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Treatment of produced water from oil and gas wells using crossflow ultrafiltration membranes

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Rice University, 1994
RICE UNIVERSITY

TREATMENT OF PRODUCED WATER FROM OIL AND GAS WELLS USING CROSSFLOW ULTRAFILTRATION MEMBRANES

by

SUSAN MOORE SANTOS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

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August, 1993
ABSTRACT

Treatment of Produced Water from Oil and Gas Wells Using Crossflow Ultrafiltration Membranes

by

Susan Moore Santos

Currently employed methods for treating produced water do not consistently meet regulatory limits on oil and grease discharge concentrations. Experiments with different produced waters using tubular, crossflow, ultrafiltration membranes demonstrated that oil and grease concentrations less than 14 mg/l (well below current regulatory limits) could be achieved. Ultrafiltration experiments on produced water and model oil emulsions demonstrate that virtually all colloidal organic materials are rejected by the membrane, while dissolved organic materials pass through it. The membrane rejects precipitated iron and suspended solids. Permeate flux behavior and the effectiveness of different cleaning procedures vary significantly among produced waters. Generalizations on permeate flux performance during ultrafiltration treatment of produced water do not appear to be warranted. Permeate flux ranged from 73 to 306 l/m²-hr depending on the produced water source and the cleaning procedures. Pilot studies on specific produced waters may be necessary to insure this process' applicability.
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DEDICATION

...to Jesse, with all my love.
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CHAPTER 1
INTRODUCTION

1.1 Problem Statement and Significance

Water is often a by-product of oil and gas production. This water is known as produced water, formation water, or brine (because of its generally high chloride level). The components of produced water generally include oil, heavy metals, radionuclides, numerous inorganic species, suspended solids, and chemicals used in treatment and hydrocarbon extraction (Stephenson, 1992). Pollution problems such as toxicity to fish and adverse effects on benthic communities in coastal environments are associated with some of the constituents of produced waters, and have led to regulations governing the treatment and disposal of most produced waters.

Currently, regulations limiting the oil content of produced waters often govern the methods for treatment and disposal of these waters. In the oil and gas industry, oil is a general term used to describe organic matter which, in produced waters, can include aliphatic and aromatic hydrocarbons, phenols, and carboxylic acids (Stephenson, 1992). These organic compounds are present in produced waters either in a dispersed (emulsified and free oil) or a dissolved form, and appear to be key factors affecting toxicity to fish and wildlife when produced waters are discharged to surface water environments (Fucik, 1992, Sauer et al., 1992).

In the U. S., produced waters may not be discharged into onshore,
navigable waters unless the produced water is being used for agriculture or wildlife propagation, in which case, the maximum daily effluent limitation for oil and grease is 35 mg/l (EPA, 1992).

Through authorization of the Clean Water Act, coastal or tidal disposal of produced water is limited to oil and grease concentrations of 48 mg/l for a maximum monthly average and 72 mg/l for a maximum daily value (EPA, 1992). Some individual states have chosen to regulate oil and grease concentrations at even lower values.

For land-based oil and gas operations, subsurface injection is the primary method for disposal of produced waters (EPA, 1987). The produced water may be reinjected into the same reservoir from which it came to aid in enhanced oil recovery (EOR) processes, reinjected into shallower saltwater formations, or reinjected into older, depleted producing formations. Produced water disposal may be located near the original reservoir, or a contract disposer may be used for offsite disposal.

Subsurface injection of produced water is not currently regulated. However, high oil and suspended solids concentrations may damage injection equipment or clog the reinjection formation. When old wells are retrofitted for produced water disposal, groundwater contamination may occur as a result of casing failure (EPA, 1987).

It can be extremely expensive to drill a disposal well for reinjection from an offshore oil and gas production platform. As a result, produced water
from offshore wells is usually discharged overboard into the ocean. Current government regulations based on the achievement of best practicable control technology currently available (BPT) dictate that no more than 48 mg/l monthly average and 72 mg/l daily maximum of oil and grease can be in discharged produced water from existing offshore platforms (EPA, 1993). The regulation also stipulates that no visible oil sheen shall be observed on the surface of the receiving body of water.

On March 4, 1993, the U.S. EPA established new regulations for oil and grease limits for produced water discharges from new offshore oil and gas sources (EPA, 1993). Limits of 29 mg/l monthly average and 42 mg/l daily maximum were set for oil and grease. These regulations establish new source performance standards (NSPS) based on best available technology economically achievable (BAT). In this case, BAT was designated as gas flotation along with upstream gravity separation and chemical addition. Under NSPS and BAT, oil and grease is also being regulated as an indicator for toxic pollutants. Zero discharge of produced sand also falls under this new regulation: oil and other contaminants can be attached to the sand particles. For permits issued under these regulations, a period of up to 36 months may be allowed for compliance from the time of the issuance of the permit for oil and grease (Randolph, 1993).

U. S. Environmental Protection Agency (EPA) Method 413.1 is the method used to determine oil and grease concentrations in produced waters for regulatory purposes in the U. S. (EPA, 1978a) (Appendix A). This method involves oil and grease extraction with Fluorocarbon-113 (Freon-
113) from the produced water sample, followed by gravimetric evaluation of the residue left after distillation of the solvent.

The methods of treatment and disposal of produced waters depend on many factors, including volume of water, type of water, location of the oil or gas field, and site-specific regulatory considerations. There is a need for produced water treatment methods that can lower the oil and grease and the suspended solids concentrations to minimize reinjection problems and meet regulatory limits. Such methods must be cost effective and, for treatment at offshore facilities, extremely compact and lightweight. Conventional treatment generally has not been successful at consistently meeting all of these criteria. Membrane filtration technologies have the potential to meet these demands.

The EPA examined the applicability of membrane filtration as a basis for BAT but concluded that membrane filtration was still in the development phase for the treatment of produced water. EPA’s sampling program clearly indicated that the technology was capable of substantially reducing the quantities of soluble and insoluble organic materials found in produced water. However, operational difficulties precluded its selection as BAT or NSPS treatment at the time of the evaluation. The quality of effluent produced by membrane processes, in particular, ultrafiltration (UF), is thought to be excellent. However, data on permeate quality, permeate flux, and cleaning procedures are very limited. Further research on the applicability of UF for the treatment of produced water is warranted.
1.2 Objective

The objective of this work is to evaluate the treatability of produced water from oil and gas wells and model oil emulsions by ultrafiltration as defined by permeate flux (flow of filtered water per surface area of membrane) and permeate quality in laboratory experiments.
CHAPTER 2
LITERATURE REVIEW

Most produced water from oil and gas wells is treated to some extent and either injected into subsurface formations or discharged into marine environments (Arnold and Maurice, 1986). Concern over groundwater contamination and toxicity of the constituents of produced waters to benthic communities in other aquatic habitats have lead to regulations governing the disposal of most produced waters.

Disposal practices generally depend on location. Land-based oil and gas operations use subsurface injection as the primary disposal method. High oil and suspended solids can cause damage to injection equipment and cause clogging of the formation (Anhaiser et al., 1992). Disposal wells may not be secure and leaks may contaminate groundwater with aromatic hydrocarbons such as benzene (EPA, 1987, Fucik, 1992).

Water produced from offshore oil and gas wells is treated and discharged overboard into the ocean, and water produced at coastal oil and gas wells is treated and usually discharged into tidal areas. Some of the constituents of produced water, such as hydrocarbons, have been identified as possible causes of toxicity to fish and have been shown to cause adverse effects in benthic communities in shallow-water, nearshore marine environments, and in river tributaries (Rabalais et al., 1992, Sauer et al., 1992). Offshore and coastal discharges are strictly regulated (EPA, 1993).
Methods for determining oil and grease concentrations and conventional treatment of produced water are reviewed in the following sections. Crossflow membrane filtration (in particular, ultrafiltration) is proposed as an alternative to conventional treatment, and a review of the basic principles of ultrafiltration follows. Previous evaluations of crossflow membrane filtration treatment of produced waters and oily wastewaters from metal processing industries are presented.

2.1 Methods for Determining Oil and Grease Concentrations

For regulatory purposes, the EPA requires its Method 413.1 to be used to measure the oil and grease content of produced water (EPA, 1978a). This method involves oil and grease extraction with Fluorocarbon-113 from the produced water sample, and then gravimetric evaluation of the residue left after distillation of the solvent (Appendix A). EPA Method 413.1 measures predominately high molecular weight organic acids and non-volatile hydrocarbons (Dyke and Bartels, 1990). Simple aromatic hydrocarbons are often volatilized during distillation of the solvent and are therefore not measured. This method can also extract non-hydrocarbon compounds such as sulfur compounds, certain organic dyes, and chlorophyll causing errors in the measurement of the true oil and grease concentration.

EPA Method 413.2 also uses Fluorocarbon-113 extraction but instead of gravimetric analysis, evaluation of the infrared absorbance of the extracted solution is performed (EPA, 1978b) (Appendix B). This method, often used on offshore platforms for convenience, usually yields higher
concentrations for oil and grease than does EPA Method 413.1 because more volatile compounds are measured.

The EPA is currently researching replacement solvents for Fluorocarbon-113. Other extraction solvents being used to measure oil and grease using gravimetric or IR analysis include hexane, dichloromethane, methylene chloride, and tetrachloroethylene (Bansal, 1975, Krug and Attard, 1990, Simms et al., 1992). These solvents extract oil and grease in varying degrees.

2.2 Conventional Treatment of Produced Water
Once well fluids leave a wellhead, they usually flow to some form of separatory tank. A separator is a vertical or horizontal tank closed to atmosphere which usually contains baffles in various configurations to aid in separation. Two-phase separators are used to separate natural gas and liquids, whereas three-phase separators are used to separate natural gas, liquid hydrocarbons, and produced water. Sometimes when processing crude oil, separators are not efficient at separating tightly emulsified oil; therefore, a gun barrel may be employed. Gun barrels are large settling tanks which have much longer residence times than separators. Hence, separation of oil and water is more efficient. Gun barrels are generally not used at offshore facilities. Once produced water leaves a separator or gun barrel, the water usually still contains high levels of hydrocarbons which need to be removed before disposal.

The method selected for treating produced water depends on several
factors, including location of oil or gas field, characteristics of the water and type of disposal. Gravity-settling skim tanks, plate coalescers, granular-media filtration systems, and gas flotation devices are widely accepted methods for treating produced water. Sometimes these methods are used in combination with each other to achieve higher efficiencies.

Gravity separation using a skim tank is usually the only treatment used before land-based reinjection of produced water into saltwater formations. Skim tanks are designed to provide long residence times during which oil drops coalesce and rise to the top of the tank and heavier suspended solids settle to the bottom. A commonly used skim basin design called an API (American Petroleum Institute) separator is horizontal and has a rectangular cross-section. API separators have large space requirements, due to long residence times. Space on offshore platforms carries a very high premium. Thus, API separators are generally unacceptable for offshore produced water treatment (Bradley, 1987). Usually, at offshore oil and gas facilities, small skim tanks are used to remove bulk suspended solids and some free oil prior to more effective treatment.

Plate coalescers depend on gravity separation to allow oil drops to rise to a plate surface where coalescence and capture can occur. Sediments slide down to the bottom of the separator where they are removed. Three types of plate coalescers are commonly used: parallel plate interceptors (PPI), corrugated plate interceptors (CPI), and cross-flow separators.

A PPI is essentially an API separator with a series of plates installed
parallel to the separator's longitudinal axis. The plates form a "V" shape so that the oil migrates up the underside of the coalescing plate and to the sides. Sediments migrate towards the middle and down to the bottom of the separator where they are removed.

The most common form of plate coalescer is the CPI. Its parallel plates are corrugated with the axis of the corrugations parallel to the direction of flow. The plate pack is inclined at an angle of 45° and the bulk water flow is forced downward. The oil sheet rises and is concentrated at the top of the corrugations. The oil is then collected in a channel and brought to the oil/water interface where it can be skimmed off. The CPI is a refinement over the PPI in that it takes up less plan area for the same drop size removal. Because the CPI is operated in laminar flow, it is an efficient settling device for sand that is not oil-wet (Arnold and Maurice, 1986). Oil-wet sand can adhere to and clog the plates, so it is best to remove most sand upstream of the CPI.

Cross-flow separators are similar to CPI's except that the water flows perpendicularly to the axis of the corrugations in the plates. This allows the plates to be aligned at a steeper angle to facilitate sediment removal. CPI's are less expensive and tend to remove oil drops more efficiently than cross-flow separators, but cross-flow separators are much better equipped at handling heavy solids loadings.

Plate coalescers have a number of advantages compared to skim basins. The PPI and the CPI require much less space for a given flow rate, and the
flow is predominately laminar so turbulence and short circuiting, which can be a problem in skim basins, are negligible. The coalescers generally outperform skim basins in removing oil drops. Effluent concentrations of oil from a skim basin are commonly between 30 and 100 mg/l, whereas a CPI will have an effluent oil concentration in the range of 15 to 30 mg/l (Bradley, 1987).

Granular-media filtration utilizes a granular-type medium to provide a large surface area on which oil drops can coalesce. It also serves as a conventional sand filter for removing suspended solids. Common filter media include sand, crushed anthracite, diatomaceous earth (DE), and black walnut shells. These separators can have upflow or downflow configurations and they almost all require backwashing. Backwashing is the process in which clean water is flushed through the filter bed in the opposite direction of the process flow. This is usually performed when effluent concentrations of oil begin to increase (breakthrough) or when the headloss through the system reaches a specified value. This type of separation removes particles extremely well but has a tendency to clog. Filtration with black walnut shells has been found to produce effluent oil concentrations of 5 to 10 mg/l. However, it is recommended that the influent oil concentration to such systems should not exceed 100 mg/l (EPA Method 413.1) (Hensley, 1992).

Flotation cells are usually used as a secondary treatment after skimming tanks have removed bulk suspended solids and a portion of the free immiscible oils. This is the most common type of treatment used on
offshore oil and gas platforms. Gas is added in the form of tiny bubbles which rise and collect a high percentage of the oil drops and some suspended solids. A froth forms at the water surface where it is skimmed off. Often flotation aids such as organic polyelectrolytes are used to improve performance (Schulz, 1993). There are two types of gas flotation generally used: dissolved gas flotation and dispersed gas flotation.

Dissolved gas flotation is a process in which gas is introduced into the water (usually air, CO₂, N₂, or natural gas) under a pressure of 280 to 410 kPa to ensure its dissolution (Bradley, 1987). When the water is depressurized in a flotation tank, tiny bubbles form and rise.

Dispersed gas units introduce bubbles by either using an inductor device or by using mechanical rotors to set up a vortex. A much higher gas/water ratio is achievable by using a dispersed gas unit instead of a dissolved gas unit. Dispersed gas units often require chemical flotation aids such as organic polyelectrolytes to meet regulatory limits on oil discharge. Tests have shown oil removals greater than 93% with chemical pretreatment (Schulz, 1993, Trapani, 1993). At a Gulf of Mexico offshore oil platform, dispersed gas flotation cell performance was monitored on four production platforms. The 1991 performance data indicate average oil effluent concentrations of 32, 27, 29, and 31 mg/l (EPA Method 413.2) for each platform (Powell, 1992).

2.3 Membrane Filtration
Pressure-driven membrane filtration is a promising alternative to
conventional treatment technologies. These membrane technologies include ultrafiltration (UF), microfiltration (MF), and nanofiltration (NF). Membrane filtration is a process which is capable of separating components of contaminated water predominantly on the basis of molecular or particle size.

Pressure-driven membrane filters are usually designed with the waste stream flowing parallel to the membrane surface. This configuration is known as crossflow filtration and is paramount in helping to minimize contaminant buildup on the membrane wall. Figure 2.1 illustrates the basic principle of crossflow membrane filtration.

![Figure 2.1: Principle of Crossflow Membrane Filtration](image)

The feed water, containing elevated levels of contaminants, flows axially through a porous tube while the filtered water (permeate) flows radially through the tube walls due to a pressure drop across the membrane (transmembrane pressure). The concentrated feed stream (retentate or recycle) exits the other end of the tube. The permeate flowrate per unit surface area of the membrane (referred to as permeate flux) is often the deciding factor in determining the applicability and cost effectiveness of
this technology.

A comparison of approximate rejection sizes for various pressure-driven membrane separation methods is shown in Figure 2.2.

Figure 2.2: Classification of Membrane Separation Processes
(adapted from Chellam and Wiesner (1991))

MF is usually used when rejection of particles larger than 0.1 μm is necessary. Often, pretreatment of the feed is required (Chen et al., 1991). One goal of pretreatment is to produce discrete solids that flocculate a portion of the emulsified oil and suspended solids in the produced water. The discrete solids deposit on the membrane surface to form a hydrophilic dynamic layer, thus preventing the oily substances and fine particles from penetrating the membrane.

UF generally rejects particles on the order of 1 nm to 100 nm, which is the size range of most macromolecules and colloidal particles (Figure 2.2). Emulsion drops are generally larger than 100 nm; therefore, UF
membranes should be able to produce an effluent virtually free of dispersed oil drops (Adamson, 1982). This method of separation rarely needs chemical pretreatment other than cleaning of the membrane. Permeate fluxes, and hence recoveries, during the processing of produced water are very competitive with recoveries typical of conventional treatment.

NF membranes are permeable to water and monovalent inorganic ions and relatively impermeable to many organic macromolecules and divalent inorganic ions (Dyke and Bartels, 1990). Problems associated with NF include the potential for precipitative fouling and low recoveries (Bansal, 1975).

Crossflow UF is a promising alternative to conventional treatment for the removal of emulsified oils and particles from produced water. It is often necessary to use a combination of conventional treatment methods (e.g. corrugated plate interceptor and dissolved gas flotation or a skim tank, a parallel plate interceptor and granular-media filtration). A greater number of unit processes increases the cost and the space needs for treatment. An UF system is extremely compact and usually requires only a small skim tank upstream to remove bulk suspended solids and a portion of the free oil. This is ideal for offshore facilities which have limited space. Moreover, none of the conventional treatments mentioned are able to handle tightly emulsified oil as effectively as UF can (VonPhul, 1993). Field experience indicates that 30 μm is a lower limit on the drop size that can be removed by plate coalescers due mainly to platform vibrations and small pressure fluctuations (Arnold and Maurice, 1986). Because of the
tendency of media to clog during granular-media filtration, it is recommended that oil influent concentrations be less than 100 mg/l (EPA Method 413.1). This limits its application and causes problems when upsets occur. UF systems can process influents with extremely high oil concentrations, and the presence of a mechanical barrier between the feed water and the effluent streams reduces oil discharges due to system upsets or operator error. Flotation cells usually need some form of chemical flotation aid to be efficient enough to meet regulatory limits; whereas, chemical pretreatment is not necessary for UF. UF systems also have fewer moving parts and low maintenance requirements.

2.4 Permeate Flux
Permeate flux is one of the most important criteria used to determine if a membrane system is feasible for treating a particular waste stream. Permeate flux is affected by the operating conditions of the system, including pressure, crossflow velocity, temperature, characteristics and concentration of the feed water, and membrane configuration and material. In particular, the accumulation of material in the feed water on, or near, the membrane may adversely affect permeate flux.

2.4.1 Concentration Polarization
Concentration polarization is a term used to describe the accumulation of materials in a dynamic layer near the membrane surface. The concentrations of rejected solutes or particles near the membrane are higher than those in the bulk flow. As water passes through the membrane, the convective flow of solute to the membrane surface is larger
than the diffusive back transport of the solute to the bulk flow. As a result, the concentration of the solute at the membrane surface increases, and a higher transmembrane pressure is required to effect permeate flux. Diffusion from the membrane surface may be either Brownian or shear-induced (Davis and Leighton, 1987). In the latter case, diffusivity is dependent on the crossflow velocity. Turbulent diffusivity may also increase back transport. In tubular membranes, turbulent diffusivity appears to be 10 to 100 times greater than Brownian and shear-induced diffusivity.

Concentration polarization is dependent on operating parameters such as pressure, temperature, feed concentration, and crossflow velocity. Solute separation efficiency is often dependent on the degree of concentration polarization and on the specific solutes making up the polarized layer (Blatt et al., 1970). The higher the flux, generally, the more rapidly concentration polarization occurs (Porter, 1972b). Negative effects of concentration polarization include a possible decrease in permeate flux, an increase in solute flux through the membrane, and precipitation of solute on the membrane wall. Concentration polarization can also cause an increase in the viscosity of the polarized layer near the wall of the membrane, which causes the flow to slow down and further increases the effects of polarization (Gill et al., 1988, Meireles et al., 1990). As concentration polarization increases contaminant concentrations near the membrane to a maximum limit, a "gel" or "cake" may also form. A gel or cake on the membrane is often the limiting layer of resistance to permeate flux through the membrane.
The following recommendations for minimizing concentration polarization have been set forth by Bruin and co-workers (1980): 1.) **Maintain a low permeate flux.** This calls for an extremely large membrane surface area. To be economical, a compact system design such as hollow fiber modules would be appropriate. 2.) **Maintain a low concentration difference between the membrane surface and the bulk fluid.** Static mixers can be used to promote turbulence, and some membrane configurations (for example, tubular) can be mechanically cleaned with a sponge to remove solutes at the surface. 3.) **Encourage back diffusion from the membrane surface.** Increasing temperature and velocity or pulsating liquid through the membrane can aid in this regard (Belfort, 1989).

### 2.4.2 Gel Polarization - Film Theory

The film theory model expresses permeate flux ($J$) in terms of concentrations and a mass transfer coefficient ($k$) (Blatt *et al*., 1970, Porter, 1972b, VanDenBerg and Smolders, 1990):

$$J = k \ln \left( \frac{C_w - C_p}{C_b - C_p} \right) \quad (2.1)$$

$C_w$, $C_b$, and $C_p$ are the concentrations at the wall, in the bulk fluid, and in the permeate, respectively. Theoretical expressions for the mass transfer coefficient have been presented by numerous investigators, but accurate estimates of practical use are difficult to obtain apriori (VanDenBerg *et al*., 1989).

Permeate flux increases with pressure until the concentration at the membrane surface reaches some critical solute concentration ($C_g$) (typically
between 20 and 70 vol\%) at which time back-diffusion balances the convective flow of solute to the membrane (Porter, 1972a). At this point, a gel or cake layer forms on the membrane surface resulting in a permeate flux that is independent of transmembrane pressure. This is termed mass-transfer-limited permeate flux (Bhave, 1991). An increase in pressure at this stage does not increase the concentration in the cake layer, but does increase its thickness (Fane, 1986). Blatt and co-workers (1970) found that at higher crossflow velocities, the pressure-independent region commences at higher pressures for a given set of operating parameters. In experiments performed by Lee and co-workers (1984) on ultrafiltration of a 5% soluble oil emulsion (contains mineral oil, surfactants and other additives), a gel layer developed above 300 kPa of transmembrane pressure and contained about 40% oil. This concentration was found to be independent of transmembrane pressure. If the permeate concentration of material limiting permeate flux is negligible, equation 2.1 simplifies to (Nabetani et al., 1990, Porter, 1972a):

\[
J = k \ln \left( \frac{C_g}{C_b} \right)
\]

(2.2)

A gel layer formed by large particles may have a negligible effect on permeate flux. Cakes or gels formed from small particles are anticipated to produce a relatively high specific resistance and can cause the permeate flux to be extremely low. Sometimes gel layer consolidation, or "hardening," due to high pressures can additionally decrease permeate flux with time (Blatt et al., 1970, Opong and Zydney, 1990).
2.4.3 Resistance Model

The flow of solvent through the membrane can be described as being proportional to a driving force $\Delta P$, and inversely proportional to the membrane resistance $R_m$, and the dynamic viscosity $\mu$,

$$J = \frac{\Delta P}{\mu(R_m)}$$

(2.3)

When a solute is present in the feed stream, concentration polarization effects can reduce the permeate flux by causing additional hydraulic resistances to develop (Fane, 1986, VanDenBerg and Smolders, 1990). The permeate flux can then be described as being inversely proportional to a sum of the resistances to permeate flow (Fane, 1984, Lainé et al., 1989, Nilsson and Persson, 1990, Shu-Sen, 1988).

$$J = \frac{\Delta P}{\mu(R_m + R_{cp} + R_c + R_a + R_p)}$$

(2.4)

The resistances are defined in Figure 2.3.

![Figure 2.3: Possible Resistances Against Solvent Transport](adapted from VanDenBerg and co-workers (1990))
2.4.4 Permeate Flux Decline Due to Fouling and Colmatage

Reductions in permeate flux are operationally attributed to membrane fouling and colmatage. Colmatage is the term used to describe reductions in permeate flux that may be recuperated by chemical cleaning and/or hydrodynamic washing of the membrane. The irreversible reduction in permeate flux is referred to as membrane fouling.

Membrane properties such as hydrophobicity and solute or particle size can influence the extent to which permeate flux decline might occur (Bonner and O'Melia, 1991). Contaminants may adsorb to the membrane surface or penetrate the membrane pores and cause clogging (Jonsson and Johansen, 1991a). Adsorption of contaminants was observed to be more pronounced in hydrophobic membranes than in hydrophilic membranes (Bil'dyukevich and Dmitrieva, 1989, Fane, 1986, McDonogh et al., 1990). Badenhop and co-workers (1970) observed that pore blockage tends to occur when the contaminant is the same size or smaller than the average membrane pore diameter. Fouling is often the limiting factor in using pressure-driven membrane processes because as permeate flux declines with time, the process can eventually be rendered uneconomical (Green and Belfort, 1980).

2.4.5 Membrane Cleaning

UF is a viable treatment option only if permeate flux and quality can be maintained over time. For the successful use of UF membranes, effective cleaning procedures should be established in laboratory and pilot studies. The following important suggestions made by Luss (1990), should be taken
into consideration when designing a cleaning program for UF membranes. The program must restore permeate flux and quality to a useful level, must not harm the membrane or other components of the system, and must be economically feasible. The cleaning procedure should also discourage microbial or fungal growth on the membrane during storage.

A number of different types of cleaning agents are used in an attempt to restore the original permeate flux after fouling has occurred. Typical agents include: oxalic acid, HCl, NaOH, and industrial surfactant cleaners such as Alconox, Triton X-100, Tergazyme, and Tergitol (Bansal, 1975). Usually, alkaline cleaners are used for oily substances, while acid is used for particulate foulants (Chen et al., 1991, Jonsson and Tragardh, 1990). Nonionic surfactants have been found to have excellent oil removal at neutral and elevated pH values (Hickman, 1991). Lee and co-workers (1984) found that a solution of sodium dodecyl sulfate (SDS), n-pentanol, and water was the most favorable compared to other cleaning agents tested for cleaning membranes fouled with oily contaminants.

Running clean water through the system for a short time at a high crossflow velocity (fastflushing) can usually remove some of the contaminants and improve permeate flux. Rogers and Sparks (1991) demonstrated that applying a negative transmembrane pressure (backflushing) to a fouled UF membrane can greatly increase the permeate flux by minimizing the effects of adsorption and pore blocking. Sometimes membranes are cleaned mechanically with sponges or swabs to remove concentrate at the membrane surface (Bruin et al., 1980).
The appropriate physical parameters for cleaning operations must be established to optimize the cleaning procedure. Hickman (1991) suggested that the crossflow velocity should be as high as the system will permit, that the transmembrane pressure should be as low as the flow conditions will allow, and that the temperature should be moderately high.

Chemical cleaning frequency is largely a function of the concentration and nature of the foulants present in a specific feed water. Cleaning time can vary from 1 hour of circulation to overnight soaking for extremely fouled membranes. The system should be well rinsed before it is returned to service.

2.4.6 Factors Affecting Permeate Flux

2.4.6.1 Pressure

Transmembrane pressure can be approximated by the following relationship:

\[ \Delta P = \left( \frac{P_{in} - P_{out}}{2} \right) - P_{permeate} \]  \hspace{1cm} (2.5)

where \( \Delta P \) is the transmembrane pressure, \( P_{in} \) is the pressure immediately upstream of the membrane modules, \( P_{out} \) is the pressure immediately downstream of the membrane modules, and \( P_{permeate} \) is the pressure on the permeate side of the membrane (Chen et al., 1991). \( P_{permeate} \) is zero if the permeate goes to atmospheric pressure. According to the resistance model, at low transmembrane pressures, membrane resistance is important and permeate flux increases linearly as transmembrane pressure increases. At higher pressures, permeate flux increases nonlinearly due to
concentration polarization and eventually becomes independent of pressure as described by gel polarization film theory (Goldsmith \textit{et al.}, 1974).

2.4.6.2 Crossflow Velocity
Crossflow velocity is the average velocity at which fluid flows through the membrane tube, parallel to the membrane surface. It is recommended that the crossflow velocity for tubular ceramic membranes be in the range of 2 to 8 m/s (Bhave, 1991). An increase in crossflow velocity increases turbulence and aids in sweeping particles and solutes away from the membrane surface (DeFilippi and Goldsmith, 1970). This helps alleviate effects of colmatage and fouling, and therefore increases the permeate flux. A number of researchers have experimentally demonstrated that an increase in crossflow velocity and turbulence increases permeate flux (Bansal, 1975, Goldsmith \textit{et al.}, 1974, Rautenbach and Schock, 1988, VanDenBerg \textit{et al.}, 1989).

2.4.6.3 Temperature
In general, higher temperatures lead to higher permeate fluxes due to a decrease in viscosity of the fluid (Mavrov \textit{et al.}, 1991). An increase in solubility of solutes, due to a higher temperature, would also tend to increase the flux (Bhave, 1991). It is best to operate with the highest temperature tolerable by the membrane to take advantage of the decrease in membrane surface area necessary for a given recovery and therefore, a decrease in the cost of the system. According to Equation 2.4, the permeate flux (\(J\)) should be in direct proportion to the inverse of the solution viscosity. Henry (1972) verified that the permeate flux-
temperature relation follows the Arrhenius form:

\[ J_T = J_{20} \ e^{s/T} \]  \hspace{1cm} (2.6)

where \( J_T \) is the membrane flux at a given temperature \( T \), \( J_{20} \) is the flux at \( T=20^\circ\text{C} \), and \( s \) is a constant. He found that flux-temperature data from a bacterial suspension yielded a linear curve of \( \ln(J_T/J_{20}) \) verses \( 1/T \), consistent with the Arrhenius form. This plot was found to have the same slope as \( \ln(\mu_{20}/\mu_T) \) verses \( 1/T \); therefore, the permeate flux dependence on temperature can be completely accounted for by the temperature-viscosity dependence (Henry, 1972). Deviation from this relationship has been observed only at extremely high solution viscosities (Shu-Sen, 1988).

2.4.6.4 Solute Size

Membranes with pore diameters on the same order of magnitude as the particles or macromolecules being filtered are more easily fouled by pore blockage and adsorption. Therefore, the membrane pores should be somewhat smaller than the material in the feed water to avoid fouling (Badenhop et al., 1970). When filtering a monodisperse system of colloids, as particle size is increased, the permeate flux has been observed to decrease, reach a minimum, and then increase (Fane, 1984). It appears that at the smallest particle sizes, back-diffusion dominates and a thinner polarized layer is deposited (McDonogh et al., 1988). As particle size is increased, the particles become too large to be back-transported by Brownian diffusion but too small to be removed by shear forces; hence, a minimum occurs in permeate flux because a maximum occurs in fouling or colmatage (Lahoussine-Turcaud et al., 1990). Lahoussine-Turcaud and co-workers found that particles near 0.2 \( \mu\text{m} \) in diameter produced the most
rapid fouling for a UF crossflow hollow fiber module with a membrane pore size of 1 nm, and the maximum particle size to have any fouling effect was a 3 μm. They concluded that large particles are less likely to deposit due to inertial lift and, deposits of larger particles are more likely to be effectively removed by shear-induced diffusion.

2.5 Permeate Quality
Permeate quality can also be a deciding factor in determining which waste treatment method to use. It is important to compare permeate solute concentration as well as solute removal efficiency. The removal efficiency is usually represented as

\[ \% \text{ Rejection} = \left(1 - \frac{C_p}{C_r}\right) \times 100 \]  

where \( C_p \) is the concentration in the permeate and \( C_r \) is the concentration in the retentate (Mahdi and Skold, 1990). A number of factors affect the rejection of macromolecules and colloids. Among these factors are size and shape of the molecule, type of membrane material, membrane configuration, solute interaction, adsorption of solutes by the membrane, chemistry effects and operating variables (Ide and Comstock, 1990). The membrane’s affinity for water (hydrophilic or hydrophobic) can have a strong effect on permeate quality and permeate flux (Laïné et al., 1989). Blatt and co-workers (1970), and Brites and dePinho (1991) found that an increase in pressure caused a decrease in rejection for a feed with one homogeneously sized component. Blatt and co-workers also found that an increase in rejection occurred for an increase in pressure for a feed having many multi-sized components. The latter case may be explained by
assuming cake-layer filtering as discussed in section 2.4.2.

2.5.1 Oil Drop Size
A rigid particle will not enter a membrane pore that is smaller than itself; whereas, an emulsified oil drop larger than a pore may enter if the transmembrane pressure is large enough to push it in. When an oil drop comes into contact with a pore opening on the wall of a membrane, the drop can be slightly deformed such that a portion of it moves into the pore. See Figure 2.4. The membrane pore is idealized as a straight cylindrical capillary and it is assumed that the two liquids are incompressible. Hysteresis (when advancing and receding contact angles are different) is neglected.

![Figure 2.4: Oil Drop Entering a Capillary](image)

For the drop to move into the pore, the capillary pressure ($P_c$) must be
overcome by the transmembrane pressure (Lee et al., 1984). The capillary pressure \((P_c)\) is the sum of the pressure drops across the two oil/water interfaces (Cline, 1989):

\[
P_c = \left( \frac{2 \gamma_{o/w}}{r^*} \right) - \left( \frac{2 \gamma_{o/w}}{R^*} \right)
\]

\(\gamma_{o/w}\) is the interfacial tension between the oil and water, \(r^*\) is the radius of curvature of the portion of the drop inside the capillary \((r^* = -r/cos\theta)\), \(\theta\) is the contact angle measured through the oil phase, and \(R^*\) is the radius of curvature of the portion of the drop outside the capillary. Equation 2.8 is based on the Young-Laplace equation. It can be seen from Figure 2.4 that as the drop moves farther into the pore, \(r^*\) remains constant and \(R^*\) decreases; therefore, the maximum value of \(P_c\) occurs when the portion of the oil drop in the capillary takes the shape of a spherical cap with radius of curvature \(r^*\).

Under the previously stated assumptions, for a given pore size, oil drop size, interfacial tension, and contact angle, Equation 2.8 can estimate the transmembrane pressure at which the oil drop will enter the pore. Application of Equation 2.8 is limited because membranes generally do not have uniform pore sizes, and the contact angle can decrease as the membrane becomes fouled.

2.5.2 Micellar-Enhanced Ultrafiltration

Dissolved, low molecular weight substances are generally not removed by ultrafiltration. However, if these substances can be made to form large aggregates, it is more likely that they can be retained by a membrane.
This concept is used in a process called micellar-enhanced ultrafiltration (MEUF) (Dharmawardana et al., 1992, Dunn et al., 1985). In MEUF, a surfactant is added to contaminated water at concentrations well above the critical micelle concentration (CMC) of the surfactant. The CMC is the concentration at which micelles (aggregates) begin to form. The solute is solubilized/adsorbed in the micelles formed by the surfactant. The micelles are large enough to be retained by the membrane, and the permeate contains only solubilized solute and surfactant monomers, both at low concentrations. The process is schematically illustrated in Figure 2.5. Ultrafiltration membranes with low molecular weight cut-off (MWCO indicates the approximate size of a solute or colloid that will be rejected by the membrane) values are best for this technology because even some of the largest micelles have molecular weights of 20,000 daltons or less (Rosen, 1989).

![Diagram of Micellar-Enhanced Ultrafiltration](image)

**Figure 2.5:** Micellar-Enhanced Ultrafiltration
(adapted from Dunn and co-workers (1985))

Early work by Bhattacharyya and co-workers (1979) showed that excellent
oil rejections were obtained (less than 10 mg/l oil (EPA Method 413.2) in the permeate) for UF experiments performed using an oil-surfactant-water solution with a feed oil concentration of 384 mg/l (EPA Method 413.2).

Jonsson and Jonsson (1991b), and Keurentjes and co-workers (1990) conducted experiments in which the effect of surfactants on UF membrane performance was evaluated, and they found that some surfactants actually caused significant decreases in permeate flux (primarily colmatage), especially for hydrophobic membranes. They attributed this behavior to adsorption of the surfactant onto the membrane surface and to concentration polarization effects.

2.5.3 Enhanced Ultrafiltration Using Powdered Activated Carbon
Another method of enhancing ultrafiltration is mixing powdered activated carbon (PAC) in the feed water to adsorb organic materials (Heneghan and Clark, 1991). The PAC particles are small enough to provide a large surface area for the adsorption of organic materials, but large enough to be rejected by an UF membrane. The PAC can also serve as a scouring agent in turbulent flow and can decrease the effect of concentration polarization and therefore, improve permeate flux.

2.6 Membrane Equipment and Configurations
2.6.1 Membrane Material
Different types of polymers can be used in the manufacturing of UF membranes. The polymers should have good chemical and thermal stability and sufficient mechanical strength to withstand applied pressures
during operation. The most commonly used membrane materials are cellulose acetate, polyamide, polyvinylidene difluoride (PVDF) and polysulfone (Cheryan, 1986, Gutman, 1987, Wiesner et al., 1992a). PVDF membranes appear to have distinct advantages over the other types mentioned, as can be seen in Table 2.1.

Table 2.1: Characteristics of Some Membranes (adapted from Gutman (1987))

<table>
<thead>
<tr>
<th>Membrane Material</th>
<th>pH range</th>
<th>Maximum temperature °C</th>
<th>Maximum chlorine mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>2-10</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>PVDF</td>
<td>1-13</td>
<td>90</td>
<td>200</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>1-13</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>Polyamide</td>
<td>2-12</td>
<td>80</td>
<td>0.1</td>
</tr>
</tbody>
</table>

PVDF has a wider pH range and can tolerate much higher concentrations of chlorine than the other materials listed. Zaidi and co-workers (1992a) have formed an extensive list of membranes potentially suitable for oil and water separation. This compilation includes membrane manufacturers, module configurations, pore sizes, and membrane materials (Table 2.2).
Table 2.2: Partial List of Ultrafiltration Membranes Suitable for Oil/Water Separation (adapted from Zaidi and co-workers (1992a))

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Configuration</th>
<th>Pore Size or MWCO</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amicon</td>
<td>flat sheet, spiral wound</td>
<td>3,000-100,000 MWCO</td>
<td>PS</td>
</tr>
<tr>
<td>Aqua Air</td>
<td>spiral wound, hollow fiber</td>
<td>1,000-15,000 MWCO</td>
<td>polymeric organic</td>
</tr>
<tr>
<td>Desalination</td>
<td>spiral wound</td>
<td>4,000-200,000 MWCO</td>
<td>thin film polymer</td>
</tr>
<tr>
<td>Hoescht/Celanese</td>
<td>spiral wound, tubular</td>
<td>10,000-40,000 MWCO</td>
<td>PES modified PAN</td>
</tr>
<tr>
<td>Nitto/Denko</td>
<td>spiral wound, tubular</td>
<td>20,000 MWCO</td>
<td>PO</td>
</tr>
<tr>
<td>Osmonics</td>
<td>spiral wound</td>
<td>100 nm - 0.1 μm</td>
<td>modified PS, PI, fluoropolymer</td>
</tr>
<tr>
<td>Patterson Candy</td>
<td>tubular, flat sheet</td>
<td>4,000-200,000 MWCO</td>
<td>PS, PES, PVDF, PAN</td>
</tr>
<tr>
<td>International</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Romicon</td>
<td>hollow fiber</td>
<td>0.005 μm</td>
<td>PP, PVC cellulose triacetate</td>
</tr>
<tr>
<td>Sartorius</td>
<td>flat sheet</td>
<td>20,000 MWCO</td>
<td>polyglucose, PP, PVDF, PTFE</td>
</tr>
<tr>
<td>Separation Dynamics Inc.</td>
<td>hollow fiber</td>
<td>40,000 MWCO</td>
<td>PS, PES, PAN, PVDF</td>
</tr>
<tr>
<td>Stork Friesland</td>
<td>tubular</td>
<td>5,000-20,000 MWCO</td>
<td>PS, polymeric organic</td>
</tr>
</tbody>
</table>

Note: PAN - polyacrylonitrile, PES - polyether sulfone, PI - polyetherimide, PP - polypropylene, PS - polysulfone, PVC - polyvinyl chloride, PVDF - polyvinylidene fluoride

Ultrafiltration membranes are often formed by a phase-inversion process. First, the polymer is dissolved in a solvent to form a solution containing 10 to 30 wt% polymer. Then the solution is cast onto a highly porous support layer typically 100 to 500 μm thick. The film is quenched in a non-solvent aqueous solution such as water. During the quenching process, the polymer is precipitated into a polymer-rich solid phase, which forms the membrane structure, and a solvent-rich liquid phase, which forms the liquid filled membrane structure (Strathmann, 1981). The thin film, or “skin”, is typically 0.1 to 2.0 μm thick. The membrane formed is referred to as an asymmetric membrane because the pores change in size from one
surface of the membrane to the other. Asymmetric membranes act as surface filters, retaining most particles at the surface.

2.6.2 Membrane Equipment
In order to compete with conventional separation methods, membrane separation equipment should be compact, reliable, and inexpensive, and have the desired separation characteristics. For compactness, membranes are usually arranged in modular configurations. The ratio of membrane surface area to unit module volume is an important design criteria. Industrial-scale facilities typically use one of four membrane geometries: tubular, hollow-fiber, plate-and-frame, and spiral-wound. Often variations or combinations of these types of units are designed to try to minimize concentration polarization and fouling (Bruin et al., 1980, Porter, 1972a). Dead-end filtration using a small flat membrane through which all of the solvent flows is used almost exclusively in laboratory separations (Fane, 1984, McDonogh et al., 1990).

Tubular membranes are shaped like long straws having a diameter anywhere from 1.0 to 2.5 cm and a length between 0.6 and 6.4 m (Strathmann, 1981). Feed water flows axially in a porous tube, while filtered water (permeate) flows radially through the tube’s porous walls due to the transmembrane pressure (usually between 100 and 500 kPa). The permeate is collected in an outer casing and the concentrated water exits the other end of the tube. These membranes can be set up in series or parallel. The flow rate through the membrane is easy to control and is usually turbulent with a Reynolds number greater than 10,000. The
tubular system is easy to clean without dismantling and can tolerate high suspended solids loadings and large particles, making it an appropriate configuration for the treatment of produced water. The membranes are not generally backflushed but chemical cleaning is necessary. This type of system has high investment and operating costs and a low membrane surface area to unit module volume, but modules are fairly inexpensive and they are easy to replace (Cheryan, 1986).

Hollow-fiber membranes are similar to tubular membranes, though they have a much smaller diameter (0.5 to 1.5 mm). They are self-supporting and are usually arranged in bundles of 50 to 3000 individual "fibers" and sealed into a tubular shell. The feed solution passes down through the center of a fiber and permeate flows through its walls. The flow through the membranes is usually laminar or in the transitional region with Reynolds numbers between 500 and 3000. The system has a very large membrane surface area per unit module volume, but it is restricted to operating pressures of less than 200 kPa (Dick, 1982). Plugging can be a problem, and the feed must be prefILTERED to remove particles above 50 to 100 μm in diameter (Gutman, 1987). Unlike tubular configurations, module replacement costs are high, regardless of surface area.

Plate-and-frame modules utilize a simple flat-sheet configuration. The membrane, the porous membrane support materials, and spacers forming the feed flow channel are clamped together and stacked between two end plates. Feed water is channeled across the surface of the membrane by the feed-side spacers. These channels are usually between 0.5 and 2.5 mm
deep. Control of concentration polarization is more difficult than in tubular configurations because this system is usually operated in laminar flow. Plugging can be a problem, and it is time-consuming to dismantle and clean the system. This type of system has a high investment cost, but membrane surface area per unit module volume is large and operating and replacement costs are low.

A spiral-wound membrane module is essentially a plate-and-frame system that has been rolled up. The membrane, the porous membrane support, and the feed flow channel are glued together on three sides and then rolled up and inserted in an outer tubular pressure cell. The feed is pumped lengthwise along the unit, while the permeate is forced through the membrane sheets into the porous membrane support and then spirals towards the perforated center collection tube. This is a very compact configuration with a high surface area per unit module volume. Capital and operating costs are low but concentration polarization may be difficult to control. The feed stream must be filtered when suspended solids are present.

2.6.3 Operational Modes
The choice of mode of operation varies by application and must be decided on a case-by-case basis. In laboratory-scale experiments, a total recycle mode is usually used. Single-pass, feed and bleed, batch operation, or variations thereof are generally used for full-scale systems.

When operating in a total recycle mode, both the permeate and the
retentate streams are returned to the feed tank. The permeate flux and the removal efficiency can be analyzed as other parameters such as temperature, crossflow velocity, and operating pressure are varied. This mode also allows evaluation of the variation of permeate flux with time for a given concentration. Also, tests can determine which cleaning agents restore the flux most effectively.

In the single-pass design, parallel trains of modules are set up in series and nothing is recycled. This type of operation is best when suspended solids loadings and contaminant concentrations are low, concentration polarization effects are negligible, and high permeate flow rates are not required.

When operating in a feed and bleed mode, the retentate is at first totally recycled until a desired concentration is reached within the loop. Then, part of the retentate stream is bled off to maintain this concentration.

In batch operations, a feed tank is installed upstream of the modules and all of the retentate is recirculated to the feed tank and concentrated as the permeate stream is discharged. This is the fastest method for concentrating a given amount of material, and it requires the least amount of membrane area, but it utilizes a large amount of energy, and heat exchangers are usually needed to control the temperature. A variation on the batch operation is to recirculate some of the retentate to the feed tank and recirculate the rest back around the modules.
2.7 Previous Evaluations of UF Treatment of Produced Waters

A limited amount of research has been performed on ultrafiltration of produced water. UF has been used for product recovery and pollution control in the metallurgical, chemical, electronic, food, and biotechnical industries for a number of years, but UF of produced water has only recently been considered (Jonsson and Tragardh, 1990). Most studies on ultrafiltration of produced waters have been conducted by industrial research laboratories. While this work has been summarized in internal reports and presentations, little has been published in the peer-reviewed literature.

Researchers at the Wastewater Technology Center in Burlington, Ontario, Canada have reviewed much of the current technology and research in the area of microfiltration and ultrafiltration of produced water (Zaidi et al., 1991, Zaidi et al., 1992a, Zaidi et al., 1992b). They have been encouraged by their results and are undertaking a comprehensive study to identify the most effective MF/UF system for the removal of oil and suspended solids generated in oil and gas recovery operations (Simms and Zaidi, 1993).

ZENON Environmental Inc., in coordination with the Canadian Department of Energy, Mines and Resources (EMR), conducted one of the most extensive studies on UF of produced water to date (Farnand and Krug, 1989, Zaidi et al., 1991, ZENON, 1990).
Experimental Results of Zenon and EMR (Phases One, Two, and Three)

In 1983, Zenon Environmental Inc. and the Canadian Department of Energy, Mines and Resources (EMR) initiated a study to test polymeric organic UF membranes for the removal of oil and suspended solids from produced water from the recovery of heavy oil (Zaidi et al., 1991). This work was conducted in three phases. In the first phase, Zenon performed bench-scale tests to screen membranes based on pure water and salt water fluxes. Zenon used bench-scale testing again in Phase Two to determine which membranes exhibited the best permeate flux and quality when filtering produced water from an oil well. Phase Three involved bench-scale and pilot-scale testing of the membranes that had the best performance during Phase Two. A variety of produced waters from different oil fields were used in Phase Three.

Phase One tests were conducted using an NRC flow cell (configuration designed by Zenon) in batch operation. Membranes were selected to evaluate their suitability for produced water treatment. Each test was run for 3 hours at a temperature of 25°C and a pressure of 712 kPa. Feed waters of either pure water or a salt solution of 1,500 mg/l were used. Membranes that showed very low permeate fluxes for these feed waters were dropped from the tests under the next phase. The membranes that continued to be tested in Phase Two include two polysulfone membranes, one cellulose membrane, one PVDF membrane, a thin-film composite membrane made by Desalination, and a proprietary membrane made by Zenon.
The membranes chosen from Phase One were again screened in Phase Two. These experiments were performed using produced water from a well-head test separator at an oilfield. The produced water characteristics are listed in Table 2.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical parameters</strong></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.75</td>
</tr>
<tr>
<td>total dissolved solids</td>
<td>784</td>
</tr>
<tr>
<td>total suspended oil</td>
<td>1602</td>
</tr>
<tr>
<td>total suspended solids</td>
<td>34</td>
</tr>
<tr>
<td>total organic carbon</td>
<td>880</td>
</tr>
<tr>
<td>filterable organic carbon</td>
<td>165</td>
</tr>
<tr>
<td>turbidity (NTU)</td>
<td>975</td>
</tr>
<tr>
<td><strong>Anions</strong></td>
<td></td>
</tr>
<tr>
<td>chloride</td>
<td>148</td>
</tr>
<tr>
<td>sulfate</td>
<td>58</td>
</tr>
<tr>
<td><strong>Cations</strong></td>
<td></td>
</tr>
<tr>
<td>sodium</td>
<td>225</td>
</tr>
<tr>
<td>potassium</td>
<td>6.5</td>
</tr>
<tr>
<td>calcium</td>
<td>1.1</td>
</tr>
<tr>
<td>magnesium</td>
<td>0.25</td>
</tr>
<tr>
<td>silica</td>
<td>82.16</td>
</tr>
<tr>
<td>barium</td>
<td>0.13</td>
</tr>
<tr>
<td>iron</td>
<td>71</td>
</tr>
</tbody>
</table>

Initially, tests were conducted using the NRC flow cells as in Phase One, with a temperature of 25°C and a transmembrane pressure of 700 kPa. The most promising membranes were then tested at varying temperatures (25°C, 45°C, and 65°C) and pH's (5.5, 7.5, and 9.5). Three types of membranes were then selected and permeate flux stability tests were performed in NRC flow cells and a modified flow cell. The membranes
chosen are listed in Table 2.4 along with their MWCO ranges.

Table 2.4: Membranes Used in Zenon Phase Two Work (adapted from Zaidi and co-workers (1991))

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Manufacturer</th>
<th>Material</th>
<th>MWCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>E500</td>
<td>Desalination</td>
<td>polysulfone</td>
<td>15,000-20,000</td>
</tr>
<tr>
<td>G10</td>
<td>Desalination</td>
<td>thin-film composite</td>
<td>6,000-10,000</td>
</tr>
<tr>
<td>CHP-CAT</td>
<td>Zenon</td>
<td>proprietary</td>
<td>15,000-20,000</td>
</tr>
</tbody>
</table>

Two different operating modes were used. To test the change in permeate quality with feed concentration, experiments were conducted in a batch mode. The permeate TOC concentration and turbidity were measured at 30, 60, and 90% volume reduction (Table 2.5).

Table 2.5: Permeate Quality for Zenon Phase Two Batch Concentration Tests (adapted from Zaidi and co-workers (1991))

<table>
<thead>
<tr>
<th></th>
<th>TOC (mg/l)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permeate at 30% Volume Reduction</td>
<td>83.0</td>
<td>2.70</td>
</tr>
<tr>
<td>CHP-CAT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G10</td>
<td>32.5</td>
<td>0.73</td>
</tr>
<tr>
<td>E500</td>
<td>64.0</td>
<td>0.89</td>
</tr>
<tr>
<td>Permeate at 60% Volume Reduction</td>
<td>85.5</td>
<td>1.60</td>
</tr>
<tr>
<td>CHP-CAT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G10</td>
<td>35.5</td>
<td>0.56</td>
</tr>
<tr>
<td>E500</td>
<td>77.0</td>
<td>0.88</td>
</tr>
<tr>
<td>Permeate at 90% Volume Reduction</td>
<td>172.0</td>
<td>3.50</td>
</tr>
<tr>
<td>CHP-CAT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G10</td>
<td>69.0</td>
<td>0.08</td>
</tr>
<tr>
<td>E500</td>
<td>127.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

Another set of experiments used a batch operation mode until there was a 90% volume reduction of the feed water, and then the system was allowed to run continuously for 300 hours in a total recycle mode. These experiments tested the permeate flux stability over time. The Zenon CHP-CAT showed the best permeation behavior, so it was chosen for further experimentation in Phase Three. The low permeation rates (less than 25 l/m²-hr) for all three membranes during the permeate flux stability tests...
were partially attributed to the low surface velocities that could be achieved in the flow cells used in these experiments.

Zenon and EMR continued their testing on produced water based on the results of Phases One and Two. Phase Three tests were conducted using reformulations of the chosen membrane material from Phase Two and other proprietary membranes. Flow cells as well as tubular membrane modules were used for these experiments, which were conducted in Zenon’s Burlington, Ontario laboratory and EMR’s laboratory in Alberta. Produced waters from various sampling locations at seven different sampling sites were tested.

Produced water from Site "A" was tested in a tubular UF system. Table 2.6 shows results for permeate flux and indicates the cleaning effects on these systems which were run at 65°C. Stable permeate fluxes between 217 and 321 l/m²-hr and good recovery after cleaning were observed for the Zenon CHP-TFC and the Zenon HPC-1076 at 90% recovery. The CHP-TFC had the best permeate quality with respect to TOC, and this membrane was later tested with other membranes that were variations of its formulation (Table 2.6).
Table 2.6: Permeate Flux and TOC Data for Zenon Phase Three Work
(adapted from Zaidi and co-workers (1991))

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Flux (l/m²-hr)</th>
<th>TOC (mg/l)</th>
<th>% Rejection</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Concentrate</td>
<td>Permeate</td>
</tr>
<tr>
<td>PES</td>
<td>525</td>
<td>229</td>
<td>1,400</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>(43 hr)</td>
<td>(94 hr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>538</td>
<td>179</td>
<td>1,000</td>
<td>180</td>
</tr>
<tr>
<td>CHP-CA</td>
<td>521</td>
<td>271</td>
<td>1,200</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>(72 hr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHP-TFC</td>
<td>200</td>
<td>217</td>
<td>1,200</td>
<td>70.5</td>
</tr>
<tr>
<td></td>
<td>(188 hr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPC-1076</td>
<td>329</td>
<td>321</td>
<td>1,100</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>(162 hr)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additional testing was performed with a variety of produced waters from different oil fields and different sampling locations. The observed permeate flux varied widely from 21 to 188 l/m²-hr. The time lapse before testing (one testing laboratory was much farther from the sample sites than the other) appeared to have a negligible effect on performance. The main factor which influenced the flux seemed to be the site from which the produced water sample originated. The variation in the initial oil concentration in the sample appeared to have little effect on the observed permeate flux. Zenon concluded, based on these bench-scale experiments, that field pilot tests were necessary to evaluate long-term performance of Zenon’s UF membranes. At the time of this review, the results of Zenon’s pilot-scale experiments were not available.

Experimental Results of Zenon and EMR (Phase Three)

As a continuation of Phase Three work, Zenon and EMR conducted experiments on ultrafiltration of produced waters from various sites and various sampling locations (Farnand and Krug, 1989). Polysulfone tubular
membranes (1.27 cm diameter) having a MWCO of between 10,000 and 15,000 were installed in a system which was operated in a feed and bleed mode. The crossflow velocity was about 1.06 m/sec. Total oil was measured by methylene chloride extraction followed by infrared analysis.

The permeate total oil concentrations were consistently less than 15 mg/l regardless of the sample locations or the retentate concentrations (between 26 and 1000 mg/l). The permeate flux ranged between 42 and 179 l/m²-hr. Produced waters which had been chemically treated prior to the ultrafiltration system with destabilizers had much lower permeate fluxes. Zenon and EMR observed that the ultrafiltration membranes fouled much more readily in the presence of free oil, and higher permeation rates were observed during UF of produced water containing stable emulsions.

An economic evaluation indicated that a permeate flux of 125 l/m²-hr would be necessary for the UF process to be less expensive than conventional processes.

Results of Zenon Pilot Tests
In 1988, Zenon began conducting pilot-scale testing on ultrafiltration of produced water from two EOR operations in Western Canada (ZENON, 1990). Pilot systems were designed to operate in batch or continuous mode. Membrane modules housed 8 tubular UF membranes (2.22 cm in diameter) in series. The systems were designed to operate with a transmembrane pressure of 310 kPa, a constant feed temperature of 73 °C and a crossflow velocity of 4.52 m/sec. The total oil concentration
(methylene chloride extraction/gravimetric analysis) in the feed water varied between 100 mg/l and 2000 mg/l. Three types of membranes were used in the tests: HEM, HST, and HSC. The HST and HSC membranes were more hydrophilic than the HEM membrane.

Each membrane type demonstrated complete separation of emulsified oil from the produced water. The membranes rejected approximately 85% of the total oil and 20% of the total dissolved oil. The total dissolved oil was measured by filtering the produced water sample with 0.45 μm filter paper and then performing the method for total oil. Virtually all of the total suspended solids and none of the total dissolved solids were rejected by the membrane. The total oil concentrations in the permeate samples generally remained constant throughout testing despite fluctuations in total oil feed concentrations.

The permeate flux was found to be dependent on feed conditions and membrane run time. Average permeate fluxes were in the range of 50 to 300 l/m²-hr. The membrane tested for the longest run time had an average flux of 122 l/m²-hr (standard deviation: 101) over 1694 operating hours.

Large permeate flux deviations were attributed to frequent cleanings and membrane fouling. A gradual decrease in permeate flux over time was observed in a number of experiments despite cleaning efforts. Clay was suspected of being the main fouling contaminant. It was speculated that clay draws oil out of an emulsion to create an oily solid which is attracted to the membrane.
Zenon performed an economic evaluation on ultrafiltration of produced water and concluded that a permeate flux of 85 l/m²-hr was necessary to be competitive with conventional technology. Based on average permeate fluxes, most of these experiments met this criterion, but longer term testing is needed.

2.8 Previous Evaluations of NF Treatment of Produced Waters
A limited number of evaluations of NF treatment of produced water have been performed. Results from Dyke and Bartels (1990) are particularly noteworthy. An offshore study was conducted to determine the feasibility of replacing flotation cells with nanofiltration (NF) membranes to treat produced water. A pilot-scale NF unit was installed on an offshore platform. For feed waters containing oil concentrations of 176 mg/l (EPA method 413.2), the permeate oil concentrations were less than 48 mg/l. Oil rejections were consistently between 72 and 89%. The feed water had a total dissolved solids concentration of 58,000 mg/l with 15 to 20% being rejected by the membrane. After two days of continuous operation at a transmembrane pressure of 1,480 kPa, the permeate flux remained between 11 and 18 l/m²-hr, providing a 7% recovery.

2.9 Previous Evaluations of MF Treatment of Produced Waters
Some work has been conducted in the laboratory and in the field with MF membranes (Bartman and Melekzadeh, 1993, Chen et al., 1991, Groves and Bartman, 1991, OOC, 1991, Oswald, 1992, Zaidi et al., 1991). Two such studies have demonstrated promising results in treating produced water with α-alumina membranes.
Experimental Results of Chen and Co-workers (1991)

An asymmetric microporous α-alumina membrane system was used to treat produced water in experiments offshore and onshore. The modules used were 0.85 m (2.8 ft) long and contained 19 channels. Pore diameters ranged from 0.2 to 0.8 μm, and the membrane thickness was 30 to 50 μm. In addition to cleaning the membranes with caustic and acid, it was also necessary to use chemical pretreatment to reduce fouling. Backpulsing and fast flushing were two techniques which also aided in reducing fouling. Backpulsing is the application of a short-duration counter pressure on the permeate side of the membrane, thereby delivering controlled pulses of permeate back through the membrane pores. Fast flushing is accomplished by increasing the feed side crossflow velocity, thereby sweeping the accumulated solids out of the filter channels.

Results indicated that the permeate flux could be sustained at 2970 l/m²-hr (1,750 gal/ft²-day), and the permeate oil concentration was less than 9 mg/l (EPA method 413.2) with a feed oil concentration varying from 28 to 583 mg/l (EPA method 413.2) (Table 2.7). The permeate concentration appeared to be independent of the feed concentration.

Table 2.7: Oil Concentration* and Rejection Characteristics for MF of Produced Water (adapted from Chen and co-workers (1991))

<table>
<thead>
<tr>
<th>Location</th>
<th>Feed (mg/l)</th>
<th>Retentate (mg/l)</th>
<th>Permeate (mg/l)</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>166-583</td>
<td>1266-3125</td>
<td>&lt;8.9</td>
<td>99.3-99.7</td>
</tr>
<tr>
<td>C</td>
<td>28-108</td>
<td>100-2900</td>
<td>&lt;5.1</td>
<td>95.0-99.8</td>
</tr>
<tr>
<td>D</td>
<td>105-574</td>
<td>&gt;215</td>
<td>3-5</td>
<td>99.1-97.7</td>
</tr>
</tbody>
</table>

* EPA method 413.2
The total suspended solids (TSS) ranged from 73 to 290 mg/l in the feed, and the permeate concentration was consistently less than 1 mg/l. Particle counts indicated 14,478 to 17,257 particles/ml larger than 2 μm in the feed and 0 to 114 particles/ml larger than 2 μm in the permeate. This corresponded to a removal efficiency of more than 99%.

Experimental Results of Separ System and Research Ltd.
Separ Systems and Research Ltd. of Calgary, Alberta, Canada performed tests using ceramic (α-alumina) MF membranes (Alcoa Separations Technology Division, Warrendale, PA) (Zaidi et al., 1991). The pore size of the membrane was 0.8 μm, the maximum transmembrane pressure was 70 kPa, and the expected permeate flux was 1,500 l/m²-hr. The feed tank was treated with either softening chemical agents (lime and sodium carbonate) to encourage precipitation of hardness, or with a small amount of lime and metal coagulants (ferric chloride and/or polyaluminum chloride) to promote a layer of solids on the membrane surface to minimize clogging of the membrane pores.

The system was operated in a batch mode, and the temperature was maintained at 50°C. The transmembrane pressure in the softening mode was between 12 and 21 kPa, and it was between 21 and 64 kPa during the non-softening mode. The pH was 10 for the softening mode and 9 for the non-softening mode. The oil concentration in the feed ranged from 100 to 2,000 mg/l, and the oil concentration in the permeate was consistently less than 10 mg/l. The method for measuring oil and grease was not specified. No oily sheen was visible, suggesting that there was no free oil in the
permeate. The total suspended solids concentration in the permeate ranged between 15 and 26 mg/l and the average flux was about 1250 l/m²-hr.

2.10 Previous Evaluation of UF Treatment of Oily Process Wastewater
Apart from evaluations of produced water treatment, many studies have been performed on UF treatment of oily wastewaters from metal processing industries (Bansal, 1975, Goldsmith et al., 1974, Krug and Attard, 1990). These industries produce wastes with very high oil concentrations and suspended solids loadings. It is difficult to compare the permeate quality from UF of metal processing wastewaters with the permeate quality from UF of produced water because in metal processing waste streams, low molecular weight ingredients containing organic carbon (corrosion inhibitors, emulsifiers, and antifoaming agents) produce a permeate with an elevated total carbon content; hence, measuring the true oil and grease concentration of a sample is difficult. A thorough review of ultrafiltration in metal processing operations is given by Pilipenko and co-workers (1987). Some of these studies are summarized below.

Experimental Results of Using an Abcor Tubular UF System
Goldsmith and co-workers (1974) performed experiments to determine if UF was a viable option for the General Electric Company River Works Plant. This plant principally manufactures aircraft engines, turbine generator sets, and gear drives. Over 1,900 m³/yr (500,000 gal/yr) of water-soluble oils and other oil-contaminated wastes are produced from heavy machine operations including various turning operations, grinding, and gear hobbing. These oil wastes had a total oil concentration between 1
and 3%. The three general types of wastes are emulsified machine coolants, synthetic and semisynthetic coolants, and oil-contaminated water. The emulsified machine coolants contain oil that has been blended with emulsifying agents and other materials, causing oil drops to form and remain in suspension. The oil for these coolants is usually a mineral oil combined with petroleum sulfonates and amine soaps to provide emulsification. Synthetic and semisynthetic coolants are inorganic liquids usually made up of borates, nitrates, nitrites, and phosphates. A small amount of mineral oil is added to this liquid to create a semisynthetic coolant. Oil-contaminated water is comprised of mechanically emulsified oils and oils held in suspension by accumulated solids during gravity separation. Laboratory and pilot-scale tests were performed using Abcor type HFA-251 tubular UF membranes with pores less than 0.005 µm in diameter. Oil concentrations were measured using EPA Method 413.2.

For the first set of experiments conducted in the laboratory, the total recycle mode was used. This permitted evaluation of the dependence of permeate flux and rejection characteristics on all operating parameters except feed concentration. The transmembrane pressure ranged from 140 to 410 kPa (20 to 60 psi). Increasing the temperature from 15 to 38°C (60 to 100°F) resulted in an approximately 50% increase in permeate flux. Over a period of more than two days of continuous operation, there was no decrease in permeate flux and no increase in permeate oil concentration.

For the second set of experiments in the laboratory, a batch mode was used and the permeate was continuously discharged. Rejection characteristics
are illustrated in Table 2.8.

<table>
<thead>
<tr>
<th>Approximate concentration ratio</th>
<th>Oil* in feed (mg/l)</th>
<th>Oil* in permeate (mg/l)</th>
<th>Oil* rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x</td>
<td>16,600</td>
<td>506</td>
<td>97.0</td>
</tr>
<tr>
<td>2x</td>
<td>37,300</td>
<td>764</td>
<td>98.0</td>
</tr>
<tr>
<td>4x</td>
<td>100,700</td>
<td>693</td>
<td>99.3</td>
</tr>
<tr>
<td>8x</td>
<td>88,200</td>
<td>405</td>
<td>99.5</td>
</tr>
<tr>
<td>15x</td>
<td>156,400</td>
<td>742</td>
<td>99.5</td>
</tr>
<tr>
<td>20x</td>
<td>227,900</td>
<td>331</td>
<td>99.9</td>
</tr>
</tbody>
</table>

* EPA method 413.2

Greater than 97.0% oil rejection was observed, and the oil content of the permeate was found to be essentially independent of the feed concentration. Goldsmith and co-workers (1974) expected this because the solubility of organic materials in the aqueous phase of a two-phase system should be independent of the relative volumes of the two phases. IR spectroscopic analysis of the feed water indicated that the relatively high oil concentrations in the permeate could be traced to the presence of an appreciable quantity of triethanolamine oleate, an organic surfactant.

During the 6-week pilot plant study, permeate fluxes were consistently above 61 l/m²-hr (35 gal/ft²-day). Fluctuations of permeate flux with time were a result of changes in operating temperatures and oil concentrations (some colmatage occurred), and not as a result of membrane fouling. It appeared that detergent emulsifiers in the coolants were highly effective in preventing buildup of an oil layer on the membrane. The permeate oil
concentration varied from 35 to 382 mg/l (EPA Method 413.2) and no free oil or visible sheen was observed. The feed was concentrated to 40%, which allowed it to be incinerated without additional fuel.

A full-scale Abcor UF facility was installed in 1973 based on the laboratory and pilot data. It was designed to treat 15,000 l/day (4,000 gal/day) of soluble oil wastes, and it cost $79,000 with 60% of this figure being the cost of the UF system including the holding tank. Analyses of permeate samples from this full-scale facility have shown oil and grease concentrations to be consistently less than 25 mg/l (EPA Method 413.2).

**Experimental Results Using a UCARSEP UF System**

Bansal (1975) reviewed the operating data of laboratory and small pilot-scale installations of UF modules, using inorganic membranes, for concentrating cutting, drawing, and other types of oily wastes, similar to the research by Goldsmith and co-workers (1974) previously discussed. The UCARSEP (a product of Union Carbide Corporation, Tuxedo, NY) UF system was used for these trials. The pore sizes of the membranes ranged from 2 to 100 nm. Before each experiment, the membranes were cleaned with one of the following cleaning agents: Alconox, oxalic acid, Tergazyme, or Tergitol (Union Carbide product #15 S-9).

For the first set of experiments, a complete recycle mode was used to determine the effect of crossflow velocity on permeate flux. A cutting oil emulsion with a feed oil content of 14.4 to 17.2% was circulated at two different crossflow velocities: 4.5 and 6.7 m/sec per tube corresponding to
Reynolds numbers of 26,000 and 39,000, respectively. The tests were conducted at 60 °C to 62 °C (140 °F to 143 °F) and 690 kPa (100 psi) average transmembrane pressure. The pH of the feed oil was between 7 and 8.

A linear decrease in permeate flux was observed over the period of one day at a crossflow velocity of 6.7 m/sec. The permeate flux was initially 244 l/m²-hr (144 gal/ft²-day) and dropped to 160 l/m²-hr (94 gal/ft²-day). A crossflow velocity of 4.5 m/sec resulted in a sharp decrease within the first five hours, from an initial flux of 207 l/m²-hr (122 gal/ft²-day) to a stable value of approximately 136 l/m²-hr (80 gal/ft²-day) which was maintained for the remainder of the test. Bansal concluded that a crossflow rate of 6.7 m/sec was preferable to a crossflow rate of 4.5 m/sec.

Over 100 industrial waste oil emulsions were tested in a batch mode of operation. The waste oils categorized were lubricating oil, rolling oil, cutting oil, vegetable oil, and drawing oil. The crossflow rate per tube was kept between 4.5 and 6.7 m/sec, and the feed pressure ranged from 345 to 690 kPa (50 to 100 psi). The temperature was between 34 °C and 71 °C (94 °F and 160 °F), and the pH was between 6.7 and 14.0. At a 12% oil concentration, the permeate flux for the cutting oils averaged 120 l/m²-hr (70 gal/ft²-day), and the other waste oils were on the order of 59 to 76 l/m²-hr (35 to 45 gal/ft²-day). The vegetable oils exhibited the lowest permeate flux. All of the oils showed a decline in permeate flux as the oil concentration in the feed was increased.
All of the oil rejections were extremely high, even though permeate oil concentrations were high during the processing of the vegetable and drawing oils (Table 2.9). During the testing of the drawing oils, the membrane became rapidly fouled, resulting in significant permeate flux decline and high oil concentrations in the permeate, possibly due to non-Newtonian viscosity behavior of the drawing oil compounds. The oil drops "solidified" into wax-like irregular blobs which adhered to the membrane surface and caused fouling.

Table 2.9: Oil Concentration and Rejection Characteristics for Waste Oils (adapted from Bansal (1975))

<table>
<thead>
<tr>
<th>Type of Oil</th>
<th>pH of feed</th>
<th>Range of Oil Concentrations*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of feed</td>
<td>Feed (%)</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>11-12</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Rolling oil</td>
<td>7.3-8.2</td>
<td>0.8-3.7</td>
</tr>
<tr>
<td>Cutting oil</td>
<td>6.7-8.3</td>
<td>0.1-3.9</td>
</tr>
<tr>
<td>Vegetable oil</td>
<td>12.0-13.9</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Drawing oil</td>
<td>9.5-14.0</td>
<td>0.1-1.5</td>
</tr>
</tbody>
</table>

*Hexane extraction method

Field tests were conducted with compressor blow down oil which had been mechanically emulsified. The average pressure ranged between 280 and 550 kPa (40 and 80 psi). The feed temperatures were between 21° and 60°C (70° and 140°F), and the crossflow rate was 4.7 m/sec per tube. The average concentration of oil in the feed was 0.16% and it was concentrated to 2.7% oil. An average permeate flux of 85 l/m²-hr (50 gal/ft²-day) was achieved over a continuous period of 18,000 hours, and the oil concentrations in the permeate ranged between 8 and 15 mg/l.
Operating cost estimates were calculated for two different scenarios for a 190,000 l/day (50,000 gal/day) unit. For a crossflow rate of 4.5 m/sec, an estimated membrane life of 3 years, and an average membrane flux of 85 l/m²-hr (50 gal/ft²-day), the operating cost would be about $0.54 per 1,000 liters ($2.0 per 1,000 gallons) of feed. The operating cost was estimated to be about $0.96 per 1,000 liters ($3.63 per 1,000 gallons) of feed for a crossflow rate of 5.6 m/sec, an estimated membrane life of 2 years, and an average membrane flux of 68 l/m²-hr (40 gal/ft²-day).

Experimental Results of Krug and Attard (1990)

Stelpipe, a large steel pipe manufacturing facility, had a number of waste streams which required treatment before being discharged into the sewer. These included rinse water contaminated primarily with oils from the pipe and cleaning chemicals used to remove the oil, and other contaminants, including polyethylene glycol and mineral oils from hydraulic fluids. Most of the oil present had been emulsified by the strong surfactants present in the cleaning solutions. UF was used exclusively until recently when the Region of Niagara declared that dichloromethane must be used instead of freon when performing an extraction to determine the oil and grease content of the water. This new method was found to give much higher oil concentrations than the method that uses freon for extraction. Dichloromethane is a more polar solvent than freon and will extract not only oil and grease, but also more surfactants and other organic materials. With the new method, the discharge was not in compliance with the regulation values; therefore, it was decided that a reverse osmosis (RO) system would be added downstream of the UF system to reduce the
permeate oil concentration. Concentrations and rejections are summarized in Table 2.10 for the UF and the RO systems.

<table>
<thead>
<tr>
<th>Date</th>
<th>UF - Oil* Feed (mg/l)</th>
<th>UF - Oil* Permeate (mg/l)</th>
<th>UF - Oil* Rejection (%)</th>
<th>RO - Oil* Permeate (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>March, 1</td>
<td>23,000</td>
<td>170</td>
<td>99.3</td>
<td>6</td>
</tr>
<tr>
<td>March, 9</td>
<td>28,000</td>
<td>200</td>
<td>99.3</td>
<td>45</td>
</tr>
<tr>
<td>March, 27</td>
<td>98,000</td>
<td>450</td>
<td>99.5</td>
<td>na</td>
</tr>
<tr>
<td>April, 2</td>
<td>103,000</td>
<td>500</td>
<td>99.5</td>
<td>na</td>
</tr>
<tr>
<td>April, 6</td>
<td>167,000</td>
<td>400</td>
<td>99.8</td>
<td>83</td>
</tr>
<tr>
<td>April, 17</td>
<td>11,000</td>
<td>180</td>
<td>98.4</td>
<td>27</td>
</tr>
<tr>
<td>April, 21</td>
<td>12,270</td>
<td>194</td>
<td>98.4</td>
<td>9</td>
</tr>
</tbody>
</table>

*Dichloromethane extraction method

Greater than 98.4% rejection of oil in the UF system was obtained. The RO system which treated the UF permeate reduced the oil concentration to 10 to 80 mg/l.

2.11 Previous Evaluations of UF Treatment of Model Oil/Water Emulsions

Synthetic oil and water mixtures have been used in an attempt to simulate metal processing oily waste streams, and one such study is discussed here (Lipp et al., 1988). UF can also be used to separate oil from solvents other than water (Koseoglu et al., 1990, Kulkarni et al., 1986).

Experimental Results Using Synthetic Oil and Water Mixtures

Factors affecting permeate flux and rejection in the ultrafiltration of oil/water emulsions were investigated, and oil drop size distributions were
analyzed (Lipp et al., 1988). Emulsions were prepared to simulate the types of wastes produced in the metal-finishing industry.

Two types of emulsions were prepared. Type "A" was made of water and a soluble oil consisting of mineral oil, surfactants, corrosion inhibitors, and other additives. Type "B" consisted of water, mineral oil, and surfactants. Experiments were performed in a stirred, batch, dead-end UF cell. Table 2.11 lists the characteristics of the membranes used. Total organic carbon (TOC) was measured, and the oil content was found by measuring turbidity and creating a calibration curve using standards.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Material</th>
<th>Nominal molecular weight cut-off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amicon YM30</td>
<td>regenerated cellulose</td>
<td>30,000</td>
</tr>
<tr>
<td>Amicon PM30</td>
<td>polysulfone</td>
<td>30,000</td>
</tr>
<tr>
<td>IRIS 3038</td>
<td>polyacrylic</td>
<td>10,000</td>
</tr>
<tr>
<td>CJT 35</td>
<td>polyamide</td>
<td>&gt; 100,000</td>
</tr>
</tbody>
</table>

The clean water flux tests (CWFT) were conducted at a transmembrane pressure of 100 kPa. Lipp characterized the fouling tendency by using the ratio $J_{wf}/J_{wi}$, where $J_{wi}$ is the clean water flux for the clean membrane, and $J_{wf}$ is the clean water flux after fouling and colmatage. Permeation rates before and after ultrafiltration of Type "A" emulsion are shown in Table 2.12.
Table 2.12: Clean Water Permeate Fluxes Before and After UF of Type "A" Oil Emulsion (adapted from Lipp and co-workers (1988))

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Initial flux $J_{wi}$ (l/m²-hr)</th>
<th>Final flux $J_{wf}$ (l/m²-hr)</th>
<th>Flux ratio $J_{wf}/J_{wi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM30</td>
<td>80</td>
<td>75</td>
<td>0.93</td>
</tr>
<tr>
<td>PM30</td>
<td>980</td>
<td>5</td>
<td>0.005</td>
</tr>
<tr>
<td>IRIS 3038</td>
<td>550</td>
<td>400</td>
<td>0.73</td>
</tr>
<tr>
<td>CJT 35</td>
<td>72</td>
<td>1</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The most hydrophilic membrane (regenerated cellulose) demonstrated the smallest fouling tendency, and the more hydrophobic membranes (polyamide, polysulfone) had the highest tendency to foul. The contact angle was measured to be less than 50° for the regenerated cellulose membrane, and about 60° for the polysulfone membrane.

Solute rejections are listed in Table 2.13 for the different types of membranes. These tests were performed at a transmembrane pressure of 200 kPa. Oil rejections were greater than 99.9% for all membranes tested, which was equivalent to less than 20 mg/l in the permeate, though the oil concentration in the feed was greater than 33,700 mg/l. The TOC rejection ranged from 96 to about 98%, which for this water corresponded to a permeate TOC concentration range of about 1,300 to 2,200 mg/l.
Table 2.13: Oil Concentration and Rejection Characteristics for UF of 5% Type "A" Oil Emulsion (adapted from Lipp and co-workers (1988))

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>TOC in feed (mg/l)</th>
<th>TOC in permeate (mg/l)</th>
<th>TOC rejection (%)</th>
<th>Oil* in feed (mg/l)</th>
<th>Oil* in permeate (mg/l)</th>
<th>Oil rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM30</td>
<td>36,250</td>
<td>1,386</td>
<td>96.2</td>
<td>33,750</td>
<td>&lt;20</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>PM30</td>
<td>36,250</td>
<td>1,338</td>
<td>96.3</td>
<td>33,750</td>
<td>&lt;20</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>PM30**</td>
<td>72,500</td>
<td>2,253</td>
<td>96.9</td>
<td>67,500</td>
<td>&lt;20</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>IRIS 3038</td>
<td>36,250</td>
<td>1,338</td>
<td>96.3</td>
<td>33,750</td>
<td>&lt;20</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>CJT 35</td>
<td>36,250</td>
<td>1,329</td>
<td>96.3</td>
<td>33,750</td>
<td>&lt;20</td>
<td>&gt;99.9</td>
</tr>
</tbody>
</table>

*Turbidity method

**10% Type "A" oil emulsion

Oil drop sizes were analyzed in the feed, the polarized gel layer, and the permeate. The results indicated that the oil drop size distributions were different for each case. A larger drop size was observed in the gel layer, providing direct evidence that coalescence was occurring. The permeate contained mostly small drops but also a few large drops indicating that some coalescence was occurring within the membrane pores. The thickness of the gel layer was estimated to be between 35 and 100 μm, and it increased significantly with feed concentration.

2.12 Previous Evaluations Summarized

UF and MF treatment of produced waters has shown promising results in the few studies that have been performed. Permeate fluxes for UF treatment range between 21 and 300 l/m²-hr and permeate fluxes for MF treatment can exceed 1250 l/m²-hr. During UF of various produced waters, the main factor that seemed to affect permeate flux was the site from which the produced water originated. The presence of free oil in the
produced water tended to cause low permeate fluxes, while UF treatment of stable emulsions demonstrated higher permeate fluxes and the membranes had a smaller tendency to foul. In one UF pilot study, clay was suspected of being the main fouling contaminant.

As with the permeate flux, the permeate TOC and oil concentrations mainly depended on the source of the produced water. For UF and MF treatment of produced water, the permeate TOC and oil concentrations generally did not change during an experiment. In one UF study, permeate oil concentrations were relatively high, ranging between 70 and 215 mg/l. Although, another study demonstrated that permeate oil concentrations of less than 15 mg/l (methylene chloride extraction/IR) could be obtained.

The NF study cited in this work demonstrated that a very high pressure (1480 kPa) was necessary to maintain a permeate flux between 11 and 18 l/m²-hr. This permeation range is much lower than that obtained by UF and MF treatment of produced water. Permeate oil concentrations were less than 48 mg/l (EPA Method 413.2), but the low recovery (7%) may make NF treatment of produced water uneconomical.

A number of evaluations of the treatment of oily process wastewaters from metal working industries have been conducted using UF. Oily process wastes have similar characteristics to those of produced water. However, oily process wastes usually have higher organic carbon contents due to high concentrations of oils and chemical additives such as corrosion
inhibitors, emulsifiers, and antifoaming agents. Permeation rates for UF treatment of these waters ranged between 59 and 120 l/m²-hr, and as in UF treatment of produced water, higher permeation rates were obtained for stable emulsions. Studies on UF of oily process wastes also indicate that the permeate flux increases with an increase in temperature and in crossflow velocity. An increase in the oil concentration in the feed stream was observed to decrease the permeate flux in one study.

Laboratory-scale experiments on UF of oily process wastes produced permeates with oil concentrations ranging between 35 and 382 mg/l (EPA Method 413.2), but industry-scale and field tests produced permeate oil concentrations less than 25 mg/l (EPA Method 413.2). As in the studies performed on produced water, variations in feed oil concentrations during experiments did not affect permeate oil concentrations.

High TOC and oil and grease (correlated with turbidity) rejections were observed during UF of model oil/water emulsions: TOC rejections were greater than 96% and oil and grease rejections were greater than 99.9%. An oil drop analysis was performed. A few large oil drops in the permeate indicated that some coalescence was occurring within the membrane pores.

Based on previous evaluations, the treatment of produced water by UF is expected to yield low TOC and oil concentrations in the permeate as long as low molecular weight chemical additives such as corrosion inhibitors are not present in the produced water. Previous evaluations indicate that permeation rates may be in the range of 21 to 300 l/m²-hr for the treatment
of produced water using UF membranes. Free oil has been shown to have a substantial fouling effect, but other constituents in the produced water have not generally been analyzed to assess what effect they might have on permeate flux decline. Because some evaluations have suggested that UF performance varies with different produced waters from different locations, further research is necessary to assess which produced water characteristics govern UF performance.
CHAPTER 3
MATERIALS AND EXPERIMENTAL METHODS

A laboratory-scale filtration unit was operated in a total recycle mode using tubular, ultrafiltration membranes to evaluate filtration performance when processing oil emulsion feed waters. Two types of feed waters were evaluated: model feed waters using laboratory prepared emulsions of hydrocarbons, and produced water from oil and gas wells. Experiments were conducted in two different ways. The first set of experiments was performed by incrementally increasing the transmembrane pressure while keeping the crossflow velocity constant. Oil concentration and crossflow velocity were varied. For the remainder of the experiments, transmembrane pressure was kept constant to observe permeation behavior and contaminant rejection with time.

3.1 Materials
3.1.1 Membrane Description
Zenon ADC, asymmetric, polymeric, ultrafiltration membranes were used for all experiments (ZENON Environmental Inc., Burlington, Ontario, CANADA, L7N 3P3). The characteristics of these tubular membranes are listed in Table 3.1. The actual membrane is a very thin porous film supported by a polyester backing. Water flows from the inside of the tube through the membrane to the outside of the tube. The membranes should not be allowed to dry out. The membrane material is of a proprietary nature.
Table 3.1: Membrane Characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>organic, polymeric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>tubular</td>
</tr>
<tr>
<td>Tube diameter (ID)</td>
<td>1.07 cm, 1.14 cm</td>
</tr>
<tr>
<td>Tube length</td>
<td>91.2 cm</td>
</tr>
<tr>
<td>Tube surface area</td>
<td>306 cm², 327 cm²</td>
</tr>
<tr>
<td>Molecular Weight Cut-Off (MWCO)</td>
<td>70,000 Daltons</td>
</tr>
<tr>
<td>Average permeate flux*</td>
<td>100-200 l/m²-hr</td>
</tr>
<tr>
<td>Estimated pore diameter</td>
<td>0.006 µm</td>
</tr>
<tr>
<td>Affinity for water</td>
<td>hydrophilic</td>
</tr>
<tr>
<td>Temperature limits</td>
<td>5 °C-60 °C</td>
</tr>
<tr>
<td>pH limits</td>
<td>2-11</td>
</tr>
<tr>
<td>Maximum pressure</td>
<td>620 kPa</td>
</tr>
<tr>
<td>Maximum chlorine concentration</td>
<td>200 mg/l</td>
</tr>
</tbody>
</table>

*as reported by manufacturer

The pore diameter shown in Table 3.1 is estimated by the following equation:

\[
d (\mu m) = 1.47 \times 10^{-4} (MWCO)^{1/3}
\]

(3.1)

This equation assumes spherical solutes were used to determine the MWCO of the membrane.

In each experiment, two tubular membranes were used in series with a length of 91.2 cm exposed to the flow for each membrane. The ADC1, ADC2, and ADC3 membranes had a diameter of 1.14 cm which corresponds to a membrane surface area of 327 cm². The remainder of the membranes used had a diameter of 1.07 cm which corresponded to a membrane surface area of 306 cm².
3.1.2 Experimental System

A laboratory-scale filtration unit supplied by ZENON Environmental Inc. was modified to accommodate pressure gauges, flowmeters, and sampling ports. The experimental system is shown in Figure 3.1.

![Experimental Ultrafiltration System Diagram](image)

**Figure 3.1: Experimental Ultrafiltration System**

A 38 liter (10 gallon) high density polyethylene (HDPE) tank was used as a feed water reservoir to the unit. The feed water was stirred using a variable speed (20-1800 rpm) Lightnin mixer (Cole-Parmer Instrument Company, Niles, IL 60714). A 115 liter (30 gallon) HDPE tank was used for rinse water. All of the valves and rigid piping are either polyvinyl chloride (PVC) or chlorinated polyvinyl chloride (CPVC), and the flexible tubing is reinforced PVC. The feed stream initially flows through a Cole-Parmer 127 mm direct reading flowmeter that has a range of 8 to 57 lpm (2 to 15 gpm) with an accuracy of +/-2.5% full scale (Cole-Parmer Instrument Company, Niles, IL 60714). The water then flows through a
Dynesco high pressure, CPVC, electrically driven, centrifugal pump and to a bypass valve which allows water to either be returned to the feed tank or to continue on through another direct reading flowmeter (Dynesco Inc., Canada). This second flowmeter indicates the rate of flow through the membrane module. The bypass valve allows for the control of pressure drop across the membrane independent of the crossflow velocity. The pump has an automatic shutoff mechanism which is activated if the temperature of the water is greater than 60°C (140°F) or if the discharge pressure is less than 83 kPa (12 psi).

A digital pressure gauge mounted upstream of the membrane module and one mounted downstream allow for a determination of headloss through the system. These gauges have a range of -97 to 3450 kPa (-14 to 500 psi) and an accuracy better than 1% (Davis Instrumentation, Baltimore, MD 21215). Each gauge has a gauge guard which protects it from suspended matter. Water flowing through the membrane is discharged to atmospheric pressure from the CPVC casings into 1/4 inch polyethylene tubing and into the feed tank. Each permeate line is fitted with a Cole-Parmer 150 mm variable area flowmeter used to determine permeate flow of less than 230 ml/min (Cole-Parmer Instrument Company, Niles, IL 60714). Larger permeate flows were measured using a graduated cylinder and stopwatch. The membrane module is aligned vertically to minimize gravitational effects. The recycle flow is returned to the feed tank. A diaphragm valve located downstream of the membrane module is used with the bypass valve to control the flow through the system and the inlet and outlet module pressures. Samples of the permeate flow were taken from sampling valves
in the permeate line, and samples of the recycle flow were taken where the recycle flow discharges into the feed tank.

3.1.3 Feed Water Description

Two types of experiments were performed: experiments with model emulsions of hydrocarbons and experiments with produced waters from oil and gas wells. In two of the experiments performed on produced water, a surfactant or powdered activated carbon (PAC) was used to try to improve membrane performance. The various feed waters and operating parameters used in these experiments are summarized in Table 3.2.

Table 3.2: Operation Variables for UF Experiments

<table>
<thead>
<tr>
<th>Experiment designation</th>
<th>Membrane designation</th>
<th>Feed water</th>
<th>Source</th>
<th>Crossflow velocity (m/sec)</th>
<th>Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>ADC1</td>
<td>0.02 vol% chlorobenzene</td>
<td></td>
<td>3.08</td>
<td>317-393</td>
</tr>
<tr>
<td>C2</td>
<td>ADC1</td>
<td>0.02 vol% chlorobenzene</td>
<td></td>
<td>1.85</td>
<td>362-424</td>
</tr>
<tr>
<td>C3</td>
<td>ADC1</td>
<td>0.2 vol% chlorobenzene</td>
<td></td>
<td>3.08</td>
<td>341-403</td>
</tr>
<tr>
<td>D1</td>
<td>ADC5</td>
<td>0.2 vol% dodecane</td>
<td></td>
<td>3.53</td>
<td>328-369</td>
</tr>
<tr>
<td>D2</td>
<td>ADC5</td>
<td>0.2 vol% dodecane</td>
<td></td>
<td>3.53</td>
<td>307-383</td>
</tr>
<tr>
<td>MJ1</td>
<td>ADC6</td>
<td>produced water</td>
<td>gas well</td>
<td>3.53</td>
<td>314-396</td>
</tr>
<tr>
<td>MJ2</td>
<td>ADC7</td>
<td>produced water</td>
<td>gas well</td>
<td>3.53</td>
<td>326-419</td>
</tr>
<tr>
<td>MJ3</td>
<td>ADC8</td>
<td>produced water</td>
<td>gas well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>MJ4</td>
<td>ADC8</td>
<td>produced water</td>
<td>gas well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>MJ5</td>
<td>ADC8</td>
<td>produced water</td>
<td>gas well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>MJ6</td>
<td>ADC8</td>
<td>produced water, surfactant*</td>
<td>gas well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>HP1</td>
<td>ADC9</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>HP2</td>
<td>ADC9</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>HP3</td>
<td>ADC9</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>HP4</td>
<td>ADC9</td>
<td>produced water, PAC**</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>LS1</td>
<td>ADC10</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>LS2</td>
<td>ADC10</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>LS3</td>
<td>ADC10</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
<tr>
<td>LS4</td>
<td>ADC10</td>
<td>produced water</td>
<td>oil well</td>
<td>3.53</td>
<td>345</td>
</tr>
</tbody>
</table>

*sodium dodecyl sulfate  
**PAC: powdered activated carbon
3.1.3.1 Model Emulsions

Experiments with model emulsions were performed to evaluate the effects of crossflow velocity and oil concentration on permeate flux and permeate quality. Special considerations were necessary in the preparations of the model feed waters due to concerns about the accurate analyses of oil drop measurements. The following section illustrates the nature of the problem and the procedure used to overcome it.

When oil and water (two immiscible liquids) are mixed together under turbulent flow conditions, such as in the experimental system used in this work, oil droplets form and break apart because of shearing and coalescing forces created by the mixing conditions. Work put into the system overcomes the surface tension at the oil/water interface and creates a large amount of interfacial area between the oil and water. When samples are taken from the turbulent system, the emulsion is thermodynamically unstable. Most of the work put into the system to create the emulsion is dissipated by viscous effect, and some of the work is stored as potential energy which is spontaneously reduced by reducing the interfacial area of drops through the process of coalescence.

If a material can be added to the system to form some type of film or barrier at the oil/water interface, the coalescence process can be minimized. Certain polymers can be used to stabilize the emulsion in a process referred to as microencapsulation. Polymeric emulsifiers and stabilizers can be made to adsorb strongly at the oil/water interface to create a mechanical barrier which "freezes" the droplets and retards the
coalescence of individual droplets (Heneghan and Clark, 1991). Through this process, the droplets can be transported, measured, and counted without a change in the original drop size distribution.

Two chemical compounds are required for the microencapsulation process - one soluble in the dispersed phase and one soluble in the continuous phase. When combined, the two encapsulating agents must polymerize with each other. Terephthaloyl chloride has been suggested by Metcalf & Eddy (1979) to be an appropriate encapsulating agent, and it is soluble in the dispersed phase (chlorobenzene) used in this work. Piperazine polymerizes with terephthaloyl chloride and is soluble in water, so it was used as the complementary encapsulating agent.

Two different types of model emulsions were used: an emulsion combining chlorobenzene, terephthaloyl chloride, piperazine, in DI water and an emulsion of dodecane in DI water. A list of some of the properties of the chemicals used for the model waters is shown in Table 3.3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>FW</th>
<th>Density (g/ml)</th>
<th>Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene*</td>
<td>C₆H₅Cl</td>
<td>112.56</td>
<td>1.107</td>
<td>0.799 (T=20 °C)</td>
</tr>
<tr>
<td>Terephthaloyl chloride*</td>
<td>C₆H₄·1, 4-(COCl)₂</td>
<td>203.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Piperazine (anhydrous)**</td>
<td>C₄H₁₀N₂</td>
<td>86.14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dodecane**</td>
<td>C₁₂H₂₆</td>
<td>170.34</td>
<td>0.748</td>
<td>1.35 (T=25 °C)</td>
</tr>
</tbody>
</table>

*Aldrich Chemical Company Inc., Milwaukee, WI 53233
**Sigma Chemical Company, St. Louis, MO 63178-9916

For the first three experiments (designated C1, C2, and C3), a solution of
either 0.02 or 0.2 vol% chlorobenzene was mixed with DI water, and then terephthaloyl chloride as 1 wt% of the chlorobenzene was added. A stock solution of piperazine as 1 wt% of the terephthaloyl chloride was prepared and a few drops were added to the samples taken during the experiment to "freeze" the drops and stabilize the emulsion for drop size measurements.

Two experiments were performed using 0.2 vol% dodecane in DI water without encapsulating agents. These experiments were designated D1 and D2.

3.1.3.2 Produced Waters
Experiments with produced waters from oil and gas wells were designed to evaluate how permeate flux and permeate quality vary with time. Produced waters used in these experiments were obtained from three different sites. The sampling locations are illustrated in Figure 3.2. Samples were taken at two different times from a gas well referred to as MJ. The water was collected immediately downstream of a two-phase, low pressure separator. Six separate experiments were performed on these waters and are designated in this work by the letters MJ followed by a number. Produced water from the second site, designated as HP, was obtained immediately downstream of a gun barrel (a settling vessel designed to separate oil and water). The third produced water tested was obtained from an oil well (LS) producing 2000 barrels of brine per day. Samples were collected from a three-phase separator that was temporarily put on line. Oil remaining in the LS produced water was separated further in the laboratory using a 5-gallon tank with a spigot at the bottom.
Figure 3.2: Produced Water Sampling Locations

X corresponds to sampling location.

MJ Gas Well

HP Oil Well

LS Oil Well
The effect of chemical pretreatment on membrane performance was evaluated. In a separate group of experiments, sodium dodecyl sulfate (C_{12}H_{25}O_{4}SNa) and powdered activated carbon (PAC) were added. Sodium dodecyl sulfate (SDS), an anionic surfactant, was added to the produced water of experiment MJ6 in three separate additions (Sigma Chemical Company, St. Louis, MO 63178-9916). If it is assumed that the produced water contains at least 0.1 M NaCl, then the critical micelle concentration (CMC) can be estimated to be 1.5x10^{-3} M (Rosen, 1989). After the permeate flux had reached a steady state value in experiment MJ6, SDS was added at fifteen minute intervals. First, 0.1 times the CMC was added, then enough SDS was added to bring the concentration to 0.4 times the CMC. For the last addition, SDS was added to bring the feed water concentration up to 1.0 times the CMC.

Darco PAC was added to the produced water in experiment HP4 after a steady flux had been reached (Darco PAC, ICI United States Inc., Wilmington, DE 19897). The average particle size of the PAC was 3.8 μm as evaluated on a Coulter Multisizer particle analyzer (Coulter Electronics Limited, Luton, England). A concentration of 20 mg/l was added directly into the feed tank.

3.2 Experimental Methods

3.2.1 Start-Up and General Operation of the UF System

The system was always filled with DI water or other fluid so that the pump would be primed. At the beginning of each experiment, both the bypass valve and the recycle valve were set to a halfway open position. All other
valves upstream of the pump were open. The start button on the unit was pressed while slowly closing the bypass valve. Once the pressure immediately upstream of the membranes passed 83 kPa (12 psi), the start button was released. The bypass valve and the recycle valve were then adjusted to obtain the desired crossflow velocity through the membranes and the desired transmembrane pressure drop. The average transmembrane pressure was approximated as the average of the pressure readings upstream and downstream of the membranes since the permeate was discharged to atmospheric pressure.

3.2.2 Experimental Procedure
For any given experiment, all valves were initially closed, and prior to turning on the pump, all valves were opened and the bypass and recycle valves were set halfway open. For experiments where particle measurements were made, electrolyte was prepared the previous day by filtering a 2.0 wt% HCl solution through a 0.45 μm filter for three hours. Sample bottles were labeled and weighed when necessary and a data sheet was prepared before each experiment. A pH reading was taken at the beginning and at the end of each produced water experiment.

First, both the small and large tanks were filled with DI water. The feed hose was connected to the small tank, and the recycle and permeate outlets were directed into a five gallon waste tank. The pump was turned on for a few seconds to allow two to three gallons of the water in the system to discharge. The recycle and permeate outlets were then attached to the rim of the small tank. The pump was again turned on and DI water was
allowed to flow at a high velocity through the system. After ten minutes, the pump was shut off and the feed hose was disconnected from the small tank. The tank was then emptied and cleaned.

Compaction of the membrane was observed so experiments with DI water were performed to determine how the feed water experiments could be conducted so as to eliminate the effects of compaction. It was determined that the following procedure eliminates compaction effects. All of the feed water experiments started with a fifty minute compaction run. The feed hose was hooked up to the large tank and the recycle and permeate hoses were directed into the waste tank. The pump was turned on for a few seconds to discharge two to three gallons of water. Then, the discharge hoses were clamped to the rim of the large tank. The pump was turned on, the bypass valve was closed all the way, and the recycle valve was adjusted to a crossflow velocity of 3.53 m/sec. The transmembrane pressure was set at 380 kPa (55 psi). While the membrane was being compacted, the feed water was prepared.

The small tank was filled with 34 liters (9 gallons) of DI water for the dodecane and chlorobenzene experiments. The appropriate amounts of chemicals were added and mixed. Produced water was transferred directly into the small tank from the field sample containers except for the LS produced water. This water was first transferred into a five gallon tank with a spigot at the bottom. The water was drawn off from the bottom so as not to include a thick layer of dark oil at the surface, thereby simulating a separator. The feed waters were usually mixed for 10 to 20 minutes
before an experiment began.

When the compaction run was finished, a clean water flux test (CWFT) was performed. CWFT's were performed before and after each experiment by running DI water through the system and incrementally increasing the transmembrane pressure so that flux readings for five to six different pressures could be taken. The crossflow velocity was kept constant at 3.53 m/sec. After the CWFT, the pump was shut off and the feed hose was disconnected from the large tank and reconnected to the small tank. Two to three gallons were discharged into the waste tank as before.

The dodecane experiments, and the MJ1 and MJ2 experiments were performed in the same manner. The pump was turned on and the bypass and recycle valves were adjusted to set an initial pressure drop of about 324 kPa (47 psi). The crossflow velocity was kept constant at 353 cm/sec throughout the experiment. At 15 minute intervals, the transmembrane pressure drop was increased. Five different pressure drops were observed for each experiment. Flux measurements were made immediately before each pressure adjustment using a graduated cylinder and a stopwatch. The chlorobenzene experiments were performed in the same way except that the time interval between pressure adjustments was 20 minutes instead of 15 minutes. The crossflow velocities were also different. Experiments C1 and C3 had crossflow velocities of 3.08 m/sec, and experiment C2 had a crossflow velocity of 1.85 m/sec.
For the remaining produced water experiments, the bypass and recycle valves were adjusted so as to have a constant transmembrane pressure drop of 50 psi and a constant crossflow velocity of 3.53 m/sec. Flux measurements were made every 7.5 minutes and samples were taken at various times. Experiments were stopped after the permeate flux was judged to have reached a steady value.

As water recirculates in the system, the temperature of the water increases due to the energy imparted by the pump. As temperature increases, the viscosity of the fluid decreases, leading to a relatively higher permeate flux. Experimental evaluation of permeate flux verses temperature in this work and in previous research (Henry, 1972) indicate that corrections of permeate flux to a reference temperature can be made as:

\[
J_{T=20} = \left( \frac{J_T \mu_T}{\mu_{T=20}} \right)
\]

(3.2)

Samples were obtained at regular intervals during the experiments. Permeate samples were collected in glass vials from the permeate sampling ports, and recycle samples were taken from the recycle outlet which emptied directly into the feed tank.

When the feed water run was finished, two or three gallons of the water in the system were discharged into the waste tank as before, and a CWFT was performed using the DI water in the large tank. The small tank was emptied, cleaned and refilled with 34 liters (9 gallons) of DI water in
preparation for the cleaning procedure as described in the next section.

3.2.3 Cleaning Procedures
After each test, the membranes were flushed with DI water for 10 minutes and then a CWFT was performed. NaOH and alkaline cleaners were used to try to remove oily substances. A sodium hydroxide (NaOH) solution having a pH of about 11 was mixed in the feed tank. This solution was circulated through the system for 20 minutes at a high velocity and then the membranes were allowed to soak for one hour. For several experiments, instead of NaOH, a 0.1 wt% solution of Alconox or Zenon's MC-4 cleaner was used. The membranes were then rinsed for fifteen minutes with DI water and another CWFT was performed in most cases.

An acid solution was used after each test except for the chlorobenzene tests. This solution was made by adding HCl to a 0.1 wt% solution of sodium benzoate (a preservative) to lower the pH to 3.5. The acid solution was circulated through the system for 10 minutes and then the system was allowed to soak until the next use. HCl was used to try to remove particulate foulants, and sodium benzoate served as a bacteriapicide and fungicide. Before a new test began, the system was rinsed twice and a CWFT was performed.

3.2.4 Analytical Methods
3.2.4.1 Total Organic Carbon
A Total Organic Carbon Analyzer was used to determine the total organic carbon (TOC) concentrations (Shimadzu Corporation, Model TOC-500,
Tokyo, Japan). This instrument utilizes a combustion-non-dispersive infrared gas analysis method to determine total carbon (TC) and inorganic carbon (IC) concentrations. The TOC concentration is typically determined by subtracting IC from TC or by first removing IC from the sample and analyzing for TC. In the latter case, IC is removed by acidifying the sample with HCl and then purging it by bubbling nitrogen gas through the sample for ten minutes. This IC-purge procedure was used to measure TOC in the HP and LS experiments. In all other experiments, TOC was measured by IC and TC channel difference. Permeate and recycle flows were sampled during every experiment. When a visible oil sheen was observed at the water/air interface of a sample, a surfactant was added to try and disperse the oil homogeneously into the water to obtain a more representative sample. Two different surfactants were used for this purpose.

For experiments HP3, HP4 and all of the LS experiments, TERGITOL nonionic surfactant 15-S-7 was used in the recycle samples (Union Carbide Chemicals and Plastics Company Inc., Danbury, CT 06817-0001). Its general formula is:

$$C_{11-13}H_{23-31}O(CH_2CH_2O)_nH$$

and its CMC is 0.0039 wt%. Enough surfactant was added to each sample to give it a concentration of 0.05% which corresponds to a TOC of 275 mg/l. This value was subtracted from the measured value determined by the TOC-500 analyzer to give the TOC concentration of the sample. This same method was used for the recycle samples from experiment HP2, except that an ionic surfactant called Enordet alpha olefin sulfonate (AOS)
14-16 was used (Ref.# 16560-185, Shell Development Company, Houston, TX 77001). A white precipitate was observed in the HP2 samples (possibly sulfate precipitation), so the TOC measurements from this experiment were considered to be inaccurate.

3.2.4.2 Total Oil and Grease

A slight modification of EPA Method 314.2 was used to determine the total recoverable oil and grease concentrations of the different produced waters. This method involves extraction with Fluorocarbon-113 of the oil and grease from the sample and then evaluation of the infrared absorbance of the extracted solution (Appendix B). A Nicolet Model 205 Fourier Transform Infrared (FTIR) Spectrometer was used to determine the peak height of the absorbance of a sample at a wavelength of 2930 cm⁻¹ which was then compared to standard solutions to determine the concentration in mg/l total oil and grease (Nicolet Instrument Corporation, Madison, WI 53711-0508). Instead of 1 liter samples, 350 ml samples were used. After the separatory procedure, the extract was diluted to 50 ml with solvent instead of 100 ml. Samples were taken during experiments MJ4, HP4, and LS4 so that a correlation could be established between total oil and grease and total organic carbon for each produced water.

3.2.4.3 Analyses of Inorganic Materials

A Perkin-Elmer Plasma 400 Emission Spectrometer was used to measure the concentrations of Ca²⁺, Mg²⁺, Ba²⁺, Zn²⁺, total Fe, total Cr, total Pb, total Hg, total Mn, and total Cu for the raw produced waters and for samples taken during experiments (Perkin-Elmer Corporation, Norwalk,
CT 06851-1196). The Plasma 400 performs sequential multielement analyses of liquid samples by atomic emission spectroscopy. A nebulizer converts the injected sample into a fine aerosol which is introduced into an argon-supported Inductively Coupled Plasma (ICP). The high temperature of the plasma atomizes the sample and promotes atomic and ionic transitions which are observable at ultraviolet and visible wavelengths. The Plasma 400 monochromator isolates the characteristic emission wavelength for each desired element. The intensity of the emission for the element is then measured to determine the concentration.

A HACH Model DR/2000 Spectrophotometer was used to analyze raw produced water samples to determine the concentrations of SiO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2-} and Al\textsuperscript{3+} (HACH Company, Loveland, CO 80539). This Spectrophotometer is a microprocessor-controlled single beam instrument that makes colorimetric measurements of aqueous samples.

3.2.4.4 Particle Measurement

A Coulter Multisizer was used to determine the number of particles, the number averaged particle size, and the volume fraction of particles for the raw produced waters and for samples taken during experiments (Coulter Electronics Limited, Luton, England). The Multisizer determines the number and size of particles suspended in a conductive liquid by monitoring the electrical current between two electrodes immersed in the conductive liquid on either side of a small aperture, through which a suspension of the particles is forced to flow. As each particle passes through the aperture, it changes the impedance between the electrodes and
produces an electrical pulse of short duration having a magnitude essentially proportional to the particle volume. The series of pulses is electronically scaled, counted, and accumulated in a number of size related channels which produces a size distribution curve. A 19 μm aperture and a 2 wt% NaCl electrolyte solution were used for particle measurements in this work. The NaCl solution was circulated through a 0.22 μm filter to obtain a virtually particle-free solution.

3.2.4.5 Turbidity
A HACH Ratio/XR Turbidimeter was used to determine the turbidity of the raw produced waters (HACH Company, Loveland, CO 80539). This instrument directs a beam of light through the test sample, and detectors measure the 90° light scatter, the forward-scattered light and the light transmitted through the sample. Linearity and color rejection are attained by electronic conditioning of the ratio of the output of the 90° detector to the sum of the other two detectors.

3.2.4.6 Zeta Potential vs. pH
A Zeta-Meter System 3.0 was used to determine how the zeta potential of the membrane varied with pH (Zeta-Meter, Inc., Long Island City, NY 11101). This instrument measures the electrophoretic mobility (a measure of the speed of a colloid relative to the strength of the electrical field) and then uses the Smoluchowski equation to approximate the zeta potential. Wet membrane material was scraped off from the inside of a tube, crushed, and then diluted in filtered DI water. The ionic strength of the crushed membrane solution was kept constant at 0.01 M using NaCl and
the pH was varied with either HCl or NaOH to obtain pH values of 3.5, 5, 7, 9, and 11. Over most of the pH values tested, the membrane appeared to be positively charged (Figure 3.3).

![Figure 3.3: Zeta Potential of the Membrane](image)
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Produced Water Characteristics

The results of analyses of each of the produced waters are shown in Table 4.1. The produced waters from the MJ gas well were taken from the same location but at different times. Although, the characteristics of these two waters are very similar, there are some differences. The TOC concentration was slightly higher, the silicon oxide concentration was much higher, and the turbidity was lower for the water from the second trip. These differences probably reflect differences in upstream separation and sampling.

The HP and the LS produced waters were quite different from those in the water obtained from the MJ well. Differences between wells may be due to differences between formations as well as differences in pretreatment before the sample location. The HP and LS wells were located within a mile of each other while the MJ well was located more than 60 miles away. Prior to analyzing the LS produced water, a funnel was used to separate and remove the brown oil layer present on the surface of the water. A similar separating procedure was also used prior to performing the LS experiments.
Table 4.1: Produced Water Characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MJ Well September gas well LPS*</th>
<th>MJ Well December gas well LPS*</th>
<th>HP Well oil well gun barrel</th>
<th>LS Well oil well 3-phase separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.31</td>
<td>5.43</td>
<td>6.66</td>
<td>6.56</td>
</tr>
<tr>
<td>TOC</td>
<td>58.4</td>
<td>68.8</td>
<td>52.9</td>
<td>354</td>
</tr>
<tr>
<td>Oil and grease** (mg/l)</td>
<td>nm</td>
<td>50.7</td>
<td>16.1</td>
<td>485</td>
</tr>
<tr>
<td>turbidity (NTU)</td>
<td>180</td>
<td>4</td>
<td>53</td>
<td>86</td>
</tr>
<tr>
<td>particles &gt; 0.4 um (#/ml)</td>
<td>3.12x10^6</td>
<td>3.58x10^6</td>
<td>3.12x10^6</td>
<td>2.69x10^6</td>
</tr>
<tr>
<td>particles &gt; 0.4 um (vol frac.)</td>
<td>7.39x10^-6</td>
<td>4.38x10^-6</td>
<td>1.17x10^-6</td>
<td>7.34x10^-6</td>
</tr>
<tr>
<td># avg. particle diameter (um)</td>
<td>2.5</td>
<td>2.0</td>
<td>1.7</td>
<td>2.5</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>650</td>
<td>537</td>
<td>33</td>
<td>48</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>248,000</td>
<td>290,000</td>
<td>101,000</td>
<td>101,000</td>
</tr>
<tr>
<td>conductivity (m mhos)</td>
<td>176</td>
<td>180</td>
<td>102</td>
<td>112</td>
</tr>
<tr>
<td>SiO₂ (mg/l)</td>
<td>16</td>
<td>69.7</td>
<td>21.6</td>
<td>23.9</td>
</tr>
<tr>
<td>total alkalinity (mg CaCO₃/l)</td>
<td>121</td>
<td>132</td>
<td>182</td>
<td>126</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/l)</td>
<td>nd</td>
<td>nd</td>
<td>1.0</td>
<td>nd</td>
</tr>
<tr>
<td>Ca²⁺ (mg/l)</td>
<td>9949</td>
<td>10345</td>
<td>1750</td>
<td>1866</td>
</tr>
<tr>
<td>Mg²⁺ (mg/l)</td>
<td>664</td>
<td>671</td>
<td>587</td>
<td>392</td>
</tr>
<tr>
<td>Ba²⁺ (mg/l)</td>
<td>255</td>
<td>281</td>
<td>76</td>
<td>96</td>
</tr>
<tr>
<td>total Fe (mg/l)</td>
<td>48.6</td>
<td>44.4</td>
<td>11.6</td>
<td>10.0</td>
</tr>
<tr>
<td>total Al (mg/l)</td>
<td>0.70</td>
<td>nm</td>
<td>0.05</td>
<td>nd</td>
</tr>
<tr>
<td>total Cr (mg/l)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Zn²⁺ (mg/l)</td>
<td>82.3</td>
<td>81.3</td>
<td>0.2</td>
<td>nd</td>
</tr>
<tr>
<td>total Pb (mg/l)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>total Hg (mg/l)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>total Mn (mg/l)</td>
<td>1.12</td>
<td>1.06</td>
<td>0.52</td>
<td>1.0</td>
</tr>
<tr>
<td>total Cu (mg/l)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

*LPS: low pressure separator

**Estimated from correlation with TOC by using EPA Method 413.2

nd-not detectable

nm-not measured
One of the most noticeable differences in the HP and LS waters was the TOC and corresponding oil and grease concentrations. The oil and grease concentrations were estimated based on correlations with TOC concentrations as discussed in section 4.2. The amount of TOC in the LS water was about 7.7 times larger than the concentration in the HP water, and the oil and grease concentration was about 30 times larger than that of the LS water. This difference may be partially attributed to the sample location. The gun barrel from which the HP water was drawn had a much larger capacity and a much longer residence time than the 3-phase separator that pretreated LS water and was more likely to separate out larger quantities of oil. Moreover, the LS samples were obtained immediately upon startup of the 3-phase separator and it is likely that very little separation actually occurred within the unit. The MJ water had a slightly higher TOC content than the HP water, and a much higher oil and grease content. An oil sheen was observed on the surface of the produced waters from the HP and LS wells but not on the surface of the MJ produced water.

Calcium, magnesium, and barium were found in much lower concentrations in the MJ water than in the HP or LS waters. There was virtually no zinc in the HP and LS waters but the MJ water had zinc concentrations of approximately 81 to 82 mg/l. There was roughly 15 times more total suspended solids in the MJ water than in the other waters and almost 3 times as much total dissolved solids. The differences in the TSS concentrations are not reflected in the values for the volume fraction of particles as measured by the particle counter. It is possible that oil
drops which may have been measured by the particle counter volatilized during the TSS tests. The HP water contained slightly less TOC and oil and grease than the MJ water did. The MJ water had about 4 times as much iron as the other produced waters and it had a lower pH.

4.2 Oil and Grease Correlation to TOC
During 3 of the produced water experiments, MJ6, HP4, and LS4, samples were taken to measure TOC and oil and grease (EPA Method 413.2). Values for these parameters were correlated for each of the 3 waters (Table 4.2, Figures 4.1, 4.2, and 4.3). The highest correlation coefficient was obtained from data for the LS produced water ($r^2=1$). In all cases, correlations are based on a very small number of samples. Note that oil and grease concentrations are higher than TOC concentrations in the LS4 experiment. These correlations are used throughout this work to estimate the oil and grease concentrations from TOC measurements.

Table 4.2: Oil and Grease Correlation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Oil and Grease* (mg/l)</th>
<th>TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MJ6</td>
<td>MJ P7</td>
<td>0.94</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>MJ P2</td>
<td>1.01</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>MJ R2</td>
<td>35.60</td>
<td>52.2</td>
</tr>
<tr>
<td></td>
<td>MJ R7</td>
<td>39.41</td>
<td>49.1</td>
</tr>
<tr>
<td>HP4</td>
<td>HP P5</td>
<td>3.94</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>HP R6</td>
<td>7.13</td>
<td>31.9</td>
</tr>
<tr>
<td></td>
<td>HP R3</td>
<td>10.72</td>
<td>33.1</td>
</tr>
<tr>
<td>LS4</td>
<td>LS P4</td>
<td>2.49</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>LS R5</td>
<td>253.25</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>LS R3</td>
<td>322.18</td>
<td>238</td>
</tr>
</tbody>
</table>

*EPA Method 413.2*
Figure 4.1: Oil and Grease Correlation for MJ Produced Water
(EPA Method 413.2)

Figure 4.2: Oil and Grease Correlation for HP Produced Water
(EPA Method 413.2)
4.3 Rejection Of Inorganic Materials

In the MJ experiments 3-6, the HP experiments, and the LS experiments, samples were analyzed for iron, manganese, magnesium, calcium, barium, and zinc to determine if any rejection of these elements occurred.

With the exception of iron, there was no apparent rejection or loss of inorganic species to the system. Iron concentrations in the permeate were much lower than those in the recycle concentration. Moreover, iron concentrations decreased in the recycle during all but one of these experiments.

The rejection of iron increased a great deal during the MJ experiments as
illustrated in Figure 4.4. This phenomena is attributed to the precipitation of iron over time and the subsequent rejection of iron precipitates by the membrane. During the experiments, the produced water changed color from a light yellowish-brown to a darker rust brown. The pH at the beginning of each experiment was near 5.4 and it increased during the experiment by almost 0.8 pH units. The feed tank was highly aerated which could have enhanced oxidation of reduced iron and stripping of CO₂. In addition to any oxidation of iron that may have taken place, higher pH may have favored iron precipitation. As more iron was oxidized and precipitated, more iron was rejected.

![Graph showing iron rejection over time](image)

**Figure 4.4: Iron Rejection for Experiments MJ3, MJ4, MJ5, and MJ6**

The iron concentration in the recycle of the MJ experiments decreased by about 10 mg/l in each experiment, and the concentration in the permeate decreased even more dramatically (Figure 4.5). The largest decrease was
Figure 4.5: Iron Concentrations for Experiments MJ3, MJ4, MJ5, and MJ6
observed in the MJ3 permeate. The iron concentration decreased from 41.3 to 8.0 mg/l over 2 hours of operation. Part of the decline in the recycle concentration may have been caused by the deposition of precipitated iron in the experimental system. Brown particles were observed sticking to the insides of the flowmeters and on the inner wall of the feed tank. Some iron precipitation may have occurred on the membrane surface or in the membrane pores. Possible effects of this precipitation on permeate flux are discussed in section 4.5.2.

The HP experiments began with iron concentrations between 8.0 and 12.1 mg/l, and 3 of the LS experiments began with an iron concentration of 8 mg/l (Figures 4.6 and 4.7). Experiment LS2 began with a concentration of 5 mg/l. These experiments started with a higher pH than the MJ experiments. The pH was approximately 6.7 and increased by about 0.7 pH units during each experiment. A higher pH may have favored precipitation of iron hydroxides. The produced water for the HP and LS experiments was very brown from the beginning. It was not determined if this color was due to the presence of precipitated iron initially in the water, clay particles, or other materials. All of the iron present was rejected after approximately 15 minutes of operation.
Figure 4.6
Iron Concentrations for Experiments HP1, HP2, HP3, and HP4

Of the 4 HP experiments, iron was detected only in permeates of experiment HP1. During this experiment, 8 mg/l of iron was lost either to the membrane and/or to the surfaces in the system. In experiments HP2 and HP3, 4 mg/l of iron was lost from the recycle flow, and there appeared to be no loss of iron during experiment HP4.
Figure 4.7: Iron Concentrations for Experiments LS1, LS2, LS3, and LS4

Experiments LS1, LS2, and LS3 each had about 1 mg/l of iron in the permeate in the beginning of the experiments. After about 30 minutes of operation, iron was no longer detected in the permeates of these experiments. During experiment LS1, it appeared that 7 mg/l of iron was lost to the surfaces in the experimental system. The iron concentration in the recycle of experiment LS2 only decreased by 2 mg/l, and in experiments LS3 and LS4, the recycle concentration decreased by 4 mg/l.

These iron losses during the HP and LS experiments may be partially due to iron precipitation on or in the membrane. The possibility of this precipitation affecting permeate flux behavior is discussed in section 4.5.2.
4.4 Rejection of Organic Materials

4.4.1 Rejection of Organic Materials During the Ultrafiltration of Model Feed Waters

The same membrane (designated ADC1) was used for all three chlorobenzene experiments (C1, C2, and C3). Each test was performed by incrementally increasing the transmembrane pressure. The model feed waters for experiments C1 and C2 contained 0.02 vol% chlorobenzene. In both experiments, almost complete breakthrough of TOC was observed - the rejection was less than 10.3% (Table 4.3).

Table 4.3: TOC Data for Experiments C1 and C2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Pressure (kPa)</th>
<th>Flux (l/m²-hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Rejection TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.00</td>
<td>317</td>
<td>193</td>
<td>45.6</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>310</td>
<td>188</td>
<td>18.5</td>
<td>25.4</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>331</td>
<td>205</td>
<td>14.9</td>
<td>15.9</td>
<td>0.0</td>
</tr>
<tr>
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<td>352</td>
<td>219</td>
<td>10.8</td>
<td>12.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>372</td>
<td>237</td>
<td>8.7</td>
<td>9.3</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1.67</td>
<td>393</td>
<td>256</td>
<td>7.8</td>
<td>7.0</td>
<td>10.3</td>
</tr>
<tr>
<td>C2</td>
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<td>348</td>
<td>nm</td>
<td>69.7</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>348</td>
<td>nm</td>
<td>45.8</td>
<td>45.5</td>
<td>0.7</td>
</tr>
<tr>
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<td>34.1</td>
<td>30.8</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>376</td>
<td>301</td>
<td>22.3</td>
<td>21.8</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>390</td>
<td>313</td>
<td>18.6</td>
<td>17.8</td>
<td>4.3</td>
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<tr>
<td></td>
<td>1.67</td>
<td>403</td>
<td>326</td>
<td>15.7</td>
<td>15.7</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>424</td>
<td>342</td>
<td>14.1</td>
<td>14.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

nm - not measured

A particle analysis indicated that there were no oil drops or other particles larger than 0.4 μm (the minimum detection limit of the instrument) in the recycle or in the permeate samples.
For experiment C1, the sampling location for the permeate was at the
discharge into the feed tank instead of immediately outside the membrane
casing. Because of the length of tubing from the membrane casing to the
feed tank, the permeate sample taken at the permeate discharge into the
feed tank was obtained relatively later in time than those subsequently
obtained immediately outside the membrane casing. The recycle sample
should be representative of the instantaneous concentration on the
concentrate side of the membrane. Since concentrations decreased over
time, permeate samples from experiment C1 had higher TOC
concentrations than did the corresponding recycle samples. After this
experiment, the sampling location was moved nearer to the membranes so
that a more representative permeate sample could be taken.

The decline in the recycle TOC concentration as illustrated in Figure 4.8
was most likely due to volatilization of the chlorobenzene. An extremely
strong odor was present during these experiments. This decline in recycle
TOC made it possible to conclude that the permeate TOC concentration
was dependent on and generally equal to the recycle TOC concentration:
the change in transmembrane pressure and the change in permeate flux had
no effect on the permeate TOC concentration during an experiment.
The model feed water for experiment C3 contained 0.2 vol% of chlorobenzene. The permeate TOC concentration was approximately equal to the recycle concentration which decreased over time. This decrease is presumably due to volatilization. The TOC concentration in the final recycle sample was about 69% less than the TOC concentration in the initial recycle sample. Permeate TOC concentrations did not appear to be dependent on transmembrane pressure or permeate flux (Table 4.4 and Figure 4.9).
Table 4.4: TOC Data for Experiment C3

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Pressure (kPa)</th>
<th>Flux (l/m²-hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Rejection TOC (%)</th>
<th>Recycle-Permeate (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>341</td>
<td>301</td>
<td>626.5</td>
<td>nm</td>
<td>nm</td>
<td>238.6</td>
</tr>
<tr>
<td>0.33</td>
<td>341</td>
<td>287</td>
<td>505.5</td>
<td>266.9</td>
<td>47.2</td>
<td>9.4</td>
</tr>
<tr>
<td>0.67</td>
<td>355</td>
<td>289</td>
<td>277.0</td>
<td>267.6</td>
<td>3.4</td>
<td>9.4</td>
</tr>
<tr>
<td>1.00</td>
<td>369</td>
<td>333</td>
<td>250.5</td>
<td>234.9</td>
<td>6.2</td>
<td>15.6</td>
</tr>
<tr>
<td>1.33</td>
<td>383</td>
<td>349</td>
<td>206.4</td>
<td>201.0</td>
<td>2.6</td>
<td>5.4</td>
</tr>
<tr>
<td>1.67</td>
<td>403</td>
<td>403</td>
<td>195.9</td>
<td>187.5</td>
<td>4.3</td>
<td>8.4</td>
</tr>
</tbody>
</table>

nm - not measured

Figure 4.9
Concentrations for Experiment C3

No oil drops or other particles larger than 0.4 µm were found in the permeate samples. A large number of particles were measured in the recycle samples (Table 4.5). The particle analyzer does not distinguish
between oil drops and other particles. However, caution was taken to filter all materials added to the feed water. Thus, particle counts are interpreted primarily as oil drop numbers. Assuming that all "particles" are drops of chlorobenzene, an oil droplet concentration, expressed as TOC can be estimated from the oil drop volume concentration. Comparison of the calculated oil drop TOC with the measured TOC (Table 4.4) shows that it is likely that most of the TOC in the recycle was dissolved and therefore passed easily through the membrane. It is possible that the terephthaloyl chloride used to "freeze" the drops affected the solubility of the chlorobenzene in water which allowed it to pass through the pores of the membrane in a dissolved or tightly emulsified form. The calculated oil drop TOC values are quite close to the difference in TOC concentrations measured in the recycle and permeate flows, suggesting that most of the oil drops were larger than 0.4 µm and were rejected by the membrane.

Table 4.5: Particle Characteristics of the Recycle Samples from Experiment C3

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Time (hr)</th>
<th># Average particle size (µm)</th>
<th>Number of drops (#/ml)</th>
<th>Calculated oil drop TOC* (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>1.652</td>
<td>8.94x10^6</td>
<td>51.0</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>1.022</td>
<td>5.04x10^6</td>
<td>4.7</td>
</tr>
<tr>
<td>3</td>
<td>0.67</td>
<td>1.125</td>
<td>5.83x10^6</td>
<td>6.9</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>1.221</td>
<td>4.65x10^6</td>
<td>9.7</td>
</tr>
<tr>
<td>5</td>
<td>1.33</td>
<td>1.202</td>
<td>4.11x10^6</td>
<td>6.9</td>
</tr>
<tr>
<td>6</td>
<td>1.67</td>
<td>1.184</td>
<td>3.95x10^6</td>
<td>6.2</td>
</tr>
</tbody>
</table>

*TOC concentration determined from particle counts

The dodecane experiments, D1 and D2, contained 0.2 vol% dodecane and
were performed in the same manner as the chlorobenzene tests. Membrane ADC5 was used for both tests. The results from these experiments were very different from the chlorobenzene test results with regards to rejection of TOC. It can be seen from Table 4.6 that in both experiments the rejection of TOC was greater than 99.4%. There was no indication that the concentration or rejection of TOC was dependent on permeate flux or transmembrane pressure.

Table 4.6: TOC Data for Experiments D1 and D2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Pressure (kPa)</th>
<th>Flux (l/m²-hr)</th>
<th>Measured Recycle TOC (mg/l)</th>
<th>Calculated Recycle TOC* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Rejection TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0.00</td>
<td>328</td>
<td>267</td>
<td>96</td>
<td>1234</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>328</td>
<td>290</td>
<td>153</td>
<td>1726</td>
<td>3.6</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>348</td>
<td>300</td>
<td>219</td>
<td>1395</td>
<td>4.2</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>362</td>
<td>325</td>
<td>227</td>
<td>1392</td>
<td>6.3</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>369</td>
<td>344</td>
<td>167</td>
<td>1389</td>
<td>7.4</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>369</td>
<td>353</td>
<td>256</td>
<td>1342</td>
<td>8.6</td>
<td>99.4</td>
</tr>
<tr>
<td>D2</td>
<td>0.00</td>
<td>310</td>
<td>357</td>
<td>35</td>
<td>1174</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>310</td>
<td>351</td>
<td>235</td>
<td>1246</td>
<td>2.4</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>324</td>
<td>365</td>
<td>356</td>
<td>1176</td>
<td>2.3</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>341</td>
<td>378</td>
<td>967</td>
<td>1206</td>
<td>2.5</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>352</td>
<td>390</td>
<td>776</td>
<td>1070</td>
<td>2.8</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>379</td>
<td>432</td>
<td>968</td>
<td>1040</td>
<td>3.5</td>
<td>99.7</td>
</tr>
</tbody>
</table>

*TOC concentration determined from particle counts
nm - not measured

The dodecane was dosed at an initial concentration of approximately 1,270 mg/l. The recycle TOC concentrations of experiment D1 as analyzed by the TOC analyzer ranged from 100 to 255 mg/l and the coefficients of variance ranged from 11 to over 100%. For experiment D2, the recycle TOC concentrations were between 133 and 967 mg/l and the coefficients
of variance were between 18 and 168%. Because of the considerable error in the TOC concentrations measured in the recycle samples, calculation of TOC concentrations from the particle volume analysis was considered to yield a more accurate estimate of the TOC in the recycle flow. Oil concentrations from particle count data were very close to those anticipated based on the initial dose of dodecane. The deviations of the calculated values from the initial dose concentration was probably due to dilution errors. The gradation lines on the feed tank have an error of +/- 2.2 liters. The coefficients of variance for the permeate TOC concentrations ranged between 2 and 15%. These were considered acceptable errors for such low concentrations.

Significant particle numbers were observed in the membrane permeates (Table 4.7). The size of these drops indicates that coalescence probably occurred in the pores or in the permeate sample containers before measurement. It can also be seen from Table 4.7 that the permeate appears to have free and dissolved oil in it. The measured TOC in the permeate is consistently higher than the TOC calculated from the particle counts in the permeate assuming all particles to be oil drops. The permeate samples in experiment D1 seemed to contain slightly more "dissolved" oil than the samples from experiment D2.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Average particle size (µm)</th>
<th>Number of drops (#/ml)</th>
<th>Permeate TOC* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Dissolved TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>0.25</td>
<td>1.403</td>
<td>2.39x10^5</td>
<td>1.8</td>
<td>3.6</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>1.286</td>
<td>3.61x10^5</td>
<td>1.6</td>
<td>4.2</td>
<td>2.6</td>
</tr>
<tr>
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<td>0.75</td>
<td>0.809</td>
<td>1.72x10^6</td>
<td>1.8</td>
<td>6.3</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.297</td>
<td>4.99x10^5</td>
<td>1.9</td>
<td>7.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>1.328</td>
<td>7.35x10^5</td>
<td>2.9</td>
<td>8.6</td>
<td>5.7</td>
</tr>
<tr>
<td>D2</td>
<td>0.25</td>
<td>1.187</td>
<td>4.36x10^5</td>
<td>1.7</td>
<td>2.4</td>
<td>0.7</td>
</tr>
<tr>
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<td>1.296</td>
<td>4.79x10^5</td>
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<td>2.3</td>
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</tr>
<tr>
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<td>0.75</td>
<td>1.213</td>
<td>3.51x10^5</td>
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<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.349</td>
<td>3.96x10^5</td>
<td>1.8</td>
<td>2.8</td>
<td>1.0</td>
</tr>
<tr>
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<td>1.25</td>
<td>1.260</td>
<td>5.85x10^5</td>
<td>2.2</td>
<td>3.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*TOC concentration determined from particle counts

Thus, these two model emulsions represent very different extremes that might be encountered in hydrocarbon-containing waters. Chlorobenzene was largely dissolved and poorly rejected, and dodecane was present mainly as oil drops and was almost completely rejected. Despite considerable differences in the phase of these hydrocarbons and the importance of phase for rejection, permeate fluxes were not significantly different.

### 4.4.2 Rejection of Organic Materials During the Ultrafiltration of Produced Waters

The feed water in experiments MJ1 and MJ2 was obtained from the first trip to the MJ gas field. Both of these experiments were performed following the same protocol used in the chlorobenzene and the dodecane
experiments. The MJ1 test was performed with an ADC6 membrane, and the MJ2 test was performed using an ADC7 membrane. The rejection and permeation behavior of this produced water falls between those of the chlorobenzene and the dodecane experiments. The rejection of TOC was 65.0% for MJ1 and 68.7% for MJ2 (Table 4.8). Differences in the permeate TOC concentrations between experiment MJ1 and experiment MJ2 are attributed to small differences in calibrating the TOC analyzer. The TOC concentrations were independent of the flux and transmembrane pressure over the ranges investigated in these experiments.

Table 4.8: TOC Data for Experiments MJ1 and MJ2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Pressure (kPa)</th>
<th>Flux (l/m²-hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Rejection TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MJ1</td>
<td>0.00</td>
<td>nm</td>
<td>nm</td>
<td>59.0</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
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<td>56.0</td>
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</tr>
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<td>52.0</td>
<td>18.7</td>
<td>64.0</td>
</tr>
<tr>
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<td>0.75</td>
<td>345.00</td>
<td>614</td>
<td>52.0</td>
<td>18.1</td>
<td>65.2</td>
</tr>
<tr>
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<td>364.00</td>
<td>640</td>
<td>53.0</td>
<td>18.8</td>
<td>64.5</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>396.00</td>
<td>693</td>
<td>52.0</td>
<td>18.4</td>
<td>64.6</td>
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<td>nm</td>
<td>59.3</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
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<td>0.25</td>
<td>331.00</td>
<td>804</td>
<td>55.5</td>
<td>17.6</td>
<td>68.3</td>
</tr>
<tr>
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<td>0.50</td>
<td>357.00</td>
<td>849</td>
<td>55.4</td>
<td>16.7</td>
<td>69.9</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>369.00</td>
<td>858</td>
<td>55.5</td>
<td>17.7</td>
<td>68.1</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>383.00</td>
<td>883</td>
<td>54.3</td>
<td>16.9</td>
<td>68.9</td>
</tr>
<tr>
<td></td>
<td>1.25</td>
<td>419.00</td>
<td>917</td>
<td>55.1</td>
<td>17.5</td>
<td>68.2</td>
</tr>
</tbody>
</table>

nm - not measured

Analysis of the permeate particle volume indicates that a small amount of the permeate TOC concentration could be attributed to free oil assuming that all particles detected were oil drops and that the drops have a density of 1000 kg/m³ and are 100% carbon (Table 4.9). At 45 minutes into
experiment MJ2, the TOC measured by particle volume analysis implies that all TOC passing through the membrane is dispersed and not dissolved. However, it is more likely that this value is incorrect, possibly due to sampling or measuring errors.

Table 4.9: Particle Characteristics and TOC Comparison of Permeate Samples from Experiments MJ1 and MJ2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th># Average particle size (µm)</th>
<th>Number of drops (#/ml)</th>
<th>Calculated Permeate TOC* (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MJ1</td>
<td>0.25</td>
<td>0.613</td>
<td>3.03x10⁶</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.617</td>
<td>6.60x10⁶</td>
<td>1.3</td>
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<tr>
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<td>0.587</td>
<td>1.23x10⁶</td>
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</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.649</td>
<td>4.99x10⁵</td>
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</tr>
<tr>
<td></td>
<td>1.25</td>
<td>0.796</td>
<td>3.96x10⁵</td>
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</tr>
<tr>
<td>MJ2</td>
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<td>2.79x10⁶</td>
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</tr>
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<td>0.648</td>
<td>5.61x10⁶</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*TOC concentration determined from particle counts

The slight decrease in recycle TOC during a test may be due to adhesion of organic materials to surfaces in the experimental system (Figure 4.10). Brown particles (possibly iron or clay) were observed to deposit on the inside walls of the feed tank just above the water line and in the tubing and flowmeters. An analysis of the recycle particle volume was not performed.
Experiments MJ3 through MJ6 were performed by keeping the transmembrane pressure constant at 345 kPa and the crossflow velocity constant at 3.53 m/s. Membrane ADC 8 was used for all of these experiments.

In experiment MJ3, the oil and grease concentration in the recycle ranged between 39.4 and 56.4 mg/l as shown in Table 4.10. These values exceed the offshore and coastal regulatory limits. The oil and grease concentrations in membrane permeates were consistently less than or equal to 2.1 mg/l; well below regulatory limits. The TOC rejection was greater than 70.0%, but the rejection of total oil and grease as estimated from correlation with TOC was greater than 95.2%. The TOC (and oil and grease) concentrations in the recycle declined slightly over the course of the test. Again, this is attributed to the adhesion of organic materials to
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Flux (l/m²-hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Oil &amp; Grease* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Oil &amp; Grease* (mg/l)</th>
<th>Rejection TOC (%)</th>
<th>Oil &amp; Grease* (%)</th>
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</thead>
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<td>nm</td>
<td>nm</td>
<td>73.6</td>
<td>95.7</td>
</tr>
<tr>
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<td>0.13</td>
<td>797</td>
<td>60.9</td>
<td>47.8</td>
<td>16.1</td>
<td>2.1</td>
<td>70.9</td>
<td>95.5</td>
</tr>
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<td>95.2</td>
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<td>70.3</td>
<td>95.2</td>
</tr>
<tr>
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<td>53.2</td>
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<td>1.3</td>
<td>71.1</td>
<td>96.6</td>
</tr>
<tr>
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<td>630</td>
<td>53.0</td>
<td>39.7</td>
<td>15.3</td>
<td>1.2</td>
<td>71.1</td>
<td>96.9</td>
</tr>
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<td>619</td>
<td>53.0</td>
<td>39.7</td>
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<td>1.2</td>
<td>71.1</td>
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</tr>
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<td>52.7</td>
<td>39.4</td>
<td>15.5</td>
<td>1.5</td>
<td>70.6</td>
<td>96.3</td>
</tr>
<tr>
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<td>623</td>
<td>53.0</td>
<td>39.7</td>
<td>15.9</td>
<td>1.9</td>
<td>70.0</td>
<td>95.3</td>
</tr>
<tr>
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<td>55.3</td>
<td>nm</td>
<td>nm</td>
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<td>72.6</td>
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<td>nm</td>
</tr>
<tr>
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<td>355</td>
<td>59.1</td>
<td>46.0</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td></td>
<td>1.13</td>
<td>353</td>
<td>59.4</td>
<td>46.3</td>
<td>16.4</td>
<td>2.4</td>
<td>72.4</td>
<td>94.9</td>
</tr>
<tr>
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<td>361</td>
<td>55.7</td>
<td>42.5</td>
<td>16.3</td>
<td>2.3</td>
<td>70.7</td>
<td>94.7</td>
</tr>
</tbody>
</table>

*correlation with TOC by EPA Method 413.2

nm - not measured
surfaces in the experimental system and to volatilization.

The permeate quality obtained in experiment MJ4 was similar to that in MJ3. However, permeate fluxes differed substantially between these experiments. It is interesting to note that oil rejection and permeate oil concentration are independent of permeate flux. Discussion of flux data is reserved for section 4.5.2.

The MJ5 experiment had slightly lower recycle concentrations but slightly higher permeate concentrations than the other MJ experiments (Table 4.11). This was evident in the rejection values (50.1 to 60.3% for the TOC rejection and 67.6 to 85.8% for the oil and grease rejection) which were lower than the other MJ experiments. The cleaning procedure was changed before this experiment; only an acid agent was used in place of surfactant or alkaline agents. It is possible that this cleaning procedure was ineffective in removing oil and that the membrane may have retained an oily residue from the previous experiment.

Table 4.11: TOC and Oil and Grease Data for Experiment MJ5

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Recycle Grease* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Permeate Grease* (mg/l)</th>
<th>Rejection TOC (%)</th>
<th>Rejection Grease* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>54.3</td>
<td>41.1</td>
<td>27.1</td>
<td>13.3</td>
<td>50.1</td>
<td>67.6</td>
</tr>
<tr>
<td>0.13</td>
<td>54.9</td>
<td>41.7</td>
<td>24.0</td>
<td>10.1</td>
<td>56.3</td>
<td>75.7</td>
</tr>
<tr>
<td>0.50</td>
<td>47.5</td>
<td>34.1</td>
<td>22.4</td>
<td>8.5</td>
<td>52.8</td>
<td>75.1</td>
</tr>
<tr>
<td>0.75</td>
<td>48.4</td>
<td>35.0</td>
<td>20.4</td>
<td>6.5</td>
<td>57.9</td>
<td>81.6</td>
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<td>34.2</td>
<td>20.0</td>
<td>6.0</td>
<td>58.0</td>
<td>82.3</td>
</tr>
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<td>46.8</td>
<td>33.4</td>
<td>19.6</td>
<td>5.6</td>
<td>58.1</td>
<td>83.1</td>
</tr>
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<td>1.88</td>
<td>47.3</td>
<td>33.9</td>
<td>18.8</td>
<td>4.8</td>
<td>60.3</td>
<td>85.8</td>
</tr>
</tbody>
</table>

*correlation with TOC by EPA Method 413.2
There was a downward trend in the recycle concentration as in the previous experiments, but there was also a downward trend in the permeate concentrations as illustrated in Figure 4.11.

![Figure 4.11](image)

Figure 4.11
TOC and Correlated Oil and Grease Concentrations for Experiment MJ5

The results from MJ6 showed similar trends except that the permeate concentrations were lower than those of MJ5 (Table 4.12). Towards the end of experiment MJ6, the membrane rejected virtually all of the oil and grease.
Table 4.12: TOC and Oil and Grease Data for Experiment MJ6

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Recycle Oil &amp; Grease* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Permeate Oil &amp; Grease* (mg/l)</th>
<th>Rejection TOC (%)</th>
<th>Rejection Oil &amp; Grease* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>54.1</td>
<td>40.9</td>
<td>16.6</td>
<td>2.6</td>
<td>69.3</td>
<td>94.7</td>
</tr>
<tr>
<td>0.13</td>
<td>52.2</td>
<td>35.6**</td>
<td>16.0</td>
<td>1.0**</td>
<td>69.3</td>
<td>97.2</td>
</tr>
<tr>
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<td>1.7</td>
<td>69.9</td>
<td>95.7</td>
</tr>
<tr>
<td>0.63</td>
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<td>15.0</td>
<td>0.9</td>
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<td>97.4</td>
</tr>
<tr>
<td>0.88</td>
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<td>14.6</td>
<td>0.5</td>
<td>71.0</td>
<td>98.6</td>
</tr>
<tr>
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</tr>
<tr>
<td>1.38</td>
<td>49.1</td>
<td>39.4**</td>
<td>14.4</td>
<td>0.9**</td>
<td>70.7</td>
<td>97.7</td>
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<td>14.4</td>
<td>0.3</td>
<td>70.4</td>
<td>99.1</td>
</tr>
</tbody>
</table>

* correlation with TOC by EPA Method 413.2
** measured value

Experiments MJ3, MJ4, MJ5 and MJ6 all had permeate oil and grease concentrations less than regulation limits. Particle analysis indicated no particles greater than 0.4 μm in the permeates of these experiments. Any organic carbon present in the permeate was either dissolved or tightly emulsified to sizes smaller than 0.4 μm.

The produced water for the HP experiments was obtained from an oil well. Membrane operating parameters were the same as those in the MJ series of experiments. An oily sheen was observed in the recycle samples of all of these experiments but not in the permeate samples.

The permeate oil and grease concentrations in experiments HP1 and HP2 varied between 3.4 and 5.2 mg/l, which is less than regulatory limits (Table 4.13). An oil sheen was observed on the surface of the recycle samples. Nothing was done to the HP1 experiment samples to try to
dissolve this oil layer; therefore, the TOC concentrations measured are most likely less than the actual concentrations. A surfactant which contained sulfate was used to try to dissolve the oil layer in the permeate samples from experiment HP2. A white precipitate formed, perhaps due to "salting out" of the sulfate groups in the surfactant. As a result, these measurements were not considered valid.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Flux (l/m²·hr)</th>
<th>Recycle TOC-not valid (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Permeate Oil &amp; Grease* (mg/l)</th>
</tr>
</thead>
<tbody>
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<td>HP1</td>
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<td>25.5</td>
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<td>3.9</td>
</tr>
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<td>274</td>
<td>27.4</td>
<td>17.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
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<td>316</td>
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<td>3.8</td>
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<tr>
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<tr>
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</tr>
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<td>14.1</td>
<td>18.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

*correlated with TOC by EPA Method 413.2

The TOC concentration in the permeate samples increased slightly at the end of each experiment. This trend may be due to an increase in dissolution of oil in the recycle flow due to an increase in temperature during the experiment. Particle analysis indicated no particles greater than 0.4 μm in the permeate.
Relative to the MJ experiments, the rejection of oil and grease was low for experiments HP3 and HP4 although the permeate concentrations were less than or equal to 5.2 mg/l. TOC rejection was less than 50% and the oil and grease rejection was less than 62% for both experiments (Table 4.14). The relatively low rejections in these experiments are mainly a function of the low recycle concentrations.

Table 4.14: TOC and Oil and Grease Data for Experiments HP3 and HP4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (hr)</th>
<th>Flux (l/m²-hr)</th>
<th>Recycle TOC (mg/l)</th>
<th>Recycle Grease* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Permeate Grease* (mg/l)</th>
<th>Rejection TOC (%)</th>
<th>Rejection Grease* (%)</th>
</tr>
</thead>
<tbody>
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<td>36.3</td>
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<td>19.3</td>
<td>4.4</td>
<td>46.8</td>
<td>57.3</td>
</tr>
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<td>28.8</td>
<td>7.7</td>
<td>19.3</td>
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<td>28.0</td>
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<td>26.1</td>
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<td>17.6</td>
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<td>4.9</td>
<td>31.2</td>
<td>40.0</td>
</tr>
<tr>
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<td>7.1</td>
<td>16.9</td>
<td>3.6</td>
<td>37.6</td>
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<td>29.1</td>
<td>7.8</td>
<td>17.9</td>
<td>3.9</td>
<td>38.5</td>
<td>49.8</td>
</tr>
<tr>
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<td>89</td>
<td>33.1</td>
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</tr>
<tr>
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<td>32.3</td>
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<td>17.4</td>
<td>3.7</td>
<td>46.1</td>
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<td>7.6</td>
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<td>3.9**</td>
<td>38.5</td>
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<td>17.9</td>
<td>3.9</td>
<td>43.9</td>
<td>45.1</td>
</tr>
</tbody>
</table>

*correlated with TOC by EPA Method 413.2  
**measured value

The oil and grease concentrations in the recycle and permeate flows are compared in Figure 4.12. The oil and grease concentrations in the permeate appear to be independent of the recycle concentrations and were not correlated with permeate flux.
Figure 4.12: Correlated Oil and Grease Concentrations for Experiments HP3 and HP4

The membrane was operated under the same conditions in the LS experiments as those used in the HP experiments. In all of the LS experiments, oil and grease rejections were high; in most cases greater than 99% (Table 4.15). TOC rejections were also very high, ranging from 94.8 to 98.7%. Permeate oil and grease concentrations for each of these experiments were far below the regulatory limits. An oily sheen was observed in the recycle samples but not in the permeate samples. The membrane appeared to reject virtually all of the free oil. There was no dependence of permeate concentration on flux.
Table 4.15: TOC and Oil and Grease Data for Experiments LS1, LS2, LS3 and LS4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time</th>
<th>Flux (l/m²·hr)</th>
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<th>Oil &amp; Grease* (mg/l)</th>
<th>Permeate TOC (mg/l)</th>
<th>Oil &amp; Grease* (mg/l)</th>
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*correlation with TOC by EPA Method 413.2
The concentrations in the recycle decreased during the course of an experiment as illustrated in Figure 4.13. Some of this loss may be due to volatilization but most of it is probably a result of organic materials sticking to surfaces in the experimental system. Large amounts of brown particles (possibly clay as well as oil) were observed on the inside walls of the feed tank and in tubing.

![Graph showing oil and grease concentration over time](image)

**Figure 4.13: Correlated Recycle Oil and Grease Concentrations for Experiments LS1, LS2, LS3, and LS4**

4.5 Permeate Flux Performance

4.5.1 Permeate Flux Performance During the Ultrafiltration of Model Feed Waters

For each model feed water experiment, the permeate flux increased as the transmembrane pressure increased (Figure 4.14). The dodecane experiments exhibited higher permeate fluxes than the chlorobenzene experiments, but the CWFT values measured before each of the dodecane
experiments were greater than those measured before the chlorobenzene experiments. It appears that the dodecane tests started with a "cleaner" membrane. Note that in no case does permeate flux verses transmembrane pressure appear to be flat (i.e. mass transfer limited).

![Graph showing permeate flux vs transmembrane pressure](image)

**Figure 4.14: Change in Permeate Flux with Pressure for Model Feed Waters**

The flux at a transmembrane pressure of 345 kPa was estimated for each of the chlorobenzene and dodecane experiments so that their performance could be compared. When CWFT values are mentioned, they have also been estimated at a transmembrane pressure of 345 kPa.

The first type of model feed water tested was a solution of chlorobenzene in DI water. Experiment C1 contained 0.02% chlorobenzene and it was operated at a crossflow velocity of 3.08 m/sec. The CWFT value
measured before the experiment began was 138 l/m²-hr.

The membrane used for the chlorobenzene experiments had been used in previous tests to determine temperature dependence, compaction behavior and the effects of cleaning agents. Consequently, the permeate flux was relatively low during the CWFT compared with new membranes.

The permeate flux during experiment C1 was significantly higher than that in the CWFT (Figure 4.15). Permeate flux was 217 l/m²-hr at a transmembrane pressure of 345 kPa during the experiment. Although a leak in the membrane was initially suspected as the cause of this increase in permeate flux, this explanation was subsequently ruled out. As previously discussed, the chlorobenzene was primarily in a dissolved form and easily passed through the membrane without fouling the membrane. It appears that the chlorobenzene may have even acted as an effective cleaning agent and removed residual Alconox which had fouled the membrane. When the membrane was subsequently "cleaned" with Alconox, the permeate flux decreased to a value that was about 98% of the initial CWFT value.
Figure 4.15: Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments C1, C2, and C3

Experiment C2 contained 0.02 vol% chlorobenzene as in experiment C1, but a lower crossflow velocity (1.85 m/sec) was used. Previous studies have indicated that an increase in crossflow velocity leads to an increase in permeate flux, mainly due to an increase in turbulence which enhances the turbulent diffusion of materials from the membrane surface. In this study, a higher permeate flux was observed at a lower crossflow velocity. It seems probable that this effect is linked to the initial permeate flux of the membrane and the residual effects of the Alconox cleaner rather than any effects on mass transport.

In experiment C2, an increase in permeate flux occurred after introducing
the chlorobenzene solution to the membrane. Permeate flux increased to 276 l/m²-hr; 2 times the value of the CWFT. After this experiment, the membranes were rinsed with clean DI water. Alconox was not applied. The permeate flux decreased slightly to a value of 263 l/m²-hr as determined when a CWFT was performed.

The stable permeate flux achieved in experiment C3 was slightly higher than the permeation rate observed during the CWFT performed before the experiment. Even though the concentration of chlorobenzene was 10 times that in experiment C2, the permeate fluxes during tests C2 and C3 were not very different. Alconox was used to "clean" the membrane after the experiment and again, the permeate flux dropped, confirming that Alconox was not an appropriate cleaner by itself.

The feed waters for the dodecane experiments contained the same amount of dodecane (0.2 vol%), and they were performed with the same crossflow velocity (3.53 m/sec). The membrane used for the dodecane experiments was first "cleaned" with Alconox to see what effect this cleaner might have on an unused membrane. The flux decreased from an initial CWFT value of 680 l/m²-hr to a flux of 329 l/m²-hr, indicating that the Alconox was, in fact, fouling the membrane. HCl and sodium benzoate were not applied to the membrane after the Alconox washing in this case.

When the D1 experiment was performed, permeate flux was only slightly less than that of the CWFT performed immediately before the experiment (Figure 4.16). The Alconox solution caused the permeate flux to decline
as before, but when a sodium benzoate and HCl solution was applied, the permeate flux increased to 1.3 times that of the original CWFT performed before the D1 experiment. The acid solution appeared to reverse the fouling effects of the Alconox detergent. The Alconox was no longer used after this experiment; instead, Zenon MC-4 (a Zenon proprietary detergent) was tested.

![Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments D1 and D2](image)

**Figure 4.16:** Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments D1 and D2

The permeate flux during the D2 experiment was only 9% less than that of the CWFT performed immediately before the experiment. When the Zenon MC-4 detergent was used, the permeate flux dropped as it had with the Alconox detergent, but the acid solution raised the permeate flux as it did after experiment D1. Once again, the acid solution seemed to reverse the deleterious effects of a detergent on permeate flux. There appeared to
be no irreversible fouling caused by the dodecane.

The two model feed waters tested demonstrated different flux behaviors. When the chlorobenzene solution was applied to the membrane, the permeate flux was higher than that of the CWFT performed immediately before the experiment. When the dodecane solution was applied to the membrane, the permeate flux decreased slightly to a value less than that of the CWFT performed before the experiment. The dodecane appeared to be present mainly as oil drops. Some of this dispersed oil could have adsorbed to the membrane or blocked the membrane pores causing the slight decline in permeate flux.

4.5.2 Permeate Flux Performance During the Ultrafiltration of Produced Waters

The MJ1 and MJ2 experiments were performed in the same way that the model feed water experiments were performed. Two different new membranes were used for these experiments. As observed in the model feed water experiments, the permeate flux increased as the transmembrane pressure increased (Figure 4.17). In both experiments, the increase in permeation rate is approximately linear with transmembrane pressure. However, experiment MJ2 permeation rates were much higher than those in MJ1. There appears to be no obvious explanation for the difference in permeate flux between the two experiments.
Permeate fluxes are compared at a transmembrane pressure of 345 kPa (Figure 4.18). The CWFT value for the new, unused membrane for experiments MJ1 was 680 l/m²-hr. When the produced water was introduced to the membrane, the flux was about 91% that of the CWFT performed immediately before the experiment. After the membrane was washed with Zenon MC-4 detergent, the permeate flux decreased. A subsequent acid wash decreased permeate flux further. Unlike experiments with dodecane, the acid solution was not able to reverse the fouling effects of the Zenon detergent.
Figure 4.18: Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments MJ1 and MJ2

The initial CWFT value for the membrane designated as ADC7 was close to that of membrane ADC6 used in experiment MJ1. However, unlike the MJ1 experiment, the permeate flux in experiment MJ2 increased to almost 1.2 times that of the initial CWFT similar to the permeation behavior observed in chlorobenzene experiments. This increase in permeation rate cannot be attributed to removal of detergent residual since the membrane had not yet been washed with detergent. The MC-4 detergent and the acid cleaner reduced the permeate flux after the MJ2 experiment to about 78% of the initial CWFT.

The remainder of the MJ experiments were performed at a constant
transmembrane pressure of 345 kPa and a crossflow velocity of 3.53 m/sec. Permeate flux as a function of time for experiments MJ3, MJ4, MJ5, and MJ6 is illustrated in Figure 4.19. The dashed lines indicate the increase or decrease in permeation rate relative to CWFT's performed between each experiment. Permeate fluxes in these experiments estimated at a transmembrane pressure of 345 kPa and normalized to the CWFT value for the fresh, unused membrane are shown in Figure 4.20.

In experiment MJ3, the initial permeate flux was 797 l/m²-hr (63 l/m²-hr higher than the initial CWFT value at 345 kPa) and it gradually decreased to a steady value of approximately 620 l/m²-hr. Inadequate compaction may have caused the initial produced water flux to be higher than the CWFT value.
Figure 4.19: Change in Permeate Flux with Time for Experiments MJ3, MJ4, MJ5, and MJ6

Membrane ADC8
Crossflow Velocity: 3.53 m/sec
Transmembrane Pressure: 345 kPa
After washing the membrane with the Zenon MC-4 cleaner followed by HCl and sodium benzoate, the flux decreased to 84% of the original CWFT value. The membrane was apparently fouled by the Zenon cleaner. The detergents in the cleaner may have adsorbed to the membrane and caused pore blockage, or may have reacted chemically with contaminants left on the membrane from the produced water. After this experiment, use of the Zenon cleaner, like the Alconox, was abandoned.

Permeate flux during the MJ4 test decreased slightly from 382 to 355 l/m²-hr (Figure 4.19). Materials in the produced water reduced permeate flux almost immediately and then apparently had little effect on permeation rate
during the remainder of the experiment.

As discussed in section 4.3, iron appeared to precipitate and deposit on surfaces during the MJ produced water experiments as evidenced by a decrease in the iron concentration in the recycle over time. Precipitation of iron on the surface of the membrane or in membrane pores may partially explain the observed permeate flux decline. This conclusion is also supported by the effect of various cleaning procedures in restoring permeate flux.

The HCl and sodium benzoate solution was very effective in restoring permeate flux after experiment MJ4; the CWFT value after using the acid solution was 560 l/m²-hr; 76% of the initial CWFT. The membranes were stored approximately two weeks in the HCl/sodium benzoate solution, which further improved membrane performance. Acid is usually used to remove mineral deposits from membranes. The efficiency of the acid wash in restoring permeate flux suggests that permeate flux decline in experiment MJ4 (and subsequent MJ experiments) may have been due to mineral deposits (such as iron) on or in the membrane.

The CWFT value determined immediately before the MJ5 experiment was 705 l/m²-hr. This value is 96% of the permeate flux determined for a fresh, unused membrane. The experiment began at a permeate flux of 448 l/m²-hr (only 64% of the CWFT value) and it declined to a steady value of 321 l/m²-hr. The initial decline in permeate flux after the CWFT may be due to the immediate precipitation of some of the iron in the produced
water: the initial concentration of iron measured during experiment MJ5 was about 4 mg/l less than that measured in the raw produced water. Experiment MJ5 exhibited a gradual decline in permeate flux similar to that observed in experiment MJ3 after an initial abrupt decrease in permeation rate from the CWFT value. The gradual decline in permeate flux is again attributed to the gradual precipitation of iron on and in the membrane.

After this test was finished, a NaOH solution and then the solution of HCl and sodium benzoate were used to try to restore the initial permeate flux with some success. The CWFT yielded a value of 638 l/m²-hr - about 87% of the permeate flux of the unused membrane. This recovery again supports the idea that mineral deposits are the cause of the permeate flux decline: the NaOH solution improved the permeate flux only slightly. The cleaning agents did not restore the membrane entirely to its initial permeate flux indicating some degree of fouling. However, this procedure for cleaning the membrane appeared to be the best used to date and this procedure was used for all the remaining experiments.

Experiment MJ6 demonstrated behavior similar to that of MJ5, starting at a permeation rate of 408 l/m²-hr and gradually decreasing to a value of 306 l/m²-hr. Again, permeate flux is most likely affected by iron precipitation. At the end of this experiment, surfactant was added to the feed water. The surfactant reduced the permeate flux. After the membrane was cleaned, the flux increased to 431 l/m²-hr, 58% of the flux of the unused membrane. It is possible that the surfactant caused more fouling than the
produced water would have alone. Discussion of the effect of surfactant on membrane performance is reserved for section 4.6.1.

The permeate fluxes reported in this work are corrected to a temperature of 20°C. In full-scale ultrafiltration facilities, the operating temperature would be maximized almost to the tolerance level of the membrane to enhance permeation rate. The maximum temperature for the membranes used in this study is 60°C. After steady state was reached in experiment MJ5, the corrected flux was about 321 l/m²-hr but the corresponding uncorrected flux was 508 l/m²-hr at a temperature of 43.2°C. Thus, cost estimates and preliminary designs should account for these higher permeation rates at higher operating temperatures.

The HP-series of experiments exhibited very different behavior from that of the MJ-series of experiments as can be seen in Figure 4.21. In experiment HP1, the permeate flux decreased rapidly and then increased back to the CWFT value over a period of 2 hours. The CWFT value for the fresh, unused membrane was 784 l/m²-hr, but the initial flux for the experiment was 534 l/m²-hr. Within the first 15 minutes of the experiment, the flux dropped to 236 l/m²-hr or 30% of the initial CWFT value (Figure 4.22). The flux then increased at a very rapid rate and leveled off at a steady value of 757 l/m²-hr. This pattern of an initial drop in permeation rate followed by a recovery was observed in most of the HP experiments. It is possible that some free oil in the produced water blocked membrane pores and decreased the permeate flux but was then gradually squeezed through and allowed the permeate flux to increase. In
Figure 4.21: Change in Permeate Flux with Time for Experiments HP1, HP2, HP3, and HP4

Membrane ADC9
Crossflow Velocity: 3.53 m/sec
Transmembrane Pressure: 345 kPa
the HP experiments, the TOC in the permeate appeared to decrease slightly in the beginning and then increase during the latter part of the experiments. While these trends might support the idea of oil passing through the pores, higher permeate concentrations might also be explained by the increase in temperature over time. As the temperature in the feed water increases, dispersed oil in the water may dissolve and pass through the membrane; hence, increases in the TOC concentrations in the permeate are observed.

![Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments HP1, HP2, HP3, and HP4](image)

Figure 4.22: Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments HP1, HP2, HP3, and HP4

The cleaning procedure, found to be effective in the MJ series of experiments resulted in a large decrease in permeate flux when applied after treating the HP water. The permeate flux decreased to 58% of the value for an unused membrane. Experiment HP2 produced similar results to those obtained in experiment HP1. However, the CWFT value for
experiment HP2 was much lower than the CWFT value for experiment HP1 (451 l/m²-hr as opposed to 784 l/m²-hr). The permeate flux for experiment HP2 initially declined to a value of 132 l/m²-hr and then increased rapidly and leveled off at a value of about 460 l/m²-hr; about the same value obtained from the CWFT performed immediately before the experiment. This behavior again may be due to effects of free oil migration through membrane pores as discussed with respect to experiment HP1.

Unlike experiment HP1, the cleaning procedure had no effect on permeate flux. Nonetheless, when the HP3 experiment began, the permeate flux decreased dramatically in the first 20 minutes of the experiment just as it had in experiments HP1 and HP2. It increased after reaching a minimum but it did so very gradually, and it did not return to its initial value. Before the experiment began, the CWFT value was 482 l/m²-hr. After initially dropping to a minimum of 182 l/m²-hr, the flux climbed to a steady value of 259 l/m²-hr. This is about 56% lower than the steady flux for experiment HP2.

The last experiment for this produced water, HP4, had an initial flux of 257 l/m²-hr which was nearly equal to the final steady value for experiment HP3 indicating that the cleaning procedure once again had little effect on permeate flux. The ineffective role of acid in restoring permeate flux suggests that mineral deposits were not the predominate cause of flux decline in the HP experiments. The permeation rate quickly decreased to a low of 70 l/m²-hr and then increased slightly to a steady flux of 73 l/m²-hr.
after which PAC was added. The uncorrected permeate flux was 117 l/m²-hr at a temperature of 39.1 °C. The results of the PAC experiment are discussed in section 4.6.2.

This produced water contains a low amount of TSS (33 mg/l) and a low amount of oil and grease (16.1 mg/l). The produced water from the MJ well contained more oil and grease (50.7 mg/l), yet its final steady state flux was 306 l/m²-hr. An oil sheen was visible in the recycle samples and not in the permeate samples of the HP experiments. No such sheen was observed in the MJ produced water. Some of the free oil may have been smeared across the surface of the membrane contributing to a reduction in permeate flux. Iron did not appear to have a substantial effect on the permeate flux during the HP experiments, but a buildup of precipitated iron on the membrane may have contributed to the overall permeate flux decline.

The LS series of experiments produced a third, very different response of permeate flux to the produced water. The CWFT value before experiment LS1 was 803 l/m²-hr, but the initial flux for the experiment was 1251 l/m²-hr - an increase of 56%. There was a small decline and then the permeate flux remained steady at a value near 1107 l/m²-hr (Figure 4.23). This somewhat unusual permeation behavior was unlike the behavior of any of the other produced water experiments, but it resembled chlorobenzene tests somewhat in that the produced water seemed to "clean" the membrane. Data on permeate quality confirmed that the membrane's integrity was intact.
Figure 4.23: Change in Permeate Flux with Time for Experiments LS1, LS2, LS3, and LS4

Membrane ADC10
Crossflow Velocity: 3.53 m/sec
Transmembrane Pressure: 345 kPa
There was a substantial decrease in permeate flux after the cleaning procedure. The flux dropped from a steady state value of 1107 l/m²-hr in experiment LS1 to 412 l/m²-hr during the CWFT; 51% of the value for an unused membrane (Figure 4.24). This decrease with "cleaning" also occurred after the first MJ experiment and the first HP experiment.

![Graph showing normalized permeate flux (J/Jo) at a transmembrane pressure of 345 kPa for Experiments LS1, LS2, LS3, and LS4.]

**Figure 4.24:** Normalized Permeate Flux (J/Jo) at a Transmembrane Pressure of 345 kPa for Experiments LS1, LS2, LS3, and LS4

The initial permeate flux for experiment LS2 (534 l/m²-hr) was an increase of 30% over that of the CWFT performed before the experiment. The permeate flux very gradually declined to an estimated steady value of 487 l/m²-hr. It appeared that the produced water restored some of the permeation capacity lost by the cleaning procedure. The permeate flux behavior for this experiment is difficult to explain.
Permeation rate decreased again after the NaOH and then the acid solution were applied. There was a slight decrease when experiment LS3 began and then the permeate flux gradually reached a steady value of 219 l/m²-hr. It can be seen in Figure 4.24 that the cleaning improved the permeate flux to a small degree after experiment LS3. The permeate flux during the LS4 experiment very gradually declined to a steady value of 184 l/m²-hr. This is only 23% of the permeate flux for the fresh, unused membrane. The final cleaning improved the flux slightly and brought it to 241 l/m²-hr - 30% of the unused membrane permeate flux. During each of the LS experiments, a large loss of organic material in the recycle stream was observed (Table 4.14). It is possible that organic material may have been deposited on the membrane which the cleaning procedure was not able to remove. Hence, with each successive experiment, the permeate flux gradually decreases. The corresponding steady permeate flux, uncorrected for temperature, was 306 l/m²-hr at a temperature of 50.5°C.

The permeation behavior observed in LS experiments was very different from that of the other experiments. Permeate flux did not change greatly during any given experiment (Figure 4.23). Most permeate flux decline occurred within the first 5 minutes of the experiment. As discussed in section 4.3, virtually all of the iron present in the HP and LS produced waters precipitated at the very beginning of each experiment; therefore, a gradual permeate flux decline due to gradual precipitation of iron was not expected and did not occur in the LS experiments. An initial immediate permeate flux decline was not observed during the LS experiments as it was in the HP experiments.
The LS produced water had about the same amount of iron and suspended solids as the HP produced water did, but the TOC and the total oil and grease were much higher. A heavy oil sheen was observed in the recycle samples but not in the permeate samples. Although one might predict that the produced water with the highest amount of free oil would foul the membrane the most, but the final steady permeate flux for experiment LS4 was 184 l/m²-hr while the final steady permeate flux for experiment HP4 was only 73 l/m²-hr before PAC was added. Thus, free oil may not be a good indicator of the fouling potential of a produced water.

4.6 Ultrafiltration Enhancement
Two strategies for enhancing permeate flux and the removal of hydrocarbons were briefly evaluated. Sodium dodecyl sulfate (a surfactant) and powdered activated carbon were added to the feed water in two separate experiments. These materials were added at the end of the experiments to compare their effects to permeate flux and rejection behavior with no additives.

When a surfactant is added to water at a concentration above its critical micelle concentration (CMC), micelles begin to form which can remove organic materials from the water. If the micelles are larger than the pore size of the membrane, they will be rejected; hence, organic material will be rejected also.

The powdered activated carbon (PAC) used in experiment HP4 was made of particles large enough to be rejected by the membrane. PAC has the
potential to influence membrane performance in two ways. The PAC could adsorb hydrocarbons, thus preventing them from passing through the membrane, and it could also "scour" the membrane surface and remove buildup of contaminants.

4.6.1 Ultrafiltration Enhancement by the Addition of Surfactant
Sodium dodecyl sulfate (SDS) was added in three separate stages at the end of experiment MJ6 after the permeate flux had reached a steady state value of 306 l/m²-hr. Immediately after the first addition, the permeate flux decreased from 306 l/m²-hr to 260 l/m²-hr and then went back up slightly to 274 l/m²-hr. Permeation rate declined again when the second surfactant addition was applied, and it continued to decline after the third addition (Figure 4.25). The experiment ended when the pressure gauges malfunctioned. The final permeate flux, 122 l/m²-hr, was 60% lower than the value before the SDS was added. This behavior is similar to what Jonsson and Jonsson (1991b), and Keurentjes and co-workers (1990) observed in their research. After using NaOH and then acid with sodium benzoate, the permeate flux greatly improved. The CWFT gave a permeate flux of 431 l/m²-hr (estimated at a pressure of 345 kPa), but this was still 32% lower than the permeate flux observed before this experiment began. This demonstrates that while colmatage was important, some of the surfactant probably adsorbs to the membrane.
When surfactant was added, a white precipitate was observed in the tubing and flowmeters. Quite possibly, the sulfate in the SDS was forming precipitates (possibly BaSO₄) in the system which could have built up on the membrane surface and reduced the permeate flux.

The first addition of surfactant should have added 21.6 mg/l TOC to the recycle stream. In fact, the concentration only rose 11.4 mg/l from the TOC measurement taken immediately before the surfactant was added (48.7 mg/l). For the second addition, the TOC concentration only rose by 25.3 mg/l when it should have risen 86.4 mg/l. The third addition of surfactant should have increased the TOC concentration past the CMC (216 mg/l) when added to the original TOC already in the water, but it only increased by 30.3 mg/l bringing the total concentration to 79 mg/l. The TOC rejection increased from 70.4% to 79% due to the increase in the
recycle TOC concentration and not because of a decrease in the permeate TOC concentration.

There are several different factors that could have affected the TOC concentration. The precipitation mentioned previously could have taken some of the carbon out of solution. A heavy foam appeared in the feed tank which probably contained a high amount of the surfactant which could also explain the low TOC concentrations.

The permeate TOC concentration increased slightly from 14.4 mg/l to 16.6 mg/l. Surfactant monomers were probably passing through the membrane and caused this increase. Because the CMC was most likely not reached, micellar enhanced UF was not expected and was not observed.

4.6.2 Ultrafiltration Enhancement by Addition of Powdered Activated Carbon (PAC)
The PAC was added during the last part of experiment HP4. In this experiment, permeate flux started at 257 l/m²-hr, decreased to a minimum of 70 l/m²-hr, and then very gradually increased to a value of 76 l/m²-hr (Figure 4.26). At this point, 20 mg/l of PAC was added. The flux continued to gradually increase to a value of 108 l/m²-hr after 1.2 total hours of operation at which time the experiment was stopped. Previous studies have shown that the addition of particles such as PAC can be used to scour the membrane walls, and hence, improve permeate flux. The permeate flux did increase slightly, but it is difficult to tell whether or not it would have continued to increase without the PAC addition.
Figure 4.26: The Change in Permeate Flux with Time with PAC Addition for Experiment HP4

Only the concentration of TOC in the permeate was measured during this phase of the experiment. Before the PAC addition, the permeate TOC concentration was 17.9 mg/l. Once the PAC was added, a concentration of 19.7 mg/l was measured. This is only a slight increase; however, it may demonstrate that the PAC was not adsorbing organic material to any significant degree.
CHAPTER 5
CONCLUSIONS

5.1 Conclusions from the Experimental Results
Ultrafiltration appears to be a promising technology for meeting oil and
grease regulations on produced water. Oil and grease concentrations in the
permeates of the produced water experiments were consistently less than
14 mg/l, well below current and anticipated regulatory limits.

The phase of the organic material in the feed stream can be extremely
important in rejection efficiency. Experiments using model feed waters
demonstrated that virtually all dissolved organic material passes through
the membrane and virtually all emulsified organic material (including free
oil) is rejected by the membrane.

The feasibility of using ultrafiltration to treat produced water largely
depends on permeate flux, which varies among produced waters. The final
steady permeate fluxes for each of the produced waters were 73, 165, and
306 l/m²-hr.

A cleaning procedure that was effective for one produced water did not
necessarily work for another. For a given produced water, cleaning
procedures seemed to produce significant changes in permeate flux, but
they did not appear to affect permeate TOC concentrations.

As expected, inorganic species are not rejected by the membrane.
However, in the case of iron, rejection was observed to increase over time. This behavior was attributed to oxidation and precipitation of the iron which was rejected in particulate form by the membrane.

Enhancement treatments such as the addition of surfactant or PAC do not appear to have a substantial effect on permeate quality. However, only a limited evaluation of enhancement treatments was done during this study. Other surfactants or other modes of addition may improve performance.

5.2 Scope for Further Research

A limited amount of research has been conducted on ultrafiltration of produced water. The effluent quality achievable warrants further investigation of this process. The limiting aspect of ultrafiltration has generally been permeate flux decline over time. Based on the experimental results of this work, it appears that precipitated iron and organic material play key roles in permeate flux behavior.

The effects of precipitating iron in produced water before an experiment begins could be compared to the effects of precipitation of iron during an experiment. Varying iron concentration and other operating parameters such as temperature, pH, and extent of aeration may help explain permeate flux behavior in some cases.

The amount and type of organic material in produced water appear to have an effect on permeate flux behavior. Quantitative evaluation of the types of organic materials in produced water may lead to a better understanding
of which of these materials affects membrane performance.

The effectiveness of a cleaning procedure can depend on what type of material is fouling the membrane. Further investigation into various cleaning procedures may lead to better predictions of effectiveness based on the characteristics of the produced water.
REFERENCES


Bartman, G.H. and B. Melekgzadeh (1993), "Crossflow Dynamic Membrane Filtration Technology as Applied to Oil Produced Water and Water Plant Wastewater Residuals." Third Annual Produced Water
Seminar of the American Filtration Society, TX Chapter, League City, TX.


University, Houston, Texas.


Hensley, J. (1992), "Technical Ways to Treat Produced Water." Second Annual Produced Water Seminar of The American Filtration Society, TX Chapter, League City, TX.


Ide, R.E. and D.L. Comstock (1990), "Ultrafiltration with Spiral Wound Membrane Technology." 51st Annual International Water Conference, Pittsburgh, PA.


Processes, Chicago, IL, 99-100.


Oswald, P.J. (1992), "Marathon's Operating Experience with the Use of Ceramic Membranes for the Filtering of Produced Water." Second Annual Produced Water Seminar of The American Filtration Society, TX Chapter, League City, TX.


Flotation Cells in a Mature Gulf of Mexico Offshore Field." Second Annual Produced Water Seminar of The American Filtration Society, TX Chapter, League City, TX


APPENDIX A

The following excerpt is taken from EPA Method 413.1 (EPA, 1978a). It is the method used to determine total recoverable oil and grease. This method involves oil and grease extraction with Fluorocarbon-113 from the produced water sample, followed by gravimetric evaluation of the residue left after distillation of the solvent.

"Method 413.1 (Gravimetric, Separatory Funnel Extraction)

1. Scope and Application
   1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through #2 fuel oils are completely or partially lost in the solvent removal operation.
   1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.
   1.4 The method covers the range from 5 to 1000 mg/l of extractable material.

2. Summary of Method
   2.1 The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.

3. Definitions
   3.1 The definition of oil and grease is based on the procedure used. The nature of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

4. Sampling and Storage
4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.

4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5. Apparatus
5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
5.2 Vacuum pump, or other source of vacuum.
5.3 Flask, boiling, 125 ml (Corning No. 4100 or equivalent).
5.4 Distilling head, Claisen or equivalent.
5.5 Filter paper, Whatman No. 40, 11 cm.

6. Reagents
6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.
6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.
6.3 Sodium sulfate, anhydrous crystal.

7. Procedure
7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.
7.3 Tare a boiling flask (pre-dried in an oven at 103°C and stored in a desiccator).

7.4 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent moistened filter paper.

NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.
7.5 Repeat (7.4) twice more, with additional portions of fresh solvent, combining all solvent in the boiling flask.
7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10-20 ml solvent and collect the rinsings in the flask.
7.7 Connect the boiling flask to the distilling head and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for reuse. A solvent blank should accompany each set of samples.
7.8 When the temperature in the distilling head reaches 50°C or the flask appears dry remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.
7.9 Cool the boiling flask in a desiccator for 30 minutes and weigh.

8. Calculation
8.1 \[\text{mg/l total oil and grease} = \frac{(R - B)}{V}\]

where:
- \(R\) = residue, gross weight of extraction flask minus the tare weight, in milligrams.
- \(B\) = blank determination, residue of equivalent volume of extraction solvent, in milligrams.
- \(V\) = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy
9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 12.6 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 93% with a standard deviation of 0.9 mg/l.

Bibliography

2. Blum, K. A., and Taras, M. J., "Determination of Emulsifying Oil
in *Industrial Wastewater*, JWPCF Research Suppl. 40, R404 (1968)."
APPENDIX B

The following excerpt is taken from EPA Method 413.2 (EPA, 1978b). It is the method used to determine total recoverable oil and grease. This method involves extraction with Fluorocarbon-113 of the oil and grease from the sample and then evaluation of the infrared absorbance of the extracted solution.

"Method 413.2 (Spectrophotometric, Infrared)

1. Scope and Application
   1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
   1.2 The method is applicable to measurement of most light petroleum fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   1.3 The method covers the range from 0.2 to 1000 mg/l of extractable material.
   1.4 While this method can be used to obtain an estimate of the oil and grease that would be measured gravimetrically, in many cases the estimate more accurately describes the parameter, as it will measure volatiles more effectively and is not susceptible to interferences such as extractable sulfur. It can be used with the Petroleum Hydrocarbon procedure to obtain an oil and grease value and a petroleum hydrocarbon value on the same sample.

2. Summary of Method
   2.1 The sample is acidified to a low pH (<2) and extracted with fluorocarbon-113. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.

3. Definitions
   3.1 The definition of oil and grease is based on the procedure used. The source of the oil and/or grease, and the presence of
extractable non-oily matter will influence the material measured and interpretation of results.

4. **Sampling and Storage**
   4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
   4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5. **Apparatus**
   5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   5.2 Infrared spectrophotometer, scanning. Non-scanning instruments may also be used but can be subject to positive interferences in complex chemical wastewaters.
   5.3 Cells, 10 mm, 50 mm, and 100 mm path length, sodium chloride or infrared grade glass.
   5.4 Filter paper, Whatman No. 40, 11 cm.

6. **Reagents**
   6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.
   6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.
   6.3 Sodium sulfate, anhydrous crystal.
   6.4 Calibration mixtures:
      6.4.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isoctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.
      6.4.2 Stock standard: Pipet 1.0 ml reference oil (6.4.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
      6.4.3 Working standards: Pipet appropriate volumes of stock standard (6.4.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.
Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer into a 100 ml volumetric flask through a funnel containing solvent-moistened filter paper. 

*NOTE:* An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent in the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5-10 ml fluorocarbon-113 and collect the rinsings in the flask. Dilute the extract to 100 ml, and stopper the flask.

7.7 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

<table>
<thead>
<tr>
<th>Pathlength</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mm</td>
<td>2-40 mg</td>
</tr>
<tr>
<td>50 mm</td>
<td>0.4-8 mg</td>
</tr>
<tr>
<td>100 mm</td>
<td>0.1-4 mg</td>
</tr>
</tbody>
</table>

7.8 Scan standards and samples from 3200 cm\(^{-1}\) to 2700 cm\(^{-1}\) with fluorocarbon-113 in the reference beam and record the results on absorbance paper. The absorbances of samples and standards are measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum at 2930 cm\(^{-1}\) and subtracting the baseline absorbance at that point. For an example of a typical oil spectrum and baseline construction, see Gruenfeld(3). Non-
scanning instruments should be operated according to manufacturer's instructions, although calibration must be performed using the standards described above (6.4). If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required.

7.9 Use a calibration plot of absorbance vs. mg oil prepared from the standards to determine the mg oil in the sample solution.

8. Calculation

8.1 \[ \text{mg/l total oil and grease} = \frac{(R \times D)}{V} \]

where:

- \( R \) = oil in solution, determined from calibration plot, in milligrams.
- \( D \) = extract dilution factor, if used.
- \( V \) = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 17.5 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 99% with a standard deviation of 1.4 mg/l.

Bibliography