

**NEW TECHNOLOGIES FOR
CONTROLLING
OILY BILGE WATER DISCHARGES**

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New Technologies for Controlling Oily Bilge Water Discharges

ABSTRACT

US military vessels are limited to oily bilge water discharge concentration of 15 ppm under 40 CFR part 1700, uniform national discharge standards (UNDS). International commercial discharge standards appear to be stabilizing at 5 ppm. In order for these regulations to have the desired effect of reducing oily bilge water discharge, improvements in treatment technology and enforcement must take place. This paper reviews developments in treatment of oily bilge water and detection of oily discharge from ships. New technologies developed to bridge the gap between oil/water separator (OWS) capability of approximately 250 ppm and discharge standard of at most 15 ppm are covered, with emphasis on cross flow membrane filtration technologies and oleophilic polymeric surfactant (PS) infused filtration devices. Developments in detection of oily discharge utilizing synthetic aperture radar (SAR) and enhanced tracking procedures are also reviewed.

INTRODUCTION

Of the oil released by vessels, 25% is reported to come from spills and 75% from operational discharges. Oily bilge discharge is second only to oily ballast tank discharge in its contribution. Historically, oily bilge water has been treated using oil/water separator (OWS) technology or discharged with minimal treatment. OWS technology alone is not capable of meeting current oily bilge water discharge standards. Discharge standard for vessels of the United States armed forces under 40 CFR part 1700, is 15 ppm. International commercial discharge standards are as low as 5 ppm. A variety of technologies have risen to fill the gap between OWS capability and discharge standards. Among these are systems based on gravity separation, size separation, chemical affinity

separation and flocculation. There has also been a gap between regulation and enforcement. Unregulated discharges have been problematic. There have been significant advances in the ability to detect such discharges in the past few years; the most significant of which is synthetic aperture radar (SAR). We will review OWS technology and developments in oily bilge water treatment and detection. For purposes of this paper we will consider engine wet exhaust treatment as similar to bilge water.

REGULATION

Section 312 of the CWA requires the Secretary of Defense and the administrator of the U.S. Environmental Protection Agency (USEPA) to develop uniform national standards to control certain discharges from vessels of the armed forces. These measures are implemented in 40 CFR, Chapter VII and Part 1700, entitled Uniform National Discharge Standards (UNDS).

The following discharges require Marine Pollution Control Devices (MPCD):

- Aqueous Film-Forming Foam
- Catapult Water Brake Tank and Post-Launch Retraction Exhaust
- Chain Locker Effluent
- Clean Ballast
- Compensated Fuel Ballast
- Controllable Pitch Propeller Hydraulic Fluid
- Deck Runoff
- Dirty Ballast
- Distillation and Reverse Osmosis Brine
- Elevator Pit Effluent
- Firemain Systems
- Gas Turbine Water Wash
- Graywater
- Hull coating Leachate

Motor Gasoline Compensating Discharge
 Non-oily Machinery Wastewater
 Photographic Laboratory drains
 Seawater Cooling Overboard Discharge
 Seawater Piping Biofouling Prevention
 Small Boat Engine Wet Exhaust
 Sonar Dome Discharge
 Submarine Bilgewater
 Surface Vessel Bilgewater/Oil-Water Separator
 Discharge
 Underwater Ship Husbandry
 Weldeck Discharges

We will address oily bilge water discharge with some discussion of small boat engine wet exhaust discharge. Discharge limit for oily bilge water under UNDS is 15 ppm but the need to have environmentally sound ships extends beyond U.S. coastal waters. European countries and other countries with large coastlines (i.e. Japan, New Zealand) have been very active in the pursuit of eliminating operational discharges in conjunction with International Maritime Organization (IMO) and independently in some areas.

Nature of Discharge (NOD)

Bilge water arises from a variety of sources, which are allowed to drain to the lowest part of the ships' hull, known as the bilge. Sources include valve and piping leaks, boiler blow-down, and condensed steam. On surface vessels, bilge water is usually transferred to a holding tank where it is stored for disposal or treated in an OWS before being discharged. Oily bilge water contains bio-accumulative persistent organic pollutants (POP's) such as polyaromatic hydrocarbons and chlorinated aromatic hydrocarbons, aromatic hydrocarbons (BTEX) and oil, copper, iron, mercury, zinc and nickel, in addition to emulsifying agents such as detergents and solvents.

TREATMENT

Gravity Separation-OWS Technology

In the past, OWS have been used exclusively for treatment of oily bilge water (OBW) however

this technology is unable to meet the 15 ppm requirement. Many OWS systems on cruise and naval ships produce an effluent in the average range of 100-250 ppm. Ships equipped with oil content monitors (OCM's) have the ability to return bilge water, not meeting discharge standards to the OWS for reprocessing.

The effluent concentration after OWS is more a measure of the degree of emulsification of the influent than of the efficiency of the OWS. With 100% non-aqueous phase pollutants, OWS are capable of achieving quite low effluent concentrations. All OWS's work based on gravity separation driven by density differences. If the suspended particles or droplets have effectively neutral buoyancy, OWS ceases to be effective. Additionally OWS's are ineffective in removing colloidal metals and soluble compounds. By definition, these are close to or at neutral buoyancy. We must look for other properties to exploit in order to achieve the desired reduction of pollutants in bilge water. The technologies discussed below can all be considered post OWS polishers, as OWS technology is optimal as a first step for bulk removal of non-aqueous phase components.

Size Separation – Membrane Technology

Cross Current Flow Membrane technologies essentially work as molecular sieves and have been used to produce pure water in municipal and industrial applications. Cross flow operations typically fall into three categories:

Ultrafiltration (UF), Nanofiltration (NF), Hyperfiltration, more commonly known as Reverse Osmosis (RO) with the following particle size and molecular weight ranges.

RO – 5 to 15 angstroms
 100 to 300 MW

Components Retained: 99% of most ions, most organics over 150 MW

Process Applications: Brackish sea water, Desalting, boiler feed purification,

blowdown reclamation, pretreatment to ion exchange, ultrapure water production.

NF – 10 to 80 angstroms
200 – 10,000 MW

Components Retained: 95% divalent ions, 40% monovalent ions, organics greater than 150-300 MW

Process Applications: Hardness removal, organic and microbiological removal, dye desalting, color removal

UF – 100 to 1000 angstroms
1,000 – 100,000 MW

Components Retained: Most organics over 1000 MW

Process Applications: Pre- and post-treatment ion exchange, beverage clarification, concentration of industrial organics and dilute suspended oils, removal of pyrogens, bacteria, viruses, and colloids.

The most commonly used of these is Reverse Osmosis due to its highest capability for removal of dissolved impurities. There are four major configurations for membrane modules: plate and frame units, hollow fiber, tubular and spiral wound. Membranes are available in a variety of materials. Some common ones are cellulosic and polyamide for RO and NF and polysulfone, ceramic and fluorinated for UF. UF has molecular weight cutoff of 1,000 to 100,000. Pressure ranges are UF – 25 to 400 psi, RO and NF operate in the 500 to 1000 psi range. Crossflow is necessary in membrane systems due to the necessity of running continuously in a self-cleaning mode. This is due to the fact that even a tiny fraction of foulant mass can have a severe effect on membrane performance. Backwashing is not possible because the polymeric membrane is coated onto a support layer. Flow reversal causes separation of membrane from support layer. All cross flow systems separate the influent wastestream into two effluent streams. These are the permeate (purified water which has passed through the membrane) and concentrate (pollutants rejected

by membrane) which must be continuously flushed away.

The inherent tendency of membranes to catch all but the smallest particle sizes renders them susceptible to fouling by organic, inorganic and biological materials. Cross current flow does not suffice in keeping the membranes clean and so they must be periodically cleaned. This can be tricky business, as membrane chemical compatibility may be similar to those of the fouling agent, in which case, the cleaner will also dissolve the membrane. Short of dissolution, membranes can be denatured by solvents, high or low pH's and temperature extremes. At the very least, membrane / cleaner compatibility must be tested. It is unlikely that membrane cleaning will ever be totally eliminated even with the use of low concentrations of chemical cleaning agents in the process stream (Ning). Effective pre-filtration of particulate and chemical fouling agents should be considered when designing a membrane filtration system.

Currently, Ultrafiltration (UF) has been the primary membrane technology utilized in post OWS bilge water polishing. RO and UF membranes are susceptible to organic and inorganic fouling. UF systems are not fine enough to capture ionic pollutants and therefore inorganic fouling has not been an issue. UF systems are able to capture most organic compounds over 1000 mw and are consequently susceptible to organic fouling.

Ceramic module ultrafiltration systems have been tested and used on naval ships for treatment of OBW with generally good results. The systems are able to achieve a reduction from approximately 232 ppm to < 5 ppm at flow of about 5 gallons per minute (GPM). Ceramic UF systems require periodic cleaning and maintenance and can be overwhelmed by concentrated slugs of influent, however they are more robust than most polymeric membranes and can withstand wider pH and temperature ranges therefore making cleaning easier. Better pre-filtration of organics (especially concentrated slugs) would probably make the system more efficient and more cost effective.

Chemical Affinity Separation-PS Technology

Chemical Affinity Separation involves the use of standard filter materials infused with curable polymeric surfactant (PS). Once cured into a substrate, the oleophilic properties of PS are transferred into a substrate, thereby greatly enhancing its' ability to attach organic compounds to its' matrix. Once attached, these compounds become hydrophobic and tend not to re-release.

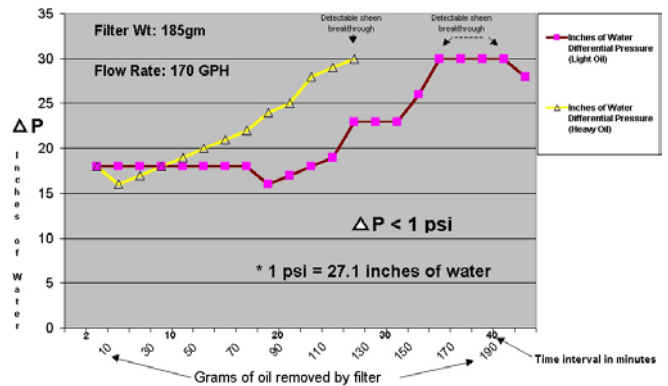
Regular 5-micron melt-blown polypropylene (MBPP) filters treated with curable viscoelastic PS results in a filter similar in capability to cross flow UF membranes for removal of organic compounds and colloidal metals. PS infused filters exhibit less than 1 psi pressure drop across the filter to saturation. (See Figure 1 and Table 1)

Table 1

Removal of Colloidal Metals	
MYCELX	
Cadmium, ICP	<0.020
Chromium, ICP	0.026
Copper, ICP	0.351
Lead, ICP	<0.10
Nickel, ICP	<0.050
Silver, ICP	<0.020
Zinc, ICP	<0.020
After Flocculation	
Cadmium, ICP	<0.020
Chromium, ICP	0.070
Copper, ICP	0.452
Lead, ICP	<0.10
Nickel, ICP	0.052
Silver, ICP	<0.020
Zinc, ICP	0.884
Holding Tanks	
Cadmium, ICP	<0.020
Chromium, ICP	0.062
Copper, ICP	1.0
Lead, ICP	0.12
Nickel, ICP	0.060
Silver, ICP	<0.020
Zinc, ICP	3.1
All Tests EPA Method 200.7	

Pressure Drop Analysis

Figure 1



ΔP vs. % Saturation

This is a critical property that enables PS to capture concentrated slugs of oil without clogging the system, therefore making them useful as pre-filters for more sensitive and therefore easily fouled filtration methods.

PS technology works by chemically immobilizing the pollutants into the filter matrix. The filters can be regenerated and the oil recovered water free by centrifugation up to 100 times. This technology has been utilized in multiple oily bilge applications in different ways, two of which are highlighted below.

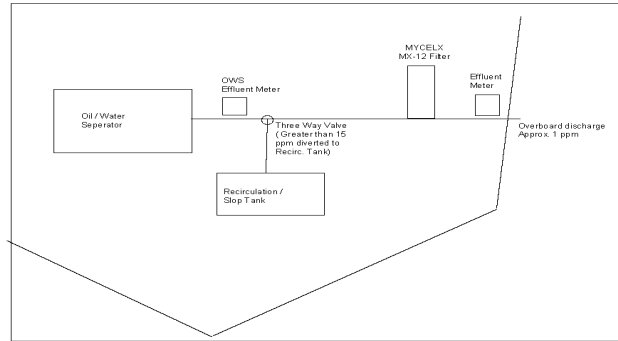
PRIMARY POLISHING TREATMENT

The pictured unit in figures 2, 3 and 4 is a MX-22 PS Technology device. It contains (22) 30-inch length, 5-micron MBPP filters infused with PS. This unit sees an average of 250 ppm post OWS effluent and discharges less than 1 ppm effluent in a single pass, even when periodically exposed to slugs as concentrated as 10,000 ppm. This system has been used for one year and has required only 1 filter set changeover. Spent filters are regenerated by centrifugation. Discarded filters are incinerated. (See Figures 2-4) It is an interesting property of PS technology that high oil loading improves its' ability to capture highly emulsified oils and colloidal metals. PS filters are not capable of capturing metals that are not organically bound.

Figure 2



Figure 5



Cruise Ship Oily Bilge Water

Figure 3



SECONDARY POLISHING

This trial was conducted in conjunction with a major cruise line on its' flagship vessel. The ship is equipped with a clay filter followed by two OWS in series and an oil content monitor. Effluent is re-circulated until a concentration of 15 ppm is achieved.

A PS MX-12 unit (twelve 30" 5 micron filters) was installed post OWS to assure a margin of safety before discharge. To date, this system has processed 99,000K gallons of 15 ppm bilge water in 3 weeks (~ 4000K gal/day) and discharge concentration has remained below 1 ppm. One filter set replacement has been required. Approximate quantity of oil removed was 15 lbs.

Figure 4



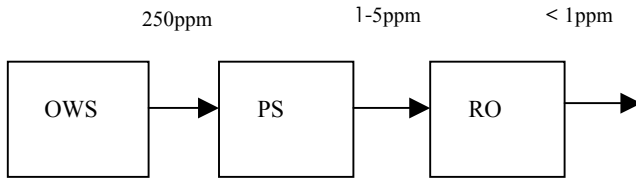
Treatment of Oily Bilge Water on Oil Drilling Ship

PRETREATMENT TO ENHANCE MEMBRANE PERFORMANCE

A third type of use for PS MX units which is being field tested for industrial applications but is also applicable to oily bilge applications is in pre-filtration to enhance the robustness and performance of membrane filtration systems. As stated earlier these systems are susceptible to organic and metallic colloid fouling. The ability of PS units to absorb concentrated slugs without breakthrough or pressure drop makes them ideal chemical prefilters to work in conjunction with membrane systems. Most of the time the membrane will see clean water greatly reducing fouling and preserving capacity. The membrane

capacity is conserved for NF or RO range pollutants. Preliminary results indicate that membrane life is extended about 20 fold while operating costs are reduced by 50%.

Figure 6



Composite Unit

We feel that similar improvements would be realized in UF membrane bilge systems currently in use. It is interesting to note, contrary to our expectations, that OBW we have encountered has not been sufficiently emulsified to require NF or RO polishing post PS MX filters. In most cases post PS effluent is BDL (below detectable limits). It appears that measures taken to segregate emulsifiers from OBW are having an effect.

OTHER METHODS

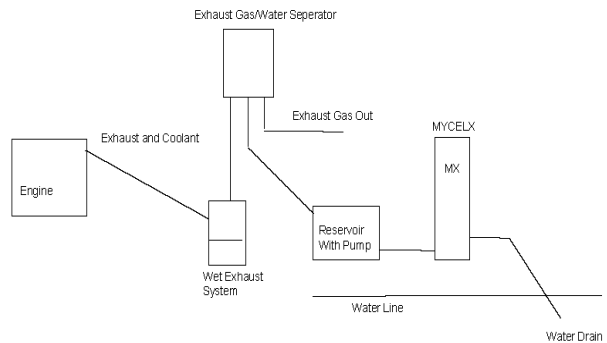
Various other methods have been developed for bilge water treatment. I will briefly mention these.

- OWS / flocculation – these systems follow OWS with flocculate in treatment tanks followed by additional filtration of effluent to remove the flocculating agent. Flocculating agent is then dewatered.
- Biological – mechanical separator followed by a biological chamber consisting of oil eating microbes supported in matrix. Microbe systems have lacked “robustness” in the past.
- Emulsifying agents, which render oil digestible to microbes.
- Burning after heating and vapor separation.

EXHAUST METHODS

Exhaust gas discharge can contain many of the pollutants present in bilge water including BTEX, metals, diesel and oils. Exhaust discharge directly into the water has become a significant waste minimization initiative. PS infused filters have been used to polish wet exhaust processed through water separation devices resulting in effluent less than 1 ppm concentration. Figure 7 is a schematic of process flow for this system. When treated this way, wet exhaust polluted water can essentially be looked at as another source of bilge water.

Figure 7



Wet Exhaust Treatment System

DETECTION OF DISCHARGES

The need to have environmentally sound ships extends beyond US coastal waters as European countries and other countries with large coastlines (i.e. Japan, New Zealand) have been very active in the pursuit of eliminating operational discharges in conjunction with International Maritime Organization (IMO) and independently in some areas.

One of the areas in which European and other foreign countries have been very active in is detection and enforcement. The development of Synthetic Aperture Radar (SAR) has made it possible to detect surface or dissolved oil day or night under a variety of weather conditions discharged above or under the surface. Synthetic aperture radar as the name implies does not

actually use a lens like conventional systems. The aperture is actually the arc described by an orbiting satellite in a given period of time. Sensors monitor scattered electromagnetic reflections in this time period and a computer image is generated. One of the interesting properties of the SAR is that higher resolutions can be achieved at greater distances due to larger lens (arc) radius.

The European space agency has been working on oil detection at sea using its SAR, ERS1 and ERS2 (European Remote Earth Sensing Satellites). These satellites have successfully been able to detect test and real spills and have been used for observing discharge trends.

A study of 660 SAR images acquired over the southern Baltic, the North Sea and the Gulf of Lyon in the Mediterranean Sea by ERS2 taken since 1996 indicates that seas are most polluted along the main shipping routes. SAR images acquired during descending (morning) and ascending (evening) satellite passes show different percentages of oil pollution, because most of the pollution occurs during night time and is still visible on the SAR images acquired in the morning time. The fact that most discharges occur at night is a strong indicator of the need for effective monitoring.

Japan has deployed a SAR system since 1991 consisting of x-band (9.55 GHz) and L-Band (1.27 GHz) resulting in high-resolution images. The purpose of CRL/NASDA is to monitor earth's environment and disasters. The United States hyperspectral NEMO satellite will also have the ability to detect oily discharges. In the past, other methods have been tested such as the use of an infrared line scanner coupled with side looking airborne radar (SLAR) to detect oil discharges from ships (ISOWAKE experiments), with mixed results.

Much work has been done up to now to detect illegal ocean discharges. It appears that SAR systems will be able to provide a higher level of detection and enforcement than was possible until recently. Besides satellite observation, other types of measures are also being considered. One idea would be to use a black

box operating on the basis of probes to indicate the level and nature of the liquids ejected. The International Maritime Organization (IMO) is studying the possibility of equipping passenger ships with a black box to record safety-related parameters so as to determine the cause of accidents, as is the case onboard aircraft. The aim is to supplement this type of equipment with "environmental indicators". A second idea would be to mark cargoes, or the fuel, with a coloring to ensure traceability and to be able to work back to the polluting vessel. A computer system for keeping tabs on shipping traffic is being put through its paces at the regional safety and emergency center (CROSS) in Jobourg (Manche). This system could be used to identify polluting vessels by spotting the whereabouts of oil slicks in relation to the route followed by ships. This approach could be used to complement the two other solutions.

DISCUSSION

Both enforcement and technology capable of meeting discharge standards are necessary to reduce oil pollution caused by ships. It appears that detection and tracking technology and the political desire to enforce regulations will make it much more difficult in the near future to discharge oily bilge water that is not in compliance with local standards. Although we primarily discussed the results of SAR imaging, there are multiple local efforts under way ranging from aerial surveillance utilizing infrared line scanners to utilization of more conventional satellite detection systems.

Regarding treatment technologies, the ultimate oily bilge water treatment technology has probably not yet been built. All the technologies mentioned in this article have their good points and weaknesses. Processes sensitive enough to capture highly emulsified or dissolved organic compounds are susceptible to fouling, requiring maintenance and expense. Conversely, processes that are not susceptible to clogging are not capable of always capturing the most highly emulsified or dissolved organic compounds.

The optimal system must be sensitive yet robust. This probably implies a 2 to 3 stage system, as adequate protection of sensitive components is probably a critical element in overall system robustness. It is also possible that OWS could be made more efficient by rendering collecting surfaces more oleophilic thereby reducing the need for pre-filtration.

The author does not believe that emulsifying agents which carboxylate paraffins thus rendering them digestible to most microbes is a prudent way to go, although probably the most facile. Use of these materials will ultimately alter nutrient balance especially in fresh water, thus leading to much faster eutrophication.

CONCLUSION

The importance of treating OBW is illustrated by the number of technologies that have developed to treat this waste stream. The ultimate oily bilge water treatment system probably has not been built yet and will most likely be a composite utilizing multiple technologies. Detection of oily discharges and the ability to track to specific ships will probably become a reality regarding enforcement within the next 5 years.

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