MYCELX TECHNOLOGIES CORPORATION

# REGULATORY AND TECHNOLOGICAL DEVELOPMENTS IN THE TREATMENT OF OILY BILGE WATER

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# REGULATORY AND TECHNOLOGICAL DEVELOPMENTS IN THE TREATMENT OF OILY BILGE WATER

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## 1. 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 technology (OWS) or discharged with minimal treatment. OWS technology alone is not capable of meeting current oily bilge water discharge standards in many cases. There has been much work in the past in regard to determining what the discharge standard should be for oily bilge water and how best to detect and monitor the discharge. The result appears to be that 15 ppm will be the standard of discharge for oily bilge water, although within localities more stringent limits exist.

A variety of technologies have arisen 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 is Synthetic Aperture Radar (SAR). This paper will review developments in detection technology and oily bilge water treatment.

## 2. Regulatory Developments

### 2.a. Regulations

In the past decade the regulatory horizon in regard to treatment and disposal of oily bilge water has changed greatly. The IMO (International Maritime Organization) has been the leader in development of regulations. The International Convention for Prevention of Pollution from Ships (MARPOL 73/78) sets the standard in regard to bilge water and other forms of ship-generated pollution. The Act to prevent pollution from ships (33.U.S.C. # 1901 et seq.) is the US legislation implementing certain provisions of MARPOL. Coast guard regulations (33 CFR # 151,153 and 155) as amended by Oil pollution act (OPA) and Clean water act require oily wastes discharged within 12 nautical miles of shore have an oil content fewer than 15 ppm. Various localities have more stringent requirements and some restrict any discharge and require onshore treatment.

The National Defense Authorization Act of 1996 amended Section 312 of the Federal Water Pollution Control Act (also known as the Clean Water Act (CWA) to require that the Secretary of Defense and the Administrator of the Environmental Protection Agency (EPA) develop UNDS (Uniform National Discharge Standards) for vessels of the armed forces. (Section 312 (n) (1)). 40 CFR Part 9 and Chapter 7 (EPA), 40 CFR Chapter 7 (Department of Defense) completes the first phase of the three phases to set UNDS for armed forces vessels. The phase 1 rule determines the type of vessel discharges that require control by MPCD's (Marine Pollution Control Devices), which includes surface bilge water and oil water separator discharge. This rule creates a new 40 CFR part 1700 establishing UNDS that apply to discharges. This regulation is promulgated under the authority of section 312 and 502 of the Clean Water Act (333 U.S.C. 1322 and 1362). Any new device must conform to MEPC .60(33) (Marine Environmental Protection Committee) as promulgated by MARPOL in which the standards of performance are set for oil filtering equipment.

**2.b. Enforcement**

Enforcement of regulations has traditionally been problematic in regard to bilge water discharges. Satellite monitoring data indicates that the highest concentration of bilge water discharge is right before sunrise, indicating that most of the discharges occur at night. Technological developments in the last two decades have made detection of illegal discharges more feasible. The technologies currently utilized for this purpose are as follows:

**2.b.1. Technologies/Sensors for Oil spill Surveillance**

- Detection of the potential presence of oil: Airborne **SLAR**, Satellite **SAR**.
- Identifying oil spills: Airborne **LFS** (Laser Fluoro Sensor).
- Determination of Oil spill thickness: Airborne **IR/UV** Line Scanner, **MWR** (Microwave Radiometer).
- Detect potential presence of a likely pollution culprit: Airborne SLAR, Satellite SAR.
- Identification of the likely pollution culprit: Airborne **FLIR** (Forward-Looking InfraRed).

**2.b.2. SAR Development**

- **Early Imaging Radar – SLAR**

The first imaging radars were Side-Looking Airborne Radars (SLAR's) developed for reconnaissance purposes. SLAR is known as "Real Aperture Radar" because its along-track resolution is determined by the size of the physical antenna footprint.

These radars at wavelengths of 2 cm, can image the Earth's surface under day/night conditions. The track resolution of SLAR is limited by antenna length.

The development of SAR (Synthetic Aperture Radar) overcomes this problem by incorporation of a pulsed coherent radar in conjunction with a synthetic aperture which is not limited by the fixed footprint of the radar dish. The size of an aperture in a SAR system is proportional to the length of the arc described by the satellite during signal collection. This results in the curious property of SAR systems having higher resolution at greater distances. SAR systems can be used at longer wavelengths than SLAR. Oil spills can often be detected in SAR imagery because the oil changes the back- scatter characteristics of the ocean. Radar back-scatter from the ocean results primarily from capillary waves through Bragg scattering. The presence of oil dampens the capillary waves, thereby decreasing radar back-scatter. Thus, oil slicks appear dark in SAR images relative to oil-free areas (Figure 1).

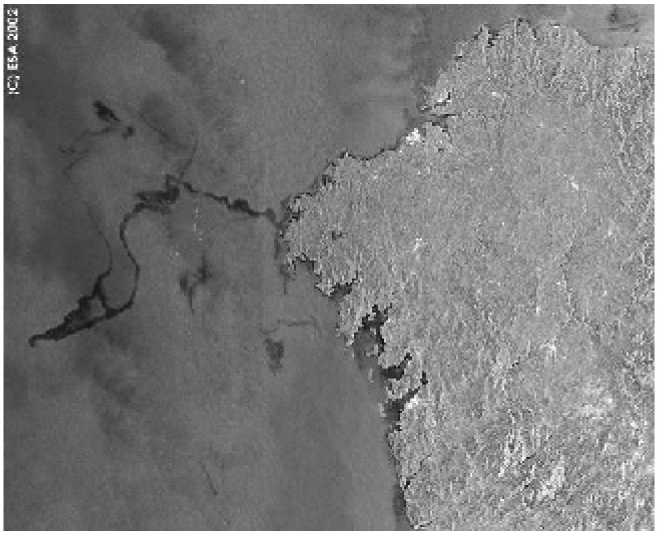


**Fig.1 The SAR Wide Swath image above was acquired over the Galician coast in Spain on 17 November 2002, i.e. few days after the Prestige tanker start to spill massive amount of oil.**

- **Seasat SAR**

The first space based imaging radar to be used for imaging of the earth was the L-band SAR on Seasat, launched in 1978. Seasat SAR was a single parameter instrument using a fixed wavelength, polarization and incidence angle and hence produced severe geometric layover distortions.

- **Shuttle imaging radars (SIR)**

SIR-A, SIR-B space based SAR's followed Seasat SAR with articulating antennas providing variable incidence angles (15-60 degrees). This demonstrated potential for using incidence angle back-scatter signatures which later led to the second generation SIR-C/X-SAR's incorporating multi-frequency, multi-polarization, variable incidence angle. The multi-parameter capability of the SIR-C/X-SAR, coupled with the introduction of routine sensor calibration, opened a new regime in SAR-based scientific applications. Oil spills are detectable and the multi-parameter capability permits oil type and oil-surfactant differentiation to be determined.

For oil spill detection, low resolution (LRI) SAR images with a spatial resolution of 100m*100m have been found to be suitable.

- **ERS-1, ERS-2**

Based upon the Seasat experience, the European space agency (ESA) embarked on the development of the ERS-1, ERS-2 satellites which incorporated a C-band SAR with a single frequency, single polarization and fixed incidence angle-23 degrees. The ERS-1 and ERS-2 are being flown in tandem mode (flying one after the other along the same track) to allow inter-ferometric processing of images from both spacecrafts. The SAR onboard the ERS satellites are the most suitable single instruments for oil spill detection onboard present and near-future satellites.

The oil spill detection capabilities of different radar satellites:

- **ERS-1, ERS-2:** Adequate for oil spill detection at low and moderate winds (2-8m/s).
- **RADARSAT-1** (Canadian Radar Satellite): acceptable for oil spills when operating in Narrow-Scan SAR-Near-Range Mode.
- **ENVISAT**: The wide Swath mode of this unit is useful in oil spill monitoring.

NOAA is exploring the possibility of participation in the Marine SAR Analysis and Interpretation system (MARSIAS) effort. This is a multinational project sponsored by the European Union with the goal of producing a comprehensive coastal ocean oil spill detection and monitoring system using SAR and other remote sensing data.

### 2.b.3. IMO Mandated Black Box

International Maritime Organization (IMO) has been studying the possibility of equipping ships with Voyage Data Recorders (VDR) and Automatic Identification Systems (AIS). The aim of is to supplement this type of equipment with "environmental indicators." The mandatory regulations for certain ships to carry VDR and AIS (MSC 73/21a2.doc Regulation 20 Annex 7) came into force on July1, 2002.

Utilization of the above should make it possible for the first time to be able to detect illegal discharges and track the discharge back to its specific vessel.

## 3. REVIEW OF CHEMISTRY OF BILGE WATER AND ESTABLISHED TREATMENT TECHNOLOGIES

### 3.a. Nature and properties of bilge water

Bilge water is a chemically complex mixture of solvents, surface active agents (surfactants, i.e. soap), metal salts such as greases and lubricants and tramp oils (i.e. compressor condensate). Some of the above are bio-accumulative persistent organic pollutants (POP's) such as polyaromatic hydrocarbons and chlorinated aromatic hydrocarbons. Others such as aromatic hydrocarbons (BTEX) and oil, copper, iron, mercury, zinc and nickel, organic metal salts in addition to detergents and solvents are aquatic toxins

Generally speaking organic non-polar compounds (oils) are not soluble in water. However if solids, solvents or surfactants are present, oils will tend to emulsify in water. The degree of emulsification is inversely proportional to the buoyancy of the micelles. If sufficient emulsification occurs to achieve neutral or closed to neutral buoyancy gravity separation devices lose their effectiveness in separating the organic compounds from water. One way to gauge the relative solubility of a surfactant and thereby the type and stability of the emulsion is the HLB (Hydrophile – Lipophile Balance) method. In this method a number between 1 and 40 is assigned to many commercial emulsifying agents, which is indicative of the balance of hydrophilic to lipophilic portions of the molecule. The higher the HLB, the more water-soluble the material. The water solubility of an emulsion or a surfactant can be used to make an approximation of its HLB which is indicative of the stability of the emulsion.

| Behavior in Water | HLB Range |
|---|---|
| No Dispersability | 1-4 |
| Poor Dispersion | 3-6 |
| Milky Dispersion After Agitation | 6-8 |
| Stable Milky Dispersion | 8-10 |
| Translucent To Clear | 10-13 |
| Clear Solution | 13+ |

The average approximated HLB is one criteria which can be used to evaluate the optimal bilge water treatment system for a particular vessel.

### 3.b. Review of principles of OWS (Oil Water Separator technology)

Oil water separators are Gravity Separation devices which utilize a difference in buoyancy of two immiscible liquids to achieve separation. There are variety of configurations which are utilized including but not limited to underflow weirs, parallel plate coalescers and centrifugation devices. OWS are very effective when two discrete phases are present. When emulsification or solvation occurs buoyancy differences are too small to be exploited utilizing existing OWS technology. In this case upstream or downstream technology must be employed in order to sufficiently clean bilge discharge. Typical bilge water concentrations range from 200-2000 ppm. The presence of neutral buoyancy particulate matter tends to further complicate the waste stream and the treatment technology. We will review some emerging technologies in regard to oily bilge water treatment which are either upstream or downstream of the OWS (as gravity separation is optimal as a first step for bulk removal of non-aqueous phase components).

## 4. EMERGING TECHNOLOGIES IN THE TREATMENT OF OILY BILGE WATER

**4.a. Biological oxidation** of OWS-treated oily bilge water in a support medium in which hydrocarbon degrading bacteria are bound by a biological glue (secreted by the bacteria). Oil and related contaminants are degraded in this bio-layer as the bacteria oxidize the hydrocarbons. One of the U.S.C.G and I.M.O approved Biological Oxidation systems is the PetroLiminator100. While biological systems can meet the proposed BOD discharge limits of 26 ppm, the effluent of the biological process contains a high concentration of non-biodegradable organics which do not consistently meet the proposed limits for COD(Chemical Oxygen Demand) and TOC (Total Organic Carbon) when exposed to high-strength oily bilge water. This necessitates post bio-oxidation treatments like Advanced Chemical Oxidation.

**4.b. Chemical Oxidation :**Oxidation processes utilizing chemical oxidizers such as peroxides especially in the presence of ultraviolet light is a well-known technology utilized in the production of high purity industrial water. Although these systems can be very effective, especially at lower influent concentrations, fouling and maintenance can result in higher than expected costs. Additionally peroxides are dangerous compounds which can become unstable and even explosive when not properly stabilized.

**4.c. Vapor Phase Extraction**: Vapor phase extraction of oily and greasy components from oily bilge water using supercritical CO2 or steam can be very effective but costs tend to be high due to the high cost of heating and cooling. Studies are still being done on the extent of recovery of carbon dioxide from bilge water and other economic concerns on the process include the recompression costs on the CO2 system.

**4.d. Surface Modified Filtration Devices:** Granular substrates and absorbents or cartridge filters can be modified with “curable polymeric surfactants” (referred to as “MYCELX”) which have affinity for emulsified droplets (Figure 2). These devices are generally used post-OWS to remove highly emulsified materials (Figures 3-6) and to bring the effluent concentration to below 1 ppm. These units have affinity for organic compounds and do not develop additional differential pressure in the presence of very thick oils or under high loading conditions. Another advantage of these units is the time invariance of the affinity reaction, resulting in a fixed footprint. A fixed size unit can handle influent concentrations over 2000 ppm and at flow rates from 5-150 gpm without affecting the effluent concentration which will remain constant at well below 5 ppm. The spent filters can be used as an alternative fuel if feasible. The disadvantage of this unit is that the spent filters cannot be discarded into the sludge tank without shredding.

**Fig.2: Partially Saturated vs. Unsaturated Filter**

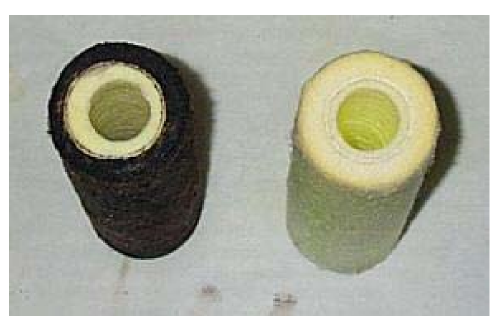

Fig.3

Fig. 5

Fig.4

Fig.6

**Fig. 3 and Fig. 4  MYCELX filters employed in treatment of Naval bilge water at 300 gpm (Photos by Kirk Abbott).**

**Fig. 5 and Fig. 6:  MYCELX filters cleaning emulsified oil on oil drilling rig. Clean water being discharged directly overboard**

**4.e. Membrane Filtration (Ultrafiltration):** It is determined that Ultrafiltration is a viable separation process for the treatment of bilge water for compliance with overboard discharge. Commercial treatments of bilge water using membranes include those with non-cellulosic and ceramic substrates. Non-cellulosic membranes are able to capture most organic compounds over 1000 (Daltons) Molecular Weight, and are consequently susceptible to irreversible membrane fouling. Ceramic membranes have been tested and used in naval ships for treatment of oily bilge water with generally good results. They require periodic cleaning and maintenance and are overwhelmed by concentrated slugs of influent. Combined Centrifugal separator/Membrane Ultrafiltration systems and Ultrafiltration/Membrane Distillation systems have also been investigated for treatment of large volumes of bilge water that contain high concentrations of emulsified and free-phase oil, as well as suspended solids.

**4.f. Flocculation:** Flocculation units are utilized in conjunction with high performance gravity separation devices (generally centrifuge) to good effect. Effluent concentrations below 15 ppm are obtainable with these systems. Centrifuge systems tend to be capital and maintenance intensive rendering them costly to operate, however they are able to achieve significant reduction in oil concentrations even with somewhat emulsified waste streams. It is necessary to get the influent to fairly low concentrations in order for the flocculation system to work optimally. Flocculation systems can be overwhelmed by high loading resulting in gel like flocculant which is difficult to handle and requires shutdown and maintenance. Often secondary treatment with carbon, clay or other absorbent is required.

## 5. DISCUSSION

The technologies for detection, identification and enforcement of oily bilge water discharges not in compliance with local and IMO regulations exist and are viable. The will to implement and enforce these regulations appears to be the limiting factor in reducing illegal oily bilge water discharges.

It is not possible to select a single bilge water treatment technology as the best for all cases. Selection of an optimum design will depend on throughput, loading, degree of emulsification and the conditions under which the units must operate, or robustness the unit must exhibit. Certainly conventional OWS is well established and is the single best technology for making the first primary cut. OWS are fully capable of achieving numbers below 15 ppm in the presence of discrete immiscible phases. Biological units function very well under conditions of moderate throughput with controlled loading. Loading spikes can overwhelm and shutdown biological units. Capital costs tend to be high and the unit can become troublesome if proper maintenance is not performed. Membrane separation technologies such as ultrafiltration are desirable in circumstances where loading is fairly low and uniform. These systems can become overwhelmed due to fouling or overloading of the membranes in which case shut down and cleaning and or membrane replacement must take place. Additionally membrane units do not have fixed footprints and require more room or dwell time in cases of higher loading or higher throughput. Initial capital outlay is high. Surface modified filtration devices exhibit high performance and the highest degree of robustness in regard to loading and throughput. These devices will not shutdown in the condition of high loading and will maintain a consistent effluent concentration and low operating pressure. Initial capital costs are low, but replacement filters are required, and the spent filters must be used for fuel or stored. Centrifugation / Flocculation units exhibit very good overall performance but the centrifuges require high degree of maintenance and initial capital outlay is high. Flocculation units involve chemical addition and can be overwhelmed if centrifuges are not working properly and influent concentrations rise too much above 200 ppm, depending on the throughput. At this time evaporation, supercritical CO2 and other chemical separation technologies do not seem to be utilized in the field very much. Additionally operating costs for these types of devices are high. Cost to operate can range from 2$/1000gallons or more to less than 50 cents/1000gallons depending on the size of the system, the loading and degree of emulsification and the unit employed.

## 5. CONCLUSION

The technology for detecting and regulating bilge water discharge now exists. Enforcement of such regulations is evermore present, and the potential for significant fines continue to mount for major violators.

There are a number of options in regard to technology for the treatment of oily bilge water. The author does not believe any single type of unit is optimal in all circumstances. The selection of the appropriate unit will depend on the type of ship (i.e. steam ship vs. gas turbine), the amount of loading, the degree of emulsification, the throughput and the robustness required of the unit, in addition to capital and operational expenses. Evaluation of average bilge water composition and degree of emulsification should be taken into account in selection of oily bilge water treatment equipment. Periodic spikes in influent concentrations should also be taken into consideration. The treatment unit should be able to operate without shutdown when challenged with isolated slugs ten times the average loading or higher.

**Acknowledgements:**

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**Primary References**:

1.Clean Water Act Section 312 (as amended by Section 325 of FY96 National Defense Authorization Act).

2. Nature of Discharge Report for Surface Vessel Bilgewater/Oil-Water Separator Discharge as amended by UNDS.

3.International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78). The 2001 amendment - Adoption: 27 April 2001; Entry into force - 1 September 2002.

4. EPA 40CFR Part 9 Chapter VIII

5."Removal of organic pollutants and warfare agents utilizing surface modified filtration devices", presented at NDIA 2003 – Hal Alper, MYCELX Technologies Corporation.

*(Secondary References available upon request).*