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TITLE

The influence of colloids and fine particles on membrane performance

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The Influence of Colloids and Fine Particles on Membrane Performance

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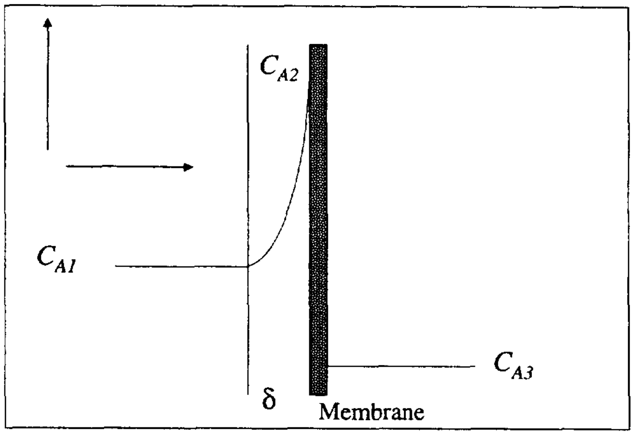
ABSTRACT

The influence of colloids and fine particles on the performance of ultrafiltration (UF) and microfiltration (MF) membranes in treating an oily wastewater mixture containing used oil was studied. The composition of this wastewater closely resembled that of wastewaters accumulating in a ship's bilge. Several membranes having molecular weight cut-offs (MWCO) spanning the full range of commercially available UF pore sizes were tested in thin channel cross-flow test cells.

The size and distribution of particles present in this wastewater was determined from dynamic light scattering (DLS) measurements, direct observations of the cake layer at the surface of the membrane and the modeling of experimentally obtained flux decline curves. The DLS measurements indicate that the synthetic bilge water prepared from used oil contains a bimodal distribution with mean radii at 89 nm and 1,340 nm. Particles in the lower distribution had radii ranging from 70 to 100 nm while those in the larger distribution ranged from 900 to 2,200 nm. The results obtained from all three techniques were in excellent agreement. Permeate flux was found to be severely affected by the presence of the smaller particles as their dimension is precisely in the range that is the most difficult to treat by cross-flow membrane filtration.

The results of the UF cross-flow tests show a substantial drop in flux for the largest pore radius tested (70 nm pore radius) versus that of a membrane having a smaller 14 nm pore radius. This suggests the entrapment of the 70-100 nm radius particles within the membrane having a 70 nm radius causing pore blockage and the serious flux decline observed for this membrane. Under these circumstances, the membrane to be used in this application should have a pore radius that is below the smaller particle distribution of 70-100 nm radius or well above a 100 nm particle radius. The microfiltration tests support these findings as pore blockage was found to be prevalent for MF membranes having a pore radius of 100 nm. MF membranes with pore radii just below this threshold performed extremely well. The results indicate that the accumulation of the sub-micron particles present in bilge water at the surface of the membrane and within membrane pores dominates membrane performance. The selection of the proper membrane pore size, particularly in MF, is critical to the success of membrane technology in this application.

Look at Concentration polarization



$$J = \frac{N_B}{c_1} = k \ln\left[\frac{C_{A2} - C_{A3}}{C_{A1} - C_{A3}}\right]$$

In the case where $C_{A3} << C_{A1}$, and $C_{A3} << C_{A2}$ (high separation)

then,

$$J = k \ln\left[\frac{C_{A2}}{C_{A1}}\right]$$

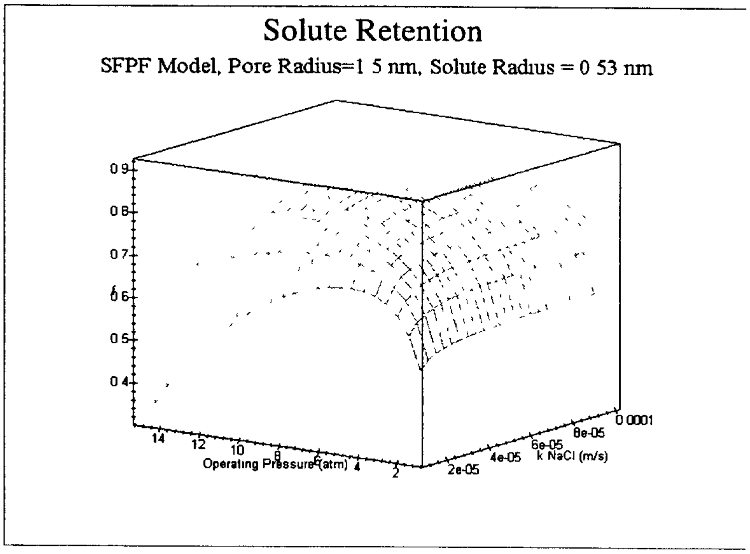
Gives rise to the gel model;

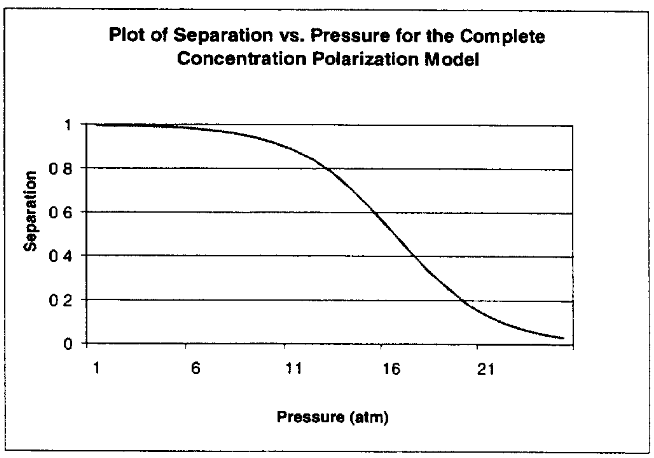
$$J = k \ln\left(\frac{C_g}{Cb}\right)$$

Where.

C_b is the bulk or feed concentration and
C_g is the concentration of a gel at the surface of the membrane

$C_g =$ 22 wt % for gelatin at 70°C,
28 wt % for human albumin,
60 wt % electrodeposition primer,
60 wt % styrene butadiene latex


Solute Retention
SFPF Model, Pore Radius=1 5 nm, Solute Radius = 0 53 nm
Operating Pressure (atm)
k NaCl (m/s)


Plot of Separation vs. Pressure for the Complete Concentration Polarization Model
Separation
Pressure (atm)

Influence of Colloidal Particulate Size on Membrane Performance and Cost

Film theory models based on Brownian back-transport from the membrane under predict permeate flux by as much as two orders of magnitude for colloidal suspensions.

Transport mechanisms for colloids and particles must be used in addition to Brownian diffusion to predict permeate flux in ultrafiltration and microfiltration.

Additional transport mechanisms are:
- shear-induced diffusion
- convective transport tangential to the membrane surface
- inertial lift

Brownian diffusivity

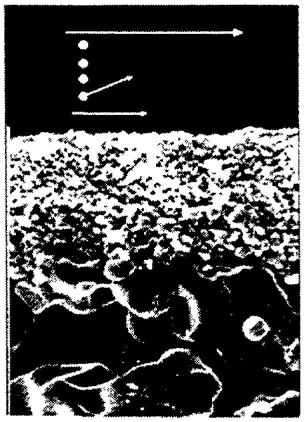
$$D_{brn} = \frac{kT}{6\pi\mu a_p}$$

Where k is Boltzmann's constant, a_p = particle radius, ϕ = particle volume fraction, T is temperature and γ is the local shear rate

Shear diffusivity

$$D_{shear} = \dot{\gamma}\ a_p^2\ (0.33\phi^2(1+0.5e^{8.8\phi}))$$

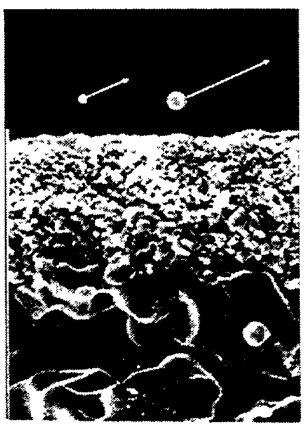
Where: a_p = particle radius,
ϕ = particle volume fraction,
T = temperature and
$\dot{\gamma}$ = local shear rate.



Lower Shear

Highest Shear at the surface of the membrane

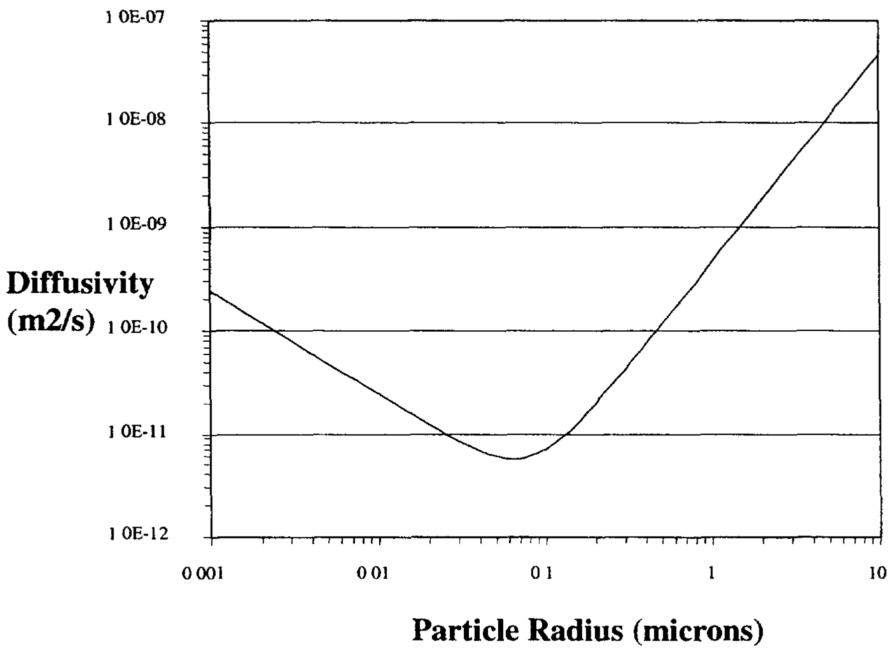
Particles move from a region of higher shear to one of lower shear



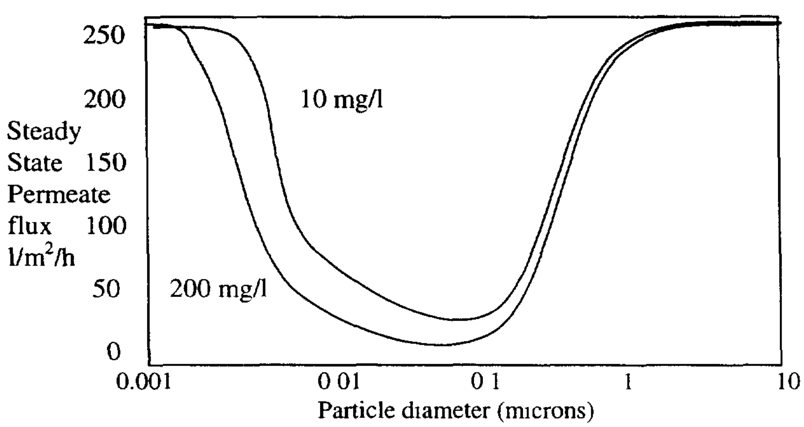
Diffusion away from the membrane is proportional to the square of the particle size.

$$D_{shear} \alpha \; a_p^2$$

The Diffusivity of a particle in solution is given by the sum of its Brownian and shear diffusivities.



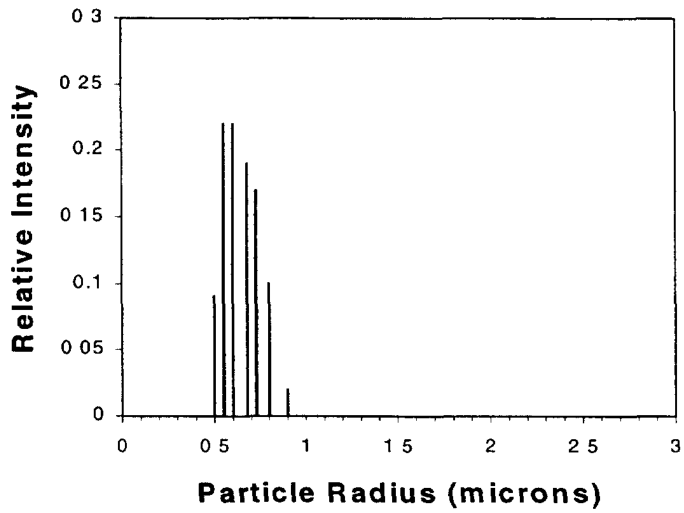
Effect of Particle Size on Permeate Flux



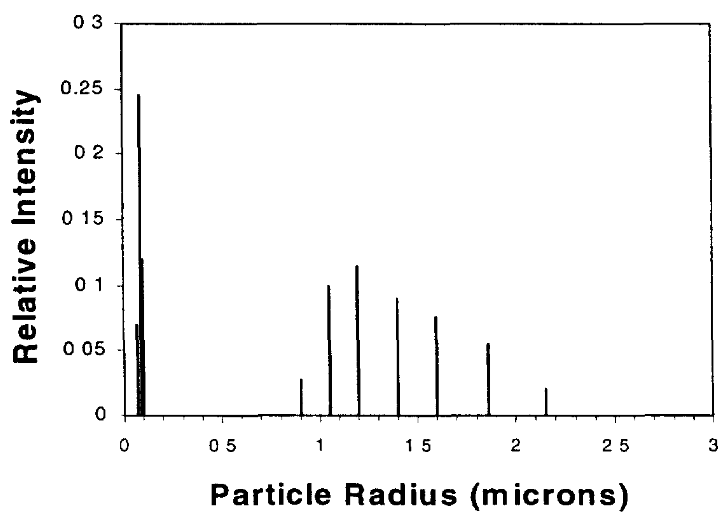
MWCO of membrane is 100,000 Daltons
Feed pressure = 100 kPa

Particle size distribution in synthetic bilge water

- Perform DLS (dynamic light scattering) measurements to determine the particle size distribution in synthetic bilge water.
- Compare bilge water prepared using new oil vs. used oil.

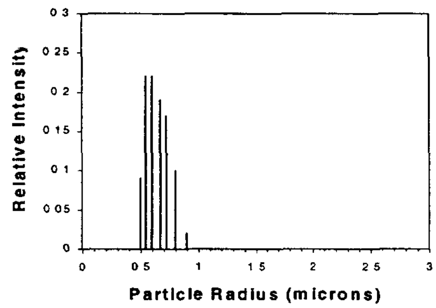


Particle size distribution for synthetic bilge water produced from new oil. Mean = 0.646 μm

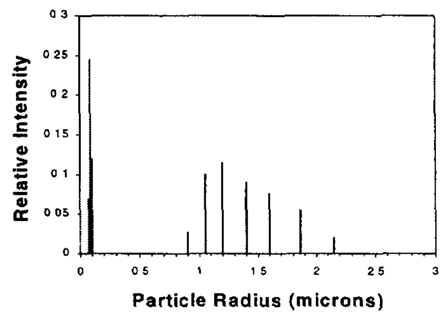


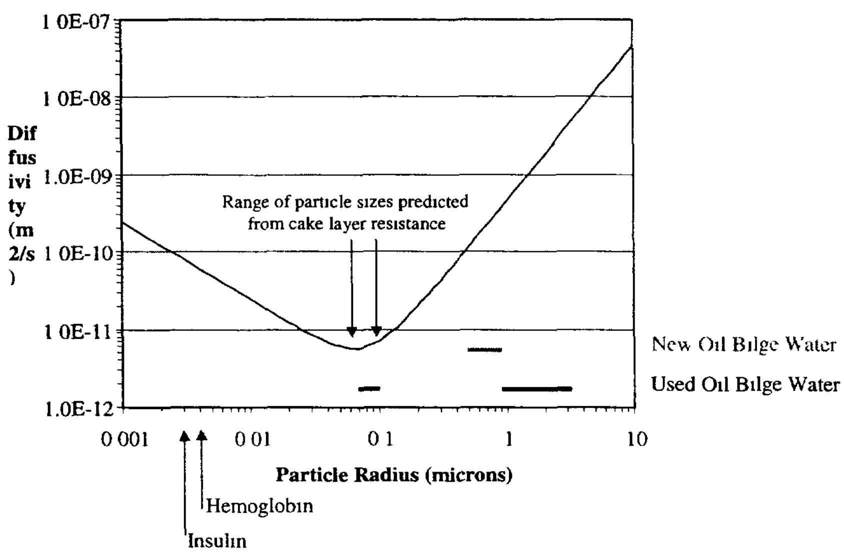
Particle size distribution for bilge water produced from used oil.

New Oil

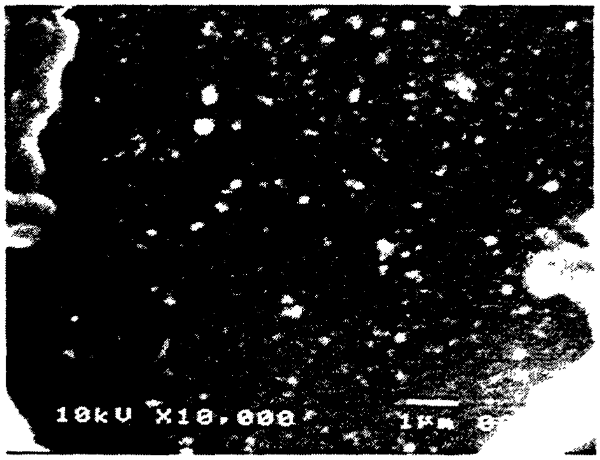


Used Oil

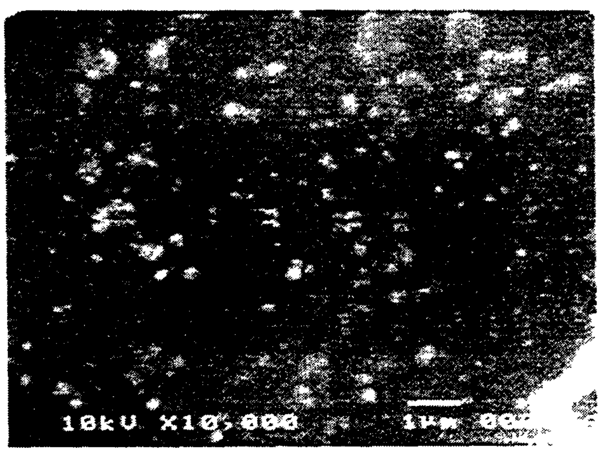




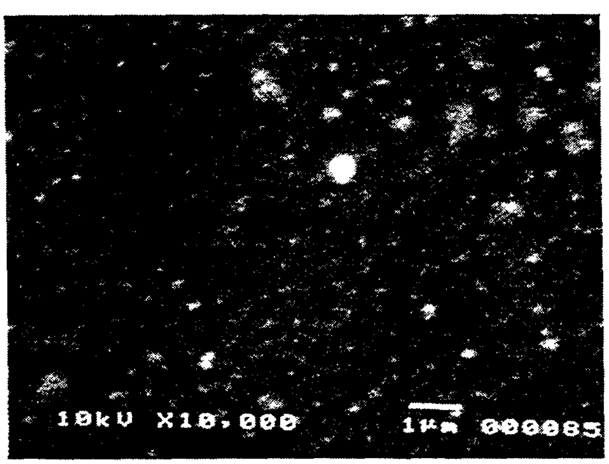
Look at the surface of Ultrafiltration membranes fouled with synthetic bilge water prepared from used oil.



Surface of a 3.5kD MWCO membrane, pore radius 0.0022 μm.



Surface of a 8kD MWCO membrane, pore radius 0.0033 μm.

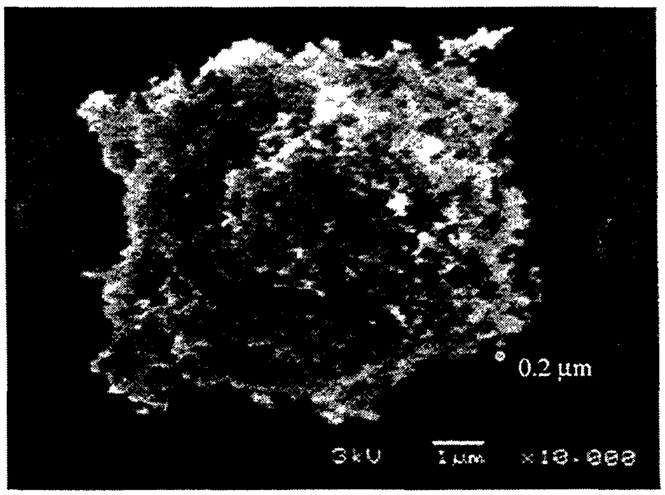


SEM of the surface of a 10kD MWCO, pore radius 0.0037 μm

Soot vs. Carbon Black

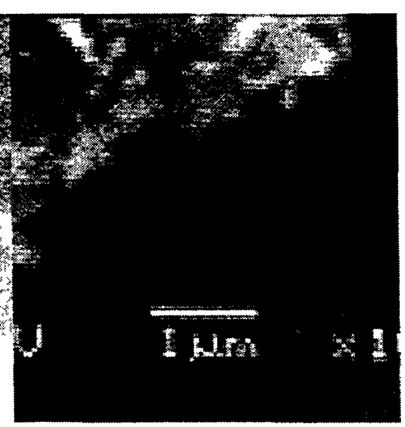
Look at size and specific gravity carbon black

- commercially available, average particle sizes ranging from 8 to 100 nm
- specific gravity of 1.7 to 1.9 (Columbian Chem. Co., 1997).
- the carbon black particles can aggregate into larger units measuring several microns.



Carbon black aggregated particle (International Steering Committee for Black Carbon Reference Materials)

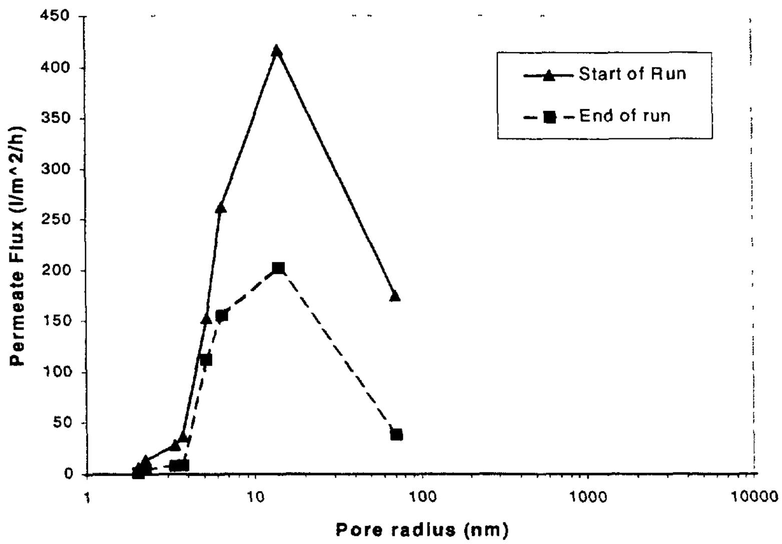
Membrane filter cake



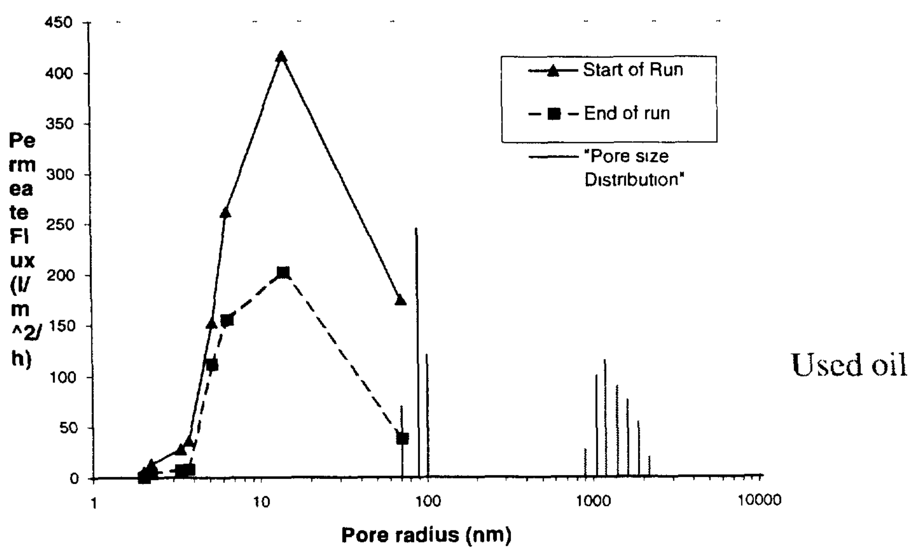
Aggregated soot.

Can we define an optimum pore size for this application ?

Flat sheet membranes in a thin channel x-flow module



Flat sheet membranes in a thin channel x-flow module and DLS measurements for used oil



Conclusions (defining an optimal pore size).

- Pore blinding was observed when a 3,600 kDalton membrane was used.
- Membranes having pore sizes above 0.1 microns could be used to allow for the passage of the 0.1 micron soot.
- Upper limit would be that observed for the passage of oil through the membrane.

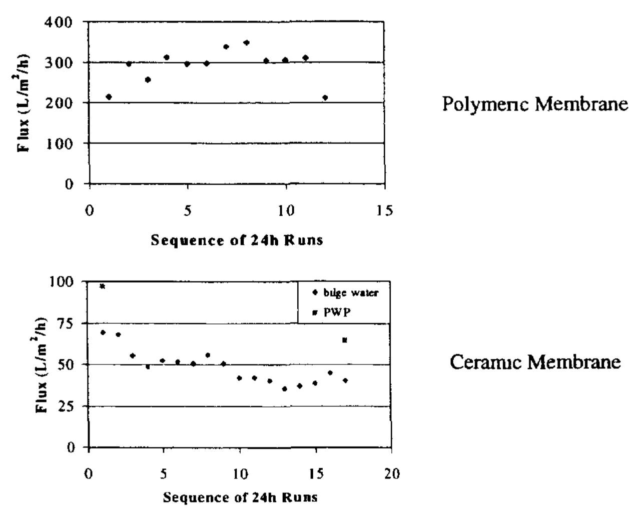
Module Testing

- Comparison of polymeric & ceramic membrane modules
- Pre-treatment – coalescence

Membrane Modules

- Polymeric:
  - KOCH CM:
    - 50K MWCO, polyacrylonitrile
  - CERAMEM:
    - 0.005micron, silica selective layer with an alumina porous substructure\\

Initial Flux Rates



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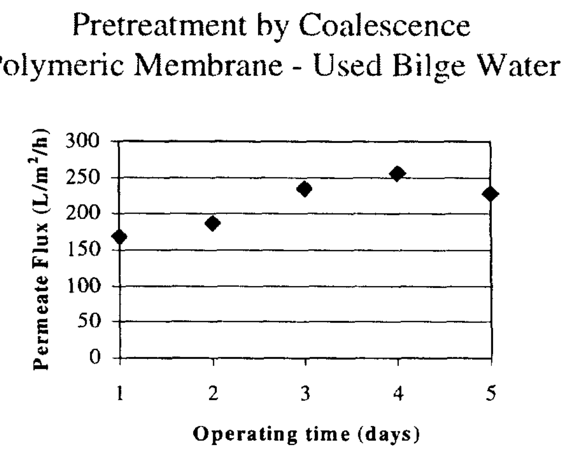
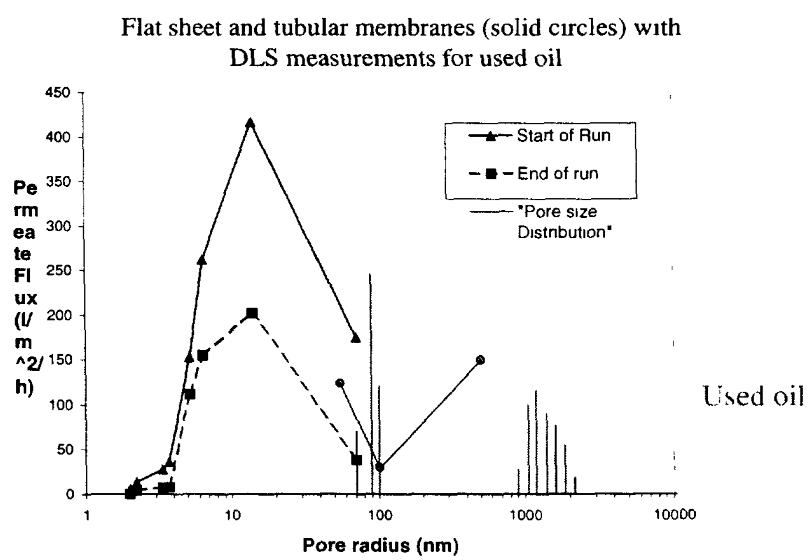


Conclusions (module testing)

- The polymeric membrane (Koch CM) appears to be more resistant to pore plugging than the ceramic membrane
- Flux Enhancement:
  - Backflushing - offers marginal improvement, for these UF membranes, but not as much as anticipated due to nature of cake layer.
  - Coalesence pre-treatment is effective in enhancing permeate flux.

Testing of new small tube membranes Carbo-cor (Koch membranes) tubular modules.



Precipitation of sparingly soluble salts.

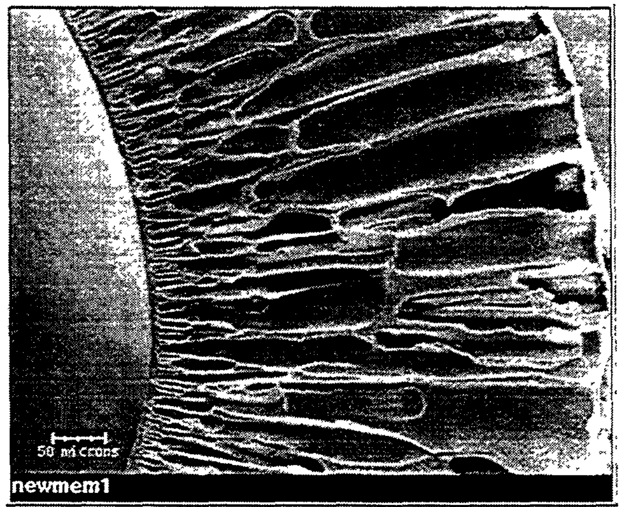
----------- EQUILIBRATED MASS DISTRIBUTION -----------

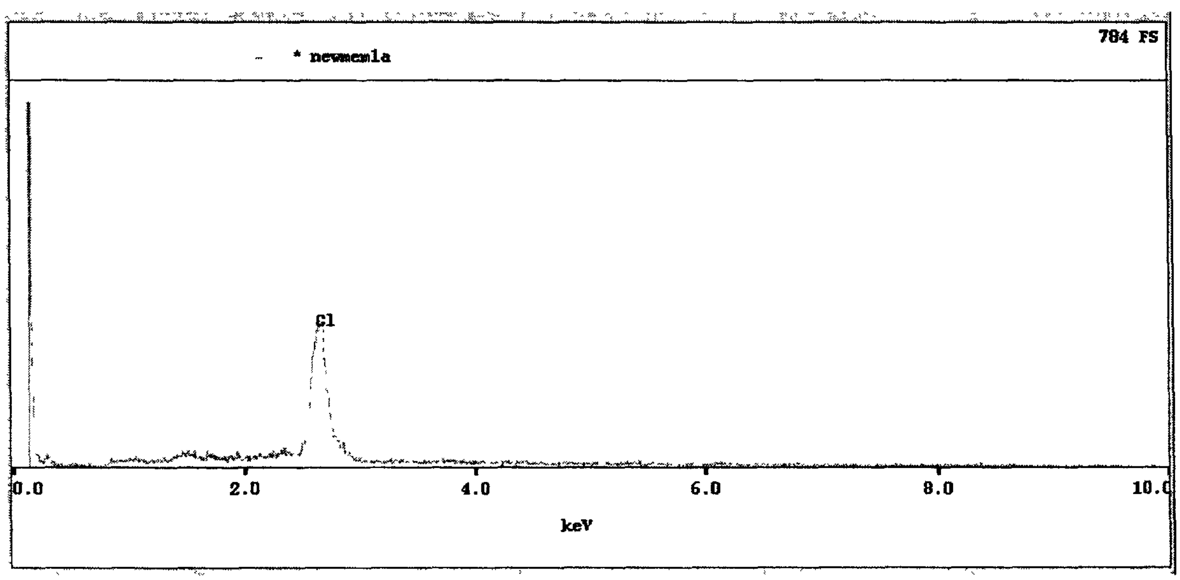
Name	DISSOLVED		SORBED		PRECIPITATED	
	mol/L	percent	mol/L	percent	mol/L	percent
F-1	3.753E-05	100.0	0.000E+00	0.0	0.000E+00	0.0
Cl-1	2.849E-01	100.0	0.000E+00	0.0	0.000E+00	0.0
Na+1	2.445E-01	100.0	0.000E+00	0.0	0.000E+00	0.0
SO4-2	1.590E-02	100.0	0.000E+00	0.0	0.000E+00	0.0
Mg+2	2.715E-02	97.5	0.000E+00	0.0	6.889E-04	2.5
Ca+2	4.628E-03	87.0	0.000E+00	0.0	6.889E-04	13.0
K+1	5.171E-03	100.0	0.000E+00	0.0	0.000E+00	0.0
Br-1	4.308E-04	100.0	0.000E+00	0.0	0.000E+00	0.0
Sr+2	8.021E-05	100.0	0.000E+00	0.0	0.000E+00	0.0
H2O	4.642E-06	100.0	0.000E+00	0.0	0.000E+00	0.0
H+1	2.160E-04	100.0	0.000E+00	0.0	0.000E+00	0.0
CO3-2	2.346E-04	14.6	0.000E+00	0.0	1.378E-03	85.4

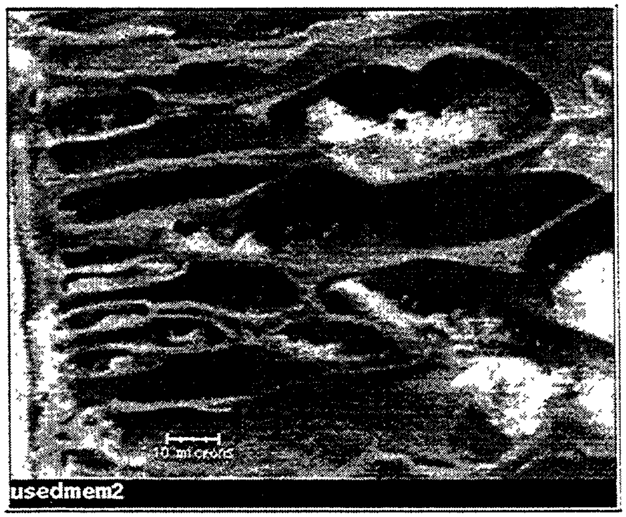
Evidence of Magnesium and Calcium carbonate precipitates in used modules from HMC ships.

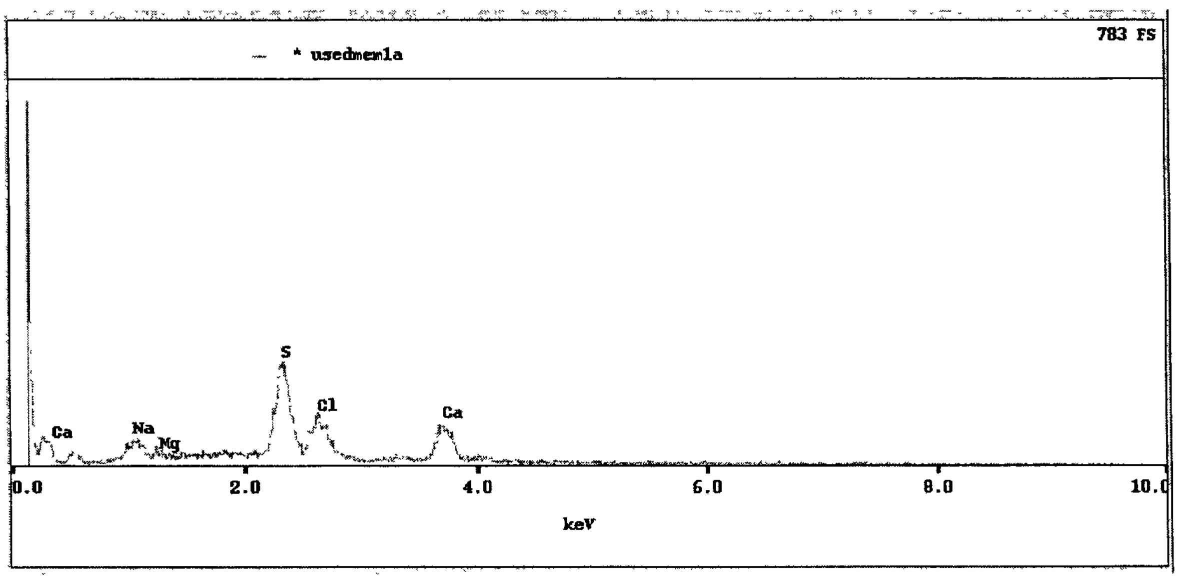
The following slides are the Scanning Electron Micrographs of clean and used membrane along with the Electron Diffractive X-ray (EDX) scans of the new and used membranes.

These results indicate that in addition to soot, sparingly soluble precipitates are present in the cake and within the membrane as evidenced by the Ca and Mg present in the EDX of the used membranes.


50 microns
newmem1


784 FS
* newmem1a
Cl
0.0
2.0
4.0
6.0
8.0
10.0
keV





ACKNOWLEGMENTS

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