#511886 (12)

Effect of Particulate Size on Membrane Performance in Bilge Water Treatment Systems

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ABSTRACT

Environmental regulations now preclude all ships, including naval vessels, from the direct overboard discharge of bilge water, primarily owing to hydrocarbon contamination. Acceptable limits for hydrocarbon contamination levels for overboard discharge in various areas have been established. However, due to the complex composition of bilge water and onboard restrictions, including available space and ship's motion, the identification of purification systems that can produce discharge fluids which meet these new acceptable low limits of contamination is extremely difficult. Many different types of systems have been tried, including coalescers and parallel plate separators, but all have problems purifying the discharge to the new low levels of contamination required. Membrane based systems can surmount these difficulties and provide an effective onboard bilge water treatment system.

A major factor affecting the quality and quantity of a membrane's permeate is the presence of emulsified oil and particulates in bilge water. Specifically, emulsions and particulates in the 0.01 to 0.1 micrometer size range accumulate readily at the surface of the membrane. In this range, particles are too large to back diffuse and too small to be swept away from the surface of the membrane. They accumulate in a layer on the surface of the membrane and greatly reduce its flux. Additionally the type of oil present in the bilge water (that is new versus used oil) can also affect membrane performance. This is related to the difference in the size and quantity of particulate in new and used oils. Used oil often contains particulate originating from oxidized hydrocarbons, carbonaceous debris, and metallic wear particles, etc. which are not likely present in new oils.

This paper will focus on the performance of various membranes in terms of separation and flux as functions of particulate loading in laboratory prepared bilge water mixtures produced using new and used oil as contaminants. The interaction of the membrane material with these different particulate contaminants and the potential effectiveness of membrane system operational parameters, such as backpulsing, to optimize separation, flux and useful lifetime will also be discussed.

Introduction

- Problem Definition
  - Environmental (Oil Discharge) Regulations
  - Shipborne Constraints
  - Bilge Water Composition
- Membrane System
  - Pre & Post Treatment
  - Membrane Selection
  - Membrane Gel Layer & Fouling
  - Effect of Operational Parameters

Problem Definition

- Environmental Regulations
  - Beyond 12 nautical miles - 100 ppm oil
  - Within 12 nautical miles - 15 ppm oil
  - Within Canadian waters - 10 ppm oil
  - Within Internal waters - 5 ppm oil
  - Arctic - 0 ppm oil

While these are the current discharge regulations it is highly preferable for a system to have the possibility of achieving increased discharge limits, due to ever increasing environmental concerns. In this vein, the Canadian Government and the International Maritime Organization (IMO) are currently examining the possibility of increasing these regulations.

One 'easy' method in which a membrane based system, could achieve more stringent discharge limits it to use membranes that have a smaller pore size.

Shipborne Constraints

- Bilge Water Concentration - 16 to 27 X
- Physical Space Constraints
  - 1.7m wide X 1.0m deep X 1.5m high
- System Automation
- Bilge Water composition will vary

An average daily bilge water production for Canadian warships – IROQUOIS and HALIFAX Classes – is approximately 3 tonnes per day. Based on this quantity a concentration approaching 30X is a minimum requirement.

The physical constraints on a ship are obvious; these particular constraints are to allow installation into the footprint of the current Oily Water Separator (SAREX Coalescer) system.

Another obvious shipborne constraint is automation. Bilge water treatment is at best a secondary requirement and therefore cannot unduly task engineering personnel.

Bilge Water Composition

- Total Oils and Greases - 2000 ppm
  - Fuel Oil - 1000 ppm
  - Lubricating Oil (New or Used) - 800 ppm
  - Hydraulic Oil - 200 ppm
- Total Suspended Solids - 500 ppm
- Total Dissolved Solids - 18 000 ppm
- Detergents - 500 ppm
- Remainder is Fresh & Sea Water

In accordance with NETE Study IT1082 – Bilge Water Characterization Study and Bilge Fluid Production Estimates - bilge water contains, on average approximately 1300 ppm oil and grease. However, this quantity can vary widely – bilge waters can contain up to 10,000 ppm oil and grease.

New vs. Used Lubricating Oil

- Approximately equal particulate size distribution
- Oxidation of Used Lubricating Oil
- Stronger Emulsion with the Used Lubricating Oil

An analysis of new and used naval diesel lubricating oil revealed a virtually identical particle size distribution. However, there exists a very real difference between the two lubricating oils. An obvious difference stems from the extreme conditions used lubricating oil has experienced. This appears to be manifested in used lubricating oil since it created a more stable oil emulsion than the new lubricating oil.

Membrane Pre & Post Treatment

- Pre Treatment:
  - Coarse Filtration
  - Hydrocyclone
  - MF Coalescence
- Post Treatment:
  - Adsorption

Membranes

- Organic Membrane
  - KOCH
  - various flat sheet membranes
- Inorganic Membranes:
  - CARBOCOR
  - CERAMEM

KOCH: Fabricated from polyacrylo nitrile (PAN) polymer. It has a molecular weight cut-off of 50,000 Daltons, which relates to a nominal pore size of roughly 0.003 microns.

CARBOCOR: Fabricated from a carbon-graphite composite material. It has a nominal pore size of 0.05 microns.

CERAMEM: A ceramic (silica) membrane. It has a nominal pore size of 0.005 microns.

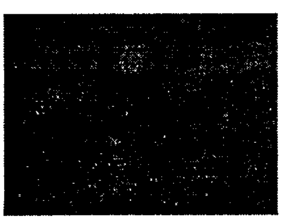
Gel Layer & Fouling

- Causes - Bilge Water Composition
  - Free Oil
  - Unstable Oil Emulsions
  - Stable Oil Emulsions
  - Particulates Size Distribution
  - Adsorption of hydrocarbons and tars on/into membrane
- Solutions
  - Pre Treatment
  - Cleaning Regime
  - Backpulsing

The oils found in the bilge water can be present either as a free oil or as an emulsion – stable and/or unstable emulsion. The free oil and unstable emulsion can be fairly easily separated from the bilge water. Therefore, to be effective, a membrane must be able to treat stable oil-water emulsions.

The following two pictures depict the emulsions created by new and used lubricating oil found in bilge water.

New vs. Used Oil Emulsion



New Oil - Bilge Water

Used Oil - Bilge Water

50 μm

The oil-water emulsion created with 'New' bilge water is a simple oil/water emulsion. Accordingly, the specific density difference between the water and oil emulsion is quite distinct.

The oil-water emulsion created with 'Used' bilge water is a more complex water in oil in water emulsion. This causes the specific gravity differential between the water and the oil emulsion to be reduced – hence it produces an emulsion which is more difficult to separate. Additionally, this emulsion appears to be more turbid – i.e. a more stable emulsion.

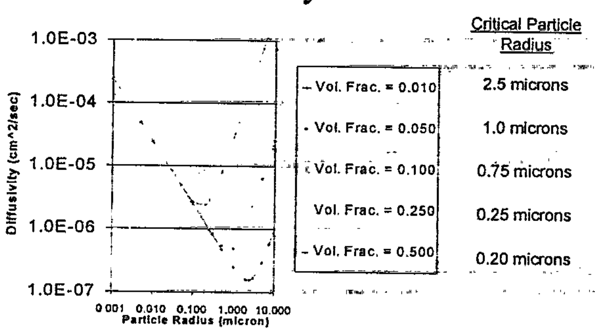
Used Oil Emulsion

Used Oil - Bilge Water 50 μm

Another picture of the 'used' bilge water oil emulsion.

In this picture the water in oil in water nature of the emulsion is very apparent.

Effect of Particle Size on Gel Layer



In membrane applications a particulate 'gel' layer forms on the membrane surface. This 'gel' layer acts as an additional filter.

This graph depicts the relationship between the oil content (volumetric fraction) in the bilge water near the surface of the membrane and the critical oil emulsion (particle) radius. This critical radius is the size of oil emulsions which would form the 'gel' layer.

Noting these critical radii and the nominal pore sizes of the membranes it can be seen that membrane pore plugging is unlikely to result.

Operational Parameters

- Pressure
- Cross-flow velocity
- Backpulsing
- Composition
- Temperature

The following operational parameters were examined for their effects on permeate quantity and quality.

Membrane theory predicts that initially permeate flux is linearly dependent on pressure. However, a point exists where the flux becomes pressure independent – due to gel polarization. As pressure is increased the permeate quality should also decrease.

Permeate flux is dependent upon cross-flow velocity. However, its effect varies depending upon laminar or turbulent flow. An increase in cross-flow velocity should result in an increase in permeate flux, but a decrease in quality.

Backpulsing – reversing permeate (clean water) flow at higher than normal system pressure – allows for the gel layer to be lifted off the membrane surface. It is expected that this would increase permeate flux and decrease quality.

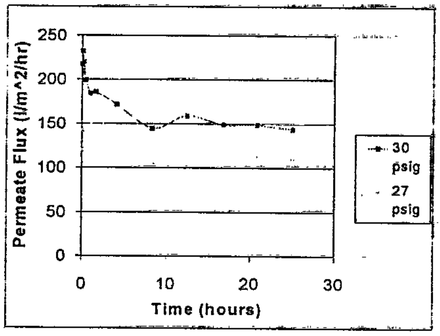
The composition of the bilge water – composed of new or used lube oil – results in a difference in permeate flux and quality.

Temperature is well documented to increase permeate flux by approximately 3% per degree Celsius.

Results

- Effect of Pressure
- Effect of Cross-Flow Velocity
- Effect of Backpulsing
- Composition: New vs. Used Lubricating Oil

Effect of Pressure
CARBOCOR Membrane

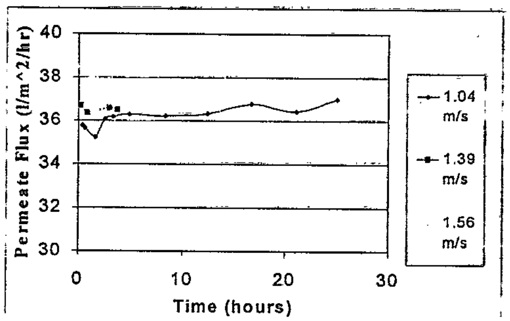


Bilge Water composed of used lube oil
Backpulsing: 5 seconds every 2 minutes

The effect of pressure is shown to be quite important – a 3 psi increase resulted in an increased flux of 40-50%. However, this increased flux was achieved with a noticeable, but not great, degradation in permeate quality.

For the pressure range tested (10-32 psi) the membrane showed no sign of entering into the pressure independent region.

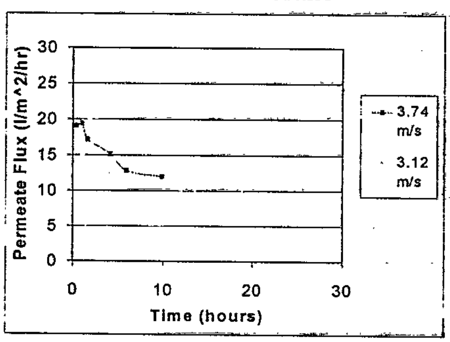
Effect of Cross-Flow Velocity
CERAMEM Module



Bilge Water composed of new lube oil
Operating Pressure = 30 psig

This and the following chart show that the cross-flow velocity has little impact on flux. However, increasing the cross-flow velocity did have a very significant negative impact on permeate quality.

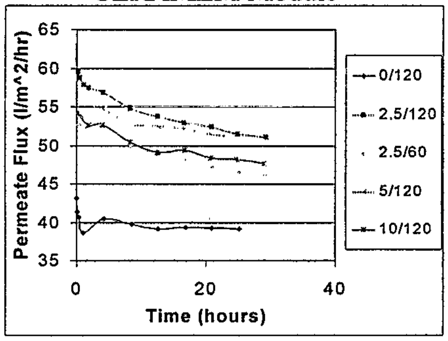
Effect of Cross-Flow Velocity
KOCH Membrane



Bilge Water composed of used lube oil
Operating Pressure = 30 psig

Effect of Backpulsing

CERAMEM Module

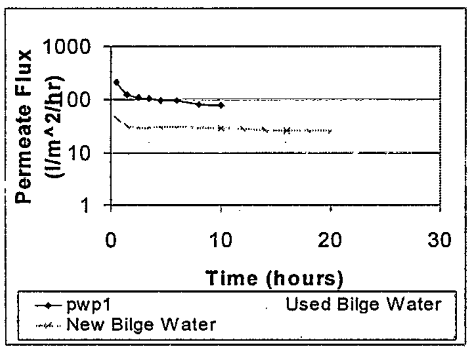


Bilge Water composed of new lube oil
Operating Pressure = 32 psig

As seen from the accompanying chart utilizing backpulsing results in a substantial flux improvement – 20 to 40%. Surprisingly, this increased flux was accompanied by little, if any, degradation in permeate quality.

Effect of Composition

KOCH M-100 Flatsheet Membrane



MWCO of Membrane = 20,000 Daltons

Early testing was conducted with flatsheet or membrane coupons. These early tests revealed differences in fluxes when treating bilge water comprised of new or used lubricating oil – with the flux of 'used' bilge water being lower than the 'new' bilge water.

Note: Tests with the membrane modules revealed that this flux degradation did not occur with the inorganic membranes.

Notes

- Fouling & subsequent cleaning requirements for organic (KOCH) membrane
- Membrane surface area
  - CERAMEM > KOCH > CARBOCOR

Organic membranes are much more susceptible to fouling than inorganic membranes and their subsequent cleaning is more cumbersome.

Membrane surface area is critical when designing membrane systems as experimental / pilot plant fluxes are expressed in volume per area per time. Scaling membrane requirements to actual system needs requires determining the overall quantity of permeate needed and then dividing the membrane flux rate into this requirement to determine the number of membranes needed. Accordingly the fact that the CERAMEM module has the greatest surface area per volume is important for optimizing space requirements - a very important shipborne variable.

CONCLUSIONS

- Membrane based systems offer a good solution to the Navy's bilge water treatment problem.
- Operators must become familiar with the effects of operational parameters.
- Bilge water composition is very important. Particularly the variance in lubricating oils.
- Membranes will foul (espically inorganic). Accordingly cleaning regime is critical.
- Membrane selection is important.