standards for UV Radiation, February 6, 1974.

