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FOSSIL ENERGY

STUDY TO DETERMINE THE TECHNICAL AND ECONOMIC FEASIBILITY OF RECLAIMING CHEMICALS USED IN MICELLAR POLYMER AND LOW TENSION SURFACTANT FLOODING

Final Report

By
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February 1978

Work Performed Under Contract No. EF-77-C-01-2600

Energy Resources Company Incorporated
Cambridge, Massachusetts

U. S. DEPARTMENT OF ENERGY

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February 1978

Prepared for

THE UNITED STATES DEPARTMENT OF ENERGY

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CHAPTER ONE

SUMMARY AND CONCLUSIONS

Energy Resources Company has developed a technology for use with enhanced oil recovery projects to achieve the following:

- Emulsion breaking - Using ultrafiltration membranes, the Energy Resources Company process can dewater an oil-in-water type emulsion expected from enhanced oil recovery projects to the point where the emulsion can be inverted and treated using conventional emulsion-treating equipment.

- Surfactant recovery - Using a tight ultrafiltration membrane or a reverse osmosis membrane, the Energy Resources Company process is capable of recovering chemicals such as surfactants used in micellar polymer flooding.

These processes find application in enhanced oil recovery projects for both economic and environmental reasons.

1.1 Process Description

The process flowsheet, Figure 1-1, shows how these two membrane processing steps are integrated into the processing scheme for produced fluids. Both ultrafiltration and reverse osmosis are filtration processes based upon the use of a porous membrane, typically polymeric material. The major difference between ultrafiltration and reverse osmosis is in the average pore size of the membrane system. The ultrafiltration membrane typically filters particles or macromolecules the size range of 0.01 microns through as much as 10 microns. Reverse osmosis systems have been developed to filter out even ionic particles the sizes of as small as 5 nanometers. As the pore size in the membrane gets smaller, two important phenomena occur:

- Flux rate - The rate at which material can be passed through the membrane decreases.

- Pressure drop - The pressure drop across the membrane increases not only because of the increased force required to drive material through the smaller pore sizes but also because retention of ionic constituents increases osmotic pressure of the fluid being filtered.

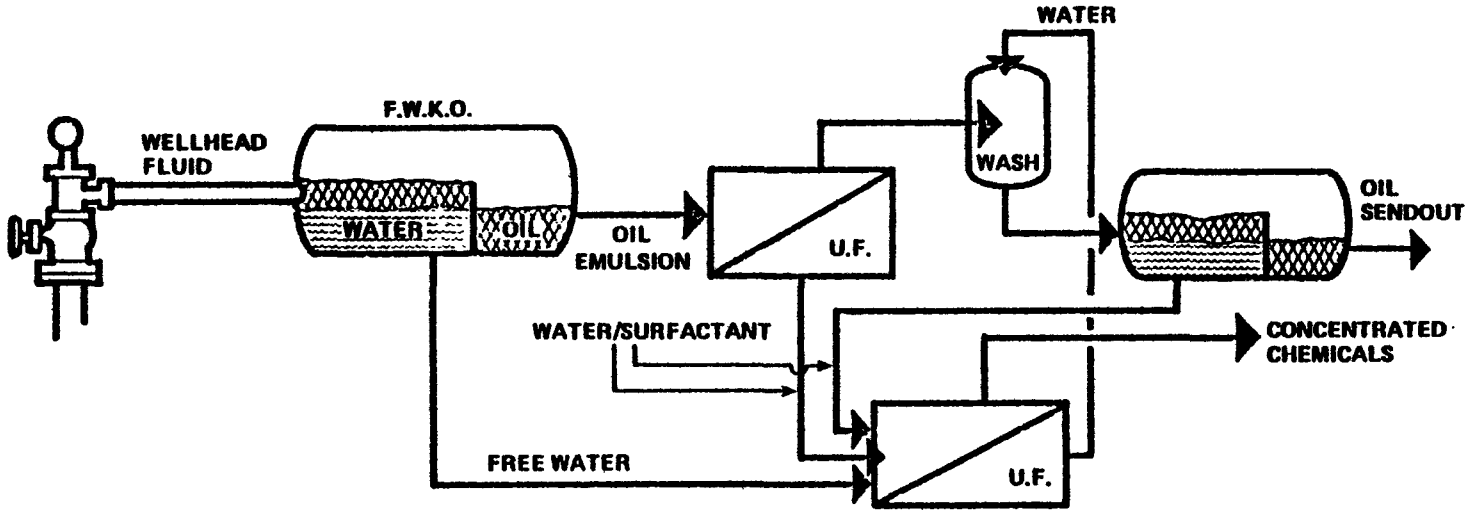

Figure 1–1. Typical oilfield process configuration.

These two phenomena have a significant impact on membrane selection and the overall economics of the two membrane processing steps of Energy Resources Company's process.

1.1.1 Emulsion Breaking Using Ultrafiltration

One of the anticipated disadvantages of the use of micellar polymer flooding is the creation of an extremely stable oil-in-water-type emulsion at the producing well. The presence of even small concentrations of surfactant can produce very stable emulsions with water-to-oil ratios (WOR) of as high as 10 or more. Such emulsions are not amenable to breaking using conventional oilfield technology and represent both a lost revenue to the micellar project and also an extremely difficult to treat environmental hazard.

At the present time such emulsions are treated using large amounts of special emulsion-breaking chemicals. The cost for breaking an oil-in-water emulsion is about a factor of 10 or more than current costs for breaking water-in-oil emulsions commonly found in primary or waterflood production with conventional oilfield equipment.

A typical oil-in-water type emulsion from enhanced oil recovery project will contain oil in micron size droplets dispersed in a continuous brine media. Ultrafiltration of the produced fluid can effectively dewater the emulsion by allowing the brine to pass through the membrane while rejecting the emulsified oil droplets. Once the emulsion has been dewatered sufficiently the emulsion will either break spontaneously or will be amenable to breaking using currently available chemical methods.

1.1.2 Surfactant Recovery Using Membrane Technology

One of the limiting factors in the implementation of micellar polymer projects is the cost of surfactant and the uncertainties about the final disposition of produced surfactant materials. The surfactant, however, can be reclaimed from produced fluids by using either a tight ultrafiltration membrane or a reverse osmosis membrane (the only difference being the effective pore size of the membrane). Two modes of surfactant recovery are possible:

- Recovery of micelles - At concentrations above the critical micelle concentration, surfactant molecules will agglomerate in extremely small droplet-like clusters on the order of 10 to 20 nanometers in

size. Such micelles behave as large macromolecules and can be separated from produced fluids using a tight ultrafiltration membrane. Water, small amounts of surfactant monomer, and electrolytes will pass through the membrane leaving a concentrated surfactant solution.

- Recovery of individual surfactant molecules - The use of a reverse osmosis system can be used to reject single surfactant molecules and even electrolyte molecules if the membrane has a sufficiently small pore size. In the case of recovering surfactant, the pore size in the membrane is needed which will reject the surfactant molecule while at the same time allowing the electrolyte to pass through the membrane so that osmotic pressure of the produced fluid need not be overcome.

By passing the produced aqueous phase through the membrane system, the surfactant can be concentrated sufficiently to allow for reuse in subsequent micellar polymer injections. This technology allows the operator to use much higher surfactant concentrations than currently used thereby resulting in improved oil efficiency and reduced formation adsorption (provided the right surfactant formulation is chosen).

1.2 Experimental Program

To determine both the technical and economic feasibility of the membrane technologies described briefly above, Energy Resources Company under contract to the Division of Oil, Gas, and Shale Technology, Department of Energy conducted an experimental program based primarily on the operation of pilot scale units to determine both the flux rate through membranes and also operating characteristics such as membrane lifetime or tendency to foul. Both an ultrafiltration pilot unit and a reverse osmosis pilot unit were constructed to carry out the tests.

The information obtained from the experimental program has been augmented by data gathered during an extensive literature search and from interviews with operators of micellar polymer floods and manufacturers of membrane equipment.

1.3 Results

1.3.1 Ultrafiltration for Emulsion Breaking

Ultrafiltration technology is an effective means for dewatering of emulsions:

Technical Evaluation

- A flux rate of up to 50 gal/day/ft^2 membrane can be achieved in oilfield service.
- The oil-in-water type emulsions can be dewatered to a WOR of 0.7 without noticeable fouling of the membrane over time.
- The dewatered emulsion will spontaneously invert or can be easily inverted using conventional chemical techniques.

Economic Evaluation

- The cost of emulsion breaking ranges from $0.07 to $0.19 per barrel of brine as shown in Table 1-1.
- The technology is competitive with proposed chemical techniques for breaking oil-in-water type emulsions for water/oil ratios of 10 or less.
- No technology (including ultrafiltration) can achieve economic oil recovery for WOR's of 100 or more, but ultrafiltration has been demonstrated as a successful pollution control measure. The cost of this application was not compared to alternative pollution control measures.

1.3.2 Surfactant Recovery by Ultrafiltration and Reverse Osmosis

Recovery of surfactant is technically and economically feasible for moderate to high inlet concentrations of surfactant.

Technical Evaluation

- The efficiency of rejection of surfactant that can be achieved at moderate inlet concentration

TABLE 1-1

ANNUAL OPERATING COSTS FOR EMULSION BREAKING

	MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 1,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 10,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 100,000 BPD (gpd/ft^2)	
	25	50	25	50	25	50
Annual operating cost, $1,000/yr						
Capital charges @ 20% over 15 yr	33	24	231	155	1,584	1,067
Routine maintenance @ 5% of cost	8	5	52	35	360	243
Membrane replacement (3-yr life)	23	12	196	98	1,400	700
Power @ $0.04/kWh	4	4	47	37	370	370
Total annual cost, $1,000/yr	68	45	516	325	3,714	2,380
Unit cost, $/bbl brine	0.19	0.12	0.14	0.09	0.10	0.07
Unit cost, $/bbl oil						
Initial WOR						
1	0.06	0.04	0.04	0.03	0.03	0.02
10	1.77	1.12	1.30	0.84	0.93	0.65
100	18.87	11.92	13.90	8.94	9.93	6.95

is in excess of 90 percent. Additional laboratory work has indicated that as much as 90 percent of the surfactant can be partioned into the aqueous phase so that an overall recovery efficiency of 80 percent of produced surfactant is achievable (see Figure 1-2).

- Flux rates for recovery of surfactant micelles is on the order of 20 gal/day/ft^2 (see Figure 1-3) with no apparent fouling of the membrane over time. The use of a true reverse osmosis membrane for recovery of surfactant molecules was not attempted within the scope of this project but based upon numbers reported in the literature, the authors believe that flux rates of only 5 to 10 gal/day/ft^2 of membrane could be achieved.

- The recovery of surfactant at low inlet concentrations (below the critical micelle concentration) requires the use of a very tight membrane which is expected to have low flux rates and high power requirements.

Economic Evaluation

- The cost of the surfactant recovery systems is slightly greater than for the ultrafiltration system used for emulsion breaking due to lower flux rates and higher pressure drops across the membrane. The costs are shown in Tables 1-2 and 1-3.

- The economics appear favorable for surfactant recovery at inlet concentrations of 0.1 weight percent or greater. Current micellar projects are not expected to have such high concentrations (although Marathon has observed one producing well with 1 percent surfactant in the produced fluids). However, high concentrations will be produced in those flood projects where extra surfactant is injected in order to improve oil recovery.

- Recovery of surfactant at inlet concentrations below 0.1 percent does not appear to be economically justifiable based upon the value of the recovered surfactant. A pretreatment step such as a froth floatation may be used to concentrate the surfactant prior to membrane filtration, but the investigation of this processing step was beyond the scope of the current project.

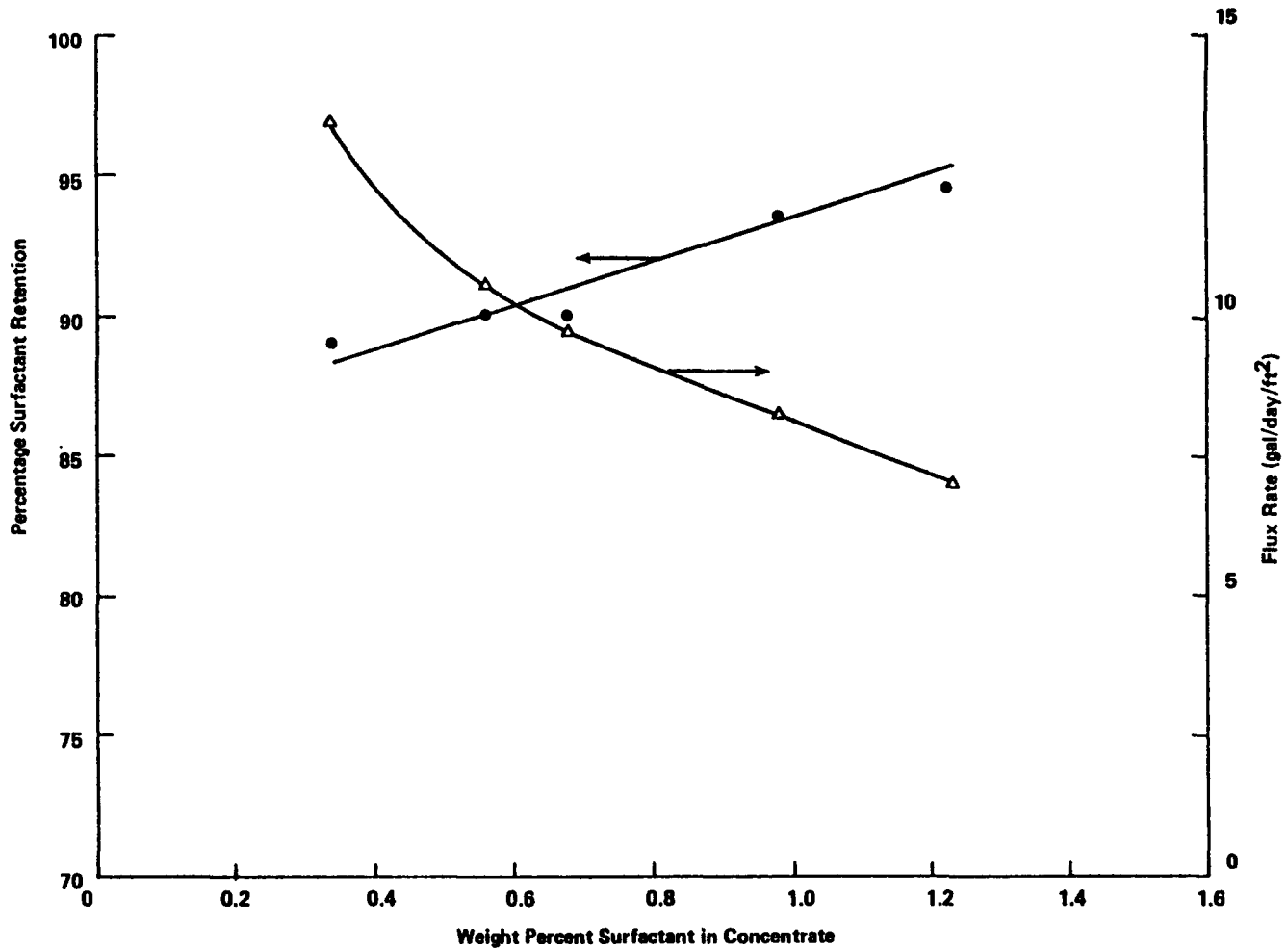

Figure 1–2. Surfactant retention and membrane flux as a function of surfactant concentration for the Rev-O-Pak 120 Membrane.

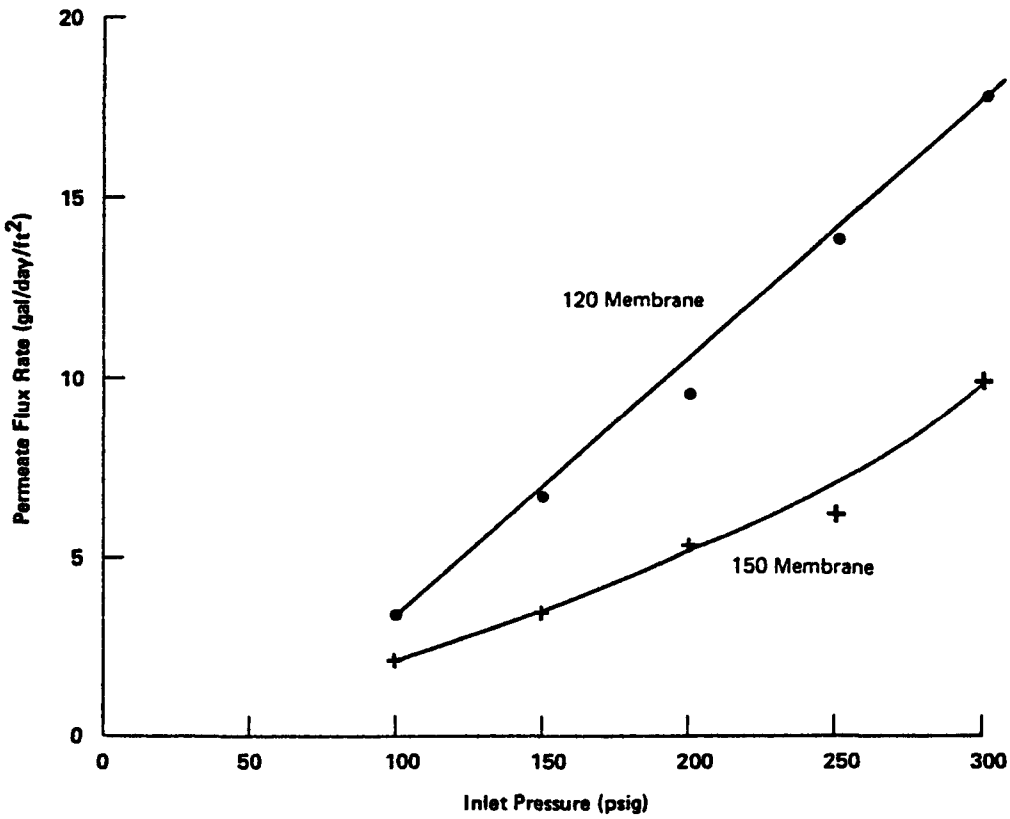

Figure 1–3. Rev-O-Pak permeate flux rates with base TRS 40 surfactant solution.

TABLE 1-2

ANNUAL OPERATING COST FOR SURFACTANT RECOVERY

	WATER FLUX (BPD)		
	1,000	10,000	100,000
Annual operating cost, $1,000			
Capital charges @ 20% over 15 years	43	271	2,035
Routine maintenance @ 5% installed cost	10	62	463
Membrane replacement	28	210	1,750
Power @ $0.04/Kwh	7	74	736
Total annual cost	88	617	4,984
Unit cost, $1 bbl brine	0.24	0.17	0.14

TABLE 1-3

ECONOMICS OF SURFACTANT RECOVERY[a]

	WATER FLUX (BPD)		
	1,000	10,000	100,000
Surfactant recovered, lb/yr			
IC 0.01%	8,200	81,800	818,000
IC 0.1%	97,100	970,900	9,709,000
IC 1.0%	996,400	9,964,500	99,645,000
Unit cost, $/lb			
IC 0.01%	10.76	7.54	6.10
IC 0.1%	0.91	0.64	0.51
IC 1.0%	0.09	0.06	0.05

[a]IC = inlet concentration. Final surfactant concentration = 10 percent.

1.4 Recommendations

1.4.1 Emulsion Breaking

1. Based on laboratory tests ultrafiltration has been shown to be technically and economically viable for enhanced oil recovery applications and should be given a field test of long duration to verify the economics and to establish membrane lifetimes.

2. Because costs for emulsion breaking are related to the rate of fluid flux through the membrane, the development of an oleophilic membrane (one which passes oil rather than water) is highly recommended. Such a membrane is expected to reduce the amount of fluid to be processed by a factor of 10 to 100, depending upon the initial WOR of the produced fluids. The cost for emulsion breaking will be proportionately reduced.

1.4.2 Surfactant Recovery

1. Efficient recovery of surfactant has been demonstrated and field tests should be initiated at floods currently experiencing high surfactant concentrations in produced fluids.

2. A reservoir modeling study should be undertaken to determine the impact on oil recovery that increased surfactant injection rates or more expensive surfactants that are less prone to slug deterioration might have and also to determine the concentration of surfactant that could be expected in the produced fluids. Such a study could be used to determine the impact that this technology might have on the economics of micellar polymer floods and ultimately on the amount of oil that might be recovered by micellar polymer flooding over the next decade.

3. If the modeling project is successful, a demonstration program should be initiated which will be based upon the injection of a large amount of surfactant to maximize oil recovery and reduce adsorption. Recovery and reuse of the surfactant should be a critical element in the demonstration program.

4. A laboratory program should be undertaken to develop a flotation system for recovering surfactants in low concentrations from brine. Such a flotation system could have both positive economic and environmental impacts on the treatment of produced fluids from enhanced oil recovery projects.

CHAPTER TWO

INTRODUCTION

The Department of Energy (previously Division of Oil and Gas and Shale Technology, Energy Research and Development Administration) has embarked on an aggressive program to develop enhanced oil recovery techniques for reclamation of additional petroleum resources considered previously to be technically unrecoverable. Several techniques are being developed, including micellar/polymer flooding, a miscible recovery technique based upon the injection of a microemulsion slug followed by a mobility control buffer. With this technology, additional displacement of oil is achieved when a microemulsion slug contacts residual oil and dissolves it (miscible displacement). To achieve the desirable effects, the slug must contain surfactants, cosurfactants, electrolytes, and polymers. Operational experience on micellar/polymer demonstration projects shows that all of these materials will be present in the produced fluids and, hence, three specific concerns that must be addressed:

- Environmental impact - The presence of surfactants or cosurfactants in produced water (along with significant amounts of solubilized oil) represents an environmental unknown. If these materials prove to be environmentally hazardous, then the disposal of produced water becomes a major environmental problem.

- Reliable operation - The presence of surfactants and cosurfactants in produced oil or water raises the possibility of the formation of highly stable emulsions which would be untreatable using conventional techniques. Such emulsions have indeed been observed in some of the early test programs.

- Potential economic incentive - Either the use of surfactant concentrations far greater than the amount normally expected to adsorb on the reservoir rock or the use of surfactants more exotic (and hence more expensive) than simple petroleum sulfonates offers significant potential for increased oil recovery. At the present time, such an approach is unattractive because the surfactants are prohibitively expensive and considered unrecoverable.

2.1 Energy Resources Co. Technology

To address the above issues, Energy Resources Co. has invented and applied for a patent on a technology based upon ultrafiltration and reverse osmosis which can be used to (1) economically treat oilfield emulsions produced from enhanced oil recovery, and (2) recover surfactants from the produced water phase. A flowsheet of the process is shown in Figure 2-1. Each of the major steps is described briefly below.

2.1.1 Free Water Knock-Out

The produced fluids from the well are passed into a conventional free water knock-out system to separate oil from water. For some enhanced recovery projects, a middle phase (emulsion), or perhaps several middle phases, are expected to form. These will be drained off and sent to the emulsion breaker.

2.1.2 Emulsion Breaking

Emulsions from enhanced oil recovery operations are expected to be of the oil-in-water type (as opposed to conventional oilfield emulsions which are the water-in-oil type). The emulsions are passed through an ultrafiltration system where the emulsion is dewatered until it reaches a point where it spontaneously inverts and breaks or where it may be economically treated with conventional equipment and chemicals. The use of ultrafiltration to dewater the emulsion greatly reduces the amount of chemicals required to break the very stable emulsions that are expected. The cost savings correspond directly to the amount of water removed from the emulsion.

2.1.3 Water Wash

The technology for surfactant recovery is based upon treating the aqueous portion of the produced fluids. Therefore, the crude may be washed or chemically doped to shift the partitioning of residual surfactants from the oil phase to the water phase.

2.1.4 Surfactant Recovery

The aqueous material containing surfactants is passed through another membrane system where the surfactant

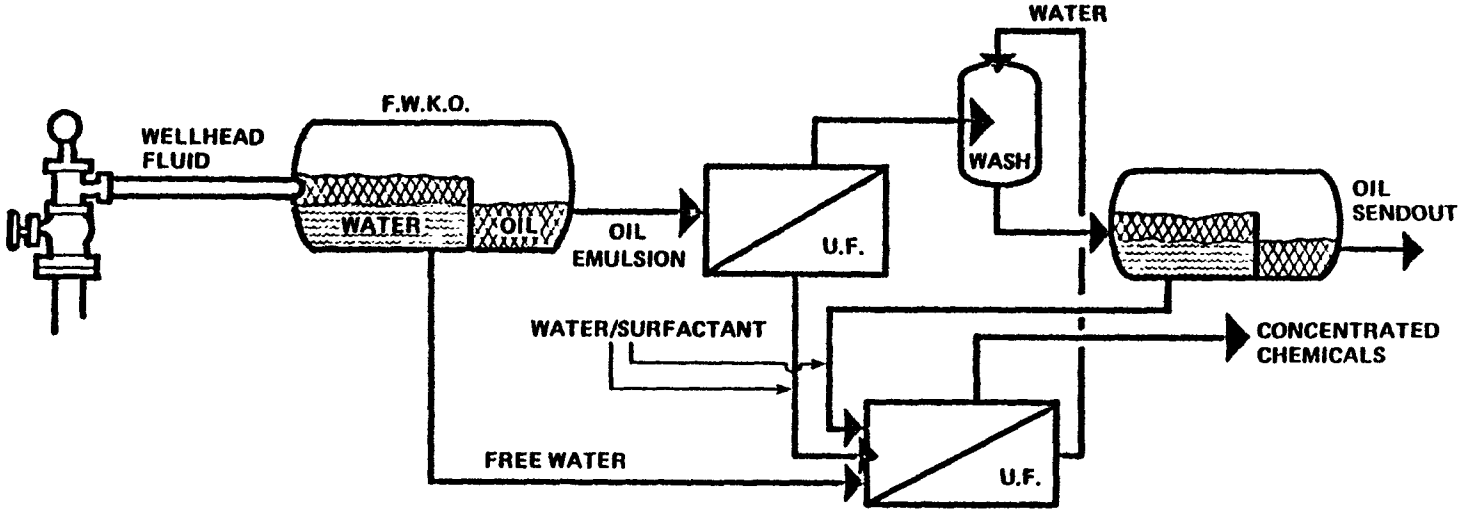

Figure 2–1. Typical oilfield process configuration.

material is retained and concentrated to the point where it may be reused. Obviously the ability to reuse surfactant would have a great impact on the cost of chemicals for micellar/polymer flooding.

2.2 Program Objectives

The objective of this program is to determine the need for and technical/economic feasibility of using Energy Resources' concepts for ultrafiltration and reverse osmosis for treating oilfield fluids and for reclaiming chemicals. This will be accomplished through the following tasks:

1. A review and evaluation of the state-of-the-art of oil/water separation techniques and the economics of oilfield emulsion separation.

2. A characterization of simulated emulsions that typify expected produced fluids from micellar/polymer floods.

3. An experimental program using ultrafiltration membranes to break the simulated emulsions and recover surfactant and water as permeate from the fluids.

4. An experimental program using reverse osmosis or ultrafiltration membranes to concentrate the surfactant in the ultrafiltration permeate and to produce a clean water stream.

5. As part of the final report, a conceptual design and cost estimate for an ultrafiltration/reverse osmosis unit for field use and an analysis of the impact of the technology on miceller/polymer flooding techniques.

2.3 Organization of Report

The Energy Resources technology addresses two specific problems inherent in enhanced oil recovery:

- The breaking of oilfield emulsions, particularly the uncommon oil-in-water type expected as a result of enhanced oil recovery (EOR) techniques.

- The recovery of surfactants in a form acceptable for reuse.

The treatment of oilfield emulsions is presented in Chapter Three. The occurrence of emulsions and current methods for treating oil and water emulsions, both in oilfield and in related practice, are presented as background information. Specific information on previous uses of ultrafiltration for emulsion breaking is presented along with the experimental data taken during this program to demonstrate both the economic and technical feasibility of the emulsion breaking technology.

The discussion of surfactant recovery is presented in Chapter Four following an outline similar to Chapter Three. Background data on the use of surfactant is presented, including information on the use of reverse osmosis or ultrafiltration membranes for molecular separations used for other applications. Experimental data on the Energy Resources Co. pilot system as well as an economic assessment are presented to show that this technology is also technically and economically feasible for those oil fields designed to take advantage of the surfactant recovery technology.

CHAPTER THREE

TREATMENT OF OILFIELD EMULSIONS

One of the more troublesome problems facing the oil production industry has been the formation of oilfield emulsions. The oil industry has been dealing with oilfield emulsions for over 50 years and has developed reasonably efficient means for breaking almost every type of emulsion currently expected with oil production. Unfortunately, oilfield emulsions currently produced are of the water-in-oil type with the oil phase being the continuous (external) phase. With the increased use of well acidization or with the advent of micellar/polymer flooding, the occurrence of oil-in-water type emulsions is also expected. Conventional equipment is inadequate for treating this type of emulsion economically.

In this section of the report, the chemistry of emulsions, their occurrence in oil fields, and current methods for treating are reviewed. The test data taken during this program on the use of ultrafiltration for treating oil-in-water type emulsions is presented along with a technical and economical assessment of the use of this technology by itself or in conjunction with conventional emulsion treating equipment.

3.1 Emulsion Chemistry and Stability[1]

When one liquid is dispersed in another the mixture is termed an emulsion. Emulsions typical of current oilfield practice are water-in-oil (W/O) with the water found in the form of extremely fine droplets and the oil as the continuous phase. Enhanced oil recovery techniques are expected to produce a second type of emulsion, an oil-in-water (O/W) emulsion where oil is dispersed as droplets in water (brine).

Emulsion chemistry relates often to the chemical nature of the interface between the oil phase and aqueous phase. For example emulsion stability is a function of the strength of the "double layer" at the interface, a distribution of charges about the interface that creates a potential difference and therefore a stabilizing effect between the two phases.

An O/W emulsion is generally not stable, although a double layer is often present. The double layer will be of the double-diffuse type with most of the potential drop occurring in the oil phase due to the low electrolyte strength in, and dielectric constant of, the oil. The charge densitites will be low - in water because of the low potential and in oil because of the very much extended double layer (see Figure 3-1). The repulsive double layer energy will then also be small, too small to counteract the attractive physical forces.

The O/W emulsion could be stabilized if a suitable surface-active substance were present at the interface. Figure 3-1 shows the influence of the adsorption of negative soap ions on the potential distribtuion (dotted curve).

Since the droplets in common emulsions are usually fairly large (1 to 10 micrometers), there is a strong tendency for separation under the influence of gravity. In this case oil droplets will rise to the surface, forming a concentrated but stable emulsion, the cream. When the repulsion is not strong enough to keep the oil droplets apart they may flocculate (aggregate) without coalescing, or they may coalesce (flow together to form a continuous oil phase).

It is also possible to disperse water in oil, but again in order to obtain stability a strong double layer must be formed in the oil phase, and this requires an increased electrolyte content. Inorganic electrolytes are usually very poorly soluble in oil, and if soluble, they are much less dissociated than in water. Some organic electrolytes, however, have large ions and can extensively dissociate in oil. Copper oleate is an example:

$$Cu(oleate)_2 \rightleftharpoons Cu(oleate)^+ + (oleate)^-$$

The cation (positive charge) is slightly more hydrophilic than the anion and hence will tend to adsorb to the aqueous phase. In this way, one obtains positively charged water droplets. Even in the presence of dissociated organic electrolytes, however, the double layer remains extended. In concentrated W/O emulsions of 50 percent/50 percent, for example, there is a considerable overlap of double layers, and the repulsion is largely overcome of necessity because the droplets are so close together. This explains the ability of these electrolytes to stabilize dilute W/O emulsions, but not concentrated ones.

The effects of the surface active species which may naturally be present in crude oils or which may be added

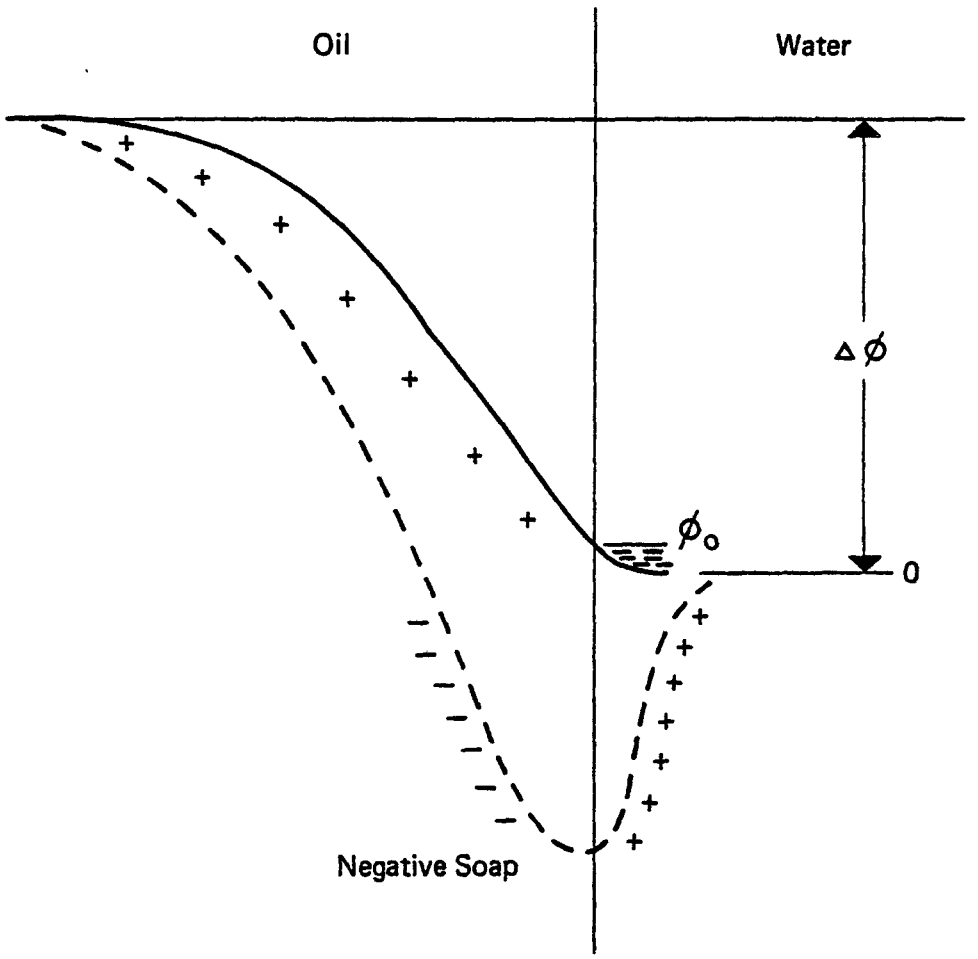

Figure 3–1. Schematic of double layer at oil/water interface.

during micellar flooding are to facilitiate emulsification and promote emulsion stability. The emulsifying agent forms an adsorbed film around the dispersed droplets which helps to prevent flocculation and coalescence. The stabilizing mechanism is complex and may vary from system to system. In general, however, the factors which control droplet flocculation are electrostatic in nature as discussed above, whereas stability against droplet coalescence depends mainly on the mechanical properties of the interfacial film. In addition to those already discussed the following factors (which depend on the nature of the surface agent and/or on the flow conditions leading to the emulsion) favor emulsion stability:

- Low interfacial tension - The adsorption of surfactant at the oil-water interfaces causes a lowering of interfacial energy, thus facilitating the development and enhancing the stability of the large interfacial areas associated with emulsions.

- A mechanically strong interfacial film - The stability of emulsions stabilized by various long-chain stabilizers arises from the mechanical protection given by the adsorbed films around the droplets, rather than from a reduction of interfacial tension. Surfactants can also stabilize in the mechanical sense. Coalescence involves droplet flocculation followed by a squeezing of film material from the region of droplet contact, and the latter is more favored with an expanded film than with a close-packed film. For example, very stable hydrocarbon O/W emulsions can be prepared with sodium cetyl sulphate plus cetyl alcohol as emulsifier (a condensed mixed film being formed at the interface), whereas the identical emulsions prepared with sodium cetyl sulphate plus oleyl alcohol (which gives an expanded mixed film) are much less stable.[2]

- High viscosity - A high viscosity simply retards the rates of creaming, coalescence, etc. This is a major factor in the stability of W/O emulsions typical of current oilfield practice.

A completely different mechanism of stabilizing emulsions which has relevance to oilfield fluids is the adsorption of solid particles at the oil/water interface. If the particulates are hydrophilic, the contact angle on the water side is small, and the particles reside on the water side of the oil/water interface, stabilizing the O/W emulsion. Oleophilic particles with a small contact angle on the oil side would lead to stabilization of the W/O emulsion. The solid particles

act as mechanical barriers to coalescence. If the continous phase is water, small quantities of electrolyte enhance emulsion stability because the particles are permitted to come closer together. However, larger amounts of electrolyte lead to flocculation and to rapid gravity separation of the emulsion, although coalescence may remain prevented. Emulsions stabilized by solid particles are called Pickering emulsions.

Whether an emulsion is of the O/W or W/O type will be mainly determined by the stabilizating mechanism. However, in some cases, the phase-volume ratio is also of some influence, the phase present in larger volume forming the continuous phase. Many O/W emulsions may be inverted into W/O emulsions by addition of suitable chemicals.

In the case of microemulsions, which are encountered in micellar floods, droplets are extremely small (1 to 50 nanometers) or are absent altogether, and flocculation and coalescence are no longer active. Microemulsions[3] are in fact not emulsions; they are colloidal solutions containing normal or inverse micelles. A micelle in an aqueous solution is an aggregate (see Figure 3-2) of surfactant molecules which forms when the surfactant concentration exceeds a certain level, the critical micellization concentration (cmc). In an organic liquid, by comparison, water is sparingly soluble, as is the typical ionic surfactant. A combination of water plus ionic surfactant will, however, be soluble over fairly wide ranges due to the formation of inverse micelles (Figure 3-3).

3.2 Occurrence of Oilfield Emulsions

3.2.1 Conventional Fields

The formation of emulsions has been a troublesome feature of the oil production business as long as the industry has been in existence. Dow noted as early as 1925 that "emulsions can form in any field that produces both oil and water, particularly when the two are subjected to mechanical agitation as, for example, from pumping or gas lift."[4] A more recent review article by Lissant[5] points out that emulsions occur as a result of the presence or occurrence of:

- Oil and water simultaneously.
- Natural emulsifiers in the produced fluids.
- Agitation or sheer.

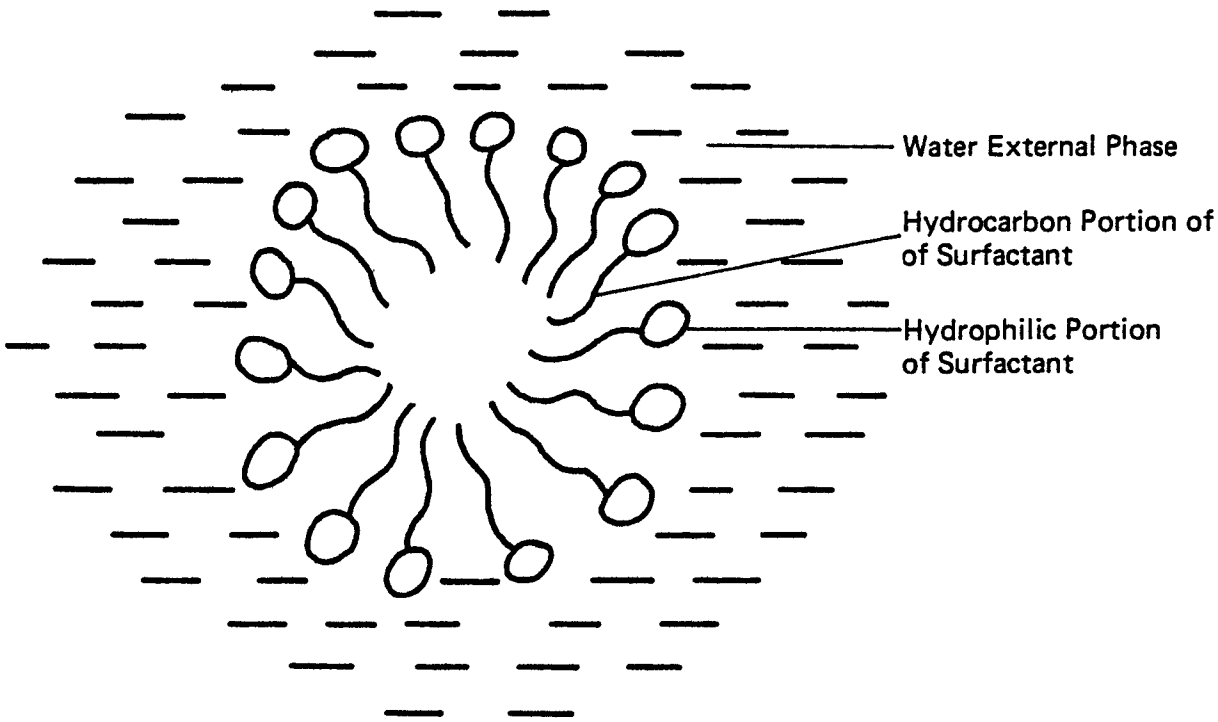

Figure 3–2. Schematic of micelle in aqueous solution.

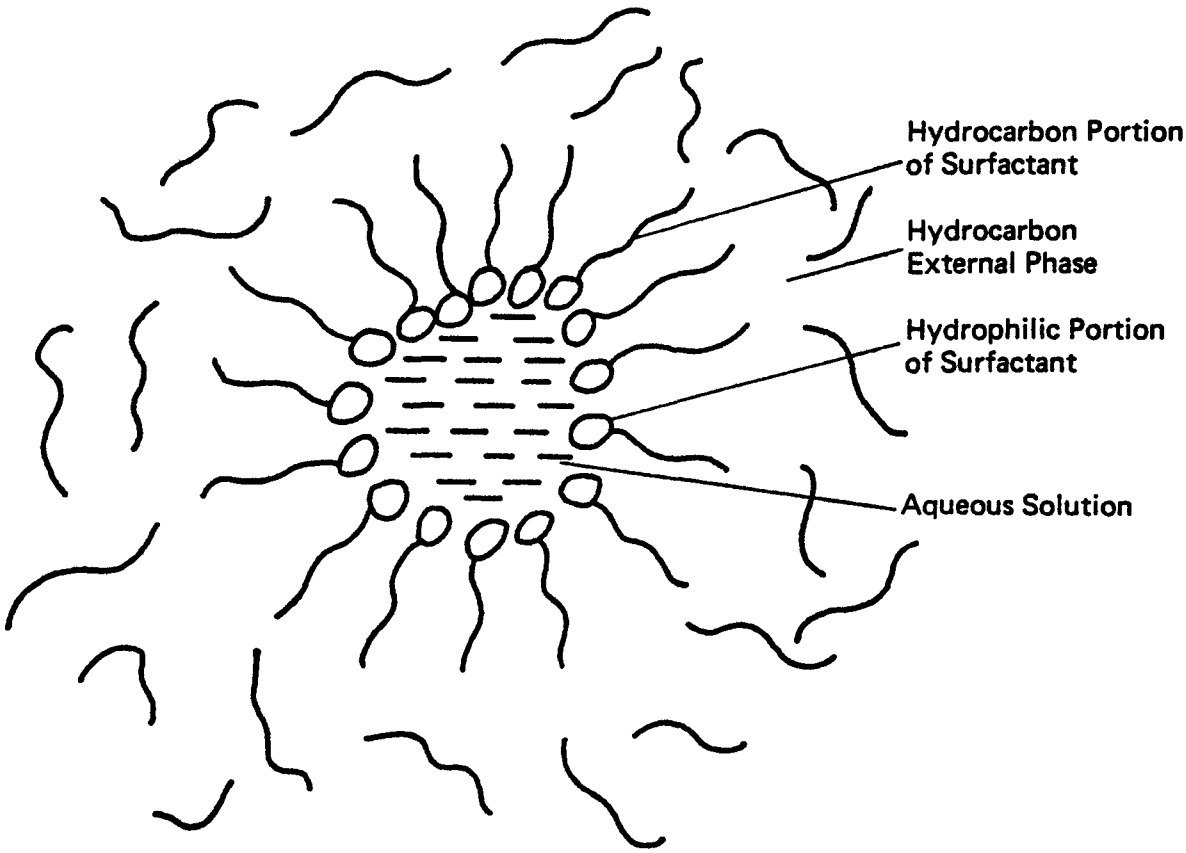

Figure 3–3. Schematic of inverse micelle.

In particular he points out that the produced emulsions are of a water-in-oil type ranging from 0.5 percent to as much as 40 percent water.

3.2.2 Enhanced Oil Recovery Projects

Enhanced oil recovery (EOR) techniques produce a whole new class of emulsions. Such emulsions will be of the oil-in-water type that are not readily broken using conventional oilfield techniques. For example, Marathon Oil Co. reports emulsion production on one of their projects as a result of a micellar/polymer flood.[6] The emulsion is believed to have formed as a result of the breakthrough of polymer and surfactant at one of the flood's producing wells. One of the characteristics of the surfactant used for micellar/ polymer floods is that it results in extremely low interfacial tension between oil and brine. Although this is to the operator's advantage while the fluids are within the reservoir, it is clearly a disadvantage at the producing well since the emulsion that results is expected to be extremely stable.

As another example of produced emulsions, Coppel reports that emulsions are formed following acidization of wells, a technique common to redrilling of old fields which often accompanies EOR projects.[7] The emulsion is believed to be caused by the presence of solids in the form of fines or precipitate from the acidization process.

3.2.3 Other Emulsions

Emulsions occur in industrial practice in many other instances besides oil production. A review of some of these situations is included here because they provide, by way of example, insight into the nature of oil-water emulsions and the corresponding methods that are used for treating these emulsions.

For the purposes of this report, two industrial emulsions have been considered:

- Wastewater emulsions - The wastewater streams from refineries or marine engine rooms include stable oil-in-water type emulsions similar to those expected with EOR techniques. Such emulsions often contain less than 1 percent oil and pose difficult water-treating problems.

- Spent lubricants - In metal drawing operations an O/W emulsion containing 5 to 10 percent oil is often used as the lubricant for the dies. Spent lubricants from this process are similar in physical characteristics to oilfield emulsions although the chemistry of the emulsion is somewhat different.

3.3 Treatment of Emulsions

3.3.1 Current Oilfield Practice

Methods for treating oilfield emulsions have evolved around three different principles:

- Gravitational settling by density differences.
- Electric dehydration - patented by Cottrell in 1911.
- Chemical breaking - first patented by Bamichel in 1914 who subsequently founded Tretolite Corp.

The conventional heater treater used commonly today combines all three principles. This device was developed during the 1930's.[8]

A typical horizontal heater treater is shown in Figure 3-4.[9] The oil phase from the oil water separators at an oil production facility will contain as much as 40 percent water in the form of a water-in-oil emulsion. In order to aid in breaking the emulsion, a demulsifying chemical may be added. The emulsion is then heated to temperatures as high as 150° F to accentuate density differences and/or passed through electrically charged plates (not shown) whereupon the oil and water will separate. Applying an electric field to the emulsion tends to force the polar water molecules in one direction. The water droplets agglomerate and coalesce, enhancing gravity separation.

The heater treater works as follows. The oil with demulsifier enters the separator on the heated side where it is contacted with the firebox tubes. As the emulsion breaks, the oil phase and the water phase collect on opposite sides of the heater. The two phases are pumped away at differing rates to maintain a proper interface level.

A variation in the conventional heater treater design is shown in Figure 3-5, showing a vertical configuration. This unit is slightly more compact than the horizontal treater and it allows for better heat exchange between the

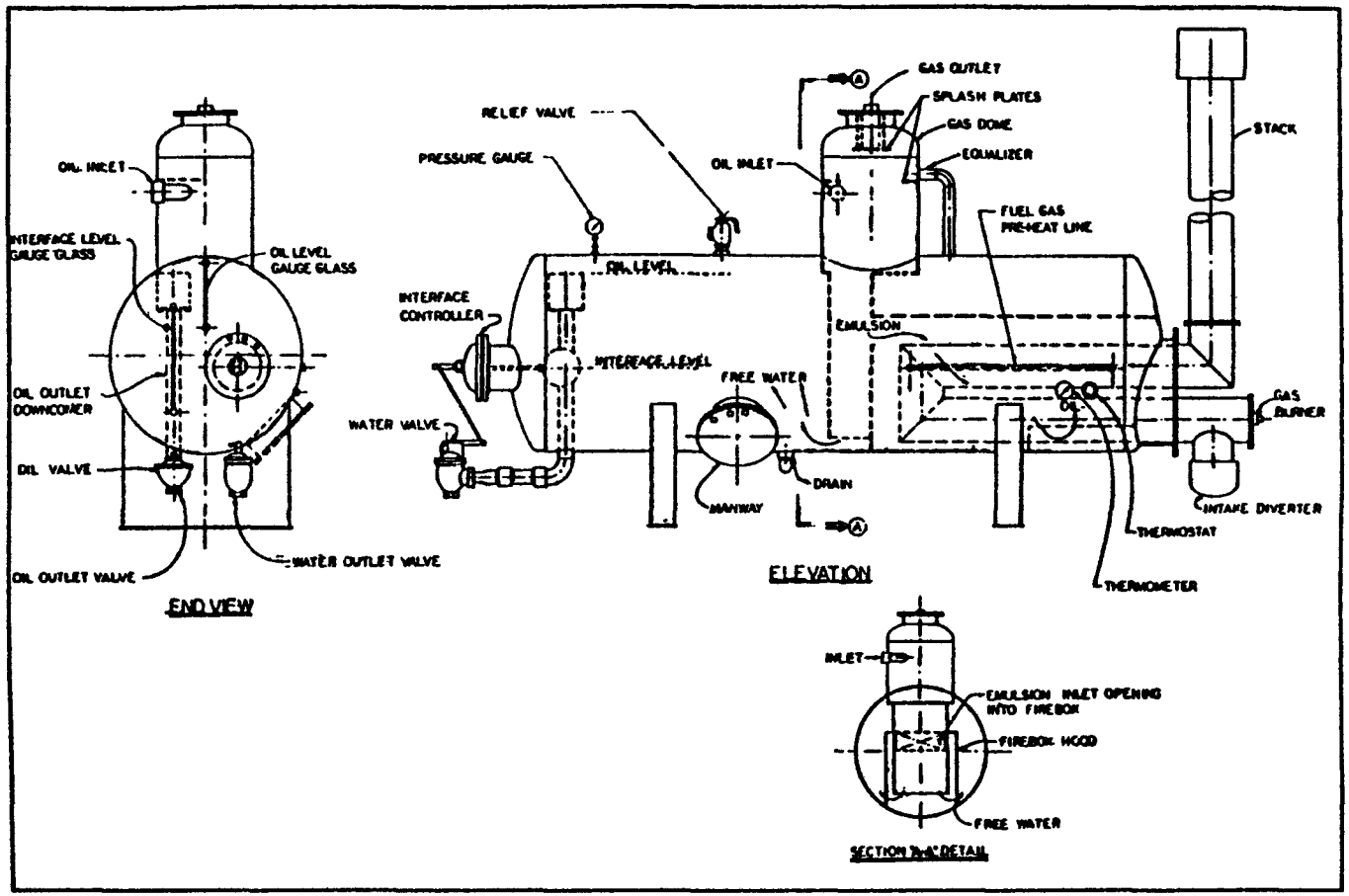

Figure 3–4. Horizontal heater treater. (Source: Sevalls Tanks Inc. Engineering Catalog, p. 465).

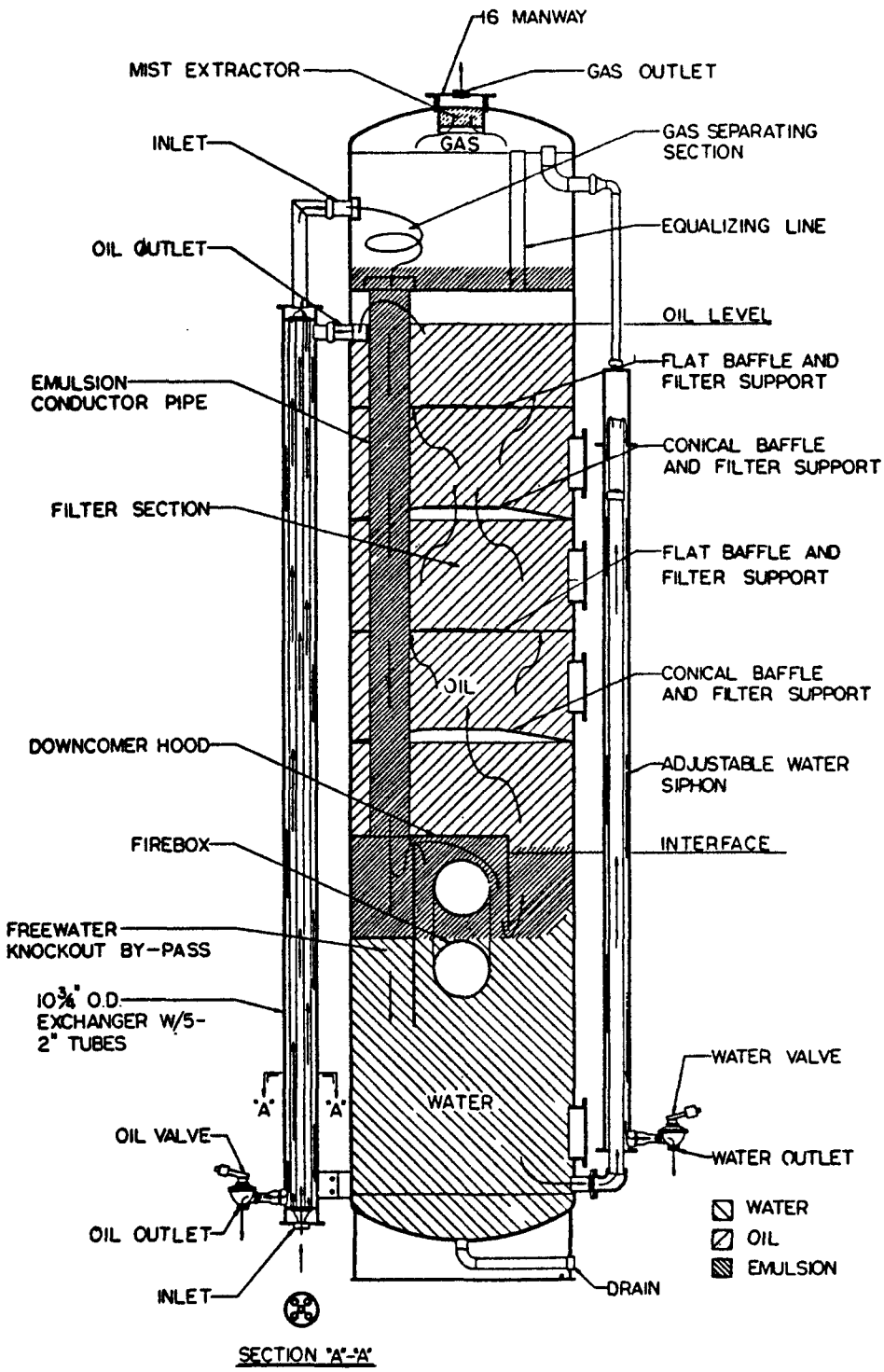

Figure 3–5. Vertical downflow treater. (Source: Sevalls Tanks Inc. Engineering Catalog, p. 409).

inlet oil emulsion and the outlet processed oil. The manufacturer claims that this design extends the life of the fire box and results in reduced fuel consumption.

3.3.2 Treatment of EOR Emulsions

Emulsions from enhanced oil recovery techniques will be of the oil-in-water type that cannot be treated using conventional oilfield equipment. For example, volumes to be processed are larger when the water phase is continuous; an electric field cannot be used if the continuous phase is a conductor. Among the methods that would be appropriate are the following:

1. Coalescence[10] - The use of porous or fibrous media can be used to promote the coalescence of oil in an oil-in-water emulsion. Although the method could be adapted for oilfield use, Lindenhofen has shown that the presence of surfactants can cause such filters/separators to fail.[11]

2. Chemical treating - Chemical treatment of oil-in-water emulsions using inorganic materials such as acids, alum, or lime as well as organic demulsifers has been reported by Nalco.[12]

3. Inversion - Another approach involving chemical methods is to invert the emulsion to a water-in-oil type using special chemicals. In the presence of surfactants, this is extremely difficult to achieve. However, if successful, the emulsion can then be broken by adding chemicals and using conventional equipment.[13]

There are very few examples of emulsion breaking for enhanced recovery projects and therefore the amount of data available is very limited. However, informal estimates of the cost suggest that breaking of oil-in-water emulsions could be as much as 10 times the cost of breaking conventional emulsions. More importantly, however, there are large uncertainties on the amount of chemicals that will be required to break oil-in-water type emulsions or the effect these chemicals might have on subsequent refining processes.

To provide additional insight into potentially viable oilfield systems, the methods of breaking industrial O/W emulsions are reviewed in the following section.

3.3.3 Related Practice for Non-Oilfield Emulsions

Oil-in-water emulsions occur in many other industries besides petroleum production. Several examples are listed in Table 3-1. Much can be learned from an investigation of how these emulsions have been treated by other industries.

Although several differences are apparent between oilfield emulsions and other industrially occurring emulsions, the two groups are also similar in that they exhibit the same physical and structural properties.

The surfactant material may be initially present in either the oil or the water, or the surfactant may be an integral part of the oil, such as a detergent in a cutting fluid. The oil, typically 3 percent by volume or less, is emulsified into the water. As in oil field production, a free water layer often exists.

Until recently many emulsions produced by industry were commonly sewered or discharged, such as in ship bilge pumping and ballasting operations. Because of environmental regulation, this option is no longer viable. An oily emulsion must be disposed of properly or broken into reusable products. In many applications such as metal cutting, the emulsified product is often recovered and separated since it is too valuable to discard.

Over a dozen different methods for recovering emulsified oil and water and breaking the emulsion have been developed. The major methods are listed in Table 3-2. The authors and references are given in Table 3-3. An annotated bibliography is given in Appendix A.

TABLE 3-1

TYPICAL SOURCES OF INDUSTRIAL OIL-IN-WATER EMULSIONS

Ship bilges and ballasting
Petroleum refineries
Paint manufacture
Rolling mills (rinsing and cooling)
Metal cutting, finishing, and electroplating
Food processing

TABLE 3-2

METHODS FOR SEPARATING OIL-WATER EMULSIONS

Membrane filtration
Ion exchange
Adsorption
Absorption
Centrifugation
Sedimentation
Heating
Chemical breaking
Chemical coagulation (flocculation)
Biological oxidation (degradation)
Electrical dehydration
Ultrasonic coagulation

3.3.3.1 Flotation and Magnetization

Flotation is based on the injection of fine air bubbles into a liquid. The oil drops adhere to the bubble surface and are removed to the water surface. Chemicals may be added to improve the efficiency of the flotation process. These chemicals, such as alum, absorb oil and form a gelatinous flock that may either be skimmed off the top or precipitated to the bottom of the vessel. Oil may be removed from an oil-in-water emulsion magnetically by the addition of a ferrofluid, which is a stable suspension of fine magnetic particles in an oil phase. The ferrofluid and the emulsified oil are miscible. The joint oil phase may then be removed by passing the fluid through a packed bed residing in a magnetic field. The force exerted by the magnetized packing material is sufficient to pull the oil droplets out from the aqueous phase and retain them on the packing. When filled to capacity, the magnet is turned off and the oil is flushed or drained out.

3.3.3.2 Coalescence

Coalescence is the term used to describe the physical promotion of uniting the interfacial boundary of droplets; i.e., consolidating smaller oil drops into bigger oil drops. The larger oil drops may then be separated by gravity. Mats, screens, and porous or fibrous materials have been used to promote coalescence. A large surface area per

TABLE 3–3

ANNOTATED REFERENCES FOR OIL–WATER EMULSION BREAKING METHODS BY AUTHOR

GENERAL REFERENCES AND REVIEWS		
Cooke	Jan	Katsuta
Takahaski	Wang	
MEMBRANE FILTRATION		
Bailey	Fluid Systems	Goldsmith (1973 and 1974)
Ladha	Markind	Oswald
Sumitomo	TJ Engineering	Trulson
FLOTATION		
Firma	George	Pollution Technical Services
Wilms		
MAGNETIZATION		
Beaucaire		
COALESCENCE		
Chambers	Fowler	Fuji
Herce	Imperial Chemical Ind.	Lock
McGrew	Mapco	Ono
Spielman (2)		
FILTRATION		
Baer	Evers	Goto
Lindenhofen	Schmidt	
ION EXCHANGE		
Shinoda		
ADSORPTION		
Vadekar		
CENTRIFUGATION		
Void		
SEDIMENTATION		
Brunsman		
HEATING		
Ackermann	Hillerbrand	Plinke
Preiss		

TABLE 3–3 (CONT.)

CHEMICAL		
Bradley	"Demulsifier"	Fledman
Jain	Lordi (2)	Markofsky
"Oil"	Ono	Otsuba
Plumbar	Sakuma	Sheikh
Tao	Yono	
CHEMICAL COAGULATION		
Ariyama (2)	Barker	Buriks
Chojnacki	Christ	Churchill
"Entwicklungs"	Fischer	Gandurina
Heinze	Kawamata	Lees
Luthy	Mongait	Schulze
Wakabayashi	Walther and Cie.	
BIOLOGICAL OXIDATION		
Hentschel	Hill	Kirby
ELECTRICAL		
Bartkievicz	Cole	Furnes
Ghisalberti	Hayano	Hettick
Jahns	Janusch	Joven
Klare	Levert	Yukawa (2)
ULTRASONIC		
Bilhartz	Kanevskii	Nagy

volume of material is required for the material to be effective. Coalescing devices such as straw filters or screens are commonly used in heater treaters in oil fields.

3.3.3.3 Filtration

Conventional filtration or conventional filtration with filter aids may also be used to retain the oil in an oil-water emulsion. However, the filter medium must be tight enough to prevent the oil from passing through the filter. But this is achieved at the cost of a high-pressure drop and pumping cost. Additionally, the oily sludge builds up on the filter and must be removed to prevent an excessive pressure drop and clogging of the filter.

3.3.3.4 Adsorption

Oil in an emulsion may be adsorbed onto the surface of a solid material such as activated carbon or polypropylene derivatives. The adsorbing medium may then be removed by gravity or filtration. Oil may also be removed by absorption into another phase, which is immiscible and will not emulsify with water.

3.3.3.5 Sedimentation

The simplest, but perhaps most expensive, approach to separating oil from water in an emulsion is by settling. The practical limit to this method is the time and space required for separation. Centrifugal forces, as in a centrifuge, may be used to enhance settling, as opposed to relying solely on gravity. Heating may also be used to change specific volume and to enhance density differences or reduce viscosity.

3.3.3.6 Other Methods

Chemicals may also be used to enhance sedimentation. Chemicals may be used to coagulate or floc the emulsified oil droplets. Chemicals that actually link to the oil droplets may be used, or salts such as calcium chloride or organic polyelectrolytes may be used to tie up the surfactant molecules at the interface and break the emulsion. O/W emulsions may also be broken through bacterial or biological action. Bacteria present in the water phase can oxidize or degrade the surfactant, freeing the oil and

breaking the emulsion. An electric field, which acts on the double layer of the emulsified droplet, may be used to coalesce the (water) droplets. This is the method conventionally used in oil fields where it is often enhanced by heating and chemical treatment. Ultrasonic methods may also be used.

Often, a combination of techniques is needed to successfully perform the job. An example of a typical problem that requires a combination of methods is described below.[14]

> Paint manufacture "D" produces various paint and finish products with latex, oil, and resin bases. Wastewater comes from clean up of paint manufacturing and packaging equipment throughout the plant and is subject to wide variations in flow and contaminate concentration and character. The plant installed a wastewater treatment system in 1961 to remove most of the oil and suspended solids before discharging the wastewater to the municipal sewer system. The treatment system consists of a holding tank followed by a full flow pressurization dissolved air flotation unit. When installed, the treatment system discharged a treated effluent described as sparkling by the treatment plant personnel. However, as the trend from oil to latex base paints has continued from the early 60's, the treated wastewater effluent quality has steadily deteriorated and now averages 1000 mg/l oil and 1500 mg/l suspended solids and a pH of 11 to 12. At the same time the municipal sewage treatment plant receiving the plants discharged wastewater for final treatment has increased their limitations on type and concentration of wastewater discharged to the sewer system. The municipal sewage treatment plant now limits the wastewater discharge to the sewer to a maximum of 250 mg/l suspended solids or oil, at a pH of 6 to 8.
>
> Laboratory chemical treatment tests on representative wastewater samples indicated that neutralization of the wastewater from a pH of 12 to 7 followed by coagulation with 150 mg/l alum and 5 mg/l cationic polyelectrolyte would result in a flotation effluent of only 50 mg/l suspended solids and no measurable oil content. The neutralization of the wastewater resulted in precipitation of the latex emulsion, which contributed most of the suspended solids in the wastewater. Most of the oil present in the wastewater was apparently adsorbed on the precipitated latex. Addition of alum then coagulated fine latex particles remaining

after neutralization and also "broke" any emulsified oils present.

Application of the above chemically treated effluent to recycle pressurization dissolved air flotation bench scale equipment indicated the existing wastewater treatment facilities could handle the chemically treated wastewater with the addition of chemical treatment facilities and minor plumbing modifications.

3.4 Ultrafiltation for Emulsion Treating

Ultrafiltration may be used to separate emulsified oil from water. This section describes the physical phenomena of membrane ultrafiltration and the current state-of-the-art of treating oil-water emulsions by ultrafiltration.

3.4.1 Ultrafiltration Membranes

Ultrafiltration utilizes semi-permeable polymeric barriers or membranes to concentrate solutes in a liquid stream. This definition also applies to reverse osmosis, but ultrafiltration differs slightly from reverse osmosis in two respects: in ultrafiltration, material transport occurs mainly by a viscous flow mechanism as opposed to diffusion in reverse osmosis membranes. This is due to structural differences in the membrane composition. Reverse osmosis membranes have a tighter structure, i.e., smaller pore size than ultrafiltration membranes. Consequently, reverse osmosis membranes can be used to separate finer particles than ultrafiltration membranes. The term ultrafiltration is generally used in describing separations involving large molecules (molecular weight greater than 500) at comparatively low concentrations. Reverse osmosis is the preferred term when osmotic pressure is significant in determining diffusion rates. As shown in Figure 3-6, the particle sizes that may be separated by either reverse osmosis or ultrafiltration overlap to some extent. This intermediate regime is often called hyperfiltration.

3.4.1.1 Process Description

Ultrafiltration membranes (ultrafilters) are used to remove macromolecules from liquid streams, to concentrate solute macromolecules in solution, and to separate macromolecules. As shown in Figure 3-7 some of the carrier liquid

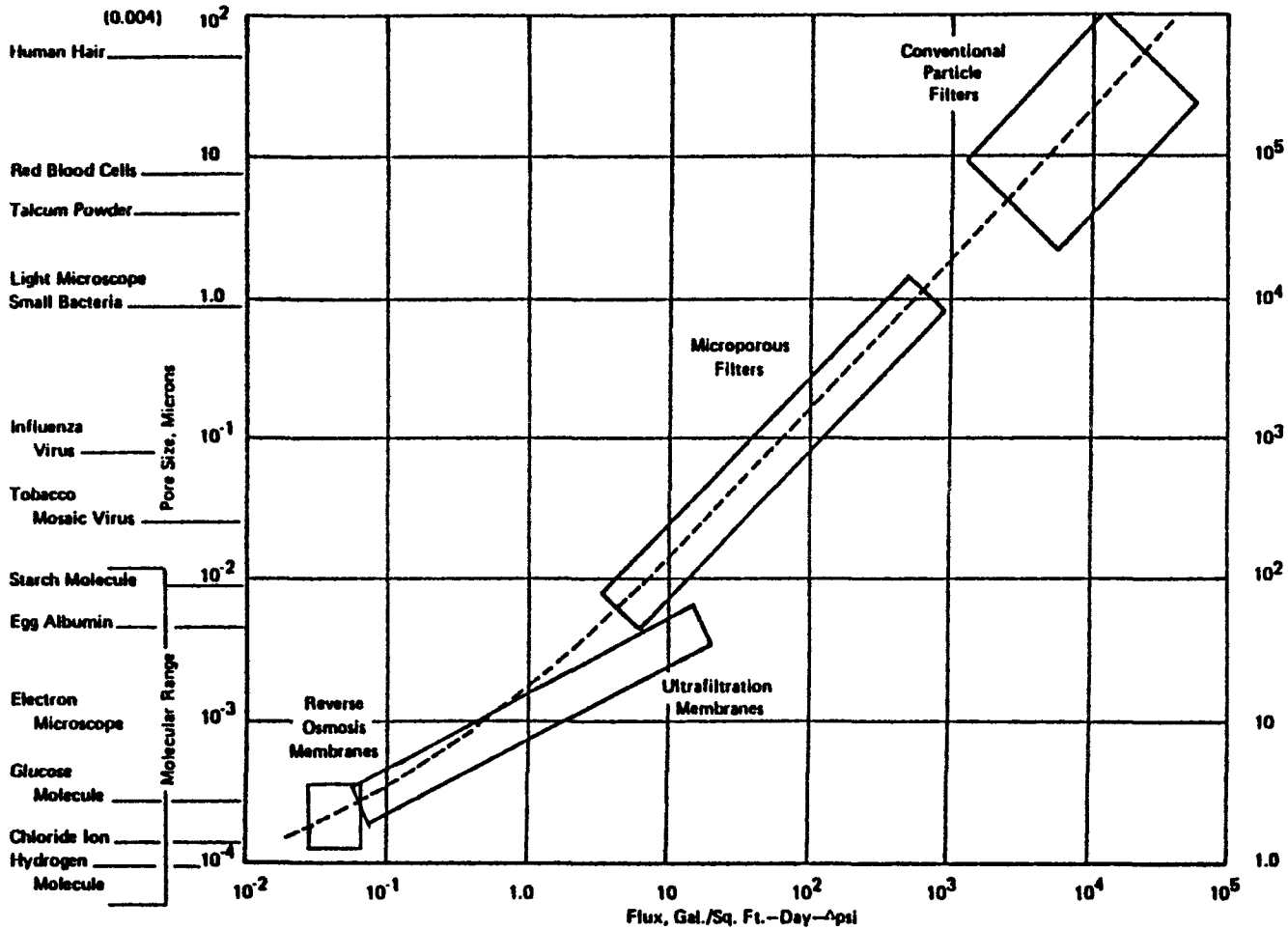

Figure 3–6. Membrane separation size range. Source: Arthur D. Little, Inc.

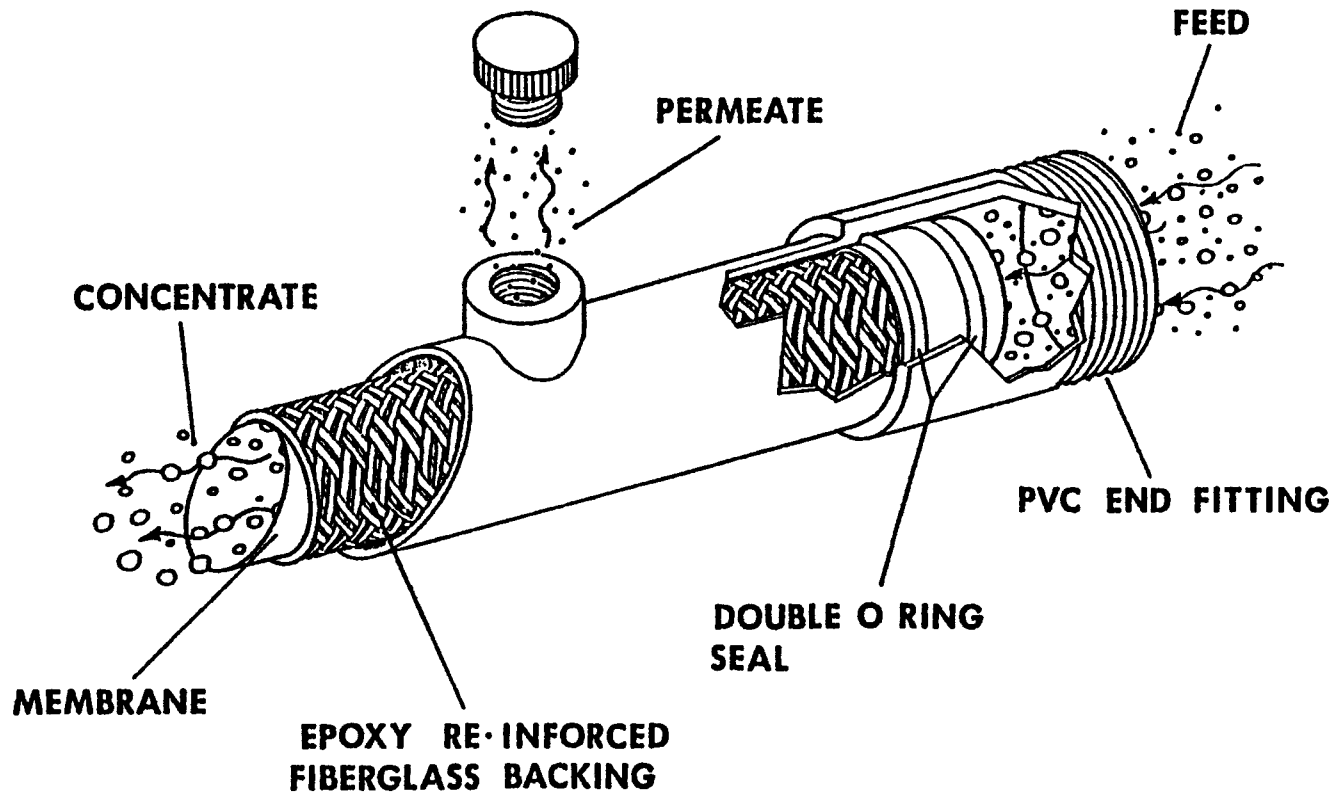

Figure 3–7. Ultrafiltration membrane.

(and smaller solute species) pass through the membrane as permeate. The macromolecular material that is too large to pass through the membrane is retained (rejected) by the membrane, and thus concentrated. By proper membrane selection different solute components may be retained. Depending on the configuration of the membrane, the permeate may pass out through or into the membrane. The membranes are typically a polymer film which is cast onto a more solid support. For ultrafiltration the driving force for separation and permeate flux is a pressure gradient across the membrane that is typically on the order of 20 to 60 lb/in^2. For reverse osmosis separations where the pore size in the membrane is much smaller and osmotic pressure in the fluid to be processed is significant, the typical pressure gradient across the membrane may be 200 to 1200 lb/in^2.

Ultrafiltration and reverse osmosis provide a method for continuous molecular separation (concentration) that does not require a phase change or interphase mass transfer. The sole energy requirement for separation is the compression energy and frictional pressure losses of the feed liquid. The energy required is much less than that required for evaporation, distillation, or heating. In addition, since the process is athermal, except for pumping friction, and involves no phase change, the materials being processed are not thermally degraded, although shearing of polymers is possible.

3.4.1.2 Currently Available Membranes

The ultrafiltration membrane itself may be made out of several different types of material such as carbon or graphite, polysulfane, polyacrylonitrile, polyvinylcarbonate and aromatic polycarbonates. The most common membrane materials are cellulose acetate and derivatives. The membrane is typically 1/3 to 2 microns thick, and thus must be supported on a more rigid material. Support material is usually a porous plastic, fiberglass, or a thicker, more porous structure of membrane material as in hollow fibers. The type of membrane material used and its chemical properties will affect the range of process conditions that may be used.

Ultrafiltration membranes of commercial interest are prepared with an asymmetric pore structure. Pore radii are smallest at the membrane surface in contact with the solution being filtered. Pore radii increase with depth from this surface. Consequently a macromolecule upon entering a pore is carried through the membrane with less and less hindrance.

In ordinary filters, by contrast, particles entering the pores collect because of internal constrictions, reducing filtration rates.

Ultrafiltration membranes are typically used to separate large macromolecules from liquid streams. Applications include membranes for artificial kidneys, blood separation, enzyme separations, removal of bacteria, protein processing in the food industry, wastewater cleanup, and separation of oil from water, which will be described below. Since ultrafilters operate essentially continuously at relatively high flux rates (permeate rate through the membrane) and at low pressure drops, they find economic application where conventional filtration is not possible. A list of general references on ultrafiltration and its application is given in Table 3-4.

3.4.1.3 Manufacturing

Ultrafiltration and reverse osmosis membrane manufacture is conceptually easy but, as practiced, is almost a black art. Chemical formulations for casting the membranes and the conditions under which the casting is done, are closely guarded company secrets. Small changes in formulation affect the structure of the membrane and the types of separations that may be made. Thus, quality control in making large quantities of membrane material is difficult and is a formidable barrier to successful entry into the field. A list of current membrane manufacturers and membrane types is given in Table 3-5. The total number of membrane manufacturers is quite small. Most membrane manufacturers sell the membranes to distributors who in turn fabricate and sell process systems for application. The manufacturers provide a technical expertise and membrane formulations to their distributors. Many distributors represent more than one membrane manufacturer in order to meet their process applications of a wide range of clients.

Figure 3-8 shows the three typical configurations for ultrafiltration membranes - the spiral-wound flat sheet, hollow fiber, and hollow tube. The latter may have either an external or internal membrane. Hollow fiber tubes are self-supporting but are consequently more sensitive to pressure drops. The operating regimes of the membranes will depend on their configuration and on the membrane material.

TABLE 3–4

REFERENCES ON ULTRAFILTRATION AND REVERSE OSMOSIS

ANNOTATED (by author)

Bhattacharyya (3)	Breslau	Buckley
Del Pico	Goldsmith (1971)	Grieves
Guetling	Havens	Hoffman
Jhawar	Kimura	Kremen
McDonald	Madsen	Nusbaum
Pattison	Porter (2)	Truby
Weissman		

GENERAL REFERENCES AND COLLECTED WORKS (not annotated)

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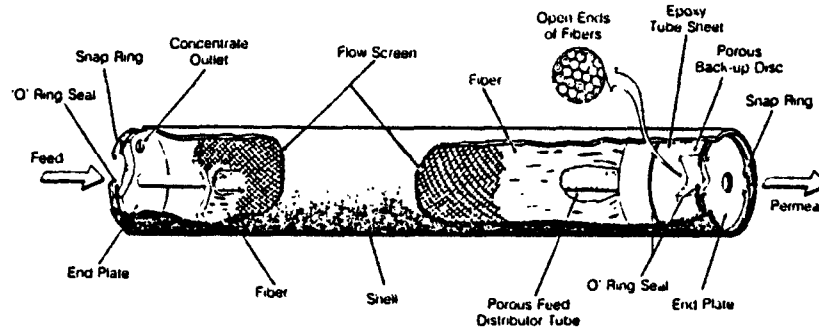
TABLE 3–5

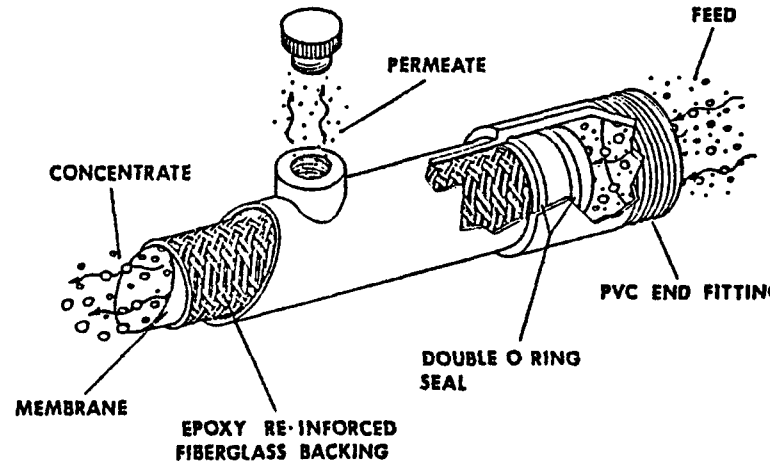
CURRENT TECHNOLOGY

Company	Geometry	Membrane Type
Abcor	1" diameter tubular membranes and spiral wound flat membranes	Originally cellulose acetate; now, other materials which are pH and temperature resistant
Dorr Oliver	Multiple flat plate	Polyelectrolyte complex (developed by Amicon)
Romicon*	Narrow channel tubular (flat sheet membrane); also hollow fibers	Dynel[R] (acrylic), cellulose acetate, Nomex[R] (nylon) polyelectrolyte complexes, others
Union Carbide	1/4" tubes	Zirconium oxide on carbon
Millipore	Multiple plate and screen cartridge	Cellulose acetate and others more solvent resistant
Osmonics	Spiral-wound modules, 2" and 4" diameter	Cellulose acetate and polyarylsulfone
Selas	Tubular	Zirconium oxide deposited in-situ on porous ceramic
Envirogenics	4" spiral wound flat membrane	Cellulose acetate
Rev-O-Pak	1/2" tubes, external membrane	Cellulose acetate and polyamide
Universal Oil Products	spiral wound flat membranes	Cellulose acetate

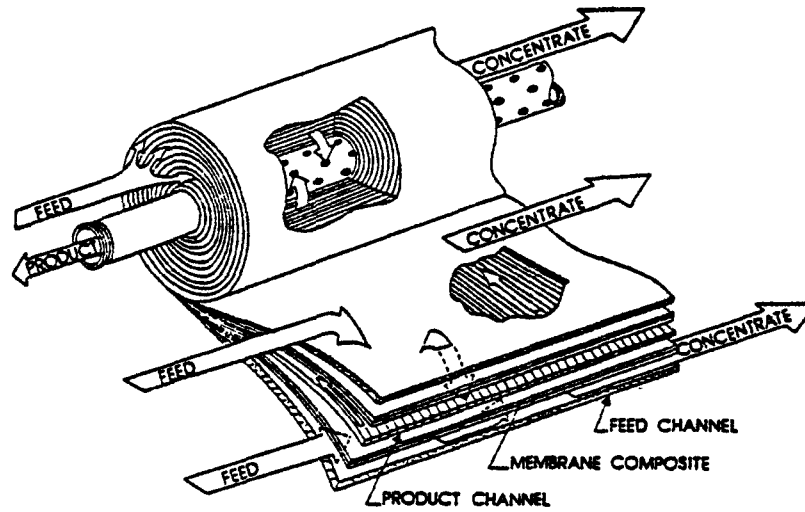
*Joint venture of Rohm & Haas and Amicon.



Hollow fiber membrane



Tubular membrane



Spiral wound membrane

Figure 3–8. Membrane configurations.

3.4.1.4 Membrane Performance

Factors that strongly influence membrane operation are temperature, pH, flow rate (superficial velocity), and pressure gradient. Excessively high temperature can cause degradation of the membrane material, especially for cellulose acetate membranes, which have a relatively narrow temperature range of operation. The pH of the feed material will also affect separation since the membrane material may react chemically with the feed. This will change the composition of the membrane and affect its structure. In any ultrafiltration system, solution bulk flow toward the membrane accompanied by solute rejection results in a concentration buildup at the membrane surface, increasing the osmotic pressure and reducing the flux rate. The concentration builds at the membrane surface until the solutes precipitate, adsorb, form a gel, or if colloidal in nature, reach the density of closely packed spheres. The thickness of the layer increases until its resistance to water transport reduces the flux to an equilibrium value such that solute transport to and from the membrane surface is at equilibrium. At this state, the flux rate is greatly reduced. To prevent the membrane from being fouled, the feed stream must have a sufficient linear velocity (shear) to remix the solution. This will prevent build-up of macromolecular material on the membrane surface, or at least inhibit this process. Consequently the feed flow rate is much higher than the permeate flux rate. For significant amounts of dewatering, several feed passes must be made.

All ultrafiltration membranes eventually foul. This is manifested by a drop-off in the permeate rate at a constant pressure drop across the membrane (or a higher pressure drop to maintain the same permeate flux). Fouled membranes may be cleaned by various methods - intermittent periods of high superficial velocity, backflushing, or chemical treatment to remove the adsorbed material. Freedom from fouling, the permeate flux rates obtainable for a given pressure drop, the feed flow rates, and the cost of manufacturing the membrane and membrane module, all affect the cost of operating the ultrafiltration system. The characteristics of the material being rejected (separated) and its concentration in the feed stream all have an effect on the operating costs of ultrafiltration.

3.4.2 Prior Art

Ultrafiltration or reverse osmosis membranes have not been used in oilfield emulsion breaking applications, but

are currently in use in treating oily wastewater. The Coast Guard has also sponsored studies to investigate the use of ultrafiltration to treat bilge waste and oily water discharges from ballasting operations. In many other operations, as in treating sewage, an emulsified phase may occur and is concentrated, but the main objective is production of a clean water stream, as opposed to separating the oil from the water. Only when the oil in the emulsion has a high value and is reusable does the objective of the separation become recovery of the oil.

Under sponsorship of the U.S. Coast Guard, Abcor, Inc. investigated the use of ultrafiltration membranes to remove and retain oil from the aqueous waste of the shipboard operations of deballisting, bilge pumping, and slop tank cleaning. The object was to produce a discharged aqueous phase with a low oil content of 10 ppm or less. A simplified schematic of the process is shown as Figure 3-9. Gravity separation is used as much as possible to separate the oil from the water and precipitate out any solids. The aqueous (emulsion) phase is pumped through the ultrafiltration membrane. Purified H_2O is produced as permeate. The concentrate, containing almost all of the oil, is recycled through the gravimetric separator.

An experimental program using Abcor's 1-inch tubular configuration membrane was conducted. Test oils were No. 6 fuel oil, a Venezuelan crude, lubricating oil, and kerosene emulsified at levels of 100 ppm to 90 percent in city water. Operating variables that were examined included pressure, feed circulation rate, and temperature. Ultrafiltration rates were very high, generally in the range of 25 to 150 gallons per day per square foot of membrane (gfd). Rates decreased with time due to fouling of the membranes. It was observed that the more stable the feed emulsions the more stable the ultrafiltration rate. Ultrafiltration rate stability was greatest for lubricating oil followed by No. 6 fuel oil, Venezuelan crude, and then kerosene.

Based on the experimental data taken, designs were prepared for systems with capacities of 10, 100, 1,000, and 10,000 gpm. Membranes in tubular and spiral wound configurations were considered. These systems were designed for shipboard installation; therefore, size and weight were important considerations. Capital cost and pumping power requirements are shown in Figure 3-10.

As of September 1976, Abcor has installed approximately 100 industrial scale plants to treat emulsified oil coolants that are typically used in machining and metal forming

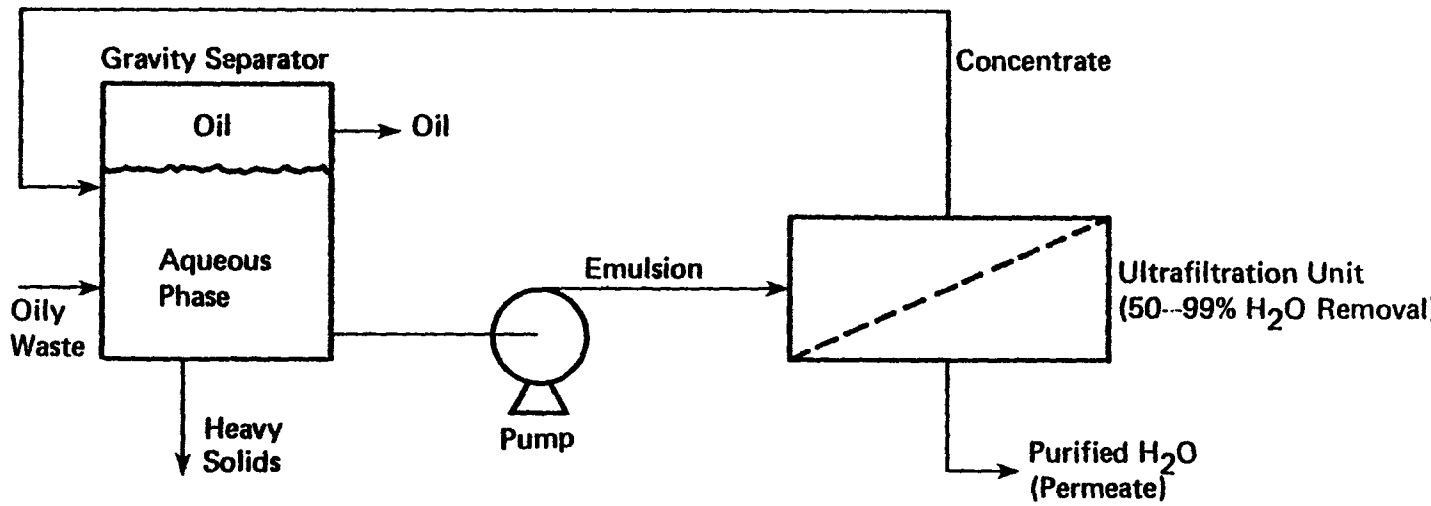


Figure 3–9. Schematic of Abcor's shipboard waste treatment plant. (R.L. Goldsmith, 1973.)

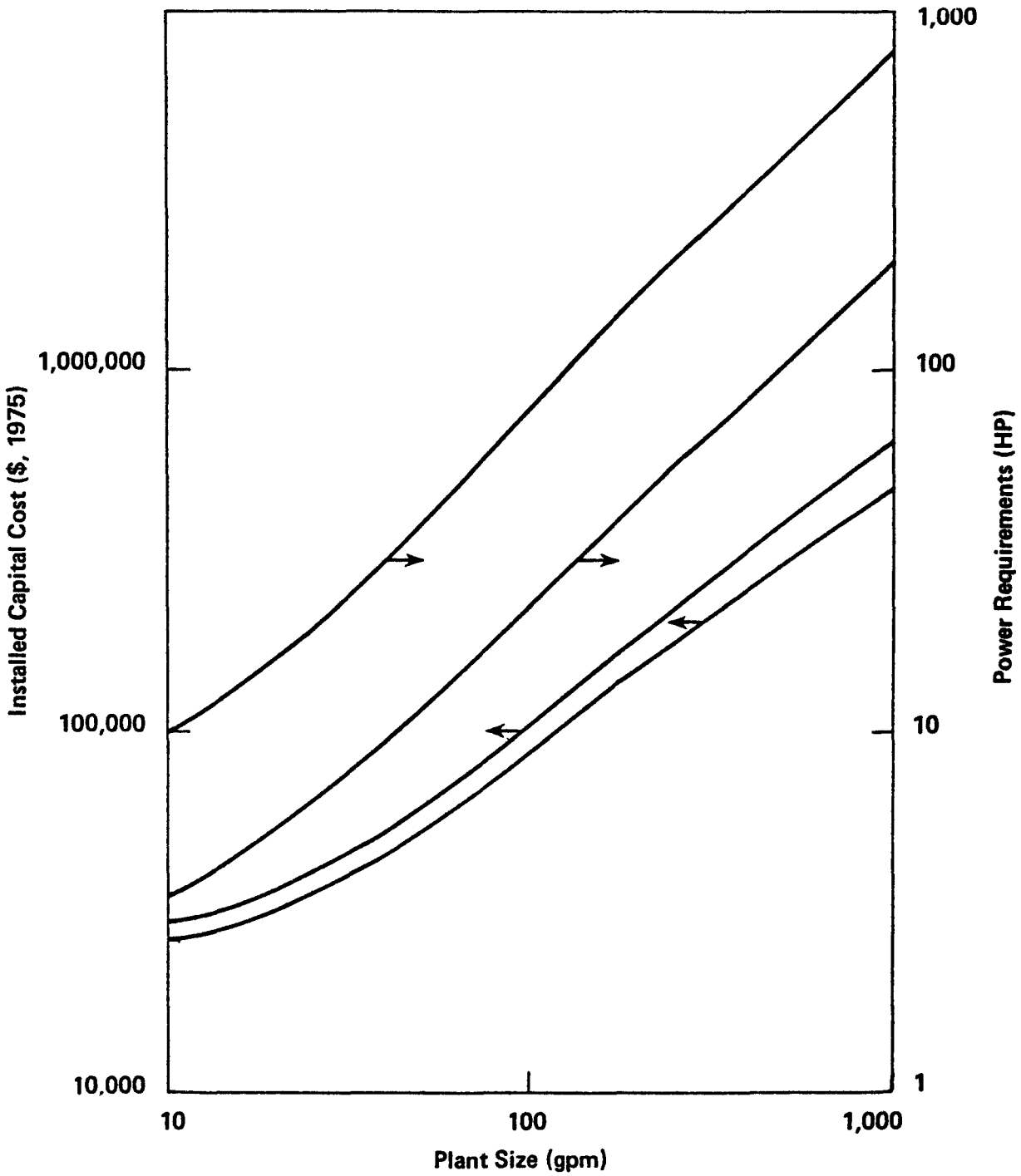


Figure 3—10. Cost and power requirements of Abcor shipboard waste treatment systems. (Goldsmith, R.L., 1973).

operations. These coolants are in increased usage since they retain a high degree of stability under a wide range of operating conditions. The emulsified oils must be cleaned or rejected when they collect an unacceptable level of dirt, metal particles, tramp oil, or start to grow bacteria. Unfortunately, they are stable, dilute emulsions of oil in water. Using ultrafiltration, the oil may be concentrated for waste haulers, chemical or thermal recovery, or incineration. Under some circumstances the concentrated emulsion may be recycled directly. The major advantage of ultrafiltration treatment of the emulsified coolants claimed by Abcor is concentration of the oil and emulsion by removal of a large portion of the water as a clean stream. Other advantages claimed are:

1. Little, if any, pretreatment.

2. No chemical additions are necessary except for detergent cleaning of the membranes.

3. No heat input is necessary.

4. The water produced as permeate can be usually sewered directly.[15]

5. No sludges are formed; the oil concentrate will sustain combustion.

6. The customer need only supply electricity and occasionally hot water.

The plants that Abcor has installed for treating emulsified oil coolants have ranged in size from a few hundred gallons per week to over 50,000 gallons per day.

A specific example[16] of an ultrafiltration plant installed by Abcor to treat soluble oil wastes is that at the General Electric Company Riverworks Plant in Lynn, Massachusetts which manufactures aircraft engines, turbine generator sets, and gear drives. Turning operations, grinding, and gear hopping produce over 500,000 gallons per year of water soluble oils and other oil contaminated wastes. The soluble wastes generated at the Riverworks facility are of three general types:

1. Emulsified machine coolants.

2. Synthetic and semi-synthetic coolants.

3. Oil contaminated water.

These products are wasted for a number of reasons but primarily for their rancid odor which is due to bacterial growth as the solutions age and become contaminated. Approximately 2,000 gallons per day of coolant must be disposed.

The previous method of disposing these coolants was incineration which placed a severe burden on the incineration facilities because of the large volume and extremely low heating value. Consequently, the coolants were gravimetrically separated and then treated chemically to break the oil emulsion and separate out an oil phase as much as possible before disposal by incineration.

After extensive pilot testing by Abcor to determine the best processing sequence and conditions for using ultrafiltration to treat the waste and to produce a dischargeable water permeate stream, a full-scale unit was built in 1973. The unit was designed to treat 4,000 gallons per day of soluble waste. A holding tank was installed to handle peak weekly accumulations. Analyses of permeate samples have shown organic extractables to be less than 25 mg/l with no detectable oil present. The total installed cost of the system was approximately $79,000. Operating costs for the system including labor, maintenance, power, and depreciation were estimated at 2.6 to 3.1 cents per gallon (1974) based on 120 operating days per year.

Universal Oil Products (UOP) and Rev-O-Pack, Inc. also sell systems designed to treat emulsified oil waste for both reuse or discharge. Specific economics will depend on the actual situation and basis used. Capital costs for the UOP system are on the order of $16,500 (1976) for a 1,500 gpd system and $45,000 for a 9,000 gpd system. Operating costs are on the order of about 3.5 cents per gallon treated. A more detailed economic analysis is shown as Table 3-6. A typical Rev-O-Pack system designed to process 3,000 gallons per day would cost approximately $24,000 (this is for a reverse osmosis system which requires no additional cleaning of the water permeate). Operating costs for this system are about 1 cent per gallon processed.

The key criteria for determining the economic viability of using ultrafiltration membranes to process oil-in-water emulsions are the following:

1. Membrane lifetime before temporary fouling.

2. Total membrane lifetime and replacement cost.

TABLE 3–6

COSTS FOR TWO DIFFERENT OIL/WATER SEPARATION EXAMPLES

	FLUID SYSTEMS DIVISION OF U.O.P. (Bulletin FS-5, 2/76)	REV-O-PACK – R.O. SYSTEM (Brochure - no number)
Size	1,500 gpd (U.G.unit)	3,000 gpd (R.O. unit)
Initial oil concentration	5%	5%
Final oil concentration	25%	Approximately 75%
Capital cost	$16,500 (1976)*	$24,000* (1976?)
Operating costs (300 days/yr)		
Capital charges	5,290	5,280†
Power ($0.02/kWh)	99	1,728
Membrane replacement	775††	1,890‡
Labor, maintenance & supplies	9,413	1,800‡‡
Total $/yr	15,577	10,698
Cents/gal	3.46	1.19

* Depends on complexity of system and is subject to change without notice.
** 5 year straight line depreciation, 7% interest, and 5% taxes and insurance.
† 10 year straight line depreciation, 7% interest, and 5% taxes and insurance.
†† 2 year life x $155 per module x 10 modules.
‡ 3 year life.
‡‡ Labor only, no supplies.

3. Flux rates as a function of time and oil concentration (flux rates decrease with increasing oil concentration).

4. Pressure requirements for a given flux rate.

5. The procedures required for cleaning and any associated costs (cleaning labor costs are usually reduced by the amount of automation possible).

While some general conclusions can be made as to the capital and operating costs for treating oil-in-water emulsions produced in metal cutting operations, the specific costs will be very dependent upon the specific components in the emulsion, the ultimate fate of the concentrated coolant, and the specifications on the water permeate. Capital costs are on the order of $5 to $10 (1977) per gpd clean permeate output. Operating costs are on the order of 1 to 3 cents per gallon of permeate produced.

3.4.3 Energy Resources' Concepts for Oilfield Emulsion Treating

3.4.3.1 Initial Concepts

The initial concept devised by Energy Resources for emulsion treating was direct demulsification of the oil field emulsion by removing water as permeate. As water (brine) is removed from the emulsion, surfactant material in the brine is also removed. As the oil concentration increases, the surfactant concentration decreases, and the emulsion is broken, as shown in Line AB in Figure 3-11. The partitioning of the surfactant between oil and water can be influenced by adding a co-surfactant or other material to the emulsion before ultrafiltration.

Unfortunately, in actual experimental work, spontaneous breaking of the emulsion never occurred. A likely explanation for the failure to break the emulsion is based on the observance that the surfactant material is retained in the oil phase (concentrate). Thus, as the brine concentration is decreased by permeate removal during ultrafiltration, the surfactant concentration in the emulsion stays approximately the same, or increases. The result, as shown in the figure, is that the surfactant concentration remains at least the same as the composition changes from A to C. The interfacial tension and emulsion stability also remain the same and the emulsion remains. While co-surfactant or other chemicals

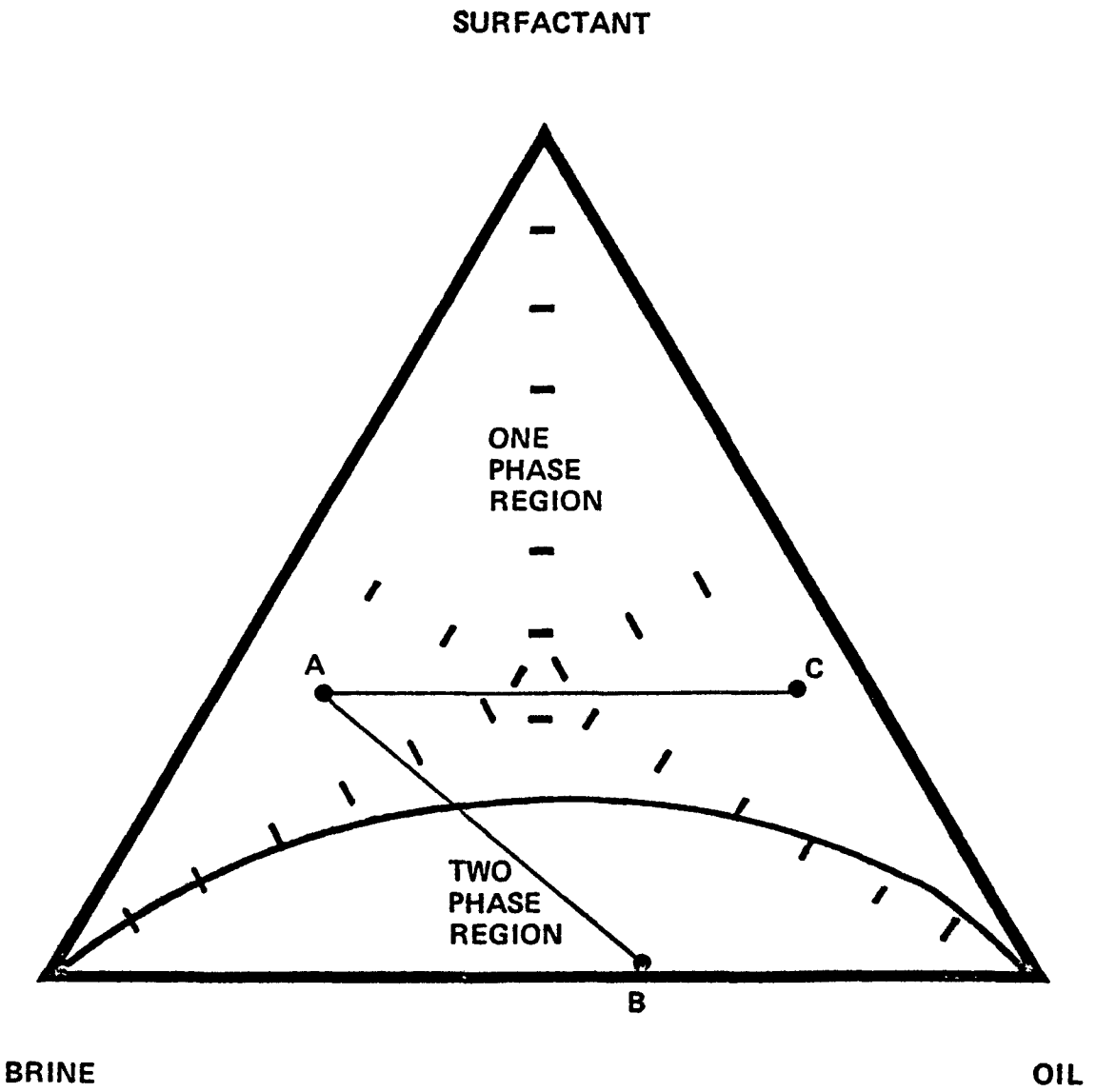


Figure 3–11. Phase relationships for emulsion breaking.

could be added to the emulsion prior to treatment to prevent the majority of the surfactant from partitioning into the oil, the cost of this method would probably be prohibitive and would also closely resemble conventional chemical treatment. Additionally, the correct formulation would vary for each emulsion to be treated and with time, since most emulsions themselves are unique.

A second concept for direct emulsion breaking was then developed. This concept calls for using reverse osmosis membranes to remove pure water from the emulsion, increasing the salt content of the emulsion. As the cationic strength of the emulsion increases, a point is reached at which the emulsion chemically breaks in a manner analogous to chemical treating. Reverse osmosis membranes that are tighter and operate with a higher pressure drop than ultrafiltration membranes are needed, since the inorganic salts must be rejected (retained) by the membrane. The amount of processing required depends on the initial cation concentration and the water/oil ratio (WOR).

This technique does not appear to be economically feasible for most cases because of the cost of de-watering at high pressure operation. Power requirements for pressure drops of several hundred pounds pressure are high and a great deal of water must be removed. As more water is removed the dissolved solids build up. More pumping is required per unit of water removed because the osmotic pressure of the emulsion increases. These trends are shown in Figures 3-12 and 3-13. In Figure 3-12, spontaneous oil and water emulsion breaking at 250 ppm divalent cation concentration is assumed. Although technically feasible, the economic prospects of this method did not warrant any further investigation as a part of this program.

3.4.3.2 Concept for Experimental Investigation

The concept for treating oil-in-water emulsions that seems to have the best technical and economic feasibility is illustrated in Figure 3-14. The ultrafiltration membrane will be used to dewater the emulsion, removing the brine or aqueous phase of the emulsion and reducing the amount of fluid that needs to be treated conventionally. Surfactant material in the aqueous phase is also removed proportionately with the water, since the membranes are loose enough to pass the surfactant molecules.

If sufficient dewatering of the emulsion occurs, the O/W emulsion will invert to a W/O emulsion. This is

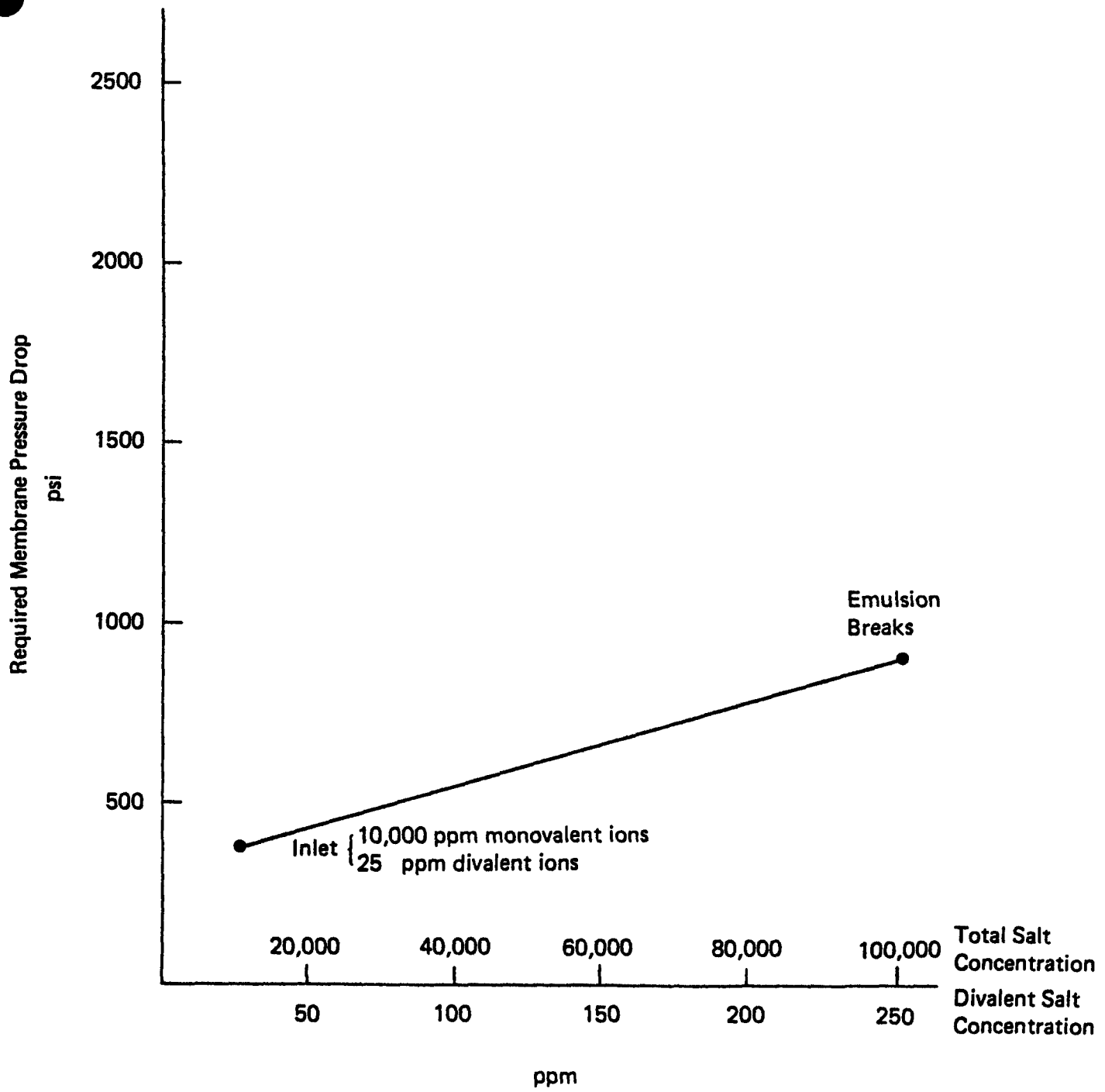


Figure 3–12. Pressure requirements for emulsion breaking by reverse osmosis.

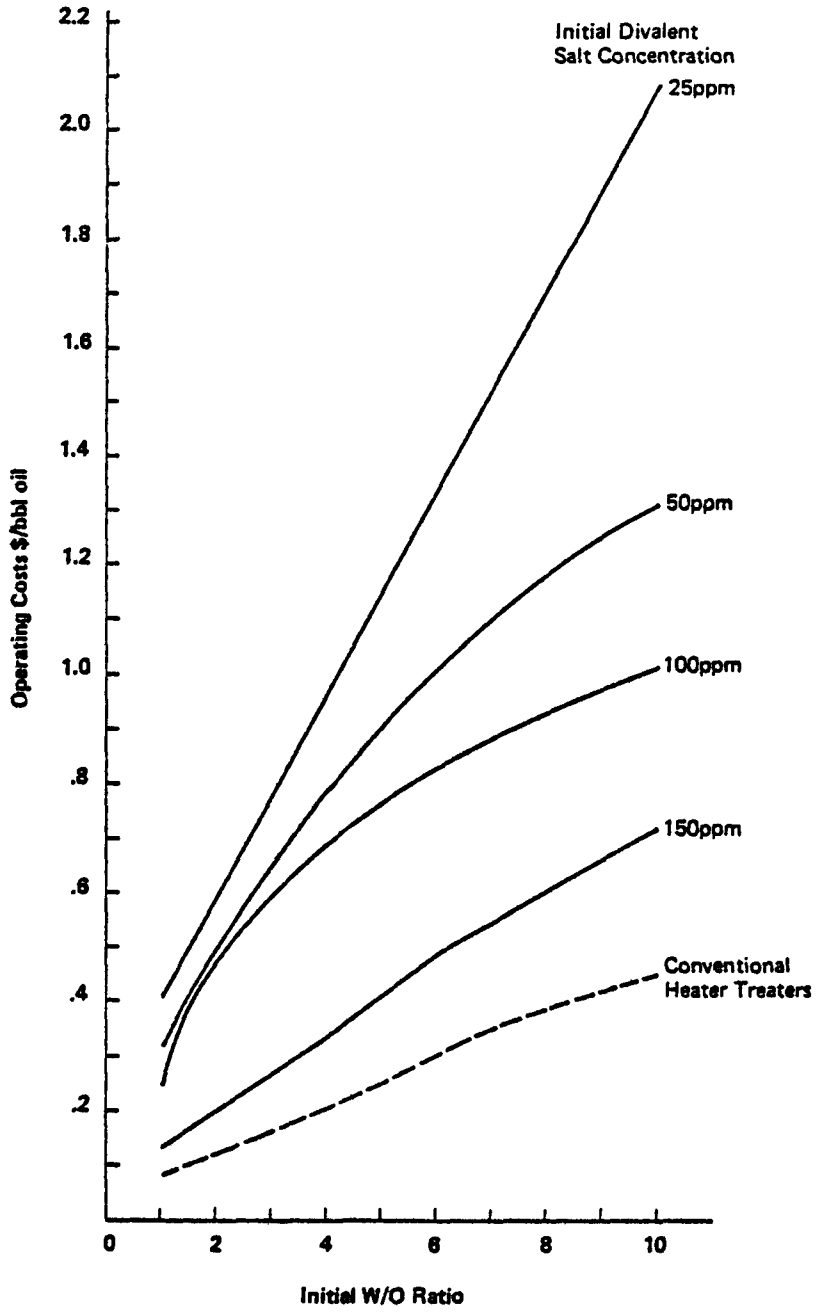


Figure 3—13. Estimated cost of emulsion breaking by reverse osmosis.

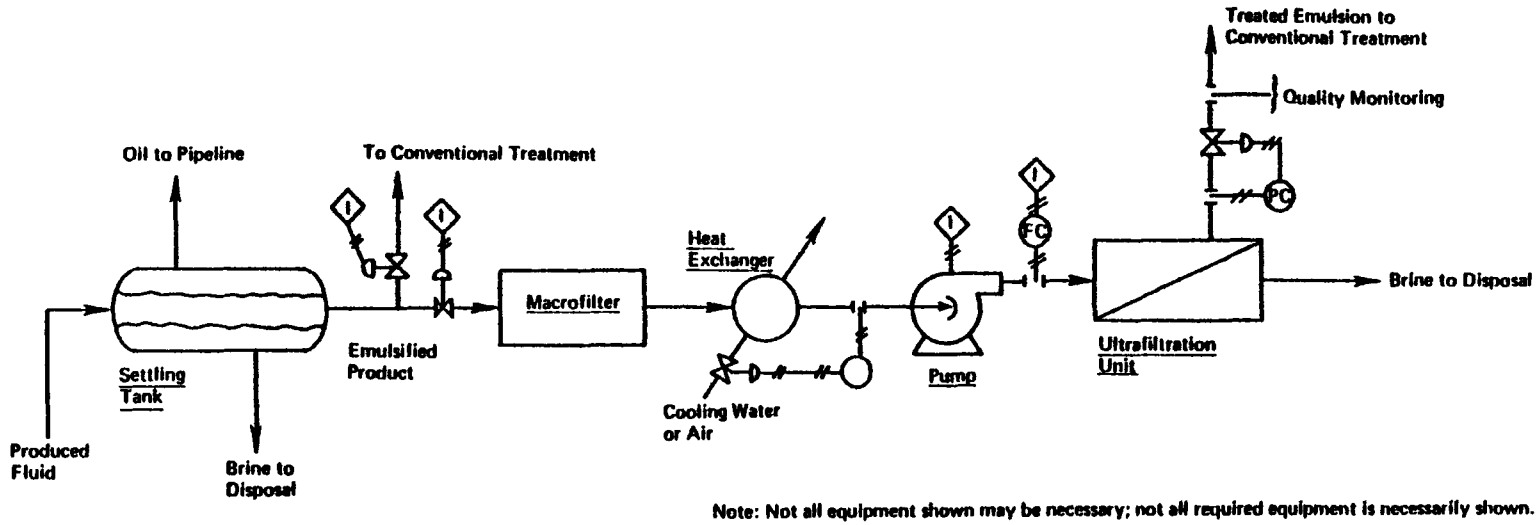


Figure 3–14. Schematic of emulsion treating field equipment.

important since the current method for treating O/W emulsions is chemical treatment to invert the emulsion to a W/O emulsion, which then can be treated conventionally in a heater-treater. Energy Resources' concept for treating the emulsion removes the chemical inversion treatment step and simultaneously reduces the amount of liquid that needs to be processed in a conventional heater-treater. Reducing the volume of fluid that needs to be processed in turn reduces the costs for fuel and chemicals in heater-treating.

Figure 3-15 is a schematic drawing of an installed system in the field. The produced fluid from a single well or group of wells is sent to a settling tank that has a short residence time. The free oil and water layers are then separated. Any emulsified phase is sent to a surge tank that feeds the ultrafiltration unit. The ultrafiltration unit consists of several parallel membrane tube paths in which the emulsion phase is dewatered continuously as the emulsion passes through the tube. The water, which is removed as permeate, is sent to surfactant recovery, process use, or is reinjected into the ground. This water will contain the same concentration of brine that is present in the aqueous phase, since the ultrafiltration membranes are not selective enough (tight enough) to reject (retain) the brine. The surfactant material will also pass through the membrane, but the oil will be rejected. After the desired amount of dewatering has been done, the dewatered emulsion (which may be inverted to a W/O emulsion) is sent to a conventional heater-treater. As can be seen in the figure, the amount of fluid that needs to be processed is greatly reduced, compared to current methods for treating O/W emulsions. The standard treatment methods, chemicals, heat, and electrostatic field, may be applied in the heater-treater as necessary.

3.4.3.3 Critical Factors and Test Plan

To investigate the feasibility of the above concept, experimental data to determine the capital plant requirements and operating costs for a conceptual field installation needed to be determined. The size and cost of an emulsion dewatering unit is almost entirely dependent on the permeate (permeate) flux rates and stream factor achievable and the membrane lifetime. Since membrane lifetimes for oil-in-water emulsions are typically on the order of 2 to 3 years, determination of membrane lifetime for oilfield applications was not within the scope of this project. The experimental effort was then focused on determining permeate flux rates and fouling times for various membranes.

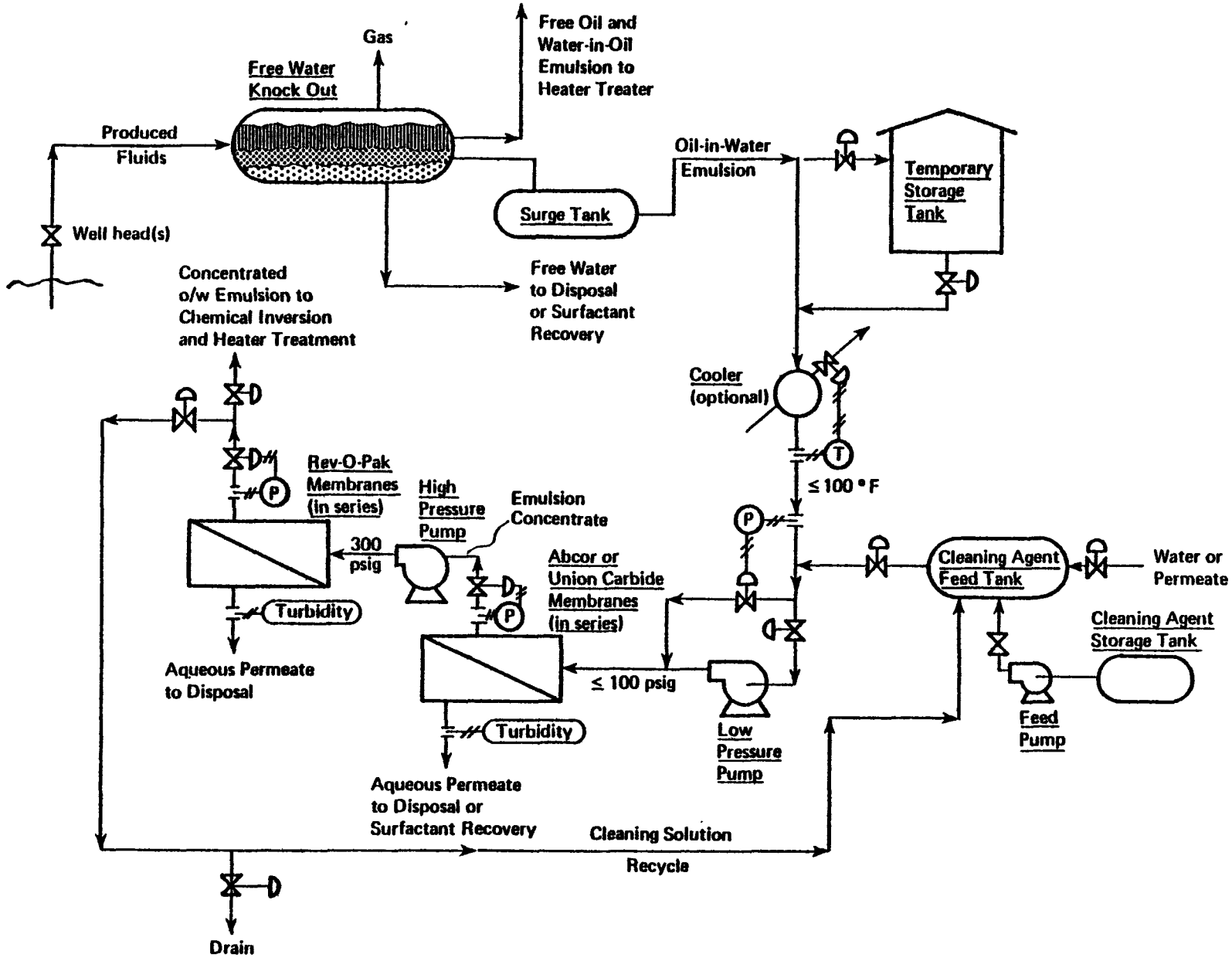


Figure 3–15.. Emulsion Dewatering.

Membrane flux rate is a function of operating temperature, operating pressure, membrane type and configuration, oil type, chemical composition of the emulsion, and oil concentration. These variables were investigated to determine the feasible operating ranges and feasible membranes for oilfield emulsion dewatering.

In order to measure flux rates for emulsion dewatering, stable emulsions of compositions resembling oilfield emulsions had to be formulated. Extremely stable emulsions were preferred since a stable emulsion presents a more difficult treatment problem in the field and also allows the use of the same emulsion with different membranes and operating conditions, thereby reducing the variability in the experimental results.

Four base case emulsions were prepared from the four oil and brine samples received from the test projects - El Dorado (Cities Services), North Burbank (Phillips), Bell Creek (Gary Operating), and Bradford Field (Penngrade). Initially, the base case emulsions were to be prepared using commercial petroleum surfactants and cosurfactants. However, stable emulsions that could be remixed when separated gravimetrically (and were therefore reusable) could not be formulated with the petroleum sulfonates on the bench scale with either a hand homogenizer or a blender. Highly stable remixable emulsions could be formulated using nonpetroleum-based, commerical surfactants. These were substituted for petroleum surfactants to speed up the testing process by providing consistent, reusable base case emulsions for testing with the various membranes under all operating conditions.

Formulation of stable remixable emulsions for membrane testing was somewhat of a black art. While a starting point for formulation could be determined by the reduction of interfacial tension between the oil and water phases, and formulations reported in the literature, a great deal of the effort that went into the formulation was trial and error. However, once the first successful formulation was determined the experience gained in reaching the formulation and the formulation composition were invaluable in preparing the other base case emulsions. The formulations used for membrane testing are given in Appendix B.

The criteria for formulating the emulsions for testing have been the following:

1. Brine concentrations less than or equal to formation water concentrations.

2. Surfactant concentrations in the total volume of synthesized material less than 1 weight percent.

3. Water-to-oil ratios in the initial mixture greater than 3.

4. Oil-in-water emulsions (water external phase).

The criteria used for emulsion stability have been the following:

1. Lack of oil-in-water phase breakdown after 2 minutes of centrifugation.

2. No phase breakdown after overnight (12 hours minimum) settling.

3. Re-emulsification by handshaking (a test tube of sample) if the emulsion separates after prolonged (24 hours or greater) settling.

4. Prolonged stability is preferred.

In all four cases, extremely stable emulsions were prepared. Better results were produced in the pilot plant than with the hand homogenizer on the bench scale. This was probably due to the greater shear possible with the centrifugal pump in the pilot plant.

Determination of flux rates at various operating conditions and with different membranes and base case emulsions was made in the manner described below. Four different ultrafiltration membranes - Abcor HFA, Union Carbide Ucarsep®, Rev-O-Pak 120, and Rev-O-Pak 150 were tested. These membranes were selected in order to examine a range of operating conditions, membrane configurations, and dewatering abilities. Price of test modules, ease of installation into the pilot plans, and availability also entered into the determination of which membranes were selected for testing.

For each membrane tested, a set of base operating parameters within the recommended operating range of the membrane was selected. For each membrane and with each of the base case emulsions, parametric changes in operating pressure, concentrate flow rate, and temperature were made around the base operating conditions. The effects of long-term operation were determined by testing each membrane with the base case fluid constantly at the base operating parameters for a period of 24 to 48 hours duration.

Initially, the long-term operation was to have paired each base case fluid with its corresponding optimum membrane (highest flux). Since flux rates for each membrane with all of the base case emulsions were fairly similar this was not attempted. During the long-term runs operating conditions, flux rate, as well as oil breakthrough into the permeate, were monitored. The long-term runs were to be terminated prematurely if either membrane flux rate fell by 50 percent or the permeate contained 1 percent or more by volume of oil.

In order to determine the effect of water-to-oil ratio (oil concentration) each membrane was tested in a transient mode with recycle of concentrate to the feed tank but external collection of permeate, reducing the aqueous content of the emulsion. For each membrane a base case emulsion was selected for testing at the base operating conditions. The runs were to continue until the feed became too viscous to pump, the emulsion broke, oil began to permeate the membrane, or until the flux rate was reduced by at least 50 percent. Besides the operating conditions, flux rate, permeate quality, and water-to-oil ratio (by material balance) were measured. The external phase of the emulsion concentrate was monitored for evidence of emulsion inversion.

3.4.3.4 Experimental Equipment

To evaluate the four membranes selected for testing, two different pilot plants were required. One (designated the low-pressure pilot plant) was constructed at Energy Resources for testing the Abcor HFA and Union Carbide membranes. The other (designated the Rev-O-Pak unit) was purchased from Rev-O-Pak Inc. The Rev-O-Pak unit is a high-pressure unit capable of accepting both ultrafiltration membranes for emulsion dewatering and tighter, higher-pressure operation membranes for surfactant recovery.

The low-pressure pilot plant is shown schematically in Figure 3-16. The unit is designed to operate over a wide range of concentrate flow rates and operating pressures to accommodate the two different membranes to be tested with the system. The pilot plant can be operated at a constant water-to-oil ratio or in a transient mode in which the water-to-oil ratio is changing.

The emulsion flows from a 30-gallon tank through the pump to the ultrafiltration membrane. A bypass loop around the pump and a ball valve are used to control flow rate to the membrane. Since the pump is a centrifugal pump, the

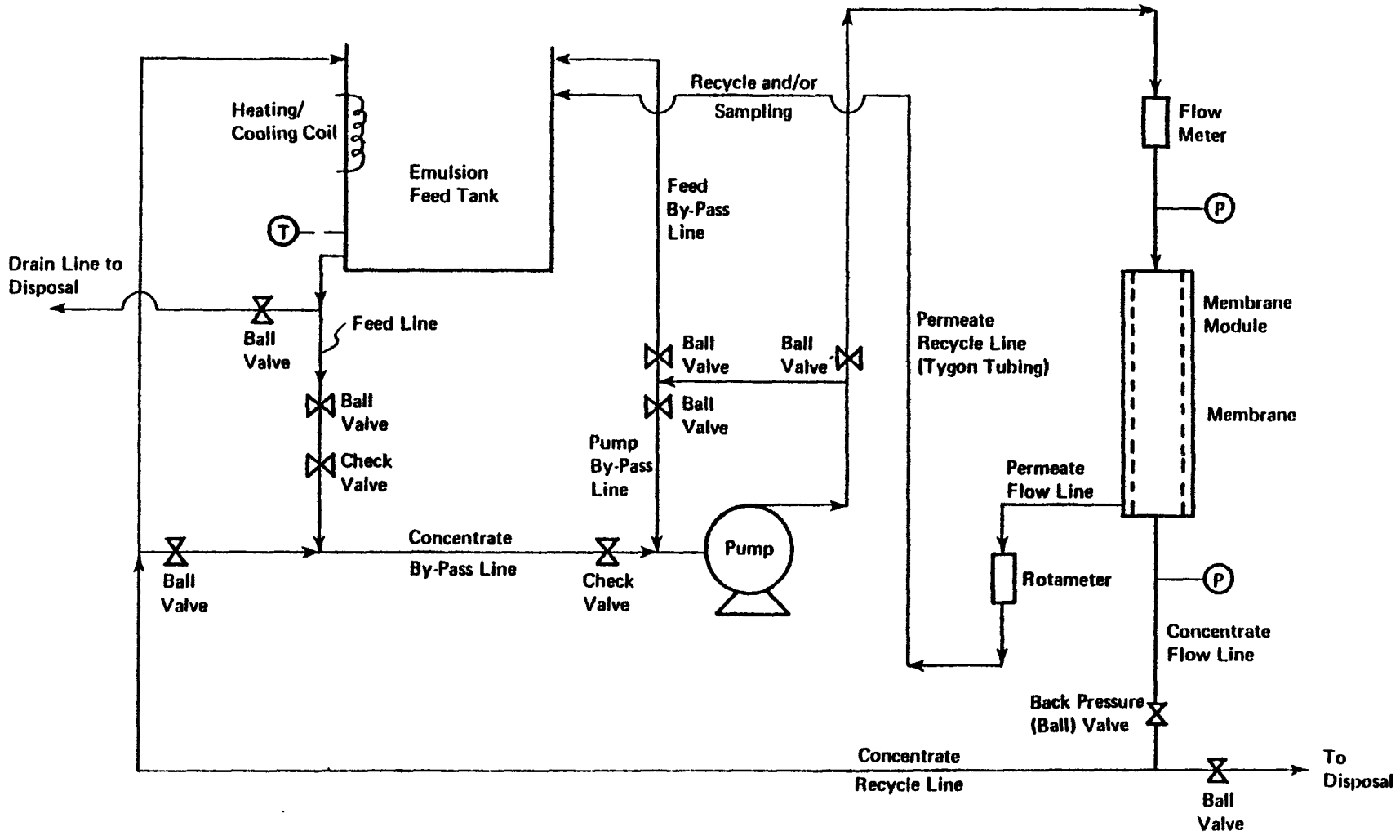


Figure 3–16. Abcor and Union Carbide ultrafiltration membrane testing system.

ball valve used to control back pressure on the membrane also has an effect on the concentrate flow rate. Fluid can be recirculated around the pump and/or returned to the feed tank for mixing without passing through the membrane. The emulsion can also be passed simultaneously through the membrane and through the recycle loop back to the feed tank. Permeate from the membrane is sent to a holding tank (transient operation) or recycled to the feed tank (constant water-to-oil ratio operation). Concentrate from the membrane can be recycled to the pump or to the feed tank.

Instrumentation on the system consists of a thermometer fitted into the feed tank, pressure gauges before and after the ultrafiltration membrane, a flowmeter upstream of the membrane to monitor volumetric flow rate, and a rotameter for measuring permeate flow rate. Permeate samples may be taken at the end of the permeate line. Concentrate samples can be taken from either the feed tank or from the feed tank drain. Instruments are bronze except for the permeate rotameter, which is glass.

All flow lines except the permeate flow lines are 1-inch diameter schedule 80 PVC piping. The permeate flow line is Tygon tubing. All valves and fittings are also made of PVC. In the temperature and pressure range expected (<150° F and <60 psig), PVC is a suitable and inexpensive material for handling oil or brine.

The centrifugal pump is sized to deliver 20 gallons per minute at approximately 50 psig. A 3-horsepower motor is required to meet these specifications. The pump internals are bronze. A ball valve and/or the pump bypass loop can be used to throttle back on the delivered flow and pressure. A centrifugal pump was chosen to avoid the stroking action of a piston pump, which might damage some ultrafiltration membranes.

The feed material is well emulsified by using the shearing action of the pump and by circulating the oil-brine fluid through the pump and directly back to the feed tank, which is made of polypropylene. The feed tank is fitted with a copper tubing coil that can be connected to a water line for heating or cooling of the emulsion.

The Rev-O-Pak pilot plant is designed and fabricated by the membrane manufacturer and is specifically made to accept all Rev-O-Pak ultrafiltration and reverse osmosis membranes. These are inserted in pressure tubes connected in series by headers. The unit purchased had eight pressure tubes; however, only the first two tubes in series were used for

data taking purposes because of the accumulative pressure drop through the tubes in series. A schematic is shown as Figure 3-17.

Emulsion from a 30-gallon polypropylene feed tank is passed through a reciprocating pump to the pressure tubes containing the membranes. Emulsion concentrate leaving the membrane tubes is recycled back to the feed tank. Pressure gauges are located before and after the membrane tubes. Operating pressure is controlled by a needle valve downstream of the membrane tubes and with an accumulator located just downstream of the pump. Since a reciprocating pump is used, emulsion concentrate flow rate is approximately equal at all operating pressures.

The temperature of the emulsion feed is controlled by a copper cooling coil inserted into the feed tank. Water from a constant-temperature bath is circulated through the coil to maintain a constant temperature. Temperature in the tank is monitored by a thermometer.

Permeate from the membranes is collected from the permeate taps and transfers to a collection bucket. The contents of the bucket are periodically returned to the feed tank for operation at a constant water-to-oil ratio. To operate the unit at a decreasing water-to-oil ratio, the permeate is stored and not returned to the feed tank.

The characteristics of the ultrafiltration membranes tested are shown in Table 3-7. Three different membrane configurations were examined, all standard commercial configurations. Both the Abcor (Figure 3-7) and Union Carbide (Figure 3-18) membranes are tubular, with the membrane supported on the inner surface of the tube. The concentrate passes through the inner annulus. Permeate fluxes across the membrane and is recovered from the outer annulus. However, major differences exist between the Abcor and Union Carbide membranes. The Abcor membrane uses a 1-inch i.d. tube and is made from cellulose acetate. The Union Carbide tube has an inside diameter of approximately one-quarter inch and is made of carbon and zirconium oxide, which gives it a higher temperature and greater pH range than the Abcor or Rev-O-Pak membranes.

Both Rev-O-Pak membranes tested had the same configuration. These membranes also use a tubular configuration, but the membrane is located outside the support. In this configuration the emulsion concentrate passes through the outer annulus of the tube as shown in Figure 3-19. Permeate is fluxed through the membrane and is collected in the inner

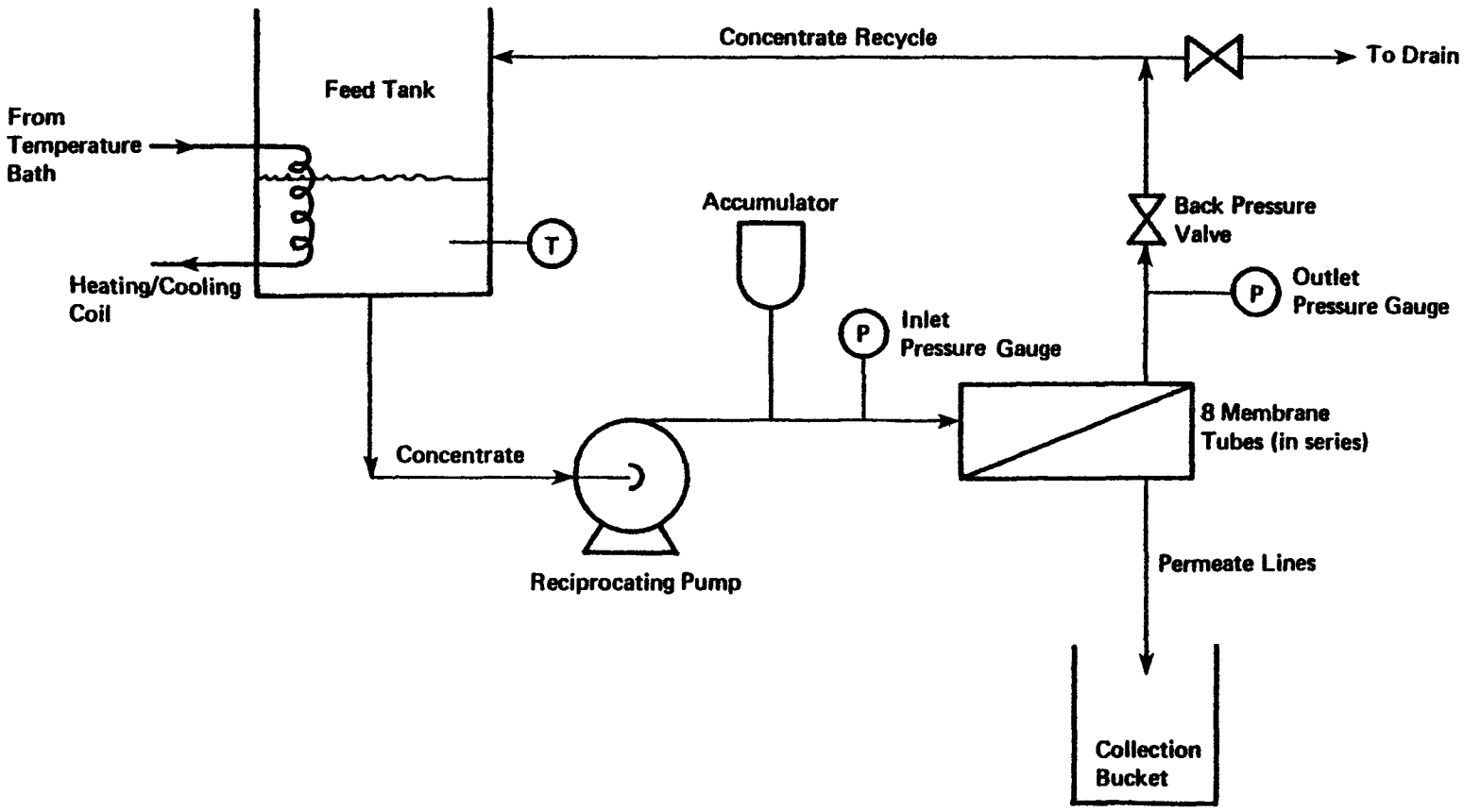


Figure 3–17. Schematic of Rev-O-Pak Pilot Plant.

TABLE 3–7

COMPARISON OF ULTRAFILTRATION MEMBRANES TESTED

	ABCOR	UNION CARBIDE	REV-O-PAK 120	REV-O-PAK 150
Membrane material	Cellulose Acetate	Carbon + Zirconium Oxide	Cellulose Acetate	Cellulose Acetate
Module membrane area	2.2 ft^2	∿0.15 ft^2*	0.5 ft^2	0.5 ft^2
Module flow diameter	1"	1/4"	∿1/2"	∿1/2"
Relative membrane tightness	4	3	2	1
Maximum temperature	120° F	200° F	108° F	108° F
pH range	2–11	1–14	2.5–7.5	2.5–7.5
Maximum pressure	60 psig	125 psig	500 psig**	500 psig**
Suggested superficial velocity	12 ft/sec	13–20 ft/sec	6.5 ft/sec	6.5 ft/sec
Relative concentrate pressure drop	2	1	3	3

* Shortened by 22% since receiving.
** At 77° F, approximately 150 psig at 108° F.

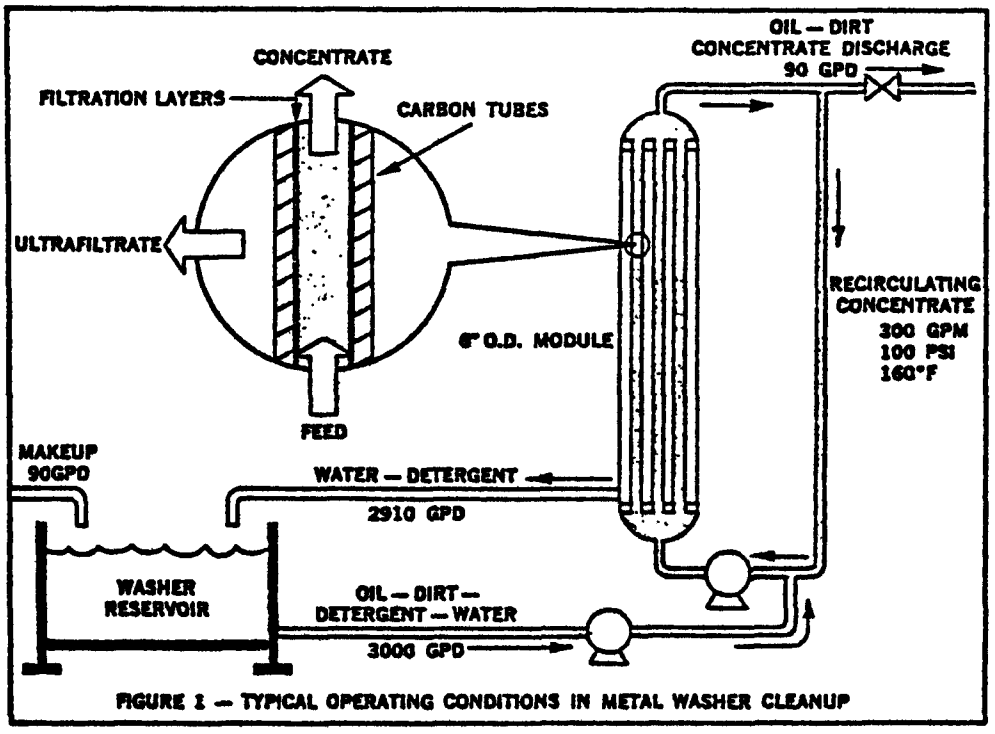


Figure 3—18. Typical operating conditions in metal washer cleanup. Source: Union Carbide sales literature.

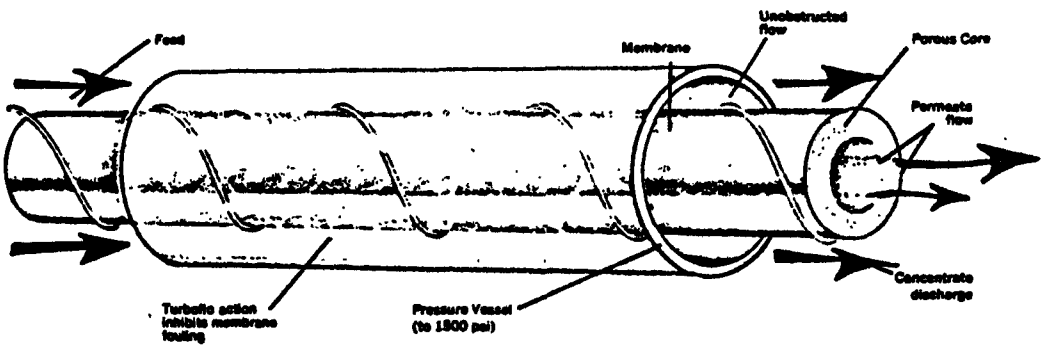


Figure 3—19. Rev-O-Pak membrane. Source: Rev-O-Pak sales literature.

annulus. The Rev-O-Pak system with the membrane on the outside of the support with the addition of patented devices for controlling and creating a turbulent flow pattern is claimed to reduce fouling and allow a higher oil concentration buildup in the concentrate.

3.4.3.5 Experiment Results and Evaluation

Typical flux rates at ordinary operating conditions for the membranes with the base case emulsions are shown in Table 3-8. Higher flux rates should be expected for the Abcor and Union Carbide membranes, since they have larger membrane pore openings.

Note that the low pressure pilot plant uses a centrifugal pump which allows a wide range of flow rates and delivery pressures; hence flow rate and inlet pressure to the membrane are not independent. Flux data as a function solely of concentrate flow rate or concentrate inlet pressure can be misleading. In Figure 3-20, the permeate flux rate as a function of concentrate flow rate is shown for similar inlet conditions with three different emulsions for the Union Carbide membrane. While the data tend to indicate that flux drops as the concentrate flow rate increases, it must be remembered that as the concentrate flow rate increases, the concentrate pressure loss through the membrane (which has a 1/4 inch flow passage) increases dramatically. Therefore, the average pressure drop across the membrane actually decreases as the concentrate flow rate increases. This is demonstrated in Table 3-9. From the table, it can be deduced that as the average concentrate pressure (of inlet and outlet conditions) increases, the flux rate across the membrane increases as expected.

A different phenomena occurs with the Abcor membrane. Since the Abcor membrane has a 1-inch concentrate flow passage, the pressure drop of the concentrate through the membrane is only on the order to 2 to 4 psig. As recommended by the manufacturer, higher concentrate flow rates tend to increase the flux by increasing permeate transport to the membrane surface and concentrate transport away from the membrane surface. For the El Dorado and North Burbank base case emulsions a linear relationship as shown in Figure 3-21 appears to exist. However, for the Bell Creek and Bradford emulsions an optimum concentrate flow rate appears to exist. Since concentrate flow rate and inlet pressure are not independent in the pilot plant, the observed maximum might not be entirely dependent on concentrate flow rate. The other pertinent variables in the data presented in Figure 3-21 are shown in Table 3-10.

TABLE 3–8

TYPICAL FLUX RATES FOR THE MEMBRANES
(gal/day/ft^2)

	PRESSURE* (psig)	NORTH BURBANK BASE CASE EMULSION**	EL DORADO BASE CASE EMULSION†	BELL CREEK BASE CASE EMULSION†	BRADFORD BASE CASE EMULSION †
Abcor	30	30.2	28.0	25.9	28.5
Union Carbide	30	25.4	24.1	24.2	–
Rev-O-Pak 120	60 – 200	10.9 – 14.6	8.1 – 10.2	9.1††	7.4 – 13.1
Rev-O-Pak 150	60 – 200	7.3 – 11.6	5.9 – 9.4	8.1††	5.9 – 11.0

* Because of the differences in membrane configurations and test equipment, not all membranes could or should be operated at the same pressure.

** Water-to-oil ratio of 3.

† Water-to-oil ratio of 4.

†† 200 psig only.

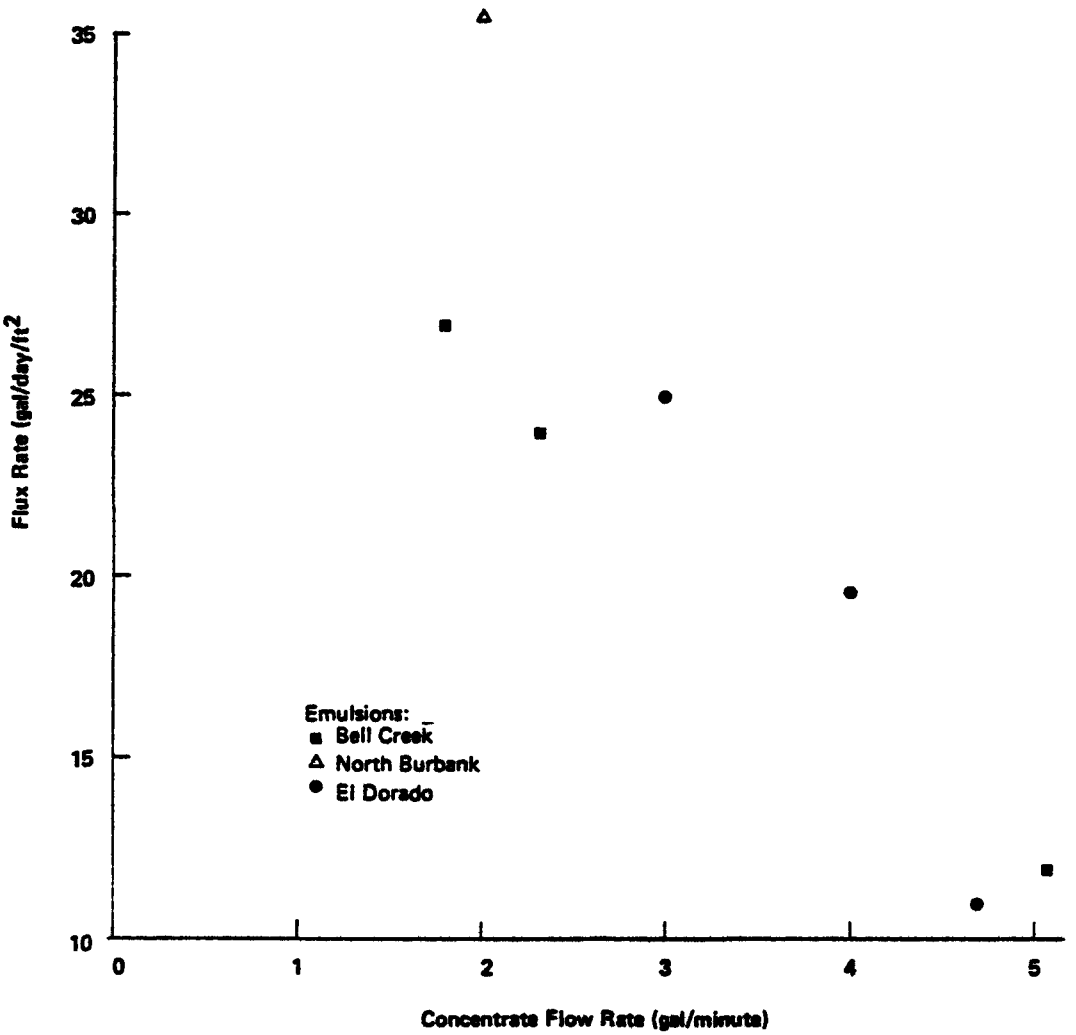


Figure 3–20. Permeate rate versus concentrate flow rate for Union Carbide membrane.

TABLE 3–9

VARIATION OF PRESSURE AND CONCENTRATE FLOW FOR UNION CARBIDE MEMBRANE

EMULSION	CONCENTRATE FLOW (gpm)	TEMPERATURE (°F)	INLET PRESSURE (psig)	OUTLET PRESSURE (psig)	FLUX RATE (gfd)
North Burbank	3.0	98	55	40	25.0
North Burbank	4.0	98	53	27	19.6
North Burbank	4.7	96	51	16	11.0
Bell Creek	1.8	100	56	50	27.0
Bell Creek	2.3	100	55	45	24.0
Bell Creek	5.1	100	50	10	12.2
El Dorado	2.0	94	50	35	35.7

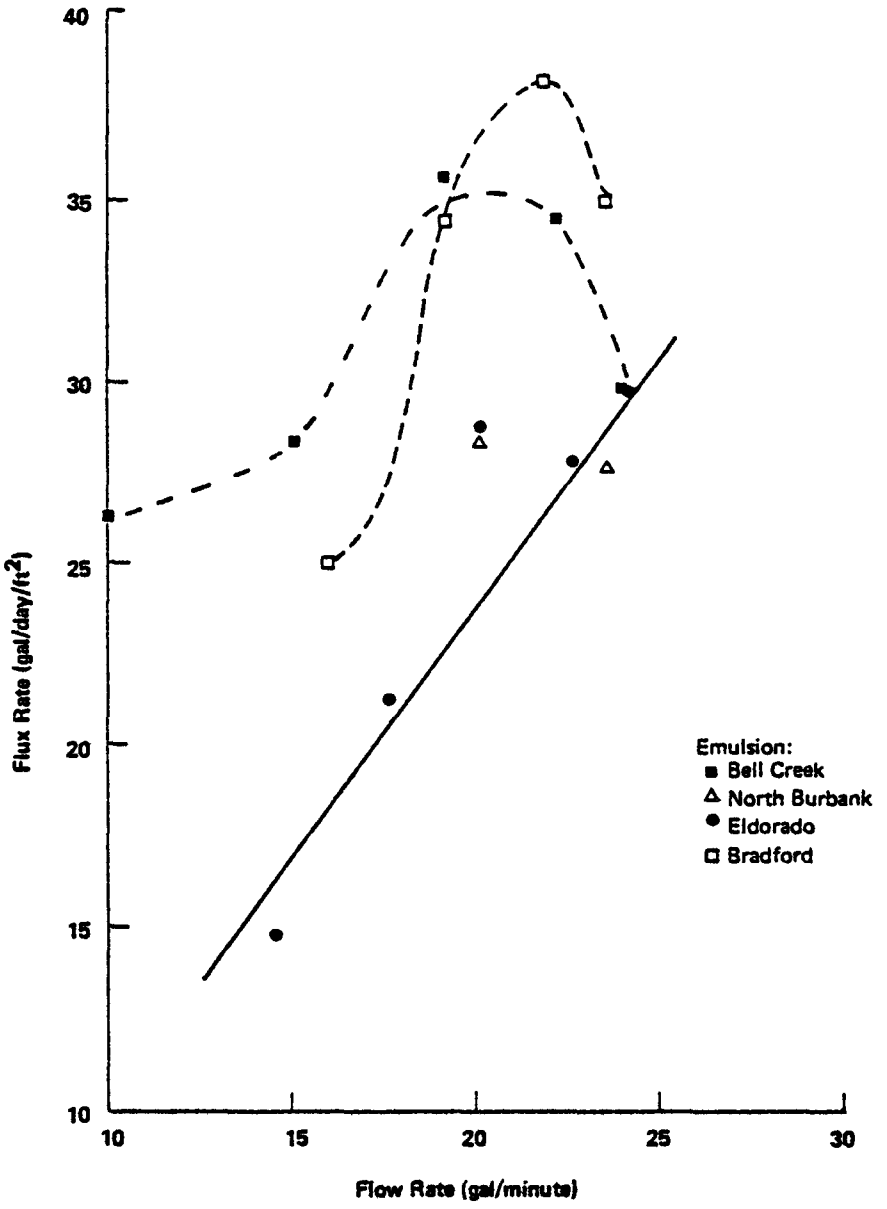


Figure 3–21. Permeate rate versus concentrate flow rate for Abcor membrane.

TABLE 3–10

VARIATION OF PRESSURE AND CONCENTRATE FLOW FOR ABCOR MEMBRANE

EMULSION	CONCENTRATE FLOW (gpm)	TEMPERATURE (°F)	INLET PRESSURE (psig)	FLUX (gfd)
North Burbank	23.5	95	22	27.7
North Burbank	20.0	95	32	28.5
El Dorado	24.0	94	20	29.8
El Dorado	22.5	94	30	27.9
El Dorado	20.0	96	35	28.8
El Dorado	17.5	102	40	21.3
El Dorado	14.5	102	45	14.8
Bell Creek	24.0	92	25	29.8
Bell Creek	22.0	92	30	34.6
Bell Creek	19.0	88	37	35.8
Bell Creek	15.0	92	44	28.3
Bell Creek	10.0	92	50	26.3
Bradford	23.5	92	25	35.2
Bradford	21.7	94	30	38.5
Bradford	19.3	92	35	34.2
Bradford	16.0	92	40	25.0

For all of the membranes tested flux rates were expected to improve with increasing temperature. (The cellulose acetate membranes [Rev-O-Pak and Abcor] have fairly low maximum temperature levels, above which the membrane begins to deteriorate.) This trend was confirmed and is shown in Figure 3-22 for the Union Carbide and Rev-O-Pak 120 membranes and Figure 3-23 for the Abcor membrane. All other operating conditions were held constant. The effect of operating temperature for the Rev-O-Pak membranes is much more pronounced during the long-term run described below.

The pilot plant for the Rev-O-Pak membranes has a positive displacement pump and, therefore, a fixed flow rate; operating pressure is then an independent variable. The effect of operating pressure on flux rate for the Rev-O-Pak membranes and three different emulsions is shown in Figure 3-24.[17]

The standard procedure for the long duration runs was initial startup in the morning followed by shutdown at the end of the working day until sufficient operating time has been accumulated. Since flux rates for the different emulsions did not seem significantly different for a particular membrane no matching or optimization of base case brines and membranes was made. The long-term run for the Union Carbide membrane using the Bell Creek base case emulsion is shown as Figure 3-25 along with the operating conditions used. No indication of fouling occurred during the duration of the run. However, there is a clear trend of increasing flux rates with duration of operation. This increase cannot be ascribed to the flow conditions such as temperature, since these were held constant during the run. The long-term run with the Abcor membrane using the Bradford emulsion is shown in Figure 3-26. Some reduction in flux rate with time occurred.

The long-term runs for the Rev-O-Pak membranes are shown in Figures 3-27 and 3-28. Here the increase in flux rates with duration of operation are probably due to temperature increase during the run since the initial startup temperature was usually about 25° to 26° C and reached approximately 36° C during the course of the day. Again, no indication of fouling was shown when the oil/water ratio was held constant.

The effects of oil content on the flux rate of the Union Carbide membrane are shown in Figure 3-29. A dramatic decrease in flux rate occurs at a water/oil ratio of about 3 to 2.5 (oil concentration of 25 to 28.5 percent oil). It was initially thought that this might be due to the duration

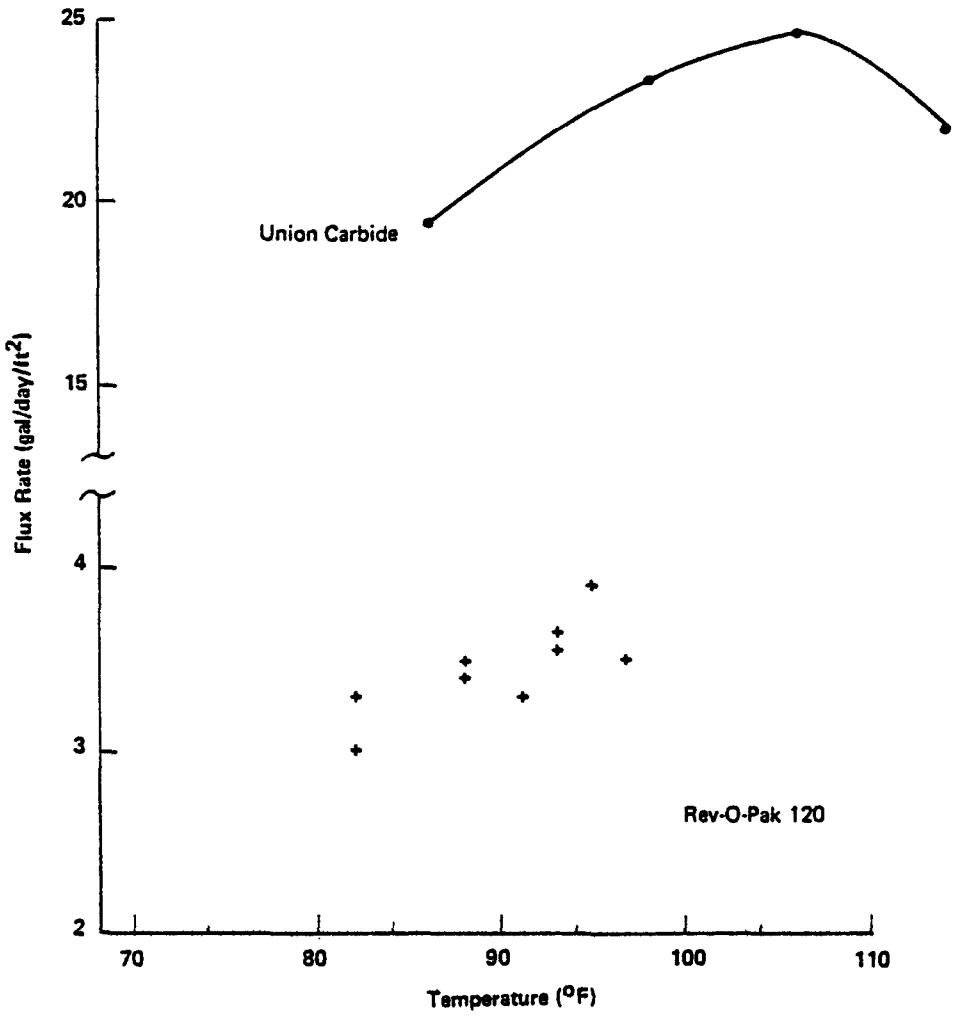


Figure 3–22. Membrane flux rate versus temperature (El Dorado emulsion).

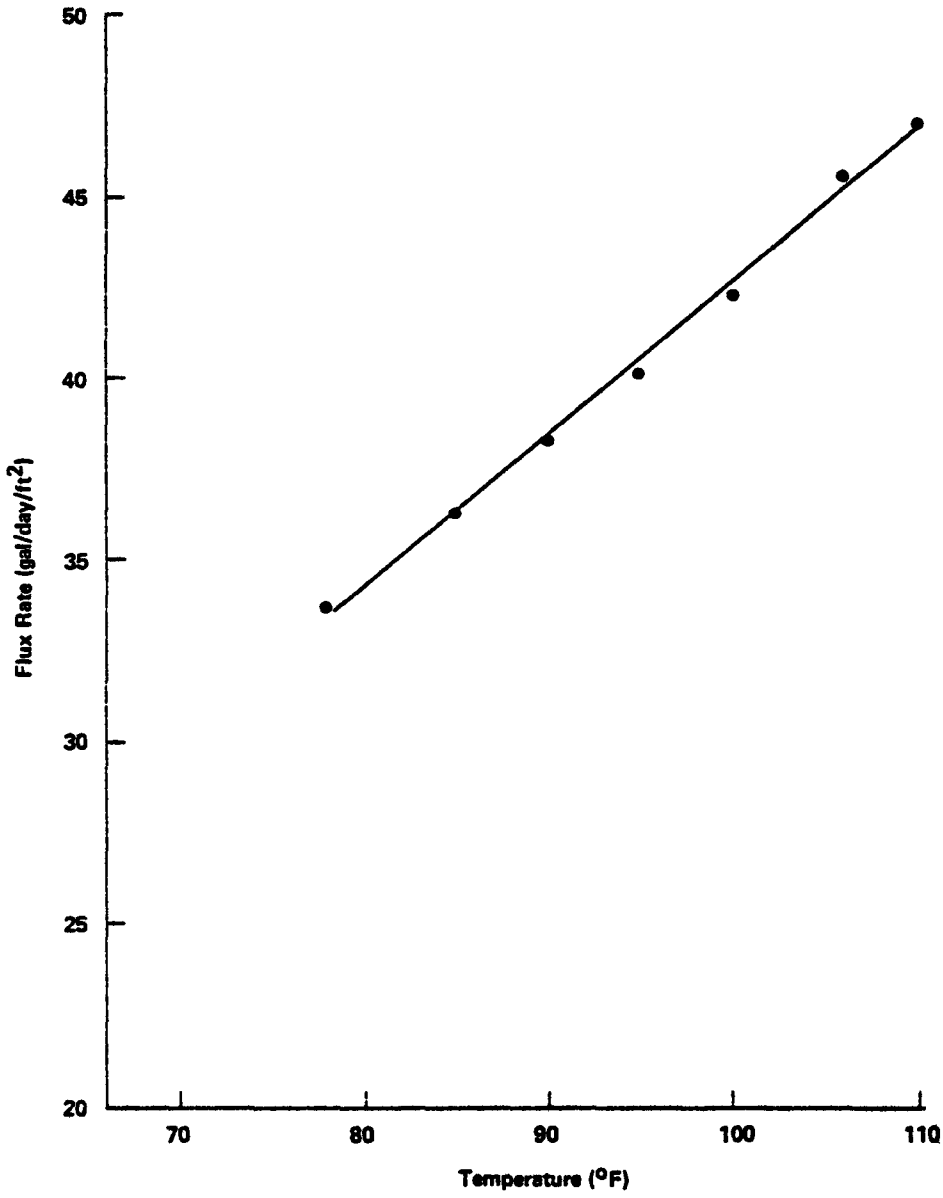


Figure 3–23. Abcor membrane flux rate versus temperature (Bradford emulsion).

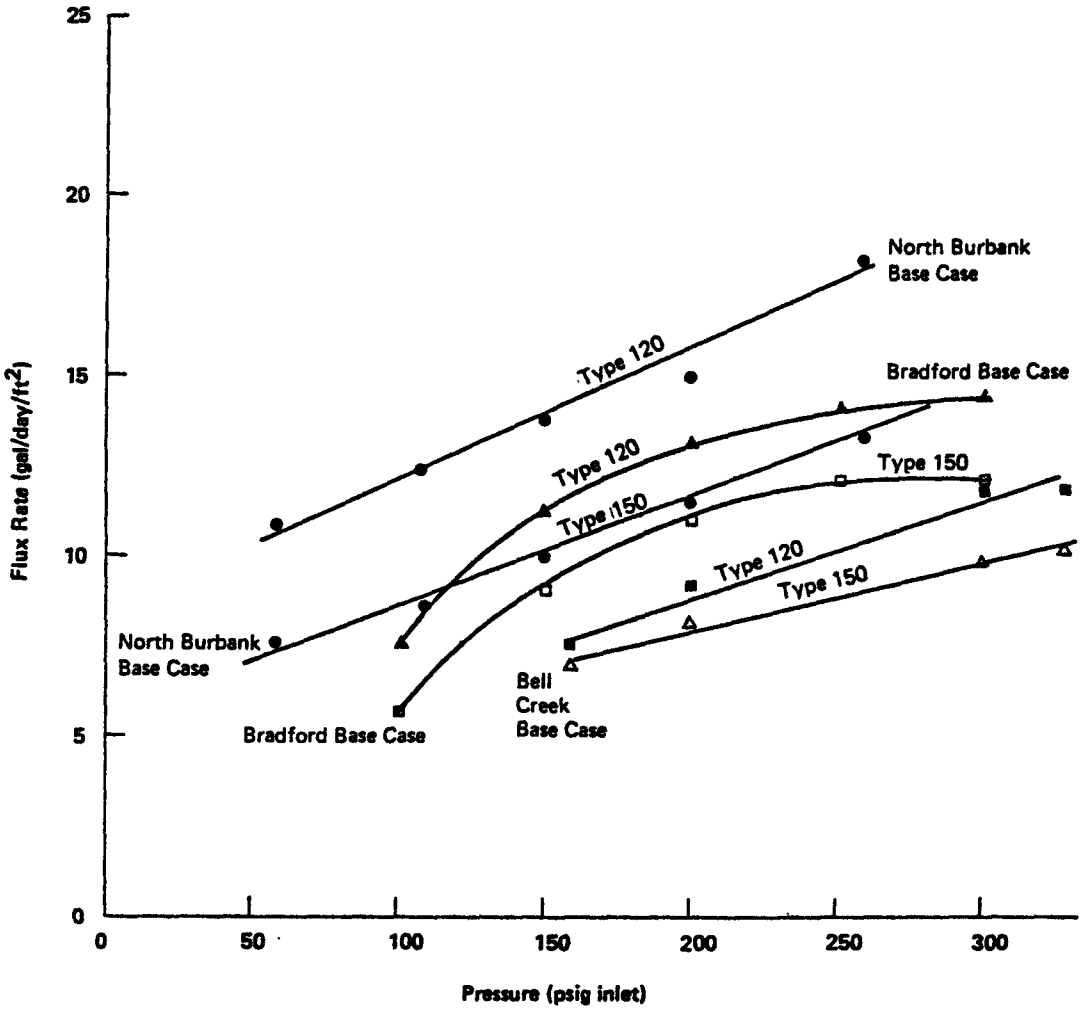


Figure 3–24. Permeate rates versus pressure for Rev-O-Pak membranes (constant flow rate).

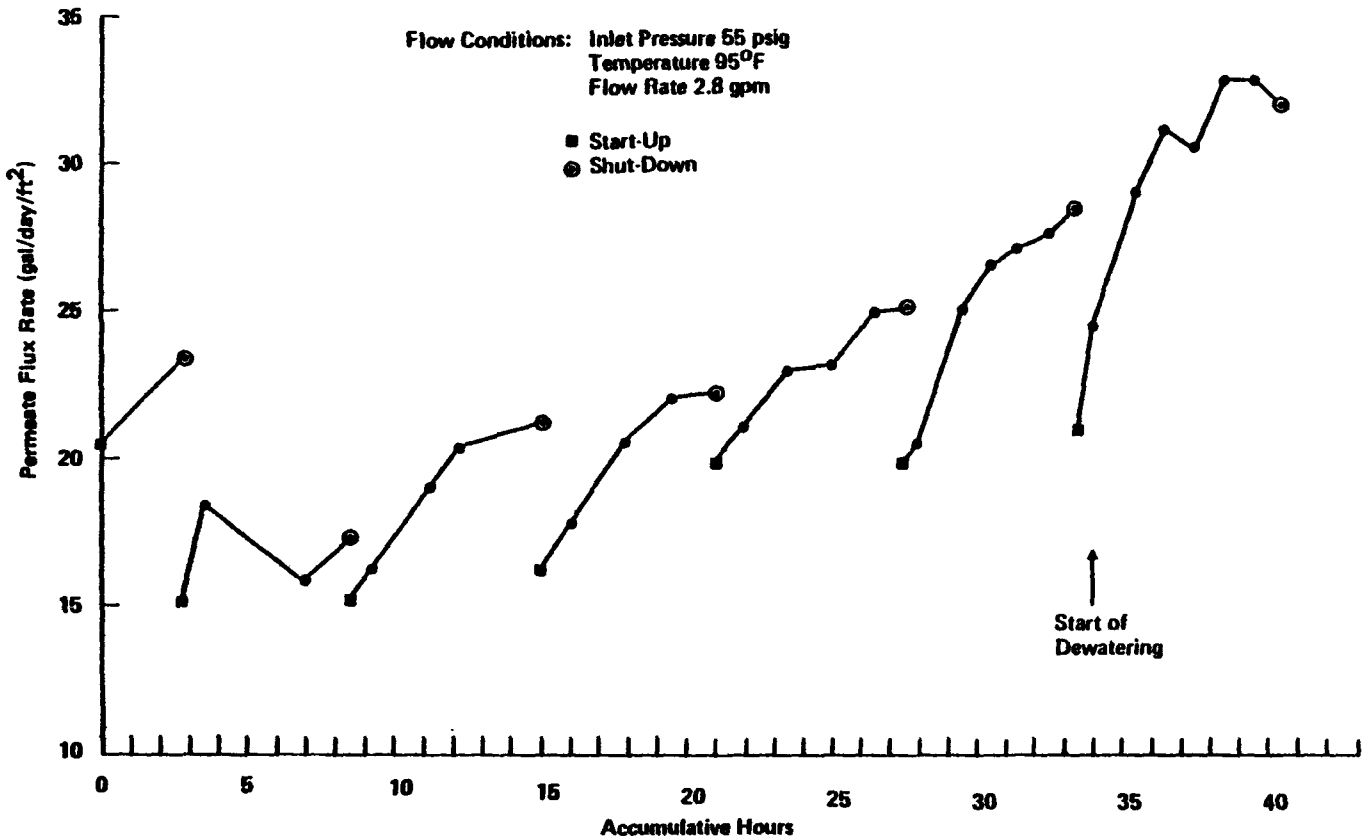


Figure 3–25. Long duration run for Union Carbide membrane (Bell Creek emulsion). Membrane in previous service for 15 hours with other emulsions.

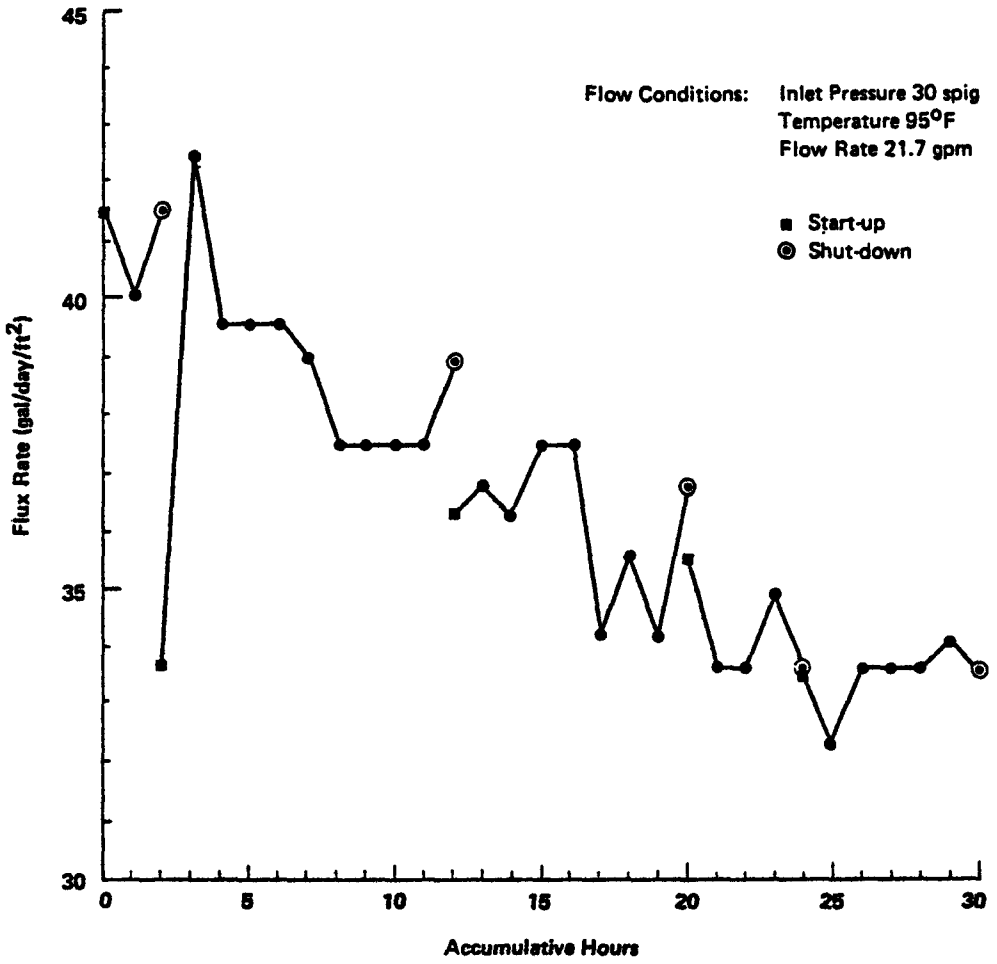


Figure 3–26. Long duration run for Abcor membrane (Bradford emulsion).

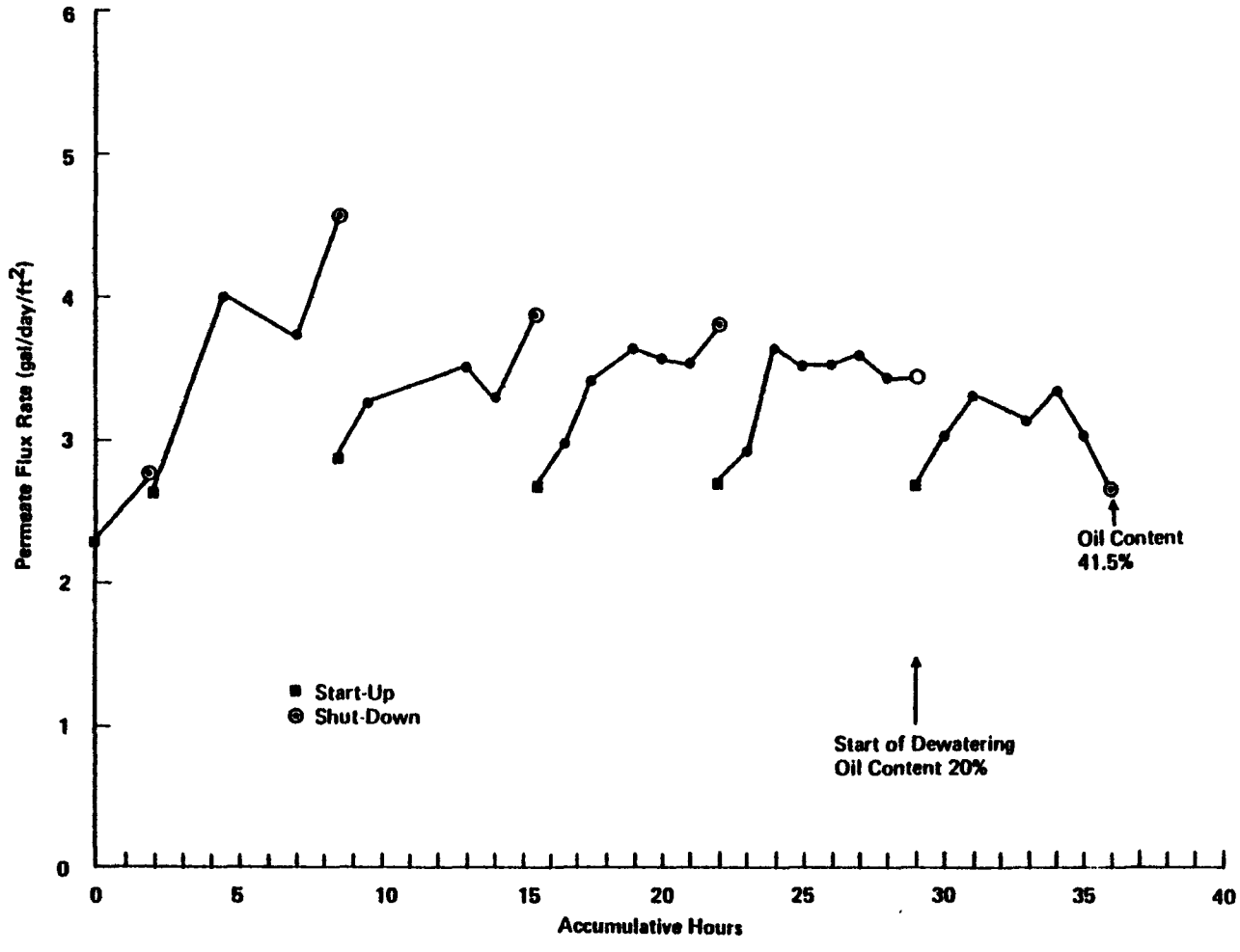


Figure 3–27. Long duration run for Rev-O-Pak 120 membrane (El Dorado emulsion).

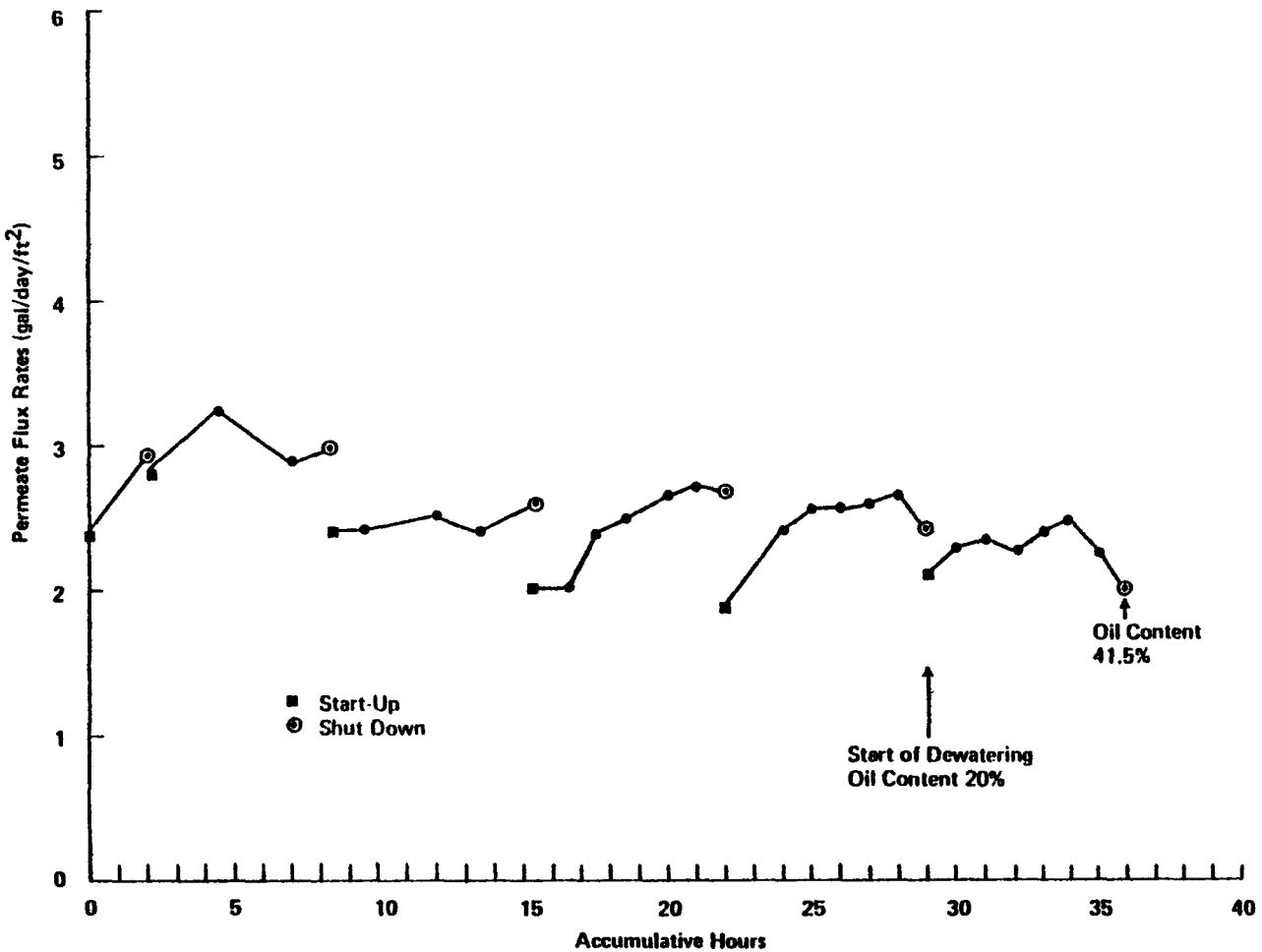


Figure 3–28. Long duration run for Rev-O-Pak 150 membrane (El Dorado emulsion).

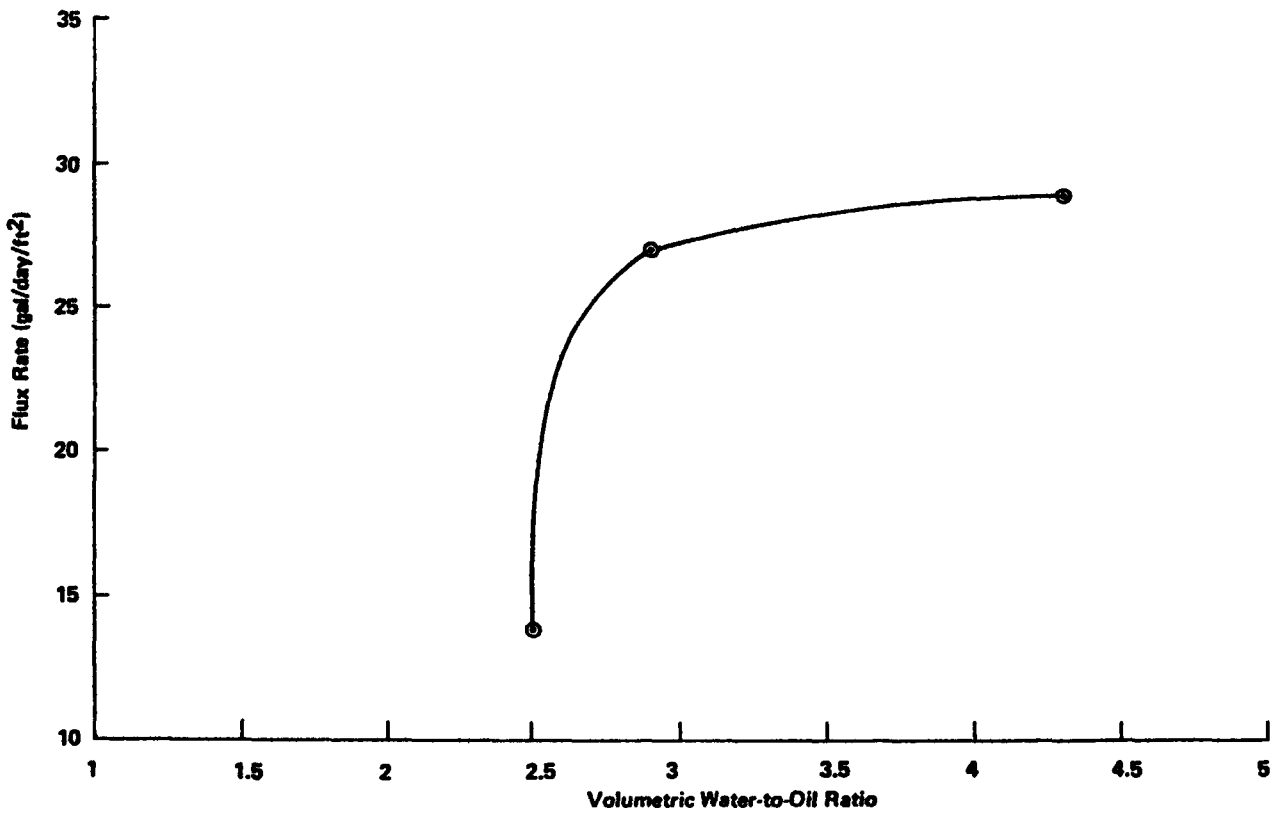


Figure 3–29. Typical membrane flux rate for Union Carbide membrane as a function of concentrate oil content (Bell Creek emulsion).

of use of the membrane. However, a discussion with a Union Carbide technical representative after the fact suggests that an oil content in the range of 25 to 30 percent is the actual operating limit of the Union Carbide membrane. This fact tends to make the Union Carbide membrane unsuitable for substantial dewatering oilfield emulsions.

The effects of oil content on the flux rate of the Abcor membrane are shown in Figure 3-30. Again, a dramatic decrease in flux rate occurs at a water-to-oil ratio of 3 to 2.5. Discussion with the manufacturer confirms this trend. The Abcor membrane would also be unsuitable for substantial dewatering applications.

The effect of oil concentration on the permeate flux rates for the Rev-O-Pak membranes is shown in Figure 3-31. Oil content of the emulsion could be increased from 20 percent to near 60 percent with only about a 40 percent drop in flux rate. This tends to confirm the manufacturers claim that this membrane configuration allows processing of high oil content streams. At water-to-oil ratios below 1, the effect of oil concentration of flux rate is quite noticeable. During all stages of the dewatering of the El Dorado base emulsion with the Rev-O-Pak membranes the emulsion concentrate remained water continuous. Up to about a 30 percent oil concentration, the oil-in-water emulsion could be easily broken by adding calcium chloride as a demulsifying agent. The calcium chloride first inverted the emulsion which could then easily be separated by gravity. The separated oil phase contained about 20 percent water based on the material balance.

At oil concentrations in the emulsion of greater than 30 percent the calcium chloride could invert the emulsion but did not produce a clean separation between water and oil. Calcium chloride addition produced an oil phase, a water phase, and an intermediate oil-in-water emulsion phase that had the consistency of a gel. Addition of tertiary amyl alcohol instead of calcium chloride produced a clean aqueous phase and a water-in-oil emulsion from the concentrated oil-in-water emulsion. Thus it seems that proper selection of chemical addition will allow inversion of the dewatered emulsion and subsequent conventional heater treatment.

As shown in Figure 3-31, the Rev-O-Pak membranes were able to reduce the volume of the emulsion to be treated by 67 percent with little loss in permeate flux rate. However, the Rev-O-Pak membranes used in this program had much lower permeate flux rates than the Abcor or Union Carbide membranes

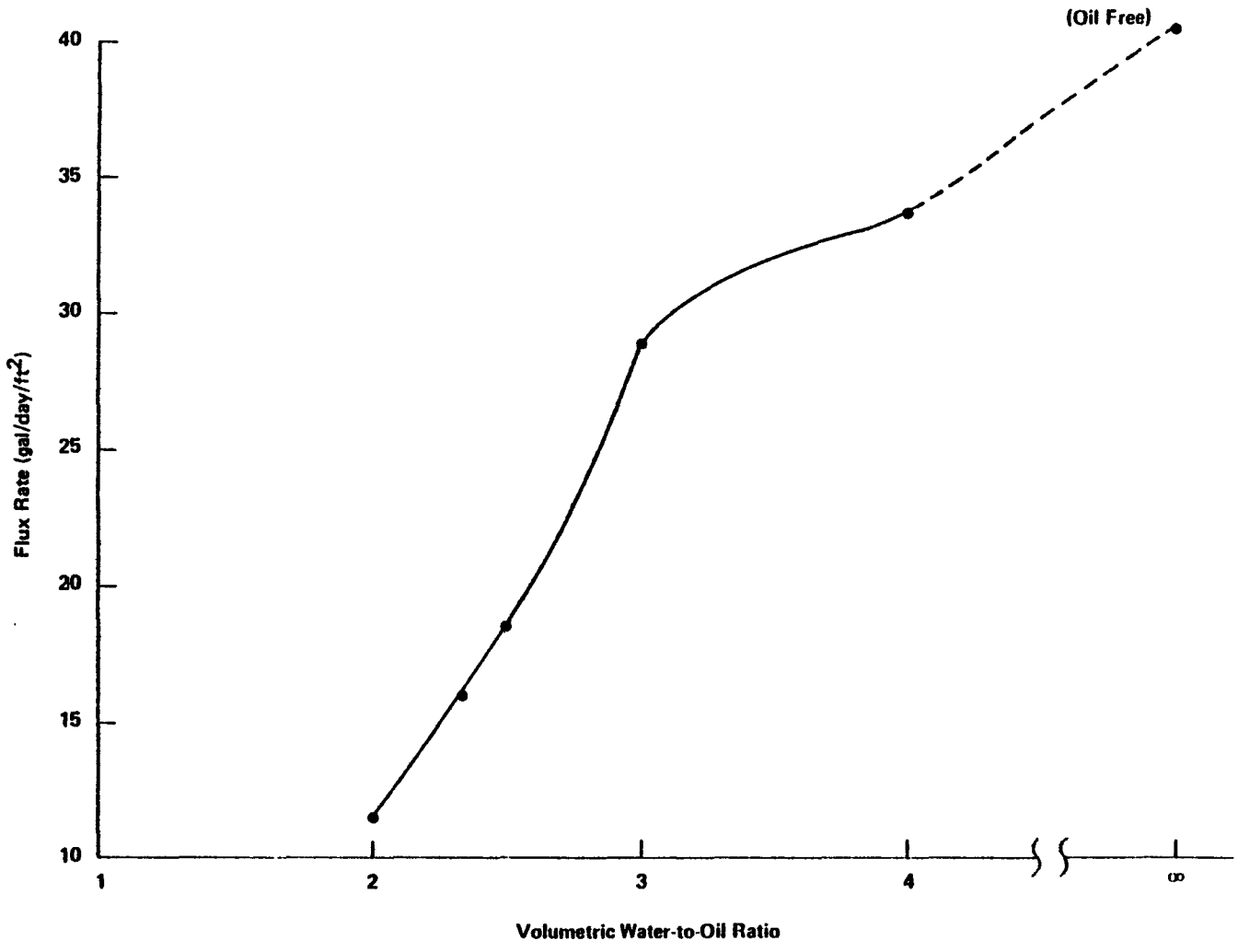


Figure 3–30. Typical membrane flux rate for Abcor membrane as a function of concentrate oil content (Bradford emulsion).

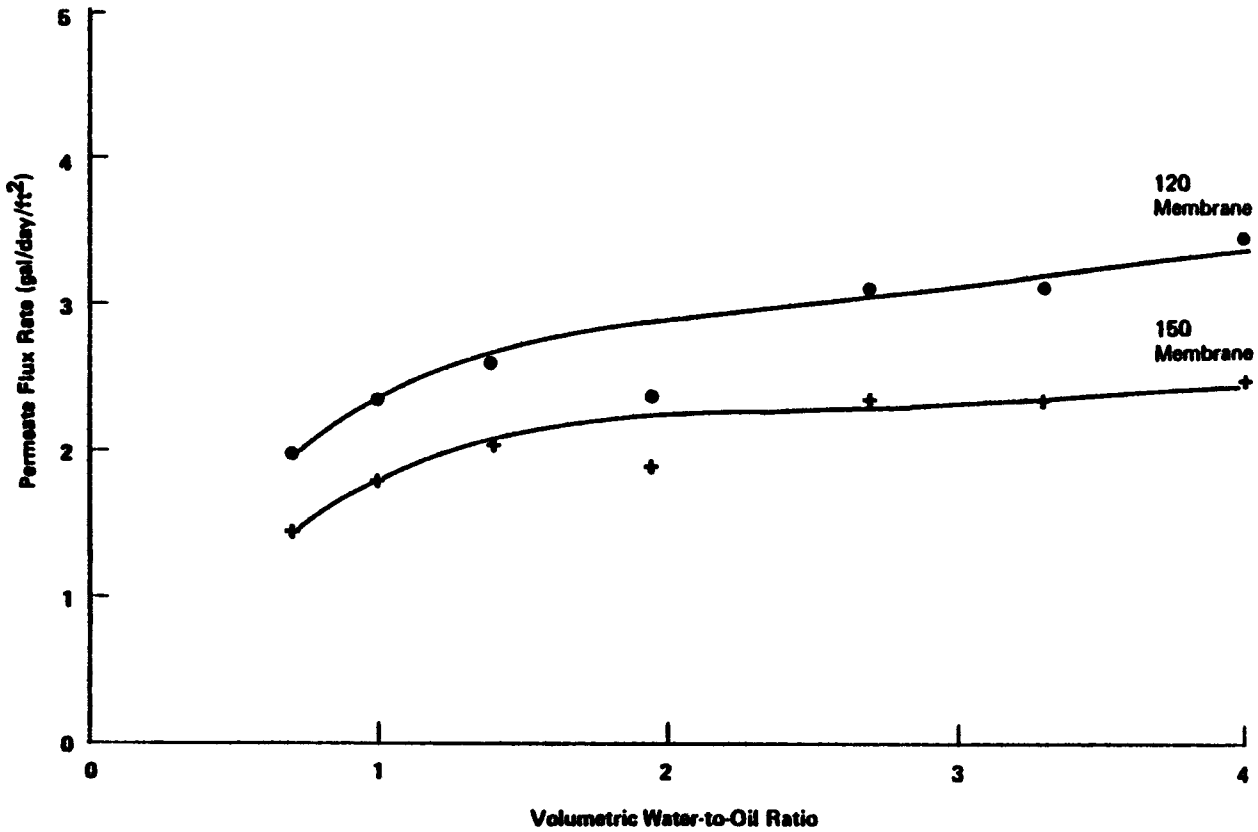


Figure 3–31. Flux rate for Rev-O-Pak membranes as a function of concentrate oil content (El Dorado emulsion).

at equal pressure driving forces. While a Rev-O-Pak membrane system could be used alone to dewater an emulsion, combination of a higher flux membrane, such as an Abcor or Union Carbide or looser Rev-O-Pak membrane, to dewater an emulsion up to an oil content of perhaps 25 to 30 percent followed by the tested Rev-O-Pak membrane to dewater the emulsion to the economic break point with conventional demulsification would be beneficial. The switch over from the high flux membrane to the Rev-O-Pak membrane would be at an oil content at which the flux rates are approximately equal although some allowance has to be given to the fact that the Rev-O-Pak membrane operates at higher pressure. If possible, wellhead pressure should be used to provide the pressure driving force for dewatering. If a high wellhead pressure is available only a Rev-O-Pak membrane might be used. However, this would disallow the use of higher flux Abcor and Union Carbide membranes. The upper pressure limit of the Abcor membrane is approximately 50 or 60 psig. The upper pressure limit of the Union Carbide membrane is nominally 125 psig but could be used in some applications up to 200 psig if care is taken with mounting the membrane in the treatment module.[18]

The use of ultrafiltration membranes to reduce the volume of an emulsion to be treated via dewatering should translate directly into a savings in the amount of chemicals required for inverting the emulsion prior to conventional treatment that is proportional to the amount of water removed. This is further discussed in the next section.

3.5 Economic Assessment

The cost of an ultrafiltration dewatering system is dependent upon the flux rate that can be achieved with a specific membrane and on the total amount of fluid that must be passed through the membrane. Current oilfield emulsions contain as much as 40 percent water, but the total amount of produced fluids requiring emulsion treating is on the same order as the amount of oil produced. In the case of O/W emulsions, however, stable emulsions could be formed with WOR as great as 10. The chemicals required to break this type of emulsion are more expensive than chemicals currently used; and, since the amount of stable emulsion per barrel of emulsified oil is 10 times as great as conventional oilfield systems, as much as 10 times the chemicals and processing volume will be required for EOR projects.

The basis for economic comparisons is shown in Table 3-11. Actual cost for this type of technology must be determined

TABLE 3-11

COST BASIS FOR EMULSION DEWATERING

	WOR OF EMULSION FOR FIELD EMULSIFIED OIL PRODUCTION OF 100 BPD			WOR OF EMULSION FOR FIELD EMULSIFIED OIL PRODUCTION OF 1,000 BPD			WOR OF EMULSION FOR FIELD EMULSIFIED OIL PRODUCTION OF 10,000 BPD		
	1	10	100	1	10	100	1	10	100
Water flux, BPD[a]	30	930	9,930	300	9,300	99,300	3,000	93,000	993,000
Water flux, gpm	1	27	290	9	270	2,900	87	2,700	29,000
Membrane area, ft^2									
@ 50 gpd/ft^2	25	780	8,300	250	7,800	83,000	2,500	78,000	830,000
@ 25 gpd/ft^2	50	1,560	16,600	500	15,600	166,000	5,000	156,000	1,660,000
Membrane cost, \$/ft^2	40	40	35	40	35	25	40	25	25

[a]Water Reduction to a WOR ratio of 0.7.

on a field-by-field basis dependent upon the WOR of the emulsified phase, the nature of the emulsion, and the relative cost of alternative technologies.

The total installed cost is shown in Table 3-12 based upon the numbers shown in Table 3-11.

The operating costs for the emulsion breaking system are shown in Table 3-13. The capital charges are based upon an amortization rate of 20 percent per year (typical of multi-national oil companies) over a period of 15 years. Note that even though a single flood project will last only 5 years from micellar slug injection to nearly completed production, most fields will be developed in stages allowing the equipment to be used over a much longer period than for a single flood pattern.

Routine maintenance is estimated at 5 percent of the installed cost for the facility. This estimate includes both labor and materials and is typical of most refinery type operations.

Since the estimated lifetime for membranes is approximately 3 years, the membrane replacement cost is one-third of the initial capital cost for the membrane module. Note that interest or inflation are not included in this estimate.

Power costs are estimated at $0.04 per kWh consumed at a rate of approximately 6 kwh per 1,000 gallons of processed fluid

The total annual costs are shown in the table along with unit costs in terms of dollars per barrel of brine treated and dollars per barrel of oil recovered. Keeping in mind that the costs of the membrane systems are primarily related to the flux of water through the membrane, the unit cost on a dollar per barrel of brine basis is roughly constant in the range from $0.10 to $0.16 per barrel of brine.

The unit cost in dollars per barrel of oil recovered ranges from a few cents per barrel at low initial WOR's to cost in excess of value of the oil for WOR's of 100. Note, however, that the same trend holds for alternatives to membrane treating of emulsions in that as the WOR increases the amount of chemicals and treatment facilities required will also increase.

The above analysis shows that the Energy Resources Co. technology is competetive with alternative methods for treating O/W emulsions. (For high WOR emulsions the emulsion treating is more of a pollution control measure than an oil

TABLE 3-12

CAPITAL COSTS FOR EMULSION BREAKING

	MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 1,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 10,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 100,000 BPD (gpd/ft^2)	
	25	50	25	50	25	50
Membrane modules, $1,000	68	34	588	294	4,200	2,100
Pumps and piping	20	20	100	100	500	500
System fabrication	40	30	200	150	1,000	750
Field installation	25	25	160	160	1,500	1,500
Total installed cost, $1,000	153	109	1,048	704	7,200	4,850

TABLE 3-13

ANNUAL OPERATING COSTS FOR EMULSION BREAKING

	MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 1,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 10,000 BPD (gpd/ft^2)		MEMBRANE FLUX RATE FOR TOTAL PRODUCED WATER FLUX OF 100,000 BPD (gpd/ft^2)	
	25	50	25	50	25	50
Annual operating cost, $1,000/yr						
Capital charges @ 20% over 15 yr	33	24	231	155	1,584	1,067
Routine maintenance @ 5% of cost	8	5	52	35	360	243
Membrane replacement (3-yr life)	23	12	196	98	1,400	700
Power @ $0.04/kWh	4	4	47	37	370	370
Total annual cost, $1,000/yr	68	45	516	325	3,714	2,380
Unit cost, $/bbl brine	0.19	0.12	0.14	0.09	0.10	0.07
Unit cost, $/bbl oil						
Initial WOR						
1	0.06	0.04	0.04	0.03	0.03	0.02
10	1.77	1.12	1.30	0.84	0.93	0.65
100	18.87	11.92	13.90	8.94	9.93	6.95

recovery operation and would not be attempted for purely economic reasons.) In addition, the Energy Resources Co. technology has several other important advantages over chemical inversion methods:

- Environmental - The ERCO technology minimizes the amount of chemicals that must be put into the emulsion in order to separate the water from oil. The water of course must be disposed of and with special chemicals may present an environmental hazard.

- Refinery operation - Some of the chemicals used for emulsion breaking may partition in the oil phase. These will be transmitted to the refinery and may have a significant impact on the refinery operation.

- Surfactant recovery - By using the membrane technology, a field planning on recovering surfactant (described in the next chapter) does not run the risk of damaging the surfactant or partitioning it in the oil phase by the addition of emulsion breaking chemicals.

One final conclusion, obvious from the data shown previously in Table 3-13, is that emulsions with water-oil ratios of 100 or better cannot be economically treated either by the membrane technology or using sophisticated chemical breaking techniques currently available. However, because the cost of the emulsion breaking is dependent upon the flux rate through the membrane, the development of an oleophilic membrane (one that passes oil rather than water) could potentially reduce the unit cost for emulsion treating to that of the unit cost for treating brine as shown in the table. Such a technology would not only eliminate the need for conventional emulsion breaking but would be competitive with conventional technology at water-oil ratios of 1 or more. In the author's opinion, stable O/W emulsions will become a more troublesome problem in the future with the advent of enhanced oil recovery techniques and hence the development of the oleophilic type membrane should be undertaken in the near future.

NOTES TO CHAPTER THREE

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14. J.L. Boyd, et al., "Treatment of Oily Wastewaters to Meet Regulatory Standards," Water 1971. AICHE Symposium Series No. 124, 1971, p.400.

15. Low molecular weight materials such as phenol that may be present in the oil will ordinarily pass through the membrane. The low molecular weight material which is considered to be hazardous such as phenol must be subsequently removed before the water may be discharged. A tighter membrane or reverse osmosis may be used to remove these contaminants.

16. R.L. Goldsmith, et al., "Ultrafiltration of Soluble Oil Wastes," WPCF Jr., 46(9) (September 1974):2183.

17. Note that between establishing the average flux rates for the El Dorado and North Burbank base case emulsions shown in Table 3-8 and taking subsequent data, the Rev-O-Pak membranes were broken during a pressure seal failure and had to be replaced. The replacement membranes showed consistent flux rates but the flux rates were lower than those determined in the initial testing.

18. Fred Morse, Union Carbide Corporation, Personal Communication, December 21, 1977.

CHAPTER FOUR

SURFACTANT RECOVERY

4.1 Introduction

At the present time the development of micellar/polymer flooding is limited primarily because of the perceived lack of economic incentives of this technology over other competing technologies. One of the problems is due to the high cost of surfactant, which at the present time cannot be recovered.

Energy Resources Co. has developed a technology based upon reverse osmosis for recovering surfactant which has both environmental and economic advantages.

4.1.1 Environmental Advantages

In a previous report to the Environmental Protection Agency,[1] Energy Resources Co. conducted an assessment of the environmental consequences of enhanced oil recovery, concluding that the present technology posed little threat to the environment but, in fact, the potential existed for the use of materials that could be toxic to the environment and which could potentially escape into groundwater resources through one of several possible mechanisms. In addition, chemicals such as surfactants have been shown to have an adverse impact on pollution control devices such as filter coalescers and hence could exhibit environmental impacts if such chemicals were eventually released to the wastewater stream of a petroleum refinery.

At the time that the environmental assessment was conducted, current practice was to design micellar slugs so that very little breakthrough of surfactant occurred. However, more recent reports with specific micellar projects have indicated the concentrations can be as high as 1 percent of the produced water.[2] Such surfactant concentrations are considerably higher than what was ever conceived of during the environmental assessment and could have major environmental implications if the produced fluids were to escape to the surrounding groundwater.

4.1.2 Economic Advantages

The ability to recovery surfactant implies two economic advantages:

- The use of more surfactants - The use of a greater quantity of surfactants than is normally practiced will result not only in an increased oil yield as a result of improved recovery efficiencies but also reduced adsorption of the surfactant on the reservoir rock. By introducing far more surfactant than is currently used in existing projects and at the same time recovering the surfactant in the produced fluids, the operator has the opportunity both to increase the project revenues (increased oil recovery) and also reduce his chemical cost (less chemical used due to reduced adsorption and also recycling of surfactant).

- Use of exotic chemicals - At the present time petroleum sulfonates are used as surfactants, one reason being their low cost. The use of more expensive chemicals often makes a given micellar/polymer project appear to be economically unattractive. However, with the ability to recover surfactants, the oilfield operator is given the opportunity to use much more exotic and, hence, much more efficient surfactants than can be currently justified.

4.2 Role of the Surfactant

The primary function of the surfactant system in micellar flooding is to achieve sufficiently low values of interfacial tension. In the case of immiscible flooding, in which adjacent oil and aqueous phases have a well-defined interface, the analysis is briefly as follows. The simplest model of an oil droplet trapped in a reservoir after water flooding is illustrated in Figure 4-1.[3] The drop is trapped at a pore constriction too small to permit further advance at the moderately high interfacial tensions, γ, experienced in water flooding. Essentially, the capillary pressures (Young-Laplace effect) across the two curved interfaces must be overcome in order to permit further advance. That is, an applied pressure difference in excess of:

$$\Delta P = P_{w2} - P_{w1} = 2\gamma(1/r_1 - 1/r_2)$$

will be required to exceed the capillary force retaining the drop.[4] A practical pressure gradient achievable in real

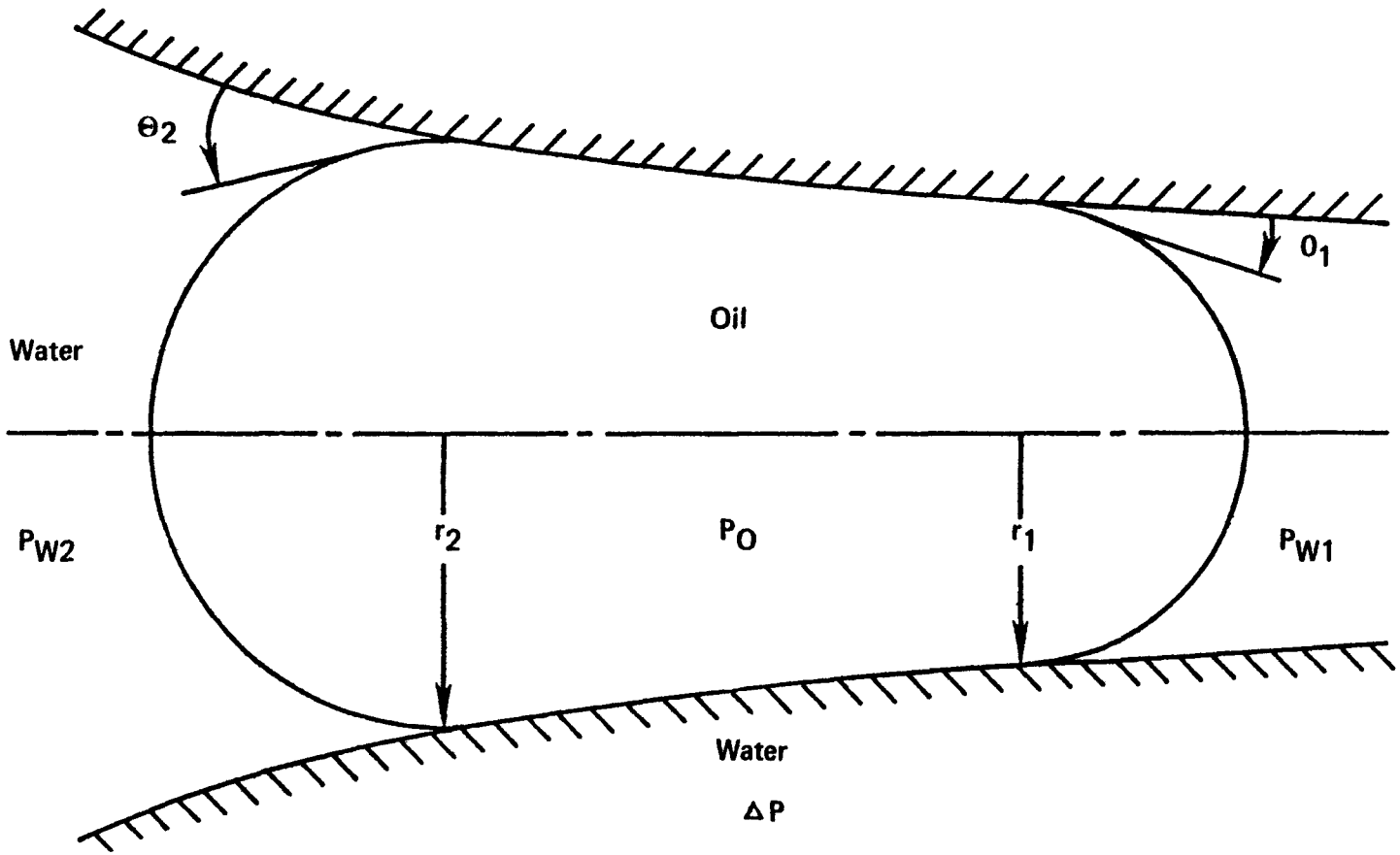

Figure 4—1. Model of an elementary oil ganglion trapped by capillarity and a pore constriction.

field situations is about 1 to 2 psi/ft, so that for typical pore radii $r_1 = 9 \times 10^{-4}$ cm and $r_2 = 4 \times 10^{-3}$ cm and for drop length = 4×10^{-2} cm, interfacial tension reduction to about 0.1 dyne/cm is needed for incipient residual oil production. Substantial oil production may require <0.01 dyne/cm.[5]

Surfactants, or surface active agents, are molecules incorporating both hydrophilic and oleophilic portions, and as a result tend to reside ("adsorb") at the oil/water interface. It is a basic consequence of thermodynamics that adsorption results in a lowering of interfacial tension. Extremely low interfacial tensions are achieved upon the addition to the system of a cosurfactant, typically a low-molecular-weight alcohol, and an electrolyte, typically NaCl or $(NH_4)_2SO_4$. Proper mixtures of these components result in microemulsions or micellar solutions characterized by interfacial tensions below 0.01 dyne/cm. Compositions varying from oil content are utilized. The range of composition can be:[6]

Surfactant	4 to 15 percent
Hydrocarbon	4 to 80 percent
Cosurfactant	Approximately 4 percent
Electrolyte	Approximately 1 percent
Water	10 to 92 percent

The process is applied by injecting a volume of micellar solution to form a slug in the reservoir. This slug moves through the reservoir displacing all of the oil and water ahead of it toward the producing well. the micellar slug is followed by a bank of polymer-thickened water for mobility control. After sufficient polymer is injected, drive water is used as in any waterflood.

Often the composition of the brine in a reservoir has an adverse effect on the micellar solution. To correct this problem, floods are started by first injecting a preflush bank of water ahead of the micellar solution, flushing the brine out of the reservoir.

Figure 4-2 shows the process under tertiary conditions. Prior waterflooding has displaced the oil to a residual immobile saturation. Only water is produced until the oil-water bank reaches the producing well. The size of the micellar solution slug usually is designed to be from 5 to 10 percent of the reservoir pore volume. Laboratory tests

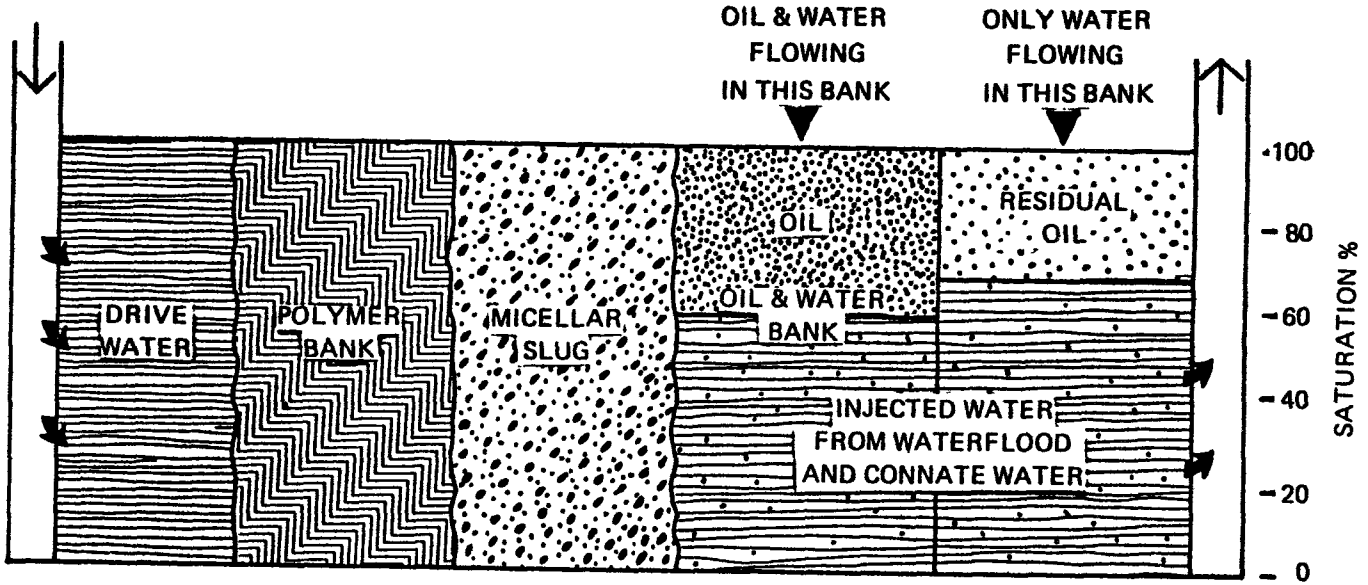

Figure 4–2. Micellar flood process used for tertiary operation.

show that a minimum 5 percent pore volume slug is required to achieve effective recovery. Adsorption of surfactant on reservoir rock and dispersion of the micellar material tend to destroy the slug. About 10 percent pore volume slug size is the maximum that present economics allow.

Micellar flooding probably is applicable to many reservoirs which have been successfully waterflooded:

- It is applicable to sandstone reservoirs, but is limited in use in carbonate reservoirs or where reservoir brines contain excessive calcium or magnesium ions. Adsorption of the surfactant is high in these type reservoirs using current micellar compositions. Further experimentation may extend the use of the process to more of these reservoirs by determining the optimum chemicals and compositions.

- The process is best applied to reservoirs with medium-gravity crude oils. Prospects with low gravity crudes probably would not be economical. A low-gravity, high-viscosity crude would call for increasing the viscosity of the micellar and polymer slugs for a favorable mobility ratio, resulting in higher cost.

- The micellar process is technically applicable for secondary recovery or tertiary recovery. If used for secondary recovery, it eliminates one set of operating costs.

In the case of anionic surfactants, once residual ganglia are effectively mobilized, a continuous oil bank is observed to form ahead of the flood front and flows at an oil saturation that depends on the resident oil-brine-rock system. Once formed, the oil bank gathers up residual ganglia at its front, continually extending its length. From the onset of oil bank formation, the function of the surfactant is to maintain continuity of the flowing oil filaments to as low a saturation as possible before they rupture and are irretrievably trapped. Since the ultimate residual saturation is established within an interfacially active environment, oil remaining behind may contain surfactant, and this loss must be accounted for in addition to that lost through adsorption and association with retained polymer.

There are a variety of interfacially active liquids that will displace residual oil from a porous medium. Independent of what type of surfactant system is injected,

once within the porous medium, the liquid system can be considered composed of three components: oil, water, and surfactant. The "oil" can be a pure hydrocarbon or as complex as a crude oil; the "water" can vary from fresh water to an oilfield brine containing a dozen or so different ions, and it may additionally contain chemicals injected in a preflush; and the "surfactant" can be a pure compound, a distribution of homologues, a petroleum sulfonate, etc., and can include cosurfactants such as ethoxylated alcohols, sulfated ethoxylated alcohols, etc., and cosolvents such as alcohols, ethers, glycols, etc. Properties of all of these can be usefully represented as functions on a pseudo-ternary diagram such as shown in Figure 4-3. The dashed line is an upper bound for compositions having current economic signficance. Surfactant concentrations in excess of about 15 percent are of no interest in relation to tertiary oil recovery.

Examples of injection compositions for all reported surfactant flooding systems are indicated by the letters A, M, S, and I in Figure 4-3. Aqueous surfactant flooding (A), the oldest of these processes, has no oil in the material injected except for that unreacted and not separated from the surfactant during manufacture. Conventional microemulsion floods (M) may have an injection composition anywhere considerably above the binodal curve and away from the shaded areas. Usually, soluble oil floods (S) utilize a substantially anhydrous composition, high in surfactant content. Immiscible microemulsion flooding (I) refers to any injection composition on or in the neighborhood of a binodal curve.

Field results are still sparse, but some effects of the primary operating variables have been inferred from the results of laboratory tests using sandstone cores. Healy et al.,[7] on the basis of their studies in which microemulsion slugs of finite size were injected, concluded the following:

1. Final oil saturation left behind the flood decreases with increased surfactant concentration, with increased flooding rate, and with increased length of travel from 4 to 16 feet.

2. Distance travelled to slug breakdown increases with increased surfactant concentration and is substantially less than that calculated on the basis of miscible displacement.

3. During an effective flood, the greater part of the oil recovered was acquired by means of immiscible displacement.

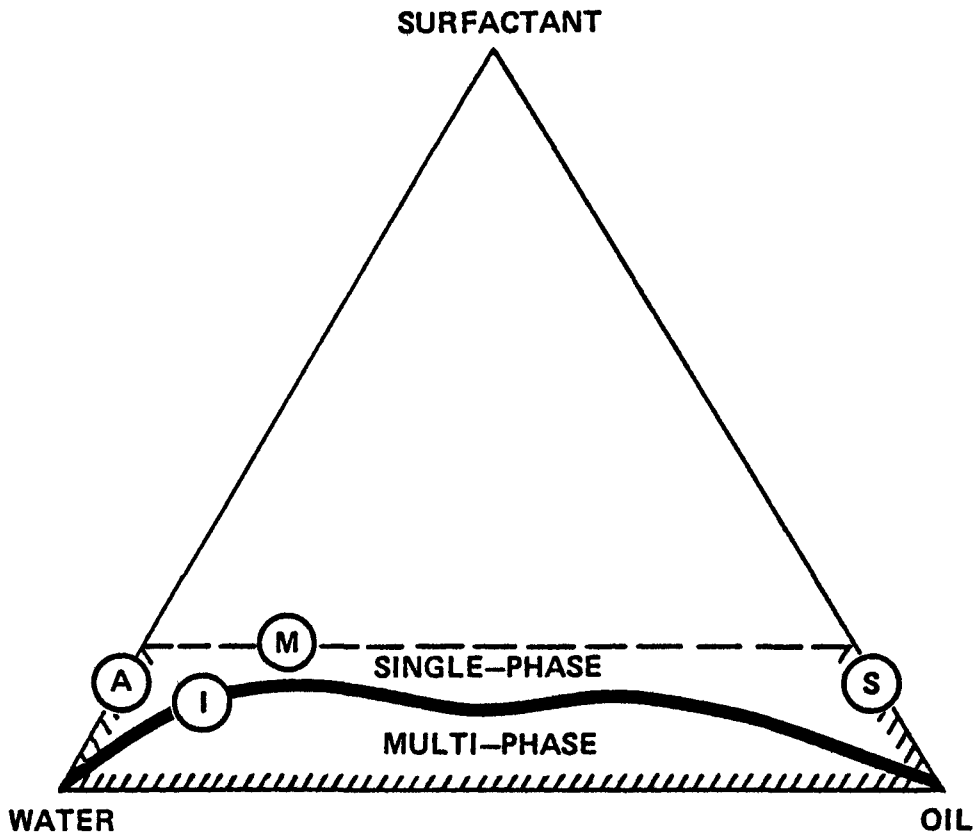

Figure 4–3. Pseudo-ternary representation of the oil-water surfactant system, showing an upper economic limit and various injection compositions of interest.

4. Nature of the external phase (i.e., water- or oil-external) is not an important variable.

5. Surfactant retention increased with increasing slug deterioration.

More generally, the following conclusion was reached:

6. Practical microemulsion flood is a locally miscible process until slug breakdown, and is an immiscible process thereafter.

4.3 Experimental Program for Surfactant Recovery

4.3.1 Prior Art

While ultrafiltration membranes are commonly used to perform protein separations in the food industry, the literature review (Appendix A) did not identify any applications of membrane technology to surfactant recovery. Work on fractionating surfactant material by molecular weight is occurring at the Department of Energy Laboratory in Morgantown, West Virginia. This is sponsored as an in-house project by the Department of Energy, and the project officer is Mr. Khris Kamanth.

In food processing operations in which ultrafiltration membranes are used to recover or separate materials, the molecular size involved is typically on the order of 5,000 to 100,000 molecular weight. These molecules are typically large proteins or carbohydrates. There are occasional applications with sugars in which the molecular weight of the material to be recovered is approximately 500. For recovery of surfactant material, the molecular weight range of interest is from approximately 300 to 600. This is the common range of most commercial petroleum sulfonates. Thus, surfactant recovery is on the low-molecular-weight end and technological fringe of ultrafiltration membrane processing.

While reverse osmosis membranes are capable of retaining (rejecting) inorganic salt molecules and could obviously retain surfactant molecules, the use of a membrane that is capable of retaining nearly all of the dissolved species present is not feasible. In order to recover surfactant for reuse or proper disposal, the concentration of the surfactant in the feed fluid must be increased on the order of 100- to 1,000-fold. Using a reverse osmosis membrane, the inorganic salt concentration of the feed fluid will also increase by nearly the same amount. As the inorganic salt concentration

of the feed fluid increases, the osmotic pressure of the fluid will also increase, increasing the pressure-driving force necessary to maintain a constant flux rate. If, for example, a feed fluid contained 1,000 ppm surfactant material and 1,000 ppm inorganic dissolved solids, an increase in concentration by a factor of 100 would produce a fluid with a surfactant concentration of 10 percent, but the salt concentration would also be 10 percent, with the resulting osmotic pressure on the order of 1,000 pounds. The pumping costs for such a scheme appear prohibitive.

The key to a successful demonstration of surfactant recovery by membrane processing is thus identifying a membrane that will reject (retain) surfactant material in the feed stream but will pass inorganic salts. Commercial membranes that are capable of such selectivity were needed before any experimental program to gauge the feasibility of surfactant recovery could be undertaken. A major effort was made to identify and obtain membranes that might meet this criteria.

4.3.2 Experiment Program

4.3.2.1 Test Plan

Initially, the surfactant recovery experimental program was to be integrated onto the end of the emulsion dewatering program in the following manner. The permeate from representative emulsions was to be processed directly with the membrane selected for surfactant recovery. This was abandoned for the following reasons:

1. Stable emulsions for emulsion dewatering could not be formulated using petroleum-based sulfonates and, therefore, any surfactant material in the emulsion dewatering permeate would not be representative of surfactant present in aqueous oilfield fluid.

2. Surfactant recovery from the aqueous phase of a produced fluid may be desirable in cases in which no emulsion is produced.

In addition to an experimental design to determine the technical feasibility of surfactant recovery, a determination of the probability that surfactant will be present in the aqueous phase of produced fluid was made. Surfactant material that is not lost in the rock structure of the field commonly partitions (equilibrates) between the aqueous and oil phases of produced fluids. Predominant partitioning of

surfactant material into either the aqueous or the oil phase significantly affects the feasibility of recovering surfactant from the aqueous phase. An experimental test plan was formulated to investigate the equilibrium values for two different petroleum sulfonates. A parametric analysis was also devised to determine the effects of salt concentration, water-to-oil ratio, and cosurfactant concentration on the partitioning. The methodology and results of the partitioning are described below.

The surfactant recovery abilities of three membranes were investigated. Two different feed solutions containing surfactant material were prepared: a high-molecular-weight surfactant mixture and a low-molecular-weight surfactant mixture. Surfactant recovery as a function of operating temperature and surfactant concentration in the feed were closely monitored. Membrane flux rates as a function of pressure, temperature, and feed concentration were also monitored. The experimental work focused on those membranes that exhibited a high surfactant retention at high flux rates since the economic feasibility of surfactant recovery is based both on retentiveness and on the capital investment in membrane area required.

4.3.2.2 Equipment Design and Experimental Procedure

For surfactant recovery both the high- and low-molecular-weight solutions were made from commercial samples of petroleum sulfonates. Witco TRS 40 (average molecular weight 330 to 350) and Witco TRS 18 (average molecular weight 490 to 520) were first dissolved in a minimum amount of distilled water, which was then mixed with the brine solution. The Witco TRS 40 solution was mixed with the brine received from the El Dorado project. The dissolved solution of TRS 18 could not be added to the El Dorado brine since it would precipitate. The TRS 18 was mixed instead with Cambridge, Massachusetts tapwater. Since the TRS 18 would not remain in solution in the presence of a high salt concentration, only the TRS 40 was used for the partitioning work.

The solution of TRS 40 and El Dorado brine was used to screen the membranes initially. The two membranes selected specifically for surfactant recovery, the Rev-O-Pak membranes, were tested first. Since both of these relatively tight membranes produced very good retention, plans to try a Universal Oil Products membrane were dropped in favor of using the Abcor membrane used in the ultrafiltration work. This decision was made in order to determine if a relatively loose membrane could still provide a high degree of surfactant

retention but produce the high flux rates expected by a relatively loose membrane. Subsequently, the TRS 40 solution was tested with the Abcor membrane.

For all three membranes and at constant surfactant concentration in the feed, the flux rates were determined as functions of temperature and operating pressure. At constant feed surfactant concentration the surfactant concentration in the permeate was measured as a function of temperature and pressure. A run was made with the TRS 40 solution and Rev-O-Pak membranes in which the permeate was collected and not returned to the feed and the surfactant concentration was allowed to increase while operating at a constant temperature and pressure. This run was continued until the flux rate had dropped by at least 50 percent.

A similar procedure was planned for the TRS 18 solution. However, since the initially measured retention by the membranes approached 100 percent the testing was cut short and assumed to be equivalent if not better than the results obtained with the TRS 40 solution.

The partitioning work was done solely with the TRS 40 solution since the TRS 18 solution was not soluble in high brine concentrations and little impact of variables other than salt concentration had been noticed with the TRS 40 work. The procedure for measuring the partitioning coefficient (actually the retention of surfactant in the aqueous phase) was as follows:

1. The materials used were El Dorado oil, El Dorado brine, TRS 40 surfactant, and ethylene glycol as a cosurfactant.

2. These constituents, in the proportions specified, were first added to a beaker swirled and then placed in a hand homogenizer. The hand homogenizer was cleaned thoroughly between each sample. The contents of the hand homogenizer were pumped through the nozzle into a collection beaker and then passed through the hand homogenizer for a second time. The resulting mixture was then added to a test tube which was hand-shaken.

3. The contents of the tube were centrifuged for approximately 5 minutes and then allowed to stand.

4. The contents of the test tube were then poured into a separatory funnel and allowed to stand for at least one-half hour.

5. The aqueous phase in the separatory funnel was drawn off and analyzed for surfactant concentration.

6. The surfactant solution used in the mixture had a known surfactant concentration. The surfactant concentration measured in the partitioned aqueous phase was compared with the surfactant concentration measured in the surfactant solution used to make up the sample. The amount of surfactant present in the aqueous phase of the sample was determined by the relative amount of surfactant measured compared with the surfactant concentration in the solution used to make the sample.

7. The method used to measure surfactant concentration, both in the partitioning work and in determining surfactant recovery, was the method described by Smith and Malmberg in SPE Paper 5306. The procedure uses a two-phase dye transfer technique based on the complexing of methylene blue with surfactant. The titration depends on the stoichiometric reaction of the cationic surfactant of the titrate with a complex of methylene blue indicator and anionic surfactant present in the solution. The methylene blue-anionic surfactant complex is soluble in chloroform and colors it. The reaction of added cationic surfactant, cetyltrimethylammonium bromide, with the complex frees the methylene blue which colors the aqueous phase. The end point was taken to be equal color in both layers or, in cases in which oil or cosurfactant obscured equal color in both layers, equal intensity of blue color in both layers was used as the end point.

The experimental equipment used with the Rev-O-Pak membranes for emulsion dewatering was used to test the Rev-O-Pak membranes for surfactant recovery. The low-pressure pilot plant which was used to test the Abcor membrane for emulsion dewatering was also used to test the Abcor membrane for surfactant recovery.

4.3.2.3 Experimental Results and Evaluation

The full range of tests were made only with the TRS 40 surfactant solution since the retention of the low molecular weight material was much higher than expected. Testing with the higher molecular weight TRS 18 solution was done only to confirm this trend. The properties of the surfactant solutions used are shown in Table 4-1.

TABLE 4-1

SURFACTANT SOLUTION PROCESSED

	SURFACTANT	
	Witco TRS 40	Witco TRS 18
Average molecular weight	330-350	470-620
% active sulfonate	42	62
Active surfactant concentration		
milliequivalents/ liter	0.01167	0.00685
weight %	0.377	0.341
Aqueous media	El Dorado brine	Cambridge tapwater[a]
TDS (mg/l)	60,000	<1,000
Membranes used	Rev-O-Pak 120, Rev-O-Pak 150 Abcor	Rev-O-Pak 120, Rev-O-Pak 150

[a]Concentrated surfactant solution (in distilled water) gelled with El Dorado brine.

A summary of the flux rates for the surfactant solutions is shown in Table 4-2. As expected, the retention by the Rev-O-Pak membranes was higher than for the Abcor membrane which has a much looser pore structure. Also as expected, the Rev-O-Pak 150 membrane had better retention than the Rev-O-Pak 120 membrane since the 120 membrane is a looser membrane.

Surfactant solutions were prepared at relatively high concentrations in order to test the ability of concentrating the surfactant to at least 4 or 5 percent by weight. If the initial surfactant concentration before processing had been on the order of 0.1 weight percent or less the volume of sample to be processed would be greatly increased as would the amount of time for running the samples.

TABLE 4-2

SUMMARY OF FLUX RATES FOR SURFACTANT CONCENTRATING

MEMBRANE	SURFAC-TANT	TEMPER-ATURE (° F)	INLET PRES-SURE (psig)	FLOW RATE (gpm)	FLUX RATE (gfd)	SURFAC-TANT RETENTION (%)
Abcor	TRS 40	77	30	22.3	14.0	~78
Rev-O-Pak 120	TRS 40	82	250	4.0	13.9	~89
Rev-O-Pak 150	TRS 40	82	250	4.0	6.3	~92
Rev-O-Pak 120	TRS 18	81	250	4.0	22.5	~98
Rev-O-Pak 150	TRS 18	81	250	4.0	19.2	~98

The permeate flux rate of the TRS 40 solution for the Rev-O-Pak membranes as a function of pressure is shown in Figure 4-4. The increase in permeate flux rate with increasing membrane pressure is nearly linear and proportionately the same as with the oil emulsions. Of greater importance is retention of surfactant by the membranes as a function of temperature. It was expected that membrane retention would fall off with an increase in operating temperature. The decrease was expected because pore size would increase with increasing temperature. Membrane retention as a function of temperature with the TRS 40 surfactant solution is shown for the three membranes tested in Figure 4-5. While the falloff in retention with temperature of the Rev-O-Pak membranes is noticeable it is not nearly as severe as the falloff experienced with the Abcor membrane. Unless temperature for processing can be held down and controlled tightly, the Abcor membrane does not seem suitable for recovering surfactant.

A major difference in membrane surfactant retention as a function of temperature occurs with the TRS 18 surfactant (Figure 4-6). The retention of the higher molecular weight surfactant material does not seem to be affected at all by

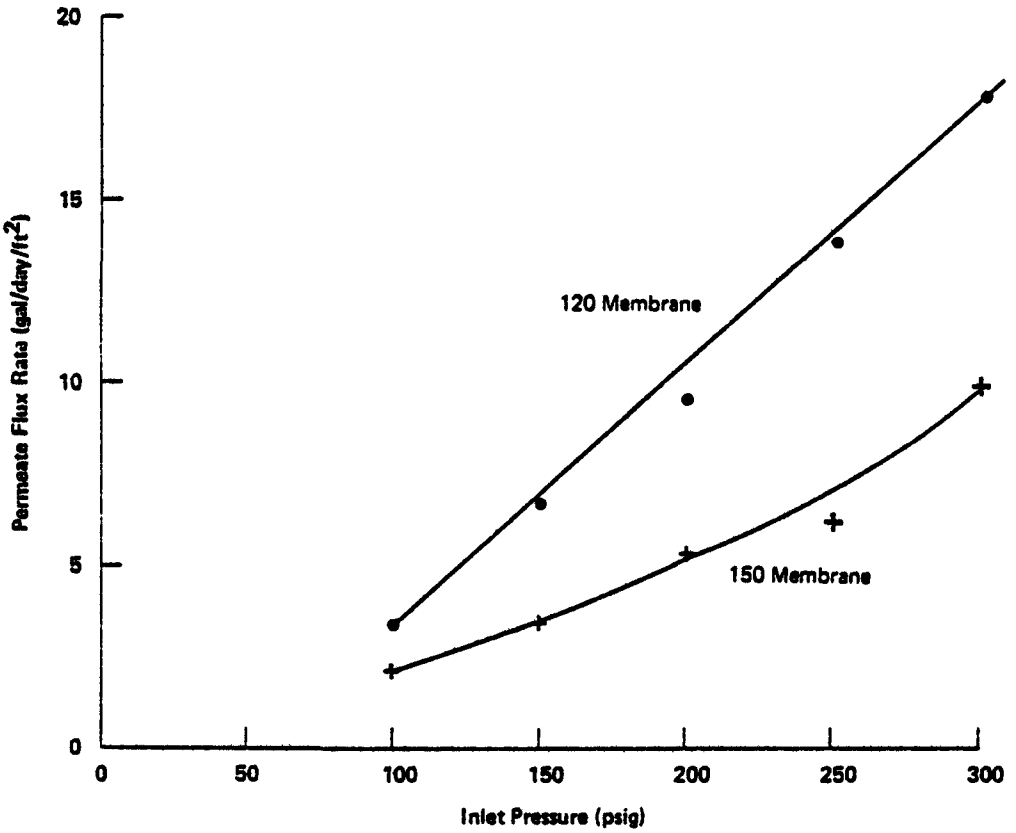

Figure 4—4. Rev-O-Pak permeate flux rates with base TRS 40 surfactant solution.

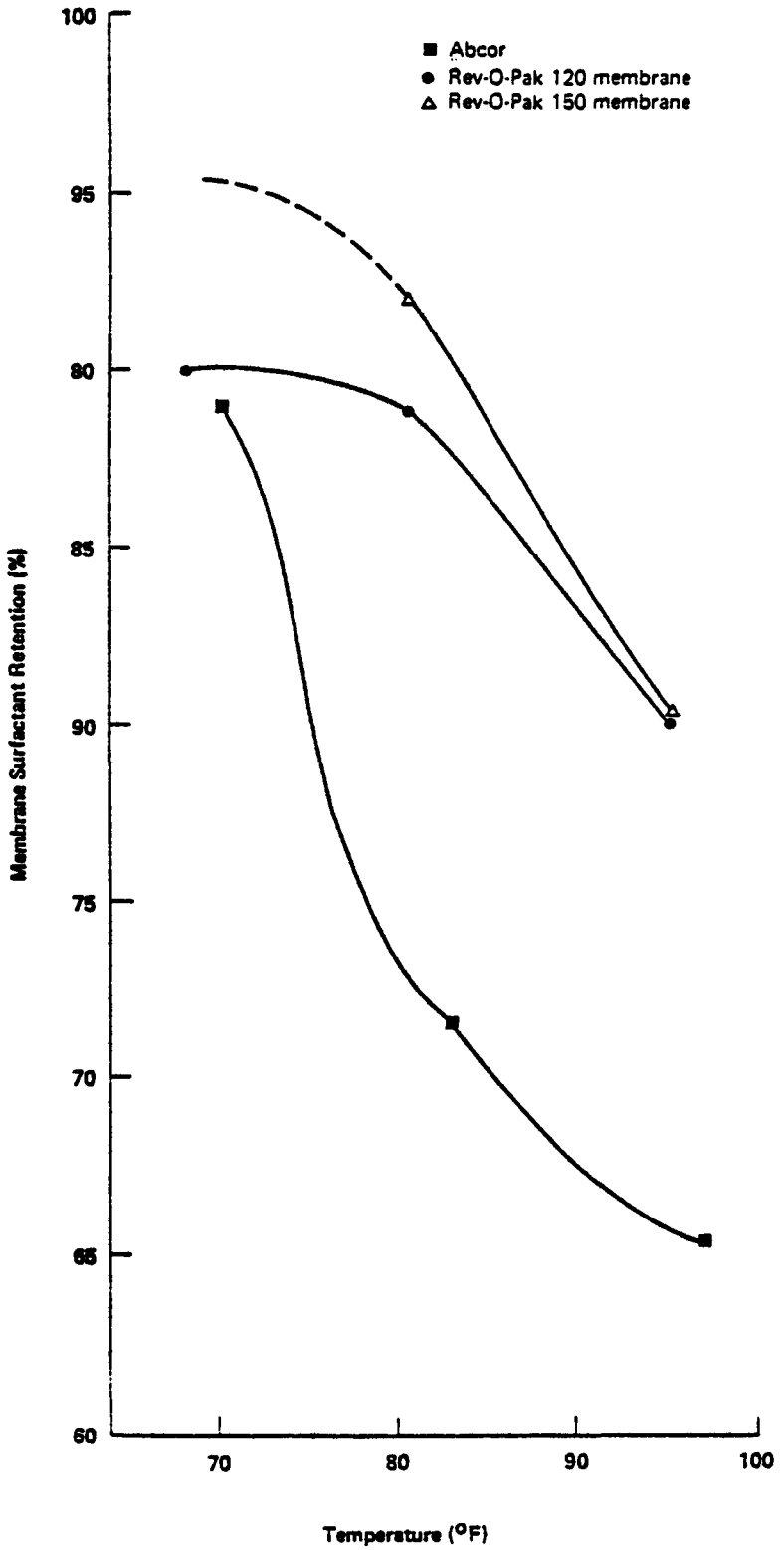

Figure 4–5. Membrane retention as a function of temperature – TRS 40 surfactant.

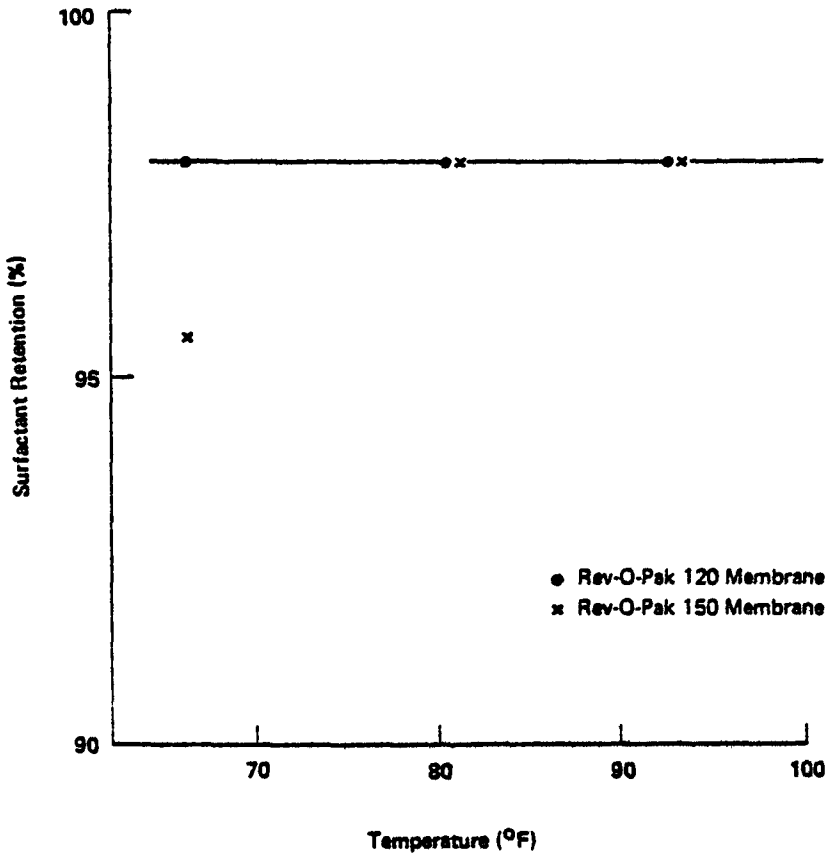

Figure 4–6. Surfactant retention as a function of temperature for TRS-18 surfactant.

the temperature for processing. This can be ascribed to two different phenomena. The individual surfactant molecules may be large enough so that they will not pass through the pores of the membrane at any operating temperature. The alternative explanation is that nearly all the surfactant in the TRS 18 solution is in micelles so that only a constant level of monomer surfactant molecule is available for transport across the membrane at any temperature.

The possibility that most of the surfactant is in micellar form and that the surfactant solution is above critical micelle concentration (CMC) might be expected by the results produced during the dewatering (concentrating) of the TRS 40 surfactant solution with the Rev-O-Pak membranes. These results are shown in Figures 4-7 and 4-8. In both cases, as expected, the permeate flux rate drops with increasing surfactant concentration. The flux rate of surfactant material across the membrane is not linearly proportional to the surfactant concentration in the bulk solution. That is, a doubling in the surfactant concentration in the bulk solution does not result in anywhere near a doubling of the surfactant loss rate. During this experiment the relative concentrations of surfactant in the concentrate and in the permeate were being measured with the methylene blue technique. The results for the concentrate were also confirmable by material balance. A similar run using the TRS 40 solution and the Abcor membrane was started. However, it had to be abandoned almost immediately due to foaming problems in the unit. Enough foam was generated with the pump so that two-phase flow was occurring through the unit and thus reliable estimates on membrane flux were impossible to obtain.

As mentioned above, the surfactant being rejected could be in micellar form and only surfactant material which has denatured or is present as monomer could be permeating across the membrane. An additional experiment was made to determine whether the high surfactant retention could be due to the formation of micelles. The TRS 18 solution was processed with the Rev-O-Pak membranes and then diluted in stages by several orders of magnitude. A standardization curve of surface tension versus surfactant concentration was made using a ring tensiometer. Surface tension measurements were used to avoid inaccuracies that could occur with the methylene blue method at low surfactant concentrations This standardization curve is shown in Figure 4-9. At each dilution of the surfactant solution permeate samples were taken and analyzed with the ring tensiometer for surfactant concentration. These results are shown in Figure 4-10. If surfactant concentration in the permeate approaches surfactant

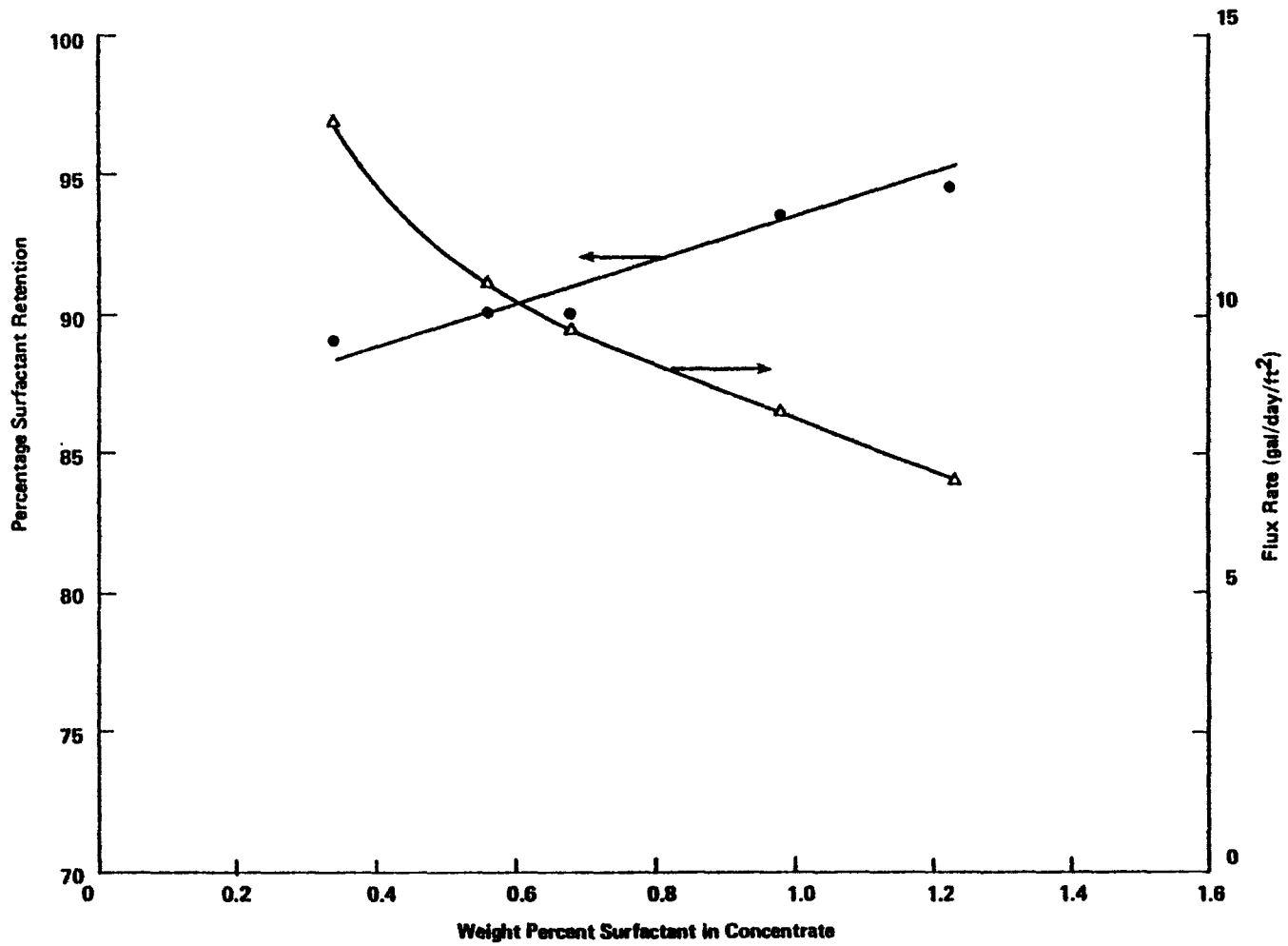

Figure 4–7. Surfactant retention and membrane flux as a function of surfactant concentration for the Rev-O-Pak 120 Membrane.

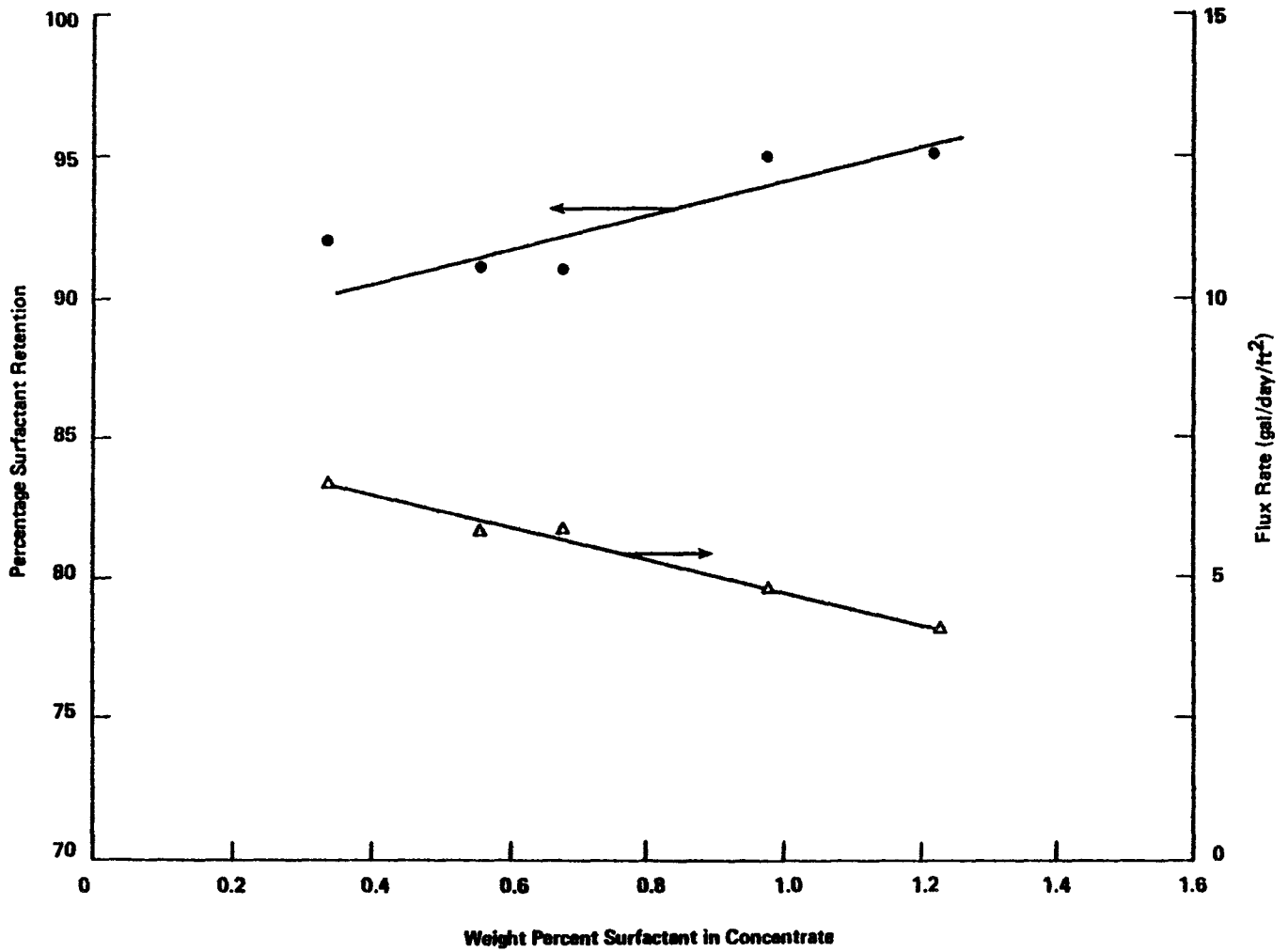

Figure 4–8. Surfactant retention and membrane flux as a function of surfactant concentration for the Rev-O-Pak 150 Membrane.

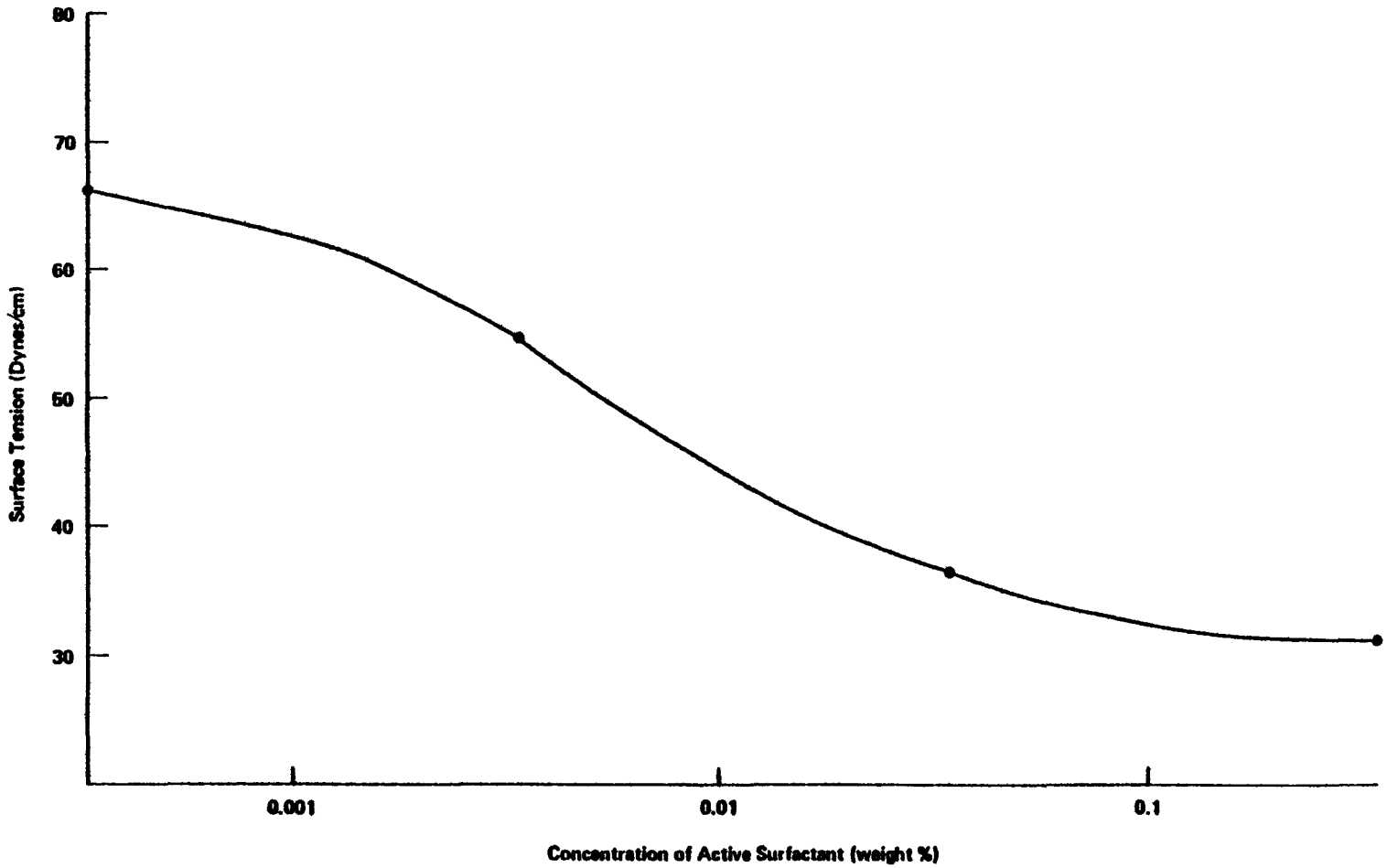

Figure 4–9. Surface tension of TRS 18 in tap water – Standardization curve.

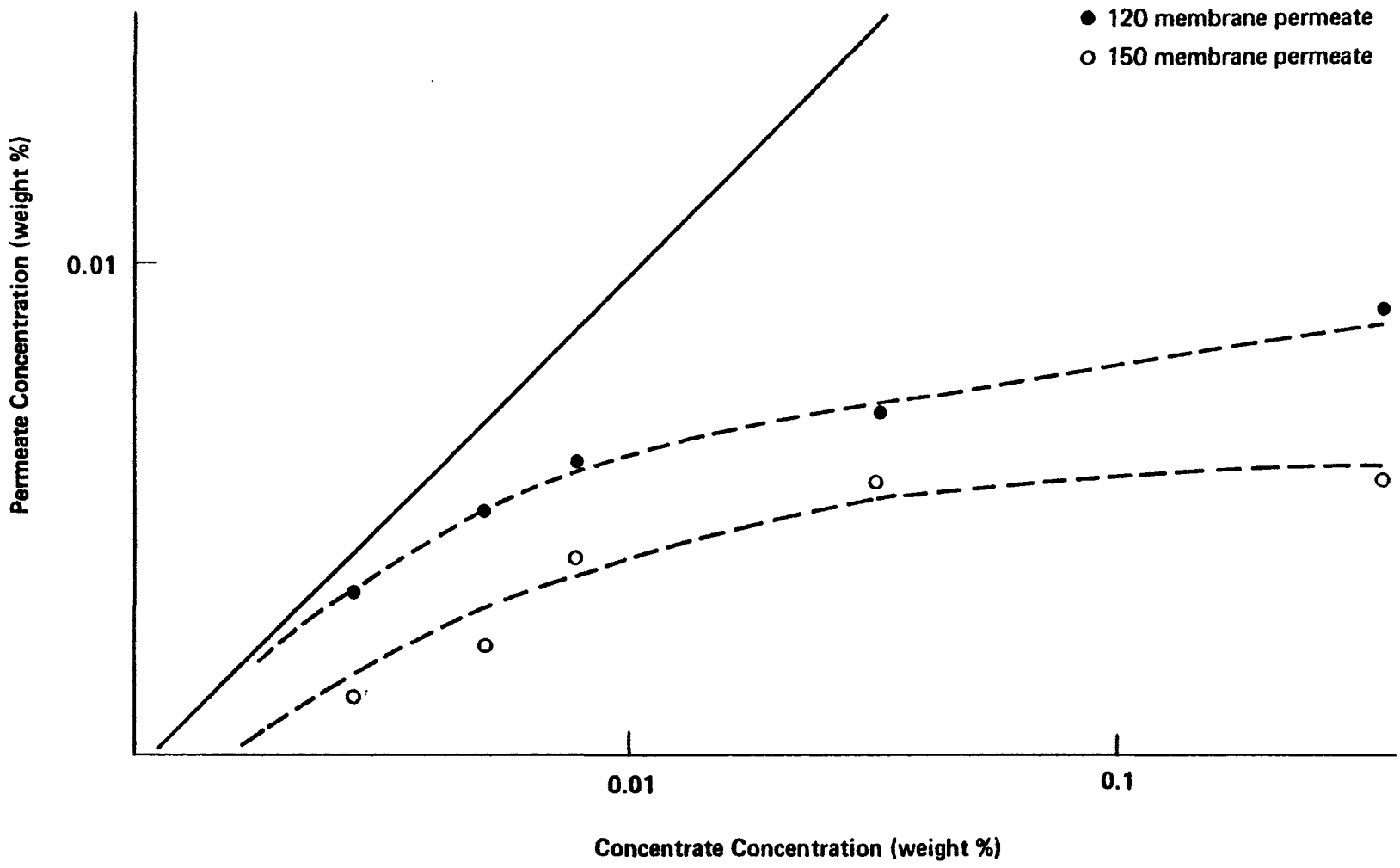

Figure 4—10. Active sulfonate distribution across Rev-O-Pak Membranes.

concentration in the concentrate the retention of the membrane is zero. This is shown by the 45° line in Figure 4-10.

Ideally, as the surfactant concentration reaches the CMC a leveling off in surface tension should occur. As shown in the standardization curve there is no clear-cut definition of the CMC. However, it would be safe to assume as the surfactant concentration decreases there is less likelihood that one is above the CMC. Referring to Figure 4-10, it is apparent as the likelihood of being below the CMC increases the retention of the surfactant by the membrane is decreasing. This indicates that at relatively high surfactant concentrations, the surfactant retention with the membranes is high because the surfactant is in micellar form.

The tight ultrafiltration membranes tested may be only capable of retaining surfactant in micellar form. The surfactant being produced in the aqueous phase of a wellhead fluid may indeed be in micellar form since salt concentration tends to suppress or reduce the concentration at which the CMC occurs.

The probability that surfactant would indeed be present in the aqueous phase instead of the oil phase was determined by the partitioning work. Table 4-3 shows the cases and results of the partitioning experiments performed with the TRS 40 solution. The methodology used to perform the experiment has been described in the above section. The effects of the three different variables are shown in Figures 4-11, 4-12, and 4-13.

While some variation in the amount of surfactant retained in the aqueous phase occurs with changes in the oil content of the mixture, the variations could also be due to changes in the water content of the oil phase with changes in oil content of the mixture. The surfactant concentration was measured in the aqueous phase of the separated sample mixture. A significant amount of water could have emulsified into the oil phase. This explanation is plausible since one would not expect a maximum in surfactant retention in the aqueous phase with increasing water content but rather increasing retention of surfactant in the aqeuous phase with increasing water content.

As shown in Figure 4-12, the effect of salt concentration on surfactant partitioning is very pronounced. Surfactant retention in the aqueous phase is improved dramaticaly with decreasing salt concentration of the mixture. The improvement in retention cannot be ascribed to the analytical technique

TABLE 4-3

PARTITIONING DATA FOR LOW MOLECULAR WEIGHT SURFACTANT[a]

CASE NO.	WATER-IN-OIL RATIO	TOTAL AQUEOUS DISSOLVED SOLIDS (mg/l)	WEIGHT % ACTIVE SURFACTANT	ACTIVE SURFACTANTS eq/l OF SAMPLE	VOLUME % COSURFACTANT[b]	ACTIVE SURFACTANT eq/l OF AQUEOUS PHASE	% TOTAL SAMPLE SURFACTANT RETAINED IN AQUEOUS PHASE[c]
1	2	60,000	0.264	0.00765	1.64	0.0049	42
2	3	60,100	0.292	0.00860	1.72	0.0039	33
3	1	59,400	0.205	0.00573	1.72	0.0034	29
4	2	30,000	0.267	0.00758	1.64	0.0058	50
5	2	15,000	0.268	0.00758	1.64	0.011	95
6	2	3,000	0.268	0.00752	1.64	0.016	137[d]
7	2	60,600	0.267	0.00770	1.00	0.0039	51
8	2	58,500	0.260	0.00752	3.22	0.0032	43
9	2	55,900	0.250	0.00729	6.25	0.0032	44

[a]Constituents are Witco TRS 40, North Burbank oil, North Burbank brine, distilled water, and ethylene glycol.

[b]Ethylene glycol.

[c]Defined by (equivalents per liter of separated aqueous phase/equivalents per liter of sample) X (liters of aqueous phase/liters of sample).

[d]Aqueous sample testing obscured by oil.

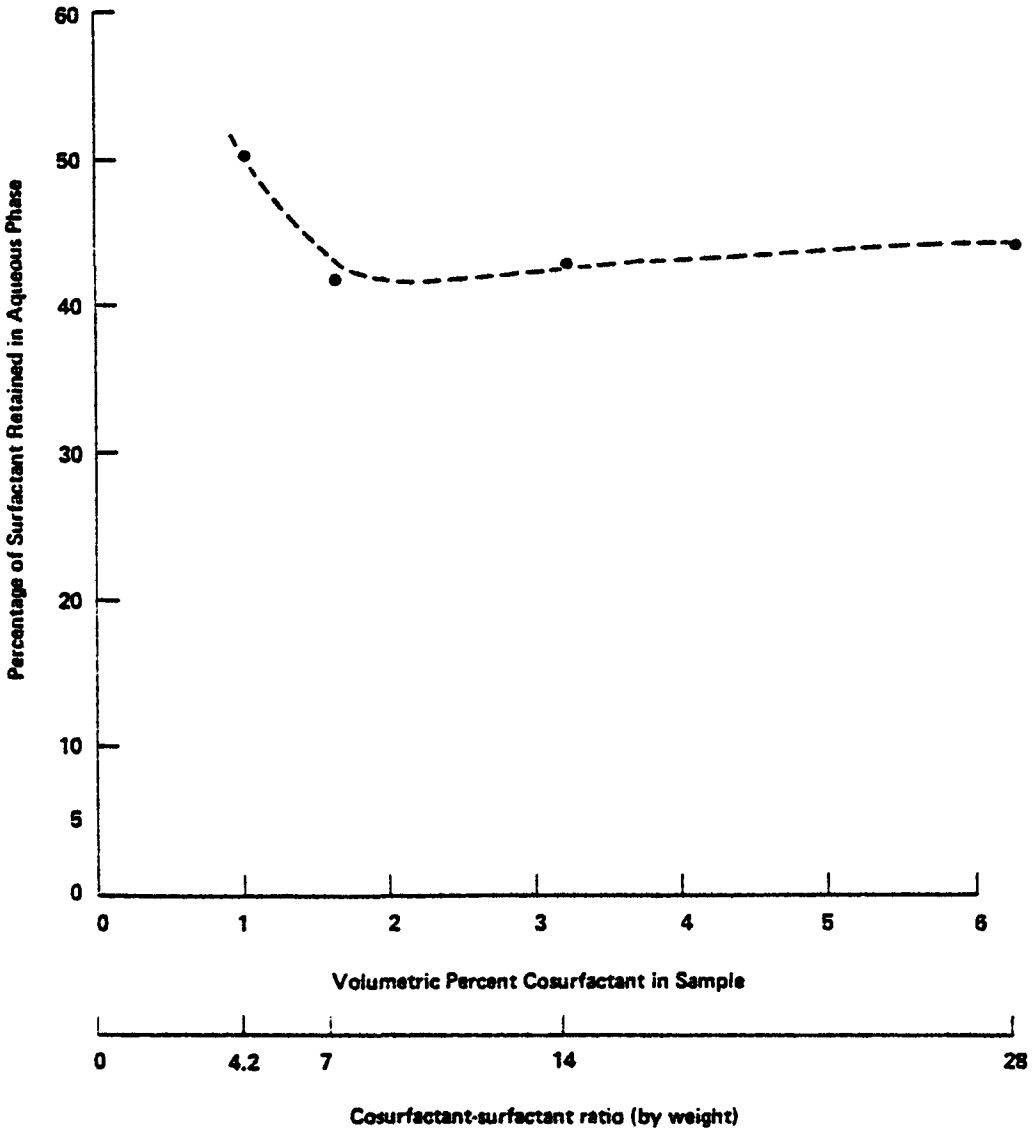

Figure 4–11. Effect of cosurfactant concentration on surfactant partioning.

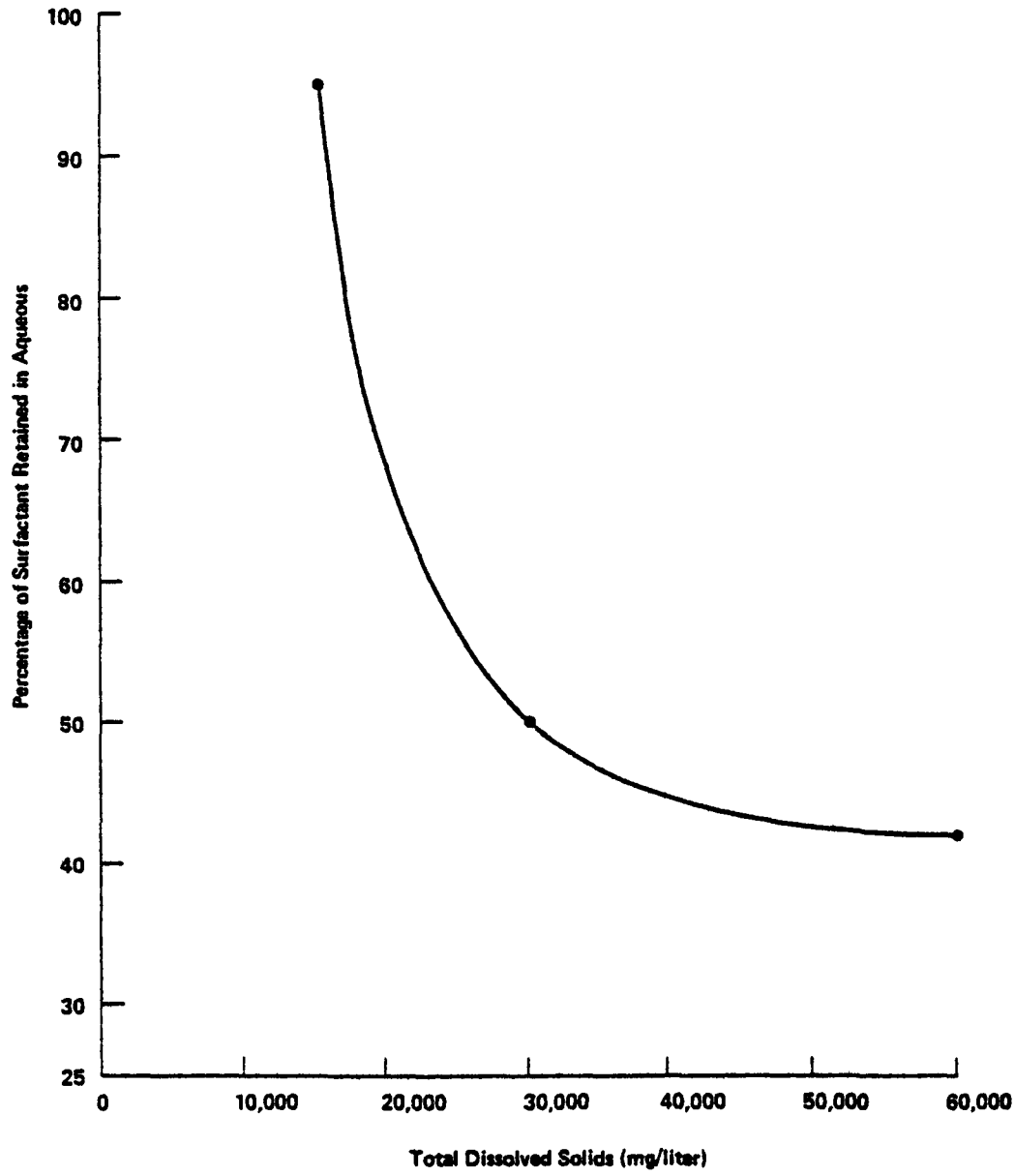

Figure 4—12. Effect of salt concentration on surfactant partioning

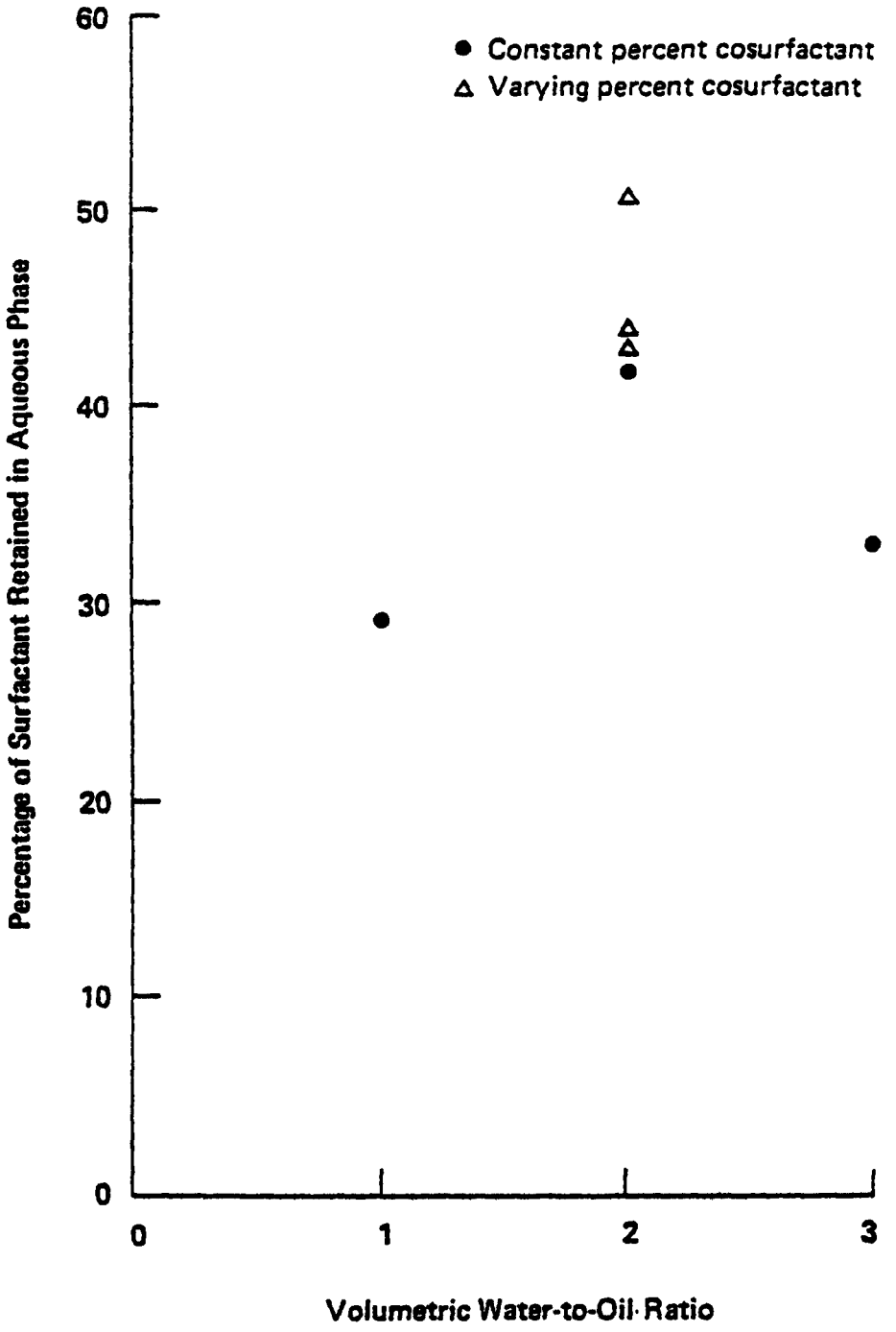

Figure 4—13. Effect of water-to-oil ratio on surfactant partioning.

for measuring surfactant since the analytical technique used produced consistently accurate measurements of surfactant concentration in brine surfactant solutions with increasing brine strength.

The effect of cosurfactant concentration on surfactant partitioning did not seem to be significant. However, only cosurfactant to surfactant ratios of greater than 4 were examined. At lower cosurfactant to surfactant ratios the effect might become more significant.

The data indicate that surfactant partitioning into the aqueous phase can be increased dramatically by reducing the salt concentration of the aqueous phase or, hopefully, that produced fluids at low salt concentrations will contain most of the surfactant in the aqueous phase. No attempt was made to determine methods for influencing surfactant partitioning into the aqueous phase by manipulating the cosurfactant or by other chemical addition. No attempt to duplicate the results noted with the TRS 40 surfactant with changes in brine concentration with the TRS 18 surfactant since the TRS 18 surfactant was insoluble when dissolved solids were present.

While results will certainly vary from field to field depending on the micellar slug used, it should be safe to assume that from 50 to 80 percent of the surfactant material in the produced fluid will be present in the aqueous phase, either naturally or by manipulation. The key unanswered question which is beyond the scope of this work is to determine the amount of surfactant material that is trapped in the resevoir in the pore structure and is not returned to the surface with the produced fluid. Recovery of a large percentage of the small amount will not suffice for economic surfactant recovery from the produced fluid.

4.4 Economic Assessment

The costs for the surfactant recovery technology are very similar to the costs of emulsion breaking shown previously in Chapter Three. The primary differences are that slightly higher pressures will be required for a surfactant recovery process since the membrane that is used will be a tighter membrane than for emulsion breaking and hence will achieve a flux rate on the order of 20 gal/day/ft^2 rather than 50 gal/day/ft^2 as is anticipated for emulsion breaking. The basis for the surfactant recovery system costs are shown in Table 4-4. Three fluid concentrations have been chosen for the parametric analysis as follows:

TABLE 4-4

SURFACTANT RECOVERY SYSTEM BASIS[a]

	1,000 BPD WATER FLUX, FLUX RATE 20 (gal/day/ft^2)			10,000 BPD WATER FLUX, FLUX RATE 20 (gal/day/ft^2)			100,000 BPD WATER FLUX, FLUX RATE 20 (gal/day/ft^2)		
	IC 0.01	IC 0.1	IC 1.0	IC 0.01	IC 0.1	IC 1.0	IC 0.01	IC 0.1	IC 1.0
Recovery, %									
Retention	80	95	98	80	95	98	80	95	98
Partition	80	80	80	80	80	80	80	80	80
Net efficiency, %	64	76	78	64	76	78	64	76	78
Total weight recovery, lb/day	22	266	2,730	224	2,660	27,300	2,240	26,600	273,000

[a]IC = inlet concentration (total surfactant weight at wellhead/weight of aqueous phase). Outlet (from recovery) concentration of surfactant is 10 percent.

- 0.01 (weight) percent - A surfactant concentration of 100 ppm has been observed in some wells. The data taken as a part of this program suggest that this is about the minimum concentration that can be treated within an acceptable pressure drop range (and flux rate) for the membrane system.

- 0.1 percent - Surfactanct concentrations of 1,000 ppm allow for high recovery efficiencies at reasonable operating pressures.

- 1 percent - This high concentration (which is currently observed at one of the Marathon floods) is about as high a surfactant concentration as could be expected for most micellar/polymer projects.

Reasonable extrapolation of the results of this program suggests retention yields and partitioning yields on the order of 80 percent or better. With further work, the authors believe that the recovery efficiency could be extended for both membrane retention and partitioning to exceed 90 percent.

The capital costs for a surfactant recovery system are shown in Table 4-5 for three different water flux rates. Costs are comparable to the capital costs estimated for the

TABLE 4-5

CAPITAL COST FOR SURFACTANT RECOVERY

	WATER FLUX (BPD)		
	1,000	10,000	100,000
Capital cost ($1,000)			
Membrane modules	84	630	5,250
Pumps and piping	30	150	750
System fabrication	50	250	1,250
Field installation	30	200	2,000
Total installed cost	194	1,230	9,250

emulsion breaking system except that more membrane area is required because of lower flux rates and larger pumps are required because of the higher pressure drop across the membrane.

The annual operating costs for surfactant recovery are shown in Table 4-6. The basis for these costs are the same as the basis for the emulsion breaking technology and the unit cost in terms of dollars per barrel of brine treated are on the order of $0.14 to $0.24 per barrel of brine.

A summary of the economics of surfactant recovery is shown in Table 4-7. The amount of surfactant that can be recovered per year is shown as a function of inlet concentration and water flux rate. The unit cost in dollars per pound of recovered surfactant clearly shows that the primary variable affecting the economic feasibility of this technology is the inlet concentration of the surfactant. At an inlet concentration of 0.1 percent, the unit cost for surfactant is on the same order as that for purchased petroleum

TABLE 4-6

ANNUAL OPERATING COST FOR SURFACTANT RECOVERY

	WATER FLUX (BPD)		
	1,000	10,000	100,000
Annual operating cost, $1,000			
Capital charges @ 20% over 15 years	43	271	2,035
Routine maintenance @ 5% installed cost	10	62	463
Membrane replacement	28	210	1,750
Power @ $0.04/Kwh	7	74	736
Total annual cost	88	617	4,984
Unit cost, $1 bbl brine	0.24	0.17	0.14

TABLE 4-7

ECONOMICS OF SURFACTANT RECOVERY[a]

	WATER FLUX (BPD)		
	1,000	10,000	100,000
Surfactant recovered, lb/yr			
IC 0.01%	8,200	81,800	818,000
IC 0.1%	97,100	970,900	9,709,000
IC 1.0%	996,400	9,964,500	99,645,000
Unit cost, $/lb			
IC 0.01%	10.76	7.54	6.10
IC 0.1%	0.91	0.64	0.51
IC 1.0%	0.09	0.06	0.05

[a]IC = inlet concentration.

sulfonates at $0.60 per pound. In flood projects using more expensive surfactants (to improve recovery efficiency or reduce adsorption), the use of the surfactant recovery technology would clearly be to the operator's advantage at this concentration or higher.

As the inlet concentration increases, the cost of surfactant recovery dramatically decreases. At concentrations of 1 percent, as currently observed in one of the Marathon floods, the surfactant can be recovered at a small percentage of the initial cost.

The economic analysis does not take into account the positive benefits from environmental protection or increased oil yields possible when high surfactant concentrations are injected (and subsequently produced).

The data also clearly shows that the use of membrane technology for extremely dilute produced fluids is not economical. The recovery of surfactants under these conditions

is possible perhaps using a froth flotation mechanism to concentrate the surfactant in much the same way that this technology is used for oily water scrubbing in refineries or offshore platforms. Unfortunately, the investigation of this processing requirement is beyond the scope of the present project.

NOTES TO CHAPTER FOUR

1. C. Braxton et al., Potential Environmental Consequences of Tertiary Oil Recovery, Environmental Protection Agency, Contract No. 68-01-1912, July 1976.

2. D.M. Burdge, Marathon Oil Company, Personal Communication, December 12, 1977.

3. R.C. Reed and R.N. Healy, Paper presented at AIChE National Meeting, Kansas City, Missouri, April 14, 1976.

4. I.I. Gardescu, Trans. AIME 136(1930):351; and J.J. Taber, Soc. Pet. Eng. J. 9(1969):3.

5. R.W. Parsons, J. Petrol. Technol. 26(1974):550.

6. E.F. Herbeck et al., Petrol. Engr. (June 1976):49.

7. R.N. Healy et al., Soc. Pet. Eng. J. 15(1975):87.

APPENDIX A

BIBLIOGRAPHY

Ackermann, U. (Holstein und Kappert Maschinenfabrik Phoenix G.m.b.H.). "System for Breaking Oil-Water Emulsions." Ger. Offen. 2,313,044 (September 19, 1974).

Aged cooling and lubricating emulsions are concentrated by evaporation. From a reservoir, measured amounts of the emulsion are pumped into a heat exchanger, and through a series of interconnected evaporators, separators, and condensers.

American Petroleum Institute. "Separation of Oil, Water, and Emulsions." In History of Petroleum Engineering, pp. 925-931. American Petroleum Institute, 1961.

Early developments in crude oil emulsion treating are described through about 1940:

1. Hay tanks: excelsior packing used to rupture films.
2. Horizontal water traps: density differences aid settling.
3. Wash (vertical) tanks.
4. Electric dehydrator: F. Cottrell, March 21, 1911 patent.
5. Chemicals: W. Barnichel (1914, first patent) and Tretolite (1916).
6. Heater-treater: developed in 1930's.

Ariyama, K. and Kurokawa, T. (Nitto Chemical Industry Co., Ltd.). "Treating Emulsified Waste Waters Containing Metals and Oils." Japan. Kokai 75,159,148 (Cl. C02C) (December 23, 1973), Appl. 74 67, 179 (June 14, 1974): 7 pp.

A metals-containing oil-water emulsified waste water is adjusted to pH <6.5 in the presence of tannin or bisphenol-A, a chelating agent, a reducing agent, and a metal collector such as a sulfide. The waste water is then flocculated with an inorganic flocculant to remove oils and metals simultaneously and effectively. Thus, a waste water containing polyoxyethylene nonyl phenyl ether 0.05 percent oils 1.0 percent, Cu 25 ppm, and Ni 25 ppm was mixed with 400 ppm of tannic acid and

100 ppm of anthanilic acid adjusted to pH 6.0, stirred, mixed with Al sulfate (200 ppm as Al_2O_3) at pH 7.0 to form a floc, and mixed with 5 ppm polyacrylamide to strengthen the floc. The floc was removed. The solution was transparent and contained Cu 0.3, Ni 0.2, and oils 1 ppm.

Ariyama, K. and Sasaki, S. (Nitto Chemical Industry Co., Ltd.). "Treatment of Waste Water Containing Metals and Emulsified Oils." Japan Kokai 75,155,053 (Cl. C02C) (December 13, 1975), Appl. 74 62,530 (June 4, 1974):5 pp.

A waste water containing metals and emulsified oils is treated with tannins at pH $\leq$6.5 and to this is added an inorganic flocculent; the flocs formed are removed; the tannin-containing liquid is adjusted to pH >9 to precipitate metals. Thus, tannic acid 400 ppm was added to a waste water containing polyoxyethylenenonylphenyl ether 0.05 percent, heavy oil 1.0 percent, Cu 25 ppm, and Ni 25 ppm. The mixture was adjusted to pH 4.0, stirred for 3 min, and to this was added $Al_2(SO_4)_3$ 200 ppm. The mixture was adjusted to pH 5.0 to form oil-containing flocs and to this was added polyacrylamide 5 ppm to harden the flocs. The flocs were removed. The aqueous phase was adjusted to pH 11.0 and stirred. The removal of precipitated metal yielded clear water containing Cu 0.5, Ni 0.2, and oil 1 ppm. When the waste water was treated without adding tannic acid, the effluent was turbid and contained Cu 9.5, Ni 5.3, and oil 4500 ppm.

Badische, A. and Soda-Fabrik, A.G. "Ethylene Oxide-1,2-Propylene Oxide Copolymers." Fr. 1,532,984 (Cl. C 08g) (July 12, 1968), Ger. Appl. (July 29, 1966):3 pp.

Poly(propylene oxide) (I) (1 part) having molecular weight 1200-2500 is polymerized with 1-4 parts ethylene oxide and then with 1-4 parts propylene oxide (with NaOMe as initiator) so that each of the poly(ethylene oxide) intermediate blocks and I exterior blocks has molecular weight 1000-3000. This block copolymer is used as a demulsifier for water-in-oil emulsions. Thus, 1 kg I having molecular weight 1500 was polymerized at 120° to 125°/5 to 6 atmospheres with 1.5 kg ethylene oxide and then with 2.0 kg propylene oxide at 130° to 135° with 10 g NaOMe as the initiator. The block copolymer (molecular weight 10,500 (20 mg) was heated with 200 g crude oil containing 105 ml water, and the mixture was allowed to cool. After 5 min and 10 min respectively, 85 percent and 99.8 percent of the water had separated. With a commercial

oxyethylated I as the demulsifier, 85 percent and 99.7 percent of the water had separated after 10 min and 40 min, respectively.

Baer, E. "A New Method of Treating Oil Emulsions in Effluents." Electroplating and Metal Finishing 18(6) (June 1965):201-203.

This article discusses a method and liquid "filter aid" used to improve de-watering (by filtration) of flocculated sludge formed during chemical (metal salt) demulsification.

Bailey, P.A. "The Treatment of Waste Emulsified Oils by Ultrafiltration." Filtration Society Symposium on Contamination, Filtration, and Disposal of Machine Tool Coolants, Birmingham, United Kingdom, September 28, 1976.

Ultrafiltration involves the use of semi-permeable membranes, generally fabricated from polymeric materials containing micropores of only tens of thousands of a micron in diameter. When emulsified oil is applied to the membrane under slight pressure, water molecules pass easily through the pores but the much larger emulsified oil particles are retained. As well as describing the principle of the process, the paper outlines practical applications, factors affecting performance, and economics.

Barker, J.E.; Foltz, V.W.; and Thompson, R.J. "Treatment of Waste Oil: Wastewater Mixtures." Chemical Engineering Progress Symposium Series 67(107) (1971):423-427.

The disposal of rinse water from the first and/or last stands of a cold-roll mill is disclosed. Small amounts of alum are used to initiate coagulation. Lime is used to promote growth of the oily floc. Air flotation, with periodic skimming of the oil, is used to separate the floc and water. The water is then sewered. The design capacity is 1500 gal/min. In 7 months of operation the plant has averaged 91 percent removal of total oil, 89 percent removal of COD and an effluent turbidity of 35 Jackson turbidity units. Oily scum (2000 to 12,000 gal/day) averaging 10 to 90 percent oil are removed daily and are used as road oil.

Bartkiewicz, B. (Politech, Warsaw, Poland). Gaz, Woda Tech. Sanit. 50(8) (1976):227-231.

Artificial emulsions of oil-in-water containing emulsifiers were treated in an electroflotation chamber with

a stainless steel cathode. The anode was either thick Al sheet or Pt-Ti wire net. A degree of purification of 99 percent was attained. When Pt-Ti anode was used, it was necessary to add $Al_2(SO_4)_3$ as a demulsifier. With the Al anode, the necessary Al ions were produced in anodic dissolution of the metal. The electrical conductivity of the solutions was increased through the addition of H_2SO_4.

Beaucaire, V.D. (Interlake, Inc.). U.S. 3,986,953 (Cl. 210-43; C02B1/20) (October 19, 1976), Appl. 456,689 (April 1, 1974):5 pp.

The oil and water emulsion is broken by waste pickling acid solution. The Fe in the waste pickling acid solution is then converted to magnetite particles which absorb the oil and then are separated. Thus, a light oil having an SUS viscosity at 100° F of 270 $\pm$ and a saponification number of $\pm$43 is treated with a pickling acid solution containing sufficient acid and Fe to break the emulsion, the pH of the solution is adjusted with lime to 7 to 12, and then oxygen is introduced under pressure to convert the Fe magnetite particles which absorb the oil.

Bhattacharyya, D.; Garrison, K.A.; Jumawan, A.B., Jr.; and Grieves, R.B. "Membrane Ultrafiltration of a Nonionic Surfactant and Inorganic Salts from Complex Aqueous Suspensions: Design for Water Refuse." AIChE Journal 21(6) (November 1975):1057-1065.

Complex aqueous suspensions containing a nonionic surfactant, phosphates, silicate, hypochlorite, oil, and kaolinite particulates are subjected to continuous flow membrane ultrafiltration with noncellulosic (Millipore PSAL) membranes. A detailed procedure is developed for scale-up of the thin channel unit to obtain the membrane area required, and resultant solute(s) rejections for any specified water recovery.

Bhattacharyya, D.; McCarthy, J.M.; and Grieves, R.B. "Charged Membrane Ultrafiltration of Inorganic Ions in Single and Multicomponent Systems." AIChE Journal 20(6) (November 1974):1206-1212.

An experimental study of the ultrafiltration of several ionic inorganic solutes (Na^+,Ca^{+2},Mg^{+2},La^{+3}/Cl^-,SO_4^{-2}, HPO_4^{-2},$H_2PO_4^-$,CrO_4^{-2},$HCrO_4^-$,HCO_3^-)using a Millipore PSAL (noncellulosic skin on cellulosic backing) negatively-charged membrane (pressure drop of 40 psi with a flow

of Reynolds number approximately equal to 2800). Tests were made on both single salt and multicomponent solutions.

For single salts, rejection fit the form $R = 1 - KC_i^a$ where $0 < a < 1.0$ ($a = 0.4$ for chlorides, 0.25 for monovalent oxyanion salts, 0.1 for divalent oxyanion salts), C_i is the inlet solute concentration, and K varies (usually below 0.4). With 2 or more salts, divalent ions significantly reduced the rejection of monovalent ions.

Bhattacharyya, D.; The, P.J.W.; and Grieves, R.B.

"Membrane Ultrafiltration to Treat Laundry Wastes and Shower Wastes for Water Reuse." University of Kentucky, Lexington, Kentucky.
An extensive experimental investigation is presented of the continuous flow, membrane ultrafiltration of (1) laundry wastes (containing linear alkylbenzene sulfonate anionic surfactants or linear alcohol ethoxylate nonionic surfactants), and (2) shower wastes. Several tight cellulose acetate (C.A.) membranes (Abcor, UOP, Gulf) and other polymeric membranes (Amicon, Millipore) are tested. C.A. membranes show poor rejection of anionic surfactants in the presence of phosphate, and practically no rejection of nonionic surfactants.

Formation of micelles at high surfactant concentration can produce a considerable flux drop due to concentration polarization.

Bilhartz, J.R. and Nellis, A.G., Jr. "Separating Oil, Water and Solids by Ultrasonic Treatment." U.S. 3,594,314 (Cl. 210-19; B 01d) (July 20, 1971), Appl. (February 12, 1969):7 pp.

This patent describes the process and apparatus for oil/water separations by subjecting waste materials to ultrasonic treatment at subcavitation power levels. After settling, the lower (aqueous) phase is further treated at cavitation power levels. Water and solids are separated by filtration or centrifugation.

Blair, C.M., Jr. "Prevention and Treatment of Petroleum Emulsions." Oil and Gas Journal 44(11) (July 21, 1945): 116-127.

This article summarizes the conditions that promote emulsion formation, and reviews the methods

used (1945) for breaking the (water-in-oil) emulsions. Film formation around water droplets is caused by natural emulsifiers in the crude (e.g., asphaltines), and is accompanied by a decrease in interfacial tension, resulting in formation of the emulsion. Other generalizations regarding emulsion formation are: (1) work, by agitation or turbulence, is necessary for formation, (2) petroleum emulsions tend to become more stable with age, and (3) oils exposed to O_2 tend to form more stable emulsions.

Three main classes of emulsion treating techniques are: (1) mechanical (sedimentation, filtration, centrifugation), (2) electrical, and (3) chemical (along with sedimentation). Each is described, with strengths and weaknesses of each method discussed.

Bradley, R.L.; Sadowski, A.J.; and Ballweber, E.G. (Nalco Chemical Co.). U.S. 3,956,117 (Cl. 210-43; B01D5/00) (May 11, 1976), Appl. 528,513 (November 29, 1974):4 pp.

Oil-in-water emulsions are broken by treatment with a polycationic water-soluble ionene polymer, which is prepared from trans-1,4-dichloro-2-butene (I) and dimethylamine with or without ethylenediamine. Thus, 187.5 g I was treated dropwise with 173 g 39 percent Me_2NH during 60 min at 30° to 35° C. The mixture was stirred 10 min, treated with 211.5 g 28.37 percent NaOH at approximately 44° and pH <10.0, heated 10 min at 45°, diluted with 220.8 g H_2O, and acidified to pH 5 to 6 with 8 g HCl to yield the trans-1,4-dichloro-2-butene-dimethylamine polymer (II) having intrinsic viscosity 0.12. An oil waste water emulsion (pH 9) from an automobile plant was adjusted to pH 5.5,treated with 35 to 80 parts per million II, and blended with alum and an acrylamide polymer. Absorbants readings taken 10 min after mixing indicated good resolution of the emulsion.

Breslau, B.R.; Agranat, E.A.; Testa, A.J.; Messinger,S; and Cross, R.A. "Hollow Fiber Ultrafiltration." Chemical Engineering Progress 71(12) (December 1975): 74-80. (Further information was obtained from a preprint by the same title and authors, from AIChE 79th National Meeting, Houston, Texas.)

This article describes Romicon's hollow fiber ultrafiltration membranes and systems. The various operation modes are explained, and cost data are presented. A

control study of protein recovery from cheese whey is presented.

Brumble, J.T. and Wilson, J.D. "Unique Design Helps Treat Hawkins Field Crude Oil." Oil and Gas Journal 70 (November 27, 1972):62-66.

This article describes a treating system designed to produce 80,000 bbl/day in Hawkins Field, Wood County, Texas. The process involves electric desalters, operating at 30 psi. The crude is washed with (recycled) fresh water (2400 bbl/day or 3 percent by volume) and passed through the desalters.

Brunsmann, J.J.; Cornelissen, J.; and Eilers, H. "Improved Oil Separation in Gravity Separators." Journal WPCF 34(1) (1962):44-55.

The installation of parallel plates in an oil separator used for treating refinery wastewater was found to improve its efficiency. Up to 60 percent further reduction in oil content was obtained. Two systems (with the plates in different configurations) were tested on both lab and full-scale experiments. The systems were evaluated based on overall oil reduction and particle size distribution of non-removed oil. [A method for determination of oil particle size distribution in a dilute, unstable system, is included in the Appendix.]

Buckley, J.D. "Reverse Osmosis: Moving from Theory to Practice." Consulting Engineer 45(5) (November 1975): 55-61.

The theory of reverse osmosis, as well as membrane configurations, are discussed. Several processes currently using reverse osmosis units are mentioned. Capital and operating costs are presented.

Buriks, R.S. and Fauke, A.R. (Petrolite Corp.). "Use of Polymeric Quaternary Ammonium Betaines as Water Clarifiers." U.S. 3,929,635 (Cl. 210-54; B01D) (December 30, 1975), Appl. 227,261 (February 17, 1972):10 pp. Division of U.S. 3,819,589.

Polymeric quaternary betaines not containing inorganic anions and useful for coagulating oils or solids in clarifying water were prepared by treating maleic anhydride-vinyl monomer copolymers with tertiary amines and alkylene oxides. Thus, a mixture of diisobutylene and maleic anhydride in PhMe containing $(Me_2CCN)_2N_2$

was heated at 90° for 4 hours to give 83.5 percent diisobutylene-maleic anhydride copolymer which was treated with trimethylamine and ethylene oxide under pressure at 55° to give 95 percent betaine. Similarly, 6 other polymeric betaines were prepared. Stirring FeS suspension in brine with 2 to 4 ppm of these polymers gave separable FeS floc. The polymers were also successfully used to break oil-in-water emulsions from crude petroleum storage tanks.

Cash, R.L.; Cayias, J.L.; Fournier, R.G.; Jacobson, J.K., Schares, T.; Schechter, R.S.; and Wade, W.H. "Modeling Crude Oils for Low Interfacial Tension." Society of Petroleum Engineering Paper No. 5813, Improved Oil Recovery Symposium, Tulsa, Okla. (March 22-24, 1976).

Based on the correlation of interfacial tension (IFT) behavior for three homologous series of hydrocarbons and a simple, mole fraction averaging procedure, it was found possible to predict IFT's for complex hydrocarbon oil/aqueous surfactant mixtures. This leads to a validation of the equivalent alkane carbon number (EACN) concept for a mixed hydrocarbon oil phase. The EACN for eight crude oils was determined, and it was found that the IFT of crudes can best be modeled by alkanes in the range of hexane to nonane.

Cash, L.; Cayias, J.L.; Fournier, G.; Macallister, D.; Schares, T.; Schechter, R.S.; and Wade, W.H. "The Application of Low Interfacial Tension Scaling Rules to Binary Hydrocarbon Mixtures." Journal of Colloid and Interface Science 59(1) (March 31, 1977): 39-44.

This article reports continued work (Cayias et al.) on correlating surfactants with low interfacial tension (IFT) in hydrocarbon-water mixtures. Scaling rules were inferred previously: for a given surfactant and brine concentration, if the C_m alkane results in an IFT minimum, then a C_m side chain on alkylbenzenes and C_{m-4} side chain on cyclohexane also give IFT minima. (For work with 1 percent NaCl and 0.2 percent Witco 10-80, m is equal to or greater than 8.

Results from similar tests with binary mixtures of hydrocarbons (from the same and different homologous series) indicate that $C_{AVG} = X_A C_A + X_B C_B$ (X_i = mole fraction) of these mixtures obeys the above laws, with m = 7.7 to 8.0.

Cayias, J.L.; Hayes, M.E.; Schechter, R.S.; and Wade, W.H. "Surfactant Aging: A Possible Detriment to Tertiary Oil Recovery." Journal of Petroleum Technology (September 1976):985-988.

This articles describes tests made on aqueous surfactant/ hydrocarbon emulsions designed to find a relationship between interfacial tension (IFT) and surfactant age. Temperature effects are also examined.

Results indicate a general rise in IFT with surfactant age, with the minimum IFT being measured with lower molecular weight species of homologous hydrocarbon series. Temperature had little effect.

Cayias, J.L.; Schechter, R.S.; and Wade, W.H. "The Measurement of Low Interfacial Tension via the Spinning Drop Technique." ACS Symposium Series, No. 8. "Adsorption at Interfaces" (1975).

This article reviews the techniques of using the "spinning drop interfacial tensiometer" for measuring the interfacial tension (IFT) between two immiscible liquids. Calculations are presented that allow one to determine the IFT by measuring the length and width of a drop of the less dense liquid (elongated by rotating in a capillary tube while surrounded by the denser liquid).

Cayias, J.L.; Schechter, R.S.; and Wade, W.H. "The Utilization of Petroleum Sulfonates for Producing Low Interfacial Tensions between Hydrocarbons and Water." Journal of Colloid and Interface Science (59)1 (March 15, 1977): 31-38.

This article reports experiments with various petroleum sulfonate (commercial) surfactants and homologous hydrocarbon series, designed to find correlations between achieving low interfacial tension (IFT) and the mixture composition.

Shell Oil Company "Martinez 470" (molecular weight 470) and Witco TRS 10-80 (M.W. 425) sulfonates were tested on series of n-alkanes, n-alkylcyclohexanes, and n-alkylbenzenes. Pronounced IFT minima were observed as a function of surfactant concentration (at 1 percent NaCl constant). For a given surfactant and brine concentration, specific members of each homologous series showed IFT minima. Higher M.W. surfactants resulted in a higher M.W. hydrocarbons showing these minima.

Chambers, D.B. (Imperial Chemical Industries Ltd.). "Separation of Oil from an Oil-In-Water Emulsion." Ger. Offen. 2,546,043 (Cl. B01D17/00) (April 22, 1976), Appl. 74/44,395 (October 14, 1974):15 pp.

Fibrous Al_2O_3, ZrO_2 and asbestos, that show positive zeta potential and have a large surface area, are effective materials in breaking negatively charged oil/water secondary emulsions. Al_2O_3 is best at pH <8.5, ZrO_2 at pH <7.7, while asbestos is not affected by pH. The surface area of Al_2O_3 is 100 to 150 m^2/g, and that of ZrO_2 5 to 15 m^2/g. The optimum diameter is 0.5 to 5 microns, with <20 percent of the fibers having diameter of >5 microns. Less than 1 percent should be nonfibrous. The fibers are in the form of a fabric, sandwiched between sheets of woven material, or preferably in the shape of a pipe. For difficultly coagulating oil particles, the emulsion is passed through a three-component structure consisting of inorganic fibers in contact with loosely bonded nonwoven and with another layer of firmly bonded nonwoven sheet.

Chojnacki, A. and Bartkiewicz, B. (Politech, Warsaw, Poland). "Removal of Surface Active Substances from Sewage Containing Emulsion Salts." Zesz. Nauk. Politech. Slask., Chem. 64A (1973):47-59.

Oil-water emulsions are broken by treatment with aqueous $MgSO_4$ and lime milk. Surfactants are removed by coagulation with $FeCl_3$, $FeSO_4$, and $Al_2(SO_4)_3$.

Christ, W.; Cyprian, J.; and Gasser, A. "Separation and Purification of Spent Oil Emulsions and Oil-Containing Waste Waters." Wasser, Luft. Betr. 12(12) (1968): 755-757 (German).

The dissociation of oil emulsions by addition of salts (with or without heating), acids, demulsifers, adsorption agents, and subsequent separation of the oil and aqueous phases with filters and separators, is discussed. After the breaking-up of the emulsion with Fe or Al salts, the solution is mixed with NaOH and subjected to flotation by flocculants. After separation of the phases, H_2O is discarded without further treatment. Oil is separated from sludge and recycled in the floation apparatus. If the emulsion contains <1 g/l oil, medium to heavy oil may be added. The oil-containing sludge is combusted. The residual oil content in the separated, nontoxic H_2O is 5.35 mg/l at pH 7.

Churchill, R.J. and Kaufman, W.J. "Waste Processing Related Surface Chemistry of Oil Refinery Wastewaters." SERL Report No. 73-3 (August 1973).

The surface chemical properties of crude oils were investigated with the objective of improving the performances of oil refinery pretreatment processes. The investigation included batch studies in "clean," chemically well-defined systems as well as continuous flow pilot plant studies on a "typical" refinery wastewater. Particular attention was directed to emulsion stabilization/destabilization.

Interfacial tension and electrostatic charge effects were investigated as factors promoting stability in crude oil-in-wastewater emulsions. Both are effective stabilization mechanisms in that, when charge effects are minimized, interfacial tension inhibits droplet coalescence and the droplets retain their individual identity. Several physicochemical parameters of the water phase were investigated and it was found that pH exerts the most profound influence on the interfacial tension and mobility resulting from its effect on crude oil surfactants. A model was developed which provides further insight into the nature of indigenous crude oil surfactants and is related to the asphaltene and resin content of the crude oil.

The use of chemical coagulants for oil removal was investigated and the hydrolyzing coagulants, Al(III) and Fe(III) performed most satisfactorily achieving oil removals in excess of 95 percent. Among those parameters indicated to be of paramount importance in obtaining maximum oil removal were segregation in initial mixing, pH of the initial coagulant solution, coagulant dose, and flocculation intensity. Several mechanisms of coagulation by hydrolyzing coagulants are indicated, primarily as a function of pH of the water. Oil removal using several commercial "demulsifier" compounds was also investigated and found to be generally inferior to the hydrolyzing coagulants alone. Similar results were obtained for polyelectrolytes, even when used as coagulant aids.

Pilot plant studies were conducted for those coagulants which performed well in the batch tests. This series of tests generally confirmed the earlier results. Several batch tests were conducted employing dissolved air flotation to remove the flocculated oil droplets. Performance was superior to that obtainable by simple gravity separation.

This project was supported in part by a grant from the National Wildlife Federation and the American Petroleum Institute.

Cole, E.A.; Mayse, W.D.; and Watson, F.D. (Petrolite Corp.) "Electric Treatment of Dispersions." U.S. 3,701,723 (Cl. 204-188; B 03c, B 01d) (October 31, 1972), Appl. 844,963 (July 25, 1969):5 pp.

An apparatus for coalescing liquid droplets (e.g., H_2O) dispersed in an oil distillate (e.g., gasoline or kerosine) is discussed. The coalesced liquid is maintained within the distillate and is separated from the distillate downstream of the coalescing electrodes.

Cooke, B. "Oil/Water Emulsions - a Crackdown on Process Wastes." Process Engineering (April 1974):64-65.

This article describes several techniques used for breaking oil/water emulsions. Several chemical approaches are mentioned, including (1) acid and flocculating agent (HCl or H_2SO_4/alum or ferric sulphate), (2) divalent salts, and (3) organic polyelectrolytes. Other methods mentioned are distillation, electroflotation, and fibrous bed breakers.

Coppel, C.P. "Factors Causing Emulsion Upsets in Surface Facilities Following Acid Stimulation." Journal of Petroleum Technology (September 1975):1060-1066.

Severe emulsion problems following acid treatment of wells are caused by the presence of solid materials. Precipitates formed in the spent acid after commingling are the most serious problem. Produced formation fines also contribute significantly to the problem.

Del Pico, J. and White, P.W. "Reverse Osmosis and Ultrafiltration, Methods of Treating Waste Water." Metal Finishing 72(8) (August 1974):29-31.

This article was written by two men from Abcor, Inc. The article is a brief overview of ultrafiltration and reverse osmosis processes and membranes. Similarities and differences (flux, pressure, etc.) between ultrafiltration and reverse osmosis are discussed. Membranes are classified as either "open" (tubular) or "compact" (hollow fiber, spiral wound) configuration. Economic rule-of-thumb guidelines are presented.

"Demulsifier Saves Oil, Reduces Pollution." Marine Engineering/Log 70(2) (February 1965):82.

This article discusses the chemical demulsifier Breaxit 7941, developed by the Esso Research and Engineering Company. Separations yield water with less than 100 ppm oil, and oil with less than 1 percent water. Laboratory and shipboard tests have been conducted.

Deutsche Gold- und Silber-Scheideanstalt vorm. "Treatment of Oil Emulsions." Roessler Fr. 1,535,801 (Cl. C 02c) (August 9, 1968), Ger. Appl. (July 22, 1966):5 pp.

The oil is separated from the H_2O by addition of salts of fatty acids or polyvalent metals. Adsorption agents suitable to the type of oil in the emulsion are used to precipitate it. Typical ratios of both additives are given along with 5 examples.

Doe, P.H. and Wade, W.H. "Alkyl Benzene Surfactants for Producing Low Interfacial Tensions Between Hydrocarbons and Water." Journal of Colloid and Interface Science 59(3) (May 1977):525-531.

The effectiveness of various alkyl benzene sulfonates in reducing hydrocarbon-water interfacial tensions (IFT) to very low values is examined. Alkyl chain length and benzene ring position are varied. Effects of salt concentration and presence of alcohols are mentioned.

Optimum salt concentrations (for IFT minimum) exist for any single hydrocarbon, with that optimum concentration increasing for higher-weight hydrocarbons of a homologous series. Water-insoluble compounds can be solubilized by adding alcohol. Alcohols also shift the hydrocarbon number of minimum IFT. Minimum IFT shifts to higher molecular weight oils as surfactant molecular weight increases. Solubility is promoted by low molecular weight surfactants, but higher molecular weight surfactants yield low IFT.

Dow, D.B. "The Formation of Oil-Field Emulsions." U.S. Bureau of Mines R.I. 2683 (March 1925).

In any well that produces water along with oil (primary recovery), emulsification can be a problem. Once water has entered the well (from any source), agitation results in emulsion formation. Emulsion formation usually results in additional expense for dewatering. (Part 1 of a 3-part study of oil field emulsions)

Dow, D.B. "Methods Used for Dehydration of Oil-Field Emulsions." U.S. Bureau of Mines R.I. 2688 (May 1925).

This article reviews the techniques used (note this was written in 1925) for dehydrating oil field emulsions. Methods discussed are: settling, heat treatment, chemical treatment (including a discussion of Tret-O-Lite), centrifugation, electrical dehydration, and filtration. (Part 2 of a 3-part study of oil field emulsions)

Dow, D.B. "Oil-Field Emulsions." U.S. Bureau of Mines Bulletin No. 250 (1926).

The information given in this paper may be summarized as follows:

(1) In the eastern fields of the United States there is little difficulty with cut oil, but in the Mid-Continent, Gulf Coast, and California fields probably one-fifth of the crude oil production is cut enough to require treating.

(2) In any field that produces water with the crude a condition favoring emulsification exists. Cutting depends upon two general factors, the nature of the crude and mechanical agitation in the process of production, whether wells are flowing or produced by the air-lift method, by the swab, and by pumping.

(3) Altering production conditions so that agitation of the oil and water are decreased while they are being raised to the surface can frequently prevent the formation of cut oil.

(4) Cut production may be treated by any of several methods developed for the dehydration of petroleum emulsions. These methods include (a) mechanical separation, (b) dehydration by heat, (c) chemical dehydration, (d) electrical dehydration, and (e) a combination of two or more methods.

(5) The fundamental physicochemical laws governing the formation of emulsions are considered theoretically with special reference to crude oil emulsions.

(6) Different methods of treating are discussed with reference to their applicability to oils of varying characteristics. A classification of different cut oils is made which should guide the producer in the selection of the correct treating process for his crude.

Dow, D.B. and Reistle, C.E., Jr. "The Physical Chemistry of Oil-Field Emulsions." U.S. Bureau of Mines R.I. 2692 (June 1925).

The laws governing the formation and resolution of oil field emulsions fall under that branch of physical chemistry dealing with colloids. The principles developed through work on commercial and pharmaceutical emulsions apply in a general way to oil field emulsions. (Part 3 of a 3-part study on oil field emulsions)

Eddy, W.G. and Eddy, H.C. "Discussion on Electrical Dehydration of Crude Oil." Industrial and Engineering Chemistry 13(11) (November 1921):1016-1017.

This article describes the theory of separating water/oil emulsions in an electric field, and also describes a typical electric dehydrator. Temperature influence is mentioned as a function of oil qualities. A typical oilfield installation is mentioned.

"Emulsion-Breaking Chemical Separates Oil from Water." Chemical Engineering 77(24) (November 2, 1970):58.

This article discusses "Nalco 7716," a nonionic polymeric polyester type compound, designed to break water-in-oil emulsions, at any pH.

Entwicklungs- und Forxchungs-Anstalt. "Removal of Oil from Waste Water." Fr. 1,505,006 (Cl. C 02c) (December 8, 1967), Austrian Appl. (December 21, 1965):7 pp.

The oil which forms an emulsion with waste water could not be removed from water under 300 mg/l. In this new process, the waste water containing oil is made alkaline and injected with pure oil and a Fe^{+3} solution in a separating container. After vigorous agitation the oil is absorbed by the flocculated hydrated Fe^{+3} and reaches the surface. The water stays in the lower layer and is clearer. This water is then reinjected with a separating agent (aqueous suspension of Fe hydrates and oil, stabilized with MgO) in a second container. After shaking and separation the purified water is still in the lower layer and the oil concentration is between 11 and 13 mg/l. The hydrated Fe^{+3} produced during the first part of the process can be used in the separating agent.

Evers, R.H. "Mixed-Media Filtration of Oily Waste Waters." Journal of Petroleum Technology (February 1975):157-163.

Mixed-media filters have been proven effective in oily waste-water filtration. Examples are given of uses with oilfield-produced water, refining waste waters, etc.

Mixed-media filters are composed of several materials, each of different size and density, to provide a filter that is coarse-to-fine in the direction of flow.

Feldman, N. (Exxon Research and Engineering Co.) "Removing Water Haze from Distillate Fuels." U.S. 4,002,558 (Cl. 208-188; C10G33/04) (January 11, 1977), Appl. 651,405 (January 22, 1976):4 pp.

The separation of undesirable haze (due to emulsified H_2O) present in distillate fuels is accelerated by the addition of an aliphatic hydroxy compound containing 5 to 10 weight percent of an inorganic salt (e.g., $MgCl_2 \cdot 6H_2O$(I), $Ni(NO_3)_2 \cdot 6H_2O$, $CaCl_2$, $CdCl_2 \cdot [2.5H_2]$. Suitable aliphatic hydroxy compounds include MeOH, EtOH, ethylene glycol, and ethylene glycol monomethyl ether. Thus, 800 ml diesel fuel was emulsified with 0.4 ml H_2O, and the rate of breakup of the emulsion was determined spectrophotometrically by measuring the amount of light transmitted through the sample. The light transmittance increased from 46 to 54 percent in 6 hours. When the emulsified fuel was mixed with 0.2 volume percent MeOH containing 5 weight percent I, the transmittance was 97 percent after 6 hours.

Firma Oto Duerr. "Separation of Oil and Water in an Oil Emulsion." Ger. Offen. 2,138,035 (Cl. C 02c, B old) (February 8, 1973), Appl. P 21 38 035.8 (July 29, 1971): 9 pp. Addition to Ger. Offen. 1,924,527.

Oil is separated from water by adding Fe, Al, or Mg hydroxides, polyelectrolytes, and a SiO_2 suspension, mixing with air in a loop reactor, removing the oil-containing sludge formed by flotation on the surface of the liquid and optional treatment in a second loop reactor for further purification of the liquid.

Fischer, G. and Schmittel, H.W. (Deutsche Abwasser-Reinigungs G.m.b.H.) "Removal of Oil From Oil-Water Emulsions." Ger. Offen. 1,912,658 (Cl. B Old) (October 1, 1970), Appl. (March 13, 1969):17 pp.

Oil-water emulsions, acidified to pH 3.5 to 4.5 with HCl solution, are treated with aqueous $Al_2(SO_4)_3$ solution acting as a demulsifier and adsorbent. The mixture is transferred to a neutralization tank, stirred with

aqueous NaOH solution causing the $Al(OH)_3$ adsorbent to be precipitated, and transferred to a settling tank containing outlets for the clarified water and adsorbent.

Fluid Systems Division, UOP, Inc. "Waste-Treatment Applications of Reverse Osmosis." A.S.M.E. Intersociety Conference on Environmental Systems, Seattle, Washington (July 29 to August 1, 1974). Paper No. 74-ENAS-41.

This paper describes two reverse osmosis waste-treatment plants being constructed (1974) and one in operation. Pilot work in several other areas, including oil-water separation (marine applications) is also described. Capital and operating costs are presented.

Fowler, L.L. "Cell Having Catalytic Layer for Coalescing Oil Droplets." U.S. 3,980,565 (Cl. 210-489; BolD27) (September 14, 1976), Appl. 202,378 (November 26, 1971):4 pp.

A cell is described for separating oil in water emulsions including provision of a catalytic means for enhancing the rate of coalescing of finely dispersed oil droplets. It comprises an elongated perforated core in which the emulsion is injected, a layer of emulsion breaking fibrous material wound about the core through which the emulsion passes, and a catalytic layer of porous material wound about the layer of fibrous material, the catalytic layer being formed of a porous flexible substrate having sprayed on particles of molten metal (Cu, Sn, Al, Ni, Zn, and alloys).

Friberg, S. "Microemulsions and Their Potentials." Chemical Technology (February 1976):124-127.

This article gives a brief overview of microemulsions - formation and potential applications. Water and certain surfactants, individually, may be insoluble in organic liquids, but together, in the proper proportion, may blend to spontaneously form (thermodynamically stable) microemulsions. High concentrations (about 15 percent by weight) of ionic surfactants are required. Lower concentrations (about 5 weight percent) of non-ionic surfactants can be used. Applications discussed include tertiary oil recovery, octane improvement (water-soluble additives), replacing diesel fuel (to cut down NO_x emissions) and for use with chemical processes to allow use of more varied catalysts.

Friberg, S. and Mondell, L. (Laboratory of Surface Chemistry, Royal Academy of Engineering Science, Stockholm,

Sweden). Phase Equilibria and Their Influence on the Properties of Emulsions." Journal of American Oil Chemists' Society 47(5) (May 1970):149-152. (English).

Phase diagrams of water-emulsifiers-oil systems have been investigated. Not only the association of the three materials into liquid crystal phases has an effect on the properties of the emulsion but also the association into micelles of the emulsifier in the oil phase influences both the type and the stability of the emulsion.

Fuji, H. "Separation of Oil Dispersions from Water by Fibrous Bed Coalescence." Kagaku Sochi 15(7) (1973):68-72. (Japanese)

Artificial oil dispersions and actual waste waters were tested in a 1-foot-square coalescer having a filter-press structure. By using commercial glass fibers (3.2 m diameter) coated with phenol-formaldehyde resin, the oil removal was nearly 100 percent at 7.5 gal/min flow rate. The oil content was reduced from 10-85 to 0-3 ppm. The pressure decrease during experiments was mainly due to the accumulation of oil in the bed and the mechanical deterioration of fibers. The service life of the bed, i.e., the performance of the coalscer, was dependent on the water temperature.

Furnes, C.D. and Allanson, J.T. (Simon-Carves Ltd.). "Treatment of Oily Sewage." Ger. Offen. 1,803,229 (Cl. C 02c) (May 14, 1969), British Appl. (October 13, 1967):17 pp.

The oil content of sewage is described by applying a potential difference to sets of electrodes immersed in the sewage. The electrolytically produced gas carries oil droplets to the surface. With sewage containing up to 2 percent oil, the cathode current density lies at 6.2×10^{-5} 6.2×10^{-4} amp/cm^2. With oil contents of 23.8 to 70 percent the current density lies at 0.00032 to 0.0011 amp/cm^2. Thus, in a 36.4 liter container there was a single, horizontal Al cathode 57.2 x 29 cm. This was separated by a gap of 1.9 cm from vertical steel anodes each 29 x 3.8 cm. The potential difference was 5 v. and the current was 0.2 amp giving a cathode current density of 0.00012 amp/cm^2. Oily sewage containing 350 ppm of oil was adjusted to pH 8 with NaOH. After 15 min in the device the sewage was cloudy

and contained 50 ppm of oil, while after 60 min it was clear and contained 20 ppm of oil.

Gale, W.W. and Sandvik, E.I. "Tertiary Surfactant Flooding: Petroleum Sulfonate Composition - Efficacy Studies." Society of Petroleum Engineers Journal 13(4) (August 1973):191-199.

This paper discusses results of a lab program to define optimum petroleum sulfonates for use in surfactant flooding. Four major criteria are: (1) low oil-water interfacial tension(IFT), (2) low adsorption, (3) compatibility with resevoir fluids, and (4) low cost.

Low IFT's are obtained using high equivalent weight (EW) components. Increased brine concentration and increased aromatic content also give lower IFT. However, high EW components exhibit high adsorption (causing large losses). Lower EW components, while showing high IFT's, suffer less from adsorption, due to increased water solubility.

Gandurina, L.V.; Zubakova, L.B.; Myasnikov, I.N.; Butseva, L.N., Zhovnirovskaya, A.B.; and Ledeneva, V.V. (USSR). "Use of Water-Soluble Polyelectrolytes for Purifying Petroleum-Containing Waste Waters." Plast. Massy 5 (1976):59-61. (Russian).

Petroleum-containing waste waters were purified by cation exchange flocculants, alone or with $Al_2(SO_4)_3$. Flocculant-polyelectrolytes of VPS series, based on vinylpyridine were used. Combined use of $Al_2(SO_4)_3$ and VPS-47 was the most effective at optimum doses of 50 g $Al_2(SO_4)_3$ and 2 g flocculant/liter. The use of the flocculant alone required a long time for waste water settling. To shorten this time, flocculation was combined with filtration. The VPS-11, molecular weight 726,000, has superior water purification efficiency, as compared to VPS-11, molecular weight 112,000. VPS-11, based on 2-methyl-5-vinylpyridine and with molecular weight $\geq$700,000, is the most efficient in waste water treatment by flotation.

George, A.L. and Manning, J.C. (George, Al, Inc.). "Method and Apparatus for Clarifying Contaminated Liquids." U.S. 3,986,954 (Cl. 210-44; B03D1/24) (October 19, 1976), Appl. 578,424 (May 19, 1975):15 pp.

The separation of contaminants in aqueous suspension,

e.g., petroleum-water emulsions, is aided by decreasing the specific gravity of the contaminants. The suspension is mixed with a gas and then pumped under pressure through a small orifice. As the suspension enters the large chamber, minute bubbles form which adhere to the particles, causing them to float. After passing through chambers designed for quiescent flow, the floating material is trapped in a trough and removed. The clarified liquid is removed through a pipe located below the sludge-collecting trough. Recirculation is possible to increase removal efficacy. Flow rates are controlled by valves in the feed and discharge lines.

Ghisalberti, F. (Ghisalberti S.P.A.). "Apparatus and Method for Breaking and Treating Stable Emulsions." Ger. Offen. 2,623,439 (Cl. BolD17/00) (December 16, 1976), Italian Appl. 75/12,627 (May 28, 1925):10 pp.

Emulsions are broken in a three-compartment apparatus by applying a d.c. current to Al electrodes. The coagulated emulsion moves to the bottom of a compartment with an inverted cone shape where it travels upwards. It then flows over the edge and drops to the inclined bottom of the surrounding third compartment from where it is pumped to a sand filter. The clarified water collects in a trough around the edge of the third compartment.

Goldsmith, R.L. "Macromolecular Ultrafiltration with Microporous Membranes." Ind. Eng. Chem. Find. 10(1) (November 1, 1971):113-120.

The mechanism of macromolecular ultrafiltration with microporous membranes is discussed, focusing on factors controlling flux (mass transfer on the feed side due to Reynolds number and concentration polarization) and solute retention (membrane pores). Data for turbulent and laminar flow, stirred-cells, and theoretical predictions are presented. Equipment and membranes are from Abcor, Inc. Studies were done on prepared solutions of Dextran (polysaccharides), fractions (Pharmacia Fine Chemicals, Inc.), and Carbowax 20M (a polyethylene glycol fraction from Union Carbide Corp.).

Goldsmith, R.L.; Roberts, D.A.; and Burne, D.L. "Ultrafiltration of Soluble Oil Wastes." Journal WPCF 46(9) (Sept. 1974):2183-2192.

Soluble oil wastes from General Electric's Lynn, Massachusetts plant were tested. Flux rates as a function of

oil concentration, pressure, temperature, and time were measured. The waste oil, containing 1 to 3 percent oil, is produced in metal cutting operations. Based on the experimental data, a plant for handling 4,000 GPD was built.

Goldsmith, R.L. and Schrab, H. (Abcor, Inc.). "Ultrafiltration Concept for Separating Oil from Water." (NTIS AD 758 - 318.) Cambridge, Massachusetts, 1973.

Study of ultrafiltration for U.S. Coast Guard. Ultrafiltration with 1-inch diameter tubular membranes produced highly-purified water from oil emulsions. For kerosine, No. 6 Fuel Oil, Venezuelan crude, and lubricating oil at input ratios of 100 ppm to 90 percent, treated water was uniformly free of visible oil and had less than 10 ppm oil. Ultrafiltration rate depended on oil type, input ratio, and operating conditions. Rates were typically 50 to 150 gallons/ft^2/day, but decreased with time due to fouling. Factors which increased emulsion stability or reduced concentration polarization minimized fouling.

Cost and physical requirements for systems of 10, 100, 1000, and 10,000 gpm were estimated for membranes in tubular and spiral wound configurations. The latter, not tested, is favored because of lower cost weight, power, and space requirements.

Goto, Y.; Daigo, Y.; and Murata, M. (Somar Mfg. Co., Ltd.). "Removal of Emulsified Oil by Filtration." Japan Kokai 75,142,491 (Cl. BolD, C09K) (November 17, 1975), Appl. 74,50,093 (May 2, 1974):4 pp.

Filters for separating oils from oil emulsions are prepared by adhering a hydrophobic synthetic fiber layer to porous materials consisting of sinterable polyethylene powder, F-containing resin powder, or mixed powder of both. Optionally, a hydrophobic synthetic fiber layer containing hydrophilic fibers may be used. This filter has high oil-removal efficiency; the concentration of oil in the resulting filtrate is decreased to <5 ppm. Thus, a super high-molecular-weight polyethylene powder (density 0.94 g/ml, melt-index <0.01 degree/min, melting point 130 to 138°C) was sintered at 250° to form a porous material with 65 percent porosity; to this porous material was adhered a layer of mixed cloth consisting of polyester fiber 65 and cotton fiber 35 percent to form a filter.

Green, E.B.; Lyborger, J.H., and Richardson, E.A. "In-Situ Acid Neutralization System Solves Facility Upset Problems." Journal of Petroleum Technology (October 1974):1153-1155.

The results of several field tests indicate that in-situ neutralization of unspent acid is effective in minimizing acid emulsion upset problems. The technique, based on the acid-consuming hydrolysis reactions of urea and various amides, can be pH controlled to return fluids amenable to conventional demulsification.

Emulsion formation in acid-stimulated wells is discussed.

Grieves, R.B.; Bhattacharyya, D.; Schomp, W.G.; and Bewley, J.L. "Membrane Ultrafiltration of a Nonionic Surfactant." AIChE Journal 19(4) (July 1973):766-774.

Aqueous solutions (1.65×10^{-4} to 1.10×10^{-2} M) of the nonionic surfactant Triton X-100 are subjected to membrane ultrafiltration over a temperature range of 22 to 50°C in a continuous flow, thin channel cell, with Reynolds numbers from 50 to 1175. Flux data is used to estimate the required membrane area and resultant ultrafiltrate concentration of surfactant to achieve any specified water recovery using series or parallel operation.

Guetling, W. "New Processing Method for Oil-Containing Wastewaters." Ind. Anz. 97(44) (1975):872-874. (German).

An ultrafiltration plant is described and illustrated. The effects of various parameters (e.g., temperature, pH) on capacity are discussed.

Guettinger, R. "Definition and Theory of Emulsions." Kosmet. Aerosole 45(6) (1972):148-151. (German).

A theoretical discussion of oil-in-water and water-in-oil emulsions is presented.

Halladay, W.B. and Crosby, R.. "Current Techniques of Treating Recovered Oils and Emulsions." Proc., American Petroleum Institute 44(III) (1964):68-73.

In 1962, the API Committee on Disposal of Refinery Wastes sent out a questionnaire regarding practices employed by refineries in treating recovered oils and emulsions. Fifty-two refineries (representing 29 oil

companies) responded. The systems can be classified as one of the following:

Cold and/or hot settling
with or without chemicals added
followed by filtration, centrifugation
or fractionation.

Special "tricks" -
recycling
hot water washing
adding off-specification oils
electric de-salters

Each of nine processes is described, and the questionnaire data are tabulated.

Havens, G.G. and Guy, D.B.. "The Use of Porous Fiber Glass Tubes for Reverse Osmosis." Chemical Engineering Progress Symposium Series 64(90) (1969):299-304.

This article discusses tests of OSMOTIK cellulose acetate membranes, using reverse osmosis for desalting operations. Many possible applications of reverse osmosis are listed. Data are somewhat outdated.

Hayano, W.; Kamogawa, K; and Yoshida, T. (Nippon Oils and Fats Co., Ltd.). "Oil-Water Separation from Emulsions." Japan. Kokai 73 44,858 (Cl. 72 Ca, 72 C35) (June 27, 1973), Appl. 71 78,918 (Oct. 7, 1971): 3 pp.

An Al electrode was immersed in an emulsion-containing surfactant and a d.c. potential was applied to separate oil from the emulsion. Thus, 1 l. waste rust preventive oil (containing kerosine, octyl alc., poly-(oxyethylene) alkylphenyl ether, and lecithin) was mixed with 1.0 percent NaCl and 0.5 percent $Al_2(SO_4)_3$, a 4 x 5 cm Al plate electrode was immersed, and d.c. potential (5 v, current density 0.5 A/cm^2) was applied for 10 min to separate an $Al(OH)_3$ floc-containing oil layer and a water layer.

Healy, R.N. and Reed, R.L. "Physicochemical Aspects of Microemulsion Flooding." Society of Petroleum Engineers Journal 14(5) (October 1974):491-501.

Whenever water, an oil, and a surfactant equilibrate at a surfactant concentration >critical micelle concentration, one or more microemulsions form. Ternary diagrams have been constructed for three specific microemulsion systems, (90 percent Isopar M, paraffinic - 10 percent

heavy aromatic naphtha oil mixture, an akyl-aryl-sulfonic acid surfactant, Exxon sulfonate FA-400, brines with Na^+ and/or Ca^{++} salts), showing the effects of salinity and cosurfactant on phase behavior, viscosity, restivity and interfacial tension (IFT). Experimental techniques are described for minimizing the extent of the multiphase region and measuring very low IFT.

Healy, R.N.; Reed, R.L.; and Stenmark, D.G. "Multiphase Microemulsion Systems." Society of Petroleum Engineers Journal 16(3) (June 1976):147-60.

Ternary microemulsion phase behavior (water/brine-oil-surfactant) is conveniently classified as Winsor's (1954) type I (excess oil/microemulsion), type II (3 phase) or type III (excess water). Effects of salinity, temperature, oil and surfactant composition and cosolvent are presented with respect to phase behavior of microemulsions. Alkyl aryl sulfonate surfactants are used.

Increasing salinity causes changes of type I to type II to type III, with decreasing microemulsion/oil interfacial tension (IFT) and increasing microemulsion/water IFT. S$\underline{q}$, optimal IFT, where $\underline{q}_{mo} = \underline{q}_{mw}$, might be a favorable operating point in oil recovery operations.

Heinze, E. (Firma Otto Duerr). "Removal of Oil from Aqueous Emulsions." Ger. Offen. 2,162,564 (Cl. C02c, B 01d) (June 28, 1973), Appl. P 21 62 564.9 (December 16, 1971):15 pp. Addition to Ger. Offen. 2,138,035 (CA 78: 161525a).

Oil was removed from aqueous emulsions (e.g., waste defatting baths or cutting oils), by addition of a mixture (equal volume parts) of used oil and 10 to 20 percent metal salt (e.g., $FeCl_3$, $MgCl_2$, Fe sulfate) solution with vigorous mixing at alkali-adjusted pH 7 to 12 for emulsion breaking and flocculation followed by phase separation in a two-step process. The mixing was performed in loop reactors with compressed air-water injection and the oil sludge was removed by flotation.

Hentschel, M.L. and Cox, T.L. "Effluent Water Treatment at Charter International Oil Company's Houston Refinery." AIChE Symposium Series 70(136) (1974):638-44.

Wastewater treatment at the Charter International Oil Company refinery in Houston features a 65,000 bbl/day (oil production) Infilco Aero-Acceltor activated sludge biological unit. Primary clarification has reduced solids 52 percent and extractable oil 82 percent. The biological unit reduces oil to approximately 1 mg/l. Performance as affected by sulfides, phenols, NH_3, oil, and flow rate is discussed. Cost data are presented. Capital costs were >$1 million (1965-70). Current operating costs are approximately 25.8 cents/1,000 gallons treated (at 1,110 gal/min flow rate).

Herce, J.A. and Heath, J.E. (Shell Oil Company). "Continuously Separating Emulsions." U.S. 3,996,157 (Cl. 252-325; B01D15/02) (December 7, 1976), Appl. 271,441 (July 13, 1972):8 pp. Division of U.S. 3,869,408.

In a method useful in treating oil discharges for recovery of oil and purified H_2O, liquid-liquid emulsions are separated by treating the emulsion with a liquid suspension of nongranular, discrete, 100 to 10,000 micron cellulose fibers to give a continuous phase and an essentially fiber-free disperse phase. Thus, adding 500 ml/min emulsion of 500 ppm 2 to 10 micron droplets of 35° API crude oil (viscosity 1 to 2 cp) in 10 percent $NaCl$-$CaCl_2$-$MgCl_2$ solution (simulated oilfield brine) to a reactor stirred at 110 to 120 rpm containing 25 g shredded waste newspaper (average fiber length and diameter 800 to 2000 and 10 microns to 15 microns, respectively) and 5 liters H_2O gives H_2O containing 3 and 4 ppm oil after 168 and 353 hours, respectively, with recovery in 353 hours of 5,295 g oil without deterioration of the shredded paper or addition of more paper.

Hettick, L. and Lucas, R. "Electro-Chemical Purification of Hydraulic Pump Power Oils." SPE Paper No. 3549 (1971).

This paper describes a process for purification of power oils (Long Beach Oil Development Company). The three essential features are: (1) conditioning the solids for transference to water phase; (2) dispersing water into the oil, creating a large interfacial area; and (3) oil/water separation in an electric field.

Hill, E.C. "Degradation of Oil Emulsions." Engineering 203 (June 16, 1967):983-984.

Oil emulsions may contain up to a ton of bacteria per

20,000 gallons. Chemical changes caused by these bacteria are removal of side chains, opening of rings, reduction of chain length, saturation and progressive oxidation. One effect is to increase the size of oil droplets, eventually producing free oil which cannot be re-emulsified. Also, loss of stable films on machine parts can lead to rapid corrosion problems.

Hillebrand, W. "Reclaiming Mineral Oils by Thermal Separation." Process Engineering (February 1975):108-109.

This article describes a plant for multi-stage evaporation of mineral oil emulsions for re-use of the oil. Influent is 10 m^3/hr of oil emulsion with oil/solids of approximately 1.2 percent.

Operating costs are approximately DM 6 to 7.00/m^3 treated emulsion (less credit for recovered oils). Investment costs are about DM 700,000 (approximately U.S. $300,000).

Hoffman, A.S.; Modell, M.; and Pan, P. "Polyacrylic Membranes for Desalination by Reverse Osmosis." Chemical Engineering Progress Symposium Series 64(90) (1969):324-325.

This article describes the preparation and performance of polyacrylic membranes for desalination by reverse osmosis. The membranes are prepared by polymerizing various mixtures of hydrophilic monomers (N-methylol-acrylamide), hydrophobic monomers (ethyl acrylate), and cross-linking monomers (trimethylolpropane trimethacrylate). The best results were slightly better than with using dense cellulose acetate (39.8 percent acetylated).

Imperial Chemical Industries Ltd. "Removal of Oil from an Oil-in-Water Emulsion." Neth. Appl. 75 02,731 (Cl. B01D) (September 15, 1975), Brit. Appl. 10,687/74 (March 1974):12 pp.

Hydrophobic textile materials were used for removal of oil from an oil-in-water emulsion. The hydrophobic textiles were prepared from poly(ethylene terephthalate) fibers, melting point 257°C, surrounded by a poly(ethylene adipate terephthalate) mantle, melting point 220°C, and coated by silane-treated SiO_2. The textile material was heated at 217°C for 10 min to improve the hydrophobic properties.

Jahns, K. "Breaking of Industrial Waste Water Emulsions." Ger. Offen. 2,301,887 (Cl. C 02c) (July 18, 1974), Appl. P 23 01 887.3 (January 16, 1973):9 pp.

Industrial waste water consisting of an emulsion containing large amounts of emulsifier of pH 11.0 was acidified to pH approximately 2.0 and electrolyzed 3 hours at 9 volts with stirring in a tank, the cathode and anode regions of which were separated by a semi-permeable membrane, to give a two phase liquid-solid system. After filtration a liquid containing approximately 7 percent sludge of pH 8.1 was obtained. For the treatment of 20 liters of the waste water, 0.1 kW·h was required.

Jain, K.D. and Sharma, M.K.(Department of Chemistry, D.A.V. Postgraduate College, Dehra Dun, India). "Physico-chemical Studies of Emulsions. II. Breaking of Emulsions by Electrolytes." Journal of the Indian Chemical Society 48(9) (1971):779-86 (English).

The effect of electrolytes on the stability and breaking of emulsions stabilized by single Surfactants, binary mixtures of surfactants, binary mixtures of protein and surfactants, and tertiary mixtures of protein and surfactants was studied. The stabilizing effect of emulsifying agents towards electrolytes increased in the order: (a) Manoxol IB (I), Manoxol OT (II), I + Tween 60 (III), II + III, I + Triton X-100(IV), II + IV, I + gelatin (V), II + V, I + III + V, II + III + V, I + IV + V, II + IV + V and (b) cetylpyridinium bromide (VI), cetyltrimethyl ammonium bromide (VII), VI + III, VII + III, VI + IV, VII + IV, VI + V, VII + V, VI + III + V, VII + III + V, VI + IV + V, VII + IV + V. The demulsification power of anions decreased in the order: PO_4^{-3}, citrate, SO_4^{-2}, $S_2O_3^{-2}$, $C_2O_4^{-2}$, CO_3^{-2}, $Cr_2O_7^{-2}$, OAc^-, Cl^-, NO_3^-, and Br^-. The demulsification power for cations decreased in the order: Al^{+3}, Fe^{+3}, Mg^{+2}, Sr^{+2}, Ba^{+2}, Co^{+2}, Cu^{+2}, K^+, Na^+, and NH_4^+.

Jan, O. "Removal of Oil and Emulsions from Waste Water, Part 2." Ind. Miljoe 4(1-2) (1973):5+. (Norwegian).

A 30 reference review.

Janusch, A.; Joven, W; and Hanke, R. (Vereinigte Oesterreichische Eisen-und Stahlwerke-Alpine Montan A.-G.). "Removal of Oil from Waste Water." Ger. Offen. 2,345,353 (Cl. C02c) (March 14, 1974), Austrian Appl. A7696/72 (September 7, 1972):17 pp.

Oil-water emulsions in waste water were broken by adjusting the pH to 6.0, passing in a first stage through a number of parallel electrolytic cells with vertical electrodes at pulsating current of current density 1 to 2 A/cm^2 and in a second stage through another group of cells at current density 0.1 to 0.2 A/cm^2, and separating the oil slurry from the aqueous phase in a settling tank. The flocculation was improved by $Al(OH)_3$ formed in the solution after partial dissolution of the Al anodes.

Jefferson, T.H. and Boulware, S.B. "Surfactants and Their Effects on Filter/Separators." Society of Automotive Engineers Paper 720863.

Surfactants in hydrocarbon fuels have harmful effects on filter/coalescer performance. The parameters most seriously affected are surface free energy, forces of adhesion, electric charge generation, and contact angle.

Surfactants tend to increase the electric charge of emulsified water droplets, increasing repulsion between droplets, resulting in incomplete coalescence. Tests regarding electrostatic charge generation in filter/separators indicate that small amounts of surfactants,

Jhawar, M. and Sleigh, J.H. "Meeting EPA Standards with Reverse Osmosis." Textile Industries (January 1975).

This article describes pilot studies using reverse osmosis for treatment of wastewater from textile plants. Performance of ROGA^R systems is described. Cost data (for 1,000,000 GPD flow) are presented.

Particular problems came from treatment of a scouring machine discharge, which included a dilute mixture of mineral oil. Membrane fouling was troublesome, and pretreatment of this stream (chemical or ultrafiltration) was recommended to remove the oil.

Jones, S.C. and Dreher, K.D. "Cosurfactants in Micellar Systems Used for Tertiary Oil Recovery." Society of Petroleum Engineers Journal 16(3) (June 1976):161-167.

This paper shows how cosurfactants affect phase behavior, control hydrocarbon and brine solubility, interact with electrolyte concentration, and change viscosity and electrical conductivity of fluids from tertiary oil recovery operations. Systems examined include a low-water-concentration oil-external micro-

emulsion, a water-external microemulsion, and "intermediate" systems for which the continuous phase is not clearly defined.

Joven, W. and Reinhart, H. "Electrolyte Method and Apparatus for Processing Aqueous Oil Emulsions." British Patent No. 1,463,022.

This patent describes a process and equipment for continous separation of oil emulsions by electrolysis, followed by settling.

Kanevskii, I.N. (Nauchno-Issled. Proekt. Inst. Redkomet. Prom., Moscow, USSR). "Improvement of Extraction in a High-Frequency Ultrasonic Field." Akust. Zh. 20(2) (1974):323-324 (Russian).

The separation of aqueous and organic phases during extraction occurs more rapidly and completely if the system is irradiated by ultrasound. The process was tested on oil-H_2O emulsions.

Katsuta, K. "Oil-Water Separation Technology." Hyomen 10(9) (1972):556-567. (Japanese).

A review on oil-water treatments (21 references).

Kawamata, T. and Kudo, Y. (Jietsuku Entorapuraizu K.K.)"Treatment of Waste Waters Containing Emulsified Oil." Japan. Kokai 75,117,251 (Cl. Co2C, BolD) (September 13, 1975), Appl. 74 23,538 (February 28, 1974):4 pp.

A polysaccharide flocculant aid containing galactomannan and a polysaccharide consisting of glucose, mannose, glucuronic acid, and pyruvic acid (molecular ratio 2.8:2.0:2.0:0.5 to 0.63) and a cationic organic flocculant are added to a waste water containing emulsified oils; the emulsified oils are demulsified and float to the surface, leaving large filamentations flocs with high filtrability in the aqueous fraction. Thus, to 50 liters of a waste water containing 5000 ppm emulsified engine oil were added 1 liter of 0.5 percent polysaccharide flocculant aid containing galactomannan and the polysaccharide and 180 ml of 1 percent polyacrylamide. The mixture was stirred for 1 min and allowed to stand. The mixture was filtered to obtain clear water, oil, and stable sludge.

Kimbler, O.K.; Reed, R.L.; and Silberberg, I.H. "Physical Characteristics of Natural Films Formed at Crude Oil-Water Interfaces." Society of Petroleum Engineers Journal 6(2) (June 1966):153-165.

Interfacial films, observed at interfaces between water and certain crude oils, may influence the efficiency of oil recovery in waterflood operations, and affect the stability of recovered emulsions. This paper presents a technique by which a modified Langmuir film balance is used to study the compressibility and collapse pressure of these films. Data are presented for several crude oil-water systems. Possible applications of these results are discussed.

Kimura, S.G. "Reverse Osmosis Performance of Sulfonated Poly (2,6-dimethylphenylene Ether) Ion Exchange Membranes." Industrial and Engineering Chemistry Product Research and Development 10(3) (1971):335-339.

Sulfonated poly (2,6-dimethylphenylene ether) cation exchange membranes show promise as reverse osmosis membranes, having 8 to 10 times as high water permeability as homogeneous cellulose acetate at the same salt rejection levels (for 1 percent NaCl feeds). Membrane performance is highly dependent on feed composition.

Kirby, T.W. "Water Conservation at a Major Refinery - Petrochemical Complex." AIChE Symposium Series 70(136) (1974):645-653.

This article describes biological waste treatment systems being used at the various plants in the Lake Charles Petrochemical Complex (Cities Services Oil Company). Separate systems are described for the lube oil and wax plant, petrochemical plant, refinery and butyl rubber plant.

Klare, H., Jr. and Sonntag, H. (Deut. Akad. Wiss., Berlin). "Chemical and Electrical Demulsification of Water-Oil Emulsions." Abh. Deut. Akad. Wiss. Berlin, Kl. Chem., Geol. Biol. 6 (1966):597-608 (pub. 1967) (German).

In a model system of two drops of 5 X 10^{-2}N KCl in n-octane with a-oleic acid monoglyceride concentrations of 0.08 to 0.300 g/l, and as emulsifier 10^{-3} to 10^{-5} of various NP emulsifiers, stable black films formed between the drops which lasted more than 120 sec; the outflow time of the dispersion medium was about 40 sec; and the thickness of the end layer was 42 $\pm$ 1 A. Higher

concentrations of emulsifiers made the films unstable. In emulsions of water drops in 0.5 g/l of the monoglyceride per liter of octane, black films were formed which lasted 120 sec when no electric field was present and the dispersion medium flowed out for 60 sec, but under 120 mv the stability was reduced to zero in some cases. When 5.0 g of the monoglyceride was used per liter of octane, the black films became unstable at 250 mv, and at 400 mv their stability was completely destroyed in most cases. Resistance to the elctric field was independent of temperature. Electric demulsification differs from electric dust removal in that the former causes particle growth in the interelectrode space but not at the electrodes themselves. The potential existing at the surfaces of the coalescing drops in contact with each other probably arises through the higher conductivity of the aqueous phase in comparison with the oil, so that between the poles of a drop, a potential exists by reason of the gradient in a distance equal to the diameter of the drop.

Kremen, S.S. "Reverse Osmosis Makes High Quality Water Now." Environmental Science and Technology 9 (April 1975): 314-318.

This article presents a basic description of the processes of osmosis and reverse osmosis, followed by specific applications and cost data for use of reverse osmosis.

Kuenzle, B. "Apparatus for Separating Liquid Petroleum Products from a Mixture of Liquid Petroleum Products and Water." (Hectronic A.-G.) Swiss 579,939 (Cl. B01D17/02) (September 30, 1976), Appl. 74/7,880 (June 10, 1974):6 pp.

The petroleum emulsion is separated from water by coalescence filters connected in a cascaded series operated under hydrostatic pressure. Each filter is fed from the bottom and the effluent is removed by an axially mounted overflow pipe and fed into the succeeding filter. The annular zone formed in the apparatus is filled with poly(tetrafluoroethylene) chips as a filtering layer.

Ladha, K.K.; Herring, M.; and Louvar, J.F. (BASF Wyandotte Corp.). "Method and Apparatus for Purifying Aqueous Streams Contaminated with Organic Materials." U.S. 4,000,065 (Cl. 210/23H) (December 28, 1976), Appl. 524,806 (November 18, 1974).

Aqueous streams contaminated with minor amounts of organic materials are separated into an aqueous fraction which is concentrated with respect to the organic contaminants and a water fraction relatively free of the organic contaminants by a method which includes a unique combination of reverse osmosis (RO) and ultrafiltration (UF). The organic contaminants include substances having molecular weights of less than 10,000 which are soluble in the aqueous stream initially but have limited solubility ranges and are precipitated therefrom upon concentration. The contaminated aqueous stream is circulated from the high pressure compartment of a RO unit to the high pressure compartment of a UF unit, then to the low pressure compartment of the UF unit, and then back to the high pressure compartment of the RO unit. The contaminants are concentrated in the high pressure compartment of the RO unit, and a portion thereof is precipitated or otherwise rendered amenable to removal along with the UF concentrate upon passing the RO concentrate from the high pressure compartment of the RO unit to the high pressure compartment of the UF unit. Soluble organic contaminants remaining in the aqueous stream are removed in the UF permeate and are recycled back to the high pressure compartment of the RO unit for further concentration and precipitation, followed by recycling to the high pressure compartment of the UF unit for removal.

Lees, R.D. and Smith, R.W. (Hercules Inc.). "Polymers for Effecting Oil-Water Separations." U.S. 3,691,086 (Cl. 252/329; B 01d) (September 12, 1972), Appl. 60,137 (July 31, 1970):7 pp.

An oil is separated from an oil-in-water emulsion system by contacting the system with a polymeric separation aid. The separation aid is either a polymer, a polymer in conjunction with a salt, or a polymer in conjunction with a salt and silica solution. The polymer is a water-soluble, cationic vinyl polymer. The salt is a water-soluble salt of a polyvalent metal.

Lefeurre, A.A.J. (Societe d'Etudes et de Realisations Industrielles S.A.) "Apparatus and Method for Treating Emulsions." Ger. Offen. 2,412,715 (September 26, 1974).

Oil is removed from aqueous emulsions by inversion of the emulsion. To an oil-containing (0.5 to 5 percent) emulsion, $CaCl_2$ (3 grams per liter) and an emulsifier of the water-in-oil type were added. Droplets of the

water-in-oil emulsion are removed by filtration through cardboard of 5 micron pore size. The water effluent contains less than 15 ppm oil.

Levert, P.P.J. and Schreiner, J. "Continuous Removal of Emulsified Fats and Oils from Waste Water." (PEC Process Engineering and Contractors Ltd.) Ger. Offen. 2,322,665 (Cl. C 02c) (March 7, 1974), Neth. Appl. 72 11,241 (August 17, 1972):17 pp.

Emulsified fats and oils were removed from waste water by adding a concentrated brine from the process, passing through a number of vertical, tubular electrolysis cells with separation into a clarified aqueous phase and an oil-containing sludge, and separating the aqueous phase into water and a concentrated brine, which was recycled to the process. The oil-containing sludge (containing 50 percent H_2O) was dehydrated by centrifuging and combusted.

Lindenhofen, H.E. "The Effect of Surfactants on the Coalescence of Emulsified Water." Filtration and Separation 5(4) (July/August 1968):317-319.

Filter/separator coalescer elements fail to remove completely emulsified water when exposed to water-fuel emulsions containing surfactants. A number of specific field problems are documented and a temporary fix is recommended. Iso-propyl alcohol flushing restores the coalescer to normal operating levels. Two controlled experiments with a corrosion inhibitor and Navy Special Fuel Oil (N.S.F.O.) contaminant, were performed to ascertain their effect on coalescer performance. The N.S.F.O. contaminant had a worse effect on the water removal characteristics of the coalescer than the corrosion inhibitor. Current theories as to why coalescers fail in the presence of surfactants were evaluated and other possible causes of failure are suggested.

Lissant, K.J. "Emulsification and Demulsification in Oil Recovery." AIChE Symposium on Improved Oil Recovery by Surfactant and Polymer Flooding, Kansas City, Missouri (April 1976).

Emulsion problems in primary oil recovery are caused by the presence of water and natural emulsifiers in the crude oil. Emulsification can be reduced by controlling the withdrawal rate, and minimizing shear producing structures in the well and producing equipment. These emulsions are water-in-oil, ranging from 0.5 percent to

about 40 percent water. Separation is usually effected in heater-treaters or electric dehydrators (e.g., in refineries with high through-put rates), combined with chemical demulsifiers.

Water flooding with surfactants (secondary or tertiary recovery) deliberately produces water-oil and oil-water emulsions.

Lock, J. "High Efficiency Oil/Water Separation." Processing (Oct. 1976):41.

Pollution Control Systems (United Kingdom) introduced their Flofoil oil/water separation process. Two different materials are used for coalescence, depending on oil droplet size. For greater than 1 micron diameter, up to 99.6 percent removal can be obtained with flow rates of up to 16 $m^3/h/m^2$ fabric, with a pressure drop of less than 1 psi. Processed water contains less than 1 ppm oil. For submicron droplets, 30 to 60 percent removal (to less than 5 ppm oil) is obtained with flows up to 10 $m^3/h/m^2$ coalescer cross section: pressure drop, 1 to 10 psi. Retention times are typically 1 to 2 (up to 6) minutes.

Lordi, R.; Manci, C.,; and Petronio, B.M. "Studies on Industrial Waters Containing Oil Emulsions II." Inquinamento 16(4) (1974) (Italian).

Emulsions studied contained anionic or nonionic emulsifiers, and additives such as a corrosion inhibitor, lubricating agent, bactericide, or anti-foaming agent. Very stable emulsions, not broken by a polyvalent metal salt alone, require additional heat or H_2SO_4 to be broken.

Lordi, R.; Manci, C.; and Petronio, B.M. "Treatment of Wastewater Containing Emulsifying Oils." Inquinamento 15(6) (1973):20-24 (Italian).

A minimum of $Al_2(SO_4)_3 \cdot 18H_2O$ is used to break oil-water emulsions emulsified with anionic compounds.

Lucas, R.N. (Petrolite Corporation, Petreco Division, 1968). "Electrical Dehydration of Thermally Produced Emulsions." SPE Paper No. 2173. Houston, Texas.

Relationships between the performance of electric dehydrators and certain properties of oilfield emulsions (bulk physical properties, charge rate, water content, particle size distribution) are examined.

Results indicate a dependence on fluid properties, charge rate, and electric field intensity, but no dependence on water content or particle size distribution.

Lucas, R.N. (Petrolite Corporation). "Uniform Electric Field Treatment for Resolving a Dispersion Consisting of Immiscible and Liquid Phases." U.S. 3,661,746 (Cl. 204/188; B 03c) (May 9, 1972), Appl. 825,015 (May 15, 1969):9 pp. Division of U.S. 3,582,527 (CA 76:5535g).

A uniform electric field is used for resolving dispersions without passing any significant amount of dispersions through the treater other than through the uniform electric field. The dispersion flows along a vertical flow axis between inlet and outlet zones. An electric field is established in the dispersion with monotonically increasing potentials in the direction of dispersion flow. The field has planes of constant potential transverse to the direction of dispersion flow. This field has sufficient intensity to resolve the dispersion at least in part into aqueous and organic phases as it passes from the inlet zone to the outlet zone. The aqueous phase gravitates downward in the electric field and is recovered near the inlet zone. The organic phase resolved from the dispersion is recovered from the outlet zone.

Luthy, R.G.; Selleck, R.E.; and Galloway, T.R. "Interfacial Phenomena Related to the Removal of Emulsified Oil from Refinery Wastewaters." SERL Report No. 75-3 (November 1975).

The purpose of this research was to identify conditions under which organic coagulants may be utilized to remove emulsified oil from refinery wastewaters and to provide a better understanding of emulsion properties which affect oil droplet flocculation and flotation.

Oil droplet properties in refinery wastewaters were found to be determined largely by water quality rather than source of oil. Emulsion stability resulted from tough, interfacial films; from electrical effects; and from solid material adsorbed at the oil-water interface.

On-line DAF pilot plant studies demonstrated oil could be removed from refinery API separator effluents to levels of 10 mg/l with a 15 mg/l dose of 75 percent charged polydiallyldimethylammonium polymer without the assistance of alum or ferric coagulants. Both influent oil concentrations and oil removal efficien-

cies were considerably higher than previously reported values. Underdosing did not affect large oil droplet removal; if oil concentrations to 25 mg/l could be tolerated, polymer dose may be reduced to 10 or possibly 7 mg/l.

Best oil removal corresponded to a polymer dose which gave net zero oil droplet charge; however, charge neutralization was not the only requirement. Efficient polymer bridging between oil droplets was also necessary. It was shown that good flocculation yielded good flotation. The process was dependent upon oil droplet size with respect to flotation, but not dependent upon oil droplet concentration with respect to depletion of polymer by adsorption.

A cost comparison indicated that the expense of polyelectrolyte treatment was more than compensated by savings in sludge disposal costs and by the value of the recovered oil. Oil recovery would also reduce environmental problems associated with oil sludge disposal.

McDonald, D.P. "Ultrafiltration Joins the Ranks of Industrial Separation Processes." Process Engineering (January 1973):76-77, 79.

This article discusses Amicon's Diaflo and Hollow Fiber ultrafiltration (UF) membranes, and thin channel UF system. "Diafiltration," more efficient than dialysis, is also discussed.

Many UF applications appear to lie in the food industry.

McGrew, J.L. (Marine Construction and Design Company). "Apparatus and Method for Coagulation for Use in Separating Oil and Water." Ger. Offen. 2,613,870 (Cl. B01D17/04) (October 21, 1976), U.S. Appl. 566,926 (April 10, 1975):31 pp.

An oil-water emulsion is separated in an apparatus having a three-dimensional network structure, (e.g., foam rubber), with a surface which sorbs oils; the pore size is $\leq D$ and the droplet size is $\leq d$. The emulsion is allowed to remain in the structure for a residence time $\geq t$, during which time the droplets are exposed to a settling force chosen so that the droplets have a settling speed r and $t \geq (D - d)/r$. The droplets coagulate on the surface and can be washed off the structure by squeezing the foam rubber. The foam

rubber can be an endless strip passing through a set of rollers which express the separated oils and water.

Madsen, R.F. et al. "Experience with Concentration and Separation of Industrial Solutions with Reverse Osmosis and Ultrafiltration." Filtration and Separation 9(5) (September/October, 1972):567-575.

This article was authored by members of the Danish Sugar Corporation (DDS). The article gives operating characteristics of DDS membranes and describes membrane modules. Several examples of current plants are discussed, with applications in the food (dairy) industry, and water desalination.

Mapco, Inc., Process and Pollution Controls Division. "Oil/Water Splitter Snags Emulsified Oil." Chemical Engineering 84(15) (July 18, 1977):77.

This article describes Mapco's Model 2000 dual-mode oil/water separator. Oleophilic, fibrous coalescer elements capture emulsified oil droplets. Operations range from 60 to 1500 gpm, with effluent water containing approximately 10 ppm oil, and free oil containing 0.5 percent water.

Markind, J. et al. "Use of Reverse Osmosis for Concentrating Waste Cutting Oils." AIChE Symposium Series 70(144) (1974):157-162.

After testing of alternative methods, Westinghouse Electric's facility in Lester, Pennsylvania switched to reverse osmosis for treating their spent oils waste stream. A pilot system was first tested (1972-1973) to determine the optimum operating parameters. A 75 micron filter was placed in-line to protect the membranes, and an activated carbon filter used to remove phenol from the permeate. Data given from several reverse osmosis runs include permeate flux and percent removal of various feed constituents.

Westinghouse membrane systems are briefly described. An economic study determined total costs to be approximately 1.4 cents/gallon (at 50,000 GPD flow), including the credit from burning (as fuel) the concentrated oil.

Markofsky, S.B. and Wood, L.L. (Grace, W.R., and Company). "Composition for Breaking Emulsions." U.S. 3,993,615 (Cl. 260-29.2TN; C08F18/24) (November 23, 1976), Appl. 423,503 (December 10, 1973):10 pp.

Demulsifiers for water-in-oil and oil-in-water emulsions were prepared by treating a diisocyanate end-capped polyol with a polyamine and quaternizing the resulting polyurea with an alkylating agent. Thus, 980 g polyethylene glycol and 326 g TDI were mixed 4 h at 50 to 60°C, and 980 g of the mixture in 1,000 ml Me_2CO was added to 103 g diethylenetriamine in 500 ml Me_2CO at 50°C. The mixture was stirred 2 hours at 60 to 65°C, and the Me_2CO was replaced by water to give an aqueous solution of the polyurea (I). I (340 g) was treated with Me_2SO_4 to give the quaternized I which gave clear aqueous phases when added to water-in-oil emulsions at 200 to 1,000 ppm.

Meijs, F.H. and Mitchell, R.W. "Studies on the Improvement of Coalescence Conditions of Oilfield Emulsions." Journal of Petroleum Technology (May 1974):563-570.

The effects of varying e, a "mixing-intensity parameter" (work per unit mass per unit time) on emulsion destabilization and equilibrium droplet size is discussed. Tests on water-in-oil emulsions were made using both a "pipe coalescer" and a "coaxial mixer". Conclusions: (1) optimum mixing intensity of approximately 5×10^3 erg/gm sec and (2) longer residence time creates better separation.

Tests on oil-in-water emulsions, using the coaxial mixer, showed an optimum e for deoiling of between 10^4 and 10^5 erg/gm sec.

Midland Oil Refineries, Ltd. "Chemical Process Slashes Cost of Treating and Recovering Waste Soluble Oils." Process Engineering (October 1972):7.

Midland Oil Refineries, Ltd. has developed a plant designed to treat and recover waste soluble oils in effluents. The process has three major operations: (1) separation of insoluble mineral oils (by gravity), (2) separation of soluble mineral oils (using chemical cracking agents with pH controlled), and (3) neutralization.

Mongait, I.L.; Zakhar'ina, S.B.; and Ishkhanova, E.G. (USSR) "Purification of Concentrated Oil-containing Waste Waters from Machine-Building Plants." Tr., Vses. Nauch. Issled. Inst. Vodosnabzh., Kanaliz., Gidrotekh Sooruzhenii Inzh. Gidrogeol. No. 28 (1970):67-71. (Russian).

The most effective way to break the emulsions used for cooling processed metallic parts is a two-step coagulation. Addition of 20 g/l of NaCl causes separation

of 80 percent of the oil. Then, the water layer is adjusted to pH 4 using H_2SO_4 and the remaining oil is liberated by addition of 1 g/l of $Al_2(SO_4)_3$.

Nagy, I. et al. (Tatabanyai Szenbanyak) "Separation of Emulsions and Suspensions by Vibration." Hungary 155,789 (Cl. C02c) (March 24, 1969), Appl. (October 20, 1966):5 pp.

The oil content of sewage or the moisture content of oils is removed by subjecting the material to ultrasound of 50 to 1,000 Hz., when the two phases separate.

Nalco Chemical Company. "Oil-in-Water Emulsion Breaking." Water Treatment Chemicals TF 97 (1975).

Chemical treatment can be used to destroy (or nullify) the surface activity of emulsifiers. Inorganic chemical treatment (Acid-alum-lime) or organic chemicals (various "demulsifiers") can be chosen. Advantages of the organic treatment are (1) lower total dissolved solids in effluent, (2) no need for final neutralization, (3) reduction in corrosion, (4) reduced alum (flocculant) usage, and (5) reduced sludge generation.

Nusbaum, I. and Sudak, R.G. (Gulf Environmental Systems, Co., San Diego, CA). "Industrial Applications of Spiral-Wound Reverse Osmosis Modules."

This article reviews some of the current applications of spiral-wound reverse osmosis membranes and systems. The spiral-wound reverse osmosis module was developed at Gulf Environmental Systems (now UOP), and is used in conjunction with isotropic reverse osmosis membranes. The following applications are discussed: (A) Water purification for: (1) electronics industry, (2) feedwater for mixed bed resin demineralizers, (3) boiler feedwater, (4) treatment of acid-mine drainage; and (B): Concentration of process streams and products in the pharmaceutical and food industries. A diagram and description of the spiral-wound module is included.

Ohtsubo, K. (Hitachi Plant Construction Engineering Company, Ltd.) "Treatment of Waste Machining Oil Emulsions." Japan. Kokai 73 47,164 (Cl. 91 C91) (July 4, 1973), Appl. 71 81,630 (October 18, 1971):3 pp.

Wastewater containing emulsified oil was treated with $CaCl_2$ and an Al or Fe salt to separate the oil, and the aqueous phase was treated with NaClO to give clean water. Thus, 200 ml waste machining oil (emulsion)

at pH 8.81, with 41 ppm suspended matter, hexane-solvent components 43,950 ppm, COD 23,200 ppm, and BOD 12,600 ppm, was stirred with 4 ml 10 percent aqueous $CaCl_2$ for 5 min, treated with 1 ml 20 percent aqueous $Al(SO_4)_3$, followed by 5 ml of 0.01 percent aqueous solution of an anionic polymer flocculant to separate the oil. The suspended matter-free aqueous phase had pH 5.56, hexane-solution components 70 ppm, COD 210 ppm, and BOD 120 ppm. The aqueous phase (200 ml) was stirred with 5 ml 10 percent aqueous NaClO and treated with 5 ml of the flocculant solution to give clean water with pH 7.78, hexane-solution components 6.0 ppm, COD 210 ppm, and BOD 100 ppm. The above process was more efficient in separating oil than one using $FeSO_4$ and $Ca(OH)_2$.

"Oil Emulsions in Metal Finishing Effluents." Electroplating and Metal Finishing (June 1965):201.

Emulsified oils from metal finishing effluents are broken chemically, with varying degree of difficulty. Aluminum sulfate generally works well (flocculation) with oil content under 100 ppm. With more oil and/or detergents, the emulsions are more stable. Similar problems exist with washing of oil-contaminated textiles.

Ono, H; Saida, T.; and Fukumura, K. (Mitsui Toatsu Chemicals, Inc.). "Separation of Oil from Wastewater Containing the Oil in the Form of Fine Droplets." Ger. Offen. 2,522,250 (Cl. C02C) (December 18, 1975), Japan Appl. 74 58,474 (May 27, 1974):13 pp.

Oil emulsions are treated with metal hydroxides or oxides to break the emulsion and adsorb the oil. HCl is added to bring the pH to 7 and dissolve the hydroxides; the oil then floats to the surface or coalesces to larger droplets which are filtered out by oleophillic synthetic or natural (e.g., peat, coconut, hemp) fibers. Thus, compressor condensate containing 300 ppm oil was treated with $Al(OH)_3$, the pH adjusted to 7 with HCl, and filtered through polypropylene fibers and then through peat to remove all but 1.2 ppm oil.

Orlov, L.N. et al. (Inst. Nefti Gaza, Ivanovo-Frankovsk, USSR). "Action of a Demulsifier on a Freshly Prepared Water-petroleum Emulsion." Neftepererab. Neftekhim. (Moscow) (1) (1972):11-12. (Russian).

Demulsifier should be added immediately after the emulsion has been prepared. If aging is permitted without a demulsifier, considerable amounts of salt

residues remain after the process. Thus, Bytkov Region petroleum was treated in 17-ton tanks. Experimental results are tabulated on salt and water concentrations before and after the process, brand and quantity of demulsifier used, and the temperature.

Oswald, E. (Guetling, Walter, Abwasser-Verfahrenstechnik und Kunststoff-Apparatebau). "Apparatus and Method for Treating Oil-Containing Wastewater." Ger. Offen. 2,401,054 (Cl. C02C) (July 31, 1975), Appl. P 24 01 054.6-25 (January 10, 1974):19 pp. Addition to Ger. Offen. 2,350,544.

Oil-containing wastewater is pumped through ultrafiltration membranes at 1 to 10 atm and 2 to 10 m/sec. The pumping pressure corresponded to the pressure drop across the membranes. A heat exchanger was placed between the pump and the membranes. The pH of the purified water was maintained at 4.5 to 8 by the automatic addition of acid or alkali.

Panchenkov, G.M.; Serikova, L.A.; and Papko, V.V. (Mosk. Inst. Neftekhim. Gozov. Prom. im. Gubkina, Moscow, USSR). "Study of the Effect of Salt Composition and Aqueous-phase pH on the Stability of Petroleum Emulsions." Neftepromysl. Delo 7 (1976):49-51. (Russian).

Asphaltenes, tars, paraffins, and porphyrins, emulsified by natural emulsifiers separated from petroleum, exhibit films, which change from rigid to rigid-elastic or elastic at pH 7 to 8 where the film strength and emulsion stability are lowest. Optimal pH (6 to 9) for breaking emulsions prepared from Tuimazin petroleum and salt solutions depends on salt buffering capacity and, at pH ≥ 8, insoluble hydroxide formation.

Panchekov, G.M. and Tsabek, L.K. (Mosk. Inst. Neftekhim. Gazov. Prom. im. Gubkina, Moscow, USSR). "Thermal (Brownian) Coagulation of an Emulsion Disturbed by Gravitational and Electric Fields." Kolloid. Zh. 31(6) (1969):887-92. (Russian).

The effect of such variables as radius of the droplet R about 1 micron, electric field E_0 about 1 to 2 kV/cm, etc. was considered for a petroleum emulsion. The critical volume of a droplet of the poly-dispersed emulsion was established by a detailed mathematical treatment of equations governing the variables. A quadratic solution was given of the equation for the thermal coagulation of an emulsion disturbed by

gravitational and external electric fields. A solution was given for exponential primary dispersion.

Pattison, D.A. "Membranes Compete for Separation Markets." Chemical Engineering 75(12) (June 3, 1968):38-40+.

This article (written in 1968), gives an overview of the potential for electrodialysis, ultrafiltration, and reverse osmosis in the context of competing with other techniques for separation of dissolved solids - namely distillation and ion exchange. Performance data are given for treatment of brackish water and seawater by membranes and systems of several manufacturers.

Petreco Division,Petrolite Corporation, Electric Dehydration/ Desalting of Crude Oils in Oilfield Production. Revision 1 - March 1975.

The first section of this booklet discusses the need to dehydrate and desalt crude oil. Following is a brief discussion of the beginnings of Tretolite and Petreco Corporations, later forming Petrolite Corporation. The nature of water found in crude, along with a brief overview of methods available for dehydrating crude oil is presented.

A section on electrical coalescing in a high voltage field presents qualitative and quantitative discussions on the topics of dehyrdation and desalting.
Lastly, a section is devoted to the special features of Petreco dehydrators, and the advantages of electrical dehydration in de-watering crude oil.

Petroleum Extension Service. Treating Oil Field Emulsions. (Third edition). Division of Extension, University of Texas at Austin, 1974.

This work is a manual designed as a complete introductory review of oil field emulsion treating. Topics discussed are oil field emulsion formation and prevention, emulsion theory, treatment principles, heat treating, chemical treating, electrical treating, treating equipment, field analysis, sampling procedures, and testing procedures.

Petrov, A.A. and Smirnov, Yu. S. (Inst. "Giprovostokneft," Kuibyshev, USSR). "Surfactants for Breaking Down Petroleum Emulsions in Petroleum Preparation." Neft. Khoz. 7 (1976):31-33. (Russian).

Testing of ethylene oxide-propylene oxide polymer derivatives of ethylenediamine, showed that polymers of mole ratio 7 to 8:1 and 3,500 to 8,000 molecular weight had the highest demulsifying capacity. The capacity somewhat increased with the molecular weight. The surfactants are water insoluble, but readily soluble in aromatic hydrocarbons, alcohols, and petroleum. Petroleum emulsions containing 30 percent water were demulsified with 25 to 30 g surfactant/ton resulting in a final water content of 0.5 percent.

Plinke, H. (Chemisch-Technisches Buero Adolf Plinke). "Separation of the Constituents of Oil-Water Emulsions." Ger. 1,810,630 (Cl. C 10m) (August 6, 1970), Appl. (November 23, 1968):6 pp.

Oil-water emulsions formed by industrial waste waters were preheated and partly vaporized in vacuum. The water component was further vaporized by heating with immersion heaters in which the oil component was burned. Oil vapors obtained in the evaporation steps were condensed. The separation could be performed continuously in a one-step or two-step installation. The process eliminates the use of flocculation agents, etc. and allows water and salts, especially nitrites, to be recovered.

Plumbar, O. (Gulf Oil Corporation). "Breaking Refinery Sewer Oil and Water Emulsions with Sodium Bicarbonate." U.S. 3,620,971 (Cl. 210/59; C 02c) (November 16, 1971), Appl. (August 21, 1973):3 pp.

A process for the breakup of refinery sewer emulsions containing 40 to 99 percent basic sediment and water (BS and W) into three distinct oil and water recoverable layers and a solids disposable layer, is based on the addition of >2 lb $NaHCO_3$ per barrel of emulsion and heating at 170° to 210° F. At high (70 percent) BS and W contents requiring large amounts of $NaHCO_3$, the $NaHCO_3$ is approximately twice as effective as Na_2CO_3 in the breakup of the emulsion.

Pollution Technical Services "Effluent Treatment by Electrolysis." Chemical and Process Engineering 53(2) (February 1972):5.

This article describes a process developed by Pollution Technical Services (U.K.) for electrolysis separation of industrial efluents. Gas bubbles formed by electrolytic action separate the phases.

Porter, M.C. "Membrane Ultrafiltration for Pollution Abatement and By-product Recovery." AIChE Symposium Series 69(129) (1973):100-122.

Although total operating costs for ultrafiltration ($0.30 to $5.00 per 1,000 gal) are greater than those for conventional waste treatment plants, ultrafiltration can accomplish recovery of valuable by-products without chemical, physical, or biological degradation. Twelve applications for ultrafiltration treatment are discussed. Amicon's hollow fiber and tubular ultrafiltration membranes are discussed, with reference to "thin-channel, cross-flow" fluid management in ultrafiltration systems. Thin-channel flow (high velocity) is used to minimize concentration polarization. Power (pumping) costs are small compared to membrane replacement costs with hollow fiber membranes.

Porter, M.C. and Michaels, A.S. "Membrane Ultrafiltration." Chemical Technology (January 1971):56-63.

This is the first of a series of articles about applying ultrafiltration in the food processing industry. Using ultrafiltration for dewatering food substances (prior to transportation, freezing, etc.) appears to have economic promise.

A brief description is given of membrane availability and uses (molecular weight cut-off, flux, etc.), and equipment technology (operational modes, avoiding of concentration polarization).

The key cost factors are membrane flux rate, life and cost (these determine pumping and equipment requirements).

Porter, M.C.; Schratter, P.; and Rigopulos, P.N. "By-Product Recovery by Ultrafiltration." Industrial Water Engineering 8(6) (June/July, 1971):18-24.

This article gives a brief introduction to Amicon's Diaflo membranes and "thin-channel" design systems.

Several examples of ultrafiltration applications (actual systems in operation) are discussed:
(1) selective fractionation of cheese whey,
(2) recovery of starch, (3) recovery of blood protein,
(4) recovery of activated carbon, (5) recovery of paint, (6) recovery of polymer latex wastes,
(7) recovery of colloidal metal oxides, and
(8) treatment of pulp and paper waste streams.

Preiss, W. "Separating Water and Oil from Emulsions." Fr. 1,556,663 (Cl. C 02c, B 01d) (February 7, 1969), Ger. Appl. (March 9, 1967):8 pp.

The apparatus contains means for heating, mixing, and clarifying emulsions, especially oil-in-water emulsions. The emulsions are treated with a decomposition agent and circulated through the apparatus while being heated to the desired decomposition temperature; the oil is then separated and purified. The apparatus gives water of high purity and is less costly than previous apparatus used for separating the components of emulsions.

Puerto, M.C. and Gale, W.W. "Estimation of Optimal Salinity and Solubilization Parameters for Alkylorthoxylene Sulfonate Mixtures." Society of Petroleum Engineers Journal 17(3) (June 1977):193-200.

Since interfacial tensions (IFT) are minimal at optimal salinity (C_D) and solubilization parameters (Vo/Vs and Vw/Vs) are related to IFT's, estimation of both properties is of great help in designing economical microemulsion flooding compositions (Healy et al., 1976).

Pure surfactants were studied, with "pure-component contributions" to C_D and Vo/Vs or Vw/Vs at C_D being determined. Mixture properties are then estimated using a weighted sum (by weight percent) of the individual contributions. Experimental results were in close agreement. Effects of various alcohols (cosolvents) on the pure-surfactant contributions were studied.

Putokhin, V.S. (USSR). "Use of Multifactor Regression Analysis in Constructing a Mathematical Model for Removing Water from Petroleum at Petroleum Fields." Neftepromysl. Delo 7(57) (1976). (Russian).

By linear multiple regression analysis, a model was constructed for the water-retaining capacity of petroleum on discharge from dewatering equipment as a function of demulsification temperature, H_2O content in the crude petroleum, and demulsifying reagent and crude petroleum consumption. The model is used to determine optimal operating conditions and control parameters.

Quitter, J.M. (How-Baker Engineers, Inc., Tyler, Texas). "Electrical Dehydrator Installed Offshore."

This article describes the world's first offshore electrical dehydration plant, serving 24 wells in the Conception Offshore Field, 2 miles at sea (Phillips Petroleum Company, California). Production, safety, and economics dictated using an electrical dehydrator offshore.

The dehydrator was designed to produce 12,000 bbl/day crude oil. Installation costs were $125,000. The 41° API Alegria Crude is almost non-conductive, reducing power costs. Operational labor costs are negligible.

The theory of coalescence in an electrical field is described. Advantages of AC over DC fields in crude dehydration are mentioned. Factors affecting settling time are considered (density difference, viscosity).

Roberts, R.J. "Electrically Energized Petroleum Demulsifier." U.S. 3,674,677 (Cl. 204/302; B 03c) (July 4, 1972), Appl. 42, 624 (June 2, 1970):7 pp.

An electrically energized horizontally disposed demulsifier , designed to eliminate potential flash hazards, accomplishes optimum coalescence by subjecting the emulsion to a high electrical field for a short time. The design prevents channeling and has low operating costs and high reliability. It is especially suited for separating water-petroleum emulsions.

Sackis, J.J. (Nalco Chemical Company) "Quaternary Ammonium Demulsifiers for Dispersed Oils." U.S. 3,585,148 (Cl. 252-344; B old) (June 15, 1971), Appl. (March 26, 1969):4 pp.

$$\begin{array}{ll} CH_2{:}CHCH_2 & R \\ & {}^{+}N \quad Cl^{-} \\ CH_2{:}CHCH_2 & R \end{array} \qquad II$$

Oil-in-water emulsions were demulsified by treatment with 100 to 1,000 ppm H_2O-soluble cationic copolymer having molecular weight $\geq$2,000 obtained by copolymering acrylamide (I) with a diallylamine quaternary compound (II). Thus, an aqueous solution of 20 percent II (R = Me) (III) at pH 6.9 ws blended with 1 percent azobisisobutyronitrile under N, and the mixture was treated with 20 percent I at 55 to 57° C to form an 80:20 I-III copolymer. The copolymer could be used to

demulsify an oil-in-water emulsion at pH just below 8. Copolymers were similarly prepared from I and II (R = CH_2CH_2OH).

Sakuma, T.; Kagahashi M.; and Nagayama, S. (Lion Fat and Oil Company, Ltd.). "Waste-Oil Emulsion Breaker." Japan Kokai 73 86,788 (Cl. 13(9)B91,91 C 91, 13(7)A21) (November 15, 1973), Appl. 72 17,839 (February 21, 1972):4 pp.

A waste-oil emulsion breaker contains mainly $R-[NR^1(:0)(CH_2)]_xNR^2R^3(:0)$ (I) or $RS(0)R^1$ (II), where R is a C_{1-16}-aliphatic hydrocarbon radical, R^1, R^2, and R^3 are C_{1-5} aliphatic hydrocarbyl. $(C_2H_4O)_nH$, and $C_3H_6O)_mH$, and n and m are 1 to 5. The emulsion breaker can be applied to waste-oil treatment in industries of pulp and paper, machinery, metals and alloys, food, etc. Thus, 100 g of a waste-oil emulsion (hydrocarbon oils 50, an emulsifier 8, rust inhibitors and extreme-pressure additives 2, and water 40 percent) was mixed with 2 percent II (R = C_6H_{13}, and R^1 = C_2H_4OH) for 5 min, and settled. The degree of separation was 100 percent. Both oil and water phases were clear, and the separation interface was definite.

Schmidt, R.; Florberg, W.; and Schneemilch, M. "Apparatus for Separating Oil-in-Water Used Emulsions, Especially Drilling Fluids." Ger. (East) 111,516 (February 20, 1975).

Oil-in-water emulsions (e.g., drilling fluids) are broken by using a filter and controlled heating.

Scholler, J. "Removal of Emulsified Oils from Waste Water." Fr. 1,475,383 (Cl. C 02c) (March 31, 1967), Ger. Appl. (April 10, 1965):6 pp.

Industrial water effluents containing oils and grease emulsified by detergents are easily purified if they are first adjusted to a pH below 4 with H_2SO_4 and then passed through a column packed with coarse quartz sand of 4 mm. diameter to separate the oil from water. Separation efficiency is approximately 95 percent. The water phase drawn off the bottom of the reactor is neutralized with lime and the remaining emulsion absorbed by the precipitated plaster is filtered out.

Shea, G.B. "Practices and Methods of Preventing and Treating Crude-Oil Emulsions." U.S. Bureau of Mines, Bulletin No. 417 (1939).

The study of conditions causing or favoring the formation of crude-oil emulsions shows that the application of certain methods or remedial measures to well and field operations frequently will modify or prevent emulsification. In discussing methods of correcting and preventing emulsification, the writer has pointed out operating practices and corrective measures that have been successful and has cited probable results of putting such methods into effect. As each emulsion and the conditions under which it is formed present an individual problem no preventive measure will prove effective or economical under all conditions. The application of remedial measures therefore should be based on a careful study of conditions, costs entailed, and benefits to be derived. The sources of emulsification in flow lines and gathering systems are more amenable to correction than those in the well. Consequently, the best progress in the prevention of emulsions has been made by the application of remedial measures on the surface of the ground.

As the extent to which emulsions can be prevented is limited, the treatment of emulsions continues to be a major operating problem in the oil fields and requires the cooperation of all concerned to attain the best results. Marked improvements have been made in the treatment of emulsified oil, and the essential features in the design and operation of chemical and electric treating plants are discussed in this report. It is pointed out also that dehydration of emulsions while they are "fresh" has an important bearing on the economics of treating.

Local conditions, the characteristics of the emulsions, and the relative merits and economies of processes generally are the deciding factors governing the selection of a dehydrating method.

It seems probable that on many properties a systematic survey of the mechanical causes of emulsification and of the economic efficiency of dehydration plants would decrease substantially the cost of producing marketable oil.

Schulze, G. "Separation of Hydrocarbons from Aqueous Solutions." Ger. Offen. 2,513,353 (Cl. C02C5/02) (October 7, 1976), Appl. (March 26, 1975):12 pp. Addition to Ger. Offen. 2,313,217.

Hydrocarbons, oil emulsions, and heavy organic loads are removed from neutralized wastewater by flocculation

after adding a stoichiometric excess of oxidant. Thus, an oil emulsion (1000 liters at 80° C, pH 7.5) having oil content 9,720 mg/l, and sulfide (free and bound) 25 mg/l, was treated with 5 liters NaClO and 1.9 kg 45 percent $FeCl_3$ solution. With vigorous aeration, the reaction was completed within 5 min. Clarification required 10 min. The oil-sludge mixture was drawn off from the surface. The remaining liquid was neutralized with 0.4 kg 10 percent aqueous NaOH and filtered by a ceramic candle filter. The purified effluent contained oil 16, COD 480, and dry residue 3,300 mg/l, and had pH 7.0. The $Fe(OH)_3$ absorbed oil amounting to 17.2 times its own weight. The effluent water, at 80°, is reusable.

Sheikh, M. "Stream Pollution Control Process by Treatment of Oil- and Phenol-Containing Industrial Sewage." U.S. 3,595,787 (Cl. 210-60; C 02c) (July 27, 1971), Appl. 542,468 (April 14, 1966):3 pp.

A stream pollution control process, comprises treating soluble oil wastes and emulsions in an industrial plant effluent, with inorganic salts and bases, to split soluble oil waste emulsions. A demulsifier is added to eliminate the tendency of the oil phase to become sticky from treatment chemicals, and to separate the oil and water phases from each other. Treating the separate phases prevents discharging oil or other pollutants into streams. The oil phase is treated to render it reusable as a soluble oil; the water phase is concentrated to make it reusable as treatment chemicals for treating further amounts of soluble oil waste emulsions and the treatment is repeated in a closed cycle arrangement.

Shernick, J.L. "Oil Field Emulsions." Industrial and Engineering Chemistry 12(2) (February 1920):133-139.

This article reviews techniques for breaking oil field emulsions (water-in-oil). Processes considered are: filtration (not feasible), evaporation (uneconomical), electrical (a.c. and d.c. fields), centrifuging (used mainly in removing traces of water), and chemicals.

Chemical techniques are detailed. Experiments are described that lead to the conclusion that the dispersed water droplets are negatively charged, and readily absorbed cations (H^+, Fe^{+3}) could be used to neutralize the charge, causing coalescence. Experiments confirm this.

Shinoda, K. "Demulsification by the Use of Ion-Exchange Resin Membrane." Journal of Colloid Science 16 (1961):85-87.

Oil-in-water emulsions, stabilized by ionic agents, can be destroyed using ion-exchange resin membranes in an electrolytic cell.

Simon, R. and Poynter, W.G. "Down-Hole Emulsification for Improving Viscous Crude Production." Journal of Petroleum Technology (December 1968):1349-1353.

This article describes the "down-hole" emulsification process used in wells that produce viscous crudes or water-oil emulsions. Addition of the proper surfactants converts these to low viscosity oil-water emulsions.

Two field tests are described. At Huntington Beach, California, pump volumetric efficiency increased from 47 to 60 percent, and required pressure drop decreased from 850 to 15 psi. Surfactant cost was made up for by reduction in pumping costs. Similar results were obtained at Kern River, California.

Nonionic surfactants are generally preferred to anionic surfactants, being cheaper and giving a lower viscosity emulsion.

Sonntag, H. and Klare, H., Jr. (Deut. Akad. Wiss., Berlin). "Influence of Water-Soluble Surfactants, External Electric Fields, and Temperature Increases on the Coalescence Stability of Water/Oil Emulsions." Tenside 4(4) (1967):104-108. (German).

The effect of adding electrolytes (KCl) and water-soluble surfactants (oxyethylated nonylphenol, Span 80, etc.), of applying external electric fields, and of increasing temperature on the stability of black films was studied on a model droplet. Larger amounts of electrolytes cause dehydration of the surface-active adsorption layers and promote demulsification through water-soluble surfactants. External electric fields led to unstable emulsions when the voltage was increased to the point where an electric discharge could take place. Higher temperature caused an increased in the rates of flocculation and coalescence. The stability of the black films already formed was not affected by temperature.

Spielman, L.A. and Goven, S.L. "Experiments in Coalescence by Flow Through Fibrous Mats." Industrial and Engineering Chemistry Fundamentals 11(1) (1972):73-83.

This paper describes experiments in coalescence of dilute oil-in-water suspensions by flow through glass fibrous mats. Incoming droplet size, fiber diameter, flow velocity, preferential wetting and oil viscosity were independently varied. Experimental results are compared with theoretical predictions.

Experimental single phase pressure drops were about 30 percent lower than predicted (due possibly to filter clamping). Results for suspension pressure drops agreed well with theory. Results confirmed that removal of drops was independent of other drop sizes and oil viscosity. Filter coefficients, $\underline{g} = -[\ln (n_L/n_o)]/L$, (where n_L and n_o are the outlet and inlet face particle number concentrations, and L is the thickness of the porous mat), were determined as a function of flow rate, droplet diameter, mat thickness, fiber diameter and oil viscosity.

Spielman, L.A. and Goven, S.L. "Theory of Coalescence Through Porous Media." Industrial and Engineering Chemistry Fundamentals 11(1) (1972):66-72.

This paper presents approximate solutions to the equations describing coalescence by flow through porous media (Spielman and Goven, Ind. Eng. Chem., 62(10) 1970b). Simplifying assumptions are made: (1) small inlet oil volume fraction and(2) moderate oil-to-water viscosity ratio. Conclusions are that the pressure drop is independent of the detailed size distribution of the dispersed phase, and the coalescence efficiency for any given size drop, while dependent upon that drop size, is independent of the overall size distribution of drops.

Steinhauff, F. "Modern Oilfield Demulsification - Part I." Petroleum (September 1962):294-296.

This first part (of a two-part article) discusses the formation of crude oil emulsions, and factors that influence their stability. Effects of emulsifying agents are mentioned. Water-in-oil emulsions are emphasized. (Part 2 deals with methods of breaking emulsions.)

Steinhauff, F. "Modern Oilfield Demulsification - Part 2." Petroleum (October 1962):335-337.

This article deals mainly with chemical demulsification of oil-water emulsions, but begins with a brief description of the electrical dehydration process.

Chemical dehydration is the "most economically important method [of breaking emulsions] used today." A brief history of demulsifiers is given, along with a discussion of the types currently used. The effects of heating (and agitating) are mentioned, in reference to Stokes' Law.

Stenzel, R.W. and Turner, D.W. (Petrolite Corp.) "Apparatus for Breaking Continuous-Oil-Phase Emulsions." Ger. 1,470,608 (CL. C 10g, B old) (February 8, 1973), U.S. Appl. 64,574 (October 24, 1960):8 pp.

The apparatus had long vertical channel-shaped outer electrodes passed by the emulsion, and long central inner electodes to reduce the bad effect of electrohydraulic turbulency in the ends of the channels (length of the channels in cm, width in cm, liquid velocity in cm/min, treatment time in min, and residual material in the oil phase in ppm given): 38, 7.6, 11.17, 3.4, 16.8; 102, 7.6, 35.56, 2.8, 0.56, respectively.

Strassner, J.E. "Effect of pH on Interfacial Films and Stability of Crude Oil-Water Emulsions." Journal of Petroleum Technology (March 1968):303-312.

Emulsions are stabilized by (1) repulsive charges on the surfaces of dispersed phase droplets and (2) films, that inhibit coalescence, around the droplets. The films contain varying organic acids and bases. The stabilizing effects can be altered by changing pH (using inorganic acids and bases). Chemical requirements for breaking the emulsions can be reduced significantly by adjusting to an optimum pH.

Stability is examined as a function of crude oil viscosity and film ratio. Generally, oils of viscosity >6 cp and >20 percent film ratio formed stable emulsions.

Natural surfactants (asphaltene and resins) stabilize best in highly acidic or basic solutions, while small concentrations of commercial surfactants operate at intermediate pH conditions.

Several examples of destabilization by pH adjustment are given.

Sumitomo Chemical Co. "Treating Oil Containing Industrial Wastes by Ultrafiltration and/or Reverse Osmosis in Closed Circuit with Incinerator." Ger. 25-49-882 (Cl. 210) (May 13, 1976), Appl. (November 6, 1975).

Process and apparatus are claimed for the disposal of aqueous effluents containing combustible organic impurities, the process comprising concentrating the liquid by ultrafiltration and/or reverse osmosis, followed by incineration of the thickened fluid, with the improvement whereby the dilute solution (filtrate) obtained from the ultrafiltration or the reverse osmosis is used in a closed circuit to cool or scrub the flue gases from the incinerator, the contact serving to decompose the organic components of the filtrate.

The effluent is thickened by ultrafiltration and the filtrate subjected to reverse osmosis, both the concentrates to be incinerated in a furnace. The flue gas may be scrubbed to reduce its temperature to below 250° C, or the heat may be recovered in a waste heat boiler before the gases enter a dust extractor from which they are discharged via a chimney.

Ultrafiltration of an effluent containing 3.5 percent oil at a rate of 1690 kg/h produced 200 kg/h of thickened fluid which was augmented by a further 50 kg/hr concentrate obtained by reverse osmosis treatment of the filtrate, the combined sludge (containing 24 percent oil) being burned with 40 kg/h of fuel oil. The filtrate from the reverse osmosis (1440 kg/h) was sprayed over the flue gases to reduce their temperature from 1050° C to 235° C. (15 pp.).

Ultrafiltration of an effluent containing 3-1/2 percent oil at a rate of 1690 kg/h produced 200 kg/h of thickened fluid which was augmented by a further 50 kg/hr concentrate obtained by reverse osmosis treatment of the filtrate, the combined sludge (containing 24 percent oil) being burned with 40 kg/h of fuel oil. The filtrate from the reverse osmosis (1440 kg/h) was sprayed over the flue gases to reduce their temperature from 1050' C to 235' C (15 pp).

TJ Engineering, Inc. "Ultrafiltration Membrane" Chemical Engineering 83(8) (April 12, 1976):168.

This article describes polysulfone membrane modules for ultrafiltration systems. They are stable for pH 0.5 to 12, T $\leq$180° F. Molecular weight cut-off is approximately 2500. At 50 psi, the TJ-439-PS20 membrane produces approximately 50 gph permeate.

Takahaski, S. and Miyata, K. "Treatment of Waste Water Containing Oil." Junkatsu 19(3) (1974):222-228. (Japanese).

Procedures for separation and removal of free and suspended oils from water are reviewed (30 references).

Tao, F.-S. (Texaco, Inc.) "Emulsion Breaking Method." U.S. 3,928,194 (December 23, 1975).

Water-in-oil emulsions are mixed with a demulsifying agent and an aqueous phase to form oil-in-water dispersions, which are separated by settling.

Truby, R. "Reverse Osmosis for Boiler Feedwater Treatment." Power Engineering 80(12) (December 1976):58-60.

This article describes several utility and industrial systems that use reverse osmosis pre-treatment of water for boilers. Savings have been realized due to reduced chemical requirement, and reduced corrosion.

Trulson, O.C. and Litz, L.M. (Union Carbide Corp.). "Ultrafiltration Apparatus and Process for the Treatment of Liquids." U.S. 3,977,967 (Cl. 210/23F) (August 31, 1976), Appl. 532,683 (December 13, 1974).

An apparatus and process are provided for the concentration and separation of components contained in liquids. The apparatus is comprised of, in part, a module containing a plurality of axially aligned, hollow tubular members having a well-defined porosity and a substantially uniform, continuous, adherent, porous coating of preformed, aggregated, inorganic metal oxide particles on their interior or exterior surface. The low molecular weight dissolved phases permeate the walls of the tubes while the larger diameter molecules are retained in the liquid. The apparatus can be operated for long periods of time with a high degree of concentration and separation of liquids. The apparatus is particularly suited for the concentration and separation of oil from mixtures of oil, water, and detergents. It is also useful in textile, paper making, and food industries. 48 Claims, 8 Drawing Figures.

Turner, D.W. (Petrolite Corp.) "Apparatus for Electrically Treating Oil-Based Emulsions Containing a Dispersed Aqueous Phase." Ger. Offen. 2,233,082 (Cl. C 10g) (February 1, 1973), U.S. Appl. 163,637 (July 19, 1971):28 pp.

The conductor between the electrodes inside the apparatus and the external voltage supply was passed through an upward directed conduct fixed onto the apparatus, a curved part and a downward directed conduct that was combined with a heat-exchanger before reaching the leading-in socket, to maintain a protective temperature drop between the high-temperature apparatus and the socket.

Turner, D.W. (Petrolite Corp.) "Electric Emulsion Breaker." Ger. 1,261,825 (Cl. B 01d) (February 29, 1968), Appl. (January 27, 1959):8 pp.

Water-in-oil emulstions are broken by passing the emulsion through two or more chambers in series fitted with electrodes. The chambvers are formed by dividing a horizontal, cylindrical tank with one or more vertical walls. The first chambers are supplied with a.c. and the last with d.c.

Turner, D.W. (Petrolite Corp.). "Systems for Electrically Treating Oil-Continuous Emulsions." U.S. 3,707,458 (Cl. 204-308; B 01d) (December 26, 1972), Appl. 202,213 (November 26, 1971):8 pp.

In an apparatus for electrically treating emulsions, an electric field is formed by an energized electrode connected to an external transformer. A first conduit extends upwardly from the vessel to a branch conduit which connexts to a pair of arm conduits extending downwardly to closed ends. A support rod extends in the first conduit from the energized electrode and connects through a horizontal support rod to an arm support rod in each conduit. Each arm support rod is secured to the top of a cylindrical insulator resting within a socket upon the closed end of the arm conduit. Heat exchangers are associated with the arm conduits at a position space from the branch conduit. The heat exchangers create a temperature gradient between the insulators and the interior of the vessel. The liquid in the vessel can be at elevated temperatures (e.g., 5000' F) while the insulators remain at low temperature (e.g., 100' F) during electric resolution of emulsions. This apparatus is suitable for electric treatment fo oil-continuous emulsions containing a dispersed aqueous phase.

Vadekar, M. and Wilson, H.S. (Exxon Research and Engineering Co.) "Removing Oil from Oily Wastewater Streams." U.S. 4,008,160 (Cl. 21023R; B01D13/00) (February 15, 1977), Appl. 600,460 (July 30, 1975):4 pp.

Oil is removed from oily wastewater streams, especially stable emulsions from refineries, by passing the stream over a particulate bed of an unprocessed poly(vinyl chloride) (I). For example, passing a sour water overhead from a steam cracker primary tower which contained 1250 volume ppm (by volume) highly olefinic emulsified oil through 15 cm^3 I (4 to 20 mesh) in the amount of 10 volumes sour water/volume I removed >99 percent of the oil, compared with 60 percent for activated carbon.

Van der Meer, P.M. (Van der Meer, H.; De Bruyne, G.W.; Sterk, R.M.C.; and Bosma, J.P.H.) "Apparatus for Separating a Suspension or a Water-In-Oil Type Emulsion." Ger. 1,258,829 (Cl. B 01d) (January 18,1968), Appl. (April 26, 1960):5 pp.

Heavy liquid or solid particles in a water-in-oil suspension or emulsion are separated by passing the latter under suitable pressure downward through a nozzle into a closed vessel, the stream of liquid from the nozzle being conducted through a ring with a funnel-shaped opening. The relation of cross-sectional areas of the liquid stream and the funnel are such that a reversal of direction of the liquid takes place under the forces that are set up. The denser particles are thus made to continue downward into the container while pure liquid, free from particles, flows upward and is discharged through openings and an outlet adjacent to the nozzle.

Vold, R.D. and Mittal, K.L. (Department of Chemistry, University of Southern California, Los Angeles, CA) "Differences in Ultracentrifugal Stability of Various Oil-In-Water Emulsions." J. Soc. Cosmet. Chem. 23(3) (1972):171-188. (English).

Studies of Nujol-water and olive oil-water emulsions stabilized with sodium dodecyl sulfate, cetylpyridinium chloride, Tween 20, or Triton X-100 show that the rate of separation of oil in an ultracentrifuge decreases with time of centrifugation, approaching zero at sufficiently long times. The marked differences in behavior of these systems suggest that the chemical nature of the oil and of the surfactant, and the molecular geometrical compatibility, may be more important than such properties as viscosity and interfacial tension.

Wakabayashi, Y. and Takado, H. (Fujikoshi, Ltd.) "Separation of Oil from Waste Emulsified Oil." Japan Kokai 76 30,585 (Cl. B01D) (March 15, 1976),

Appl. 74 104,004 (September 10, 1974):3 pp. (Japanese).

An oil-water separating agent for waste emulsified oil, such as spent cutting oil, is made by adding 0.6 ± 0.2 percent of a polymer flocculant to a powdered mixture containing $CaCl_2$-impregnated pozzolan 60 ± 5, polyaluminum chloride 25 ± 5, and Na_2CO_3 13 + 2 percent. Thus, a powdered mixture containing $CaCl_2$-impregnated pozzolan 62, polyaluminum chloride 25, and Na_2CO_3 13 percent was mixed with 0.6 percent of a polymer flocculant (molecular weight 3×10^6). The oil-water separating agent 25 percent was added to 200 liters of a waste emulsified oil solution (pH 9.4) containing 4.8 percent oil to adjust the pH to 6.0 to 6.5, followed by stirring, settling, and filtering, to obtain a transparent solution containing 5 ppm oil.

Walther & Cie. A.G. (Cologne, W. Germany) "Oil-Emulsion Breaking Plant." Chemical Engineering 83(25) (November 22, 1976):94.

This article describes a plant, called "Oecomat," for treating almost all kinds of emulsions. The unit produces a sludge of approximately 40 percent water, and an effluent with <20 mg/l oil.

Wang, L.K.; Yang, J.Y.; and Dahms, D.B. "Separation of Emulsified Oil from Water." Chemistry and Industry (July 5, 1975):562-564.

This article is a state-of-the-art review of techniques for separating emulsified oil from water. Treatments examined are: flotation, magnetization, fibrous coalescence, filtration (layer and membrane), adsorption and absorption, centrifugation, sedimentation, chemical coagulation, heating (evaporation) and biological oxidation. (40 references)

Waterman, L.C. "Electrical Coalescers." Chemical Engineering Progress 61(10) (October 1965):51-57.

The petroleum industry relies on electrostatic coalescers to purify crude petroleum of its connate sediments and corrosion inducing salts. Two mechanisms promoting separation are presented. Several processes using electrical coalescers are discussed.

Waterman, L.C. and Winslow, J.P. "Electrical Demulsification Processes and Equipment." World Petroleum 37(13) (December 1966):58.

Electrostatic coalescers are used: (1) in conjunction with crude oil production to reduce water content, (2) prior to distillation to reduce corrosion and fouling of equipment, and (3) in treatment of final products.

The effect of the electric field is to overcome the resistance to coalescence established by the films about the droplets of the dispersed phase (water). The mechanism of droplet coalescence is discussed. Heat and pressure are used to decrease the oil viscosity. Crude dehydration is efficient and cheaper using a.c.

A d.c. process, "electrofining," is used for treatment of final products. Similarities, differences, equipment and electrical requirements for electrostatic precipitation and electrofining are discussed in detail.

Watson, F.D. (Petrolite Corp.) "Three Phase Energized Electrical Treater." U.S. 3,794,578 (Cl. 204-305; B 03c) (February 26, 1974), Appl. 317,914 (December 26, 1972):6 pp.

An electric field treater operated with three-phase a.c. is used for resolving a dispersion formed of a continuous oil phase and dispersed water. It comprises a metal vessel which includes a dispersion inlet and outlets to remove the continuous oil phase and the coalesced water phase. A transformer arrangement energized from three-phase a.c. provides in three secondary windings elevated voltages for energizing three electrodes mounted in electrical isolation within the vessel. Two of the secondary windings are phased 120° apart and energize the electrodes mounted to each side of the third electrode. The third electrode is energized by a third secondary winding which is phased 60° apart from the other two secondary windings. High tension conductors interconnect the secondary windings with the electrodes. The side-positioned electrodes are energized to substantially the same potential as the third electrode and all the electrodes are at the same potential as the metal sidewalls of the vessel.

Weissman, B.J.; Smith, C.V., Jr.; and Okey, R.W. "Performance of Membrane Systems in Treating Water and Sewage." Chemical Engineering Progress Symposium Series 64(90) (1969):285-290.

Three prototype ultrafiltration systems were built and operated in Connecticut for treating: (1) raw sewage,

(2) secondary effluent, and (3) moderately contaminated water. Non-cellulosic organic polymer membranes (anisotropic) in cartridges of 20 square feet were used.

BOD reduction was >95 perent; TSS reduction was 100 percent. Superficial velocities of 4 to 6 ft/sec were used to minimize concentration polarization (to maintain high flux). With the sewage treatment plant, membrane cleaning was required about every 1 to 2 months, with irreversible fouling becoming substantial after about 6 months.

Economic estimates are presented at $2 to $5 per square foot of membrane, with a 6 month membrane lifetime. Projected capital costs (for up to 60,000 GPD processed) are presented graphically. Operating costs are estimated at $0.50 to $1.60/1000 gal.

For sewage treatment, conventional means become cheaper at approximately >20,000 to 50,000 GPD. Water treatment appears cheapr by conventional means, but ultrafiltration allows portability.

Wilms, H. (Wilms G.m.b.H.) "Separation of Water-Oil Emulsions." Ger. Offen. 2,503,350 (Cl. B01D17/04) (July 29, 1976), Appl. (January 28, 1975):8 pp.

Oil-in-water emulsions are broken by feeding the emulsion continuously into one tank where the pH is controlled and a reagent is added for breaking the emulsion. The mixed solution is passed into another tank and treated by bubbling fine air bubbles through to separate the oil at the top. The oil on the surface is removed at the effluent end of the tank by rotating disks dipped in the solution. The clarified water is transferred to another tank where it is neutralized (e.g., by NaOH or milk of lime).

Wilson, P.M.; Murphy, C.L.; and Foster, W.R. "The Effects of Sulfonate Molecular Weight and Salt Concentration on the Interfacial Tension of Oil-Brine-Surfactant Systems." Society of Petroleum Engineers Paper No. 5812, Improved Oil Recovery Symposim, Tulsa, Oklahoma, (March 22-24, 1976).

Synthetic and petroleum sulfonates produce lowest interfacial tensions (IFT) in aqueous solutions against Loma Novia crude oil when the sulfonate has an average equivalent weight of about 400 to 410 (hydrocarbon equivalent weight of about 305 prior to sulfonation).

Adjusting the electrolyte content of the aqueous phase also affects IFT, with NaCl being more effective than Na_2SO_4, Na_2CO_3, or $Na_5P_3O_{10}$ in reducing IFT. Mixtures of petroleum sulfonates are often more effective in lowering IFT than individual sulfonates used separately.

Woelfin, W. (Petrolite Corp.) "Apparatus for Electrically Breaking and/or Desalting Water-In-Oil Emulsions." Ger. 1,420,894 (Cl. C 10g, B 01d) (August 17, 1972), Appl. P 14 20 894.7-44 (July 17, 1958):7 pp.

A horizontal closed cylinder is provided with lattice electrodes placed in parallel planes to the long axis of the cylinder and above the central axis. The lattices consist of metal rods or concentric rings on a quadrilateral frame to which are attached insulators and connections to an external source. Inlets for the emulsion are situated below the central axis of the cylinder. The cylinder has a bottom outlet piping system with valves for the collected water and upper outlet for the dewatered or desalted oil produced by the breaking or desalting of the emulsion in an electric field between the lattice electrodes.

Yano, S. (Nippon Mining Co., Ltd.) "Oil Emulsion Wastewater Treatment." Japan Kokai 75 47,452 (April 26, 1975).

Oils are separated from petroleum emulsion containing wastewaters using $Ca(OH)_2$ and $Al_2(SO_4)_3$. An oil-containing alkaline wastewater from a petrochemical plant was treated with $CaCl_2$ at pH 6 to 10, aerated, and further treated with aluminum sulfate. The pH was adjusted to 7.5 to 8.0. After standing, scum, water, and precipitate were separated.

Yukawa, H. (Gunma University, Maebashi, Japan) "Electrochemical Separation for Dispersed Systems." Kagaku Kogyo 22(5) (1971):674-680. (Japanese).

An electrochemical separation of emulsions, (e.g., oil-in-water and water-in-oil systems), and an electroosmotic filtration were investigated. Experiments were made on an emulsion of C_5H_6, $PhNH_2$, $PhNO_2$, and kerosine. The rate of moving of the emulsion boundary was proportional to the applied electric field strength. In the case of $PhNH_2$, the moving rate was 19 cm/hr in a field strength of 10 V/cm, compared to 0.2 cm/hr without the applied field. The filtration rate of water from slurries by electroosmosis was proportional to the field strength applied between either the filter bed or the

cake. In the case of a clay slurry, the amount of filtrate when applying a field of 12 V/cm was 14.2 times that where there was no applied field.

Yukawa, H.; Kanai, S.; Shimoyama, O; and Kurino, T. (Department of Chemical Engineering, Gunma University, Kiryu, Japan). "Separation of Particles from Emulsions Exposed to Electric Potential." Kagaku Kogaku 35(6) (1971):656-663. (Japanese).

For oil-in-water emulsions of C_6H_6, kerosine, $PhNH_2$, and $PhNO_2$, the separability of the dispersed particles was to $P^{1/2}$, where P is the total electric power. The separating efficiency for continuous operation was proportional to $P^{0.62}$.

APPENDIX B

TABLE B-1

EMULSION COMPOSITIONS
(Volume %)

	PHILLIPS NORTH BURBANK	CITGO EL DORADO	PENNGRADE BRADFORD	GARY OPERATING BELL CREEK
Oil	33	20	20	20
Brine[a]	64	63.7	76.3	63.7
Ethylene glycol	2.6	6.5	-	6.5
SDBS[b]	0.2	0.4	0.3	0.4
Methyl ethyl ketone	-	-	1.6	-
Isobutyl alcohol	-	-	1.6	-
Alcohol ether sulfate	0.08	0.16	0.1	0.16
Sodium xylene sulfonate	0.08	0.16	0.1	0.16
Other	-	9.1[c]	-	9.1[d]
	99.96	100.02	100	100.02

[a]Brine compositions follow.
[b]Sodium dodecylbenzene sulfonate.
[c]North Burbank emulsion as seed.
[d]El Dorado emulsion as seed.

TABLE B-2

FORMATION WATER COMPOSITIONS

	FORMATION WATER (AS RECEIVED) (mg/l)			
	BELL CREEK	EL DORADO	BRADFORD	NORTH BURBANK
Calcium	90	1,960	328	4,220
Magnesium	36	1,220	112	1,050
Sodium	77	21,300	2,510	19,400
Sulfate	33	11	2	0
Chloride	78	39,400	4,610	40,600
Total TDS	726	64,900	8,100	66,400

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