DOE/ER/30133--H1-Vol.2

DE90 011770

MEMBRANE SEPARATION SYSTEMS
- A RESEARCH & DEVELOPMENT NEEDS ASSESSMENT

by the
Department of Energy Membrane Separation Systems
Research Needs Assessment Group

Final Report

Volume II

March 1990

Prepared by:

R.W. Baker
E.L. Cussler
W. Eykamp
W.J. Koros
R.L. Riley
H. Strathmann

Under Contract No. DE-AC01-88ER30133

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

VOLUME II

INTRODUCTION TO VOLUME II	viii
CHAPTER ONE: MEMBRANE AND MODULE PREPARATION by R. W. Baker, Membrane Technology and Research, Inc.	1-1
1.1 SYMMETRICAL MEMBRANES	1-3
1.1.1 Dense Symmetrical Membranes	1-3
1.1.2 Microporous Symmetrical Membranes	1-6
1.2 ASYMMETRIC MEMBRANES	1-10
1.2.1 Phase Inversion (Solution-Precipitation) Membranes	1-10
1.2.2 Interfacial Composite Membranes	1-19
1.2.3 Solution Cast Composite Membranes	1-22
1.2.4 Plasma Deposit in Membranes	1-24
1.2.5 Dynamically Formed Membranes	1-26
1.2.6 Reactive Surface Treatment	1-26
1.3 CERAMIC AND METAL MEMBRANES	1-27
1.3.1 Dense Metal Membranes	1-27
1.3.2 Microporous Metal Membranes	1-27
1.3.3 Ceramic Membranes	1-27
1.3.4 Molecular Sieve Membranes	1-28
1.4 LIQUID MEMBRANES	1-32
1.5 HOLLOW-FIBER MEMBRANES	1-33
1.5.1 Solution (Wet) Spinning	1-35
1.5.2 Melt Spinning	1-35
1.6 MEMBRANE MODULES	1-37
1.6.1 Spiral-Wound Modules	1-37
1.6.2 Hollow-Fiber Modules	1-40
1.6.3 Plate-and-Frame Modules	1-40
1.6.4 Tubular Systems	1-40
1.6.5 Module Selection	1-40
1.7 CURRENT AREAS OF MEMBRANE AND MODULE RESEARCH .	1-44
REFERENCES	1-46
CHAPTER TWO: PERVAPORATION by R. W. Baker, Membrane Technology and Research, Inc.	2-1
2.1 PROCESS OVERVIEW	2-1
2.1.1 Design Features	2-4
2.1.2 Pervaporation Membranes	2-6
2.1.3 Pervaporation Modules	2-6
2.1.4 Historical Trends	2-9

2.2	CURRENT APPLICATIONS, ENERGY BASICS AND ECONOMICS .	2-10
2.2.1	Dehydration of Solvents	2-11
2.2.2	Water Purification	2-14
2.2.3	Pollution Control	2-19
2.2.4	Solvent Recovery	2-21
2.2.5	Organic-Organic Separations	2-24
2.3	INDUSTRIAL SUPPLIERS	2-26
2.4	SOURCES OF INNOVATION	2-30
2.5	FUTURE DIRECTIONS	2-32
2.5.1	Solvent Dehydration	2-32
2.5.2	Water Purification	2-34
2.5.3	Organic-Organic Separations	2-34
2.6	DOE RESEARCH OPPORTUNITIES	2-35
2.6.1	Priority Ranking	2-36
	REFERENCES	2-37

CHAPTER THREE: GAS SEPARATION 3-1
by W. J. Koros, University of Texas, Austin

3.1	INTRODUCTION	3-1
3.2	FUNDAMENTALS	3-3
3.3	MEMBRANE SYSTEM PROPERTIES	3-5
3.4	MODULE AND SYSTEM DESIGN FEATURES.	3-7
3.5	HISTORICAL PERSPECTIVE	3-11
3.6	CURRENT TECHNICAL TRENDS IN THE GAS SEPARATION FIELD	3-12
3.6.1	Polymeric Membrane Materials	3-12
3.6.2	Plasticization Effects.	3-15
3.6.3	Nonstandard Membrane Materials	3-17
3.6.4	Advanced Membrane Structures	3-17
3.6.5	Surface Treatment to Increase Selectivity	3-17
3.6.6	System Design and Operating Trends	3-18
3.7	APPLICATIONS.	3-19
3.7.1	Hydrogen Separations	3-19
3.7.2	Oxygen-Nitrogen Separations.	3-23
3.7.3	Acid Gas Separations	3-26
3.7.4	Vapor-Gas Separations.	3-28
3.7.5	Nitrogen-Hydrocarbon Separations	3-29
3.7.6	Helium Separations	3-30

3.8	ENERGY BASICS	3-30
3.9	ECONOMICS	3-35
3.10	SUPPLIERS	3-35
3.11	SOURCES OF INNOVATION	3-37
3.11.1	Research Centers and Groups	3-37
3.11.2	Support of Membrane-Based Gas Separation	3-40
3.12	FUTURE DIRECTIONS	3-40
3.12.1	Industrial Opportunities	3-40
3.12.2	Domestic Opportunities	3-41
3.13	RESEARCH OPPORTUNITIES	3-41
3.13.1	Ultrathin Defect-Free Membrane Formation Process	3-41
3.13.2	Highly Oxygen-Selective Materials	3-44
3.13.3	Polymers, Membranes and Modules for Demanding Service	3-44
3.13.4	Improved Composite Membrane Formation Process	3-44
3.13.5	Reactive Surface Modifications	3-45
3.13.6	High-Temperature Resistant Membranes	3-45
3.13.7	Refinement of Guidelines and Analytical Methods for Material Selection	3-45
3.13.8	Extremely Highly Oxygen-Selective Membrane Materials	3-46
3.13.9	Physical Surface Modification by Antiplasticization	3-46
3.13.10	Concentration of Products from Dilute Streams	3-46
	REFERENCES	3-47

CHAPTER FOUR: COUPLED AND FACILITATED TRANSPORT 4-1

by E. L. Cussler, University of Minnesota

4.1	PROCESS OVERVIEW	4-1
4.1.1	The Basic Process	4-1
4.1.2	Membrane Features	4-3
4.1.3	Membrane and Module Design Factors	4-7
4.1.4	Historical Trends	4-9
4.2	CURRENT APPLICATIONS	4-9
4.3	ENERGY BASICS	4-12
4.4	ECONOMICS	4-14
4.4.1	Metals	4-14
4.4.2	Gases	4-15
4.4.3	Biochemicals	4-16
4.4.4	Sensors	4-17
4.5	SUPPLIER INDUSTRY	4-17

4.6	RESEARCH CENTERS AND GROUPS	4-17
4.7	CURRENT RESEARCH	4-18
4.8	FUTURE DIRECTIONS	4-19
4.8.1	Metal Separations	4-19
4.8.2	Gases	4-21
4.8.3	Biochemicals	4-24
4.8.4	Hydrocarbon Separations	4-25
4.8.5	Water Removal	4-25
4.8.6	Sensors	4-25
4.9	RESEARCH OPPORTUNITIES: SUMMARY AND CONCLUSIONS .	4-26
	REFERENCES	4-30

CHAPTER FIVE: REVERSE OSMOSIS 5-1

by R. L. Riley, Separation Systems Technology, Inc.

5.1	PROCESS OVERVIEW	5-1
5.1.1	The Basic Process	5-1
5.1.2	Membranes	5-5
5.1.3	Modules	5-5
5.1.4	Systems	5-9
5.2	THE REVERSE OSMOSIS INDUSTRY	5-14
5.2.1	Current Desalination Plant Inventory	5-14
5.2.2	Marketing of Membrane Products	5-16
5.2.3	Future Direction of the Reverse Osmosis Membrane Industry	5-18
5.3	REVERSE OSMOSIS APPLICATIONS	5-18
5.4	REVERSE OSMOSIS CAPITAL AND OPERATING COSTS	5-20
5.5	IDENTIFICATION OF REVERSE OSMOSIS PROCESS NEEDS	5-24
5.5.1	Membrane Fouling	5-24
5.5.2	Seawater Desalination	5-27
5.5.3	Energy Recovery for Large Seawater Desalination Systems . .	5-30
5.5.4	Low-Pressure Reverse Osmosis Desalination	5-33
5.5.5	Ultra-low Pressure Reverse Osmosis Desalination	5-35
5.6	DOE RESEARCH OPPORTUNITIES	5-37
5.6.1	Projected Reverse Osmosis Market: 1989-1994	5-37
5.6.2	Research and Development: Past and Present	5-37
5.6.3	Research and Development: Energy Reduction	5-39
5.6.4	Thin-Film Composite Membrane Research	5-39
5.6.5	Membrane Fouling: Bacterial Adhesion to Membrane Surfaces	5-42
5.6.6	Spiral-wound Element Optimization	5-43
5.6.7	Future Directions and Research Topics of Interest for Reverse Osmosis Systems and Applications	5-44

5.6.8	Summary of Potential Government-Sponsored Energy Savings Programs	5-50
REFERENCES		5-52
CHAPTER SIX: MICROFILTRATION by W. Eykamp, University of California, Berkeley		6-1
6.1	OVERVIEW	6-1
6.2	DEFINITIONS AND THEORY	6-2
6.3	DESIGN CONSIDERATIONS	6-9
6.3.1	Dead-end vs. Crossflow Operation	6-9
6.3.2	Module Design Considerations	6-11
6.4	STATUS OF THE MICROFILTRATION INDUSTRY	6-14
6.4.1	Background	6-14
6.4.2	Suppliers	6-14
6.4.3	Membrane Trends	6-16
6.4.4	Module Trends	6-20
6.4.5	Process Trends	6-20
6.5	APPLICATIONS FOR MICROFILTRATION TECHNOLOGY	6-20
6.5.1	Current Applications	6-20
6.5.2	Future Applications	6-21
6.5.3	Industry Directions	6-24
6.6	PROCESS ECONOMICS	6-25
6.7	ENERGY CONSIDERATIONS	6-27
6.8	OPPORTUNITIES IN THE INDUSTRY	6-28
6.8.1	Commercially-Funded Opportunities	6-28
6.8.2	Opportunities for Governmental Research Participation	6-28
REFERENCES		6-31
CHAPTER SEVEN: ULTRAFILTRATION by W. Eykamp, University of California, Berkeley		7-1
7.1	PROCESS OVERVIEW	7-1
7.1.1	The Gel Model	7-3
7.1.2	Concentration Polarization	7-8
7.1.3	Plugging	7-8
7.1.4	Fouling	7-9
7.1.5	Flux Enhancement	7-10
7.1.6	Module Designs	7-11

7.1.7	Design Trends	7-11
7.2	APPLICATIONS	7-13
7.2.1	Recovery of Electrocoat Paint	7-13
7.2.2	Fractionation of Whey	7-13
7.2.3	Concentration of Textile Sizing	7-13
7.2.4	Recovery of Oily Wastewater	7-16
7.2.5	Concentration of Gelatin	7-16
7.2.6	Cheese Production	7-16
7.2.7	Juice	7-16
7.3	ENERGY BASICS	7-18
7.3.1	Direct Energy Use vs. Competing-Processes	7-19
7.3.2	Indirect Energy Savings	7-19
7.4	ECONOMICS	7-20
7.4.1	Typical Equipment Costs	7-20
7.4.2	Downstream Costs	7-23
7.4.3	Product Recovery	7-23
7.4.4	Selectivity	7-25
7.5	SUPPLIER INDUSTRY	7-25
7.6	SOURCES OF INNOVATION	7-26
7.6.1	Suppliers	7-26
7.6.2	Users	7-27
7.6.3	Universities	7-28
7.6.4	Government	7-28
7.6.5	Foreign Activities	7-28
7.7	FUTURE DIRECTIONS	7-28
7.8	RESEARCH NEEDS	7-31
7.9	DOE RESEARCH OPPORTUNITIES	7-34
	REFERENCES	7-35

CHAPTER EIGHT: ELECTRODIALYSIS 8-1
by H. Strathmann, Fraunhofer Institut für Grenzflächen und
Bioverfahrenstechnik

8.1	INTRODUCTION	8-1
8.2	PROCESS OVERVIEW	8-1
8.2.1	The Principle of the Process and Definition of Terms	8-1
8.2.2	Design Features and their Consequences	8-8
8.2.3	Ion-Exchange Membranes Used in Electrodialysis	8-13
8.2.4	Historical Developments	8-17

8.3	CURRENT APPLICATIONS OF ELECTRODIALYSIS	8-18
8.3.1	Desalination of Brackish Water by Electrodialysis	8-18
8.3.2	Production of Table Salt	8-20
8.3.3	Electrodialysis in Wastewater Treatment.	8-20
8.3.4	Electrodialysis in the Food and Pharmaceutical Industries . . .	8-21
8.3.5	Production of Ultrapure Water	8-21
8.3.6	Other Electrodialysis-Related Processes	8-23
8.4	ELECTRODIALYSIS ENERGY REQUIREMENT	8-26
8.4.1	Minimum Energy Required for the Separation of Water from a Solution	8-26
8.4.2	Practical Energy Requirement in Electrodialysis Desalination	8-26
8.4.2.1	Energy requirements for transfer of ions from the product solution to the brine	8-27
8.4.2.2	Pump energy requirements	8-28
8.4.2.3	Energy requirement for the electrochemical electrode reactions	8-28
8.4.3	Energy Consumption in Electrodialysis Compared with Reverse Osmosis	8-28
8.5	ELECTRODIALYSIS SYSTEM DESIGN AND ECONOMICS	8-30
8.5.1	Process Flow Description.	8-30
8.5.2	Electrodialysis Plant Components	8-30
8.5.2.1	The electrodialysis stack	8-30
8.5.2.2	The electric power supply	8-32
8.5.2.3	The hydraulic flow system	8-32
8.5.2.4	Process control devices	8-32
8.5.3	Electrodialysis Process Costs	8-32
8.5.3.1	Capital.	8-32
8.5.3.2	Operating costs	8-35
8.5.3.3	Total electrodialysis process costs	8-35
8.6	SUPPLIER INDUSTRY	8-38
8.7	SOURCES OF INNOVATION - CURRENT RESEARCH	8-40
8.7.1	Stack Design Research	8-40
8.7.2	Membrane Research	8-41
8.7.3	Basic Studies on Process Improvements	8-42
8.8	FUTURE DEVELOPMENTS	8-44
8.8.1	Areas of New Opportunity	8-44
8.8.2	Impact of Present R&D Activities on the Future Use of Electrodialysis	8-44
8.8.3	Future Research Directions.	8-49
	REFERENCES	8-51
9.1	GLOSSARY OF SYMBOLS AND ABBREVIATIONS	9-1

INTRODUCTION TO VOLUME II

Industrial separation processes consume a significant portion of the energy used in the United States. A 1986 survey by the Office of Industrial Programs estimated that about 4.2 quads of energy are expended annually on distillation, drying and evaporation operations.¹ This survey also concluded that over 0.8 quads of energy could be saved in the chemical, petroleum and food industries alone if these industries adopted membrane separation systems more widely.

Membrane separation systems offer significant advantages over existing separation processes. In addition to consuming less energy than conventional processes, membrane systems are compact and modular, enabling easy retrofit to existing industrial processes. The present study was commissioned by the Department of Energy, Office of Program Analysis, to identify and prioritize membrane research needs in light of DOE's mission.

This report was prepared by a group of six experts representing various fields of membrane technology. The group consisted of Dr. Richard W. Baker (Membrane Technology & Research, Inc.), Dr. Edward Cussler (University of Minnesota), Dr. William Eykamp (University of California at Berkeley), Dr. William J. Koros (University of Texas at Austin), Mr. Robert L. Riley (Separation Systems Technology, Inc.) and Dr. Heiner Strathmann (Fraunhofer Institute, West Germany). Dr. Eykamp served as Principal Investigator for the program. Dr. Amulya Athayde (MTR) served as program coordinator for the project. Dr. Athayde and Ms. Janet Farrant (MTR) edited the report.

Seven major membrane processes were covered: four developed processes, microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and electrodialysis (ED); two developing processes, gas separation with polymer membranes and pervaporation; and one yet-to-be-developed process, facilitated transport.

The first three processes, microfiltration, ultrafiltration, and reverse osmosis, are related filtration techniques, in which a solution containing dissolved or suspended solutes is forced through a membrane filter. The solvent passes through the membrane; the solutes are retained. These processes differ principally in the size of the particles separated by the membrane.

Microfiltration is considered to refer to membranes that have pore diameters from 0.1 μm (1,000 Å) to 10 μm . Microfiltration membranes are used to filter suspended particulates, bacteria or large colloids from solutions. Ultrafiltration refers to membranes having pore diameters in the range 20–1,000 Å. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solution. In the case of reverse osmosis, the membrane pores are so small, in the range of 5–20 Å in diameter, that they are within the range of the thermal motion of the polymer chains. Reverse osmosis membranes are used to separate dissolved microsolute, such as salt, from water. The principal application of reverse osmosis is the production of drinking water from brackish groundwater, or the sea.

The fourth fully developed membrane process is electrodialysis, in which charged membranes are used to separate ions from aqueous solutions under the driving force of an electrical potential difference. The process utilizes an electrodialysis stack, built on the filter-press principle, and containing several hundred individual cells formed by a pair of anion and cation exchange membranes. The principal application of electrodialysis is the desalting of brackish groundwater.

Gas separation with membranes is the more mature of the two developing technologies. In gas separation, a mixed gas feed at an elevated pressure is passed across the surface of a membrane that is selectively permeable to one component of the feed. The membrane separation process produces a permeate enriched in the more permeable species and a residue enriched in the less permeable species. Current applications are the separation of hydrogen from argon, nitrogen and methane in ammonia plants, the production of nitrogen from air and the separation of carbon dioxide from methane in natural gas operations.

Pervaporation is a relatively new process that has elements in common with reverse osmosis and gas separation. In pervaporation, a liquid mixture is placed in contact with one side of a membrane and the permeate is removed as a vapor from the other. The mass flux is brought about by maintaining the vapor pressure on the permeate side of the membrane lower than the potential pressure of the feed liquid. Currently, the only industrial application of pervaporation is the dehydration of organic solvents. However, pervaporation processes are being developed for the removal of dissolved organics from water and the separation of organic solvent mixtures.

The final membrane process studied in the report is facilitated transport. This process falls under the heading of "to be developed" technology. Facilitated transport usually employs liquid membranes containing a complexing or carrier agent. The carrier agent reacts with one permeating component on the feed side of the membrane and then diffuses across the membrane to release the permeant on the product side of the membrane. The carrier agent is then reformed and diffuses back to the feed side of the membrane. The carrier agent thus acts as a shuttle to selectively transport one component from the feed to the product side of the membrane.

Each of the authors was assigned primary responsibility for a topic area as shown below.

<u>Topic</u>	<u>Author</u>
Pervaporation	Richard Baker
Gas Separation	William Koros
Facilitated and Coupled Transport	Edward Cussler
Reverse Osmosis	Robert Riley
Microfiltration and Ultrafiltration	William Eykamp
Electrodialysis	Heiner Strathmann

The role of the authors was to assess the current state of membranes in their particular section, identify present and future applications where membrane separations could result in significant energy savings and suggest research directions and specific research needs required to achieve these energy savings

within a 5-20 year time frame. The authors as a group also performed the prioritization of the overall research needs.

Volume I of this report is devoted to a description of the methodology used in preparing the report, an introductory outline of membrane processes, a breakdown of current Federal support of membrane-related research in DOE and other Government agencies, and an analysis of the findings and recommendations of the group.

Volume II supports Volume I by providing detailed source information in light of which the findings of Volume I can be interpreted. Volume II contains eight chapters. The first discusses membrane and module preparation techniques. The same general methods can be used to prepare membranes for use in diverse separation applications, so it was decided to make a separate chapter of this topic, rather than repeating essentially the same information in several individual application chapters. Chapters Two through Eight take the areas of membrane technology one by one, and provide an overview of the process fundamentals, a discussion of the present technology and applications, and the limitations and opportunities for the future. For each area, a list of high-priority research items was identified and the relative importance of the items, in terms of impact on the industry, energy savings and likelihood for realization, was prepared. The top five or seven items in these individual lists were used by the group of authors to prepare the master table of 38 priority research needs that forms the basis of much of the discussion in Volume I.

REFERENCES

1. The DOE Industrial Energy Program: Research and Development in Separation Technology, 1987. DOE Publication number DOE/NBM-8002773.

CHAPTER ONE

MEMBRANE AND MODULE PREPARATION

TABLE OF CONTENTS

1.1 SYMMETRICAL MEMBRANES	1-3
1.1.1 Dense Symmetrical Membranes	1-3
1.1.1.1 Solution casting	1-3
1.1.1.2 Melt pressing	1-3
1.1.2 Microporous Symmetrical Membranes	1-6
1.1.2.1 Irradiation	1-6
1.1.2.2 Stretching	1-6
1.1.2.3 Template leaching	1-10
1.2 ASYMMETRIC MEMBRANES	1-10
1.2.1 Phase Inversion (Solution-Precipitation) Membranes	1-10
1.2.1.1 Polymer precipitation by thermal gelation	1-11
1.2.1.2 Polymer precipitation by solvent evaporation	1-15
1.2.1.3 Polymer precipitation by imbibition of water vapor	1-15
1.2.1.4 Polymer precipitation by immersion in a non-solvent bath	1-17
1.2.2 Interfacial Composite Membranes	1-19
1.2.3 Solution Cast Composite Membranes	1-22
1.2.2 Plasma Deposit in Membranes	1-24
1.2.5 Dynamically Formed Membranes	1-26
1.2.6 Reactive Surface Treatment	1-26
1.3 CERAMIC AND METAL MEMBRANES	1-27
1.3.1 Dense Metal Membranes	1-27
1.3.2 Microporous Metal Membranes	1-27
1.3.3 Ceramic Membranes	1-27
1.3.4 Molecular Sieve Membranes	1-28
1.4 LIQUID MEMBRANES	1-32
1.5 HOLLOW-FIBER MEMBRANES	1-33
1.5.1 Solution (Wet) Spinning	1-35
1.5.2 Melt Spinning	1-35
1.6 MEMBRANE MODULES	1-37
1.6.1 Spiral-Wound Modules	1-37
1.6.2 Hollow-Fiber Modules	1-40
1.6.3 Plate-and-Frame Modules	1-40
1.6.4 Tubular Systems	1-40
1.6.5 Module Selection	1-40
1.7 CURRENT AREAS OF MEMBRANE AND MODULE RESEARCH .	1-44
REFERENCES	1-46

CHAPTER ONE

MEMBRANE AND MODULE PREPARATION

by

R.W. Baker, Membrane Technology and Research, Inc.
Menlo Park, CA

The present surge of interest in the use of membranes to separate gases and liquids was prompted by two developments: first, the ability to produce high flux, essentially defect-free membranes on a large scale; second, the ability to form these membranes into compact, high-surface-area, economical membrane modules. These major breakthroughs took place in the 1960s and early 1970s, principally because of a large infusion of U.S. Government support into reverse osmosis research via the Office of Saline Water. Adaption of reverse osmosis membrane and module technology to other membrane processes took place in the 1970s and 1980s.

In this section, we will briefly review the principal methods of manufacturing membranes and membrane modules. Membranes applicable to diverse separation problems are made by the same general techniques. In fact, selecting a self-consistent membrane organization method based on either application, structure or preparation method, is impossible. Figure 1-1 illustrates the problem.¹ We see that gas separation membranes can be symmetrical, asymmetric or even liquid. Porous membranes can be used for ultrafiltration, microfiltration or even molecular sieving. Hollow-fiber modules can be used for gas separation, pervaporation, reverse osmosis, dialysis and so on. For the purposes of this section, we have organized the discussion by membrane structure: symmetrical membranes, asymmetric membranes, ceramic and metal membranes, and liquid membranes.

Symmetrical membranes are uniformly isotropic throughout. The membranes can be porous or dense, but the permeability of the membrane material does not change from point to point within the membrane. Asymmetric membranes, on the other hand, typically have a relatively dense, thin surface layer supported on an open, often microporous substrate. The surface layer generally performs the separation and is the principal barrier to flow through the membrane. The open support layer provides mechanical strength.

Ceramic and metal membranes can be both symmetrical or asymmetric. However, these membranes are grouped separately from polymeric membranes because the preparation methods are so different.

Liquid membranes are the final membrane category. The permselective barrier in these membranes is a liquid phase, often containing dissolved carriers which selectively react with specific permeants to enhance their transport rates through the membranes. Because the membrane barrier material is a liquid, unique preparation methods are used. In their simplest form, liquid membranes consist of an immobilized phase held in the pores of a microporous support membrane; in another form the liquid is contained as the skin of a bubble in a liquid emulsion system.

MTR-006-WD

Figure 1-1. Membrane classification.¹

The membrane organization scheme described above works fairly well. However, a major preparation technique, solution precipitation, also known as phase inversion, is used to make both symmetrical and asymmetric membranes. To avoid needless repetition, the technique has been described under asymmetric membranes only. The major membrane structures are shown in Figure 1-2.

1.1 SYMMETRICAL MEMBRANES

1.1.1 Dense Symmetrical Membranes

Dense symmetrical membranes are widely used in R & D and other laboratory work to characterize membrane properties. These membranes are rarely used commercially, however, because the transmembrane flux is too low for practical separation processes. The membranes are prepared by a solution casting or a thermal melt-pressing process.

1.1.1.1 Solution casting

Solution casting uses a casting knife or drawdown bar to draw an even film of an appropriate polymer solution across a casting plate. The casting knife consists of a steel blade, resting on two runners, arranged to form a precise gap between the blade and the plate on which the film is cast. A typical hand-casting knife is shown in Figure 1-3. After the casting has been drawn, it is left to stand, and the solvent evaporates to leave a thin, uniform polymer film.

A good polymer casting solution is sufficiently viscous to prevent the solution from running over the casting plate. Typical casting solution concentrations are in the range 15-20 wt% polymer.

Solvents having high boiling points are inappropriate for solution casting, because their low volatility demands long evaporation times. During an extended evaporation period, the cast film can absorb sufficient atmospheric water to precipitate the polymer, producing a mottled, hazy surface. If limited polymer solubility dictates the use of a high boiling solvent, a spin casting technique proposed by Kaelble can be employed.² The apparatus used in this technique is shown in Figure 1-4. It consists of a hollow aluminum cylinder with a lip, fitted with a removable plastic liner. The cylinder is spun and the casting solution is poured into it. Centrifugal force pushes the solution to the cylinder walls. As the solvent evaporates, it leaves a dense film at the surface of the casting solution; this more concentrated polymer material is then forced back into the solution by the high centrifugal force, bringing fresh unevaporated solvent to the surface. This action results in rapid solvent evaporation, more than ten times faster than normal plate-cast films, and allows solution-cast films to be prepared from relatively nonvolatile solvents.

1.1.1.2 Melt pressing

Many polymers do not dissolve in suitable casting solvents. Such polymers, including polyethylene, polypropylene, and nylons can be made into membranes by melt pressing.

Symmetrical Membranes

Nucleation Track Membrane

Microporous Phase-Inversion Membrane

Asymmetrical Membranes

Loeb-Sourirajan Phase-Inversion Membrane

Silicone-Rubber Coated Composite Membrane

Electrolytically-Deposited Membrane

Multilayer Ceramic Membrane

Figure 1-2. Types of membrane structures.

Figure 1-3. A typical hand-casting knife. (Courtesy of Paul N. Gardner Company, Inc. Pompano Beach, FL.)

MTR-034-F

Figure 1-4. Schematic of a spin-casting mold. (From Kaelble.)

Melt pressing, or melt forming, involves sandwiching the polymer at high pressure between two heated plates. A pressure of 2,000-5,000 psi is applied for 0.5 to 5 minutes, while holding the plates just above the melting point of the polymer. The optimum pressing temperature is the lowest temperature that yields a membrane of completely fused polymer of the desired thickness. If the polymer contains air or is in pellet form, massing the material on a rubber mill before pressing improves results.

To prevent the membrane from sticking to the press plates, the polymer is usually placed between two sheets of Teflon-coated foil or non-waterproof cellophane. Cellophane does not stick to the plates and, if dampened with water after molding, it strips easily from the membranes. To make films thicker than 100 μm , metal shims or forms of an appropriate thickness are placed between the plates. The best technique for making thinner membranes is free-form pressing. A typical laboratory process used to make melt-formed films is shown in Figure 1-5.

1.1.2 Microporous Symmetrical Membranes

A number of proprietary processes have been developed to produce symmetrical microporous membranes. The more important are outlined below.

1.1.2.1 Irradiation

Nucleation track membranes were first developed by the Nuclepore Corporation.^{3,4} The two-step process is illustrated in Figure 1-6. A polymer film is first irradiated with charged particles from a nuclear reactor. As the particles pass through the film, they break polymer chains in the film and leave behind sensitized tracks. The film is then passed through an etch solution bath. This bath preferentially etches the polymer along the sensitized nucleation tracks, thereby forming pores. The length of time the film is exposed to radiation in the reactor determines the number of pores in the film; the etch time determines the pore diameter. This process was initially used on mica wafers, but is now used to prepare polyester or polycarbonate membranes. A scanning electron micrograph of a nucleation track membrane is shown in Figure 1-7.

1.1.2.2 Stretching

Microporous membranes can also be made from crystalline polymer films by orienting and stretching the film. This is a multistep process. In the first step, a highly oriented crystalline film is produced by extruding the polymer at close to its melting point coupled with a very rapid drawdown.^{5,6}

After cooling, the film is stretched a second time, up to 300%, in the machine direction of the film. This second elongation deforms the crystalline structure of the film and produces slit-like voids 200 to 2,500 Å wide. A scanning electron micrograph of such a film is shown in Figure 1-8. The membranes made by Celanese Separation Products, sold under the trade name Celgard®, and the membranes made by W. L. Gore, sold under the trade name Gore-Tex®, are made by this type of process.⁷

Figure 1-5. A typical laboratory press used to form melt-pressed membranes. (Courtesy of Fred S. Carver, Inc., Menomonee Falls, WI.)

Step 1: Polycarbonate film is first exposed to charged particles in a nuclear reactor

Step 2: The tracks left by the particles are preferentially etched into uniform, cylindrical pores

MTR-036-F

Figure 1-6. Two-step process of manufacturing nucleation track membranes.

Figure 1-7. Scanning electron micrograph of a typical nucleation track membrane.

0 2 μm

Figure 1-8. Scanning electron micrograph of a typical expanded polypropylene film membrane, in this case Celgard. (Reprinted with permission from Cierenbaum et al., *Ind. Eng. Chem. Proc. Res. Develop.* 13, 2. Copyright 1974 American Chemical Society.)

1.1.2.3 Template leaching

Template leaching is not widely used, but offers an alternative manufacturing technique for insoluble polymers. A homogeneous film is prepared from a mixture of the membrane matrix material and a leachable component. After the film has been formed, the leachable component is removed with a suitable solvent and a microporous membrane is formed.^{8,9,10} The same general method is used to prepare microporous glass.¹¹

1.2 ASYMMETRIC MEMBRANES

In industrial applications, symmetrical membranes have been almost completely displaced by asymmetric membranes, which have much higher fluxes. Asymmetric membranes have a thin, finely microporous or dense permselective layer supported on a more open porous substrate. Hindsight makes it clear that many of the membranes produced in the 1930s and 1940s were of the asymmetric type, although this was not realized at the time. The asymmetric structure was not recognized until Loeb and Sourirajan prepared the first high-flux, asymmetric, reverse osmosis membranes by what is now known as the Loeb-Sourirajan technique.¹² Loeb and Sourirajan's work was a critical breakthrough in membrane technology. The reverse osmosis membranes they produced were an order of magnitude more permeable than any symmetrical membrane produced up to that time. More importantly, the demonstration of the benefits of the asymmetric structure paved the way for developers of other membrane separation processes. Improvements in asymmetric membrane preparation methods and properties were accelerated by the increasing availability in the late 1960s of scanning electron microscopes, the use of which enabled the effects of structural modifications to be easily assessed.

1.2.1 Phase Inversion (Solution-Precipitation) Membranes

Phase inversion, also known as solution precipitation or polymer precipitation, is the most important asymmetric membrane preparation method. In this process, a clear polymer solution is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and a liquid, polymer-poor phase that forms the membrane pores. If the precipitation process is rapid, the pore-forming liquid droplets tend to be small and the membranes formed are markedly asymmetric. If precipitation proceeds slowly, the pore-forming liquid droplets tend to agglomerate while the casting solution is still fluid, so that the final pores are relatively large. These membranes have a more symmetrical structure.

Polymer precipitation from a solution can be achieved in several ways, such as cooling, solvent evaporation, or imbibition of water. Preparation of membranes by all of these techniques has been reviewed in the literature.

The simplest technique is thermal gelation, in which a hot one-phase casting solution is used to cast a film. The cast film cools, reaching the point at which polymer precipitation occurs. As the solution cools further, precipitation continues. The process can be represented by the phase diagram shown in Figure 1-9. The pore volume in the final membrane is largely determined by the initial composition of the cast film, because this determines the ratio of the polymer to liquid phase in the cooled film. However, the spatial distribution and size of the pores is largely determined by the rate of cooling and, hence, precipitation, of the film. In general, rapid cooling leads to membranes with small pores.

Solvent evaporation is another method of forming asymmetric membranes. This technique uses a solvent casting solution consisting of a polymer dissolved in a mixture of a good volatile solvent and a less volatile nonsolvent (typically water or alcohol). When a film of this solution is cast and allowed to evaporate, the good volatile solvent leaves first. The film becomes enriched in the nonsolvent and finally precipitates. This precipitation process can be represented as a pathway through a three-component phase diagram, as shown in Figure 1-10.

Finally, the casting solution can be precipitated using imbibition of water, either as vapor from a humid atmosphere or by immersion in a water bath. This precipitation process can also be represented as a pathway through a phase diagram, as shown in Figure 1-11. This is the Loeb-Sourirajan process.

The use of phase diagrams of the type shown in Figures 1-9, 1-10 and 1-11 to understand the formation mechanism of phase-inversion membranes has been an area of considerable research in the last 10-15 years.¹³⁻¹⁶ The models that have been developed are complex, and will not be reviewed here. Although the theories are well developed, it is still not possible to predict membrane structures only from the phase diagram and solution properties. However, phase diagrams do allow the effects of principal membrane preparation variables to be rationalized and are of considerable value in designing membrane development processes.

1.2.1.1 Polymer precipitation by thermal gelation

The thermal gelation method of making microporous membranes was first commercialized on a large scale by Akzo.^{17,18} Akzo markets microporous polypropylene and polyvinylidene fluoride membranes under the trade name Accurel®.

Polypropylene membranes are prepared from a solution of polypropylene in N,N-bis(2-hydroxyethyl)tallowamine. The amine and polypropylene form a clear solution at temperatures above 100-150°. Upon cooling, the solvent and polymer phases separate to form a microporous structure. If the solution is cooled slowly, an open cell structure of the type shown in Figure 1-12 results. The interconnecting passageways between cells are generally in the micron range. If the solution is cooled and precipitated rapidly, a much finer structure is formed, as shown in Figure 1-13. The rate of cooling is therefore a key parameter determining the final structure of the membrane.

MTR-040-GRP

Figure 1-9. Phase diagram showing the composition pathway traveled by the casting solution during thermal gelation.

Figure 1-10. Phase diagram showing the composition pathway traveled by a casting solution during the preparation of porous membranes by solvent evaporation.

MTR-039-GRP

Figure 1-11. Phase diagram showing the composition pathway traveled by a coating solution during the preparation of porous membranes by water imbibition.

Figure 1-12. Type I "Open Cell" structure of polypropylene formed at low cooling rates (2,400X).

Figure 1-13. Type II "Lacy" structure of polypropylene formed at high cooling rates (2,000X).

A simplified process flowsheet of the membrane preparation process is shown in Figure 1-14. The hot polymer solution is cast onto a water-cooled chill roll, which cools the solution causing the polymer to precipitate. The precipitated film is passed to an extraction tank containing methanol, ethanol or isopropanol, which extracts the solvent. Finally, the membrane is dried, sent to a laser inspection station, trimmed and rolled up. The process shown in Figure 1-14 is used to make flat-sheet membranes. The preparation of hollow-fiber membranes by the same general technique has also been described.¹⁹

1.2.1.2 Polymer precipitation by solvent evaporation

This technique was one of the earliest methods of making microporous membranes to be developed, and was used by Bechhold, Elford, Pierce, Ferry and others in the 1920s and 1930s.²⁰⁻²² In the method's simplest form, a polymer is dissolved in a two-component solvent mixture consisting of a volatile good solvent such as methylene chloride, and an involatile poor solvent, such as water or ethanol. This two-component polymer solution is cast on a glass plate. As the good, volatile solvent evaporates the casting solution is enriched in the poor, non-volatile solvent. The polymer precipitates, forming the membrane structure. The solvent evaporation-precipitation process may be continued until the membrane has completely formed, or the process can be stopped and the membrane structure fixed by immersing the cast film into a precipitation bath of water or other nonsolvent.

Many factors determine the porosity and pore size of membranes formed by the solvent evaporation method. In general, increasing the nonsolvent content of the casting solution, or decreasing the polymer concentration, increases porosity. It is important that the nonsolvent be completely incompatible with the polymer. If partly compatible nonsolvents are used, the precipitating polymer phase contains sufficient residual solvent to allow it to flow and collapse as the solvent evaporates. The result is a dense rather than microporous film.

1.2.1.3 Polymer precipitation by imbibition of water vapor

Preparation of microporous membranes by simple solvent evaporation alone is not widely practiced. However, a combination of solvent evaporation with precipitation by imbibition of water vapor from a humid atmosphere is the basis of most commercial phase-inversion processes. The processes involve proprietary technology that is not normally disclosed by membrane developers. However, during the development of composite reverse osmosis membranes at Gulf General Atomic, Riley et al. prepared this type of membrane and described the technology in some detail in a series of Office of Saline Water Reports.²³ These reports remain the best published description of this technique.

Figure 1-14. Simplified process flowsheet for membrane preparation by thermal gelation.

The type of equipment used by Riley et al. is shown in Figure 1-15. The casting solution typically consists of a blend of cellulose acetate and cellulose nitrate dissolved in a mixture of volatile solvents, such as acetone, and involatile nonsolvents, such as water, ethanol or ethylene glycol. The polymer solution is cast onto a continuous stainless steel belt. The cast film then passes through a series of environmental chambers. Hot humid air is usually circulated through the first chamber. The film loses the volatile solvent by evaporation and simultaneously absorbs water from the atmosphere. The total precipitation process is slow, taking about 10 minutes to complete. As a result the membrane structure is fairly symmetrical. After precipitation, the membrane passes to a second oven through which hot dry air is circulated to evaporate the remaining solvent and dry the film. The formed membrane is then wound on a take-up roll. Typical casting speeds are of the order of 1-2 ft/min.

1.2.1.4 Polymer precipitation by immersion in a nonsolvent bath (Loeb-Sourirajan process)

The Loeb-Sourirajan process is the single most important membrane-preparation technique. A casting machine used in the process is shown in Figure 1-16.²⁴ A solution containing approximately 20 wt% of dissolved polymer is cast on a moving drum or paper web. The cast film is precipitated by immersion in a bath of water. The water rapidly precipitates the top surface of the cast film, forming an extremely dense permselective skin. The skin slows down the entry of water into the underlying polymer solution, which thus precipitates much more slowly, forming a more porous substructure. Depending on the polymer, the casting solution and other parameters, the dense skin varies from 0.1-1.0 μm thick. Loeb and Sourirajan were working in the field of reverse osmosis.¹² Later, others adapted the technique to make membranes for other applications, including ultrafiltration and gas separation.²⁵⁻²⁷ Ultrafiltration and gas separation membranes have the same asymmetric structure found in reverse osmosis membranes, but the skin layer of ultrafiltration membranes contains small pores 50-200 Å in diameter.

A major drawback of gas separation membranes made by the Loeb-Sourirajan process is the existence of minute membrane defects. These defects, caused by gas bubbles, dust particles and support fabric imperfections, are almost impossible to eliminate. Such defects do not significantly affect the performance of asymmetric membranes used in liquid separation operations, such as ultrafiltration and reverse osmosis, but can be disastrous in gas separation applications. In the early 1970s, Browall showed that membrane defects could be overcome by coating the membrane with a thin layer of relatively permeable material.²⁸ If the coating was sufficiently thin, it did not change the properties of the underlying permselective layer, but it did plug membrane defects, preventing simple Poiseuille gas flow through the defect.

MTR-038-F

Figure 1-15. Schematic of casting machine used to make microporous membranes by water imbibition.

MTR-039-F

Figure 1-16. Schematic of Loeb-Sourirajan membrane casting machine.

Later, Henis and Tripodi, at Monsanto,²⁷ applied this concept to sealing defects in polysulfone Loeb-Sourirajan membranes with silicone rubber. The form of the Monsanto membrane is shown in Figure 1-17. The silicone rubber layer does not function as a selective barrier but rather plugs up defects, thereby reducing non-diffusive gas flow. The flow of gas through the portion of the silicone rubber layer over the pore is very high compared to the flow through the defect-free portion of the membrane. However, because the total area of the membrane subject to defects is very small, the total gas flow through these plugged defects is negligible. Because the polysulfone selective layer no longer has to be completely free of defects, the Monsanto membrane can be made thinner than is possible with an uncoated Loeb-Sourirajan membrane. The increase in flux brought about by decreasing the thickness of the permselective skin layer more than compensates for the slight reduction in flux due to the silicone rubber sealing layer.

A scanning electron micrograph of a Loeb-Sourirajan membrane is shown in Figure 1-18. In this example, the permselective film has deliberately been made thicker than normal to better show the dense surface layer. Loeb-Sourirajan membranes can have skin layers thinner than 0.1 μm .

Cellulose acetate Loeb-Sourirajan reverse osmosis membranes were introduced commercially in the 1960s. Since then, many other polymers have been fabricated into asymmetric membranes in attempts to improve membrane properties. In the reverse osmosis area, these attempts have had limited success, the only significant example being DuPont's polyamide membrane. In gas separation and ultrafiltration a number of membranes with useful properties have been made. However, the early work on asymmetric membranes has spawned numerous other technologies in which a microporous membrane is used as a support to carry another thin, dense separating layer. The preparation of such membranes is now discussed.

1.2.2 Interfacial Composite Membranes

In the early 1960s, Cadotte at North Star Research developed an entirely new method of making asymmetric membranes that produced reverse osmosis membranes with dramatically improved salt rejections and water fluxes.²⁹ In this method an aqueous solution of reactive prepolymer, such as polyamine, is first deposited in the pores of a microporous support membrane, typically a polysulfone Loeb-Sourirajan ultrafiltration membrane. The amine loaded support is then immersed in a water immiscible solvent solution containing a reactant, for example, a diacid chloride in hexane. The amine and acid chloride then react at the interface of the two solutions to form a densely crosslinked, extremely thin membrane layer. This type of membrane is shown schematically in Figure 1-19. The first membrane made by Cadotte was based on the reaction of polyethylenimine crosslinked with toluene-2,4-diisocyanate, shown in Figure 1-20. The process was later refined by Cadotte et al.³⁰ and Riley et al.³¹ in the U.S. and Nitto in Japan.³²

Figure 1-17. Schematic of Loeb-Sourirajan and Monsanto gas separation membranes.

Figure 1-18. Scanning electron micrograph of an asymmetric Loeb-Sourirajan membrane

Figure 1-19. Schematic of the interfacial polymerization procedure.

Figure 1-20. Idealized structure of polyethylenimine crosslinked with toluene 2,4-diisocyanate.

Membranes made by interfacial polymerization have a dense, highly crosslinked interfacial polymer layer formed on the surface of the support membrane at the interface of the two solutions. A less crosslinked, more permeable hydrogel layer forms under this surface layer and fills the pores of the support membrane. Since the dense crosslinked polymer can only form at the interface, it is extremely thin, on the order of 0.1 μm or less, and the flux of permeate is high. Because the polymer is highly crosslinked, its selectivity is also high. The first reverse osmosis membranes made this way were up to an order of magnitude less salt-permeable than other membranes with comparable water fluxes.

When used for gas separation, interfacial polymerization membranes are less interesting. This is because of the water-swollen hydrogel that fills the pores of the support membrane. In reverse osmosis, this layer is highly water-swollen and offers little resistance to the flow of water. When the membrane is dried and used in gas separations, however, the gel becomes a rigid glass with very low gas permeability. This glassy polymer fills the membrane pores and, as a result, defect-free interfacial composite membranes usually have low gas fluxes although their selectivities can be good.

1.2.3 Solution Cast Composite Membranes

Another very important type of composite membrane is formed by solution casting a thin (0.5-2.0 μm) film on a suitable microporous film. The first membranes of this type were prepared by Ward, Browall and others at General Electric using a type of Langmuir trough system.³³ In this system a dilute polymer solution in a volatile water-insoluble solvent is spread over the surface of a water filled trough. The thin polymer film formed on the water surface is then picked up on a microporous support. This technique was developed into a semicontinuous process at General Electric but has not proved reliable enough for large-scale commercial use.

Currently, most solution cast composite membranes are prepared by a technique pioneered by Riley and others at UOP.³⁴ In this technique, a polymer solution is directly cast onto the microporous support film. It is important that the support film be clean, defect-free and very finely microporous, to prevent penetration of the coating solution into the pores. If these conditions are met, a liquid layer 50-100 μm thick can be coated onto the support, which after evaporation leaves a thin permselective film, 0.5-2- μm thick. This technique was used by Hennis and Tripodi to form the Monsanto Prism® gas separation membranes²⁷ and at Membrane Technology & Research to form pervaporation and organic solvent/air separation membranes.³⁵ A scanning electron micrograph of this type of membrane is shown in Figure 1-21.³⁶

Figure 1- 21. Scanning electron micrograph of a silicone rubber composite membrane (courtesy of H. Strathmann).

1.2.4 Plasma Polymerization Membranes

Plasma polymerization of films was first used to form electrical insulation and protective coatings, but a number of workers have also prepared permselective membranes in this way.³⁷⁻⁴⁰ However, plasma polymerization membranes have never been produced on a commercial scale. A typical, simple plasma polymerization apparatus is shown in Figure 1-22. Most workers have used RF fields at frequencies of 2-50 MHz to generate the plasma. In a typical plasma experiment helium, argon, or other inert gas is introduced at a pressure of 50-100 millitorr and a plasma is initiated. Monomer vapor is then introduced to bring the total pressure to 200-300 millitorr. These conditions are maintained for a period of 1-10 minutes. During this time, an ultrathin polymer film is deposited on the membrane sample held in the plasma field.

Monomer polymerization proceeds by a complex mechanism involving ionized molecules and radicals and is completely different from conventional polymerization reactions. In general, the polymer films are highly crosslinked and may contain radicals which slowly react on standing. The stoichiometry of the film may also be quite different from the original monomer due to fragmentation of monomer molecules during the plasma polymerization process. It is difficult to predict the susceptibility of monomers to plasma polymerization or the nature of the resulting polymer film. For example, many vinyl and acrylic monomers polymerize very slowly, while unconventional monomers such as benzene and hexane polymerize readily. The vapor pressure of the monomers, the power and voltage used in the discharge reaction, the type and the temperature of the substrate all affect the polymerization reaction. The inert gas used in the plasma may also enter into the reaction. Nitrogen and carbon monoxide, for example, are particularly reactive. In summary, the products of plasma polymerization are ill defined and vary according to the experimental procedures. However, the films produced can be made very thin and have been shown to be quite permselective.

The most extensive studies of plasma polymerized membranes have been performed by Yasuda, who has tried to develop high-performance reverse osmosis membranes by depositing plasma films onto microporous polysulfone films.^{37,38} Other workers have also studied the gas permeability of plasma polymerized films. For example, Stancell and Spencer³⁹ were able to obtain a plasma membrane with a selectivity α_{H_2/CH_4} of almost 300, while Kawakami et al.⁴⁰ have reported plasma membranes with a selectivity α_{O_2/N_2} of 5.8. Both of these selectivities are very high when compared to the selectivity of other membranes. The plasma films were also quite thin and had a high flux. However, in both cases the plasma film was formed on a substrate made from thick, dense polymer films 25-100 μm thick. As a result, the flux through the overall composite membrane was still low.

MTR-035-F

Figure 1- 22. Simple plasma coating apparatus.

1.2.5 Dynamically Formed Membranes

In the late 1960s and early 1970s, a great deal of attention was devoted to preparing dynamically formed anisotropic membranes, principally by Johnson, Kraus and others at Oak Ridge National Laboratories.^{41,42} The general procedure used is to form a layer of inorganic or polymeric colloids on the surface of a microporous support membrane by filtering a solution containing suspended colloid through the support membrane. A thin layer of colloids is then laid down on the membrane surface and acts as a semipermeable membrane. Over a period of time the colloidal surface layer erodes or dissolves and the membrane's performance falls. The support membrane is then cleaned and a new layer of colloid is deposited. In the early development of this technique a wide variety of support membranes were used, ranging from conventional ultrafiltration membranes to fire hoses. In recent years microporous ceramic or carbon tubes have emerged as the most commonly used materials. Typical colloidal materials are polyvinyl methylether, acrylic acid copolymers, or hydrated metal oxides such as zirconium hydroxide.

Dynamically formed membranes were pursued for many years as reverse osmosis membranes because they had very high water fluxes and relatively good salt rejection, especially with brackish water feeds. However, the membranes proved to be unstable and difficult to reproduce reliably and consistently. For these reasons, and because high-performance interfacial composite membranes were developed in the meantime, dynamically formed membranes gradually fell out of favor. Gaston County Corporation, using microporous carbon tube supports, is the only commercial supplier of dynamic membrane equipment. The principal application is polyvinyl alcohol recovery in textile dyeing operations.

1.2.6 Reactive Surface Treatment

Recently a number of groups have sought to improve the properties of asymmetric gas separation membranes by chemically modifying the surface permselective layer. For example, Langsam at Air Products has treated films of poly(trimethylsilyl-1-propyne) with diluted fluorine gas.⁴³⁻⁴⁵ This treatment chemically reacts fluorine with the polymer structure in the first 100-200 Å-thick surface layer. This treatment produces a dramatic improvement in selectivity with a modest reduction in permeability. The surface treated polymer is superior to conventional polymers, even though the permeability is less than that for untreated poly(trimethylsilyl-1-propyne).

Calculations of the permeability and selectivity for the treated surface layer indicate that permeation through this layer is a diffusion controlled process. Since the untreated poly(trimethylsilyl-1-propyne) has extremely high free volume and correspondingly high permeant diffusivity, it is evident that the fluorination is reducing the free volume of the surface layer and thereby decreasing the diffusivity of the permeant.

1.3 CERAMIC AND METAL MEMBRANES

1.3.1 Dense Metal Membranes

Palladium and palladium alloy membranes can be used to separate hydrogen from other gases. Palladium membranes were extensively studied during the 1950s and 1960s and a commercial plant to separate hydrogen from refinery off-gas was installed by Union Carbide.^{46,47} The plant used palladium/silver alloy membranes in the form of 25 μm -thick films. The technique used to make the membrane is not known, but films of this thickness could be made by standard metal casting and rolling technology. A number of problems, including long-term membrane stability under the high temperature operating conditions, were encountered and the plant was replaced by pressure-swing adsorption systems.

Small-scale systems, used to produce ultrapure hydrogen for specialized applications, are currently marketed by Johnson Matthey and Co. These systems also use palladium/silver alloy membranes, based on those developed by Hunter.^{48,49} Membranes with much thinner effective palladium layers than were used in the Union Carbide installation can now be made. One technique that has been used is to form a composite membrane, with a metal substrate, onto which is coated a thin layer of palladium or palladium alloy.⁵⁰ The palladium layer can be applied by spraying, electrochemical deposition, or by vacuum methods, such as evaporation or sputtering. Coating thicknesses on the order of a few microns or less can be achieved. Johnson Matthey and Co. holds several patents covering this type of technology, including techniques in which composites are coated on both sides with palladium and then rolled down to form a very thin composite film.⁵¹ The exact nature of the membranes used in their present systems is proprietary.

1.3.2 Microporous Metal Membranes

Recently, Alcan International^{51,52} and Alusuisse^{53,54} have begun to produce microporous aluminum membranes. The production methods used are proprietary, but both use an electrochemical technique. In the Alcan process aluminum metal substrate is subjected to electrolysis using an electrolyte such as oxalic or phosphoric acid. This forms a porous aluminum oxide film on the anode. The pore size and structure of the oxide film is controlled by varying the voltage. Once formed, the oxide film is removed from the anode by etching. The membranes have a tightly controlled pore size distribution and can be produced with pore diameters ranging from 0.02–2.0 μm .

1.3.3 Ceramic Membranes

The major advantage of ceramic membranes is that they are chemically extremely inert and can be used at high temperatures, where polymer films fail. Ceramic membranes can be made by three processes: sintering, leaching and sol-gel methods. Sintering involves taking a colloidal suspension of particles, forming a coagulated thin film, and then heat treating the film to form a continuous, porous structure. The pore sizes of sintered films are relatively large, of the order of 10–100 μm . In the leaching process, a glass sheet or capillary incorporating two intermixed phases is treated with an acid that will dissolve one of the phases. Smaller pores can be obtained by this method, but

the uniformity of the structure is difficult to control. The preparation of ceramic membranes by a sol-gel technique is the newest approach, and offers the greatest potential for making membranes suitable for gas separation.

Figure 1-23 summarizes the available sol-gel processes.⁵⁵ The process on the right of the figure involves the hydrolysis of metal alkoxides in a water-alcohol solution. The hydrolyzed alkoxides are polymerized to form a chemical gel, which is dried and heat treated to form a rigid oxide network held together by chemical bonds. This process is difficult to carry out, because the hydrolysis and polymerization must be carefully controlled. If the hydrolysis reaction proceeds too far, precipitation of hydrous metal oxides from the solution starts to occur, causing agglomerations of particulates in the sol.

In the process on the left, complete hydrolysis is allowed to occur. Bases or acids are added to break up the precipitate into small particles. Various reactions based on electrostatic interactions at the surface of the particles take place. The result is a colloidal solution. Organic binders are added to the solution and a physical gel is formed. The gel is then heat treated as before to form the ceramic membrane.

The sol-gel technique has mostly been used to prepare alumina membranes to date. Figure 1-24 shows a cross section of a composite alumina membrane made by slip casting successive sols with different particle sizes onto a porous ceramic support. Silica or titanic membranes could also be made using the same principles. Anderson et al.⁵⁶ have made unsupported titanium dioxide membranes with pore sizes of 50 Å or less by the sol-gel process shown in Figure 1-25.

1.3.4 Molecular Sieve Membranes

A common, albeit, inaccurate analogy used to describe a membrane is that of a sieve, with smaller species passing through a porous barrier while the larger species are retained. In practice, most membranes rely on the permeant-selective properties of a non-porous barrier, whether it be liquid, polymer or metal, to separate the components of a mixture. One could use a porous barrier, if it were sufficiently finely porous to achieve a sieving at the molecular level. However, until recently membranes with the necessary pore size and pore distribution were not known.

Recent developments in the field of inorganic membranes offer promise of the development and commercialization of molecular-sieve type membranes in the next decade, especially for gas separation applications. A substantial amount of work on molecular sieve membranes is being performed in Israel, where the membranes are closest to scale-up. Soffer, Koresh and co-workers have been working on carbon membranes obtained by heating polymeric hollow fibers to between 500-800°C in an inert atmosphere or in a vacuum, which reduces the polymer to carbon.⁵⁷ The membranes are reported to have pore diameters between 2-5 Å.

Figure 1-23. Three ways to obtain inorganic membranes.

Figure 1-24. Cross-sectional scanning electron micrograph of a three-layered alumina membrane/support (pores of 0.2, 0.8 and 10 μm , respectively, in each layer).

MTR-005-WD

Figure 1-25. Preparation route for particulate and polymeric ceramic membranes.

In the United States, PPG Industries is active in the area of molecular sieve membranes and is believed to have developed 10Å-diameter glass hollow-fiber membranes with carbon dioxide/methane selectivity of 50.¹¹ Beaver describes the process used for producing microporous glass hollow-fiber membranes by a leaching process. The starting material for the membranes is a glass containing at least 30-70% silica, as well as oxides of zirconium, hafnium or titanium and extractable materials. The extractable materials comprise one or more boron-containing compounds and alkali metal oxides and/or alkaline earth metal oxides. Glass hollow fibers produced by melt extrusion are treated with dilute hydrochloric acid at 90°C for 2-4 hours to leach out the extractable materials, washed to remove residual acid and then dried. This technique has been used to produce hollow fibers membranes with 8-10 Å-diameter pores.

1.4 LIQUID MEMBRANES

Liquid membranes containing carriers to facilitate selective transport of gases or ions were a subject of considerable research in the 1960s and 1970s. Although still being worked on in a number of laboratories, the development of much more selective conventional polymer membranes in recent years has diminished interest in these films.

The earliest liquid membrane experiments were done by biologists, using natural carriers contained in cell walls. As early as 1890, Pfeffer postulated transport properties in membranes using carriers. Perhaps the first coupled transport experiment was performed by Osterhout, who studied the transport of ammonia across algae cell walls.⁵⁸ By the 1950s the carrier concept was well developed, and workers began to develop synthetic biomembrane analogues of the natural systems. For example, in the mid-1960s, Sollner and Shean⁵⁹ studied a number of coupled transport systems using inverted U-tubes, shown in Figure 1-26a. At the same time, Bloch and Vofsi published the first of several papers in which coupled transport was applied to hydrometallurgical separations, namely the separation of uranium using phosphate esters.⁶⁰ Because phosphate esters were also plasticizers for polyvinyl chloride (PVC), Bloch and Vofsi prepared immobilized liquid films by dissolving the esters in a PVC matrix. Typically, the PVC/ester film was cast on a paper support. Researchers actively pursued this work until the late 1960s. At that time, interest in this approach lagged, apparently because the fluxes obtained did not make the process competitive with conventional separation processes. Some workers are continuing to apply these membranes to metal separations, but most current interest in PVC matrix membranes is in their use in ion selective membrane electrodes.⁶¹

Following the work of Bloch and Vofsi, two other methods of producing immobilized liquid films were introduced. Both are still under development. In the first approach, the liquid carrier phase is held by capillarity within the pores of a microporous substrate, as shown in Figure 1-26b. This approach was first used by Miyauchi⁶² and further developed by Baker et al.⁶³ and by Largman and Sifniades.⁶⁴ The principal objective of this early work was the recovery of copper and other metals from hydrometallurgical solutions. Despite considerable effort on the laboratory scale, the process has never become commercial. The

major problem is instability of the liquid carrier phase in the microporous membrane support.

The second type of immobilized liquid carrier is the emulsion or "bubble" membrane. In this technique a surfactant-stabilized emulsion is produced as shown in Figure 1-26c. The organic carrier phase forms the wall of the emulsion droplet separating the aqueous feed from the aqueous product solutions. Metal ions are concentrated in the interior of the droplets. When sufficient metal has been extracted, emulsion droplets are separated from the feed and the emulsion is broken, liberating a concentrated product solution and an organic carrier phase. The carrier phase is decanted from the product solution and recycled to make more emulsion droplets. The principal technical problem is the stability of the liquid membrane. Ideally, the emulsion membranes must be completely stable during the extraction step, to prevent mixing of the two aqueous phases, but must be completely broken and easily separated in the stripping step. Achieving this level of control over emulsion stability has proved difficult.

The emulsion membrane technique was popularized and fully developed by Li and his co-workers at Exxon.^{65,66} Starting in the late 1950s and continuing for more than twenty years, the Exxon group's work led to the installation of the first pilot plant in 1979. However, the process is still not commercial, although a number of pilot plants have been installed, principally on hydrometallurgical feed streams. Another important group working independently on the problem at about the same time was Cussler et al. at Carnegie Mellon University.⁶⁷ More recent workers in the field include Halwachs and Schurgerl⁶⁸ in West Germany, Marr and Kapp in Austria,⁶⁹ Stelmaszek et al. in Poland,⁷⁰ Martin and Davis in the United Kingdom,⁷¹ and Danesi et al.,⁷² Noble et al.,⁷³ and Lamb, Christensen and Izatt⁷⁴ in the United States.

1.5 HOLLOW-FIBER MEMBRANES

Most of the techniques described above were originally developed to produce flat-sheet membranes. However, most techniques can be adapted to produce membranes in the form of thin tubes or fibers. Formation of membranes into hollow fibers has a number of advantages, one of the most important of which is the ability to form compact modules with very high surface areas. This advantage is offset, however, by the lower fluxes of hollow-fiber membranes compared to flat-sheet membranes made from the same materials. Nonetheless, the development of hollow-fiber membranes by Mahon and the group at Dow Chemical in 1960,^{75,76} and their later commercialization by Dow Chemical, DuPont, Monsanto and others, represents one of the major events in membrane technology.

Hollow fibers are usually on the order of 25-200 μm in diameter. They can be made with a homogeneous dense structure, or more preferably as a microporous structure having a dense permselective layer on the outside or inside surface. The dense surface layer can be integral, or separately coated. The fibers are packed into bundles and potted into tubes to form a membrane module. More than a kilometer of fibers is required to form a membrane module with a surface area of one square meter. Since no breaks or defects are allowed in a module, this requires very high standards of reproducibility and quality control.

(a) U-Tube Liquid Membranes

(b) Supported Liquid Membranes

(c) Emulsion Liquid Membranes

Figure 1-26. A schematic illustration of three types of liquid membranes.

Hollow-fiber fabrication methods can be divided into two classes. The most common is solution spinning, in which a 20-30% polymer solution is extruded and precipitated into a bath of nonsolvent. Solution spinning allows fibers with the asymmetric Loeb-Sourirajan structure to be made. An alternative technique is melt spinning, in which a hot polymer melt is extruded from an appropriate die and is then cooled and solidified in air or a quench tank. Melt-spun fibers are usually dense and have lower fluxes than solution-spun fibers, but, because the fiber can be stretched after it leaves the die, very fine fibers can be made. Melt spinning can also be used with polymers such as poly(trimethylpentene) which are not soluble in convenient solvents and are therefore difficult to form by wet spinning.

1.5.1 Solution (Wet) Spinning

The most widely used solution spinnerette system was first devised by Mahon.^{75,76} The spinnerette consists of two concentric capillaries, the outer capillary having a diameter of approximately 400 μm and the central capillary having an outer diameter of approximately 200 μm and an inner diameter of 100 μm . Polymer solution is forced through the outer capillary while air or liquid is forced through the inner one. The rate at which the core fluid is injected into the fibers relative to the flow of polymer solution governs the ultimate wall thickness of the fiber. Figure 1-27 shows a cross-section of this type of spinnerette. Unlike solution-spun textile fibers, solution-spun hollow fibers are not stretched after leaving the spinnerette.

A complete hollow-fiber spinning system is shown in Figure 1-28. Fibers are formed almost instantaneously as the polymer solution leaves the spinnerette. The amount of evaporation time between the solution's exit from the spinnerette and its entrance into the coagulation bath has been found to be a critical variable by the Monsanto group. If water is forced through the inner capillary, an asymmetric hollow fiber is formed with the skin on the inside. If air under a few pounds of pressure, or an inert liquid, is forced through the inner capillary to maintain the hollow core, the skin is formed on the outside of the fiber by immersion into a suitable coagulation bath.

Wet-spinning of this type of hollow fiber is a well-developed technology, especially in the preparation of dialysis membranes for use in artificial kidneys. Systems that can spin more than 100 fibers simultaneously on an around-the-clock basis are in operation.

1.5.2 Melt Spinning

In melt spinning, the polymer is extruded through the outer capillary of the spinnerette as a hot melt, the spinnerette assembly being maintained at a temperature between 100-300°C. The polymer can either be used pure or loaded with up to 50 wt% of various plasticizers. Melt-spun fibers can be stretched as they leave the spinnerette, facilitating the production of very thin fibers. This is a major advantage of melt spinning over solution spinning. The dense nature of melt-spun fibers leads to lower fluxes than can be obtained with solution-spun fibers, but because of the enormous membrane surface area of hollow-fiber systems this need not be a problem.

MTR-041-F

Figure 1-27. A spinnerette design used in solution-spinning of hollow-fiber membranes.

MTR-042-F

Figure 1-28. A hollow-fiber solution-spinning system.

Substantial changes in the fiber properties can be made by varying the added plasticizer. A particularly interesting additive is one which is completely miscible with the melt at the higher temperature of the spinnerette, but becomes incompatible with the polymer at room temperature. If the additive is soluble, it can then be leached from the fiber, leaving minute voids behind. This produces a mechanism for making microporous melt-spun fibers.

1.6 MEMBRANE MODULES

A useful membrane process requires the development of a membrane module containing large surface areas of membrane. The development of the technology to produce low cost membrane modules was one of the breakthroughs that led to the commercialization of membrane processes in the 1960s and 1970s. The earliest designs were based on simple filtration technology and consisted of flat sheets of membrane held in a type of filter press. These are called plate and frame modules. Systems containing a number of membrane tubes were developed at about the same time. Both of these systems are still used, but because of their relatively high cost they have been largely displaced by two other designs, the spiral-wound and hollow-fiber module. These designs are illustrated in Figure 1-29.

1.6.1 Spiral-Wound Modules

Spiral-wound modules were originally used for artificial kidneys, but were fully developed for reverse osmosis systems. This work, carried out by UOP under sponsorship of the Office of Saline Water (later the Office of Water Research and Technology) resulted in a number of spiral-wound designs.⁷⁷⁻⁷⁹ The design shown in Figure 1-30 is the first and simplest design, consisting of a membrane envelope wound around a perforated central collection tube. The wound module is placed inside a tubular pressure vessel and feed gas is circulated axially down the module across the membrane envelope. A portion of the feed permeates into the membrane envelope, where it spirals towards the center and exits via the collection tube.

Simple laboratory spiral-wound modules 12-inches-long and 2-inches in diameter consist of a simple membrane envelope wrapped around the collection tube. The membrane area of these modules is typically 2-3 ft². Commercial spiral-wound modules are typically 36-40 inches long and have diameters of 4, 6, 8, and 12 inches. These modules typically consist of a number of membrane envelopes, each with an area of approximately 20 ft², wrapped around the central collection pipe. This type of multileaf design is illustrated in Figure 1-31.⁷⁷ Multileaf designs are used to minimize the pressure drop encountered by the permeate gas traveling towards the central pipe. If a simple membrane envelope were used this would amount to a permeate spacer length of 5-25 meters, producing a very large pressure drop, especially with high flux membranes.

Plate and Frame Module

Tubular Module

Capillary (Spaghetti) Module

Hollow Fiber Module

Spiral Wound Module

Figure 1-29. Schematics of the principal membrane module designs.

Figure 1-30. Spiral-wound membrane module.

Figure 1-31. Schematic of a four-leaf, spiral-wound module.

1.6.2 Hollow-Fiber Modules

Hollow-fiber membrane modules are formed in two basic geometries. The first is the closed-end design illustrated in Figure 1-32 and used, for example, by Monsanto in their gas separation systems or DuPont in their reverse osmosis fiber systems. In this module, a loop of fiber or a closed bundle is contained in a pressure vessel. The system is pressurized from the shell side and permeate passes through the fiber wall and exits via the open fiber ends. This design is easy to make and allows very large fiber membrane areas to be contained in an economical system. Because the fiber wall must support a considerable hydrostatic pressure, these fibers usually have a small diameter, on the order of 100 μm ID and 150-200 μm OD.

The second type of hollow-fiber module is the flow through system illustrated in Figure 1-33. The fibers in this type of unit are open at both ends. In this system, the feed fluid can be circulated on the inside or the outside of the fibers. To minimize pressure drops in the inside of the fibers, the fibers often have larger diameters than the very fine fibers used in closed loop systems. These so-called spaghetti fibers are used in ultrafiltration, pervaporation and in some low to medium pressure gas applications, with the feed being circulated through the lumen of the fibers. Feed pressures are usually limited to less than 150 psig in this type of application.

1.6.3 Plate-and-Frame Modules

Plate-and-frame modules were among the earliest types of membrane systems and the design has its origins in the conventional filter-press. Membrane feed spacers and product spacers are layered together between two end plates, as illustrated in Figure 1-34. A number of plate-and-frame units have been developed for small-scale applications, but these units are expensive compared to the alternatives and leaks caused by the many gasket seals are a serious problem. The use of plate-and-frame modules is now generally limited to electrodialysis and pervaporation systems or small ultrafiltration and reverse osmosis systems.

1.6.4 Tubular Systems

Tubular modules are now used in only a few ultrafiltration applications where the benefit of resistance to membrane fouling because of good fluid hydrodynamics overcomes the problem of their high capital cost.

1.6.5 Module Selection

The choice of an appropriate module design for a particular membrane separation is a balance of a number of factors. The principal factors that enter into this decision are listed in Table 1-1.

The paper clip illustrates the relative size of the hollow fibers inside a Prism Alpha separator.

Figure 1-32. Schematic of a Monsanto Prism® closed-end module.

Figure 1-33. Schematic of a capillary membrane module.

Figure 1-34. Schematic of plate-and-frame membrane system.

Cost, although always important, is a difficult factor to quantify. The actual selling price of membrane modules varies widely depending on the application. Generally, high-pressure modules are more expensive than low-pressure or vacuum systems. The selling price also depends on the volume of the application and the pricing structure adopted by the industry. For example, membranes for reverse osmosis of brackish water are produced by many manufacturers. As a result, competition is severe and prices are low. Similar modules used in other separations are much more expensive. Our estimate of the cost of producing membrane modules is given in Table 1-1; the selling price is typically two to five times higher.

Table 1-1. Characteristics of the Major Module Designs

	Hollow Fine Fibers	Capillary Fibers	Spiral- Wound	Plate- and-Frame	Tubular
Manufactur- ing cost (\$/m ²)	5 - 20	20 - 100	30 - 100	100 - 300	50 - 200
Packing density	high	moderate	moderate	low	low
Resistance to fouling	very poor	good	moderate	good	very good
Parasitic pressure drops	high	moderate	moderate	moderate	low
Suitable for high pressure operation?	yes	no	yes	can be done with difficulty	can be done with difficulty
Limited to specific types of membranes?	yes	yes	no	no	no

A second major factor determining module selection is resistance to fouling. Membrane fouling is a particularly important problem in liquid separations such as reverse osmosis and ultrafiltration. In gas separation applications fouling is more easily controlled.

A third factor is the ease with which various membrane materials can be fabricated into a particular module design. Almost all membranes can be formed into plate and frame modules, for example, but relatively few materials can be fabricated into hollow fine fibers or capillary fibers. Finally, the suitability of the module design for high pressure operation and the relative magnitude of pressure drops on the feed and permeate sides of the membrane can sometimes be important considerations.

In reverse osmosis, most modules are of the hollow fine fiber or spiral-wound design. Plate-and-frame and tubular modules are used in a few applications where membrane fouling is particularly severe, for example, food applications or processing of heavily contaminated industrial water. Currently, spiral-wound modules appear to be displacing hollow fiber designs because they are inherently more fouling resistant and feed pretreatment costs are therefore lower. Also, the thin film interfacial composite membranes that are the best reverse osmosis membranes now available, cannot be fabricated into hollow fine fiber form.

In ultrafiltration applications, hollow fine fibers have never been seriously considered because of their susceptibility to fouling. If the feed solution is extremely fouling, tubular or plate-and-frame systems are used. In recent years, however, spiral modules with improved resistance to fouling have been developed and these modules are increasingly displacing the more expensive plate-and-frame and tubular systems. Capillary systems are also used in some ultrafiltration applications.

In high pressure gas separation applications, hollow fine fibers appear to have a major segment of the market. Hollow-fiber modules are clearly the lowest cost design per unit membrane area, and the poor resistance of hollow-fiber modules to fouling is not a problem in gas separation applications. High pressure gas separations also require glassy rigid polymer materials such as polysulfone, polycarbonate, and polyimides, all of which can easily be formed into hollow fine fibers. Of the major companies servicing this area only Separex and W.R. Grace use spiral-wound modules.

Spiral-wound modules are much more commonly used in low pressure or vacuum gas separation applications, for example, the production of oxygen-enriched air, or the separation of organic vapors from air. In these applications, the feed gas is at close to ambient pressure and a vacuum is drawn on the permeate side of the membrane. Parasitic pressure drops on the permeate side of the membrane and the difficulty in making high-performance hollow fine fiber membranes from the rubbery polymers used in these membranes both militate against the hollow fine fiber designs.

Pervaporation has the same type of operational constraints as low pressure gas separation. Pressure drops on the permeate side of the membrane must be small and many pervaporation membrane materials are rubbery. For this reason, spiral-wound modules and plate-and-frame systems are both being used. Plate-and-frame systems are competitive in this application despite their high cost primarily because they can be operated at high temperatures with relatively aggressive feed solutions, where spiral-wound systems would fail.

1.7 CURRENT AREAS OF MEMBRANE AND MODULE RESEARCH

During the past 40 years membrane technology has moved from laboratory to industrial scale. Annual sales of the four developed membrane processes, microfiltration, ultrafiltration, reverse osmosis and electrodialysis, are of the order of \$1 billion. More than one million square meters of membranes are installed in industrial plants using these processes around the world. Because these processes

are now developed, opportunities for technological breakthroughs in new membranes and modules with dramatic consequences are limited. A survey of the patent literature shows this. Currently between 80-100 U.S. patents on various improvements to microfiltration, ultrafiltration, reverse osmosis or electrodialysis membranes and modules are issued annually. Almost all of these patents cover small improvements to existing techniques or systems. Progress in these areas will continue in the future but is likely to occur through a large number of small, incremental advances.

Areas in which breakthroughs in membrane and module technology are occurring are gas separation and, to a lesser extent, pervaporation and facilitated transport. These are developing processes and a number of innovative concepts are being explored that could produce major changes. The total number of U.S. patents on membrane and module preparation in these areas in 1988-9 was between 60-80. Although nearly equal in number to the established process patents, the flavor of these patents taken together is quite different. They are, in general, more innovative; some cover substantial advances. Gas separation, therefore, currently represents the advancing frontier of modern membrane technology.

REFERENCES

1. R. Rautenbach and R. Albert, Membrane Processes, John Wiley & Sons, Chichester, England (1989).
2. D.H. Kaelble, "Spin Casting of Polymer Films," J. Appl. Polym. Sci. **9**, 1209 (1965).
3. R.L. Fleischer, P.B. Price and R.M. Walker, "Solid-State Track Detectors: Applications to Nuclear Science and Geophysics," Ann. Review Nucl. Sci. **15**, 1 (1965).
4. R.L. Fleischer, P.B. Price and R.M. Walker, Nuclear Tracks in Solids," Sci. American **220** (June 30, 1969).
5. H.S. Bierenbaum, R.B. Isaacson, M.L. Druin and S.G. Plovan, "Microporous Polymeric Films," Ind. Eng. Chem., Prod. Res. Develop. **13**(1), 2 (1974).
6. Okugama, U.S. Patent 4,585,604.
7. R.W. Gore, U.S. Patent 4,187,390 (Feb. 1980).
8. U.S. Patent 3,532,527.
9. K. Gerlach, E. Kressler and W. Henne, U.S. Patent 4,708,799 (1987).
10. T. Ichikawa, K. Takahara, K. Shimoda, Y. Seita and M. Emi, U.S. Patent 4,708,800 (1987).
11. R.P. Beaver, U.S. Patent 4,778,499 (Oct. 1988).
12. S. Loeb and S. Sourirajan, "Sea Water Demineralization by Means of an Osmotic Membrane," Saline Water Conversation, Vol. 2, R.F. Gould (Ed.), ACS Symposium Series 38, American Chemical Society, Washington, DC, p. 117 (1963).
13. H. Strathmann, K. Kock, P. Amar and R.W. Baker, "The Formation Mechanism of Asymmetric Membranes," Desalination **16**, 179 (1975).
14. H. Strathmann and K. Kock, "The Formation Mechanism of Phase Inversion Membranes," Desalination **21**, 241 (1977).
15. J.G. Wijmans and C.A. Smolders, "Preparation of Asymmetric Membranes by the Phase Inversion Process," in Synthetic Membranes: Science, Engineering and Applications, P.M. Bungay, H.K. Lonsdale and M.N. de Pinho (Eds.), D. Reidel, Dordrecht, The Netherlands (1986).
16. M.H.V. Mulder, J. Oude Hendrikman, J.G. Wijmans and C.A. Smolders, "A Rationale for the Preparation of Asymmetric Pervaporation Membranes," J. Appl. Polym. Sci. **30**, 2805 (1985).
17. A.J. Castro, U.S. Patent 4,247,498 (1981).

18. W.C. Hiatt, G.H. Vitzhum, K.B. Wagener, K. Gerlach and C. Josefiak, "Microporous Membranes via Upper Critical Temperature Phase Separation," in Materials Science of Synthetic Membranes, D.R. Lloyd (Ed.), American Chemical Society, Washington, D.C. (1985).
19. W. Henne, M. Pelger, K. Gerlach and J. Tretzel, in Plasma Separation and Plasma Fractionation, M.J. Lysaght and H.J. Gurland (Eds.), S. Karger AG, Basel, Switzerland (1983).
20. W.J. Elford, "Principles Governing the Preparation of Membranes Having Graded Porosities, The Properties of "Gradocol" Membranes as Ultrafilters," Trans. Far. Soc. 33, 1094 (1937).
21. R. Zsigmondy and W. Bachmann, "Uber neue filter," Z. Anorg. Chem. 103, 119 (1918).
22. J.D. Ferry, "Ultrafilter Membranes and Ultrafiltration," Chem Rev. 18, 373 (1936).
23. R.L. Riley, H.K. Lonsdale, L.D. LaGrange and C.R. Lyons, "Development of Ultrathin Membranes," Office of Saline Water Report No. 386, PB# 207036. Jan. (1969).
24. B.J. Epperson and L.J. Burnett, "Development and Demonstration of a Spiral-Wound Thin-Film Composite Membrane System for the Economical Production of Oxygen-Enriched Air," Final Report Department of Energy No. CS/40294. November (1983).
25. A.S. Michaels, U.S. patent 3,615,024 (Oct. 1971).
26. J.M.S. Henis and M.K. Tripodi, "A Novel Approach to Gas Separations Using Composite Hollow Fiber Membranes," Sep. Sci. & Tech. 15, 1059 (1980).
27. J.M.S. Henis and M.K. Tripodi, U.S. Patent 4,230,463 (1980).
28. W.R. Browall, U.S. Patent 3,980,456 (Sept. 1976).
29. L.T. Rozelle, J.E. Cadotte, K.E. Cobian and C.V. Kopp, Jr., "Non-Polysaccharide Membranes for Reverse Osmosis, NS-100 Membranes," S. Sourirajan (Ed.), National Research Council of Canada Pub. NRCC 15627, (1977).
30. J.E. Cadotte, "Evolution of Composite Reverse Osmosis Membranes," in Materials Science of Synthetic Membranes, D.R. Lloyd (Ed.), American Chemical Society, Washington, D.C. (1985).
31. R.L. Riley, R.L. Fox, C.R. Lyons, C.E. Milstead, N.W. Seroy and M. Tagami, Desalination 19, 113 (1976).

32. Y. Kamiyama, N. Yoshioka, K. Matsui and E. Nakagome, "New Thin-Film Composite Reverse Osmosis Membranes and Spiral-Wound Modules," Desalination **51**, 79 (1984).
33. W.J. Ward, W.R. Browall and R.M. Salemme, "Ultrathin Silicone Rubber Membranes for Gas Separation," J. Membrane Sci. **1**, 99 (1976).
34. R.L. Riley and R.L. Grabowsky, "Preparation of Gas Separation Membranes," U.S. Patent 4,234,701 (January 1984).
35. R.W. Baker, U.S. Patent 4,553,983 (Nov. 1985).
36. H.S. Strathmann, private communication.
37. H. Yasuda, "Plasma Polymerization for Protective Coatings and Composite Membranes," J. Memb. Sci. **18**, 273, (1984).
38. H. Yasuda, "Composite Reverse Osmosis Membranes Prepared by Plasma Polymerization," in Reverse Osmosis and Synthetic Membranes, S. Sourirajan (Ed.), National Research Council of Canada (1977).
39. A.R. Stancell and A.T. Spencer, "Composite Permselective Membrane by Deposition of an Ultrathin Coating from a Plasma," J. Appl. Poly. Sci. **16**, 1505 (1972).
40. M. Kawakami, Y. Yamashita, M. Iwamoto and S. Kagawa, "Modification of Gas Permeabilities of Polymer Membranes by Plasma Coating," J. Memb. Sci. **19**, 249 (1984).
41. K.A. Kraus, A.J. Shor and J.S. Johnson, Desalination, **2**, 243 (1967).
42. J.S. Johnson, K.A. Kraus, S.M. Fleming, H.D. Cochran and J.J. Perona, Desalination, **5**, 359 (1968).
43. M. Langsam, U.S. Patent 4,657,564 (1987).
44. M. Langsam, A.C. Savoca, U.S. Patent 4,759,776 (July 1988).
45. M. Langsam, M. Anand, E.J. Karwacki, Presented at the 2nd Annual National Meeting of the North American Membrane Society, Syracuse, NY, (June 1-3, 1988).
46. R.B. McBride, D.L. McKinley, Chem. Eng. Prog. **61**, 81 (1965).
47. R.B. McBride, R.T. Nelson and R.S. Hovey, U.S. Patent 3,336,730 (1967).
48. J.B. Hunter, U.S. Patent 2,773,561 (1956).
49. J.B. Hunter, Platinum Met. Rev. **4**, 130 (1960).
50. R.W. Baker, J. Louie, P.H. Pfromm and J.G. Wijmans, U.S. Patent 4,857,080, (August 1989).

51. A.S. Darling, British Patent 1,292,025 (1972).
52. U.S. Patent 4,717,455.
53. U.S. Patent 4,722,771.
54. R.C. Furneaux et al., "The Formation of Controlled Porosity Membranes from Anodically Oxidized Aluminium," Nature **337**, No. 6203, 147-9, (1989).
55. H.P. Hsieh, "Inorganic Membranes," in New Membrane Materials and Processes for Separation, K.K. Sirkar & D.R. Lloyd (Eds.), AIChE Symposium Series, 84, p.1 (1988).
56. M.A. Anderson, M.S. Gieselmann, Q. Xu, J. Membr. Sci. **39**, 243 (1988).
57. A. Soffer, J.E. Koresh and S.S. Saggy, U.S. Patent 4,685,940 (1987).
58. W.J.V. Osterhout, Physiology **21**, 125-32 (1935).
59. G.M. Shean and K. Sollner, Annals of the New York Academy of Sciences, **137**, 759-76 (1966).
60. R. Bloch, A. Finkelstein, O. Kedem and D. Vofsi, "Metal Ion Separation by Dialysis Through Solvent Membranes," I&EC Process Design and Development, **6**, 231-37 (1967).
61. G.J. Moody and J.D.R. Thomas, "Polyvinyl Chloride Matrix Membrane Ion-Selective Electrodes" in Ion-Selective Electrode Methodology, A.K. Covington (Ed.), CRC Press: Boca Raton, FL, 111 (1979).
62. T. Miyauchi, U.S. Patent 4,051,230, (1977).
63. R.W. Baker, M.E. Tuttle, D.J. Kelly and H.K. Lonsdale, "Coupled Transport Membranes," J. Membr. Sci. **2**, 213- 233 (1977).
64. T. Largman and S. Sifniades, "Recovery of Copper from Aqueous Solutions by Means of Supported Liquid Membranes," Hydrometallurgy **3**, 153-162 (1978).
65. N.N. Li and A.L. Shrier, "Liquid Membrane Water Treating" in Recent Developments in Separation Science, Vol. 1, CRC Press: Cleveland, OH (1972).
66. R.P. Cahn and N.N. Li, "Hydrocarbon Separation by Liquid Membrane Processes" in Membrane Separation Processes, P. Meares (Ed.), Elsevier: Amsterdam, 328 (1975).
67. E.L. Cussler, Multicomponent Diffusion, Elsevier: Amsterdam (1976).
68. W. Volkel, W. Poppe, W. Halwachs and K. Schurgerl, "Extraction of Free Phenols from Blood by a Liquid Membrane Enzyme Reactor," J. Membr. Sci. **11**, 333 (1982).

69. R. Marr and A. Kopp, Chem. Ing. Tech. 52:5, 399 (1980).
70. J. Stelmazek, J. Membr. Sci., 2, 197 (1977).
71. T.P. Martin and G.A. Davies, "The Extraction of Copper From Dilute Aqueous Solutions Using a Liquid Membrane Process," Hydrometall. 2, 315 (1976/1977).
72. P.R. Danesi, J. Membr. Sci., 20, 231 (1984).
73. A.L. Bunge and R.D. Noble, "A Diffusion Model for Reversible Consumption in Emulsion Liquid Membranes," J. Membr. Sci. 21, 55 (1984).
74. R.M. Izatt, R.M. Haws, J.D. Lamb, D.V. Dearden, P.R. Brown, D.W. McBride, Jr. and J.J. Christensen, J. Membr. Sci., 20, 273 (1984).
75. H.I. Mahon, U.S. Patent 3,228,876 (1966).
76. H.I. Mahon, U.S. Patent 3,228,877 (1966).
77. D.T. Bray, U.S. Patent 3,417,870 (1968).
78. J. Westmoreland, U.S. 3,367,504 (1968).
79. S.S. Kremen, "Technology and Engineering of ROGA Spiral Wound Reverse Osmosis Membranes," in Reverse Osmosis and Synthetic Membranes, S. Sourirajan (Ed.), Natinal Research Council of Canada, Ottawa (1977).

CHAPTER TWO
PERVAPORATION
TABLE OF CONTENTS

2.1	PROCESS OVERVIEW	2-1
2.1.1	Design Features	2-4
2.1.2	Pervaporation Membranes	2-6
2.1.3	Pervaporation Modules	2-6
2.1.4	Historical Trends	2-9
2.2	CURRENT APPLICATIONS, ENERGY BASICS AND ECONOMICS .	2-10
2.2.1	Dehydration of Solvents	2-11
2.2.2	Water Purification	2-14
2.2.3	Pollution Control	2-19
2.2.4	Solvent Recovery	2-21
2.2.5	Organic-Organic Separations	2-24
2.3	INDUSTRIAL SUPPLIERS	2-26
2.4	SOURCES OF INNOVATION	2-30
2.5	FUTURE DIRECTIONS	2-32
2.5.1	Solvent Dehydration	2-32
2.5.2	Water Purification	2-34
2.5.3	Organic-Organic Separations	2-34
2.6	DOE RESEARCH OPPORTUNITIES	2-35
2.6.1	Priority Ranking	2-36
2.6.1.1	Solvent dehydration	2-36
2.6.1.2	Water purification	2-36
2.6.1.3	Organic-organic separations	2-36
	REFERENCES	2-37

CHAPTER TWO

PERVAPORATION

by

R.W. Baker, Membrane Technology and Research, Inc.
Menlo Park CA

2.1 PROCESS OVERVIEW

Pervaporation is a membrane process used to separate mixtures of dissolved solvents. The process is shown schematically in Figure 2-1. A liquid mixture contacts one side of a membrane; the permeate is removed as a vapor from the other side. Transport through the membrane is induced by the difference in partial pressure between the liquid feed solution and the permeate vapor. This partial-pressure difference can be maintained in several ways. In the laboratory a vacuum pump is usually used to draw a vacuum on the permeate side of the system. Industrially, the permeate vacuum is most economically generated by cooling the permeate vapor, causing it to condense. The components of the feed solution permeate the membrane at rates determined by their feed solution vapor pressures, that is, their relative volatilities and their intrinsic permeabilities through the membrane. Pervaporation has elements in common with air and steam stripping, in that the more volatile contaminants are usually, although not necessarily, preferentially concentrated in the permeate. However, during pervaporation no air is entrained with the permeating organic, and the permeate solution is many times more concentrated than the feed solution, so that its subsequent treatment is straightforward.

The separation factor, β_{pervap} , achieved by a pervaporation process can be defined in the conventional way as

$$\beta_{\text{pervap}} = \frac{c''_i/c''_j}{c'_i/c'_j} \quad , \quad (1)$$

where c'_i and c'_j are the concentrations of components i and j on the feed liquid side and c''_i and c''_j are the concentrations of components i and j on the permeate side of the membrane. Because the permeate is a vapor, c''_i and c''_j can be replaced by p''_i and p''_j , the vapor pressures of components i and j on the permeate side of the membrane. The separation achieved can then be expressed by the equation

$$\beta_{\text{pervap}} = \frac{p''_i/p''_j}{c'_i/c'_j} \quad (2)$$

$$\text{Flux} = \frac{\text{Total quantity passed through membrane}}{\text{Membrane area time}}$$

$$\text{Separation factor } (\beta_{\text{pervap}}) = \frac{\text{ratio of components in permeate vapor}}{\text{ratio of components in feed solution}}$$

$$\beta_{\text{pervap}} = \frac{p''_i/p''_j}{c'_i/c'_j}$$

Figure 2-1. Schematic of pervaporation process.

The most convenient mathematical method of describing pervaporation is to divide the overall separation processes into two steps. The first is evaporation of the feed liquid to form a (hypothetical) saturated vapor phase on the feed side of the membrane. The second is permeation of this vapor through the membrane to the low pressure permeate side of the membrane. Although no evaporation actually takes place on the feed side of the membrane during pervaporation, this approach is mathematically simple and is thermodynamically completely equivalent to the physical process. The evaporation step from the feed liquid to the saturated vapor phase produces a separation, β_{evap} which can be defined as the ratio of the components' concentrations in the feed vapor to their concentrations in feed liquid

$$\beta_{\text{evap}} = \frac{p'_i/p'_j}{c'_i/c'_j} \quad , \quad (3)$$

where p'_i and p'_j are the partial vapor pressures of the components i and j in equilibrium with the feed solution.

The second permeation step of components i and j through the membrane is directly related to conventional gas permeation. The separation achieved in this step, β_{mem} , can be defined as the ratio of components in the permeate vapor to the ratio of components in the feed vapor,

$$\beta_{\text{mem}} = \frac{p''_i/p''_j}{p'_i/p'_j} \quad . \quad (4)$$

From the definitions given in Equations (1-4), we can write the equality,

$$\beta_{\text{pervap}} = \beta_{\text{evap}} \cdot \beta_{\text{mem}} \quad . \quad (5)$$

This equation shows that the separation achieved in pervaporation is equal to the product of the separation achieved by evaporation of the liquid and the separation achieved by permeation of the components through a membrane. To achieve good separations both terms should be large. It follows that, in general, pervaporation is most suited to the removal of volatile components from relatively involatile components, because β_{evap} will then be large. However, if the membrane is sufficiently selective and β_{mem} is large, nonvolatile components can be made to permeate the membrane preferentially.

It can be shown that Equation (5) can be rewritten as

$$\beta_{\text{pervap}} = \beta_{\text{evap}} \cdot \alpha_{\text{mem}} \left[\frac{p'_i/p''_i}{p'_j/p''_j} \right] \cdot \frac{p'_j}{p'_i} \quad , \quad (6)$$

where α_{mem} is the membrane selectivity, that is the ratio of the individual component permeabilities,

$$\alpha_{\text{mem}} = \frac{P_i}{P_j} \quad . \quad (7)$$

Equation (6) is useful in defining the contributions to the separation achieved in a pervaporation process. The first contribution is the simple evaporation term β_{evap} . This term can be obtained from the vapor-liquid equilibrium diagram and is the same factor that determines the efficiency of a distillation process. The second term α_{mem} reflects the intrinsic permeation selectivity of the membrane. The third term

$$\left(\frac{p'_i - p''_i}{p'_j - p''_j} \right) \cdot \frac{p'_j}{p'_i}$$

reflects the particular operating conditions of the pervaporation process.

To obtain the maximum possible separation for a particular mixture the membrane permeation selectivity should be much greater than 1, and there should be the maximum possible difference between the feed and permeate vapor partial pressures.

2.1.1 Design Features

As described above, transport through pervaporation membranes is produced by maintaining a vapor pressure gradient across the membrane. The vapor pressure gradient used to produce a flow across a pervaporation membrane can be generated in a number of ways. Figure 2-2 illustrates a number of possible processes.

In the laboratory, the low vapor pressure required on the permeate side of the membrane is most conveniently produced with a vacuum pump as shown in Figure 2-2a. On a commercial scale, however, the vacuum pumps required would be impossibly large. An attractive alternative to vacuum operation, illustrated in Figure 2-2b, is to cool the permeate vapor to condense the liquid. The feed solution may also be heated. In this process, sometimes called thermopervaporation, the driving force is the difference in vapor pressure between the hot feed solution and the cold permeate liquid at the temperature of the condenser. Because the cost of providing the cooling and heating required is much less than the cost of a vacuum pump, as well as being operationally more reliable, this type of system is preferred in commercial operations.

A third possibility, illustrated in Figure 2-2c, is to sweep the permeate side of the membrane with a carrier gas (normally air). In the example shown, the carrier gas is cooled to condense and recover the permeate vapor and the gas is recirculated. This mode of operation has little to offer compared to temperature gradient-driven pervaporation, since both require cooling water for the condenser. However, if the permeate has no value and can be discarded without condensation (for example, in the pervaporative dehydration of an organic solvent with an extremely selective membrane), this is the preferred mode of operation. In this case, the permeate would contain only water plus a trace of organic solvent and could be discharged or incinerated at a low cost. No cooling water is required.¹ An alternative carrier gas system uses a condensable gas, such as steam, as the carrier sweep fluid. This system is illustrated in Figure 2-2d.

a) Vacuum driven pervaporation

b) Temperature gradient driven pervaporation

c) Carrier gas pervaporation

d) Pervaporation with a condensable carrier

e) Pervaporation with a two-phase permeate and partial recycle

f) Pervaporation with fractional condensation of the permeate

MTR-028-1S

Figure 2-2. Schematics of possible pervaporation process configurations.

Low-grade steam is often available at very low cost and if the permeate were immiscible in the condensed carrier water, it could be recovered by decantation. The condensed water would contain some dissolved solvent and could be recycled to the evaporator and then to the permeate side of the module. This mode of operation is limited to water-immiscible permeates and to feed streams in which contamination of the feed liquid by water vapor permeating from sweep gas is not a problem. A possible example would be the removal of low concentrations of toluene and similar organic solvents from aqueous feed streams.

The final two pervaporation processes illustrated in Figures 2-2e and 2-2f are systems of particular interest for removing low concentrations of dissolved organic compounds from water. The system shown in Figure 2-2e could be used when the permeating solvent has a limited solubility in water. In this case, the condensed permeate liquid will often separate into two phases: an organic phase, which can be treated for reuse, and an aqueous phase saturated with organic solvent, which can be recycled to the feed stream for reprocessing. The system shown in Figure 2-2f shows two condensers in series. In this case, a second, partial separation can be achieved, in addition to the pervaporation separation. This would be useful, for example, in the separation of dilute alcohol-water feeds. Thus, the alcohol-enriched permeate would be separated into a water-rich fraction that might be recycled to the pervaporation unit and a second, highly enriched alcohol fraction.²

2.1.2 Pervaporation Membranes

The selectivity of pervaporation membranes can vary substantially and has a critical effect on the overall separation obtained. The range of results that can be obtained for the same solutions and different membranes is illustrated in Figure 2-3 for the separation of acetone from water. The figure shows the concentration of acetone in the permeate as a function of the concentration in the feed. The two membranes shown have dramatically different properties. The pervaporation selectivity varies with concentration. At 20 wt% acetone in the feed, silicone rubber has a pervaporation selectivity of approximately 16 favoring acetone; the crosslinked polyvinyl alcohol (PVA) membrane has a pervaporation selectivity of only 0.3 and selectively removes water.

The acetone-selective, silicone rubber membrane is best used to treat dilute acetone feed streams, concentrating most of the acetone in a small volume of permeate. The water-selective, polyvinyl alcohol membrane is best used to treat concentrated acetone feed streams containing only a few percent water. Most of the water is then removed and concentrated in the permeate. Both membranes are more selective than distillation, which relies on the vapor-liquid equilibrium to achieve a separation.

2.1.3 Pervaporation Modules

Pervaporation applications often involve hot, organic-solvent-containing feed solutions. These solutions can degrade the seals and plastic components of membrane modules. As a result, the first-generation commercial pervaporation modules installed have been made from stainless steel and are of the plate-and-frame design. Figure 2-4 shows a single cell of a multicell pervaporation stack. These cells can be made in various sizes. The largest currently produced incorporates membranes with a membrane area of 1.5 m².

MTR-034-GRP

Figure 2-3. The pervaporation separation of acetone-water mixtures achieved with a PVA, water-selective membrane, and an acetone-selective, silicone rubber membrane (source: GFT literature).

MTR-043-F

Figure 2-4. A pervaporation plate-and-frame module.

In recent years attempts have been made to switch to lower cost module designs. Membrane Technology and Research (MTR) and Air Products have both used spiral-wound modules for pervaporation. British Petroleum is also said to be developing a tubular module system.

2.1.4 Historical Trends

The origins of pervaporation can be traced to the 19th century, but the process was first studied in a systematic fashion by Binning, Lee and co-workers at American Oil in the early 1950s.³ Binning and Lee were interested in applying the process to the separation of organic mixtures. Although this work was pursued for a number of years and several patents were obtained, the process was not commercialized, because membrane fabrication technology available then did not allow the high-performance membranes and modules required for a commercially competitive process to be made. By the 1980s, however, advancements in membrane technology made it possible to prepare economically viable pervaporation systems. The surge of interest in the process starting in 1980 is illustrated in Figure 2-5, which tabulates the increase in the quantity of pervaporation literature over the last 40 years.

Pervaporation has now been commercialized for two applications. The first and by far the most important is the separation of water from concentrated alcohol solutions. GFT of Hamburg, West Germany, the leader in this field, installed their first major plant in 1982.⁴ Currently, more than 100 plants have been installed by GFT for this application.⁵ The second application is the separation of small amounts of organic solvents from contaminated waters, for which the technology has been developed by MTR.⁶ Both of the current commercial processes concentrate on the separation of organics from water. This separation is relatively easy, because organic solvents and water, due to their difference in polarity, exhibit distinct membrane permeation properties. The separation is also amenable to membrane pervaporation because the feed solutions are relatively non-aggressive and do not chemically degrade the membrane.

No commercial systems have yet been developed for the separation of the more industrially significant organic/organic mixtures. However, current technology now makes development of pervaporation for these applications possible and the process is being actively researched in a number of laboratories. The first pilot-plant results for an organic-organic application, the separation of methanol from methyltertbutyl ether/isobutene mixtures, was recently reported by Air Products.^{7,8} Texaco is also working on organic-organic separations.⁹ This is a particularly favorable application and currently available cellulose acetate membranes give good separation. It can only be a matter of time, however, before much more commercially significant organic-organic separations are attempted using pervaporation.

2.2 CURRENT APPLICATIONS, ENERGY BASICS AND ECONOMICS

There are three current applications of pervaporation; dehydration of solvents, water purification, and organic-organic separations as an alternative to distillation. Currently dehydration of solvents, in particular ethanol and isopropanol, is the only process installed on a large scale. However, as the technology develops, the other applications are expected to grow. Separation of organic mixtures, in particular, could become a major application. Each of these applications is treated separately below. The energy considerations and system economics vary from application to application and are discussed in the individual application sections.

Figure 2-5. Pervaporation citations in Chemical Abstracts for the years 1959-1988.

2.2.1 Dehydration of Solvents

More than 100 plants have been installed for the dehydration of ethanol by pervaporation. This is a particularly favorable application because ethanol forms an azeotrope with water at 95% and there is a need for a 99.5% pure product.

A comparison of the separation of ethanol and water obtained by a pervaporation membrane (GFT polyvinyl alcohol composite membrane) and the separation obtained by distillation is shown in Figure 2-6. Because of the ethanol-water azeotrope at 95% ethanol, the concentration of ethanol from fermentation feeds to high degrees of purity requires rectification with a benzene entrainer, some sort of molecular-sieve drying process, or a liquid-liquid extraction process. All of these processes are expensive. The existence of extremely water-selective pervaporation membranes, however, means that pervaporation systems can produce almost pure ethanol (>99.9% ethanol from a 90% ethanol feed). The permeate stream contains approximately 50% ethanol and can be recirculated back to the distillation column.

An energy and cost comparison of a very small ethanol/water separation plant from GFT is shown in Table 2-1. Pervaporation is less capital and energy intensive than distillation or adsorption processes. These savings produce a cost reduction of 3-5¢/gallon of ethanol produced. However, because of the modular nature of the process, the costs of pervaporation are not as sensitive to economies of scale as are the costs of distillation and adsorption processes. Figure 2-7 shows GFT cost data for ethanol dehydration plants varying from 100 to 10,000 L/h. Costs of plants above 100 L/h capacity scale almost linearly with capacity. Distillation costs, on the other hand, scale at a rate proportional to 0.6-0.7 times the power consumption. Thus, distillation remains the most economical process for large plants. The cross-over point at which distillation becomes preferable to pervaporation from an energy and economic point of view currently appears to be about 10×10^6 gal/year (5,000 L/h) processing capacity.

Table 2-1. Separation Options for Small Scale EtOH/Water
(Basis: 1,000 L/day, 99.5 wt% EtOH)⁵

	<u>Pervaporation</u>	<u>Distillation</u>	<u>Adsorption</u>
System cost	\$ 75,000	\$140,000	\$ 90,000
Pumps	3 kW	2 kW	2 kW
Steam	45 kg/h @ 1.8 bar	70 kg/h @ 7.3 bar	90 kg/h @ 7.3 bar, 220°C
Entrainer	--	3 L/day	--

MTR-036-GRP

Figure 2-6. Separation of ethanol/water mixtures by distillation and GFT's polyvinyl alcohol pervaporation membrane.

MTR-041-GRP

Figure 2-7. Cost of ethanol dehydration plants as a function of plant capacity.¹⁰ Costs in \$/liter/hour capacity are shown.

A flow scheme for an integrated distillation-pervaporation plant operating on 5% ethanol feed from a fermentation mash is shown in Figure 2-8. The distillation column produces an ethanol stream containing 85-90% ethanol, which is fed to the pervaporation system. To maximize the vapor pressure difference across the membrane, the pervaporation module usually operates at a temperature of 105-130°C with a corresponding feed stream vapor pressure of 2-6 atmospheres. Despite these harsh conditions, the membrane lifetime is good and qualified guarantees for up to four years are given.

Figure 2-8 shows a single-stage pervaporation unit. In practice, at least three pervaporation stages are usually used in series, with additional heat being supplied to the ethanol feed between each stage. This compensates for pervaporative cooling of the feed and maintains the feed at 80°C. The heat required is obtained by thermally integrating the pervaporation system with the condenser of the final distillation column. Most of the energy used in the process is therefore low grade heat. Generally, about 0.5 kg of steam is required for each kilogram of ethanol produced. The energy consumption of the pervaporation process is, therefore, about 2,000 Btu/gal of product, less than 20% of the energy used in azeotropic distillation, which typically is in the range 11,000-12,000 Btu/gal. Moreover, pervaporation uses very low-grade steam, which is available in most industrial plants at very little cost.

Although most of the installed solvent dehydration systems have been for ethanol dehydration, dehydration of other solvents including isopropanol, glycols, acetone and methylene chloride, has been considered. Schematics of pervaporation processes for these types of separation are shown in Figure 2-9. These processes are all in the pilot-plant or demonstration-plant stage.

2.2.2 Water Purification

A number of applications exist for pervaporation in the removal or recovery of organic solvents from water. If the aqueous stream is very dilute, pollution control is the principal economic driving force. However, if the stream contains more than 1-2% solvent, recovery for eventual reuse can significantly enhance the process economics.

A number of membranes have been used for the separation of solvents from water and are discussed in the literature.^{6,10-14} Usually the membranes are made from rubbery polymers such as silicone rubber, polybutadiene, natural rubber, polyether copolymers and the like. Some typical results for a commercial organic-solvent-selective membrane are shown in Figure 2-10. This membrane has high selectivities for hydrophobic volatile solvents such as benzene, 1,1,2-trichloroethylene and chloroform. It has high selectivities for solvents of intermediate hydrophobic character such as ethyl acetate, methyl ethyl ketone, and acetone, but only modest selectivities with relatively hydrophilic solvents such as ethanol, methanol and acetic acid. This pattern of behavior is typical of most membranes, although there are substantial differences between different membrane materials. Some comparative data for the separation of toluene and trichloroethylene from dilute aqueous solutions are shown in Figure 2-11. In these particular experiments, the ethene-propene terpolymer membrane was significantly more selective than, for example, silicone rubber.

MTR-032-F

Figure 2-8. Integrated distillation/pervaporation plant for ethanol recovery from fermenters.

MTR-033-F

Figure 2-9. A schematic of various types of pervaporation solvent dehydration systems.

Figure 2-10. Separation of organic solvents from water by pervaporation using a commercial membrane (MTR CODE-100, Membrane Technology and Research, Inc.).

Figure 2-11. Comparative selectivities for toluene and trichloroethylene from water and various rubber membranes.

There is very little data on membranes with high selectivities for polar solvents such as ethanol and methanol. The most promising results to date have been obtained with silicone rubber membranes containing dispersed zeolite particles.¹⁵ It appears that ethanol preferentially permeates through the pores of the zeolite particles and membranes have been produced in the laboratory with ethanol:water selectivities of 40 or more. Membranes with these characteristics could find a substantial application in fermentation and solvent recovery applications if they can be made on a large scale.

2.2.3 Pollution Control

The costs of pervaporation treatment for pollution control vary widely, depending on the solvent and the fractional removal of solvent required. A sample cost calculation is given below for the application of a pervaporation system to a polluted ground-water. The process is illustrated in Figure 2-12. In this example, a 20,000 gal/day groundwater stream is assumed to be polluted with 1,000 ppm (0.1%) of 1,1,2-trichloroethane. The pervaporation separation factor assumed for this solvent is approximately 200, with a transmembrane flux of 1.0 L/m²·h. Both of these figures are easily achievable with current membranes. Using these values and a computer model, it can be shown that 99% removal of the solvent can be achieved with 85 m² of membrane, producing a permeate stream containing 4.1% 1,1,2-trichloroethane.⁷ This solvent is relatively insoluble in water. Therefore, on condensation, the permeate spontaneously separates into a pure solvent stream which can be decanted for reuse or incineration, and an aqueous stream containing 0.4% solvent, which can be returned to the incoming feed for further treatment. The economics of this process are summarized in Table 2-2, based on data from MTR. These costs appear to be very attractive. The capital cost of the plant is equivalent to a cost of \$7.75/gal-day capacity. The operating cost is \$18.8/1,000 gal feed. These costs compare favorably with other waste treatment methods.

Table 2-2. Capital and Operating Costs of a 20,000-gal/day PerVap System to Remove 1,1,2-Trichloroethane from Wastewater

Capital Cost	\$155,000
Operating Cost	
Depreciation at 15%	\$ 22,800
Labor (10% of capital)	15,500
Module Replacement (3-year life)	15,000
Energy	<u>60,000</u>
	\$113,300/yr
Operating Cost	\$18.8/1,000 gal feed

MTR-030-1S

	<u>Feed</u>	<u>Permeate</u>	<u>Residue</u>
Flow (gal/day)	20,000	500	19,980
Concentration (%)	0.1	4.1	0.001
Membrane pervaporation enrichment			200
Membrane flux	1.0 (L/m ² ·h)		
Membrane area	85 (m ²)		

Figure 2-12. Flow diagram and design parameters of an MTR PerVap system to treat a 0.1% 1,1,2-trichloroethane stream.

2.2.4 Solvent Recovery

If the concentration of solvent in the feedstream is sufficiently high, solvent recovery for its own sake becomes economically attractive. An application of this type is shown in Figure 2-13.⁶ This stream contains 2% ethyl acetate and the object is to recover 90% of the solvent. As shown, the pervaporation system produces a permeate containing 45.7% solvent, which spontaneously separates into an organic phase of 96.7% solvent suitable for reuse, and an aqueous phase. The aqueous phase from the permeate is recycled to the feed stream.

The capital cost of a 20,000 gallon/day plant is \$140,000 and the operating costs, as shown in Table 2-3, are approximately \$107,000, or \$0.98/gal of solvent recovered. The current cost of technical grade ethyl acetate is approximately \$5/gal, so the system has a pay-back time of only a few months.

Table 2-3. Capital and Operating Costs of a 20,000 gal/day Pervaporation System to Recover Ethyl Acetate

Capital Cost	\$140,000
Operating Costs	
Depreciation at 15%	21,000
Labor (10% of capital)	14,000
Module Replacement (3 year life)	12,000
Energy	<u>60,000</u>
	\$107,000/yr
Operating Cost	\$17.8/1,000 gal feed
Operating Cost	\$ 0.98/gal solvent recovered

Pervaporation would be more widely applied in solvent recovery operations if membranes more selective for hydrophilic polar solvents were available. Existing membrane materials, such as silicone rubber, have pervaporation selectivities, β_{pervap} , for this type of solvent typically in the range 5-10. If materials having selectivities in the range 40-50 could be made for solvents such as acetic acid, formic acid, ethanol or methanol, pervaporation could easily compete with distillation or solvent extraction. Membranes with this type of selectivity have been reported on a laboratory-scale, but have yet to be tested industrially.

Calculations of the type given above suggest that pervaporation can be economically applied to a wide range of aqueous industrial streams. The process is still very new and its ultimate competitive position compared to more conventional techniques is uncertain. Figure 2-14 shows the solvent concentration range in which pervaporation is believed most competitive. When the feedstream contains less than 100 ppm solvent, carbon adsorption beds become small and this is probably the preferred technique. Similarly, when the stream contains more than 5-10% solvent, distillation, steam stripping or incineration will probably be less expensive than pervaporation. However, in the intermediate range of between 100 ppm and 5% solvent, pervaporation will find a number of important applications.

	<u>Feed</u>	<u>Permeate</u>	<u>Residue</u>
Flow (gal/day)	20,000	800	19,600
Concentration (%)	2.0	45.7	0.2

Membrane pervaporation enrichment	100
Membrane flux, pure water	1.0 (kg/m ² .h)
.2% ethyl acetate	2.0 (kg/m ² .h)
Membrane area	70 (m ²)

Figure 2-13. Flow diagram and design parameters of an MTR PerVap system to treat a 2% ethyl acetate stream.

MTR-037-GRP

Figure 2-14. Costs of pervaporation water purification systems compared to those of competitive technologies.

2.2.5 Organic-Organic Separations

The final application of pervaporation membranes is the separation of organic solvent mixtures. Currently this is the least developed application of pervaporation. However, if problems associated with membrane and module stability under the relatively harsh conditions required for these separations can be solved, this could prove to be a major membrane application around the year 2000.

In 1976 distillation energy consumption was estimated to be two quads (one quad equals 10^{15} Btu), which equals 3% of the entire national energy usage.¹⁶ In principle, pervaporation could be used as a substitute or supplement to distillation processes with substantial cost and energy savings. This is definitely true for the separation of azeotropes and close boiling liquids, which are difficult to separate by conventional distillation techniques. A list of major distillation separations that consume more than 2,000 Btu/lb of product to perform is given in Table 2-4. Replacement of even some of these separations by a low-energy pervaporation process could have a major impact on national energy use.

Table 2-4. Major Distillation Separation Processes Using More Than 2,000 Btu/lb of Product

Process Description	U.S. Distillation Energy Consumption (Quads/yr)	Specific Distillation Energy Consumption (Btu/lb product)	Key Components Light/Heavy
Ethylbenzene/gasoline fractionation	0.00355	11,582	Ethylbenzene/p-xylene
Adipic Acid: air oxidation of cyclohexane	0.00336	2,210	--
Methyl ethyl ketone from n-butylene	0.00279	5,470	Sec-butanol/water
Glycerine using peracetic acid	0.00492	11,618	Dilsobutyl-ketone/heavy impurities, water/glycerine
Ethanol: direct hydration of ethylene	0.0105	8,784	Ethanol azeotrope/water
Vinyl acetate monomer from ethylene and acetic acid	0.00453	3,061	Vinyl acetate-water azeotrope/acetic acid water azeotrope
Phenol from cumene	0.00437	2,005	Cumene/phenol
o-Xylene	0.00603	5,689	m-xylene/o-xylene
Acetic acid acetaldehyde oxidation	0.00574	2,362	Water/acetic acid

It is unlikely that a pervaporation process would perform the entire separation required for any item on the list. In practice, a hybrid distillation-pervaporation process would be used. Such a process is shown in Figure 2-15. In the process shown in Figure 2-15, a 50/50 azeotropic mixture is fractionated into two approximately equal streams, each containing 85% of one of the components.

These streams are then sent to distillation columns to produce pure components and a recycled azeotrope stream. A key feature of this process is that only a relatively modest separation of the azeotropic mixture by the membrane is required to make the separation feasible. Of course, membranes with very high selectivities are more efficient than those with lower selectivities, but in this application a membrane with a selectivity as low as 5-10 might be economically viable, depending on the solvent mixture and the alternative treatments available.

A number of workers have studied membranes for the separation of organic mixtures and membranes have been developed which appear to be remarkably selective, even for relatively similar compounds. Some typical results from Aptel are shown in Figure 2-16.¹⁷ The principal problem hindering the development of commercial systems for this type of application is the lack of membranes and modules able to withstand long-term exposure to organic compounds at the elevated temperatures required for pervaporation.

Membrane and module stability problems do not appear to be insurmountable, however, as shown by the successful demonstration of a pervaporation process for the separation of methanol from an isobutene/methyltertbutyl ether (MTBE) mixture. This mixture occurs during the production of MTBE; the product from the reactor is an alcohol/ether/hydrocarbon raffinate stream in which the alcohol/ether and the alcohol/hydrocarbon both form azeotropes. The product stream is treated by pervaporation to yield a pure alcohol permeate, which can be recycled to the etherification process. This process has been developed by Separex, a division of Air Products (currently owned by Hoechst-Celanese Corp.), using cellulose acetate membranes. The separation factor for methanol from MTBE is 1,000 or more with cellulose acetate membranes. Two alternative ways of integrating the pervaporation process into a complete reaction scheme are illustrated in Figure 2-17.^{7,8} These membranes are reported to work well for feed methanol concentrations up to 6%. Above this concentration, the membrane becomes plasticized and selectivity is lost.

2.3 INDUSTRIAL SUPPLIERS

The current industrial suppliers are listed in Table 2-5. GFT is the industry leader with more than 90% of the current market, primarily alcohol dehydration plants in Europe. However, this is a rapidly evolving technology and the industry structure may be very different in a few years time. The table only shows companies that have announced the development of pilot-scale or full industrial systems. The list is probably incomplete, because a number of major oil companies are believed to be evaluating pervaporation systems, particularly for organic-organic separations, although no announcements have appeared in the patent or technical literature. The current pervaporation market is probably less than \$8 million/year but is growing.

Figure 2-15. Schematic of a combined pervaporation-rectification process for the separation of a 50/50 azeotropic mixture.

MTR-038-GRP

Figure 2-16. Fraction of benzene or cyclohexane in product vs. feed mixture composition for pervaporation at reflux temperature of two binaries (benzene/cyclohexane and cyclohexene/cyclohexane). A 20- μ m, crosslinked alloy membrane was used.¹⁶

MTBE Reaction Chemistry

Pervaporation Process before Debutanizer

Pervaporation on Debutanizer Sidedraw

MTR-031-F

Figure 2-17. Methods of integrating pervaporation membranes in the recovery of methanol from the MTBE production process.^{7,8}

Table 2-5. Industrial Suppliers

Company	Application	Membranes/Modules	Comments
GFT	Solvent dehydration	Crosslinked PVA composite membranes. Plate-and-frame modules.	Founded by G.F. Tüsel, now a division of Ceraver. GFT the major pervaporation company. Concentrating on alcohol dehydration, they have over 100 plants installed. Mitsui is their Japanese distributor.
Lurgi	Solvent dehydration	GFT PVA membranes. Plate-and-frame modules.	Use GFT membranes, but their own plate-and-frame modules based on existing heat exchanger technology. Have installed a number of alcohol dehydration plants.
Membrane Technology & Research	Solvent recovery	Composite membranes. Spiral-wound modules.	Sells plants in the 5-10 thousand gallon/day range for water pollution control.
British Petroleum (Kalsep)	Solvent dehydration	Composite membranes based on ion-exchange polymers. Tubular and plate-and-frame modules.	Some small plants operating. Mostly water/isopropanol.
Air Products (Separex)	Organic-organic separation, methanol/MTBE	Cellulose acetate membranes. Spiral-wound modules.	Small pilot system operating at field site (2 gal/h) on an MTBE vent stream.
Texaco	Solvent dehydration especially ethylene glycol, isopropyl alcohol, organic/organic separation	Their own composite membranes in GFT plate-and-frame modules.	

2.4 SOURCES OF INNOVATION

Pervaporation is still one of the less developed areas of membrane technology and the number of research groups of any size is small. Table 2-6 lists the major institutions and key personnel, where known.

Table 2-6. Major Membrane Technology Institutions and Key Personnel

Company/Institution	Key Personnel
<u>Industrial Companies</u>	
Air Products and Chemicals, Allentown, Pennsylvania	M.S. Chen
British Petroleum, Cleveland, Ohio	J. Davis
Exxon, Baton Rouge, Louisiana	
GFT, Boonton, New Jersey	H.E.A. Brüscke, H.L. Fleming
Koninklijke/Shell Laboratory, Amsterdam, The Netherlands	
Lurgi GmbH, Frankfurt, West Germany	V. Sander
Membrane Technology & Research, Menlo Park, California	R.W. Baker, J.G. Wijmans
<u>Academic and Nonprofit Institutions</u>	
University of Twente, Enschede, The Netherlands	M.H.V. Mulder, C.A. Smolders
University of Maine, Orono, Maine	E. Thompson
University of Syracuse, Syracuse, New York	S.A. Stern
State University of New York, Syracuse, New York	I. Cabasso
University of Cincinnati, Cincinnati, Ohio	S-T. Hwang
GKSS, Geesthacht West Germany	K.W. Böddeker, K.-V. Peinemann
Fraunhofer IGB Stuttgart, West Germany	H. Strathmann
Ecole Nationale, Nancy, France	J. Neel
TNO, Zeist, The Netherlands	F.F. Vercanteren

2.5 FUTURE DIRECTIONS

2.5.1 Solvent Dehydration

Currently solvent dehydration is the major commercial application and research area of interest for pervaporation. For example, at the Third International Pervaporation Conference in Nancy, France, in 1988, more than two thirds of the papers presented dealt with solvent dehydration applications. Of these, more than half dealt with the dehydration of ethanol. Nonetheless, although of considerable current interest, this application is to a large extent a solved problem.

The current industry leader is GFT, who use a polyvinyl alcohol-based membrane. This membrane is extremely selective and future improvements in module selectivity are unlikely to change the overall dehydration process economics dramatically. However, a number of other membranes have been reported, particularly those based on ion-exchange polymers. Figure 2-18 shows a permeate composition vs. feed composition performance curve for one of these membranes.¹⁸

Comparison of this figure with data for the GFT polyvinyl alcohol membrane illustrated in Figure 2-6 shows that the membrane selectivities are comparable or a little less. With newer versions of the membranes, these results could probably be improved. The principal advantage these membranes may offer is higher fluxes, which could reduce process costs by reducing the amount of membrane area required and hence the module costs. However, current plate-and-frame modules already have heat and mass transfer problems, even at existing fluxes. It may be difficult to exploit new higher-flux membranes without making corresponding improvements in module design and performance.

Development of better modules is the principal area where an investment of research resources would lead to significant cost savings. Current commercial plate-and-frame modules are made from stainless steel. These modules are reliable, resistant to solvent attack and can withstand high pressure and temperature operations. However, they are extremely expensive, almost ten times the cost of spiral-wound modules, for example. Development of spiral-wound or hollow-fiber modules able to withstand the operating conditions encountered in solvent dehydration would lower costs significantly, allowing much wider use of the process.

MTR-042-GRP

Figure 2-18. Separation of ethanol-water feed solutions with Nafion® ion-exchange, hollow-fiber membranes with various counter-ions.¹⁸

2.5.2 Water Purification

Water purification by pervaporation has yet to be demonstrated on an industrial scale. Application and process development is, therefore, a high-priority research area. Major applications exist in pollution control, solvent recovery and waste reduction. Aroma and flavor recovery from wastewaters in the food and flavor and fragrance industries is another promising opportunity.

Current water-purification membranes are sufficiently permselective for hydrophobic solvents, but are inadequate for handling hydrophilic solvents such as ethanol, methanol, acetic acid and formic acid. These solvents, being freely water miscible, are found in many industrial process and waste streams. Many industrial water streams that would be candidates for pervaporation contain significant quantities of hydrophilic solvents. Development of more selective membranes for these solvents is urgently required. The inclusion of zeolites or other molecular sieving materials into polymer membranes, discussed in Section 2.2.2 may also be worth pursuing further.

2.5.3 Organic-Organic Separations

The separation of organic solvent mixtures represents by far the largest opportunity for major energy and cost savings. It is estimated that 40% of the total energy consumed by the chemical processing industry is used in distillation operations. Not only does distillation use large amounts of energy, but it is not an effective separation method in many cases. In particular, distillation is not well-suited to separating mixtures of components with similar boiling points or mixtures that form azeotropes. Currently, when standard distillation is unsuitable, extractive distillation, liquid/liquid separation or some other technique must be used. Azeotropic mixtures are an obvious target application for a pervaporation process. However, if suitable membranes and modules can be developed, more widespread applications to the entire chemical industry could be considered. It is unlikely that pervaporation would be used to perform complete separations; pervaporation systems are likely to find their best applications in hybrid processes where an optimized distillation/pervaporation operation is performed. The pervaporation units would perform a first, crude, low-cost separation, leaving the distillation columns to perform a polishing operation.

The lack of membranes and modules able to withstand aggressive solvent mixtures under the operating conditions of pervaporation is the key problem hindering the application of pervaporation to organic mixtures. Very little work on membranes able to separate organic mixtures has been reported in the literature. This is a good research opportunity. If membranes were available, they could probably be used with plate-and-frame modules, but these modules are so expensive they will only be used commercially in few, very favorable situations. Widespread application of organic-selective pervaporation membranes requires the development of solvent-resistant, hollow-fiber or spiral-wound modules.

In addition to module and membrane development, research must be performed on overall system design. Pervaporation units will be used in combination with other processes. Effective ways of integrating these processes are required. Heat integration is a particularly important and undeveloped area.

Support of research in the broad topic areas listed above is likely to produce an across-the-board improvement in organic-organic pervaporation systems. However, to encourage industrial acceptance of the process, focused research aimed at specific, particularly favorable applications of pervaporation should be encouraged. If pervaporation systems could be developed for one or two applications, even if they are small, niche applications, it would encourage further development of the process into broader, much more economically significant areas.

2.6 DOE RESEARCH OPPORTUNITIES

Based on the discussion above, a list of recommended research topics has been developed. The topics are listed in Table 2-7 and ranked by order of priority within application.

Table 2-7. Pervaporation Priority Research Topics

Research Topic	Prospect For Realization	Importance	Comments
Membranes for organic-organic separations	Very Good	10	If sufficiently selective membranes could be made, pervaporation could replace distillation in many separations
Better solvent-resistant modules	Excellent	10	Current modules cannot be used with organic solvents and are also very expensive
Better membranes for the removal of organic solvents from water	Very Good	7	More solvent-selective membranes are required, especially for hydrophilic solvents
Plant designs and studies	Good	7	Pervaporation will probably be used in hybrid systems for organic-organic separations. System design studies are needed to guide research
Dehydration membranes for acidic, basic, and concentrated aqueous solvent streams	Good	7	Would be of use in breaking many common aqueous-organic azeotropes

2.6.1 Priority Ranking

2.6.1.1 Solvent dehydration

Generally, this is a relatively developed area. Several companies are active and commercializing plants. Better membranes would help to reduce costs, but the principal problem is the high cost of plate-and-frame modules.

- Development of new module design would reduce costs.

2.6.1.2 Water purification

This process has been demonstrated at the pilot level, but not in the field.

- Current membranes are inadequate for ethanol, methanol, and other hydrophilic solvents. Several areas of current membrane research look promising. This could have a big impact in the fermentation industry.
- Current membranes are inadequate for high-boiling solvents, phenols, glycols, etc. Improved membranes are also required here.
- Results from demonstration plants are required to encourage industry acceptance.

2.6.1.3 Organic-organic separations

This area is now only being developed for niche applications. The big potential application is azeotropes and closely-boiling solvent mixtures.

- Current membranes are inadequate. Some research on improved membrane material is underway, but few materials have been formulated into high-performance membranes. The theory behind the materials selection process is weak.
- It is pointless to develop better materials and membranes unless they can be formulated into high-surface-area modules. Research is required here.
- Development of a few new niche opportunities would be useful to encourage the early acceptance of the program.
- System design and applications development of these membranes is also unexplored. Research is required here.

REFERENCES

1. R. DeVellis et al., U. S. Patent 4,846,977 (July, 1989).
2. West German Patent P 3610011.0 (1986).
3. R.C. Binning, R.J. Lee, J.F. Jennings and E.C. Martin, "Separation of Liquid Mixtures by Permeation," Ind. & Eng. Chem. **53**, 45 (1961).
4. A.H. Ballweg, H.E.A. Bruschke, W.H. Schneider and G.F. Tüsel, "Pervaporation Membranes," in Proceedings of the Fifth International Alcohol Fuels Symposium, Auckland, New Zealand, 13-18 May 1982, John McIndoe, Dunedin, New Zealand (1982).
5. H.E.A. Bruschke, "State of the Art of Pervaporation," in Proceedings of Third International Conference on Pervaporation in the Chemical Industry, Nancy, France, R. Bakish (Ed.) (1988).
6. I. Blume, J.G. Wijmans and R.W. Baker, "The Separation of Dissolved Organics from Water by Pervaporation," J. Memb. Sci., in press.
7. M.S.K. Chen, G.S. Markicwicz and K.G. Venugopal, "Development of Membrane Pervaporation Trim Process for Methanol Recovery from CH₃OH/MTBE/C₄ mixtures," AIChE Spring Meeting, Houston (1989).
8. M.S. Chen, R.M. Eng, J.L. Glazer and C.G. Wensley, "Pervaporation Processes for Separating Alcohols from Ethers," U.S. Patent 4,774,365 (September, 1988).
9. V.M. Shah, C.R. Bartels, M. Pasternak and J. Reale, "Opportunities for Membranes in the Production of Octane Improvers," paper presented at AIChE Spring National Meeting, Houston, TX, April 2-6 (1989).
10. H.L. Fleming, "Membrane Pervaporation Separation of Organic/Aqueous Mixtures," International Conference on Fuel Alcohols and Chemicals, Guadalajara, Mexico, (1989).
11. Y.M. Lee, D. Bourgeois and G.Belfort, "Selection of Polymer Materials for Pervaporation," in Proceedings of Second International Conference on Pervaporation, San Antonio, TX, R. Bakish (Ed.) (1987).
12. H.H. Nijhuis, M.H.V. Mulder and C.A. Smolders, "Selection of Elastomeric Membranes for the Removal of Volatile Organic Components from Water," in Proceedings of the Third International Conference on Pervaporation in the Chemical Industry, Nancy, France, R. Bakish (Ed.) (1988).
13. C.-M. Bell, F.-J. Gerner, and H. Strathmann, "Selection of Polymers for Pervaporation Membranes," J. Memb. Sci. **36**, 315 (1988).

14. G. Bengston and K.W. Böddeker, "Pervaporation of Low Volatiles from Water," in Proceedings of the Third International Conference on Pervaporation in the Chemical Industry, Nancy, France, R. Bakish (Ed.) (1988).
15. H.J.C. Hennepe, D. Bargemann, M.H.V. Mulder and C.A. Smolders, "Zeolite Filled Silicone Rubber Membranes, Part I", J. Memb. Sci. 35, 39 (1987).
16. T.W. Mix, J.S. Dweak, M.Weinberg and R.C. Armstrong, "Energy Conservation in Distillation," a report to the U.S. Department of Energy (DOE/CD/40259), (July, 1987).
17. P. Aptel, N. Challard, J. Cuny and J. Neel, "Application of the Pervaporation Process to Separate Azeotropic Mixtures," J. Memb. Sci. 4, 271 (1978).
18. I. Cabasso, Z.Z. Lin, "The permselectivity selectivity of ion-exchange membranes for non-electrolyte liquid mixtures," J. Memb. Sci. 24, 101 (1988).

CHAPTER THREE
GAS SEPARATION
TABLE OF CONTENTS

3.1	INTRODUCTION	3-1
3.2	FUNDAMENTALS	3-3
3.3	MEMBRANE SYSTEM PROPERTIES	3-5
3.4	MODULE AND SYSTEM DESIGN FEATURES.	3-7
3.5	HISTORICAL PERSPECTIVE	3-11
3.6	CURRENT TECHNICAL TRENDS IN THE GAS SEPARATION FIELD	3-12
3.6.1	Polymeric Membrane Materials	3-12
3.6.2	Plasticization Effects	3-15
3.6.3	Nonstandard Membrane Materials	3-17
3.6.4	Advanced Membrane Structures	3-17
3.6.5	Surface Treatment to Increase Selectivity.	3-17
3.6.6	System Design and Operating Trends	3-18
3.7	APPLICATIONS.	3-19
3.7.1	Hydrogen Separations	3-19
3.7.2	Oxygen-Nitrogen Separations	3-23
3.7.3	Acid Gas Separations	3-26
3.7.4	Vapor-Gas Separations	3-28
3.7.5	Nitrogen-Hydrocarbon Separations.	3-29
3.7.6	Helium Separations	3-30
3.8	ENERGY BASICS	3-30
3.9	ECONOMICS	3-35
3.10	SUPPLIERS	3-35
3.11	SOURCES OF INNOVATION	3-37
3.11.1	Research Centers and Groups	3-37
3.11.2	Support of Membrane-Based Gas Separation	3-40
3.11.2.1	United States	3-40
3.11.2.2	Foreign	3-40
3.12	FUTURE DIRECTIONS	3-40
3.12.1	Industrial Opportunities	3-40
3.12.2	Domestic Opportunities	3-41

3.13	RESEARCH OPPORTUNITIES	3-41
3.13.1	Ultrathin Defect-Free Membrane Formation Process	3-41
3.13.2	Highly Oxygen-Selective Materials	3-44
3.13.3	Polymers, Membranes and Modules for Demanding Service .	3-44
3.13.4	Improved Composite Membrane Formation Process	3-44
3.13.5	Reactive Surface Modifications	3-45
3.13.6	High-Temperature Resistant Membranes	3-45
3.13.7	Refinement of Guidelines and Analytical Methods for Material Selection	3-45
3.13.8	Extremely Highly Oxygen-Selective Membrane Materials . .	3-46
3.13.9	Physical Surface Modification by Antiplasticization	3-46
3.13.10	Concentration of Products from Dilute Streams	3-46
REFERENCES		3-47

CHAPTER THREE

GAS SEPARATION

by W. J. Koros, University of Texas, Austin, Texas

3.1 INTRODUCTION

The separations of oxygen and nitrogen from air, and hydrogen from carbon monoxide, methane or nitrogen, are large consumers of energy in the chemical processing industry. In general, purified gases are more valuable than arbitrary mixtures of two or more components, since pure components provide the option of formulating an optimum mixture for particular applications. Moreover, in some cases, such as the inert blanketing of chemically sensitive products, a pure gas stream is desired.

Energy-intensive compression of feed streams is often needed to provide the driving force for permeation in membrane-based separations. In their simplest ideal forms, represented schematically in Figure 3-1, membranes appear to act as molecular-scale filters that take a mixture of two gases, A and B, into the feed port of the module and produce a pure permeate containing pure A and a nonpermeate containing pure B. Real membranes can approach the simplicity and separation efficiency of such idealized devices, but, more usually, complex recycling of some of the permeate or nonpermeate stream may be needed because perfect selection of all of the A and B molecules cannot be achieved in a single pass. Optimization of the properties of the membrane to achieve the most efficient separation is important to avoid expensive and cumbersome systems that fail to achieve the attractive simplicity of ideal membranes.¹

In principle, as shown in Figure 3-2, three basic types of membranes can be used for gas separations. The third type, solution-diffusion membranes (Figure 3-2d), is dominant in current devices. In these membranes, the gas dissolves in the membrane material and diffuses through the membrane down a gradient of concentration. Ultramicroporous (pores $<7\text{\AA}$ in diameter) molecular-sieve membranes (Figure 3-2c) have received increasing attention recently because of claims that they may offer higher productivities and selectivities than solution-diffusion membranes.² Many questions remain to be answered concerning the durability, freedom from fouling and ease of large-scale manufacture of ultramicroporous membranes, and further investigation does appear to be justified.

So-called "Knudsen" diffusion membranes (Figure 3-2b) cannot compete commercially with the two preceding types due to their low selectivity between molecules. Pores exist in the barrier layer of these membranes, but the pores are smaller in diameter than the distance a molecule would travel in the gas phase between collisions, on the order of 50 to 100 $\text{\AA}$ in diameter or more. The relative rates of flow across the membrane for an equimolar feed for typical gases are given by the inverse square root ratio of the molecular weights of the gases. For a 50/50 mixture of nitrogen and hydrogen, this would mean that for every 3.7 molecules of hydrogen that permeated, 1 molecule of nitrogen would permeate. This separation factor is too low to be commercially attractive. As indicated in Figure 3-2a, if pores are even larger than those that permit Knudsen separation, nonselective permeation by viscous flow occurs, and this is obviously of no use in separation processes.

Figure 3-1. Generalized representations of an ideal membrane separation process.

Figure 3-2. Membrane-based gas transport and separation mechanisms.

3.2 FUNDAMENTALS

High-performance nonporous polymeric and ultramicroporous carbon membranes can achieve relative passage rates favoring hydrogen over nitrogen exceeding 100, and they form the basis for simple, convenient processes to separate a wide spectrum of gas pairs. The ultramicroporous membranes (Figure 3-2c) are believed to have a tortuous, but continuous network of passages connecting the upstream and the downstream face of the membrane.³ Solution-diffusion membranes have no continuous passages, but rely on the thermally agitated motion of chain segments comprising the polymer matrix to generate transient penetrant-scale gaps that allow diffusion from the upstream to the downstream face of the membrane.³ The penetrants undergo random jumps, but because there is a higher concentration of them at the upstream face than the downstream face, a diffusive flow occurs toward the downstream face.

By varying the chemical nature of the polymer, one can change the size distribution of the randomly occurring gaps to retard the movement of one species, while allowing the movement of the other. This is said to be a "mobility selectivity" mechanism. A similar mobility control can be exercised in ultramicroporous materials by controlling the size distribution in the network of available passages to favor one of the components relative to the other. If one could perfectly control this distribution, a true molecular-sieving process would occur and infinite selectivity would be achieved. The essential impossibility of such a situation is suggested by the data in Table 3-1, which shows the effective sieving dimensions of various important penetrants as measured by exclusion from crystalline cages in zeolites.⁴ It is amazing that, for both ultramicroporous and solution-diffusion membranes, mobility selectivities of 2,000 have been reported for helium over methane which differ by only 1.2Å in minimum dimension.⁵ The ability to regulate the distribution of transient-gap sizes in solution-diffusion membranes is achieved by the use of molecules with highly hindered segmental motions and packing. Typically, these materials are noncrystalline and are referred to as glassy polymers.⁶ Indeed, they are organic analogs to ordinary inorganic glass. The rates of diffusion through glassy polymers are sufficiently high to allow their use as membrane materials, because the segmental motions are more pronounced than in the inorganic materials. If one heats a glassy polymer to a sufficiently high temperature, it eventually begins to behave as a rubbery material and loses its mobility selectivity.

The mobility selectivity mechanism is not the only factor determining membrane operation. Selectivity is determined, not only by the relative jumping frequency of molecules A and B, but also by the relative concentrations available for jumping. These concentrations are determined by the relative sorptivity of gases A and B in the nonporous polymer or in the ultramicroporous network. One can speak of a "solubility selectivity" analogous to the mobility selectivity mentioned above,⁷ and the product of the solubility and mobility selectivities determines the overall selectivity of the membrane. A good measure of the relative solubilities of two gases is given by their respective boiling point.⁵ For instance, helium and nitrogen have normal boiling points of 4°K and 112°K, respectively, indicating that helium is less condensable and will tend to have a much lower sorption level in polymers and ultramicroporous media compared to nitrogen. Subtle effects due to interactions between the membrane material and gases are also seen sometimes, but they tend to be small and can be ignored in most cases.

Table 3-1. Minimum kinetic (sieving) diameters of various penetrants taken from the zeolite literature.⁴

Penetrant	He	H ₂	NO	CO ₂	Ar	O ₂	N ₂	CO	CH ₄	C ₂ H ₄	Xe	C ₃ H ₈	n-C ₄	CF ₂ Cl ₂	C ₃ H ₆	CF ₄	i-C ₄
Kinetic Diameter (Å)	2.6	2.89	3.17	3.3	3.4	3.46	3.64	3.76	3.8	3.9	3.96	4.3	4.3	4.4	4.5	4.7	5.0

It is possible for the mobility selectivity and the solubility selectivity to complement each other or to oppose each other. For the polymer materials cited above that have a mobility selectivity of over 2,000 for helium from methane, the solubility selectivity for helium relative to methane is 1/16, so the product of these two gives an overall selectivity well above 100 for helium relative to methane.⁵ For other gas pairs, such as carbon dioxide and methane, the two factors both favor carbon dioxide over methane since carbon dioxide is smaller and also more condensable. Typically, rubbery and glassy materials with similar chemical natures (i.e., similar percentages of polar vs. nonpolar moieties in the chain) have similar sorption properties for gases. In fact, glassy materials often have higher sorption capacities than their flexible rubbery analogs, because of the presence of unrelaxed packing defects present in the glassy polymers that are not present in the rubbery state.^{7,8}

The relative rates of permeation of two components in an actual gas mixture are usually within 10 to 15% of the rates measured with pure gases, so long as equivalent pressure differences of the two components exist between the upstream and downstream faces of the membrane.⁹ This approximation breaks down at the point of "transport plasticization", where the presence of a penetrant affects the local rate of diffusion of another nearby penetrant by altering polymer segmental motions. As the sorbed penetrants increase the ease of segmental motions, the size range of the transient gaps tends to be less sharply controlled, and the mobility selectivity begins to fall. In a loose fashion, one can say that the previously glassy material starts to behave in a more "rubberlike" fashion; however, it is really still a glassy material in most cases. In operating a membrane, one must be on the lookout for such selectivity losses compared to the pure component case, since they signal the onset of problem conditions for that membrane material.

Another factor that affects the selectivity significantly is the operating temperature of the membrane. Increasing the operating temperature gives rise to a strong increase in polymer segmental motions, causing exponential increases in molecular diffusion rates. However, higher temperatures tend to generate larger, less size-discriminating gaps in the polymer matrix. Penetrants also become less condensable as the temperature rises. The net results of these changes are generally lower selectivities, but higher permeabilities. Permeability is the product of the diffusivity and solubility parameters, and characterizes a penetrant's ability to move across a membrane of given thickness under a given differential pressure drive force. Permeability is a fundamental property of the

membrane material and permeant.¹⁰ In a practical membrane separation process, one is generally forced to accept lower selectivities if higher productivities are achieved by increasing the temperature of operation.

3.3 MEMBRANE SYSTEM PROPERTIES

It is convenient to divide the discussion of important properties for gas separation membranes into technical and practical categories. Technical requirements refer to those characteristics that must be present for the system to even be considered for use in gas separation applications. Practical requirements, on the other hand, relate to the characteristics that are important in making a technically acceptable system competitive with alternative technologies, such as cryogenic distillation or pressure-swing adsorption.

Because the solution-diffusion permeation process is slow relative to Knudsen and nonselective viscous-flow transport mechanisms, an area fraction containing nonselective pores even as small as 10^{-5} in the membrane surface is sufficient to render a membrane effectively useless. The most critically important technical requirement for solution-diffusion membranes, therefore, is to attain a perfect pore-free selective layer. The selective layer must, of course, also be able to maintain its defect-free character over the entire working life of the membrane in the presence of system upsets and long-term pressurization.

For molecular-sieve membranes, a similar standard of perfection must be met to ensure that essentially no continuous pores with sizes greater than a certain critical size exist between the upstream and downstream membrane faces. The exact size limit is not clear at present, since it may be that the effective constriction sizes responsible for the molecular-sieving mechanism may be influenced by the species that are, themselves, permeating. Adsorption on the walls of the passageways may reduce the effective openings well below that of the "dry" substrate. Unsubstantiated claims suggest that pore sizes as large as $10\text{\AA}$ in the dry substrate may be closed down to the $3\text{-}4\text{\AA}$ level likely to be needed for molecular sieving of materials like carbon dioxide and methane. Ultramicroporous membranes, like nonporous membranes, must adhere to rigorous standards, because the pores must remain sufficiently clear of condensable molecules or contaminants that would tend to inhibit the rapid passage of desired product to the downstream side.

Because industrially important gas streams contain condensable and aggressively sorptive or even reactive components, it is often desirable to pretreat the gas to remove such components prior to feeding the gases to the module. Pretreatment is not a major problem and competitive separation processes such as pressure swing adsorption (PSA) also use feed pretreatments. However, the more robust the membrane system is in its ability to accept unconditioned feeds, the more attractive it is in terms of flexibility and ease of operation.

Besides the above technical requirements, practical requirements demand that a membrane should offer commercially attractive fluxes. Even for materials with relatively high intrinsic permeabilities, commercially attractive fluxes require that the effective thickness of the membrane be made as small as possible without introducing defects that destroy the intrinsic selectivity of the material. For

practical purposes, therefore, even high productivity polymers are generally not used in a dense film form because of the enormous membrane areas that would be required to treat commercial-size gas streams.

To achieve sufficiently thin selective layers ($<2,000\text{\AA}$) and yet maintain mechanical integrity, "asymmetric" membrane structures with complex morphologies, such as those shown in Figure 3-3b-d, are favored over the simple dense film shown in Figure 3-3a. Membranes comprised of cellulose acetate or aromatic polyamides typify the "integrally skinned" membranes shown in Figure 3-3b. Cellulose acetate and the aromatic polyamides can be formed with nonporous skins using a process based on the original Loeb-Sourirajan techniques sometimes called wet phase inversion.^{11,12} Recently, a wide spectrum of other materials have also been shown to be formable in this manner.¹³

Figure 3-3. Membrane types useful for solution-diffusion separations of gas mixtures.

Polysulfone and many other attractive polymers can easily be made into almost thin skin structures, but until recently it has been difficult to prepare a truly perfect defect-free skin. To permit the use of such materials, therefore, the "caulked" composite membrane structure shown in Figure 3-3c was introduced.¹⁴ The caulking procedure is useful, because it allows rapid production rates of the basic membrane without extreme attention to the elimination of defects. Defects are patched in a later processing step by coating the membrane with a dilute solution of silicone rubber. Because the silicone rubber layer is relatively thin and has a high permeability, it seals defects in the base membrane without affecting the intrinsic permeability properties of the membrane.

The membrane sealing approach described above derives from an earlier type of membrane in which a porous nonselective support is coated with a second material with desirable solution-diffusion separation properties.¹⁵ The support is produced by wet phase inversion (Loeb-Sourirajan process), and the ultrathin, selective skin can be produced by a variety of techniques, of which dip coating, doctor-knife application or plasma polymerization are the most common. This technique permits one to decouple the support function of the membrane from the basic separation function of the skin.

In addition to flux, a practical membrane system must achieve certain upstream or downstream product stream compositions. The ideal membrane separation factor, that is the ratio of the intrinsic permeabilities of the two penetrants, should be as high as possible to allow flexibility in setting transmembrane pressure differences, while still meeting product-purity requirements. The ideal separation factor also affects the energy used in compressing the feed gas. Membrane selectivity also determines if multistage system designs are needed to meet the required product compositions. Unfortunately, high ideal membrane permselectivities often correlate with low intrinsic membrane permeabilities, and this forces a compromise between productivity and selectivity of the membrane material used. The trade-off between intrinsic membrane permeability and selectivity is the major issue concerning scientists searching for new polymers from which to make the separating layers of gas-separation membranes. This important issue will be summarized in a later section.

3.4 MODULE AND SYSTEM DESIGN FEATURES

The total gas flow from the upstream to the downstream side in a membrane module (Figure 3-1) is determined by the integrated product of the flux and the membrane area in the module. In principle, one can achieve satisfactory production rates by simply increasing the area density (membrane area per unit volume) in the module. Means of packaging gas-separation membranes, illustrated in Figure 3-4, include plate-and-frame, spiral-wound and hollow-fiber modules. The origins and attributes of the various module designs are discussed fully in Chapter One.

(a) Plate and frame module of GKSS.

(b) Spiral wound module of Separex® Air Products.

(c) Monsanto's Prism® separator for H_2 separation, typical of shell side gas fed hollow fiber modules.

Figure 3-4. Gas separation module types.

The plate-and-frame approach gives the lowest surface area/unit-volume ratio. GKSS, of West Germany, has developed this technology for almost fifteen years, and as much as 200 ft² of membranes per ft³ of module can be achieved with their efficient arrangement of the central collection tube, support frames and permeate channels. This is roughly twice the area density available in early plate-and-frame systems.

The hollow-fiber and spiral-wound module configurations, shown in Figures 3-4b and 3-4c, achieve substantially higher area densities. For example, a 15-fold increase in permeation area per unit volume (to 3,000 ft² of membrane per ft³) can be achieved by replacing even the advanced GKSS plate-and-frame module with 200- μ m outside diameter fibers packed at a 50% void factor in a 10-inch-diameter shell. Even higher area densities can be achieved by using smaller diameter fibers and higher packing densities, the limiting factor being pressure drop in the fibers and shell.

The spiral-wound configuration provides area densities intermediate between the plate-and-frame and typical hollow-fiber modules, with 1,000 ft² of membrane per ft³ of module being typical. As in the plate-and-frame case, this number might be increased somewhat by optimization, but it will not approach the roughly 3,000 ft² of membrane per ft³ of module in the 200- μ m hollow-fiber example cited above.

Based on the need to maximize production rates, it appears that hollow-fiber modules will eventually dominate the gas separation field. However, other factors are also important. Until recently, it was possible to form the permselective skins on flat membranes two to three times thinner than the skins on asymmetric hollow-fibers. This meant the overall productivities of spiral-wound and hollow-fiber membrane modules were similar. Recently, however, hollow fibers of roughly 400- μ m outside diameter were introduced by the Monsanto in their Prism[®] Alpha module that had a caulked thin-skin of 500Å thick. A 500Å skin corresponds roughly to that achievable in spiral-wound systems. If other, more advanced, membrane materials can be produced in equally thin selective layers in hollow-fiber form, this module configuration will likely dominate the field. In the absence of such capability, the spiral-wound and hollow-fiber modules will both remain popular.

In high-pressure gas-separation applications such as hydrogen and carbon dioxide separations, the pressurized feed gas is usually introduced on the shell side of the hollow fiber. Fibers are much stronger under compression than expansion and if individual fibers fail, they do so by being crushed closed. This means they no longer contribute to the total membrane area, but they do not serve as bypasses to contaminate the permeate with feed gas. The flows in such modules have aspects of both countercurrent and crossflow patterns.¹

For low-pressure applications where fiber failures are less likely, for example the production of nitrogen from air, bore-side feed is common, even if the skin layer is on the outer fiber surface. An advantage of this configuration is that channeling and other flow distribution problems are eliminated. Approximate crossflow or countercurrent flow patterns can be achieved with bore feed by using a central collection tube (cross flow) or by removing product from the shell at the same end as the feed entered (countercurrent).

Detailed proprietary computer models are used by suppliers to simulate the behavior of their particular system under conditions of varying composition, pressure, upstream to downstream pressure ratio and stage-cut. The stage-cut is the fraction of the incoming feed stream that passes through the membrane as permeate. Higher membrane selectivities minimize the stage-cut by limiting the amount of the undesired component that passes through the membrane. For nitrogen enrichment of air, where the residue is the desired stream, this means lower compression costs are incurred to produce a given quantity of product gas at the required purity. For hydrogen separation, where the permeate is the most valuable stream, higher selectivities allow higher fractional recoveries of valuable product, without falling below the product purity specification.

Gas separation membrane processes, in common with all rate-determined unit operations, suffer depletion of the driving force, in this case, the partial pressure difference along the unit. Except with an extraordinarily permselective membrane, high-purity permeate cannot be produced unless the partial pressure of the faster permeating gas in the feed stream is maintained at a relatively high level. For cases such as helium recovery from natural gas, where the initial concentration of helium is <1%, a single-stage unit will not produce high-purity helium with current membranes. Moreover, in many cases, production of a high-purity permeate and high-purity residue is required simultaneously. In these cases, more than one module stage is required.

Systems requiring multiple compression operations are unattractive because of high capital and operating costs, so most system designs are limited to two or three module stages.¹⁶ Nevertheless, to complete an adequate engineering and economic analysis of even two or three stage systems is a complex problem. Spillman notes that due to their novelty, early publications concerning the use of membranes often ignored the importance of optimization of the system design.¹⁷ A more mature consideration of recycle and other optimization options can make membranes the clearly favored choice for a particular separation, even though a membrane process may have appeared marginally viable previously.

Spillman further notes that working with membrane design requires an objective consideration of economically acceptable recovery rates. The value of lost product should be considered an operating cost, similar to other expenses. In some cases, membranes do not neatly replace existing separation processes and a rethinking of the process logic may be beneficial. The nature of the separation is different than, say, for PSA, so process changes are sometimes necessary, and the specific impact of these process changes must be considered.

A typical situation is illustrated by the separation of hydrogen in refinery streams. In a membrane process the purified hydrogen is produced at low pressure. PSA, on the other hand, delivers the hydrogen at close to the feed pressure. Which process is selected will depend on the pressure at which the product hydrogen is to be used. Increased familiarity of plant designers with membranes, coupled with increasingly sophisticated computer software, should promote the use of membranes while avoiding inappropriate applications.

3.5 HISTORICAL PERSPECTIVE

Gas separation using polymeric membranes was first reported over 150 years ago by Mitchell in a study with hydrogen and carbon dioxide mixtures.¹⁸ In 1866, Graham made the next important step in understanding the permeation process.¹⁹ He postulated that permeation involves a solution-diffusion mechanism by which penetrants first dissolved in the upstream face of the membrane were then transported through it by the same process as that occurring in the diffusion of liquids. Graham demonstrated that atmospheric air could be enriched from 21% to 41% oxygen using a natural rubber membrane, and that increasing the thickness of a pinhole-free membrane reduces the permeation rate, but does not affect the selectivity.

The above advances were not matched by a practical means of applying the permeation process to large-scale separation of gas streams. Early attempts by Union Carbide to apply plate-and-frame technology for helium separation were not successful, because the fluxes were too low to be of commercial interest.²⁰ The discoveries of Loeb and Sourirajan in developing integrally-skinned asymmetric membranes (Figure 3-3b) were not applied immediately to gases, because the porous substructure collapsed upon drying and multiple defects were introduced in the selecting skin.²¹

In the 1970s, discovery of the extraordinarily high permeability of silicone rubber encouraged a group at General Electric (GE) to develop a novel process for ultrathin membranes based on silicone rubber or silicone rubber/polycarbonate copolymers.^{22,23} Pinholes were eliminated by laminating multiple layers to yield separating layers of 1,000Å supported on a microporous substrate. The membranes were housed in plate-and-frame forms to yield modules with orders of magnitude higher productivity than found in the original work by Union Carbide. This research at GE laid the groundwork for later developments in composite membranes discussed earlier (Figure 3-3d). The Oxygen Enrichment Company was started as a result of the work at GE to produce oxygen-enriched air systems for home medical use. This company continues to supply products based on this technology. The technology did not develop to the industrial production of oxygen-enriched air because the membrane fabrication process and system performance were not adequate for large-scale, less-costly applications.

In 1970, a process that allowed asymmetric cellulose acetate membranes to be dried and used in gas separation applications was developed, but not pursued.²⁴ The field was dormant until 1977, when a group at Du Pont applied melt-spinning technology to produce polyester hollow-fine-fibers with inside diameters of 36 μm for high-pressure hydrogen applications.²⁵ Instead of seeking to increase flux by minimizing membrane thickness, Du Pont accommodated the low flux using incredible area densities, approaching 10,000 ft^2 of membrane/ ft^3 . Because of their robust, dense walls, the fibers were fed on the bore side without danger of fiber failure.

A patent by Du Pont in the 1970s²⁶ also identified many glassy polymer materials with unusually high intrinsic permeabilities. These materials had much better potential than the low productivity polyester for gas separation in hollow-fine-fiber melt-spun form. In asymmetric membrane forms, these are attractive even today. The technology was mothballed in 1979, as Du Pont focused on reverse osmosis.

Coincident with Du Pont's withdrawal from the gas separation field, Monsanto announced the revolutionary concept of the "resistance composite", or "caulked membrane" (Figure 3-3c).^{14,27} The clever approach involved applying a thin coating over, or applying a vacuum to suck silicone rubber into, surface defects present in asymmetric hollow fibers. The coating eliminates Knudsen and viscous flow that undermined the intrinsic solution-diffusion selectivity of the skin. Although used commercially only for the polysulfone material, it was clear that the approach and patent coverage was general and would also have been applicable to materials such as those described in the Du Pont patent. Monsanto chose to work with standard polysulfone because of its ready availability, adequate properties and easy processability. Timing was excellent, because of the "energy crisis", and Monsanto moved strongly into the hydrogen separation field. Initial applications were hydrogen recovery from ammonia purge streams, refinery and petrochemical off-gases.

Most gas-separation work to date has been performed with polymeric membranes. However, membranes made from palladium-silver alloys have been the subject of substantial research and limited commercial development.²⁸ These membranes have extremely high hydrogen/methane selectivities, and can be operated at elevated pressures and temperatures above 400°C. These systems are still available today, but have not been a large scale commercial success.

3.6 CURRENT TECHNICAL TRENDS IN THE GAS SEPARATION FIELD

3.6.1 Polymeric Membrane Materials

Identification of advanced materials has been an important driving force propelling gas separation membrane technology in recent years. An indication of the advances in performance that may be possible with new membrane materials is given in Figure 3-5. The figure shows "best-case" permeability/selectivity curves attainable with present commercial polymers. In fact, most individual commercial materials fall below the lines, either in permeability, selectivity or both. For example, commercially available polyvinyl fluoride has a selectivity of 170 for helium/methane but a helium permeability of 1 Barrer. On the other hand, silicone rubber and polyphenylene oxide have helium permeabilities of 300 and 105 Barrers, respectively, but helium/methane selectivities of 0.4 and 24. Similar situations apply for the other two gas pairs in Figure 3-5.

Several studies have reported materials that deviate favorably from the standard correlation line defined by the properties of commercially available materials, although generalized correlations of polymer properties and separation are not yet possible.^{5,29,30} Within a given family of polymers, however, rules can be identified to guide the optimization process. Figure 3-5 shows data points for two classes of materials, the polycarbonates and polyimides, to which such optimization procedures have been applied. The polymers and their structures are identified in Table 3-2. The results in this figure are typical of the new-generation polymers, which offer higher permeability at equivalent selectivity, or higher selectivity and higher permeability, than the points on the present "best-case" lines. The field of membrane material selection is complex. The most important points can be distilled into two rules of thumb, summarized below and discussed in more detail in recent publications.³¹

Figure 3-5. Typical trade-off between selectivity and permeability for gas separation systems. The solid lines represent best case expectations based on commercial materials. The numbers and letters refer to material in Table 3-2.

1. Structural modifications that simultaneously inhibit chain packing and the torsional mobility around flexible linkages in the polymer backbone tend to cause either: a) simultaneous increases in both the permeability and selectivity, or b) a significant increase in permeability with negligible loss in selectivity.
2. Modifications that reduce the concentration of the most mobile linkages in a polymer backbone tend to increase selectivity without undesirable reductions in permeability so long as the modification does not significantly reduce intersegmental d-spacings.

Table 3-2. Systematically varied polyimides and polycarbonates illustrating the value of structure-property optimization for improving the trade-off between selectivity and permeability.

Polyimides		Polycarbonates	
PMDA-ODA (1)		Standard bisphenol-A Polycarbonate (a) PC
PMDA-MDA (2)		Hexafluorinated bisphenol-A Polycarbonate (b) HFPC
PMDA-IPDA (3)		Tetramethyl bisphenol-A Polycarbonate (c) TMPC
PMDA-DAF (4)		Hexafluorinated Tetramethyl bisphenol-A Polycarbonate (d) HFTMPC
6FDA-ODA (5)
6FDA-MDA (6)
6FDA-IPDA (7)
6FDA-DAF (8)

The application of membranes at high temperatures in aggressive chemical environments may require the use of structures with intractable skins comprised of exotic polymers. This area is likely to be of increasing interest as experience is gained in module formation for such demanding applications. If an organic membrane existed now with the ability to sustain extended operation above 200°C, the potting and other components in the module would need to be upgraded for this service, and virtually no research seems to be underway in this regard. The polyimides and aramides are probably the best materials studied to date for potential high-temperature applications. Data for permeation of carbon dioxide and nitrogen as a function of temperature indicate a much lower temperature dependence of permeation for rigid polyimides, as compared to most commercial glassy materials.²² This indicates that rigid materials like the polyimides are less affected by increases in temperature than the standard glassy polymers with lower glass transition temperatures. The ability to maintain glassy-state separation properties at elevated temperatures may find application in membrane-reactor hybrid processes.³³

3.6.2 Plasticization Effects

As previously discussed, plasticization of the membrane polymer by a sorbed permeant can affect the permeability and selectivity properties significantly. An illustration of apparent plasticization behavior is shown in Figure 3-6. The permeability of carbon dioxide in silicone rubber and various substituted polycarbonates is seen to vary considerably with upstream pressure. In each case, downstream pressure was maintained at less than 10 mm Hg.³¹

For standard unconditioned polycarbonate, the upturn point in permeability is not reached until roughly 600 psia carbon dioxide pressure. For hexafluorinated tetramethyl bisphenol-A polycarbonate, HFTMPC, the point is reached at only about 250 psia, due to the much higher solubility in this "open", packing-inhibited material. In terms of permissible carbon dioxide partial pressure prior to the onset of plasticization, tetramethyl bisphenol-A polycarbonate, TMPC, and HFTMPC may be less attractive than standard polycarbonate, because of their high sorption coefficient caused by larger d-spacing. These data suggest that useful operating ranges for different polymer materials will vary considerably. Further research is needed to better understand these preliminary observations.

Figure 3-6. Carbon dioxide permeability at 35°C for silicone rubber and the polycarbonate polymers in Table 3-2 as a function of upstream CO₂ pressure.

PC: Standard bisphenol-A polycarbonate
 HFPC: Hexafluorinated bisphenol-A polycarbonate
 TMPC: Tetramethyl bisphenol-A polycarbonate
 HFTMPC: Hexafluorinated tetramethyl bisphenol-A polycarbonate

3.6.3 Nonstandard Membrane Materials

Carbon, molecular-sieve membranes formed by pyrolysis of unspecified polymer precursors are being developed by Rotem, the commercial arm of the Israeli nuclear research center in conjunction with the Swedish Gas Company, Aga.^{2,34} Helium fluxes through the membranes of 200×10^{-6} cm³(STP)/cm²·s·cmHg and hydrogen/methane selectivities above 1,000, based on pure gases, have been reported.² The materials, however, have not been tested thoroughly in mixed gas streams. Due to their ultramicroporous structure, they are likely to have serious problems with "plugging" by condensable agents such as water. It may be possible to eliminate adsorption problems by operating at high temperatures, without the need for major feed pretreatment. This area appears to have considerable potential, if the inherently fragile nature of the membranes can be dealt with.

In principle, ceramic and glass membrane materials offer similar properties, although the minimum pore sizes attainable are currently around 25Å for ceramics and 10Å for glass. These dimensions are 2-6 times larger than the minimum dimensions of the various molecules that are of interest in gas separation. As noted earlier, molecular adsorption onto pore walls may reduce the effective pore size in some cases. Moreover, at low temperatures, the possibility of additional transport modes, such as surface diffusion of condensable agents, playing a part in the separation process may make ceramic or glass membranes viable. Systematic, fundamental studies are needed to assess the true potential of the approach.

3.6.4 Advanced Membrane Structures

Integrally-skinned asymmetric membranes, made by the Loeb-Sourirajan process, are commonly used in commercial membrane gas separation. Although the Loeb and Sourirajan approach has successfully been applied to defect-free cellulosic-based asymmetric membranes, it has been found difficult to prepare thin-skinned defect-free membranes from other polymers. The "caulking" process used by Monsanto in the original Prism®, and later Prism® Alpha, products with standard polysulfone provides a solution to this problem, but patent coverage precludes its generalized use by other companies in the field.²⁷

The preparation of ultrathin, flat-sheet asymmetric gas-separation membranes has recently been reported for polyethersulfone and polyetherimide by GKSS.³⁵ The membranes showed some skin-layer defects that had to be post-treated, but the Monsanto patent was avoided using a different post-treatment procedure.¹³ An approach that eliminates the need for post-treatment, yet produces an ultrathin, defect-free skin on flat-sheet membranes, has recently been reported.³⁶ For optimum value, new skin-formation processes should be applicable to both hollow-fiber and flat-sheet membranes. Work in this area is likely to be an important activity in the future.

3.6.5 Surface Treatment to Increase Selectivity

Two types of surface treatment have been considered: (i) reactive and (ii) physical (antiplasticization). Techniques in the reactive category include fluorination, silylation and photochemical crosslinking.³⁷⁻³⁸ Fluorination of polytrimethyl-silylpropyne (PTMSP) has been studied at Air Products. Recent data

from Air Products suggest that fluorinated PTMSP exhibits stable properties under exposure to organic materials such as vacuum pump oil, a result that conflicts with earlier studies.³⁹ However, there are reports that a lower-flux, but perhaps more reliable polymethylpentene material is the basis for a fluorinated membrane that will be introduced in the near future. Presumably, the fluorination will produce increases in selectivity as in the case of the PTMSP.

Photochemical crosslinking of labile benzophenone groups has been described by Du Pont for polyimides based on benzophenone dianhydride.³⁶ This approach produced large increases in the selectivity of a dense film, with small reductions in apparent permeability. As in the case of fluorination, however, the reduction in the permeability of the outer skin was probably very high. If the entire thin skin of an asymmetric membrane were treated by either a fluorination or photochemical process, very significant reductions in flux might be expected as compared to the unmodified material. The key to producing useful materials seems to be to use an intrinsically high-flux material to form a thin-skinned ($\approx 1,000\text{\AA}$) asymmetric membrane from that material and then to reactively surface treat the skin layer. If fully developed, this technique could result in membranes in which attractive productivities are maintained, along with significantly improved selectivities.

The incorporation of physically bound components into polysulfone has been reported to increase selectivity by an antiplasticization phenomenon.^{40,41} The effect is believed to result from the inhibition of chain motions by the antiplasticizers. It is not desirable to load the entire membrane with antiplasticizers, because loss of mechanical properties occurs. Even if extremely nonvolatile components are used as the antiplasticizing agents, calculations suggest that the small skin volume and the extremely high passage rates of permeating gases through the skins will effectively remove the antiplasticizing agents in a relatively short period of time ($<3\text{-}6$ months), so this approach appears much less attractive than the reactive ones noted above.

3.6.6 System Design and Operating Trends

Little activity appears to be under way with regard to the design and operation of modules. A notable exception to this is a patent by A/G Technology relating to the use of a bore-side feed for hollow-fiber modules.⁴² Both bore-side and tube-side feeds have been used since the beginning of hollow-fiber membrane technology. Indeed, the first Du Pont hollow-fiber module for hydrogen separation was based on tube-side feed. The current Du Pont, Monsanto, UOP and Dow modules for hydrogen separation are all believed to use tube-side feed.

For low-pressure applications such as nitrogen enrichment, where fiber failures are unlikely, bore-side feed is common. The details of internal flow paths are proprietary. Designs that give behavior from countercurrent to crossflow and mixtures of the two are believed to exist. Differences in product takeoff and feed introduction points also result in a range of possible configurations.

More significant differences exist in the internal and external design details for gas separation membrane units than are found in reverse osmosis units, for example. The standardization that came about in reverse osmosis technology as a result of the information exchange provided by the Office of Saline Water Research program is absent from the gas separation scene; instead each company has taken its own divergent path. As the technology matures some measure of standardization may emerge due in part to competition for the replacement module market.

Module and system design for gas separation applications are a complex issue. System designs require consideration of numerous possible scenarios including single-stage, multistage, recycle and so on. The design is typically done by the supplier, using a proprietary computer program to optimize the system configuration and minimize the cost based on known or required selectivity and productivity parameters. This trend promotes user dependence upon the supplier for innovation. For some applications, for example, production of nitrogen from air for blanketing or inerting, this situation may be perfectly satisfactory. On the other hand, in petrochemical and refinery hydrogen applications, the user may view the membrane system as one of many integral and interacting unit operations in a plant. Sophisticated system-design programs, able to consider multiple case studies, are likely to be developed by the user, without concern for the details of module internals. Using module performance information from suppliers, such programs allow independent consideration of different vendor suggestions as well as user proposed flowsheet options. In this respect, users may well become an important source of innovation.

3.7 APPLICATIONS

Table 3-3 summarizes currently commercial and precommercial applications of membrane-based gas separations. The key features of the various separation types are discussed below.

3.7.1 Hydrogen Separations

The first membrane-based, gas-separation systems were used for hydrogen separation, from ammonia purge gas streams, and to adjust the hydrogen/carbon monoxide ratio in synthesis gas.

Table 3-3. Current and Developing Applications of Membrane-Based Separations

Gas Components: Application	Comments & Key Technical Problems
H_2/N_2 : Ammonia Purge Gas H_2/CH_4 : Refinery H_2 recovery H_2/CO : Synthesis gas ratio adjustment	Successful.... condensibles (H_2O or NH_3) must be removed Successful, but condensible hydrocarbons undesirable or fatal Successful, but condensible methanol must be removed
O_2/N_2 : N_2 enriched inerting medium Home medical oxygen enrichment O_2 enriched burner gas Highly- O_2 (>90%) enriched gas	Practical for 95%... marginal for 98%+ , next generation membranes (higher selectivity) will improve position vs PSA Technology exists, no serious problems but small market Higher temperature burner designs needed.... new generation of membranes possibly adequate productivity- α for economics Selectivity of polymeric membranes much too low ... $\alpha = 60$ needed
Acid gases/ Hydrocarbons : CO_2 recovery from bio and landfill gases CO_2 recovery from well injections H_2S removal from sour gas	Successful.... condensible organics removed even in competitive PSA process and water scrub requires water cleanup for pollution control.... better productivity- α tradeoff is desirable Successful, but condensibles must be removed and better productivity- α and plasticization resistance is desirable No known installations, but current or emerging membranes may work
H_2O / Hydrocarbons: Natural gas drying H_2O / Air : Air dehydration must be overcome	Effective, but hydrocarbon losses to permeate marginally acceptable Effective, for intermediate dewpoints, concentration polarization in permeate
Hydrocarbons / Air : Pollution control, solvent recovery Hydrocarbons(CH_4)/ N_2 : Upgrading of low BTU gas	Successful for chlorinated hydrocarbons. Permeate tends to become oxygen enriched (flammability concern) and vacuum system design is exotic Current membranes are not selective enough to avoid excessive loss of methane into the permeate stream
He / Hydrocarbons : Helium recovery from gas wells He/N_2 : Helium recovery from diving air mixtures	Low He feed concentrations require multistage operation, market is small Feasible, market is small

Hydrogen separations from highly supercritical gases, such as methane, carbon monoxide, and nitrogen are easy to achieve by membranes, because of the extremely high diffusion coefficient of hydrogen relative to all other molecules except helium. Even though solubility factors are not favorable for hydrogen, the diffusion contribution dominates and gives overall high selectivities. For example, the hydrogen/methane selectivity of some of the new rigid polyimide and polyaramide membranes is about 200. An example of Monsanto's use of membranes for synthesis gas composition adjustment is the production of methanol from synthesis gas. Monsanto has published a study of a plant in Texas City producing 100×10^6 gal/yr of methanol.⁴³ The combined methanol/syngas process, shown in Figure 3-7, requires a hydrogen:carbon dioxide ratio of 3:1 for feed to the reactor/interchanger. The overall flow diagram is shown in Figure 3-7a and the separator flow diagram indicating the detailed process conditions is shown in Figure 3-7b. The separator train involves two parallel banks of four 10-ft long, 8-in diameter modules arranged in series, to handle the 4,150 scfm of feed gas at 682 psig. Specific information about the 8-in-diameter modules is proprietary, but if one assumes a standard 200 μ m OD fiber and a 50% packing factor, roughly 80,000 ft² of total membrane area is present in the compact separator train.

The feed stream leaving the methanol scrubber is saturated with water and is preheated prior to entering the separator train to prevent condensation on the membranes. The permeate gas, consisting largely of hydrogen and carbon dioxide is sent back to the synthesis reactor, while the nonpermeate from the last separator is sent to the fuel header to be burned. Roughly half of the available hydrogen and carbon dioxide is recovered, leading to a net increase of 2.4% in methanol production, simply by elimination of the wasted raw materials lost in the purge. The slightly slower permeation rate of carbon dioxide relative to hydrogen requires the addition of a small amount of carbon dioxide makeup gas to the recycle stream to maintain the 3:1 stoichiometry required. Accounting for this supplemental carbon dioxide and a debit for the lost fuel value of the reclaimed raw materials, the permeator installation permitted an impressive 13% reduction in variable costs per gallon of methanol.

Monsanto's success encouraged companies with technology in asymmetric cellulose acetate, which could be dried out without the need for a caulking post treatment, to enter the gas separation market. In the early 1980s, Dow (Cynara), Grace, Envirogenics and Separex began to market gas separation systems. Except for the hollow-fiber Cynara product, all modules were spiral-wound. Except for the Envirogenics module, all of these products are still being sold and have had a measure of acceptance. Separex, which was recently purchased by Hoechst-Celanese, has sold more modules for hydrogen separation than the rest of the cellulose acetate manufacturers. Air Products showed that by using 18.5 million standard cubic feet/day (mmscfd) of a typical synthesis gas feed stream comprised of 73% hydrogen and 24% carbon monoxide, the feed to the methanol reactor could be adjusted to match the stoichiometry needed in the synthesis reactor. The permeate from the process was 98% hydrogen, and Air Products indicated that cost of the membrane system was less than half the cost of a competitive pressure swing adsorption (PSA) system.⁴⁴

Figure 3-7a. Schematic representation of complete oxo-alcohol process showing the relationship of the two banks of 8-in. diameter, 10-ft-long Prism® separators.

Figure 3-7b. Detailed flow, pressure and composition diagram for the Prism® separator system in Figure 3-7a.

Spillman summarizes numerous other hydrogen recovery case studies involving ammonia synthesis and refinery applications.¹⁷ A specific example is the recovery of 98% pure hydrogen from a 15 mmscfd stream containing 75% hydrogen by means of a Du Pont polyaramide hollow-fiber membrane system. The stream originates from a hydrodesulfurization purge stream in a Conoco refinery. The investment and operating costs of the membrane system, compared with PSA, cryogenic treatment and incremental reforming in a hydrogen plant are shown in Figure 3-8.

Figure 3-8. Comparison between process economics for hydrogen recovery for a hydrodesulfurization (HDS) purge gas stream.¹⁷

The excellent temperature stability of the newer, high-performance materials should allow their use at temperatures above 100°C in the future, so long as potting materials capable of high-temperature operation can be developed.

3.7.2 Oxygen-Nitrogen Separations

Membranes can be used to separate air to yield either nitrogen- or oxygen-enriched air as the final product. For production of nitrogen-enriched air, the stage-cut (fraction of feed air passing through the membrane) is set to allow sufficient oxygen to pass through the membrane to reduce its mole fraction to whatever level is desired. In a perfectly permselective membrane, at zero

downstream pressure, the stage-cut could be set at roughly 21%, pure oxygen collected as permeate and pure nitrogen collected as residue. The current generation of membranes have oxygen/nitrogen selectivities of 4-5, but higher ideal separation factors are becoming available. The next generation of modules will probably operate with stage-cuts of less than 45% to produce high purity nitrogen.

By far the largest current application is to produce nitrogen-enriched air for inerting of foods, fuels, etc. In 1987, Monsanto introduced their Prism Alpha® membranes, asymmetric membranes with an improved structure that gives rise to a thinner selective skin layer.

A/G Technology, a small company with experience in ethylcellulose, hollow-fiber spinning, entered the air separation market and carved out a niche in small-scale nitrogen inerting systems. Union Carbide's hollow-fiber composite membrane system was also introduced successfully for both nitrogen inerting and hydrogen separation applications in 1987. A large membrane plant to produce inerting nitrogen upon demand was started up at Johnson & Johnson in 1988 and appears to have been successful.

The nitrogen-enriched air market represents a huge potential opportunity for membrane systems, but entrenched gas companies can reduce liquid nitrogen costs to inhibit market-share losses to membranes. Nevertheless, gas suppliers have begun to accept that membranes will cause eventual loss of markets from conventional technologies. The result is the formation of numerous joint ventures between membrane suppliers and gas companies, for example Du Pont/Air Liquide, Dow/British Oxygen, Akzo/Air Products, Rotem/Aga and Allied Signal/Union Carbide.

The current generation of membranes seem to be extremely attractive for 95% nitrogen; however, PSA is a strong competitor for the 98%+ market. Recent patents and announcements by Dow of higher selectivity polyester carbonate materials suggest that the 99%+ market may soon be at least partially served by membranes.

The evolving picture in the air separation field is illustrated by Figure 3-9 in which the shaded area indicates the improvement in capability of membranes since 1985.¹⁷ Even prior to the introduction of the next generation membranes, PSA is being challenged for the 98%+ market. A case quoted by Spillman shows that a metal powder facility using 286,000 scf of nitrogen per month spends \$0.53/cscf for liquid nitrogen plus tank metal. A Prism® Alpha system producing 99% nitrogen is claimed to yield a nitrogen cost of \$0.26 per cscf, amounting to over a 50% savings compared to delivered liquid nitrogen, even when capital and maintenance costs are included.¹⁷

A recent comparison between A/G Technology's ethylcellulose hollow-fiber module and PSA for the production of 95% nitrogen indicated roughly equivalent costs of \$0.13/cscf. Replacing the ethylcellulose membranes with a higher selectivity material, such as polysulfone, would favor the membrane option. Moreover, membrane units are light and simple compared with PSA, so in applications such as aircraft fuel tank inerting they would tend to be favored.

Figure 3-9. Updated comparison of air separation technologies and sources for nitrogen gas. The shading reflects advances in gas separation membranes made since the original figure was prepared in 1985.¹⁷

Except for home medical uses, membrane-generated, oxygen-enriched air is not currently a significant market. A 45-50% oxygen-enriched air permeate is at the limit of what can be achieved with present membranes. The Japanese have identified oxygen-enriched air feeds to burners as an important priority. A commercial installation by Osaka Gas Company to generate oxygen-enriched air for improved methane combustion efficiency, described in a 1983 paper, is believed to be the first of its kind in the world.⁴⁶ A four-year DOE-supported study of the use of oxygen-enriched air in a copper tube annealing furnace was demonstrated to be practical using even the low-selectivity materials available ten years ago.⁴⁷ The use of membrane-produced, oxygen-enriched air for combustion applications appears to be a sleeping giant. Improved membranes with suitable productivity and selectivity will soon be available to make the oxygen-enriched burner feed market attractive. A/G Technology's assessment of the relative cost of available oxygen in 35% oxygen-enriched air indicates a cost of only \$28 per ton for membranes compared with \$42 per ton for PSA.⁴⁸ Ward and co-workers, in an article published in 1986, indicate that even at \$55/ton the economics of oxygen enrichment for burners appear attractive. The article shows that, with high-efficiency modules, it is technically feasible to save roughly 40% of natural gas fuel costs by operating with 30% oxygen feeds.⁴⁹ As burner designs evolve to accommodate inexpensive oxygen-enriched air sources, this aspect of membrane technology will likely burgeon.

The use of sterile, oxygen-enriched air for biotechnology is also a market that is likely to develop as the systems for air processing become more familiar to the public.

3.7.3 Acid Gas Separations

Currently, the principal application in this category comprises carbon dioxide removal from a variety of gas streams containing primarily methane as the second component. Such gases arise from landfills and from enhanced oil recovery (EOR) projects. Enhanced oil recovery operations involve the injection of high-pressure (2,000 psia) carbon dioxide into a reservoir via an injection well, and removal of carbon dioxide, light gases and oil from production wells around the periphery of the injection well. Monsanto, Dow and Grace have all been active in the area of membrane systems to recover the injected carbon dioxide. A Dow installation at a Sun Oil field has run successfully for over five years without replacement modules, considerably longer than the original two- to three-year lifetime expectations. The membrane modules are still owned by Dow, so careful control of module exposure to adverse conditions has been maintained.

A complete study of a typical carbon dioxide recovery system in an EOR application has been done by Shell.⁵⁰ In this study, the 95% carbon dioxide permeate stream from the membrane can be used for reinjection; the nonpermeate stream, containing 98.5% methane, forms pipeline quality natural gas. Spillman has shown that multistage membrane systems can be competitive with recovery of carbon dioxide by the conventional diethylamine (DEA) process, even at carbon dioxide concentrations as low as 5%.¹⁷ By resorting to multistage processing, it appears that membranes provide markedly less expensive processing costs than amines for this case as well as the higher carbon dioxide concentration cases. The difference between the single-stage membrane, the optimized multistage membrane and the DEA process is illustrated in Figure 3-10 and Table 3-4.

Table 3-4. Detailed economic comparison between amine treatment and optimized multistage membrane process for CO₂ removal from natural gas.¹⁷

CO ₂ Content of Feed	5%	10%	15%	20%	30%	40%
Amine						
Capital (Millions of Dollars)	3.35	4.54	5.45	6.21	7.50	8.56
Expenses (Millions of Dollars/Year)	1.22	1.81	2.33	2.82	3.73	4.58
Lost Product (Millions of Dollars/Year)	0.02	0.04	0.07	0.09	0.14	0.19
Capital Charge (Millions of Dollars/Year)	0.91	1.23	1.48	1.68	2.03	2.32
Processing Cost (Dollars/MSCF Feed)	0.17	0.24	0.30	0.36	0.46	0.55
Membrane (Multistage Process)						
Capital (Millions of Dollars)	1.86	3.33	3.87	3.69	3.37	3.32
Expenses (Millions of Dollars/Year)	0.53	0.85	0.97	1.00	0.98	0.96
Lost Product (Millions of Dollars/Year)	0.43	0.69	0.93	1.24	1.54	1.49
Capital Charge (Millions of Dollars/Year)	0.51	0.90	1.05	1.00	0.91	0.90
Processing Cost (Dollars/MSCF Feed)	0.11	0.19	0.23	0.25	0.27	0.26

* 37.2 MMSCFD at 725 psig (1,000,000 m³/day at 5.0 MPa).

Figure 3-10. Economic comparison between amine treatment, single-stage and optimized multistage membrane processes for CO₂ removal from natural gas.¹⁷

Spillman further notes that although the methane loss for membrane systems may exceed that in amine systems, the fuel requirements to operate the amine unit more than offset these losses in the overall economics.

Current indications are that using membrane separations in natural gases and in EOR applications looks very promising. Even in the case of future, large-scale EOR projects (which are currently on hold due to low oil prices), it may be wise to build a small- to medium-scale startup cryogenic plant to handle the base load and add additional capacity only as it is needed during the aging of the field as carbon dioxide concentrations increase.

EOR is by no means the only opportunity for carbon dioxide selective membranes. Naturally occurring gases containing up to 50% carbon dioxide are also excellent candidates for membrane-based gas separation processes. The range of feed pressures and compositions in these cases can cover a broad spectrum; streams containing more than 15% carbon dioxide look most attractive for membranes. Schendel et al.⁵¹ have recognized that, in many applications, membranes will be able to compete with cryogenic systems, even when the cost comparison favors cryogenics, because of the flexible and modular nature of membrane systems.

In addition to the naturally occurring sources of methane, gases produced from municipal waste or landfills can produce a methane-rich gas containing up to 45% carbon dioxide with various impurities that must be dealt with. It has been estimated that the municipal waste from U.S. cities, if properly processed, could produce up to 200×10^9 scf/year of methane.⁵² Moreover, since landfills tend to be near urban centers, the cost of moving the gas is minimized.

In such applications, membranes will have to compete with a variety of other technologies including water scrubbing, PSA and direct use of the contaminated gas as a low-energy fuel. Typical landfill gases contain significant amounts (100-200 ppm) of chlorinated hydrocarbons, as well as a broad spectrum of other hydrocarbons. Thus, the clean-up and use of the gas via PSA or membranes is preferable to direct combustion.

For both natural gas and landfill gas applications, more selective and productive membranes would improve the economics by reducing hydrocarbon losses to the permeate. Particularly for high-pressure applications, plasticization of the membrane by carbon dioxide or hydrocarbons may reduce the membrane performance. Identification and development of new materials that can resist plasticization would be valuable.

3.7.4 Vapor-Gas Separations

Separation of water vapor from natural gas and other streams, and separation of organic vapors from air and other streams, are both areas of current and future opportunity for membranes.

Dehydration of natural gases occurs spontaneously during carbon dioxide removal, because water vapor has a high intrinsic permeability and the downstream mole fraction tends to be maintained at a low level by the high downstream mole fraction of carbon dioxide. In this case, it is easy to meet the

0.014% limit on allowable water in the residue gas.¹⁷ In the absence of carbon dioxide, a tendency exists for downstream water vapor concentration polarization to occur. Concentration polarization can be eliminated by allowing sufficient hydrocarbon permeation, but this leads to undesirable product loss, so the use of triethylene glycol solvent drying is generally preferred for relatively pure natural gases without carbon dioxide.¹⁷

Small-scale dehydration of air is possible using a clever approach developed by Monsanto in their Cactus® system. The tendency for undesirable reductions in driving force due to concentration polarization at the downstream membrane surface is eliminated by allowing a small nonselective bypass of air through uncaulked defects in the otherwise selective membrane skin. The system allows economical production of low dew point (-10°C) air without excessive losses due to transmembrane air flows, and it provides a trouble-free source of dry air for many small laboratory and instrumentation applications.

Removal of volatile organics, especially chlorinated and chlorofluorinated hydrocarbons from air have attractive ecological as well as economic driving forces. Spiral-wound membrane systems for this application are marketed by Membrane Technology and Research, Inc. GKSS has worked in the same area, using a plate-and-frame unit that minimizes vacuum losses in the permeate channels. The system designs currently proposed for the application require careful module design and pump selection.

3.7.5 Nitrogen-Hydrocarbon Separations

This separation need arises due to the presence of small amounts (5-15%) of nitrogen impurities in some natural gas reservoirs. Also, the use of nitrogen as a displacement fluid in enhanced oil recovery operations has been suggested. The nitrogen/methane separation is a very difficult one to achieve using membranes. For rubbery membrane materials, the higher condensability of methane favors it as the permeate material. Even in glassy materials, the solubility selectivity generally overcomes the slight mobility selectivity favoring the more compact nitrogen and gives an overall selectivity near unity. Some glassy polymers with highly restricted motions have given selectivities as high as three in favor of nitrogen. The attractive aspect of the more selective glassy polymers is their tendency to pass nitrogen over methane, so it is not necessary to lose pressurization of the product gas. Such selectivities, however, are still too low for commercial viability.

The possibility of incorporating nitrogen complexing groups to promote nitrogen solubility selectivity has not been pursued as a means of complementing the already favorable mobility selectivity for this pair of gases in highly rigid glassy polymers. In fact, a serious potential difficulty exists in this case unless the complexing interactions are very weak. If the complexing is not weak, the diffusion coefficient of the nitrogen may be suppressed, thereby undermining the nitrogen/methane mobility selectivity at the expense of the improved solubility selectivity.

3.7.6 Helium Separations

Helium is a very small molecule and, in the case of hydrogen, a number of high-selectivity and good-productivity membranes already exist. For example, helium can readily be recovered from diving gases by means of a membrane unit. Helium recovery from natural gases is also potentially possible, although the low helium concentration (<1-1.5%) would favor a multistage unit.

3.8 ENERGY BASICS

Idealized and actual gas separation membrane processes are very different. Figure 3-11 shows an idealized, reversible system. Two perfectly selective membranes allow permeation of oxygen and nitrogen compared to the partial pressures in the feed. Only reversible work is performed to raise the exit pressure back to one atmosphere for the two pure-component streams.

Clearly, such a reversible process with differential driving forces would require an infinite amount of membrane surface area. Actual membrane processes, using finite membrane area and finite partial pressure driving forces require more energy consumption than the ideal reversible amount. Nevertheless, some useful statistics about membrane systems can be derived by knowing the theoretical minimum energy requirement. The calculation below is for air at one atmosphere and 20°C.

For an open isothermal, steady state process, the energy balance, in terms of the Gibbs free energy, G , of the inlet and outlet streams can be written:⁵³

$$G_{\text{out}} - G_{\text{in}} = \int \Delta W - \int T \Delta S_{\text{gen}} \quad , \quad (1)$$

where ΔW is the net work and ΔS_{gen} is the entropy change associated with the process. For a reversible system, $\Delta S_{\text{gen}} = 0$, so total work equals the sum of the work done on the nitrogen and oxygen permeate streams:

$$G_{\text{out}} - G_{\text{in}} = \int \Delta W_1 + \Delta W_2 = W \quad . \quad (2)$$

Since the Gibbs free energy is an extensive property that is determined by the number of moles (n) and the chemical potential (μ) of the various streams:

$$G_{\text{out}} = (n_{\text{N}_2} \mu_{\text{N}_2} + n_{\text{O}_2} \mu_{\text{O}_2})_{\text{P}} + (n_{\text{N}_2} \mu_{\text{N}_2} + n_{\text{O}_2} \mu_{\text{O}_2})_{\text{R}} \quad , \quad (3)$$

where P and R denote the permeate and residue streams, and

$$G_{\text{in}} = (n_{\text{N}_2} \mu_{\text{N}_2} + n_{\text{O}_2} \mu_{\text{O}_2})_{\text{F}} \quad , \quad (4)$$

where F denotes the feedstream.

MTR-052-F

Figure 3-11. Representation of an idealized isothermal reversible membrane separator for producing pure oxygen and pure nitrogen at 1 atm from a feed of air at 20°C.

For an ideal gas, we have:

$$\mu_i = \mu_i^\circ + RT \ln p_i = \mu_i^\circ + RT \ln y_i + RT \ln p \quad ; \quad (5)$$

$p = 1$ atmosphere in all cases here, so

$$\mu_i = \mu_i^\circ + RT \ln y_i \quad (6)$$

Associated with one ton of oxygen, there are:

$$(2000/32) \times 454 \text{ gmol oxygen} = 28,375 \text{ gmol oxygen}$$

and

$$(0.79/0.21) 28,375 \text{ gmol nitrogen} = 106,774 \text{ gmol nitrogen.}$$

Substituting into equation (2), the $n \mu_i^\circ$ terms cancel each other, so:

$$W = 43.8 \text{ kWh/ton air separated} \quad .$$

The individual work requirements to produce the $0.79/0.21 = 3.76$ tons of pure nitrogen, W_1 , and the 1 ton of pure oxygen, W_2 , respectively are:

$$\begin{aligned} W_1 &= 17.14 \text{ kWh (or 4.56 kWh/ton nitrogen)} \\ W_2 &= 30.16 \text{ kWh per ton oxygen} \quad . \end{aligned}$$

For oxygen enrichment applications, W_2 is the pertinent value to consider. Ward et al. suggest the use of the concept of "tons of equivalent pure oxygen" oxygen (EPO₂) to allow comparison of membrane and other approaches for producing oxygen enriched air streams.⁴⁹ "Equivalent pure oxygen" is the amount of pure oxygen needed to be blended with air to make a particular mixture of oxygen-enriched air. For example, 100 moles of 35% oxygen enriched air can be made by blending 17.7 mole of pure oxygen with 82.3 moles of air. The resulting mixture, therefore, contains 17.7 moles of equivalent pure oxygen (EPO₂):

To produce 10 tons of available oxygen in a 35% oxygen-enriched air, therefore, $10/0.35 = 28.57$ tons of air are delivered. Of the 10 tons of oxygen in the air, 4.94 tons are supplied as EPO₂. If this oxygen is obtained from a reversible separation like that described above, an ideal energy cost of $30.16 \times 4.94 \text{ kWh} = 149 \text{ kWh}$ for the 10 tons of available oxygen would result. The actual energy cost to produce EPO₂ by standard cryogenic plants ranges from 275–375 kWh/ton.⁴⁷ Assuming a midrange value of 325 kWh/ton EPO₂ gives the 1600 estimate shown in Table 3–5 for comparison to the ideal 149 kWh value. PSA processes have been estimated to operate at 400 kWh/ton EPO₂, thereby yielding the energy cost of 1976 kWh indicated in the table.

A/G Technology has estimated the cost to produce 10 tons per day available oxygen in a 35% oxygen enriched air stream using their ethyl cellulose membranes as opposed to a standard PSA approach (see Table 3-6).⁴⁸ If operated in a pressurized mode rather than with a vacuum downstream, the power costs for the membrane unit approach those of the PSA unit. The vacuum mode of operation is more energy efficient, because only the permeate must be compressed as opposed to the entire feed in "pressurized" mode. Estimated power costs for the membrane system were \$86 for the membrane system and \$131 for the PSA system, suggesting that the membrane process is somewhat more energy efficient than the PSA process in this case. If the 2,000 kWh energy value noted in Table 3-5 is used with the \$131 cost of power quoted by A/G Technology for the PSA case, they indicate a reasonable energy cost of 6.6¢/kWh at the time of the 1985 analysis. This number allows estimation of the 1300 kWh value shown in Table 3-5 based on the \$86 value quoted by A/G Technology for production of 10 tons of available oxygen using their membrane system.

For all of the actual separation cases, the energy cost is well above the theoretical minimum value of 149 kWh, because practical processes must be carried out at finite rates and are less energy efficient than those carried out reversibly. Further productivity increases in membranes may provide the opportunity to reduce the driving forces required to achieve economical production rates, thereby even further improving their position relative to the other separation processes in terms of energy efficiency. As noted previously, however, energy costs are only one aspect of the strong attraction of membrane systems. Their convenience, flexibility and overall operating costs are even more important. This point is made in Table 3-6 from the article by A/G Technology in comparing the total cost to deliver ten tons per day of available oxygen as a 35% oxygen-enriched stream.

"Vacuum Swing Adsorption" (VSA), which operates between essentially atmospheric pressure and a vacuum, rather than between an elevated pressure and one atmosphere, allows energy savings by requiring compression of only the oxygen-enriched product gas rather than the entire feed. In this case, the energy efficiency of the adsorption and membrane operations are probably similar.

Table 3-5. Comparison of energy consumption by different processes for tons per day of available oxygen in a 35% oxygen enriched air stream. If the adsorption process is run as VSA (vacuum swing adsorption) it is likely that it will be more similar in energy use to the membrane than is the case for PSA.⁴⁹

Type of Process	Energy Requirement (kW-hr/ton EPO ₂)
Reversible isothermal (blended pure O ₂ with air to make 35%)	149
Cryogenic production of 99.5% (blended with air to make 35%)	1600
Pressure swing adsorption production 90% O ₂ (blended with air to make 35%)	2000
Typical current generation membrane for direct production of 35% O ₂ containing air with no post blending	1300

Table 3-6. Cost comparisons for 35% oxygen-enriched air (10 tons/day available oxygen).⁴⁸

	A/G Technology Membranes	PSA
Installed Capital Cost (Thousands of Dollars)	288.00	552.00
Expenses (\$/day)		
Membrane Replacement	38.00	—
Power	86.00	131.00
Capital Charges	105.00	202.00
Depreciation	33.00	63.00
Other	18.00	27.00
Total (Dollars/Day)	280.00	423.00
Total (Dollars/Ton)	28.00	42.00

3.9 ECONOMICS

Evolution of more advanced materials such as the polymers indicated in Figure 3-5 and Table 3-2 will eventually reduce the need for multistage and recycle approaches to achieving required product specifications for one or both the permeate and nonpermeate streams. In general, however, selection of optimized approaches for using membranes in a given application will remain complex and is best done with the aid of detailed computer programs to allow complete analysis of numerous candidate process layouts. The application examples in Table 3-3 and the earlier case study results by Shell referred to in the section on the historical development of the field illustrate the versatility of gas separation membrane technology.⁵⁰ It is this very versatility that places membranes in competition with a diverse array of competitive technologies.

Spillman has presented a useful analysis emphasizing the importance of objective consideration of economic factors when evaluating competitive technologies such as membranes, PSA, cryogenic, chemical and physical solvent candidates for a given application.¹⁷ He notes that issues such as the pressure level at which the products can be delivered, e.g., in nitrogen inverting or hydrogen recovery, are sometimes deciding factors of equal or greater importance to the absolute recovery of the desired component. Also, as illustrated by the use of membranes to reduce carbon dioxide concentrations prior to feeding to a cryogenic plant for enhanced oil recovery operations, hybrid approaches involving membranes with another separation process may sometimes be the best strategy.

3.10 SUPPLIERS

Table 3-7 summarizes the principal suppliers of commercial-scale equipment for gas-separation applications. As can be seen, the only company offering equipment in all application areas at present is Monsanto. Even the other large players have focused on two or three specific topics, and the field is made up of a large number of smaller companies, or larger companies with relatively small membrane groups, that are attacking the niche markets.

For the larger companies, it appears that joint ventures with companies that supply gas by other means will continue to flourish. An across-the-board capability to handle gas-separation problems regardless of the volume, pressure or composition of the feed will obviously put a supplier in a strong position with regard to the competition. Furthermore, the optimum solution to any particular gas separation problem may well involve a hybrid process incorporating two or more individual technologies, such as membranes plus pressure swing adsorption for high-purity separations, or membranes plus compression-condensation for the most cost-effective pollution control approach.

As the industry becomes more mature, it may also become increasingly standardized as companies compete with one another for the replacement module market.

Table 3-7. Commercial-scale membrane suppliers and gas separation module types for each supplier.

Company	CO ₂	H ₂	O ₂	N ₂	Other*	Module Type**
A/G Technology (AVIR)	x		x	x		HF
Air Products (Separex)	x	x			x	SW
Asahi Glass (HISEP)			x	x		
Cynara (Dow)	x					HF
Dow (Generon)				x		HF
DuPont	x	x		x		HF
GKSS		x			x	PF
Grace Membrane Systems	x	x			x	SW
Membrane Tech. & Resch.					x	SW
Monsanto	x	x		x	x	HF
Nippon Kokan					x	
Osaka Gas			x			
Oxygen Enrichement Co.			x			PF
Perma Pure					x	HF
Techmashexport			x			PF
Teijin Ltd.			x			
Toyobo			x			HF
Ube Industries		x			x	HF
Union Carbide (Linde)		x		x		HF
UOP/Union Carbide		x				

* Included solvent vapor recovery, dehumidification and/or helium recovery.

** SW = spiral wound, HF = hollow fiber, PF = plate and frame.

For the small companies, with limited resources and expertise to undertake large-scale plant engineering, the trend to go after niche markets will continue. The gas separation field is young enough and open enough to accommodate many successful small companies, at least through the short to medium range future. A/G Technology is very effectively marketing its ethylcellulose hollow-fiber modules. Membrane Technology and Research, Inc. has announced membranes for removing organic vapors from air, and for removing higher hydrocarbons from natural gas, which may place it in a favorable position.

3.11 SOURCES OF INNOVATION

3.11.1 Research Centers and Groups

As indicated earlier, industrial users often rely upon the suppliers of systems for innovation in the details of membrane materials, membrane structure and system design. This trend is promoted by suppliers who have found it attractive to either sell self-contained systems or, in some cases, to provide gas as a utility to a customer who merely rents the system. Although complex computer programs are usually needed to accurately assess the true potential of membranes compared to competitive technologies, small users can still promote innovation in the field. By proposing novel applications and challenging the existing state of the art in membranes, users can help establish goals to drive the fundamental material science and applied engineering research being supported in academia by both government and industry. Technical meetings and conferences are valuable forums for the interchange of such information and for keeping users apprised of the rapidly expanding capabilities of gas separation membrane systems.

The field of gas separation membrane research is extremely active at the present time. Tables 3-8a and 3-8b list locations where sufficient concentration of effort exists to indicate that a significant contribution to the field is occurring. Major groups are identified by an asterisk. Table 3-8a covers industrial research centers; Table 3-8b covers academia. For the larger industrial groups, over ten professional scientists and engineers are typically involved in the indicated activities. Similarly, in academia, five to ten graduate students may be involved in activities with multiple faculty at a given location. Activities in facilitated transport, discussed in Chapter Four, are not included.

The entries in the "activities" column are based on publicly available information; where activities are not indicated, they may exist but have not been publicized. Most of the commercial suppliers listed earlier in Table 3-7, are expected to have capabilities in at least the last three categories, and have been so indicated in Tables 3-8a and 3-8b. Where a joint venture is in place, the name of the principal partner with the major strength in gas membranes is given. Multiple addresses are given in cases where specific activities are carried out at different locations, but some overall coordination of effort exists. Often, but not always, the second partner in a joint venture provides market access and knowledge, rather than membrane expertise.

Table 3-8a. Industrial Research Centers and Groups Contributing to the Development of Membrane-Based Gas Separation. NM refers to organizations conducting research into new materials; F refers to membrane formation; MDM to module design and modeling; ST to system testing.

Organization & Location	Activities			
	NM	F	MDM	ST
A/G Technology Needham, MA 02194		X	X	X
Air Products/Akzo Allentown, PA 18195 Anaheim, CA 92806	X	X	X	X
Aashi Glass, Inc. Yokohama, Japan	X	X	X	X
Bend Research Bend OR 97701		X	X	X
Dow Chemical Co./British Oxygen Co. Midland, Michigan 48674 Walnut Creek, CA	X	X	X	X
Dow-Corning Co. Midland, MI 48686	X			
E. I. DuPont/ Air Liquide Wilmington, Delaware 19898	X	X	X	X
Exxon Annandale, N. J.		X	X	
Eniricerche Rome, Italy	X			
General Electric/ Oxygen Enrichment, Inc. Schenectady, NY 12301	X			
GKSS Geestacht, West Germany		X	X	X
Grace Membrane Systems Columbia, MD 21044		X	X	X
Hoechst-Celanese Summit, N. J.	X	X		
Innovative Membrane Systems/ Union Carbide/Allied Signal Norwood, MA 02062 & Tonawanda, NY 10591 Des Plaines, IL 6001	X	X	X	X
Nippon Kokan, Inc. (need information here)	X	X	X	X
Membrane Technology & Research Menlo Park, CA 94025		X	X	X
Monsanto St. Louis, MO 63167		X	X	X
Osaka Gas, Inc. Osaka, Japan	X	X	X	X
Rotem/ AGA Negev, Israel	X	X		
Separex Biella, Italy	X			
Sepracor Inc. Marlboro, MA 01752	X	X	X	
Shell, Inc. Amsterdam, Netherlands	X	X	X	X
Technosherport Vladimir, USSR	X	X	X	X
Texaco, Inc. Beacon, NY 12508		X	X	
Ube Industries	X	X	X	X

Table 3-8b. Academic, Government and Private Research Institutes Contributing to the Development of Membrane-Based Gas Separation. NM refers to organizations conducting research into new materials; F refers to membrane formation; MDM to module design and modeling; ST to system testing.

Organization & Location	Activities			
	NM	F	MDM	ST
Case Western Reserve University Cleveland, OH	X			
Chung Yuan University Chungli, Taiwan	X			
Democritos Nuclear Research Center Athens, Greece	X			
EG&G Idaho, Inc. Idaho Falls, ID 83415	X			
Imperial College London, UK	X			
Institute of Chemistry , Academia Sinica Beijing, China	X			
Johns Hopkins University, Baltimore, MD		X		
Max Planck Institute for Biophysik Frankfurt Am Main, West Germany		X		
Meiji University Kawasaki, Japan	X			
National Institute of Science and Technology Boulder, CO	X			
North Carolina State University Raleigh, N. C.	X		X	
Rutgers University New Brunswick, NJ	X			
Stevens Institute of Technology Hoboken, NJ 07030			X	X
Syracuse University Syracuse, NY	X		X	
SUNY, Syracuse Syracuse, NY	X	X		
University of Aachen Aachen, West Germany			X	
University of Calabria Calabria, Italy	X	X		
University of Cincinnati Cincinnati, OH			X	
University of Colorado Boulder, CO		X		
University of Missouri Rolla, MO	X			
University of Texas Austin, Texas 78712	X	X		X
University of Tokyo Tokyo, Japan		X		
University of Twente Twente, Netherlands	X	X		
SRI International Menlo Park, CA	X		X	

3.11.2 Support of Membrane-Based Gas Separation

3.11.2.1 United States

To date, the bulk of the funding for gas separation research has come from industrial sources that see long-term opportunities in this area. The major companies identified in the preceding table have made multimillion dollar investments to develop technology to promote their position in this rapidly growing field. In addition to the industrial support, various U.S. private and governmental organizations have provided limited support. Included in the above funding sources are the National Science Foundation, the Department of Energy and the Small Business Innovation Research (SBIR) program within these organizations. Except for scattered fundamental grants, and highly mission-oriented projects funded by Defense Advanced Research Projects Agency (DARPA), the Department of Defense has not helped significantly to promote gas separations using membranes. This is surprising, especially given the advantages provided to a mobile military unit by potential fuel savings if oxygen-enriched air is used in an advanced internal combustion engine. Moreover, weight and space savings associated with the possibility of on-board generation of inert atmospheres for aircraft and ship fuel tanks is an area that would seem to merit much more attention by the military than it has received.

3.11.2.2 Foreign

Foreign industrial activities in the membrane-based gas separation area are significant, with those in Europe and Japan being the most intense. As in the United States, university and institute funding is much less apparent than in the industrial arena.

3.12 FUTURE DIRECTIONS

The worldwide market for industrial or home uses of membranes will ultimately be determined by the cost-to-service ratio achievable with these products. Originally unavailable markets, such as nitrogen inerting, have recently become available as the cost-to-service ratio decreases. The membrane module, and sometimes the membrane material itself, are critical elements in determining this ratio. Other system components and their complexities must be engineered to accommodate for membrane deficiencies, thereby adding costs. First generation products have achieved commercial success with essentially non-tailored materials, but longer term success will require more attention to the membrane material and membrane structure itself.

3.12.1 Industrial Opportunities

In the near future, industrial opportunities will fit into one of the existing categories listed in Table 3-3. Existing products, however, are marginally useful or unacceptable for some of these applications. The one factor that would do most to speed commercial success would be improvements in membrane materials and membranes. A listing of application areas in terms of anticipated future importance is given in Table 3-9, with brief explanatory comments. The "Prospects" column is intended to reflect the current assessment of the likelihood

that problems preventing the implementation of membranes for the cited application area have been, or will be resolved within the next 5-20 year period. The "Importance" column represents the consensus of opinions from the working group meeting at the 1989 North American Membrane Society (NAMS) meeting. A high rating on a scale from 1-10 indicates that the application is likely to be significantly important to the United States in the energy conservation field. The "Comments" column mentions technical, economic or related constraints and factors that may impact the implementation of the process.

3.12.2 Domestic Opportunities

In overall dollar value, applications of membrane-based gas separation will likely be predominately in the industrial sphere, at least for the next 5-10 years. However, the simplicity of the membrane process presents some attractive possibilities for new consumer markets for an increasingly environmentally sensitive public. Potentially, industrial burner and furnace designs based on oxygen-enriched feeds may find their way into the home-heating market as energy costs rise and concern for carbon dioxide emissions increases. The compactness and minimal service needs for such systems are attractive. Similarly, less reliance on refrigeration to reduce spoilage of certain types of foods and other oxygen-sensitive articles in shipment may ultimately find an analog in more energy-efficient home storage. Development of practical, small-scale digesters for generation of methane from wastes in rural or isolated installations appears technically feasible, but dependent upon simple, efficient membrane system. Such developments are likely to require time to be achieved, but on a society-wide basis, they amount to very significant developments. Moreover, such potential developments add an additional dimension and driving force for promoting industrial scale membranes which will be the eventual source of technology for such consumer products.

3.13 RESEARCH OPPORTUNITIES

Potential areas of research emphasis are described in Table 3-10. The topics are ranked semiquantitatively according to their prospects for realization as well as their importance in addressing the application areas in Table 3-9. The rankings are based on an integration of all of the preceding discussions of the various sections as well as discussions of the panel convened at the 1989 NAMS meeting.

3.13.1 Ultrathin Defect-Free Membrane Formation Process

An attractive, achievable opportunity would entail the development of a convenient general process to produce truly defect-free, asymmetric membranes with ultrathin skins less than 500Å thick. The availability of such membranes, especially in hollow-fiber form, would provide major improvement in all gas separation systems. Monsanto has a process for spinning ultrathin-skinned standard polysulfone, but it is not readily applicable to other polymers. A process that could handle more selective, existing commercial polymers, such as polyetherimide (PEI), as well as new custom-made materials, would be a major breakthrough. Moreover, such a process could be used to form membranes that would serve as a basis for post-reaction modification of highly productive, low selectivity materials (item #5 in Table 3-10).

Table 3-9. Future Directions for Membrane-Based Gas Separation

Application Area	Prospects	Importance	Comments
1. N ₂ enrichment of air	excellent	10	Major market...share determined by cost- benefit position vs. PSA & cryogenic. Higher selectivity and productivity units needed to cut compression costs and module size, resp.
2. Low level O ₂ enrichment of air	excellent	8	Major market... similar considerations to #1, except possible additional opportunities exist if one can separate O ₂ from a compressed gas stream at high temperature (300°C) for cogeneration processes
3. Hydrogen separation	excellent	7	Large market, but diversely distributed. Good materials exist for super critical gases (CO, N ₂ , & CH ₄) but not CO ₂ . Higher temperature module of interest.
4. Acid gases separation from hydrocarbons & H ₂	good	8	Significant market, but more plasticization- resistant, high selectivity materials needed to compete with cryogenic in new plants if goal is to use only membranes.
5. Helium recovery	good	1	Workable systems exist, however, market is limited. PSA and membranes appear competitive.
6. Hydrocarbon and chloro-fluoro hydrocarbon separation from air or nitrogen	fair	5	Silicone rubber works well, but system design needs a lot of work. Potential danger due to O ₂ concentration in the permeate.
7. Air dehydration	fair	5	Small scale process for eliminating H ₂ O concentration polarization using an internal recycle or an air sweep through a controlled porosity skin limits acceptable, but inefficient for large scale.
8. Natural gas dehydration	fair	4	In absence of additional permeable impurities like CO ₂ , CH ₄ losses associated with H ₂ O concentration polarization are too high. A more CH ₄ rejecting membrane might work if water permeability is not too low.
9. N ₂ removal from natural gas	poor	7	Solubility selectivity and mobility selectivity oppose each other, and both are low. Nitrogen complexing agents that may allow increasing the solubility of N ₂ relative to CH ₄ may be useful if they do not destroy the mobility selectivity associated with rigid glasses like the imides in Table 3.
10. High level (90%+) O ₂ enrichment of air	poor	6	Much more selective membrane materials will be needed to do this with conventional polymers. It appears likely that facilitated transport may be the method of choice if membranes are to be used for this application.
11. Selective methane removal from butane or ethane streams	poor	5	Although size differences favor passage of methane, condensibility favors heavier penetrants, and good selectivity is not likely to be achievable at economical fluxes. Few data
12. Acid gas removal from flue gases	poor	7	Difficult to do well with membranes, since concentration driving force is low. Only hope is by facilitated transport membranes.

Table 3-10. Research Topics of Future Interest for Membrane-Based Gas Separation

Research Topic	Prospects	Importance	Comments
1. Development of convenient and generally applicable method for producing membranes with ultrathin ($<500\text{\AA}$) defect-free skins	good	10	Would allow broad usage of advanced materials — even better if done in hollow fiber form
2. Higher O_2/N_2 selectivity ($\alpha \sim 8-10$) and productivity polymer ($P \sim 2-3$ Barrer for O_2) capable of being formed with a $500\text{\AA}$ defect-free skin to provide oxygen $P/l > 1 \times 10^{-4}$ cc(STP) / sec $\text{cm}^2\text{cm Hg}$	good	10	Experimental materials approach these intrinsic α and P numbers, but no ability to spin form them in ultrathin form has been reported. Again, more valuable in hollow fiber form.
3a. Membrane material with high selectivity for CO_2 and H_2S separation from CH_4 ($\alpha > 45$) and H_2 ($\alpha > 20$) at high CO_2 and H_2S partial pressures. 3b. Improved module designs, materials for module construction at high CO_2 and H_2S partial pressures	good	7	Will become more important as the acid gas partial pressure in the feed from EOR projects increases .
4. Development of a convenient and generally applicable method for forming composite hollow fibers with ultrathin ($<500\text{\AA}$) defect-free skins	good - fair	10	Same as #1, but even more valuable if possible since only a small amount of valuable advanced materials need to be used if only the selecting is composed of such materials.
5. Reactive treatments for increasing the selectivity of a preformed ultra-thin selective skin without excessive flux losses	good-fair	6	Attractive if it is generally applicable. Both fluorination and photochemical crosslinking have been demonstrated on dense films and on a relatively thick ($1 \mu\text{m}$) composite membrane, but not on thin $<1000\text{\AA}$ membranes
6a. Industrial survey to define needs for exotic high temperature organic and inorganic membranes 6b. High temperature membranes	good fair	5 ?	Should be done before large expenditures are made to develop high temperature materials, since the current market is unclear. High temperature O_2 selective membrane for cogeneration and membrane reactors may be important.
7. Refine & quantify guidelines and analytical methods to streamline selection of polymers for high efficiency separations	good	6	Much progress has been made, but steady longterm building of this capability provides a good basis for opening potential new markets and preventing displacement by foreign products
8. Highly oxygen selective membrane ($\alpha \sim 12-15$ for O_2/N_2) with good stability and a O_2 $P/l \geq 0.5-1 \times 10^{-4}$ cc(STP) / sec $\text{cm}^2\text{cm Hg}$	poor	8	Carbon fiber membranes or facilitated transport membranes may meet α and P/l goals. Carbon membranes may be too difficult to handle to permit economical formation of large modules, and facilitated transport membranes are unlikely to be stable over extended periods.
9. Physical treatments (antiplasticization) to increase the α of a preformed ultra thin selective skin without excessive reductions in P/l	poor	2	Unlikely to be stable over extended periods if present only in thin ($<1000 \text{\AA}$ selecting layer), and deleterious to mechanical properties if present throughout whole membrane.
10. Concentration of products from dilute streams	very poor	7	Facilitated transport membranes are more appropriate for this type of application

There seems to be nothing inherently preventing the achievement of this goal, and lab-scale demonstrations with flat asymmetric membranes have already been achieved. Elimination of defects by simple coatings is precluded by a Monsanto patent, so for the field to advance in general for all suppliers, intrinsically perfect skins or more elaborate post-treatments not covered by the Monsanto "caulking" process to heal defects are needed. Such a project should also involve an improved understanding of membrane formation fundamentals and would require the implementation of more advanced spinning technology than exists in the field at the present time.

3.13.2 Highly Oxygen-Selective Materials

Another achievable project of specific applicability involves the discovery of a stable, intermediate permeability membrane with an oxygen/nitrogen selectivity of 7-10. The membrane should be able to be formed into sufficiently thin skins to provide transmembrane fluxes on the order of $100 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2\text{-s-cmHg}$ in a high efficiency hollow-fiber form. Such a membrane would place strong pressure on PSA, even for the 99% nitrogen market. Although liquid membranes achieve this selectivity, their flux is not good and stability is poor. Assuming that formation of ultrathin, defect-free skins can be achieved, polymers with intrinsic properties almost good enough to achieve the above goals are known. Therefore, it is likely that this goal will be achieved if sufficient resources are focused on it.

3.13.3 Polymers, Membranes and Modules for Demanding Service

This item relates to the development of more robust membrane materials and modules capable of operation in extreme environments. This objective is likely to be important in enhanced oil recovery processes in the presence of strongly interacting high-pressure carbon dioxide feeds. For this application microporous ceramic or glassy membranes may have some real potential. It has been noted that surface flow of the more condensable component seems to provide selectivity of that component relative to methane. This is a surprising finding that needs more careful scrutiny.

3.13.4 Improved Composite Membrane Formation Process

The development of a process for producing ultrathin, defect-free composite membranes is important. If such a process could be developed in a generally applicable form for use with most advanced materials, a high-productivity and high-selectivity coating could be applied on an inexpensive support. It would then be feasible to use even expensive materials to produce high performance modules without sacrificing economic attractiveness.

This is a difficult problem, but one well worth pursuing. Work done at Union Carbide, IPRI (Japan), Air Products and MTR with thin ($<1,500\text{\AA}$) coatings on fibers or flat membranes suggests the feasibility of the approach. The surface-to-volume advantages of hollow-fibers compared to spiral units make them the most attractive as a composite support; however, formation of a perfect ultrathin composite hollow-fiber membrane is a formidable objective. Cabasso suggests the use of an intermediate layer on which to place the selective layer to help channel permeate flow to the pores of the underlying support.⁵⁴ The issue of optimum composite membrane structure deserves considerable attention.

3.13.5 Reactive Surface Modifications

Surface modification by plasma, photochemical reactions, fluorination or other reactive treatments is an attractive way to produce "asymmetric, asymmetric" membranes. The procedure, in principle, allows treatment of just the outer layer of otherwise relatively thick, but defect-free asymmetric membrane produced by conventional technology. Surface modification may be applicable to even commercially available polymers with unacceptably low intrinsic selectivities, but with relatively high intrinsic permeabilities.

Laboratory demonstrations of various manifestations of the approach exist (plasma, bromination, fluorination, photochemical), but a commitment is required by industry to scale up the technology, and the expense and problems are likely to be significant. Monsanto's attempts to surface-treat polyphenylene oxide (PPO) was abandoned because of technical difficulties. Nevertheless, there are no inherent barriers preventing the development of surface-modification technology.

3.13.6 High-Temperature Resistant Membranes

The development of high-temperature resistant membranes is a topic of considerable scientific interest, but it is not clear whether the availability of such materials would really make a significant impact on energy consumption. A study to look specifically at the energy implications of temperature-resistant membranes and modules would be useful. As for Item 3, ceramic, carbon or glass membranes may have application here if an economic and energy study justify costs.

Examples of such applications could include hydrogen separations where it may ultimately be possible to link reactors and membranes to influence the direction of reactions by removal or introduction of hydrogen to force the products to a favorable form. Moreover, the possibility of high-temperature oxygen-selective membranes for use in cogeneration processes has been suggested.

3.13.7 Refinement of Guidelines and Analytical Methods for Membrane Material Selection

A great deal of progress has been made in recent years in developing optimization strategies for improving the trade-off between permeability and selectivity for members within a given class of polymers. Little general understanding exists, however, about general principles that would allow one to decide on which family of polymers to perform such optimization procedures. Moreover, the current approaches are very empirical and experimentally intensive. As an investment in the long-term viability of the United States membrane industry, steady improvements in the understanding of fundamental factors governing the detailed permeation process need to be made. An example of such a study is the evaluation of the free volume cavities available for diffusion of molecular penetrants through glassy polymers by applying a Monte Carlo technique to a model of the energy states of polymer segments within a closed cube.⁵⁵

3.13.8 Extremely Highly Oxygen-Selective Membrane Materials

A potentially very significant, but difficult to achieve, opportunity would be offered by a stable, highly oxygen-selective, highly productive membrane. If an oxygen/nitrogen selectivity of 12-15 could be achieved with a flux of $50-100 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$, membranes would have ready access to even intermediate (50-60% oxygen) markets. Such a membrane would also potentially displace PSA for all nitrogen production and all oxygen production except the highest purity markets (>90%). Although liquid membranes offer this selectivity, their flux and stability are poor. A more likely hope in this respect would be the Rotem carbon fibers; however, they may be impractical due to handling problems as well as potential "plugging" due to the presence of condensable components competing for diffusion pathways.

3.13.9 Physical Surface Modification by Antiplasticization

The use of antiplasticizing agents loaded into the selective layers of membranes seems to be unreasonable for long term operation. Even if the agent has an incredibly low vapor pressure, the large quantities of gas passing through the membrane and the minuscule amount of agent present should tend to cause unacceptably rapid removal even at ambient temperatures. Under elevated temperature conditions the situation is even less attractive and not worthy of support.

3.13.10 Concentration of Products from Dilute Streams

The ability to selectively collect dilute components as a concentrated permeate product is typically very poor for most applications using conventional membranes. An exception to this rule is, however, given by the case of helium separation from natural gas. Helium may be present at concentrations below 5%, but the high selectivity of current glassy membranes for the helium/methane system makes the separation relatively straightforward.

The larger and more important problem of removing acid gases from flue gases illustrates the more commonly encountered situation involving dilute solution processing. The limited selectivity relative to nitrogen that is available for gases such as sulfur dioxide and carbon dioxide that are present in dilute concentrations in flue gases precludes economical removal using conventional membranes. Facilitated transport membranes, on the other hand, appear to be appropriate for this type of application, but are typically not well suited for the higher concentration ranges due to saturation of carrier capacity. Therefore, facilitated transport and conventional membranes can be viewed as complementary to each other in terms of covering a broad spectrum of feed compositions.

REFERENCES

1. Koros, W.J. and Chern, R.T., "Separation of Gaseous Mixtures Using Polymer Membranes", Chap.20 in Handbook of Separation Process Technology, R. W. Rousseau (ed), John Wiley and Sons, New York, (1987).
2. Koresh, J. and Soffer, A., Sepr. Sci., and Techn., **22**, 973 (1987).
3. Felder, R.M. and G.S. Huvard, Methods of Experimental Physics, **16c**, 315 (1980).
4. Breck, D.W., Zeolite Molecular Sieves, John Wiley and Sons, New York, (1974).
5. Kim, T.H., Koros, W.J. and Husk, G.R., Sepr. Sci., and Techn., **23**, 1611 (1988).
6. Billmeyer, F.W., Textbook of Polymer Science, 2nd Edition, John Wiley and Sons, New York (1971).
7. Koros, W.J., J. Polym. Sci., Polym. Phys. Ed., **23**, 1611 (1985).
8. Chern, R.T., Koros, W.J., Sanders, E.S., Chen, S.H. and Hopfenberg, H.B., in Industrial Gas Separations, ACS Symposium Series 223, ed. by T.E. Whyte, C.M. Yon, and E.H. Wagener, pg. 47 , 1983.
9. O'Brien, K.C., Koros, W.J., Barbari, T.A., and Sanders, E.S., J. Membr. Sci., **29**, 229 (1986).
10. Stannett, V.T., Chapter 2 in Diffusion in Polymers, ed. by J. Crank and G. Park, Academic Press (1968).
11. Gantzel, P.K. and Merten, U., I&EC Proc., Des., Dev., **8**, 84 (1969).
12. H.H. Hoehn, "Aromatic Polyamide Membranes", in Materials Science of Synthetic Membranes, ed. D. R. Lloyd, ACS Symposium Series 269, pg. 81 , 1985.
13. Pinnau, I. and Koros, W.J., " Integrally-Skinned-Asymmetric Gas Separation Membranes Based on Bisphenol-A Polymers", paper presented at the International Symposium in Suzdal, USSR, Feb., 1989.
14. Henis, J.M.S. and Tripodi, M.K., Sepr. Sci., and Techn., **15**, 1059 (1980).
15. Cadotte J., "Composite Reverse Osmosis Membrane", in Materials Science of Synthetic Membranes, ed. D. R. Lloyd, ACS Symposium Series 269, pg. 273 , 1985.
16. Matson, S.L., Lopez, J. and Quinn, J.A., Chem. Engr. Sci., **38**, 503 (1983).

17. Spillman, R.W., "Economics of Gas Separation by Membranes," Chem. Eng. Prog., **85**, 41 (1989).
18. Mitchell, J.K., Philadelphia J. Med. Sci., **13**, p. 36 (1831).
19. Graham, T., Philos. Mag., **32**, 401 (1866).
20. Stern, S.A., Sinclair, T.F., Gareis, P.J., Vahldieck, N.P. and Mohr, P.H., "Performance of a Variable Volume Permeation Cell," I. & E.C., **57**, 49 (1965).
21. Loeb, S., and Sourirajan, S., "Sea Water Demineralization by Means of an Osmotic Membrane," Adv. Chem. Ser., **38**, 117 (1962).
22. Ward, W.J., Browall, W.R., and R.M. Salemm, "Ultrathin Silicone/Polycarbonate Membranes for Gas Separation Processes," J. Membr. Sci., **1**, 99 (1976).
23. Ward, W.J., U. S. Patent 4,279,855, July (1981).
24. U. Merten and P.K. Cantzel, U.S. Patent 3,415,038, December (1968).
25. Gardner, R.J., Crane, R.A. and Hannan, J.F., "Hollow Fiber Permeator for Separating Gases," Chem. Eng. Prog., **73**, 76 (1977).
26. Hoehn, H.H. and J.W. Richter, U.S. Patent Re. 30,351, July (1980).
27. Henis, J.M.S. and Tripodi, M.K., U.S. Patent 4,230,463, October (1980).
28. Hunter, J.B. et al., U.S. Patents 2,961,061 November (1960), and 3,254,956 June (1966).
29. Pye, D.G., Hoehn, H.H., and Panar, M., "Measurement of Gas Permeability of Polymers. I. Permeation in Constant Volume/Variable Pressure Apparatus," J. Appl. Polym. Sci., **20**, 287 (1976). Pye, D.G., Hoehn, H.H., and Panar, M., "Measurement of Gas Permeability of Polymers. II. Apparatus for Determination of Mixed Gases and Vapors," J. Apply. Polym. Sci., **20**, 1921 (1976).
30. Pilato, L., Litz, L., Hargitay, B., Osborne, R., C., Farnham, A., Kawakami, J., Fritze, P., and McGrath, J., "Polymers for Permselective Gas Separations," ACS Preprints, **16**(2), 42 (1975).
31. Koros, W.J. and Hellums, M.W., "Gas Separation Membrane Material Selection Criteria: Differences for Weakly and Strongly Interacting Feed Components", paper presented at the Fifth International Conference on Fluid Properties and Phase Equilibria, May (1989).
32. Kim, T.H., Koros, W.J., and Husk, G.R., "Temperature Effects on Gas Permselection Properties in Hexafluoro Aromatic Polyimides", J. Membr. Sci., in press.

33. Shinnar, R., "Thermodynamic Analysis in Chemical Process and Reactor Design," Chem. Eng. Sci., 43, 2303 (1988).
34. Chu, W., "Hydrogen purifiers: Reliable technology in demanding times," American Laboratory, Feb. (1989).
35. Peinemann, K.V., U.S. Patent 4,746,333, May (1988), and Peinemann, K.V., Pinnau, I. and Wind, J., "Polyethersulfone and Polyetherimide Membranes with High Selectivities for Gas Separation", International Workshop on Membranes for Gas and Vapor Separation, Mar. 7-9, 1988, Qiryat Anivim, Israel.
36. Hayes, R.A., U.S. Patent 4,717,393, January (1988).
37. Mohr, J. M., and Paul, D. R., "Surface Fluorination of Composite Membranes for Gas Separations", Meeting of North American Membrane Society, Austin, Texas, May, 1989.
38. Langsam, M., U.S. Patent 4,657,564, April (1987).
39. Hopfenberg, H.B., Witchey, L.C., and Chern, R.T., "Sorption and Transport of Organic Vapors in Poly(1-trimethylsilyl-1-propyne)", paper presented at the 1987 Annual AIChE meeting, New York, November (1987).
40. Brooks, et al., U.S. Patent 4,575,385, March (1986).
41. Murphy, M.K., Beaver, E.R., and Rice, A.W., "Post Treatment of Graded Asymmetric Membranes for Gas Application", paper presented at the AIChE 1989 Spring National Meeting in Houston, Texas, April (1989).
42. Gollan, A., U.S. Patent 4,734,106, March (1988).
43. Burmaster, B.M. and Carter, D.C., "Increased Methanol Production Using Prism Separators", paper presented at AIChE Symposium, Houston, Tx, March (1983).
44. Schott, M.E., Houston, C.D., Glazer, J.L., and DiMartino, S.P., "Membrane H₂/CO Ratio Adjustment," paper presented at AIChE Symposium, Houston, Tx, April (1987).
45. Nakamura, A., and Minoru, H., "Novel Polyimide Membrane for Hydrogen Separation," Chem. Econ. and Eng. Rev., 117, 41 (1985).
46. H. Ito and M. Watabe, "Oxygen Enriched Air Conversion System by Membranes", Maku 18 No. 5, 372 (1983).
47. Epperson, B.J., and Burnett, L.J., "Development and Demonstration of a Spiral-Wound Thin-Film Composite Membrane System for the Economical Production of Oxygen-Enriched Air", Final Report on Contract No. DE-AC01-79CS40294, Report No. DOE/CS/40294.

48. Gollan, A. and Kleper, M.H., "Membrane Based Air Separation," AICHE Symp. Ser.250, 82, pp. 35, (1986).
49. Matson, S.L., Ward, W.J., Kimura, S.G., and Browall, W.R., "Membrane Oxygen Enrichment, II. Economic Assessment," J. Membr. Sci., 29, 79 (1986).
50. Youn, K.C., Blytas, G.C., and H. H. Wall, "Role of Membrane Technology in the Recovery of Carbon Dioxide: Economics and Future Prospects", paper presented at Gas Processors Association Regional Meeting, Houston, TX, Nov. (1983).
51. Schendel, R.L., Mariz, C.L., and Mak, J.Y., "Is Permeation Competitive," Hydrocarbon Process., 62, 58 (1983).
52. Kumar, R., and Van Sloun, J.K., "Purification by Adsorptive Separation," Chem. Eng. Prog., 85, 34 (1989).
53. Denbigh, K., The Principles of Chemical Equilibrium, 3rd edition, Cambridge University Press, New York, (1978).
54. Lundy, K. A. and Cabasso, I., "Analysis and Construction of Multilayer Composite Membranes for the Separation of Gas Mixtures," Ind. Eng. Chem. Res., 28, 742 (1989).
55. V.M. Shah, S.A. Stern and P.J. Ludovice, "Estimation of the Free Volume in Polymers by Means of a Monte Carlo Technique," Macromolecules, 22, 4660 (1989).

CHAPTER FOUR

FACILITATED TRANSPORT

TABLE OF CONTENTS

4.1	PROCESS OVERVIEW	4-1
4.1.1	The Basic Process	4-1
4.1.2	Membrane Features	4-3
4.1.3	Membrane and Module Design Factors	4-7
4.1.4	Historical Trends	4-9
4.2	CURRENT APPLICATIONS	4-9
4.3	ENERGY BASICS	4-12
4.4	ECONOMICS	4-14
4.4.1	Metals	4-14
4.4.2	Gases	4-15
4.4.2.1	Air separation	4-15
4.4.2.2	Acid gases	4-15
4.4.2.3	Olefin-alkanes and other separations	4-16
4.4.3	Biochemicals	4-16
4.4.4	Sensors	4-17
4.5	SUPPLIER INDUSTRY	4-17
4.6	RESEARCH CENTERS AND GROUPS	4-17
4.7	CURRENT RESEARCH	4-18
4.8	FUTURE DIRECTIONS	4-19
4.8.1	Metal Separations	4-19
4.8.2	Gases	4-21
4.8.3	Biochemicals	4-24
4.8.4	Hydrocarbon Separations	4-25
4.8.5	Water Removal	4-25
4.8.6	Sensors	4-25
4.9	RESEARCH OPPORTUNITIES: SUMMARY AND CONCLUSIONS .	4-26
	REFERENCES	4-30

CHAPTER FOUR

FACILITATED TRANSPORT

by

E.L. Cussler

Department of Chemical Engineering and Materials Science,
University of Minnesota

4.1 PROCESS OVERVIEW

4.1.1 The Basic Process

Facilitated transport is a form of extraction carried out in a membrane. As such, it is different from most of the other membrane processes described in this report. Many of these, for example ultrafiltration, are alternative forms of filtration. Others, especially gas separations and pervaporation, depend on diffusion and solubility in thin polymer films. In contrast, facilitated transport involves specific chemical reactions like those in extraction.¹

Facilitated transport usually has four characteristics that make it different from other membrane separations:

- (1) It is highly selective.
- (2) It reaches a maximum flux at high concentration differences.
- (3) It can often concentrate as well as separate a given solute.
- (4) It is easily poisoned.

Characteristics (2) and (3) are the most powerful evidence that facilitated transport is occurring.

The way in which facilitated transport works is shown schematically in Figure 4-1. The U-tube at the top of this figure contains two aqueous solutions separated by a denser chloroform solution. The aqueous solution on the left contains mixed alkali metal chlorides; the solution on the right is initially water. The chloroform solution contains dibenzo-18-crown-6, a macrocyclic polyether. An additive like this polyether is called a "mobile carrier".² With time, salts in the left-hand solution in Figure 4-1 dissolve in the chloroform and diffuse to the right-hand solution. This dissolution is enhanced or "facilitated" by as much as a million times by the mobile carrier. Moreover, the enhancement is selective: in this case, the flux of potassium chloride is four thousand times greater than that of lithium chloride.

Figure 4-1. Facilitated Transport as Extraction. The extraction system at the top of the figure mimics the facilitated diffusion in the membrane at the bottom of the figure.

The process at the top of Figure 4-1 is obviously an extraction. The reduction from extraction to facilitated transport is made possible by reducing the chloroform phase to a thin sheet, perhaps 30 μm thick, as suggested at the bottom of Figure 4-1. This thin sheet is stabilized by capillary forces within the pores of a microporous hydrophobic polymer membrane. Celgard® membranes, made from microporous polypropylene are a common choice. As before, potassium chloride is selectively extracted from the left-hand "feed" solution into the membrane; the mobile carrier greatly facilitates the salt's diffusion, and the right hand "stripping" solution removes the solutes from the membrane.

The example of facilitated transport illustrated in Figure 4-1 involves the separation of metal ions with a carrier that selectively reacts with one ion and not with the others in the solution. These carriers are widely used in solvent extraction under the name liquid ion-exchange (LIX) reagents. Another type of facilitated transport process uses carriers that will selectively react with and transport one component of a gas mixture. One of the most widely studied gas separation facilitated transport processes is the separation of oxygen from air. Hemoglobin is a well known natural carrier for oxygen, and many other synthetic carriers are also known.

In the past, most facilitated transport membranes used selective carriers dissolved in an organic liquid solvent. In conventional forms of the process, the carrier-solvent solution is immobilized in the pores of a microporous membrane. If the solvent is nonvolatile and insoluble in the surrounding media, the pores of the microporous membrane are made sufficiently small that the liquid is immobilized by capillarity. Such immobilized liquid membranes (ILMs) are easily made, and are normally stable for periods of days, weeks or even months, but not longer.

A second type of facilitated transport membrane is the emulsion liquid membrane (ELM), first developed by Li at Exxon.³ In these membranes, the solvent-carrier and the aqueous product solution are emulsified together to form an oil-in-water emulsion. This emulsion is then re-emulsified in the feed solution, forming a water-in-oil-in-water emulsion. The carrier-solvent phase is the oil phase, and forms the walls of an emulsion droplet separating the aqueous feed solution from the aqueous product solution. Permeate ions are concentrated in the interior of the emulsion droplets. When sufficient permeate has been extracted, the droplets are separated from the feed solution and the emulsion is broken, liberating a concentrated product solution and an organic carrier phase. The organic carrier phase is decanted from the product solution and recycled to make more emulsion droplets.

4.1.2 Membrane Features

Facilitated membrane diffusion can be much more selective than other forms of membrane transport,³⁻⁵ but the membranes used in the process are usually unstable. This instability is a tremendous disadvantage, and is the reason why this method is not commercially practiced.

The characteristics of facilitated diffusion are illustrated by the values in Table 4-1, which compares diffusion coefficient, separation factor and thickness for polymer membranes and for facilitated transport membranes. The speed of any membrane separation is directly proportional to the membrane's diffusion coefficient and inversely proportional to the membrane's thickness. The diffusion coefficient in polymer membranes is much smaller than that in liquid membranes, but the thickness of the polymer membranes is also much smaller. As a result, polymer membranes may show separations with speeds comparable to those of facilitated diffusion.

Table 4-1. Representative Membrane Characteristics. Facilitated transport membranes offer fast diffusion and good selectivity, but are thicker than polymer membranes.

	Diffusion coefficient (cm ² /sec)	Separation Factor	Thickness (cm)
Glassy polymer membrane	10 ⁻⁸	4	10 ⁻⁵
Rubbery polymer membrane	10 ⁻⁶	1.3	10 ⁻⁴
Facilitated transport membrane (liquid)	10 ⁻⁵	50	10 ⁻³

The high selectivity of facilitated transport comes from the chemical reactions between the diffusing solutes and the mobile carrier. These chemical reactions cover the spectrum of chemistry used in extraction and absorption. In the system in Figure 4-1, both potassium chloride and lithium chloride are largely insoluble in the chloroform membrane unless they are complexed. The potassium ions are strongly complexed by the crown compound, but lithium ions are only weakly complexed; this is why this membrane is much more selective for potassium chloride than for lithium chloride.

The coupling between diffusion and chemical reaction gives facilitated diffusion another unusual feature: the flux is not always proportional to the solute concentration difference between the feed and permeate side. At low solute concentration, doubling the concentration difference often doubles the flux, but at high solute concentration, doubling the concentration difference may have no effect on the flux at all. This unusual non-linearity occurs because at high solute concentration, the reactive carrier is fully utilized. In other words, essentially all the carrier molecules are complexed on the feed side of the membrane, and essentially none are complexed on the permeate side of the membrane. Increasing the feed concentration has no effect, therefore, because no additional complexed solutes can be formed. The resulting data are sometimes confused with dual mode sorption, a similar, but less well defined effect, which is described in the section on gas separations.

Because facilitated transport involves coupled diffusion and chemical reaction, it can sometimes concentrate as well as separate a specific solute. Such concentration is sometimes called "coupled transport". An example, given in Figure 4-2, shows how a feed solution containing 100 ppm copper can produce a stripping solution with 1,200 ppm copper. The energy for this separation usually comes from a second reaction, often implicit and often involving a pH change. In the copper case, it is the reaction of the carrier with acid. Again, the process is like extraction, where such concentration is common.

Although facilitated transport membranes are highly selective, they suffer from a major problem, namely instability, that has precluded industrial adoption. Four main causes of membrane instability have been identified: solvent loss, carrier loss, osmotic imbalances, and spontaneous emulsification.^{6,7} Each merits more discussion:

Solvent Loss: Solvent loss occurs when the liquid membrane solvent dissolves in the adjacent solutions and eventually ruptures. As a result, facilitated transport solvents are usually chosen for their relative insolubility in the adjacent solutions. In practice, rupture usually occurs for some other reason, before the solvent in the membrane has dissolved significantly, so this mechanism is only infrequently a significant cause of instability.

Carrier Loss: The mobile carrier makes the diffusing solutes more soluble in the membrane. Unfortunately, the diffusing solutes also tend to make the mobile carrier more soluble in the adjacent solutions. Moreover, many carriers are chemically unstable, including many proposed for separating oxygen from air. These disadvantages can sometimes be reduced by modifying the carrier chemistry, for example reducing its water solubility by adding side chains to the mobile carrier, just as is done in extraction.

Osmotic Imbalances: A facilitated transport system often involves concentration differences between the feed and the permeate solution that are 1.0 M or higher. These imply osmotic pressure differences of 40 atmospheres or more. Such pressure differences can force the liquid membrane out of the pores of the polymer support. This effect can be reduced by using supports with very small pores or good wetting, but it remains a chief cause of membrane instability.

Spontaneous Emulsification: Most membrane additives are amphoteric. For example, the oximes used to extract copper ions from aqueous solution into kerosene can also extract some water. This water is sometimes "stranded" within the membrane, eventually producing trails of water droplets which coalesce into channels across the membrane. Such emulsification is less well studied than the osmotic imbalances, but it may also be a serious cause of membrane rupture.

Other factors that may influence the membrane performance are membrane viscosity, membrane density and support wetting. These issues are less significant than those concerned with membrane stability.

MTR-052-GRP

Figure 4-2. Copper concentration by facilitated transport. While the basic feed contains only 100 ppm copper, the acidic product has over 1000 ppm copper.¹

4.1.3 Membrane and Module Design Factors

Immobilized Liquid Membranes: As described above, liquid membranes for facilitated transport can be stabilized in the pores of a microporous polymer membrane. Ideally, the microporous membrane supports should have very small pores, so that the effects of any applied pressures are minimized. The pores should also be as homogeneous as possible. In practice, many ultrafiltration and microfiltration membranes work well. Hydrophobic microporous polypropylene membranes are commonly used.

The membrane support should have a large surface area per volume to allow a large flux per volume. Plate-and-frame and hollow-fiber supports, such as those shown in Figures 4-3a and 4-3b, are often used. Capillary hollow-fiber systems are generally preferred. The support is prepared simply by wetting it with the membrane liquid. Sometimes, this wetting is enhanced with vacuum or pressure, but this is rarely essential.

Emulsion Liquid Membranes: A second method of using facilitated transport membranes is as water-in-oil-in-water emulsions, shown in Figure 4-3c.^{3,8,9} An example of an emulsion liquid membrane would be droplets of water emulsified by rapid stirring in a chloroform solution of surfactant and of mobile carrier, then dispersed in the mixed salt feed solution by slow stirring. Salts like potassium chloride diffuse from the mixed feed across the chloroform into the internal phase. This method is also called "double emulsion membranes," "liquid surfactant membranes," and "detergent liquid membranes."

The advantage of emulsion liquid membranes is the large area per volume, which enables separations to take place at great speed. The principal disadvantage is the complexity. The membrane separation may be fast, but the emulsion manufacture, the emulsion separation, and the recovery of the internal phase from the centers of the droplets can be extremely difficult.^{10,11}

Membrane Contactors: A final method of employing facilitated diffusion is to make a membrane contactor. A membrane contactor typically uses a hollow-fiber module containing microporous membranes, as shown in Figure 4-3d. Feed flows through the lumens of the hollow fibers, and extractant flows countercurrently on the shell side of this module. Solute entering in the feed is removed by the extractant. The solute is later stripped from the extractant under different conditions in a second module. This process is really a hybrid, combining aspects of both conventional extraction and liquid membranes. Alternatively, one can use two sets of hollow fibers immersed in a "liquid membrane" solution. One set of fibers carries the feed, and the other contains the product stream. In either case, the membrane contactor performs the same function as a packed tower.

Membrane contactors exhibit the advantages of liquid membranes, but avoid disadvantages of absorption and extraction.^{12,13} They have a large area per volume and hence produce fast separations. They are unaffected by loading, by flooding, or by density differences between feed and extract. In this sense, they are a poor man's centrifugal extractor. Membrane stability problems are avoided by essentially putting one membrane interface in an extraction module and the other interface in a stripping module. However, although the performance of

(a) Flat Sheet Membranes

(b) Hollow Fiber Membranes

(c) Emulsion Liquid Membranes

(d) Hollow Fiber Contactor

Figure 4-3. Module Geometries. Most facilitated diffusion systems borrow modules from ultrafiltration. The exception is the emulsion liquid membrane geometry shown in (c).

membrane contactors in the laboratory is excellent, their performance under industrial conditions is only currently being explored. The energy requirements of such a system have yet to be clarified.

4.1.4 Historical Trends

Studies of facilitated transport originated in biochemistry.¹⁰ Living membranes often show fluxes that are faster and more selective than would be expected to be achieved by the membrane components. Living membranes often concentrate specific solutes, but are easily poisoned by particular drugs. These observations led to the postulates of mobile carriers. Theories of mobile carriers were later tested by studies on blood, where hemoglobin facilitates diffusion of oxygen and of carbon dioxide.

The high fluxes, high selectivity and specific concentration achieved in biological membranes spurred research into synthetic membranes and carriers. The simultaneous development of microporous polymer films abetted this development by providing membrane supports. By 1975, facilitated transport processes were being studied for acid gas treatment, metal ion recovery, and drug purification. None of these processes became commercial. Ironically, biochemical interest also waned, deflected into studies of chemically selective pores.

Since 1980, the most important research studies in the field of facilitated transport have focussed on membrane stability, an issue which remains unresolved.

4.2 CURRENT APPLICATIONS

Many fundamental studies of facilitated transport systems have been performed. Table 4-2 summarizes a recent review by Noble et al.⁸, and shows the broad scope of facilitated diffusion research to date.

The solutes shown can be roughly divided into three groups. The largest group includes metals, especially in their ionic forms. This group underscores the similarity between facilitated transport and extraction. A second group, gases, builds on parallels between facilitated transport and absorption. A third group consists of organics of moderate molecular weight, with an emerging bias towards pharmaceuticals. These fundamental studies have elucidated the detailed chemistry responsible for many types of facilitated diffusion.

In contrast to these fundamental efforts, commercial successes are sparse. The most serious, publicly detailed effort has been by Rolf Marr and his associates at the University of Graz, in Austria.⁹ These workers developed a large-scale emulsion liquid membrane process for the selective extraction of zinc from textile waste. The process is shown schematically in Figure 4-4. They used liquid membranes of diamines dissolved in kerosene. The product solution is first emulsified in the carrier medium. This emulsion is then re-emulsified with the feed solution. In the permeation step the zinc migrates into the interior product solution. The emulsion is then passed to a settler and the feed solution, now stripped of zinc, is removed as a raffinate. In a final step, the carrier-product emulsion phase is passed to a de-emulsifier where the emulsion is broken to produce a carrier solution, which is recycled, and a product solution containing

Table 4-2. Fundamental Studies of Facilitated Transport. ⁸

Permeable Species	Solvent or Surfactant	Carrier Species	Support
CO	DMSO	CuSCN, <i>N</i> -Methylimidazole	Poly(trimethylvinylsilane)
CO ₂ , H ₂ S/H ₂ , CO	H ₂ O, NMP	EDA, Hindered Amines	PFSA
CO/CH ₄	DMSO	CuCl and VCl ₃	Poly(trimethylvinylsilane)
CO ₂ /N ₂	H ₂ O	K ₂ CO ₃	Porous Polypropylene
CO ₂ /O ₂ and N ₂	Polyethylene Glycol	Ca, Na	Bulk Liquid
H ₂ S, CO ₂	H ₂ O	Carbonate	
H ₂ S/CO ₂	H ₂ O	Carbonate, Ethanolamine	Bulk Liquid
NO	<i>N</i> -Cyclohexyl-2-pyrrolidone	Fe(II), Zn(II)	Bulk Liquid
O ₂	DMF	Silicon Carbonate	Cellulose Acetate
O ₂ and CO	DMF	4-Vinylpyridine	Porous PTFE Film
O ₂ /N ₂	DMSO	(Co) Polyamine Chelate	Poly(trimethylvinylsilane)
O ₂ /N ₂	DMSO	(Ni) Pyridine Complex	Porous PTFE Film
O ₂ /N ₂	DMSO	<i>N, N'</i> -bis(2-aminobenzal)EDA	Polyarylene
O ₂ /N ₂	DMSO	Dipropylenetriamine Co Salt	Bulk Liquid
Cd, Hg, And Zn	PheMe	<i>m</i> -Dicyclohexano-18-crown-6	Bulk Liquid
Ac, Na, Ba, Co, Ni, Cu, Zn, Ag	CH ₂ Cl	Polyfluoroalkyl, -alkenyl Ion Exchangers	Bulk Liquid
Acetic Acid		Tertiary Amines	
Acetic Acid		Trioctylphosphineoxide	
Acetic, Benzoic, and Phenylacetic Acid;		LiOH	
Phenol and <i>m</i> -Cresol			
Ag ⁺	Cumene Solutions	DEHPA	Teflon
AgBr ₂ (-)	Toluene	DC18C ₆	Bulk Liquid
AgBr ₂ (-)		Macrocycles	
Alkali Cations	Chloroform	Polynactin, DB-18-C-6	Bulk Liquid
Alkali Metals	CH ₂ Cl ₂	Macrocycles	Bulk Liquid
Am		Amines and Alkylphosphoric Acids	
Am ³⁺ , Eu ³⁺	Decaline/ <i>N</i> -Dodecane	Neutral/Acidic Organic Phosphates	Composite Porous Films
Am(III)	Diethylbenzene	(Carbamoylmethyl) Phosphine	Polypropylene Film
Amino Acids	Diethylbenzene	Macrocycles	Bulk Liquid
Aminoalkyl Sulfonic, -carboxylic Acids	CHCl ₃	Tetraoctylammonium Bromide	Bulk Liquid
Benzene/Cyclohexane	H ₂ O	AgNO ₃	Porous PTFE Film
Bilirubin		Hexadecyltrimethylammonium Bromide	Bulk Liquid
C ₃ H ₆ /CH ₄	H ₂ O	Ag ⁺	Porous Film
Cd ²⁺		Aliquat 336	
Cd, Zn, Hg, Au		Macrocycle	
Co(II)/Ni(II)	H ₂ O	Dialkylphosphinic Acid/ <i>tert</i> -Alkylammonium Salt	Composite Porous Films
		Bis(Ethylhexyl)phosphate	
Co, U		Trioctylamine	
Cr	<i>N</i> -Decane	Alamine 336	Porous Polypropylene Film
Cr	Oil		
Cr ⁶⁺		Amine	

Table 4-2 continued

Permeable Species	Solvent or Surfactant	Carrier Species	Support
Cr ⁴⁺ , Hg ²⁺		Alamine 336	
Cr(VI)	Organic Solvent	Trioctylamine	Bulk Liquid
Cr(VI), Re(VII)	Organic Solvent	Quaternary Ammonium Chlorides	Bulk Liquid
Cr, Zn, Re, Tc V	SPAN 80	Allquat 336	
Cs, Sr, Co, U, Ce, Tc		DEHPA	
Cs, Sr, Co, U, Ce, Tc		8-Hydroxyquinoline	
Cu	ECA 5025, ECA 4360	2-Hydroxy-5-alkylbenzophenone	
Cu	Kerosene	Primary Amine	Porous Polypropylene Film
Cu	Kerosene	N-510 and P 204	Bulk Liquid
Cu	N-Dodecane	Diethylhexylphosphorous Acid	
Cu		2-Hydroxy-5-nonylbenzophenone oxime	Film
Cu	Dispersol	SME529	
Cu	Dodecane	Bis(2-Ethylhexylphosphoric Acid	Porous Hollow Fibers
Cu		LIX64N	
Cu		LIX65N	
Cu		LIX64N, Acorga P5100, 300	
Cu ²⁺ and H ⁺	Toluene	β -Hydroxy-oxime	Porous Polypropylene Film
Cu ²⁺ , NH ₄ ⁺	H ₂ O	Stearic Acid	
Cu, Co, Zn, Ni	H ₂ O	Di(2-Ethylhexyl)phosphoric Acid	Bulk Liquid
Cu, Ni, Zn	CH ₂ Cl ₂	Lipophilic Tetraamines	Bulk Liquid
Enantiomeric Enrichment	H ₂ O	Cyclodextrins	
Ethylene/Ethane	H ₂ O	AgNO ₃	Porous Film
Fe(III)	C ₂ H ₅ Cl ₂	18-Crown-6 Macrocycle	Bulk Liquid
Fe, Co	Organic Solvent	Methyltrioctylammonium	Bulk Liquid
H ⁺	Oil	Tridodecylamine	Electrode
H ₂ PO ₄ (-)		Oxomolybdenum(V)tetraphenyl Porphorin	
Halides	1,2-Dichloroethane	Ammonioimides	
Hg	CHCl ₃	Macrocycles	Bulk Liquid
Hg		Dibutylbenzoylthiourea	Bulk Liquid
HNO ₃	Decane	TBP, TAA	
HNO ₃	Diethylbenzene	Trilaurylamine	Bulk Liquid
Hydrocarbons	H ₂ O	Sulfolane, TEG	
K and Na Picrates		Crown Ethers	Bulk Liquid
L-Amino Acids		ADGEN 464	
L-Leu, L-Trp Me Esters		Dibenzo-18-crown-6	Bulk Liquid
La, Sm, Er, Fe, Ca, Na		Crown Ethers DB-18-C-6, B-15C-5	Bulk Liquid
Lanthanides, La, Sm, Gd, Er		DEHPA	
Li ⁺ , K ⁺ , Na ⁺		Octamethyltetraoxaquarterane	Bulk Liquid
Li ⁺ , Na ⁺ , K ⁺	CH ₂ Cl ₂	Monoaza Crown Ethers	Bulk Liquid
Metal M(+), M(2+) Cations	CHCl ₃	Amino Acids and Polypeptides	Bulk Liquid
Metal Nitrates, Pb, Ag, Tl		Macrocycles	

the separated zinc. The zinc process was installed in Lenzing, Austria, where it processed 1,000 m³/hr for at least six months.

Other efforts to demonstrate industrial processes have been stillborn. General Electric explored the possibility of acid gas removal using an aqueous carbonate liquid membrane supported by cellulose acetate.⁴ The project was abandoned at the pilot stage. Bend Research and General Mills Chemicals (now a division of Henkel) both studied copper removal using an oxime solution. They apparently abandoned the work because they found no compelling advantages over conventional extraction. Recovery of uranium from ore leach solutions was also developed by Bend Research to the pilot-plant stage, using amines immobilized in hollow-fiber modules. This work was also abandoned because of stability problems. In by far the largest effort, Exxon studied the recovery of metals and of drugs using emulsion liquid membranes, a geometry on which they hold broad patents, now beginning to expire.^{3,15,16,17} Both uranium and copper recovery were investigated, but neither process became commercial. One additional effort, a collaboration with Mitsui Chemical for recovering dissolved mercury, reached the pilot scale, but has since been abandoned.

Many Chinese and Eastern European commercial efforts on facilitated transport apparently continue, for reasons that are not clear. Pilot units for processing chromium and other metals are reported to be operating in China. The future prospects of these efforts are unknown.

4.3 ENERGY BASICS

Facilitated transport competes with gas absorption and with liquid extraction, but not with evaporation. It uses pressure differences or chemical energy, not thermal energy. As a result, facilitated transport membranes will have little effect on the direct use of thermal energy.

Facilitated transport systems tend to require the same amount of energy as conventional gas absorption and liquid extraction. For example, hydrogen sulfide separated by facilitated diffusion from flue gas must use a high-pressure feed and either a low-pressure product or a steam sweep. As a second example, copper recovered from dilute solution by facilitated diffusion requires almost the same acid per mole of copper as is required in liquid extraction. For the same separation, a similar amount of energy is needed.

The advantage of facilitated transport membrane processes lies not in their energy consumption, but in their speed. Facilitated membrane processes are much faster than their conventional counterparts. Used in the form of membrane contactors, facilitated transport processes are about eighty times faster than absorption towers of equal volume, and six hundred times faster than extraction columns of equal volume. This greater speed is primarily the result of the very large surface area per volume possible in membrane devices. This surface area can be achieved at a wide range of flows, independent of the constraints of loading and flooding which can compromise conventional unit operations. Although facilitated transport membranes are likely to be ten times more expensive per volume than existing equipment, their speed and space efficiency still offer some real potential for cost savings. This advantage alone, however, may not provide sufficient motivation to displace fully depreciated equipment in a

MTR-047-F

Figure 4-4. A schematic of the only commercialized facilitated transport system that has been built. This Austrian process uses emulsion liquid membranes to recover dissolved zinc.

stable chemical process industry. It could, however, have substantial impact in other smaller-scale applications, especially pharmaceuticals.

4.4 ECONOMICS

Only one commercial-sized facilitated transport membrane system has been installed, so no sensible discussion of the economics of the process is possible. It is possible, however, to highlight product areas where commercialization has been considered and identify the improvements necessary to make commercialization attractive. Four such product areas are obvious: metals, gases, biochemicals, and sensors.

4.4.1 Metals

Key metals of interest in the non-ferrous industry are copper and uranium. Not surprisingly, this is where most facilitated transport systems have been investigated.^{1,9,16,18} Both immobilized liquid membranes and emulsion liquid membranes have been used; both work effectively; both have been tried at the pilot scale; both have been abandoned.

The full development of facilitated transport membrane systems for these applications may have been inhibited by a general depression in the metals industry. Recent increases in copper prices, and interest in superconductivity research using rare earths, make it worth reviewing the possible advantages for facilitated transport of metals.

Energy Use: The energy use of facilitated membrane separations will be similar to that of extractions. In some cases, facilitated transport can operate with "dirty" feeds which require filtration before liquid-liquid extraction. There is no energy advantage in using facilitated transport membranes rather than conventional extraction processes.

Separation Speed: Membrane separations can be hundreds of times faster than conventional extractions. For copper, this speed is not a significant advantage, because existing conventional extractions take only about twenty minutes per stage. For hazardous materials, however, including radioactive isotopes, it means the equipment can be much smaller. For these hazardous materials, there is an opportunity.

Extractant Costs: The amount of extractant inventory is dramatically reduced. Solvent entrainment in the raffinate is usually minor with supported liquid membranes, but can be significant in conventional extraction. However, extractant losses caused by dissolution in the feed solution are the same as those in extraction. Advantages here are minor except for very expensive extractants.

Stable Membranes: One of the advantages of membrane technology in general is that membrane systems run reliably with minimal operator attention. Currently, all liquid membranes have major stability problems. The ability to perform facilitated transport in stable membranes would be a major advance. Improved membrane stability is the key to better economics for metal separations.

4.4.2 Gases

Gas separations using facilitated diffusion have focused on three areas: oxygen separation from air, acid gas treatment and olefin-alkane separation. In each case, the attraction of facilitated diffusion comes from high speed and higher selectivity. Some processes also claim lower regeneration costs, and hence energy savings. The chief concern again is membrane stability.

4.4.2.1 Air separation

Oxygen and nitrogen are produced industrially in greater quantities than all chemicals except sulfuric acid, so their separation is of major importance and has been studied for many years. The minimum energy consumption possible to perform an oxygen/nitrogen separation, based on the free energy of unmixing, is about 0.09 kWh/m³ of oxygen. This separation is now carried out commercially by cryogenic distillation, pressure swing adsorption, and polymer membranes. The energy currently used for cryogenic distillation is 0.4 kWh/m³ of oxygen, or less than five times the thermodynamic minimum. The energy used by pressure swing adsorption (PSA) is somewhat higher. The capital costs of a PSA system are, however, lower than those of a cryogenic unit for small to medium sized installations.

Commercial polymer membrane-based air-separation units have been successful, especially in producing nitrogen-enriched air for inert blanketing. The wide application of membrane separation has been inhibited by membrane selectivity. Facilitated transport offers higher selectivity, so it could, in theory at least, outperform diffusion through polymer materials. Thus the outlook for facilitated transport in gas separation is unfocused but positive.

Past studies of facilitated transport have used solutes to complex oxygen, and hence enhance its flux across the membrane.¹⁹⁻²² In most studies, porphyrins or Schiff bases were used as complexing agents. The first successful systems used these solutes in immobilized liquid membranes, which gave selective separations but were not stable.²⁴ In this case, the instability comes largely from the chemical decay of the carriers, not from failure of the membrane films. No published studies discussing the energy required for facilitated transport are available.

Other studies have explored facilitated oxygen transport systems in which the oxygen complexing solutes are contained in solid films. Recently, some Japanese groups have succeeded in making oxygen-selective membranes in this way.^{23,24} These membranes are apparently not yet stable, and the basis for their claimed success is frail. However, they do show characteristics of facilitated diffusion, and may become a truly major advance.

4.4.2.2 Acid gases

Acid gas feed streams are best organized under three subheadings: flue-gas desulfurization, industrial gas treating and organic sulfur removal. In flue-gas desulfurization, the target is to remove 90% or more of the 0.2% sulfur dioxide present in the gas. In gas treating, the goal is to reduce the concentration of carbon dioxide and hydrogen sulfide to perhaps 100 ppm (4 ppm for hydrogen

sulfide in natural gas). In the third case, organic sulfur concentrations are to be reduced to 1 ppm or less.

Currently, these separations are accomplished by gas absorption. When the feed concentrations are high, the acid gases are dissolved in non-reactive ("physical") solvents. When the feed concentrations are lower, the acid gases are more easily removed with reactive ("chemical") solvents. Many of these chemical solvents are synthesized to react reversibly; these are the best candidates for facilitated diffusion.

Many workers have studied facilitated diffusion as a means of separating acid gases.^{4,25,26} Their efforts show that the diffusion process has the same energy use and selectivity as conventional gas absorption. It is much faster per volume of equipment. However, membrane stability and membrane fouling remain major, unresolved concerns. Moreover, new chemical solvents of greater capacity have essentially increased the capacity of existing gas absorbers, and hence reduced the need for new technology. As in the case of metals, facilitated transport has not shown compelling advantages over currently practiced technology.

4.4.2.3 Olefin-alkanes and other separations

The separation of olefins from alkanes can only be accomplished effectively by absorption or distillation. Thus facilitated transport can achieve savings in energy and improvements in selectivity. The selectivities for facilitated transport membranes should exceed those in conventional polymer membranes.

Past efforts at olefin/alkane separations have exploited the reactions of olefins with metal ions, such as Ag^+ , Cu^+ , and Hg^+ .^{27,28} Originally, the ions were used in aqueous nitrate solutions; later, in cation exchange membranes. Within these membranes, ions are electrostatically tethered but still mobile, even in the absence of water. As a result, such membranes avoid many of the stability problems that plague facilitated diffusion.

Pez, et al., at Air Products, have recently developed molten salt membranes for ammonia/hydrogen and other separations.²⁹⁻³¹ Their results suggest that the transport mechanism through the molten salt may be similar to that in ion-exchange membranes. Both the ammonia separations and olefin/alkane separations will be especially attractive if the feed is already at high pressure. The technology to perform these separations works well at laboratory scale. Given that this is the one area of facilitated diffusion where stability is not an overwhelming difficulty, the time appears ripe for scale-up and commercial exploitation.

4.4.3 Biochemicals

Specialty chemicals, especially high value added materials, such as antibiotics and proteins, are frequently mentioned as candidates for facilitated transport separations. Although facilitated transport systems will work, the energy demands and extractant costs will be comparable with those of conventional processes in most cases.

Fast facilitated diffusion may be superior to slower conventional extraction for unstable solutes. For example, penicillin is stable as the sodium salt but unstable as the free acid. It is purified by adding acid to the salt to make the free acid, extracting the free acid into a solvent such as amyl acetate, and stripping the salt out of the acetate with base. The faster the extraction, the greater the yield. However, although facilitated extraction has been a common idea for fifteen years, it is not practiced commercially for penicillin purification.

4.4.4 Sensors

Facilitated diffusion is used in a variety of chemical sensors, especially for biochemicals. It works well, offering high selectivity. However, the market for biochemical sensors is extremely fragmented, with literally hundreds of small, highly specialized uses. As a result, the tendency is for instrument manufacturers to produce generic electrode assemblies, into which the buyer installs his own selective chemical system. There is little potential, within the context of the present study, for recommending development efforts that would have any impact in such a market.

4.5 SUPPLIER INDUSTRY

There are currently no suppliers of equipment for facilitated transport.

4.6 RESEARCH CENTERS AND GROUPS

Table 4-3 summarizes the research centers and investigators active in facilitated transport research. The list is broken down by membrane type.

The first group, which is the largest and most diverse, includes work that extends beyond the boundaries of liquid membrane studies. This group includes the greatest numbers outside of the United States. Advances in this area may well continue to be scientifically successful, but are unlikely to be practiced commercially.

The second group, which focuses on membrane contactors, is now entering commercial practice. The scientific development of this area is largely complete: the design equations are known, the key operating steps are well established, and some important applications have been identified. So far, much of the work has been academic. What is needed is encouragement for more commercial applications. This is especially true in the area of acid gases and antibiotics.

The third group lists those studying solid membranes capable of facilitated diffusion. Interestingly, the group has a large number of industrial scientists, a reflection of the major potential gain. At present, these industrial scientists are aiming at specific separations, like those of air or of olefin-alkanes. Their academic counterparts aim more at exposing mechanisms, rather than developing processes.

Table 4-3. Facilitated Transport Researchers

TOPIC/Investigator*	Area of Interest
<u>LIQUID MEMBRANES</u>	
<u>Noble and Pellegrino</u> (NIST)	Best review article
Bunge (Colorado School of Mines)	Metals
Danesi (Europ. Atomic Energy)	Rare earths
Freisen (Bend Research)	Air
Rolf Marr (U. of Graz)	Commercial zinc process
Noble (U. of Colorado)	Good theoretical perspective
Stroeve (UC Davis)	Facilitation by micelles
Wasan (Illinois Inst. of Tech)	Emulsion liquid membranes
Govind (U. of Cincinnati)	Air
<u>MEMBRANE CONTACTORS</u>	
<u>Sirkar</u> (Stevens Institute of Tech.)	Liquid extraction
Aptel (Toulouse U.)	Water
Callahan (Hoechst-Celanese)	Gold
Cussler (U. of Minnesota)	Acid gases; proteins
Fane (U. of New South Wales)	Membrane distillation
<u>SOLID MEMBRANES</u>	
<u>Cussler</u> (U. of Minnesota)	One of few analyses
Ho (Exxon)	Olefin-alkane
Nishide (Waseda U.)	Air
Noble (U. of Colorado)	Theory
Pez (Air Products & Chemicals)	Molten salt glasses
Way (Oregon State)	Air
Yoshikawa (Kyoto U.)	Acid gases

* The underlined author is a good starting point.

4.7 CURRENT RESEARCH

Facilitated transport remains a specialized research area, which is practiced mostly in the academic sphere. A listing of published authors would show a number from industry, but would be misleading, because many industrial scientists only publish their work after it has been abandoned.

The most active industrial program in this area is at Air Products and Chemicals, where facilitated diffusion of ammonia and other gases through molten salts are being examined. The company has recently been awarded a contract of \$1.2 million from the DOE, Office of Industrial Programs, for further development of the work.

At Air Products and Chemicals, viscous, extremely low volatility liquids and molten salts are used as liquid membranes. These membranes can withstand pressure differences and high temperatures. Although the first membranes of this type to be developed were molten salts that needed to be operated at temperatures in excess of 400°C, the newer systems are based on polyamine liquids that can be used at room temperature.

Pez et al. have described a facilitated transport membrane for oxygen/nitrogen separation based on molten lithium nitrate.³⁰ The molten salt is supported in the pores of a stainless steel mesh and the membrane is operated at 429°C. Nitrite ions act as the carrier to selectively transport oxygen across the membrane as nitrate ions. Nitrogen does not react with the salt and hence its permeation rate is minimal. A similar approach is used for ammonia separation, using zinc chloride as the molten salt.³¹

The Air Products group has also studied membranes based on salts that are molten at room temperature. These materials are also referred to as "ionic liquids". Examples are triethylammonium chlorocuprate and ammonium thiocyanate. The former has been used as a liquid membrane for the separation of carbon monoxide from nitrogen, a separation not yet achievable with polymer membranes. The latter liquifies in the presence of ammonia to form an electrically conducting liquid membrane.

A refinement is the use of molten salt hydrates, which resemble molten salts, but include some bound water molecules.²⁹ Molten salt hydrates typically have lower melting points, and can dissolve larger volumes of gas, than molten salts themselves. For example, Air Products used tetramethylammonium fluoride tetrahydrate in a liquid membrane for the selective separation of carbon dioxide from mixtures containing hydrogen and methane.

4.8 FUTURE DIRECTIONS

Potential applications for facilitated transport are listed and rated in Table 4-4. The most promising area in the metal separation category is copper extraction, and in the gas separation category, oxygen/nitrogen separation from air. The technology is not attractive for hydrocarbon separations or water separations, both of which can be accomplished much more efficiently by other membrane-based technologies.

4.8.1 Metal Separations

The key areas of interest for the use of facilitated transport in metal separation continue to be copper and uranium extractions. Recent sharp increases in copper prices make improvements in existing copper producing processes, and development of new processes, worthwhile. The market for uranium is less predictable, because it will always depend on the acceptability of nuclear power generation.

If superconducting materials begin to be developed on a large scale, there will be a rapid growth in the demand for rare earths to make these materials. Rare earths could be separated effectively by facilitated transport. However, any research support for this area should wait until needs are clearer.

Table 4-4. Applications for Facilitated Transport

Application Area	Importance	Prospects for Realization	Comments
<u>Metal Separation</u>			
Copper Extraction	8	Good	Stable membranes with the speed and selectivity of facilitated diffusion remain the key.
Uranium Purification	5	Fair	
Rare Earth Recovery	3	Fair	
<u>Gases</u>			
Air	10	Good	This area is the most varied and will need different responses to different challenges.
Acid gases	6	Good	
Hydrogen/Methane	2	Poor	
<u>Biochemicals</u>			
Commodities	2	Fair	Facilitated transport will work, but it is unlikely to be used commercially. Membrane contactors will become standard for antibiotics and flavors.
Antibiotics	8	Excellent	
Flavors	5	Fair	
Proteins	1	Poor	
<u>Hydrocarbon Separation</u>			
Olefin-Alkane	6	Good	The olefin-alkane effort merits more work. The other separations are better done with other membranes.
Aromatic-Aliphatic	3	Poor	
Linear-Branched	3	Poor	
Solvent Recovery	6	Poor	
<u>Water Removal</u>			
Ethanol-Water	2	Poor	Pervaporation and ultrafiltration have greater promise.
Gelatin-Water	2	Poor	

Facilitated transport of metals will develop in two directions. First, membrane stability must be improved. Efforts to date to improve liquid membrane stability have been partially successful, but have not provided compelling reasons to abandon extraction. Staging membranes currently seems impractical.³² Another approach is to accept that the carrier liquid will be lost or degraded and to replace it periodically. Such a technique seems cruder and less elegant than, for example, the "contained liquid membranes" of Sirkar.¹³ However, membrane reloading may merit some further consideration.

The obvious alternative to improving liquid membrane stability is to foster development of solid facilitated transport membranes containing reactive groups responsible for selective separations.^{23,24} The reactive groups are parallels of the mobile carriers in liquid membranes; reflecting this parallel, they are sometimes called "chained carriers" or "caged carriers." The mechanism by which solid facilitated transport membranes work is not yet understood. Authors often use words like "hopping" and "flexing," and analogies with "bucket brigades" or "chemically selective pores." One group has whimsically discussed performance in terms of Tarzan paddling a canoe vs. swinging from a vine, as shown in Figure 4-5.

Research into solid membranes capable of facilitated diffusion is a key area that merits fundamental support. The public and academic research effort should initially focus on gaining a better understanding of the transport mechanisms. This will aid parallel industrial efforts to develop practical systems.

Facilitated transport of copper and uranium could be improved by using membrane contactors, which do not suffer so severely as liquid membranes from problems associated with carrier loss or degradation. A membrane contactor typically uses a membrane module containing microporous hollow fibers to carry out an existing liquid-liquid extraction. It can also use one module containing two types of hollow fibers, one for feed and one for product. The result can be a fast, efficient separation effected at a fraction of the cost of a centrifugal or conventional extraction. However, the performance of a membrane contactor under the conditions actually found in the metals industry remains unknown. Investigating membrane contactors, at least for copper separations, deserves support for development.

In summary then, for metal separations, the most worthwhile areas in which to commit research resources, are:

1. Understanding and developing solid facilitated transport membranes.
2. Developing membrane contactors.

A lower priority, but of some merit, is to find improved ways to reload membranes with liquid carriers.

4.8.2 Gases

Facilitated transport of gases continues to be dominated by questions of membrane stability. Improved membrane stability is being actively pursued by various uncoordinated strategies, of which three stand out. First and most dramatically, several groups are using ionic mobile carriers tethered electrostatically within ion-exchange membranes. So long as the ions within the membrane are protected from side reactions, the membranes will be stable.

(a) Mobile Carriers

(b) Chained Carriers

Figure 4-5. Transport Mechanisms. Facilitated transport in liquid membranes used mobile carriers functioning as in (a); the parallel process in solid membranes requires partially mobile carriers schematically suggested by Tarzan's vines.

Second, other groups are using non-porous glasses or gels as membranes. The most promising membrane materials are the molten salts developed by Air Products. Third, some workers are using membranes with smaller, well defined pore sizes, including microporous ceramics. All of these efforts are in the relatively early stages of development, and it is too early to assess their ultimate success.

Interestingly, efforts to improve membrane stability are without definite targets. Everyone believes that improved stability is vital, but there is no consensus as to whether an acceptable membrane stability would be measured in weeks, months or years.

The key gas separations for facilitated transport are those of air and of acid gases. The most important gas separation is that of air, where polymer membranes are only modestly selective, and where significant improvement in performance might be achieved by facilitated transport membranes. The second important separation is that of acid gases, which can probably be improved by facilitated diffusion. Other important gas separations, like hydrogen-nitrogen and carbon dioxide-methane, are poor candidates for the method.

The success of polymer membranes for air separation has had a major impact throughout the chemical and chemical engineering industries, and has been a factor in the increased interest in membrane separations by large corporations and the U.S. government. Polymeric membranes do not exhibit high oxygen/nitrogen selectivities. The increased chemical selectivity possible with facilitated diffusion has spurred development of reactive solutions which complex oxygen. Reactive solutions make good liquid membranes, but the research effort has stalled for two reasons. First, the solutions are often too reactive: they complex oxygen and dimerize so strongly that stripping is difficult. This excess reactivity can probably be solved by new chemistry, in a comparable way to that in which temperature- and pressure-sensitive amines were developed for acid gas absorption. The second reason is, of course, the lack of membrane stability, an area where there continues to be ongoing research.

Facilitated transport of oxygen in solid membranes continues to attract major research efforts, many in industry. Unfortunately, failures are rarely published, so that many unknowingly repeat earlier unsuccessful ventures. The situation can be almost comic; for example, at least five different groups have found that hemoglobin analogues in rubbery polymer films do not facilitate oxygen transport. In spite of this, major effort for oxygen facilitation in solid membranes will and should continue, spurred by recent reports of Japanese success. The problem is too important to ignore, and the rewards for the development of stable facilitated transport membranes for oxygen/nitrogen separation would be substantial.

The separation of acid gases by means of facilitated diffusion is technically feasible, but has not been vigorously pursued and is not practiced commercially. The lack of interest may reflect direct competition with polymer membranes or with gas absorption, where new reactive liquids have increased the capacity of old equipment. Solid facilitated transport membranes suitable for carrying out

acid gas separations might be possible, but do not seem to be under active development.

A new direction for facilitated diffusion of acid gases uses membrane contactors. The fundamentals of the process are in place, but the practical utility has yet to be demonstrated. Demonstrating this utility merits more technical effort. A second direction in acid gas treatment is the use of ceramic membranes as liquid membrane supports. Ceramic membranes presently have a low surface area per volume, but they do have small pores and remain stable at high temperatures. They can remove low concentrations of gases such as hydrogen sulfide without feed recompression, though they are less effective than absorption. This direction has yet to show compelling advantages over gas absorption.

In gas separation, research into oxygen facilitation in solid membranes is most important. Work on solid facilitated transport membranes for other separations has merit, as does further development work on membrane contactors

4.8.3 Biochemicals

Facilitated transport continues to be viewed as a natural separation technique for unstable, costly biochemicals, where fast, high-purity separations are imperative. This view is oversimplified.

Some interesting biochemical examples of facilitated transport aim at chiral separations. These require mobile carriers selective for, for example, a d-isomer. Existing carriers are not sufficiently selective to be commercially attractive. Alternatively, some workers have used a "membrane reactor," which uses an enzyme to oxidize the d-isomer and a membrane to separate the l-isomer and the oxidized form of the d-isomer. Membrane reactors of this type, although they do not use facilitated diffusion, may be appropriate to perform the same types of biochemical separations as could be done by facilitated transport.

However, despite the superficial match between biochemical products and facilitated transport processes, a major research effort in this area is not justified. To understand why, a comparison should be made between the production methods for commodity chemicals, such as those made by Exxon Chemical Company, and specialized pharmaceuticals, as manufactured by the Upjohn Company, for example. Exxon's 23 well defined chemical products are made on the large scale, each by dedicated equipment working 24 hours a day. The equipment is optimized for each product. An efficient production line of this type is basic to profitability in commodity chemicals. Upjohn's 343 products, on the other hand, are made on the small scale. For specialized drugs and products, the annual demand may be 20 kg or less. As a result, production is carried out batchwise, on non-dedicated units that may be operating under far from optimal conditions for that particular application. However, Upjohn's strategy is entirely appropriate to the market, where highly sophisticated equipment lying idle for most of the time would be completely impractical.

The new biotechnology products now beginning to come onto the market also fall into the specialized, limited market category. For example, the anticipated demand for tissue plasminogen activator (TPA), an agent proven to dissolve blood

clots, is around 80 kg/year. Factor VIIIc, used in treating hemophilia, is consumed at the rate of about 60 grams/year in the United States, and is supplied by five competing companies. Even bovine growth hormone, expected to be a major biotechnology product, has an expected demand of about 20 tons/year. It is not feasible to devote a major effort to develop facilitated transport systems to be used in making this type of product, when the advantages to be gained over other already well developed membrane and non-membrane processes are marginal. For example, ultrafiltration, a fully mature membrane technology, can perform a variety of biological separations adequately. For solvent recovery in the pharmaceutical industry, gas separation membranes or pervaporation membranes would work as well, or better than facilitated transport membranes.

In the biotechnology area, therefore, a facilitated transport research effort is not recommended.

4.8.4 Hydrocarbon Separations

As discussed in Section 4.4.2.3, facilitated transport can effectively separate olefins and alkanes. The membranes used for this separation, which are cation exchangers with mobile carrier metal ions, are stable. However, this promising direction for facilitated diffusion has stalled. Industrial development has ceased, and academic research has tended to shift to air separations. It is not clear why this opportunity is not being pursued, particularly as energy and cost savings could probably be achieved by a facilitated transport process.

These stalled olefin separations are the only promising application for facilitated transport of hydrocarbons. Aliphatic and aromatic hydrocarbons are better separated by distillation. When this fails, pervaporation is a better choice than facilitated diffusion. The exception might be if azeotropes inhibit distillation and if highly selective complexing of aromatics is possible. Linear vs. branched hydrocarbons are more effectively separated by adsorption. Solvent recovery, potentially a large area, is better approached with polymer membranes. Except for olefins, facilitated diffusion is a bad choice for hydrocarbon separations.

4.8.5 Water Removal

One can imagine mobile carriers which would react with molecules of water and facilitate their transport. These carriers might even produce greater speed and selectivity than can be attained by other means. However, these advantages would probably be outweighed by membrane stability problems. At least at present, facilitated transport is a poor second choice compared with pervaporation and ultrafiltration.

4.8.6 Sensors

Although facilitated transport is not commonly used for commercial separations, it is often used for chemical sensors. For example, to measure the concentration of glucose in the presence of other sugars, one can cover a pH electrode with a liquid membrane containing glucose oxidase. This enzyme oxidizes glucose, producing a pH change sensed by the electrode. Such facilitated transport electrodes are common and effective, especially when they concentrate the solute of interest, and hence amplify the basic signal.

The development of these sensors will continue. It merits technical effort, though not necessarily by DOE. For example, a sensor for the AIDS virus seems better suited to NIH sponsorship, but a sensor for plastic explosive might be of DOE interest. Each of these sensors might be made more sensitive by use of facilitated diffusion.

4.9 RESEARCH OPPORTUNITIES: SUMMARY AND CONCLUSIONS

Facilitated transport is more selective and less stable than other types of membrane separations. It does not merit dramatically increased technical effort. However, it does provide some opportunities which, if selectively pursued, can yield major advances.

Eight research opportunities are given in order of importance in Table 4-5. These opportunities echo the conclusions of the earlier sections. Three are concerned with solid membranes showing facilitated transport capabilities; three focus on membrane contactors; and only two deal with conventional liquid membranes. Each group merits more discussion.

The group loosely defined as solid membranes includes molten salt membranes, which are much less volatile than ordinary liquid membranes, and gels, which have higher viscosity and a more pronounced structure. The three projects on solid facilitated diffusion parallel similar efforts that might be carried out with other types of membranes. That for air, which is most important, will compete with cryogenic distillation and with pressure swing adsorption. That for olefins competes with adsorption and extraction. The study of solid transport mechanisms is more fundamental and longer term.

Interestingly, all three solid membrane topics probably require more chemistry than engineering. For example, for air separations, the goal should be the synthesis of still more oxygen-complexing species stable under process conditions. At present, the goal need not include optimal membrane geometry, mass transfer and concentration polarization, and mathematical modeling. We need a process which has the potential of working well before we can demand its optimization.

The second group of topics, dealing with membrane contactors, have a bastardized background but a bright future. The modules used for membrane contactors are based on cheap, simple hollow fibers, not expensive, exotic units. Such modules can contain liquid membrane solutions with attractive properties.

Membrane contactors will be a significant growth area in the next five years. As designs are optimized, many applications will appear where substantial energy savings are possible. Membrane contactors seem immediately valuable for drugs, where they can give extractions of one hundred stages for less investment than conventional equipment containing five stages. Applications to gas absorption are less certain. Flue gases are the best defined short-term target, but aeration and chlorinated hydrocarbon stripping may also prove attractive long-term targets.

Table 4-5.Future Research Directions for Facilitated Transport

Research Topic	Importance	Prospects for Realization	Comments
Solid facilitated oxygen selective membranes	10	Good	Air separations of higher selectivity are a target common to all types of membranes.
Optimal design of membrane contactors	8	Excellent	As membranes get better, module design maximizing mass transfer per dollar becomes key.
Solid facilitated olefin-selective membranes	6	Fair	Membrane life is the key question, especially with sulfide contaminants.
Membrane contactors for copper and uranium	5	Excellent	Dramatic successes for drugs can be repeated with metals and possibly with toxic waste.
Membrane contactors for flue gases and for aeration	4	Good	Success in the field is less certain than success in the lab.
Mechanisms of solid facilitated transport	4	Fair	Chemical reactions for facilitated transport promise improved selectivity.
Enhanced liquid membrane stability	2	Fair	Even if successfully made, liquid membranes have not proved superior to extraction.
Liquid membranes for biotechnology	1	Excellent	Systems work, but applications are very small scale; chances of acceptance are remote.

The last two topics in Table 4-5, both of which involve conventional liquid membranes, are of lower priority. That on membrane stability, which is the more important, should include setting targets for membrane stability, and measuring how closely existing membranes approach these targets. At present, although everyone agrees that stability is crucial, no one has considered whether a stability measured in weeks, months or years would be technically or economically acceptable. Finally, although liquid membranes will give good separations of biochemicals, they are unlikely to be used commercially for the reasons detailed in Section 4.8.3.

A possible time line describing these efforts is shown in Figure 4-6. The clear region in this figure represents fundamental research; the shaded region is development work; and the stippled region indicates practice. The width of the bars represents the amount of effort merited.

While this line is speculative, its implications seem reasonable. Liquid membranes represent a small, almost entirely fundamental effort which will get smaller as other forms of facilitated diffusion become more attractive. Membrane contactors already have their fundamentals in place; they should see rapid development and commercialization. Facilitated transport in solid membranes both has the greatest promise and the greatest problems. It will require the most fundamental work before it becomes practical.

Six areas where little research appears to be warranted are:

1. Alcohol-water separations;
2. Emulsion liquid membranes;
3. Facilitated diffusion of proteins;
4. Hydrocarbons, excluding olefins;
5. Mathematical models of liquid membranes; and
6. Mathematical models of staged membranes.

These topics are unlikely to produce significant advances in our use or knowledge of facilitated transport.

Figure 4-6. A Proposed Time Line for Facilitated Transport. The clear region represents fundamental research; the shaded region is development work; and the stippled region indicates practice. The width of the bars represents the amount of effort merited.

REFERENCES

1. Cussler, E. L., Diffusion, Cambridge, London (1984).
2. Izatt, R. M., R. L. Bruening, J. D. Lamb, and J. S. Bradshaw, "Design of Macrocycles to Perform Cation Separations in Liquid Membrane Systems," paper at Second Annual National Meeting of the North American Membrane Society, Syracuse, N.Y., June, 1988.
3. N.N. Li, U.S. Patent 3,410,794 (1968).
4. Ward, W. J., "Analytical and Experimental Studies of Facilitated Transport," AIChE J., **16** 405 (1970).
5. Cussler, E. L., "Membranes Which Pump," AIChE J. **17**, 1300-1303 (1971).
6. P.R. Danesi, L.Reichley-Yinger and P.G. Richert, "Life-Time of Supported Membranes," J. Memb. Sci. **31**, 117-145 (1987).
7. A.M. Neplenbroek, D. Bargeman and C.A. Smolders, "Stability of Supported Liquid Membranes," paper presented at 7th European Summer School in Membranes Science, Twente University, June, 1989.
8. Noble, R. D., C. A. Koval, and J. J. Pellegrino, "Facilitated Transport Membrane Systems," Chem. Engr. Prog., **85**(3) 58-70 (1989).
9. Draxler, J. W. Furst, and R. Marr, "Separation of Metal Species by Emulsion Liquid Membranes," J. Memb. Sci., **38**, 281 (1989).
10. Sharma, A., A. N. Goswami, and R. Kuishma, "Use of Additives to Enhance the Selectivity of Liquid Surfactant Membranes," J. Memb. Sci., **40**, 329 (1989).
11. Nakashio, F., M. Gato, M. Matsumoto, J. Irie, and K. Kondo, "Role of Surfactants in the Behavior of Emulsion Liquid Membranes - Development of New Surfactants," J. Memb. Sci., **38**, 249 (1988).
12. Yang, M.C., and E. L. Cussler, "Artificial Gills," J. Memb. Sci., **42**, 273 (1989).
13. Prasad, R., and K. K. Sirkar, "Dispersion-Free Solvent Extraction with Microporous Hollow-Fiber Modules," AIChE J. **33**, 1057 (1987).
14. Stein, W. D., Transport and Diffusion Across Cell Membranes, Academic Press, Orlando, 1986.
15. Li, N. N., R. P. Cahn, and A. L. Shier, "Water in Oil Emulsions Useful in Liquid Membrane," U.S. Patent #4,360,448, Nov. 23, 1982.

16. N.N. Li, R.P. Cahn, D. Naden and R.W.M. Lai, "Liquid Membrane Processes for Copper Extraction," Hydrometall. **9**, 277 (1983).
17. E.S. Matulevicius and N.N. Li, "Facilitated Transport Through Liquid Membranes," Sep and Pur. Methods **4:1**, 73 (1975).
18. Baker, R. W., "Extraction of Metal Ions from Aqueous Solution," U.S. Patent #4,437,994, Mar. 20, 1984.
19. R.J. Bassett and J.S. Schultz, "Nonequilibrium Facilitated Diffusion of Oxygen Through Membranes of Aqueous Cobaltodihistidine," Biochim. Biophys. Acta **211** 194 (1970).
20. I.C. Roman and R.W. Baker, "Method and Apparatus for Producing Oxygen and Nitrogen and Membrane Therefor," U.S. Patent 4,542,010 (September 17, 1985).
21. R.W. Baker, I.C. Roman and H.K. Lonsdale, "Liquid Membranes for the Production of Oxygen-Enriched Air. I. Introduction and Passive Liquid Membranes," J. Memb. Sci. **31** 15-29 (1987).
22. B.M. Johnson, R.W. Baker, S.L. Matson, K.L. Smith, I.C. Roman, M.E. Tuttle and H.K. Lonsdale, "Liquid Membranes for the Production of Oxygen-Enriched Air. II. Facilitated-Transport Membranes," J. Memb. Sci. **31** 31-67 (1987).
23. Nishide, H., M. Ohyanagi, O. Okada, and E. Tsuchida, "Dual Mode Transport of Molecular Oxygen in a Membrane Containing a Cobalt Porphyrin Complex as a Fixed Carrier," Macromolecules, **20**, 417-422, (1987).
- 24.. Nishide, H., and E. Tsuchida, "Facilitated Transport of Oxygen Through the Membrane of Metalloporphyrin Polymers," paper at Second Annual National Meeting of the North American Membrane Society, Syracuse, N.Y., June, 1988.
25. Kimura, S. G., W. J. Ward, III, and S. L. Matson, "Facilitated Separation of a Select Gas Through and Ion Exchange Membrane," U.S. Patent #4,318,714, Mar. 9, 1982.
26. Matson, S. L., K. Eric, L. Lee, D. T. Friesen, and D. J. Kelly, "Acid Gas Scrubbing by Composite Solvent-Swollen Membranes," U.S. Patent #4,737,166, Apr. 12, 1988.
27. Hughes, R. D., J. A. Mahoney, and E. F. Steigelman, "Olefin Separation by Facilitated Transport Membranes," Recent Devel. Sep. Sci., **9**, 173 (1986).
28. Teramoto, M., H. Matsuyama, T. Yamashiro, and S. Okamoto, "Separation of Ethylene from Ethane by a Flowing Liquid Membrane Using Silver Nitrate as a Carrier," J. Memb. Sci., **45**, 115 (1989).
29. Pez, G. P., et al., U.S. Patent 4,761,164, 1988.

30. Pez, G. P., and L. V. Laciak, "Ammonia Separation Using Semipermeable Membranes," U.S. Patent #4,762,635, Aug. 9, 1988.
31. Pez, G. P., and R. T. Carlin, "Method for Gas Separation," U.S. Patent #4,617,029, Oct. 14, 1986.
32. Danesi, P. R., "Separations by Supported Liquid Membrane Cascades," U.S. Patent #4,617,125, Oct. 14, 1986.

CHAPTER FIVE

REVERSE OSMOSIS

TABLE OF CONTENTS

5.1	PROCESS OVERVIEW	5-1
5.1.1	The Basic Process	5-1
5.1.2	Membranes	5-5
5.1.3	Modules	5-5
5.1.4	Systems	5-9
5.2	THE REVERSE OSMOSIS INDUSTRY	5-14
5.2.1	Current Desalination Plant Inventory	5-14
5.2.1.1	Membrane sales	5-14
5.2.2	Marketing of Membrane Products	5-16
5.2.3	Future Direction of the Reverse Osmosis Membrane Industry	5-18
5.3	REVERSE OSMOSIS APPLICATIONS	5-18
5.4	REVERSE OSMOSIS CAPITAL AND OPERATING COSTS	5-20
5.5	IDENTIFICATION OF REVERSE OSMOSIS PROCESS NEEDS	5-24
5.5.1	Membrane Fouling	5-24
5.5.2	Seawater Desalination	5-27
5.5.3	Energy Recovery for Large Seawater Desalination Systems	5-30
5.5.4	Low-Pressure Reverse Osmosis Desalination	5-33
5.5.5	Ultra-Low-Pressure Reverse Osmosis Desalination	5-35
5.6	DOE RESEARCH OPPORTUNITIES	5-37
5.6.1	Projected Reverse Osmosis Market: 1989-1994	5-37
5.6.2	Research and Development: Past and Present	5-37
5.6.3	Research and Development: Energy Reduction	5-39
5.6.4	Thin-Film Composite Membrane Research	5-39
5.6.4.1	Increasing water production efficiency	5-39
5.6.4.2	Seawater reverse osmosis membranes	5-40
5.6.4.3	Ultra-low-pressure membranes	5-41
5.6.5	Membrane Fouling: Bacterial Adhesion to Membrane Surfaces	5-42
5.6.6	Spiral-wound Element Optimization	5-43
5.6.7	Future Directions and Research Topics of Interest for Reverse Osmosis Systems and Applications	5-44
5.6.8	Summary of Potential Government-Sponsored Energy Saving Programs	5-50
	REFERENCES	5-52

CHAPTER FIVE

REVERSE OSMOSIS

by R. L. Riley, Separation Systems Technology, Inc.

5.1 PROCESS OVERVIEW

5.1.1 The Basic Process

Reverse osmosis (RO), the first membrane-based separation process to be widely commercialized, is a liquid/liquid separation process that uses a dense semipermeable membrane, highly permeable to water and highly impermeable to microorganisms, colloids, dissolved salts and organics. Figure 5-1 is a schematic representation of the process.

A pressurized feed solution is passed over one surface of the membrane. As long as the applied pressure is greater than the osmotic pressure of the feed solution, "pure" water will flow from the more concentrated solution to the more dilute through the membrane. If other variables are kept constant, the water flow rate is proportional to the net pressure. The osmotic pressures of some typical solutions are listed in Table 5-1.

Table 5-1. Typical Osmotic Pressures at 25°C (77°F)

Compound	Concentration (mg/L)	Concentration (moles/L)	Osmotic Pressure (psi)
NaCl	35,000	0.60	398
Seawater	32,000	-	340
NaCl	2,000	0.0342	22.8
Brackish water	2-5,000	-	15-40
NaHCO ₃	1,000	0.0119	12.8
Na SO ₄	1,000	0.00705	6.0
Mg SO ₄	1,000	0.00831	3.6
MgCl ₂	1,000	0.0105	9.7
CaCl ₂	1,000	0.009	8.3
Sucrose	1,000	0.00292	1.05
Dextrose	1,000	0.0055	2.0

Reverse osmosis is widely used to remove salts from seawater or brackish water. An ideal desalination membrane would allow unhindered water passage, with complete rejection of dissolved salts. In practice, both water and salts cross the membrane barrier, but at differing rates. There are two principal models for the transport process: the solution-diffusion model, first described by Lonsdale, Merten and Riley¹, and the capillary pore model, described by Sourirajan,² both of which describe the reverse osmosis process. However, the solution-diffusion model is more widely accepted.

SCHEMATIC OF THE REVERSE OSMOSIS PROCESS

Figure 5-1. Schematic of the reverse osmosis process.

The performance characteristics that describe a reverse osmosis system are the product water flux, the salt flux, the salt rejection and the water recovery. The equations that define these terms are given below. The water flux, F_w (g/cm²·sec), and the salt flux, F_s (g/cm²·sec), are linked to the pressure and concentration gradients across the membrane. From the solution-diffusion model, these terms are described by the equations:

$$F_w = A(\Delta p - \Delta \pi) \quad , \quad (1)$$

where A is the water permeability constant (g/cm²·sec·atm), Δp is the pressure differential across the membrane (atm), and $\Delta \pi$ is the osmotic pressure differential across the membrane, and

$$F_s = B(C_1 - C_2) \quad , \quad (2)$$

where B is the salt permeability constant (cm/sec), and $C_1 - C_2$ is the salt concentration difference across the membrane (g/cm³). Thus, the water flux is proportional to the applied pressure but the salt flux is independent of the applied pressure. This means the membrane appears to become more selective as the pressure is increased. In reverse osmosis, the membrane selectivity is normally measured by a term called the salt rejection, R , which is proportional to the fractional depletion of salt in the product water compared to the feed. The salt rejection is defined as

$$R = \left[1 - \frac{C_p}{C_f} \right] \times 100\% \quad , \quad (3)$$

where C_p is the concentration of the product water and C_f is the concentration of the feed water. Finally, the fraction of the feed water that is produced as a purified product is called the % recovery of a reverse osmosis system, and is defined as

$$\% \text{ recovery} = \frac{N_p}{N_f} \times 100\% \quad , \quad (4)$$

where N_p is the product flow rate from the reverse osmosis system and N_f is the feed solution flow rate to the reverse osmosis system.

Figure 5-2 shows the effects of pressure, temperature, and water recovery on the membrane flux and product water quality of reverse osmosis membranes. These are generalized curves and deviations can be expected depending on the nature and concentration of the feed solution. Figures 5-2a and 5-2b show the effect of applied pressure on membrane flux and product water quality. Figures 5-2c and 5-2d show the effect of feed temperature on membrane flux and product water quality. Finally, Figures 5-2e and 5-2f show the effect of water recovery on membrane flux and product water quality.

**EFFECT of APPLIED PRESSURE,
FEED TEMPERATURE and WATER RECOVERY on the
MEMBRANE FLUX and PRODUCT WATER QUALITY
of REVERSE OSMOSIS MEMBRANES**

Figure 5-2. Schematic curves showing the effect of pressure, temperature, and water recovery on the performance of reverse osmosis systems.

An efficient reverse osmosis process, that is a process that achieves a high water flow at low energy expenditure, should meet the following requirements:

- a) High intrinsic water permeability with low intrinsic salt permeability.
- b) Large membrane surface area.
- c) Low pressure drop across the membrane.
- d) Very thin, defect-free membrane.

5.1.2 Membranes

Loeb and Sourirajan developed the first asymmetric, cellulose diacetate membranes.^{3,4} A major research and development effort, using their work as a basis, took place through the 1960s and 1970s, with substantial sponsorship by the Department of the Interior, Office of Saline Water. Figure 5-3 summarizes the key developments that have occurred over the past thirty years in membrane development for desalination. Today, asymmetric, flat-sheet membranes made from cellulose triacetate/cellulose diacetate blends are widely used in the industry for brackish water treatment. Cellulose triacetate hollow fibers are in limited use for seawater treatment, but most seawater plants use hollow-fiber or more commonly thin-film composite membranes made from aromatic polyamides. Thin-film composites made from aryl-alkyl polyetherurea and other polymers are also used.

Cellulose acetate membranes are rugged, resistant to moderate levels of chlorine and inexpensive. They are susceptible to bacteriological attack, and to hydrolysis when exposed to strongly basic solutions. The newer materials offer better performance than cellulose acetate membranes in some circumstances. Some have negatively charged surfaces, which enhance their rejection of sulfate, carbonate or phosphate ions, for example. However, they tend to be less chlorine-resistant and more susceptible to oxidation. Table 5-2 summarizes the properties of the two main types of commercial polyamide and polysulfone composite membranes.

5.1.3 Modules

Reverse osmosis membranes are prepared in the form of hollow fibers or flat sheets. The membranes are then packaged into modules designed to enable a large membrane area to be contained in a small volume. Hollow fibers are made into bundles, several of which are contained within one housing, to form a single module, or permeator. The feed solution flows on the outside of the fibers, in contact with the dense skin layer. DuPont is the principal company manufacturing hollow-fiber modules. Figure 5-4 shows a schematic drawing of a DuPont module. This module is designed for single-stage seawater desalination, and it contains 2.3 million individual fibers enclosed in an 8-in-diameter, 5-ft-long pressure vessel. Hollow fiber modules offer a very high membrane area at a relatively low cost. However, these modules are susceptible to fouling by suspended matter in the feed solution and this is a major operating problem.

Figure 5-3. Key developments in reverse osmosis membrane development.

Table 5-2. Comparative Properties of Commercial Thin-Film Composite Membranes

Comparative Properties of Commercial Thin-film Composite Membranes		
	Aryl-Alkyl <u>Polyetherurea</u>	Crosslinked Fully Aromatic <u>Polyamide</u>
Seawater Capability	Yes	Yes
Brackish Water Capability	Yes	Yes
Low Pressure Capability	Marginal	Yes
Thin-film Thickness (A)*		
Seawater	500	2000
Brackish	250	2000
Low Pressure	<250 (Marginal)	2000
Intermediate Layer Between		
Thin Film and Support	Yes	No
Silica Rejection	Moderate	High
Organic Rejection	Moderate	High
Chlorine Tolerance	None	Limited
Oxidant Tolerance	None	Limited
Temperature Stability	Process Dependent	Stable to 45 C
Membrane Surface Charge	Positive	Negative
Cleaning Agents (anionic)	Incompatible	Compatible
Cleaning Agents (cationic)	Compatible	Incompatible
Acid Cleaning Limits	pH 3.5	pH 1
Alkaline Cleaning Limits	pH 12	pH 12

Angstrom Units: 1 micron = 10,000 angstroms

Figure 5-4. Schematic drawing of a DuPont hollow-fiber module for single-stage seawater desalination.

Spiral-wound modules are the more widely used configuration throughout the industry, principally because they are less susceptible to fouling. In these modules, flat-sheet membranes are made in long rolls, 40 or 60 inches wide. Between two and six spiral-wound modules are then placed in a single pressure vessel. A schematic of a spiral-wound module and pressure vessel assembly are shown in Figure 5-5. The features and advantages of spiral-wound modules for use in reverse osmosis are:

<u>Features</u>	<u>Advantages</u>
Large membrane surface area	Compact membrane plants
Compact packaging	Low initial capital costs
Optimum feedwater passages	High surface flow velocity Reduced polarization effects Higher permeate output Increased salt rejection
Simple, rugged, disposable design	Low replacement costs

Reverse osmosis spiral-wound modules were originally designed to operate optimally at 12-17 gallon/ft²-day. Higher flow rates would be desirable, but lead to major fouling problems. The nature of the spacer materials, especially the feed channel spacer material, is also an important aspect of reverse osmosis technology.

5.1.4 Systems

The factor which has the greatest influence on reverse osmosis membrane system design is fouling, caused by particulate and colloidal matter that become concentrated at the membrane surface. Pretreatment is used to remove particulate matter from the feed water, but is seldom completely effective. The concentration of foulants at the membrane surface increases with increasing permeate flux and product recovery rate. A system designed to operate at a high permeate flux is likely to experience high fouling rates and will require frequent chemical cleaning.

A measure commonly used to determine the clarity of the feed water and its membrane fouling potential is the Silt Density Index (SDI). Determining the feed water's SDI involves measuring the necessary time to filter a fixed volume (usually 500 mL) of feed water through a clean filter pad. The test is repeated with the same pad 15 minutes after the first test. The SDI is calculated from the change in time required to filter the feed water sample through the clean versus the fouled filter pad. To make SDI measurements comparable, a constant applied pressure of 30 psig and a Millipore 0.45- μ m filter pad are commonly used for this test.

SOURCE O.K. Burris et al., "The USAID Desalination Manual" U.S. Agency for International Development, Washington, DC prepared by CH2M Hill International Corp., August 1980

Figure 5-5. A schematic drawing of a spiral-wound module and pressure vessel assembly.

A very low SDI is particularly important for hollow-fiber modules, and a feed water SDI of 3.0 is considered the maximum value to which these modules can be exposed. Spiral-wound elements are more tolerant to particulate matter fouling and a feed water SDI of 3.0-5.0 is normally specified. Obviously, a lower value for the feed water is beneficial to both types of membrane systems.

Typical pretreatment processes are media filtration (sand, anthracite, etc.) and cartridge filtration. The media filters may be preceded by coagulation and sedimentation for highly turbid waters.

Chemical dosing is also required for scale control and for dechlorination if the raw seawater is chlorinated. Typical chemicals are:

- Sulfuric acid for pH control and calcium carbonate scale prevention.
- Antiscalants/scale inhibitors for prevention of calcium carbonate and sulfate scale.
- Sodium bisulfite for dechlorination and inhibition of fouling.

Typical design guidelines for spiral-wound polyamide type membrane elements in a seawater desalination system are shown in Table 5-3.

Table 5-3. Typical Design Guidelines for Spiral-wound Modules using Polyamide-type Thin-film Composite Membranes

Silt density index	3-5 (or less)
Maximum permeate flux	20 gal/ft ² -day
Maximum water recovery for 40-inch elements	15%
Maximum permeate flow rate per 40-inch element	
8 x 40-in.	6,000 gal/day
4 x 40-in.	1,500 gal/day
2.5 x 40-in.	500 gal/day
Maximum feed flow rate for 40-inch elements	
8 x 40-in.	60 gal/min
4 x 40-in.	16 gal/min
2.5 x 40-in.	6 gal/min
Standard salt rejection (avg.)	99.5%
Standard salt rejection (min.)	99.3%

Figure 5-6 shows a diagram for a typical reverse osmosis desalination plant, which could apply to either seawater or brackish water desalination. In this flow diagram, the pressure vessel does not necessarily indicate a single vessel, but generally is an array of pressure vessels, as shown in Figure 5-7. For brackish water applications, each six-element pressure vessel is designed to operate at 50% water recovery. Thus, assuming a feed flow of 100 gal/min, the module array in Figure 5-7a represent a 75% water recovery system, while the array in Figure 5-7b represents 87.5% recovery. Obviously, a system operating at the highest possible water recovery is desirable, since the overall operating costs will be reduced. The level of water recovery that can be attained is dictated by the feed water composition. In the absence of high concentrations of salts, particularly sulfates, carbonates, etc. that can cause scaling, high water recovery

Figure 5-6. Flow diagram of a typical reverse osmosis desalination plant.

TWO POSSIBLE SPIRAL-WOUND MODULE ARRAYS for RO

Figure 5-7. Two possible spiral-wound module arrays for reverse osmosis. Assuming a feed flow of 100 gal/min, a) represents a 75% water recovery system and b) represents 87.5% recovery.

levels generally can be attained. For seawater desalination systems, however, the overall water recovery is limited to about 45%, due to the high osmotic pressure of the seawater brine in the final array of the system. At this point the osmotic pressure approaches the applied pressure and, consequently, the net driving force becomes so small that the permeate flow becomes uneconomically small. This occurrence will be discussed later, along with the effect on plant operating costs.

5.2 THE REVERSE OSMOSIS INDUSTRY

5.2.1 Current Desalination Plant Inventory

Worldwide, more than 6,235 desalting plants were in operation at the beginning of 1988, with a total capacity of 3,178,500,000 gallons per day. Figure 5-8 shows a breakdown of this total with respect to desalination methods, worldwide location, and type of feedwater.

Presently, there are about 750 desalination plants operating in the United States with individual capacities in excess of 25,000 gallons per day. This translates into a combined capacity of about 200 million gallons per day. Reverse osmosis accounts for about 75% of this capacity, with about 70% of the plants used for industrial purposes. There are many smaller reverse osmosis plants in operation, but their combined capacity is relatively low. These applications include point-of-use home RO systems, mobile military units, pleasure boats and merchant ships, small industries, off-shore drilling rigs, etc.⁶

5.2.1.1 Membrane sales

Recent figures indicate that sales of desalination membranes by U.S. industry are approximately \$85 million/year. Even with an increasing share of the world's desalination market, U.S. manufacturers have been hit hard by stiff competition and declining profits. The domestic membrane industry has experienced great change with an overall trend toward fewer, but generally larger, companies during the last few years. Some firms have been acquired by larger chemical corporations involved in water treatment and/or process separation. Price cutting, particularly in spiral elements, has been severe, thereby lowering gross margins and making membrane products commodity items. Declining profits have forced some firms to go out of business.

The U.S. desalination membrane market continues to be dominated by sales of small to moderate-size RO plants, replacement membrane elements, and plants for military uses. Sales of home water RO units continue to climb rapidly, encouraged by public concerns about water pollution. Potential international competition in the U.S. market, especially from the Japanese, is a concern. Some efforts have been made to introduce membrane systems into domestic industrial applications, primarily aimed at process waste-water treatment and recovery of valuable materials. Since these waste streams are so diverse, major investments are often required to develop such markets in industries where other technologies are entrenched. However, many of these older technologies are energy intensive, e.g., distillation or other evaporative methods, so the benefits of reverse osmosis will become increasingly important as energy prices rise. More stringent application of discharge limits under the EPA's National Pollutant Discharge Elimination System will also help the market to grow. As the cost of membrane

CURRENT WORLDWIDE DESALINATION PROCESS CAPACITIES

Figure 5-8. Worldwide desalination process capacity, location and feedwater type.⁵ (MSF: multistage flash, RO: reverse osmosis).

systems decrease, accompanied by energy reductions in low-pressure operations, desalination of industrial waste streams will be a more attractive alternative to established treatment systems, especially in areas where water supplies are limited and water reuse becomes a necessity.⁶

Estimated worldwide 1988 sales of reverse osmosis membrane are shown in Table 5-4. The figures have been adjusted for recent fluctuations in the U.S. dollar exchange rate.

Table 5-4. The Reverse Osmosis Membrane Industry

Company	Location	Estimated Sales of Company Manufactured Membrane Products (\$ millions)		
		Hollow Fiber	Spiral Elements	Total
DuPont	USA	24*	5	29
Dow/Filmtec	USA	--	26	26
Fluid Systems/ UOP	USA	--	13	13
Hydranautics/ Nitro-Denko	USA/ Japan	--	12	12
Desalination Systems	USA	--	5	5
Millipore	USA	--	3	3
Osmonics	USA	--	3	3
Toray	Japan	--	12	12
Toyobo	Japan	4*	--	4
Others	World	--	11	11
Total		28	90	118

* Membrane permeator includes pressure vessel

Table 5-5 presents a breakdown of the total estimated membrane sales by membrane type. Pressure vessel sales are not included, except for hollow-fiber membrane permeators, which include the pressure vessel as a complete package.

5.2.2 Marketing of Membrane Products

The previous discussion has focused on membrane sales only, ignoring plant design and operation. At the present time, only one major membrane company, Nitro-Denko/Hydranautics, supplies systems other than small pilot units. All other domestic companies have abandoned plant and system sales, due to lack of profitability and the necessity of maintaining a large engineering and equipment fabrication staff. Plant design and construction is handled by original equipment manufacturers (OEMs).

Table 5-5. Estimated 1988 Reverse Osmosis Membrane Market Share by Membrane Type

	% of Total	\$ (millions)	Trend
<u>Membrane Configuration</u>			
Hollow fibers	26.2	28	Decreasing
Spiral-wound	73.8	90	Increasing
<u>Membrane Type</u>			
Spiral polyamide composite	45.4	52.7	Increasing
Cellulose acetate blend	28.3	37.3	Stable
<u>Replacement Market</u>			
Spiral-wound (all types)	20.0	44.5	Increasing

Table 5-6 lists representative OEMs and engineering companies engaged in reverse osmosis plant design.

Table 5-6. OEMs and Engineering Firms Involved in Reverse Osmosis Plant Design and Construction

<u>OEMs</u>	<u>Engineering Companies</u>
Aqua Design	Bechtel
Arrowhead	Black and Veach
Culligan	Burns and Roe
Gaco Systems, Inc.	CH2M Hill, Inc.
Graver Water Systems	Stone and Webster
Ionics	VBB-SWECO
L.A. Water Treatment	
Polymetrics	

The OEM designs and builds the plant according to the guidelines for elements, vessel arrays and operating conditions set by the membrane manufacturer. Most membrane elements are standardized as far as size and flow rates are concerned, and are thus interchangeable, so OEMs buy freely from all membrane manufacturers. Customers typically purchase from the OEM tendering the lowest bid. In these competitive conditions, it is hard for both membrane makers and OEMs to ensure that recommended operating standards are adhered to. This is an industry weakness.

5.2.3 Future Direction of the Reverse Osmosis Membrane Industry

In the next decade, the large membrane-producing companies will increase market share by acquiring technology from smaller, more innovative companies. Thus, the number of membrane companies will decrease. At present, in spite of the size and softness of the membrane market, a number of large corporations with little, if any, membrane experience are anticipating entry into the business.

Since the development of the crosslinked, fully aromatic polyamide thin-film composite membrane by Cadotte in 1977, emphasis has focused on this membrane type throughout the industry. Several dominant membrane companies have directed their attention to methods of circumventing the patents protecting this technology, in lieu of research and development on new membranes with superior properties, principally chlorine resistance.

The ultimately successful companies will be characterized by:

- Ability to make high-quality products, consistently, reliably, efficiently.
- Strong proprietary and patent positions.
- Strong, effective R&D effort.
- Ability to offer oxidation-resistant, high-performance membranes.
- Technically trained, customer-oriented marketing and support operation.
- Development of strong OEMs with product loyalty.
- International marketing and manufacturing capability.

These attributes will be achieved by effective, dedicated management rather than by acquisition.

5.3 REVERSE OSMOSIS APPLICATIONS

Figure 5-9 shows estimated reverse osmosis membrane sales worldwide for 1988, by application area. Projections for 1998 are also given.

The largest single application area at present is desalination of seawater and brackish waters, which accounts for about 50% of total sales. The remaining sales are directed to diverse applications, ranging from industrial process water, to water for medical use and for food processing. Applications showing the highest projected growth rate percentages are purification of relatively dilute streams such as industrial process water, ultrapure/medical, and small package sales. Lowest projected increases are in seawater, brackish water, and food applications.

The sales of home "under the sink" reverse osmosis units is a rapidly rising segment of the reverse osmosis market in the United States and Europe. However, these systems are very wasteful of water and use 5-10 gallons of tap water for each gallon of water processed, thereby dumping what is generally considered potable water. Sales of these units could, therefore, be regulated in the future.

Figure 5.9. Principal applications of reverse osmosis and estimated worldwide sales of membrane products (projected annual growth rate, 1988-1998).

Although reverse osmosis membrane sales for food processing applications represent only a small percentage of the total sales, with a modest projected growth rate, the food industry is very energy intensive. Thus adoption of alternate low-energy separations such as reverse osmosis could result in considerable energy savings. Many of the food materials requiring separation are dilute suspensions and solutions, and are ideal candidates for concentration by reverse osmosis. Reclamation of wastewater and high-temperature process waters are good applications.⁶

To date, three U.S. companies have obtained FDA approval for use of their membrane modules in food processing applications. These are:

- The DuPont B-15 linear aromatic polyamide hollow fiber permeator.
- The FilmTec/Dow FT-30 crosslinked fully aromatic polyamide and NF-40 polypiperazineamide thin-film composite spiral-wound membrane elements.
- The Fluid Systems/UOP thin-film composite spiral-wound aryl-alkyl polyetherurea membrane elements.

U.S. industry consumes about 8 billion gallons of fresh water daily; industrial and commercial facilities discharge about 18 billion gallons of wastewater daily, mostly into open water supplies or sewage systems.⁶ Both supply of high quality water and treatment of wastewater offer opportunities for reverse osmosis technology. Table 5-7 lists industries and reverse osmosis markets within that industry, grouped by their maturity status. There is significant potential for applying desalination technology to reclamation and reuse of wastewaters. If drought conditions continue in the Western United States, desalination of brackish waters or wastewaters may become increasingly attractive, but relatively high costs will make the installation of seawater desalination plants unlikely.

5.4 REVERSE OSMOSIS CAPITAL AND OPERATING COSTS

Four techniques can be used to remove salts from water:

- Distillation - Multiple-effect (ME), Multi-stage flash (MSF), Vapor compression (VC) and Solar.
- Reverse Osmosis (RO).
- Electrodialysis (ED).
- Ion Exchange (IX).

Selection of the most appropriate technology depends on many factors including the water analysis, the desired quality of the treated water, the level of pretreatment required, the availability of energy, and waste disposal. Both reverse osmosis and electrodialysis membranes can be tailored to the application, based on the feed water composition. Table 5-8 shows the various methods available for desalination based on the nature of the feed. Ion exchange and electrodialysis are generally preferred for very dilute streams while distillation is preferred for very concentrated streams. Reverse osmosis is the best technique for streams containing 3,000 to 10,000 ppm salt but is still widely used for streams more dilute than 3,000 ppm and streams as concentrated as seawater at 35,000 ppm salt.

Table 5-7. Reverse Osmosis Market Applications

Status	Industry	Applications
Mature	Desalination	Potable Water Production Seawater Brackish Water Municipal Wastewater Reclamation
	Ultrapure Water	Semiconductor manufacturing Pharmaceuticals Medical Uses
Growing	Utilities and Power Generation	Boiler Feedwater Cooling Tower Blowdown Recycle
	Point of Use	Home Reverse Osmosis
Emerging	Chemical Process Industries	Process Water Production and Reuse Effluent Disposal and Water Reuse Water/Organic Liquid Separation Organic Liquid Mixtures Separation
	Metals and Metal Finishing	Mining Effluent Treatment Plating Rinse Water Reuse and Recovery of Metals
	Food Processing	Dairy Processing Sweeteners Concentration Juice and Beverage Processing Production of Light Beer and Wine Waste Stream Processing
	Textiles	Dyeing and Finishing Chemical Recovery Water Reuse
	Pulp and Paper	Effluent Disposal and Water Reuse
	Biotechnology/Medical	Fermentation Products Recovery and Purification
	Analytical	Isolation, Concentration, and Identification of Solutes and Particles
	Hazardous Substance Removal	Removal of Environmental Pollutants from Surface and Groundwaters

Table 5-8. Methods of Desalination

Technique	Typical Applications			
	Brackish Water		Seawater	Higher Salinity Brines
	3,000 ppm	3,000-10,000 ppm	35,000 ppm	
Distillation	t	s	P	P
Electrodialysis	P	s	t	
Reverse osmosis	P	P	P	s
Ion exchange	P			

Key: P = Preferred application
s = Secondary application
t = Technically possible, but not economical

Source: Office of Technology Assessment, 1987.

Although desalination costs have decreased significantly in the last 20 years, cost remains a primary factor in selecting a particular desalination technique for water treatment. Figure 5-10 shows a comparison of estimated desalination operating costs based on plant size. These costs include capital and operating costs for plants producing 1 to 5 million gallons per day of potable water (in 1985 dollars). Costs include plant construction (amortized over 20 years), pretreatment, desalination, brine disposal, and maintenance. As Figure 5-10 shows, there is a significant decrease in cost with increasing plant size for seawater desalination, but only a slight decrease in cost with increasing plant size for brackish water plants.

Table 5-9 shows the current capital and operating costs for seawater and brackish water desalination plants. These costs are strongly influenced by several factors, as previously indicated. Consequently, the range of the total costs does not closely agree with the costs shown in Figure 5-10.

Table 5-9. Capital and Operating Costs for Seawater and Brackish Water Desalination by Reverse Osmosis

Type of Water	Capital Costs (\$/gal-day)	Operating Costs (\$/1000 gal of product)
Seawater	4.00 - 10.00	2.50 - 4.00
Brackish	0.60 - 1.60	1.00 - 1.25

Figure 5-10. Comparison of estimated desalination operating costs based on plant size. (MSF: multistage flash, RO: reverse osmosis, ME: multiple-effect evaporation, ED: electrodialysis).

The estimated energy requirements associated with the various types of desalination processes are shown in Table 5-10. These energy costs are a function of feed solution salt concentration. The effect of the salt concentration in brackish water on energy usage is less marked with reverse osmosis than with other technologies. The principal effect as far as RO is concerned is an increase in the osmotic pressure of the feed solution. Higher pressures (400 psi) are used for desalination of brackish feeds, in the 3500-8000 mg/L range. Lower pressure operations are used with low feedwater concentrations.

Table 5-10. Estimated Energy Requirements for Desalination Processes

Process Type	Energy Requirements	
	kWh/m ³	kWh/1,000 gal
Distillation	15	56
Electrodialysis		
Seawater	>50*	>100*
Brackish Water	4	15
Reverse Osmosis		
Seawater	7	26
Brackish Water (400 net psi)	2	7.6
(200 net psi)	0.8-1.5	3.0 - 5.7

* Electrodialysis is not economical for seawater desalination. Energy consumption is approximately 5 kWh for each 1000 mg/L salt reduction per each 1,000 gal. of purified water.

The development of energy saving, low-pressure, thin-film composite membranes has made reverse osmosis superior to low pressure distillation/evaporation processes for seawater desalination. Energy recovery systems would enable further reductions in energy consumption to be made.

5.5 IDENTIFICATION OF REVERSE OSMOSIS PROCESS NEEDS

5.5.1 Membrane Fouling

Membrane fouling is a major factor determining the operating cost and membrane lifetime in reverse osmosis plants. If operated properly the life of reverse osmosis membranes is excellent. Cellulose acetate blend membranes and polyamide thin-film composite membranes have been operated without significant deterioration on brackish water feeds for up to 12 years.

Several types of fouling can occur in reverse osmosis systems depending on the feed water. The most common type of fouling is due to suspended particles. Reverse osmosis membranes are designed to remove dissolved solids, not suspended solids. Thus, for successful long-term operation, suspended solids must be removed from the feed stream before the stream enters the reverse osmosis plant. Failure to remove particulates results in these solids being deposited as a cake on the membrane surface. This type of fouling is a severe problem in hollow-fiber modules.⁷

A second type of fouling is membrane scaling. Scaling is most commonly produced when the solubility limits of either silica, barium sulfate, calcium sulfate, strontium sulfate, calcium carbonate, and/or calcium fluoride are exceeded. Exceeding the solubility limit causes the insoluble salt to precipitate on the membrane surface. Chemical analysis of the feed stream is required to establish the correct reverse osmosis plant design and operating parameters. It is essential that a plant operate at the design recovery chosen to avoid precipitation and subsequent scaling on the membrane surface.

A third cause of membrane fouling is bacteria. Reverse osmosis membrane surfaces are particularly susceptible to microbial colonization and biofilm formation.⁸ The development of a microbial biofilm on the feedwater membrane surface has been shown to result in a decline in membrane flux and lower the overall energy efficiency of the system. Bacterial attachment and colonization in the permeate channel has the potential to rapidly deteriorate permeate water quality. In recent years, Ridgway and coworkers have systematically explored the fundamental mechanism and kinetics of bacterial attachment to membrane surfaces.⁹⁻¹² The cumulative effects of membrane biofouling are increased cleaning and maintenance costs, deterioration of product water flow and quality, and significantly reduced membrane life.

Other types of fouling which can occur are the precipitation of metal oxides, iron fouling, colloidal sulfur, silica, silt, and organics.

All of these membrane fouling problems are controlled by using a correct plant design including adequate pretreatment of the feed and proper plant operation and maintenance. It is now well accepted that scaling and fouling were the major problems inhibiting the initial acceptance of reverse osmosis.

The type of pretreatment required for a particular feed is quite variable and will depend on the feed water and the membrane module used. Pretreatment may include coagulation and settling and filtration to remove suspended solids, and disinfection with chlorine is commonly used to kill microorganisms. When chlorine-sensitive, thin-film membranes are used, dechlorination of the feed will then be required, a factor that tends to inhibit the use of these membranes. Scaling is usually controlled by addition of acid, polyphosphates, or polymer-based additives. These pretreatment steps are all standard water treatment techniques, but taken together, their cost can be very significant. Typically, the cost of pretreatment may account for up to 30% of the total operating cost of a desalination plant.

Irrespective of the level of pretreatment, some degree of fouling will occur in a reverse osmosis system over a period of time. Periodic cleaning and flushing of the system is then required to maintain high productivity and long membrane life. With good pretreatment, periodic cleaning will maintain a high level of productivity, as illustrated in Figure 5-11.¹³ When pretreatment is inadequate, frequent cleaning is required. In addition, cleaning is then less effective in restoring membrane productivity, leading to reduced membrane life. A membrane system should be cleaned when:

Figure 5-11. Membrane productivity as a function of operating time.

- Productivity is reduced by more than 10%.
- Element pressure drop increases by 15% or more.
- Salt passage increases noticeably.
- Feed pressure requirements increase by more than 10%.
- Fouling/scaling situation requires preventative cleaning.
- Before extended shutdowns.

Chemical cleaning solutions have been developed empirically that are quite effective, provided the system is cleaned on a proper schedule. Cleaning chemicals, formulations, and procedures must be selected that are compatible with the membrane and effective for removing the scale or foulant present. Due to the complexity of most feedwaters, where both inorganic and organic foulants are present, the cleaning operation generally is a two-step process. Inorganic mineral salts deposition usually requires an acidic cleaning solution formulation, whereas organic foulants such as algae and silt require alkaline cleaning. The selection of chemical cleaners is hindered by the sensitivity of most reverse osmosis membranes to such factors as temperature, pH, oxidation, membrane surface charge, etc. The development of more durable membrane polymers would allow a more widespread use of strong cleaners.

5.5.2 Seawater Desalination

Currently, seawater plants are designed and operated with spiral-wound polyamide type thin-film composite membranes in a single-stage mode at operating pressures of 800 to 1000 psi, producing 300 mg/L product water quality at rates of 9 gal/ft²-day and water recovery levels of 45%.¹⁴

Five classes of membranes are commercially used for seawater desalination today. They are:

- Cellulose triacetate hollow-fine fibers.
- Fully aromatic linear polyamide hollow-fine fibers.
- Spiral-wound crosslinked fully polyamide type thin-film composite membranes.
- Spiral-wound aryl-alkyl polyetherurea type thin-film composite membranes.
- Spiral-wound crosslinked polyether thin-film composite membranes.

The performance characteristics of the dominant seawater desalination membranes are shown in Figure 5-12.¹⁵

With the exception of cellulose triacetate hollow-fine fibers, the other membranes are rapidly degraded in an oxidizing environment. This limitation creates major problems in designing for effective pretreatment, cost of pretreatment chemicals, fouling by microorganisms, decreased membrane performance, and reduced membrane life.

Figure 5-12. Performance characteristics of membranes operating on seawater at 56 kg/cm², 25°C.

To date, few seawater desalination plants have operated without difficulty. The common factors in those plants that have operated efficiently are:

- A reducing (redox potential) seawater feed.
- An oxygen-free (anaerobic) seawater feed taken from a seawater well that has been filtered through the surrounding strata.
- High levels of sodium bisulfite in the seawater feed (40 to 50 mg/L) to remove oxygen and/or chlorine if the feed has been chlorinated.

Most difficulties have been encountered with plants operating from surface seawater intakes where chlorination is required to control growth of both algae and microorganisms. In these cases, chlorination must be followed by dechlorination to protect the polyamide type membranes. Dechlorination is generally carried out by adding sodium bisulfite at an amount slightly in excess (6 to 8 mg/L) of that stoichiometrically required to remove the 1 to 2 mg/L residual chlorine that is present. This amount of sodium bisulfite is insufficient to remove chlorine since oxygen, which is present in seawater at approximately 7 to 8 mg/L, competes with chlorine for sodium bisulfite. As a result, very small amounts of chlorine or oxidation potential remain, as determined by redox measurements. Approximately 50 mg/L of sodium bisulfite is required to totally remove the dissolved oxygen present in seawater. It is now known that the presence of heavy metals, commonly deposited on the surface of these membranes in a seawater desalination environment, accelerates degradation of polyamide type membranes by chlorine. As a result, even small traces of residual chlorine can rapidly degrade the membrane.

Attack of polyamide type membranes by dissolved oxygen in seawater in the presence of heavy metals is also a concern. Japanese researchers have shown this type of attack does occur with some membranes. They have concluded that heavy metals catalyze the dissolved oxygen to an active state that is very aggressive toward the membrane. With these membranes, both chlorine and dissolved oxygen are totally removed with a combination of vacuum deoxygenation and sodium bisulfite.¹⁵

Because of these residual chlorine problems, the most successful polyamide membrane seawater desalination plants employ large quantities of sodium bisulfite to remove chlorine and dissolved oxygen and create a reducing environment to protect the membrane. The addition of sodium bisulfite at the 50 mg/L levels is equivalent to approximately 900 pounds of sodium bisulfate per million gallons of seawater processed. This adds approximately \$0.20 per thousand gallons to the cost of the product water. This cost is clearly a disadvantage for the process, not to mention the logistics burden of transportation and storage of large quantities of the chemical.

Low levels of copper sulfate have been used effectively to treat seawater feeds to reverse osmosis plants to control algae. Its effectiveness as a biocide, however, has not been well documented. Furthermore, the discharge of copper sulfate into the seawater environment is undesirable.

Currently, seawater desalination by reverse osmosis is viewed with considerable conservatism. However, as increasing energy costs make distillation processes more costly, the inherent energy advantage of reverse osmosis will give the process an increasing share of the growing market. Toward that goal, membrane manufacturers must:

- Develop an improved understanding of seawater pretreatment chemistry.
- Develop a better understanding of the limitations of their products.
- Develop high performance membranes from polymer materials that do not degrade in oxidative seawater environments.
- Develop membranes that are not dependent on periodic surface treatments with chemicals to restore and maintain membrane performance.
- Develop membranes from polymers exhibiting low levels of bacteria attachment to minimize fouling.
- Employ efficient energy recovery systems to reduce the operating costs of seawater desalination.

Single-stage seawater desalination systems are generally limited to a maximum of 45% water recovery when operating on seawater feeds with total dissolved solids in the 35,000 to 38,000 mg/L range. The limiting factor in plant operation and water recovery is the high osmotic pressure observed in the final elements in a membrane pressure vessel, severely reducing the net pressure, or driving force, to produce sufficient permeate flow and permeate concentration.

Figure 5-13 shows the effect on the osmotic pressure of the feed and the net driving force as the seawater traverses through each element in the pressure vessel. It is the net driving pressure that dictates both flow rate and membrane rejection in all membrane systems. Considerable savings in both capital and operating costs would be realized by a thinner membrane barrier, because plant operation could be carried out at a lower pressure.

5.5.3 Energy Recovery for Large Seawater Desalination Systems

To lower the energy requirement and the high cost per gallon of fresh water from large seawater desalination plants, energy recovery systems to recover the energy contained in the pressurized concentrated brine streams are essential. An energy recovery system allows a smaller, less costly motor to be used and results in a significant savings in the cost per gallon of product water produced.¹⁶ This effect is illustrated in Figure 5-14. Energy savings of 35% are typical when energy recovery systems are used. Although energy recovery systems are best suited for high-pressure desalination systems, energy savings are also available for low-pressure reverse osmosis membrane systems.

There are three types of energy recovery devices used on reverse osmosis plants today. All are well developed and operate at high recovery efficiencies.

- Pelton wheel, supplied by Calder of England and Haywood Tyler in the U.S.: recovers 85-90% of hydraulic energy of the brine.
- Multistage reverse running centrifugal pump, supplied by Pompes-Ginard of France and Johnson Pumps, Goulds Pumps, and Worthington Pumps in the U.S.: 80-90% hydraulic energy recovery.
- Hydraulic work exchanger across piston or bladder: 90-95% hydraulic energy recovery when used on small systems.

Figure 5-13. Effect of water recovery on the seawater feed osmotic pressure and net driving pressure.

Figure 5-14. Energy cost vs. operating pressure for seawater desalination systems employing energy recovery devices.

5.5.4 Low-Pressure Reverse Osmosis Desalination

In the past, brackish water reverse osmosis desalination plants operated at applied pressures of 400 to 600 psi. Today, with the development of higher flux membranes, both capital and operating costs of the reverse osmosis process can be reduced by operating brackish water plants at pressures between 200 and 250 psi. Low-pressure operation also means these high-flux membrane systems operate within the constraints of the spiral element design (12-17 gallons/ft²-day), thus minimizing membrane fouling that would occur if higher pressure were used. The significant energy savings achieved are illustrated in Table 5-11, which shows the comparative energy requirements of a membrane system operated at 400 and 200 psi.

Table 5-11. Energy Requirements of Reverse Osmosis Brackish Water Membranes

Process Type	Energy Requirements	
	kWh/m ³	kWh/1,000 gal
Brackish Water - 400 psi	2	7.6
Brackish Water - 200 psi	0.8-1.5	3.0-5.7

In addition to the increased productivity exhibited by the new low-pressure reverse osmosis membranes, they show enhanced selectivity to both inorganic and organic solutes and, in some cases, increased tolerance to oxidizing agents. These properties make the membrane particularly attractive for a wide variety of applications, including brackish water desalination. These applications include:

- High purity water processing for the electronic, power, and pharmaceutical industries.
- Industrial feed and process water treatment.
- Industrial wastewater treatment.
- Municipal wastewater treatment.
- Potable water production.
- Hazardous waste processing.
- Point of use/point of entry.
- Desalting irrigation water.

A comparison of the desalination performance of several commercially available low-pressure membranes is shown in Figure 5-15.¹⁵ These low-pressure reverse osmosis membranes have significantly lower operating costs, improved water quality, and reduced capital costs. It is anticipated, therefore, that these membranes will soon become the state-of-the-art design for new and replacement plants and will have a higher than normal growth rate. This growth should also allow membrane manufacturers to increase gross margins by producing an improved product which will help stabilize the industry in this period of price instability.

Figure 5-15. Desalination performance of several commercially available low-pressure membranes. Feed: 1,500 mg/L NaCl at 15 kg/cm², 25°C.

5.5.5. Ultra-Low-Pressure Reverse Osmosis Desalination

The ultra-low-pressure reverse osmosis process is commonly referred to as nanofiltration or "loose reverse osmosis". A nanofiltration membrane permeates monovalent ions and rejects divalent and multivalent ions, as well as organic compounds having molecular weights greater than 200. As the name implies, nanofiltration membranes reject molecules sized on the order of one nanometer. Nanofiltration is a low-energy alternative to reverse osmosis when only partial desalination is required.

Nanofiltration membranes are thin-film composite membranes, either charged or non-charged. They are currently being commercialized by several membrane manufacturers. A comparison of desalination performance of these commercial membranes is shown in Figure 5-16.²³

These membranes typically exhibit rejections of 20 to 80% for salts of monovalent ions. For salts with divalent ions and organics having molecular weights about 200, the rejections are 90 to 99%. Thus, these membranes are well suited for:

- Removal of color and total organic carbon (TOC).
- Removal of trihalomethane precursors (humic and fulvic acids) from potable water supplies prior to chlorination.
- Removal of hardness and overall reduction of total dissolved solids.
- Partial desalination of water (water softening) and food applications.
- Concentration of valuable chemicals in the food and pharmaceutical industries.
- Concentration of enzyme preparations.
- Nitrate, selenium, and radium removal from groundwater in potable water production.
- Industrial process and waste separations.

For most water with dissolved solids below 2,000 mg/L, nanofiltration membranes can produce potable water at pressures of 70 to 100 psi. However, a low-pressure reverse osmosis plant operating at 200 psi can produce a higher quality permeate.

Taylor et al.,¹⁷ in a survey of ten operating nanofiltration and reverse osmosis membrane plants concluded that the capital cost for a nanofiltration plant is equivalent to a reverse osmosis plant. Although pumps, valves, piping, etc. are less expensive for a nanofiltration plant, the same membrane area will be required because the fouling potential is the same for both membrane types. The lower cost for construction is offset by the higher cost of the nanofiltration membranes. The membrane cost represents only about 11% of the total cost of the permeate produced. Thus, the initial membrane price is not as important as the membrane and plant reliability.

Estimated cost data for a 38,000 m³/day (10 MGD) low-pressure reverse osmosis plant operating at 240 psi and 75% recovery give a projected water cost of \$0.38/m³ permeate. An equivalent nanofiltration plant operating at 100 psi is about 7% cheaper, due to the lower pumping costs. The relative cost advantage for nanofiltration membranes compared with reverse osmosis membranes is, therefore, slight, but will increase as energy costs rise. These ultra-low-pressure membranes are currently finding acceptance in Florida for softening groundwater. The future for these reverse osmosis membranes appears to be bright.

Figure 5-16. A comparison of the desalination performance of several commercial ultra-low-pressure membranes operating on a 500 mg/L NaCl feed at 7.5 kg/cm², 25°C.

5.6 DOE RESEARCH OPPORTUNITIES

5.6.1 Projected Reverse Osmosis Market: 1989-1994

A significant number of large desalination plants, both multistage flash (MSF) and reverse osmosis, are slated to be built between now and the early 1990s, primarily in the Middle East, Spain, and Florida in the United States. New plant construction for 1988 is estimated at 440 mgd; estimates for 1989 and 1990 are for 220 mgd. Projections through 1994 include 267 mgd of new construction for that year. If projections are realized, this would increase the present world capacity of 3 billion gpd by more than 33%.⁵

About 50% of this new capacity would be MSF, with 41% reverse osmosis. This includes 100 mgd of brackish water reverse osmosis in South Florida over the intermediate time range 1993-1994. These plants will utilize low-pressure and ultra-low-pressure energy-efficient membranes for brackish groundwater desalting, water softening, and trihalomethane precursor removal.

Presently, Spain with 12.3% of desalination plant sales is the fastest growing worldwide market. This market is focused on seawater desalination in the Canary Islands using reverse osmosis.

The use of desalination as a water treatment process will continue to increase worldwide. In the United States, reverse osmosis will be the most rapidly accepted process. This process will be used primarily for:

- Desalting brackish groundwater for potable purposes.
- Treating municipal waste water.
- Industrial process water.

Some bias against desalination technologies still exists, particularly in the area of municipal water treatment. Conventional processes are still preferred by some consulting engineering firms who design the plants, by water utilities that build and operate the plants, and by public health agencies. This bias is expected to decrease significantly with the introduction of new and improved low- and ultra-low-pressure membranes. These membranes, because of their inherent lower energy requirements, will be dominant factors in expanding the reverse osmosis market.

5.6.2 Research and Development: Past and Present

Between 1952 and 1982, Federal funding for desalination research, development, and demonstration averaged about \$11.5 million per year (as appropriated) - about \$30 million per year in 1985 dollars. This program, a portion of which was directed to membrane processes, was primarily responsible for the development of reverse osmosis. As shown in Figure 5-17, the program peaked in 1967 and was virtually nonexistent in 1974.⁶ By that time, the United States had established a technological leadership role for reverse osmosis desalination throughout the world. The technology developed under this program was made freely available throughout the world through workshops and the wide distribution of published papers. The western drought of 1976-77 renewed interest in membrane improvement for reverse osmosis and additional funding was provided at a rate of about \$10 million per year until 1981 when the program was officially terminated.

Figure 5-17. Annual Federal funding for desalination research and development.²⁷ Between one-half and two-thirds of the money was spent on membrane research.

Since the termination of the Federally-funded desalting program, most U.S. companies have committed little, if any, funding for reverse osmosis membrane research and development. Further, with worldwide membrane product sales of \$118 million per year and due to the low or negative profit margins associated with the competitiveness of the industry, it is unlikely that this situation will change. Much of the present research and development effort is applied research, rather than basic research, directed toward the development of specific products or improving plant efficiencies. Most of this work is done within private companies. There are no industry coordinated research efforts being conducted at this time. In addition, there is little, if any, research being conducted in U.S. universities. As a result, many of the dominant patents upon which the U.S. membrane industry was built have expired, leaving most membrane manufacturers with a weak or non-existent patent position. In the private sector, the level and focus of research and development is controlled largely by the marketplace. In this case, development costs are indirectly passed on to the end user.

The reverse osmosis industry is presently unable to justify sponsoring significant amounts of research and development to maintain world leadership. For the most part, the industry believes that a Federal program should assist on a cost sharing basis where individual companies could retain a proprietary position. Such a program would improve the competitive position of the U.S. membrane industry in foreign markets, as well as benefit municipal and industrial users of this technology in the U.S.

5.6.3 Research and Development: Energy Reduction

Reverse osmosis is a low-energy desalination process because, unlike distillation, no phase change occurs. Significant advances have been made over the past decade in membrane polymers, structures, and configurations that have reduced energy consumption. However, reverse osmosis is still far from the theoretical minimum energy requirements of the process. In the following section, areas of research directed toward reducing the energy requirements of the reverse osmosis process are described.

5.6.4 Thin-Film Composite Membrane Research

5.6.4.1 Increasing water production efficiency

Thin-film composite membranes for desalination were created by the reverse osmosis industry primarily because asymmetric membranes were unable to provide the transport properties required for seawater desalination. The work that led to the development of these membranes was empirical and limited to polyamide-type membrane systems. The water production efficiency of these membranes, as described below, is only about 30% of the theoretical value. Thus, energy consumption is high even with the new low-pressure membrane systems.

The development of the thin-film composite membrane was undertaken soon after it was realized that the Loeb-Sourirajan method was not a general membrane preparation method that could be applied to a wide variety of polymer materials. Thin-film composite membranes, for the most part, are made by an interfacial process that is carried out continuously on the surface of a porous supporting membrane.¹⁸ The thin semipermeable film consists of a polyamide-type polymer, while the porous supporting membrane is polysulfone. This method of membrane processing provides the opportunity to optimize each specific component of the membrane structure to attain maximum

theoretical water productivity and/or minimum theoretical energy consumption. The discussion that follows describes how the energy consumption required by state-of-the-art thin-film composite membranes can be reduced significantly.

- Theoretically, the thin, dense film can be made on the order of 200 Å thick, five to ten times thinner than either asymmetric or current commercial thin-film composite membranes. Attainment of such film thicknesses has been demonstrated. Reduction of the thickness of these films can significantly reduce the energy consumption of the process, since the water throughput through the thin polymer film is inversely proportional to thickness for a given set of operating conditions.
- Both the thin barrier film and the porous supporting membrane can be made from different polymer materials, each optimized for its own specific function.
- The surface pore size, pore size distribution, and surface porosity of the porous supporting membrane must be such that flow through the thin-film is not hindered. Commercial thin-film composite membranes operate at only about 30% efficiency because of flow restrictions.¹⁹
- The charge on the surface of the thin-film barrier can be varied and controlled. To minimize energy consumption, interactions between the membrane surface and feed components that will increase resistance to flow must be avoided. Ideally, membrane surfaces should be neutral.

Research opportunities abound in the area of membrane optimization -- which leads to reduced energy consumption. Other research opportunities in this area are suggested below:

- Present thin-film composite membranes are limited to operating temperatures of 40–50°C. For example, composite membranes are required for the food industry that are capable of operating up to 100°C for energy savings and to control the growth of microorganisms by sterilization.²⁰
- Attachment of biocides, surfactants, anti-foulants, anti-scalants, and enzymes at the thin-film interface with the feed stream is of interest to minimize fouling, thereby reducing the pressure drop across the membrane element and energy consumption. Experimental investigation of surface attachment is needed.²¹
- Develop new types of interfacially formed thin-film systems that are capable of withstanding a constant level of chlorine (an effective biocide) at 0.5 to 2.0 mg/L for periods of three to five years.

5.6.4.2 Seawater reverse osmosis membranes

There is a need to improve the stability and reliability of the present state-of-the-art polyamide-type reverse osmosis seawater membranes. This is particularly needed for plants operating on open seawater intakes where disinfection by chlorination is required to control growth of microorganisms. The sensitivity of these membranes to chlorine and oxidizing agents is such that chlorination/dechlorination is required when chlorine is used as a disinfectant in pretreatment. Today, there is a lack of understanding by both membrane manufacturers and OEMs of how to successfully dechlorinate a seawater feed to polyamide-type thin-film composite membranes at a reasonable cost. A number of large seawater desalination plants have been lost due to insufficient dechlorination.

To improve the reliability of the reverse osmosis seawater desalination process, the following areas of research should be considered:

- Development of seawater membranes from oxidation-resistant polymeric materials.
- Development of effective methods for disinfecting seawater feeds at competitive costs that do not damage polyamide type membranes.
- Development of a comprehensive understanding of the process of dechlorinating seawater with sodium bisulfite and/or sulfur dioxide. Determine the influences of dissolved, heavy metals, etc. on the process.
- Analysis of the effects of dissolved oxygen in seawater, if any, on the stability of polyamide type membranes.
- Comprehensive evaluation of the oxidation-reduction (redox potential) characteristics of pretreated seawater and the influence, if any, it has on membrane degradation.

As previously discussed, research should be directed toward increasing the water production efficiency of polyamide type thin-film composite membranes, because significant energy savings could be attained by operating reverse osmosis plants at lower applied pressures.

5.6.4.2 Low-pressure membranes

The economic advantages of low pressure (200-240 psig) membranes are lower energy consumption and operating costs. For these reasons, older reverse osmosis plants are being retrofitted and converted to low-pressure operation.²²

The membranes used in these processes, for the most part, are not new developments, but material and morphological optimizations of current technology. These long-overdue improvements have been demonstrated with both asymmetric cellulose acetate and thin-film composite membranes. Low-pressure asymmetric cellulose acetate membranes are now operating at the 5 mgd Orange County Water District's reverse osmosis plant on a municipal waste water feed at significantly reduced energy costs.

Even though great strides have been made, these membranes retain the material limitations of the original system with respect to temperature, bacterial adhesion, lack of oxidation resistance, etc. Research and development efforts are required to develop new membrane materials that overcome these limitations. Thin-film composite membrane systems offer the greatest promise to attain these objectives.²³

5.6.4.3 Ultra-low-pressure membranes

The ultra-low-pressure membrane process (<100 psig) is not strictly defined. Unlike normal reverse osmosis, the process operates at lower pressures and allows selective permeation of ionic salts and small solutes. The transport characteristics of these membranes fall into the area between reverse osmosis and ultrafiltration and they are commonly referred to as nanofiltration membranes.

The development of nanofiltration membranes is relatively new, with only a limited number of products in the marketplace today. The potential for this process looks particularly promising since the energy consumption is significantly less than for low-pressure membranes operating on the same application. This savings has been shown to be as much as 15%.²⁴

Most of the ultra-low-pressure membranes developed to date are thin-film composite membrane structures, whose performance characteristics are determined primarily by the chemistry, structure, and thickness of the thin-film barrier surface.

Directed research efforts in this area should result in the development of membranes capable of operating at still lower energy consumption. The focus of this future research, however, should be on improving the selective permeation between various inorganic and organic solutes at ultra-low applied pressures. In addition, it is desirable for the membranes to be resistant to oxidation, stable at high temperatures, and solvent-resistant.

5.6.5 Membrane Fouling: Bacterial Adhesion to Membrane Surfaces

Chlorine is perhaps the most commonly employed disinfectant in the pretreatment of water to control microorganisms. Unfortunately, many types of bacteria exhibit resistance to this biocide, and those microorganisms comprising an attached biofilm in a reverse osmosis membrane element may be entirely resistant to the biocidal effects of such halogen disinfectants. Furthermore, chlorine cannot be used with polyamide type membranes, since this oxidant rapidly deteriorates these membranes with a dramatic loss in salt rejection. Given the limitations of chlorine, and the current lack of alternative biocides, it is no surprise that bacteria and other microbes have been demonstrated to rapidly adhere to and colonize both the feedwater and permeate channel surfaces in membrane elements. The major symptoms associated with microbial fouling of membrane surfaces are:

- A gradual decline in water flow per unit membrane area.
- An associated increase in transmembrane operating pressure of the system, which may eventually exceed the manufacturer's specifications.
- A gradual increase in salt transport through the membrane.
- A gradual deterioration of permeate quality with increasing bacterial count in the permeate.

The cumulative effects of membrane biofouling are greatly increased cleaning frequency and significantly reduced membrane life. These factors result in increased operating and maintenance costs which adversely affect the overall efficiency and economics of the reverse osmosis process. Increased energy consumption is associated with both cleaning operations and reduced water productivity.

Fundamental research is needed in most aspects of membrane biofouling. Investigation of the specific changes in biofilm chemistry and ultrastructure that affect membrane performance is required. Knowledge is also required concerning the specific biochemical and/or environmental signals that must regulate microbial population fluctuations on the membrane surface. It is also important to identify and characterize the repertoire of fouling microorganisms and subcellular components that are most significant in terms of loss in membrane performance.

The bacterial adhesion process is fundamental to the often serious biofouling problems encountered in reverse osmosis systems. Currently, there is a very limited understanding of the adhesion process, although research methods have recently been developed which have the potential to greatly expand our knowledge in this critical area.¹¹ Thus, it is imperative that a detailed understanding of the subcellular and molecular mechanisms of adhesion exhibited by fouling bacteria be acquired before truly effective measures for controlling biofouling in reverse osmosis membrane systems can be designed and implemented.

The current inability to effectively and reliably control microbial adhesion and biofouling in reverse osmosis systems suggests that this is an area needing considerable further investigation. Some worthy research goals in the area of membrane biofouling might include:

- Additional research on the types of fouling bacteria, their specific adsorption behavior and kinetic attributes, and the molecular basis for their attachment to different membrane polymers operated under differing feedwater conditions.
- Exploration and development of innovative membrane polymers having significantly reduced affinity for microbes implicated in the biofouling process.
- Development of alternative biocidal agents that exhibit greater activity against biofilm bacteria.
- Development of novel and cost-effective pretreatment methods which are more capable of removing biofouling type microorganisms from feedwater streams.
- Development of reverse osmosis cleaning formulations which display increased ability to disrupt and solubilize microbial biofilms without adversely affecting membrane performance.
- Establishment of appropriate mathematic algorithms which can be utilized to predictively model biofouling in reverse osmosis membrane systems. Such a model would be extremely useful in the earliest stages of new plant design and engineering, when membrane selection, long-term performance, and operating and maintenance costs must be predicted with a reasonable level of confidence and accuracy.

5.6.6. Spiral-wound Element Optimization

The design of the spiral-wound element has not changed appreciably since its early development in the late 1960s. With the development of low- and ultra-low-pressure membranes, the design and material selection becomes more important. For example, the net pressure may be on the order of 70 psig for ultra-low-pressure and 180 psig for low-pressure membranes. Thus, flow resistance within the element, or differential pressure, becomes a significant percentage of the net pressure.

The differential pressure across the element is approximately linear with feed flow rate. A typical differential pressure drop for a new 40-inch low-pressure (214 psig) element, as designated by the manufacturer's specification, is <14 psi. The differential pressure for a vessel of six elements is <29 psi. A large amount of this flow resistance can be attributed to the turbulence-promoting mesh-screen type feed spacer separating the membrane sheets within the spiral element. Thus, for a low-pressure membrane element that operates at a net driving pressure 190 psig, a pressure drop of 29 psig reduces the net driving pressure by 15%. Such elements are generally cleaned when the pressure drop increases by a factor of 1.5, or 43.5 psig for a vessel of six elements.

This condition reduces the net driving pressure by 15%. If the plant operates at a constant flow, this requires a significant increase in operating pressure and energy consumption.

It becomes apparent that the pressure drop within a spiral element becomes a restricting factor in setting the lower limits at which low-pressure membranes can operate. Development work is needed to improve the efficiency of the spiral element for low net pressure operations by:

- Selecting new spacer materials that have a low affinity for bacteria adhesion to minimize fouling.
- Selecting spacer designs that are amenable to and assist cleaning. Present type spacer materials trap suspended solids within the cells of the mesh screen, particularly after cleaning.
- Designing spacer configurations that are more effective turbulence promoters and offer less resistance to flow.
- Designing spacer materials that minimize stagnant areas within the element. The efficiency of present elements is significantly reduced by areas of low feed flow and stagnation near the product water tube.
- Optimizing the design of anti-telescoping devices with respect to flow resistance.

Such improvements in element materials and design would enhance the energy efficiency of membrane processes that operate at low net driving pressures. Processes of this type are a rapidly growing segment of the market and exhibit the greatest potential for energy reduction.

5.6.7. Future Directions and Research Topics of Interest for Reverse Osmosis Systems and Applications

Despite the success of membranes developed for reverse osmosis applications during the past 25 years, considerable research efforts are warranted to achieve the full potential of this process with significant reductions in overall cost and energy expenditures. Tables 5-12 and 5-13 outline future directions and topics of interest for research on reverse osmosis systems and applications, respectively. The importance of each topic is rated on a scale of 1 to 10, with the higher number showing the larger degree of importance.

Table 5.12. Future Directions for Reverse Osmosis Applications

Topic	Prospect for Realization	Importance	Comments/Problems
<u>Seawater</u>	Excellent	5	The reliability of single-stage seawater reverse osmosis process requires further improvement to make the process more competitive with conventional processes. Improvements in membrane flux, selectivity and oxidative stability are required.
<u>Brackish Water</u>			
Surface	Excellent	7	Greater selectivity at lower pressures desirable for reducing energy and capital costs. Membrane fouling a major problem on these complex feeds.
Well	Excellent	10	Greater selectivity at lower pressures desirable for reducing energy and capital costs.
Softening	Excellent	7	A rapidly growing market, particularly in the Florida area for softening underground water. Also promising for seawater softening of feeds to reverse osmosis and distillation plants. Requires ultra-low-pressure membranes that can discriminate between monovalent and divalent ions.
<u>Water Reclamation</u>			
Municipal waste	Excellent	7	Bacteria fouling of the membrane surface is the major obstacle limiting this application. Membranes are required that exhibit low levels of bacteria attachment, oxidation resistance and are capable of operating at low pressure to reduce energy and capital costs.
Agricultural Drainage	Fair	2	Very complex and difficult high-fouling feedstreams that contribute to high system costs. Requires low-pressure membranes.
Industrial waste	Good	5	Very complex and difficult high-fouling feedstreams that contribute to severe membrane fouling.

Table 5.12. continued

Topic	Prospect for Realization	Importance	Comments/Problems
<u>Process Water</u>			
Boiler water	Excellent	8	Requires highly selective membranes capable of producing a very high quality product water at low pressures. The rejection of silica must be high.
Ultrapure water	Excellent	7	This application requires the highest quality of membrane element and manufacturing. The membrane product must be free of any leachable materials into the ultrapure water product stream.
Dewatering	Fair	3	Dewatering of a feedstream results in a concentrate of high solids contents. Improvement in membrane packaging is necessary to minimize fouling in this application.
High temperature	Fair	2	Energy savings can often be attained by processing high-temperature feedstreams. For this application, a high-temperature stable membrane package is required.

Table 5.13. Research Topics of Future Interest for Reverse-Osmosis Systems and Applications

(SW = Seawater, BW = Brackish Water, WR = Water Reclamation, PW = Process Water)

Topic	Prospect for Realization	Importance				Comments/Requirements
		SW	BW	WP	PW	
<u>Thin-Film Composite Membrane Research</u>						
						Thin-film composite membranes in use today are first generation technology. As a result, the potential for improvement is excellent.
Increasing water flux	Excellent	5	8	8	8	Commercial thin-film composite membranes operate at about 30% of theoretical efficiency because of flow restrictions within the membrane. Modest improvement could reduce the energy consumption of the reverse osmosis process significantly.
Seawater membrane	Excellent	8	-	-	-	Single-stage seawater desalination is the most cost effective mode of operation. Membrane improvements in water flux, selectivity and oxidation resistance are necessary to improve the reliability and competitiveness of the process.
Low-pressure membrane	Excellent	-	8	8	8	Thin-film composite membrane systems offer the greatest potential to achieve this objective. Material and morphological optimization of current membrane systems are required.
Ultra-low-pressure membrane	Excellent	-	5	6	8	The need to achieve better resolution in the separation of ions/molecules of different types but similar sizes at ultra-low pressure is increasing.

Table 5.13. continued

(SW = Seawater, BW = Brackish Water, WR = Water Reclamation, PW = Process Water)

Topic	Prospect for Realization	Importance				Comments/Requirements
		SW	BW	WP	PW	
Oxidation-resistant membrane	Good	10	7	10	7	Commercial polyamide reverse osmosis membranes rapidly deteriorate in the presence of oxidizing agents such as chlorine, hydrogen peroxide, etc. This deficiency has slowed the acceptance of the process in some areas.
High-temperature	Excellent	1	3	3	8	Current membranes are limited to applications that do not exceed 35-40°C. Many applications, particularly in the process water areas require high-temperature stable membranes. Modification of existing thin-film composite membranes can be made to achieve this objective.
<u>Bacterial Attachment to Membrane Surfaces</u>	Excellent	6	4	10	4	Bacteria fouling of membrane surfaces reduces productivity. Affinity of microorganisms for different membranes is markedly different. Elucidation of attachment mechanism required to select optimal membrane material and surface morphology.
<u>Spiral-wound Element Improvement</u>	Excellent	4	4	9	6	New feed spacer designs are necessary to minimize fouling and enhance the efficiency of membrane cleaning. Current feed spacers trap suspended solids within the interstices of the feed spacer, making them difficult to remove during cleaning.

Table 5.13. continued

(SW = Seawater, BW = Brackish Water, WR = Water Reclamation, PW = Process Water)

Topic	Prospect for Realization	Importance				Comments/Requirements
		SW	BW	WP	PW	
<u>Pretreatment/Fouling Cleaning</u>	Excellent	4	4	9	6	The need for greater volumes processed before fouling/scaling and subsequent cleaning of the membrane system equates directly to a lower cost.
Improved pretreatment	Good	9	7	9	8	Improvement of classical pretreatment methods that will enhance the reduction of suspended solids in feedstreams to reverse osmosis systems is desired.
Chlorination/ Dechlorination	Good	10	4	3	3	Process improvements are required to protect chlorine-sensitive TFC polyamide membranes.
Colloidal Fouling	Good	6	8	6	4	The AL/FE/Si-humic acid colloidal complex, present in surface waters, is particularly troublesome. Improved pretreatment and cleaning processes are needed.
Other Foulants	Good	7	6	6	8	Adsorption of organic materials on membrane surfaces is a major problem with complex feed waters containing organic materials.
Scaling (CaCO ₃ , BaSO ₄ , etc.)	Excellent	1	2	2	4	Commonly used polyacrylic acid anti-scalant materials are adequate.
Silica Anti-Scalant	Good	1	6	6	7	An anti-scalant is needed to increase the water recovery of reverse osmosis plants operating on high silica feeds.

Table 5.13. continued

(SW = Seawater, BW = Brackish Water, WR = Water Reclamation, PW = Process Water)

Topic	Prospect for Realization	Importance				Comments/Requirements
		SW	BW	WP	PW	
Disinfectants	Good	7	4	10	4	Non-THM producing disinfectants are needed to control membrane fouling by micro-organisms.
Cleaning Improvements	Excellent	6	6	9	5	Membrane cleaning is not always successful; it remains a trial-and-error operation.
<u>Energy Recovery Devices</u>	Poor	2	2	2	2	State of the art energy recovery devices are relatively efficient.

5.6.8. Summary of Potential Government-Sponsored Energy Saving Programs

The Federal Government will be one of the largest beneficiaries of energy-saving advancements that may result from the aforementioned research and development. With both the military program and the Bureau of Reclamation's 72 mgd Yuma reverse osmosis desalination plant, the Federal Government has been the largest purchaser of reverse osmosis elements.²⁵ Unfortunately, membrane elements scheduled to go on line at the Yuma Desalination Plant in 1991 are dated technology. The asymmetric cellulose diacetate membrane elements contracted for the Yuma plant will operate at 400 psig and above on high-salinity irrigation drainage return water to the Colorado River before entering Mexico. Difficulties were encountered with these membranes in the pilot test program with respect to fouling and membrane stability that have not been satisfactorily resolved. Thus, additional membrane elements were added to the plant to compensate for unacceptable high fouling rates.

The estimated water cost from the plant is about \$0.80 per 1000 gallons. The operating costs have increased about 50% over the original estimates, based primarily on order of magnitude changes in energy prices. With that as emphasis, the Federal Government must more actively pursue cost-saving potentials. Areas to consider are low-pressure, chlorine-resistant membranes that are less susceptible to fouling, off-peak electrical operation, particularly seasonal, and cogeneration.

Federal support of research and development for the development of energy-saving reverse osmosis membranes and demonstration projects is in the Federal Government's interest. If research and development is left to the private sector, the level of effort will be controlled largely by the market demand. This type of research and development is usually focused on the short-term and has not proven successful for the U.S. desalination industry. The primary issue, then, is not how much research should be conducted, but who should fund it - the Federal Government or the users of desalination. Since the Federal Government is one of the largest users of reverse osmosis technology in the U.S., their participation seems apparent.

The market for membrane processes will be driven not only by energy reduction, but also by stringent standards for drinking water, hazardous waste disposal, industrial wastewater discharge, municipal wastewater, etc. For the most part, these processes would utilize the same energy-efficient membranes requiring similar performance characteristics.

Government and private industry could cooperate in the joint development of new low-pressure, energy-efficient membrane systems for all these applications. The development test facilities at the Yuma plant could be used both by the Federal Government and private industry. To utilize the available resources, the Federal program could be a cooperative one between Departments involved in supporting desalination research. A return to high energy prices would tend to elevate the priorities associated with such a program.

REFERENCES

1. H.K. Lonsdale, U. Merten and R.L. Riley, "Transport Properties of Cellulose Acetate Osmotic Membranes," J. Appl. Poly. Sci. **9**, 1344 (1965).
2. S. Sourirajan, "Reverse Osmosis", Academic Press, New York (1970).
3. S. Loeb and S. Sourirajan, Adv. Chem. Ser. **38**, 117 (1962).
4. S. Loeb and S. Sourirajan, "High Flow Porous Membranes for Separating Water from Saline Solutions", U.S. Patent 3,133,132, May 12, (1964).
5. K. Wangnick, 1988 IDA Worldwide Desalting Plants Inventory Report No. 10, June/July, (1988).
6. U.S. Congress, Office of Technology Assessment, Using Desalination Technologies for Water Treatment, OTA-BP-0-46, U.S. Government Printing Office, Washington, D.C., March (1988).
7. J.W. Kaakinen and C.D. Moody, "Characteristics of Reverse Osmosis Membrane Fouling at the Yuma Desalting Test Facility", in: S. Sourirajan and T. Matsuura (Ed.), Reverse Osmosis and Ultrafiltration, ACS Symposium Series 281, 359-382, Washington, D.C. (1985).
8. H.F. Ridgway, C. Justice, A. Kelly, and B.H. Olson, "Microbial Fouling of Reverse Osmosis Membranes Used in Advanced Wastewater Treatment Technology: Chemical, Bacteriological and Ultrastructural Analyses", Applied and Environmental Microbiology, **45**, 1066-1084 (1983).
9. H.F. Ridgway, M.G. Rigby, and D.G. Argo, "Adhesion of a Mycobacterium to Cellulose Diacetate Membranes Used in Reverse Osmosis", Applied and Environmental Microbiology, **47**, 61-67 (1984).
10. H.F. Ridgway, C.A. Justice, C. Whittaker, D.G. Argo, and B.H. Olson, "Biofilm Fouling of Reverse Osmosis Membranes: Its Nature and Effect of Water for Reuse", J. Amer. Water Works Assn., **76**, 94-102 (1984).
11. H.F. Ridgway, D.M. Rodgers, and D.G. Argo, "Effect of Surfactants on the Adhesion of Mycobacteria to Reverse Osmosis Membranes", Proc. of the Semiconductor Pure Water Conference, San Francisco, California (1986).
12. H.F. Ridgway, "Microbial Adhesion and Biofouling of Reverse Osmosis", in B. Parekh (Ed.), Reverse Osmosis Technology: Applications for High-Purity Water Production, Marcel-Dekker, Inc., New York (1988).
13. C.T. Sackinger, "Seawater Reverse Osmosis System Design", Permasep Products, DuPont Company Technical Manual.

14. K. Frank, "Seawater Reverse Osmosis Plant Performance at Lanzarote, Canary Islands", Proceedings of the National Water Supply Improvement Association Conference, San Diego, California, July 31 - August 4 (1988).
15. M. Kurihara, Toray Industries, Tokyo, Japan, October (1988).
16. Calder RO Turbines Technical Product Literature, Calder, Limited, England.
17. J.S. Taylor, et al, "Applying Membrane Processes to Ground Water Sources for Trihalomethane Control, Research and Technology", J. Amer. Water Works Assn., Vol. 79, No. 8, 72-82, August (1988).
18. R.L. Riley, "Thin-Film Composite Reverse Osmosis Membranes: Development Needs and Opportunities", Proceedings Membrane Technology/Planning conference, Boston, Massachusetts, November 5-7 (1986).
19. H.K. Lonsdale, et al., "Transport in Composite Reverse Osmosis Membranes", Chapter 6 in Membrane Processes in Industry and Biomedicine, M. Bier (Ed.), Plenum Press, New York (1971).
20. R.L. Riley, "Reverse Osmosis Apparatus", U.S. Patent 4,411,787, March 25 (1983).
21. J. Stefarik, J. Williams, and H.F. Ridgway, "Analysis of Biofilm from Reverse Osmosis Membranes by Computer Programmed Polyacrylamide Gel Electrophoresis", presented at the 18th Meeting of the American Society for Microbiology, New Orleans, Louisiana, May 4-18 (1989).
22. F. Crowds, "System Economic Advantages of a Low Pressure Spiral RO System Using Thin Composite Membranes", Ultrapure Water, July/August (1984).
23. R.G. Sudak, et al., "Procurement of New Reverse Osmosis Membranes: The Water Factory 21 Experience", Proceedings of the National Water Supply Improvement Association Conference, San Diego, California, July 31-August 4 (1988).
24. J.E. Cadotte, et al., "Nanofiltration Membranes Broaden the Use of Membrane Separation Technology", Desalination, 70, Nos. 1-3, November (1988).
25. K.M. Trompeter, "The Yuma Desalting Plant - A Water Quality Solution", Proceedings of the National Water Supply Improvement Association Conference, San Diego, California, July 31-August 4 (1988).

CHAPTER SIX
MICROFILTRATION
TABLE OF CONTENTS

6.1 OVERVIEW	6-1
6.2 DEFINITIONS AND THEORY	6-2
6.3 DESIGN CONSIDERATIONS	6-9
6.3.1 Dead-end vs. Crossflow Operation	6-9
6.3.2 Module Design Considerations	6-11
6.3.2.1 Dead-end filter housings	6-12
6.3.2.2 Crossflow devices	6-12
6.4 STATUS OF THE MICROFILTRATION INDUSTRY	6-14
6.4.1 Background	6-14
6.4.2 Suppliers	6-14
6.4.3 Membrane Trends	6-16
6.4.4 Module Trends	6-20
6.4.5 Process Trends	6-20
6.5 APPLICATIONS FOR MICROFILTRATION TECHNOLOGY	6-20
6.5.1 Current Applications	6-20
6.5.2 Future Applications	6-21
6.5.2.1 Water treatment	6-23
6.5.2.2 Sewage treatment	6-23
6.5.2.3 Clarification: diatomaceous earth replacement	6-23
6.5.2.4 Fuels	6-24
6.5.3 Industry Directions	6-24
6.6 PROCESS ECONOMICS	6-25
6.7 ENERGY CONSIDERATIONS	6-27
6.8 OPPORTUNITIES IN THE INDUSTRY	6-28
6.8.1 Commercially-Funded Opportunities	6-28
6.8.2 Opportunities for Governmental Research Participation	6-28
REFERENCES	6-31

CHAPTER SIX

MICROFILTRATION

by William Eykamp, University of California, Berkeley

6.1 OVERVIEW

Of the membrane processes included in this study, microfiltration is by far the most widely used, with total sales greater than the combined sales of all the other membrane processes covered.

For all its economic size, microfiltration is surprisingly invisible. It is ubiquitous, with innumerable small applications. A huge fraction of the market for microfiltration is for disposable devices, primarily for sterile filtration in the pharmaceutical industry, and for filtration in semiconductor fabrication processes.

The heart of the microfiltration field is sterile filtration,¹ using microfilters with pores so small that microorganisms cannot pass through them. These disposable filters, typically in the form of pleated cartridges, are sold to a variety of users, but the major customer is the pharmaceutical industry. Although there is intense competition for new sales in this market, stable relationships between suppliers and customers are the rule. The cost of switching to a new supplier can be high and, thus, there is little incentive for substitution of one supplier's product for another's.

The replacement market for sterile filtration cartridges is quite large. Microfiltration cartridges used as vent air filters may last for months, but those used to filter batches of liquid may have a useful life measured in hours. These membranes may sell for little more than \$10/ft², an order of magnitude below some other membranes covered in this report. But costs to manufacture in the volumes required by the market leave a healthy margin for selling costs, research and development, and profit. Cash generated by the business, and the competition within it, provide a steady stream of innovation in the industry.

A second major application for microfilters is in the electronics industry for the fabrication of semiconductors. As semiconductor devices shrink in size, the conductive paths on their surfaces get closer together. Dirt particles represent potential short circuits in the semiconductor device. Therefore, filtration of various streams throughout the manufacturing process is a vital concern. For microfiltration companies schooled in the sterile filtration discipline, the electronics applications seemed made-to-order. A particularly attractive application in this industry is final filtration of the water used to rinse semiconductors during fabrication. Most of this water is first treated by a reverse osmosis membrane. Since this is a much finer filter than a microfilter, this water contains only a small amount of dirt from the piping and equipment. Thus, microfilters used in this process have long lifetimes. Another area in which microfiltration has been applied in the semiconductor industry is in filtering the gases and liquids used as reactants in making a chip. These chemicals are often very aggressive, and cannot be prefiltered by reverse osmosis membranes, so these streams are a challenge and an opportunity for microfilter manufacturers. The electronics industry has proven to be a strong market for microfiltration, and is now second only to sterilizing filtration.

In both of the major microfiltration applications, sterile filtration and semiconductor fabrication, energy considerations are less important than other issues such as product quality. Some of the sterile microfiltration applications replace thermal sterilization. In these cases, there is a direct energy saving in the process and an indirect saving through avoidance of heat exchange equipment, which has energy-intensive fabrication requirements. Energy is a negligible consideration in the electronics applications. Other applications for microfiltration, particularly some of the emerging potential applications, may offer significant energy advantages over alternative methods. Therefore, the emphasis of this report will be less on current dominant applications of microfiltration, where energy is not a significant issue, and more on less developed process applications.

6.2 DEFINITIONS AND THEORY

Microfiltration is a process for separating material of colloidal size and larger from true solutions. It is usually practiced using membranes. In this report, only microfiltration accomplished by membranes is covered. Microfilters are typically rated by pore size, and by convention have pore diameters in the range 0.1-10 μm . A photomicrograph of the surface of a typical microfiltration membrane is shown in Figure 6-1. A microfiltration membrane is generally porous enough to pass molecules which are in true solution even if they are very large. Thus, microfilters can be used to sterilize solutions, because they may be prepared with pores smaller than 0.3 μm , the diameter of the smallest bacterium, *Pseudomonas diminuta*.

There are several key characteristics necessary for efficient microfiltration membranes. These are (1) pore size uniformity, (2) pore density, and (3) the thinness of the active layer or the layer in which the pores are at their minimum diameter. The impact of these parameters on the flow through the membrane can be seen by examining the governing equation for flow through the pores of a membrane, Poiseuille's law:

$$Q/A = \left[\frac{\pi \Delta p}{8 \mu \delta} \right] \sum n_i d_i^4 \quad , \quad (1)$$

where Q/A is the volumetric flow rate per unit membrane area, Δp is the pressure drop across the membrane, μ is the solution viscosity, δ is the thickness of the active pore layer, and d_i is the diameters of the individual pores in the unit area A .

Figure 6-1. A surface photomicrograph of a typical microfiltration membrane. Membrane shown is Nylon 66 with 0.2 μm pores.

The importance of pore size uniformity is evident, since a membrane will not reliably retain anything smaller than the largest pore, which determines its rating. Smaller pores contribute far less to flow. According to Poiseuille's law, a pore 0.9 times as large as the rated pore size contributes only two-thirds as much flow. Pore length may be minimized by making the active layer δ (in which the pores are at their minimum diameter) as thin as possible. The importance of pore density is especially important in dead-end filtration.

The most uniform pore sizes are found in membranes made by the track-etch process, illustrated in Figure 6-2. Track-etched membranes are made by exposing a polymer sheet to a beam of radiation, then selectively etching away the tracks where the polymer was damaged by the radiation. Photomicrographs of these membranes (Figure 6-3) show a uniformity of pore size difficult to find in membranes formed by other techniques. The pictures also show that the number of pores per area is low. Track-etched membranes cannot be made with high pore densities because of the probability of track intersection, which would result in pores too large for the rating. Polymer strength dictates a minimum film thickness for the membrane which, in the case of the cylindrically shaped pores found in track-etched membranes, governs the pore length.

Membrane pore size is rated by, and tested with, latex particles, bacteria, direct microscopic examination, and bubble point. The bubble point procedure measures the diameter of the largest pore by forcing air through the wetted membrane until a bubble appears. This procedure is illustrated in Figure 6-4. The bubble point is a function of pore diameter and surface tension.

Photomicrographs of membranes made by a new technique, the anodic oxidation of aluminum, show a membrane structure with promise for producing membranes with high densities of thin, uniform pores. An example is shown in Figure 6-5. These membranes should be very useful for many low-solids dead-end filtration applications.

Microfiltration membranes are made in several different forms. One of the most common is the pore filter. As shown in Figure 6-3, a photomicrograph of this type of membrane looks like a plate with cylindrical holes drilled in it. These filters are usually prepared by the track-etch method, described in more detail below. There are, however, many techniques for preparing microfiltration membranes, and they result in physical structures quite different from the pore filter. Like ultrafiltration and reverse osmosis membranes, some microfiltration membranes have conically shaped pores, with the small end of the truncated cone facing the process fluid. In this structure, any particle passing through the small end of the pore encounters a progressively more open path as it passes through the filter. All the filtration is done at the surface, where the "funnel" is narrowest. This feature can significantly reduce plugging and enhance mass transfer.

Other common ways of preparing microfiltration membranes result in structures that resemble porous beds of spheres, slits, and fibrous structures. The final membrane form may be flat-sheet, ceramic monolith, tube, capillary, or fiber, and these may be further modified in preparing various forms of modules.

Figure 6-2. Track-etch process for capillary-pore membranes.

Figure 6-3. Photomicrograph of a Nuclepore® membrane made by the track-etch method.

Figure 6-4. Procedure used in determining bubble-point.

Figure 6-5. Photomicrograph of an Alcan electrolytically deposited alumina membrane.

Microfiltration membranes can be operated in two ways: 1) as a straight-through filter, known as dead-end filtration, or 2) in crossflow mode. In dead-end filtration, all of the feed solution is forced through the membrane by an applied pressure. This is illustrated in Figure 6-6a. Retained particles are collected on or in the membrane. Dead-end filtration requires only the energy necessary to force the fluid through the filter. In the simplest applications, a laboratory vacuum or simple pump provide enough motive force to drive the application at an acceptable rate. The ideal energy requirement, if rate is not critical, is negligibly low. The dead-end microfiltration membrane may be in one of many different forms (flat-sheet, pleated cartridge, capillary, tube, etc.)

The second way to operate microfiltration membranes is in crossflow. In this operational mode, shown in Figure 6-6b, the fluid to be filtered is pumped across the membrane parallel to its surface. Crossflow microfiltration produces two solutions; a clear filtrate and a retentate containing most of the retained particles in the solution. By maintaining a high velocity across the membrane, the retained material is swept off the membrane surface. Thus, crossflow is used when significant quantities of material will be retained by the membrane, resulting in plugging and fouling.

A principal difference in the operation of these two schemes is conversion per pass, or the amount of solution that passes through the membrane. In dead-end filtration, essentially all of the fluid entering the filter emerges as permeate, so the conversion is roughly 100%, all occurring in the first pass. For a crossflow filter, far more of the feed passes by the membrane than passes through it, and conversion per pass is often less than 20%. Recycle permits the ultimate conversion to be much higher, however.

Another difference between dead-end and crossflow operation is the energy required. The energy requirements of the crossflow method of operation are many times higher than those of dead-end flow, because energy is required to pump the fluid across the membrane surface. However, for high solids applications, and for those where the solids would normally plug the filter when it is operating as a dead-end filter, crossflow is the method of choice.

6.3 DESIGN CONSIDERATIONS

The optimum design of a microfiltration membrane system depends on a number of parameters and on the characteristics of the feed stream to be treated. Two important design considerations are 1) the choice of operational mode, either dead-end or crossflow, and 2) module design. Both of these are discussed below.

6.3.1 Dead-end vs. Crossflow Operation

One important characteristic of a feed stream is the level of solids that must be retained by the microfilter. The higher the level of solids, the higher the likelihood that crossflow filtration will be used.

Typically, streams containing high loadings of solids ($>0.5\%$) are processed by membrane filters operating in crossflow. The operation of microfilters in crossflow is similar to the operation of ultrafilters. The major difference is in

Dead-end filtration

a) Dead-end filtration

Cross-flow filtration

b) Crossflow filtration

Figure 6-6. Schematic representations of a) dead-end and b) crossflow operation of microfiltration membranes.

the behavior of the polarized layer near the membrane. The limit to the rate at which a crossflow device produces permeate is paradoxically the rate at which solids retained by the membrane can redisperse into the bulk feed flowing past the surface. Were it otherwise, the crossflow filter would be acting as a dead-end filter, where the solids simply build up at the filter face. Using the theory and concepts developed for reverse osmosis and ultrafiltration, the molecular diffusivity of the retained material is one direct determinate of how fast it diffuses away from the surface. The colloidal material retained by a microfilter has even a lower diffusivity than the macrosolutes in ultrafiltration. The redispersion rate of retained material is thus calculated to be very low. In fact, microfiltration rates are often quite high compared to ultrafiltration, even at lower crossflow velocity. The explanation seems to lie in a shear enhanced particle diffusivity which results in dramatic increases in flux.² The final state of the solids retained in crossflow filtration differs from conventional dead-end filtration. Crossflow devices produce a concentrated liquid retentate, not a dry cake. As this retentate is recycled, it becomes more concentrated in retained solids, the driving force for redispersion of material retained by the membrane declines, and filtration rates decline. Ultimately, there comes a point where it is not economical to concentrate further. Depending on the nature and value of the permeate and the retentate, techniques exist to achieve high recovery of the products.

Membrane filters operating on feeds with medium loadings of solids ($<0.5\%$) are generally operated in dead-end flow. Commonly, the surface of the membrane is protected by a guard filter made of packed glass or asbestos fibers, which entrains most of the larger solids before they reach the membrane. The structure acts as a depth filter backed by a membrane filter. Some of these devices are quite sophisticated, because both prefilter and membrane filter can be charged to give superior non-plugging characteristics. In some applications, these composite structural filters attain the same outstanding characteristics as asbestos filters.

Fluids with low solid loadings ($<0.1\%$) are almost always filtered in dead-end flow, where the membrane acts as an absolute filter as fluid passes directly through it. For some time, track-etched filters dominated this market. Now, other membranes compete successfully.

Earlier, reference was made to membranes with conical pores, and the desirability of this shape for the prevention of plugging. In some low-solids loading applications, these membranes are run "upside down", that is, with the wide part of the cone towards the process stream. In this way, the cone serves as a trap for particles. This configuration mimics that of a structured filter which wraps a coarse filter outside progressively finer filters. Although the membrane eventually plugs, its dirt holding capacity is increased. This operating scheme is only appropriate where the load of material to be retained is low.

6.3.2 Module Design Considerations

For a membrane to be a useful device, it must be packaged in a way that permits the membrane to operate efficiently. Many types of membrane holders and devices are available.

6.3.2.1 Dead-end filter housings

Disk holders: Disk holders represent the simplest membrane filter housing, and their design has evolved slowly since their introduction in the 1950s. The membrane is fitted between two plates, a porous one on which the membrane filter is supported, and a feed plate containing a cavity to permit the fluid to contact the membrane freely. The devices are usually plastic or stainless steel, and the membrane is usually sealed with an O-ring.

Pleated cartridges: Many membranes are pleated, then formed into a cylinder, substantially increasing the membrane area that can be fit into a given volume. The devices resemble the familiar automotive air filter. End caps are generally attached using curable liquid or melt sealants. Cartridges are then fitted into housings, either singly or in groups. The housings are simple pressure vessels, although their design may become elaborate.

Dead-end spiral: Spiral-wound modules are popular crossflow devices, widely used in reverse osmosis and ultrafiltration. A hybrid crossflow/dead-end filter is being manufactured for microfiltration using the principle of running a spiral-wound module as a dead-end filter. During initial operation, until significant solids have built up, most of the feed passes across the membrane, becoming dead-ended only near the outlet of the sealed spiral device. When filled with solids, the spiral operates totally as a dead-end filter.

Air-pulsed capillary: A novel system to handle retained solids is employed by Memtec (Australia). Their device, illustrated in Figure 6-7, operates as a pulse-cleaned, dead-end and crossflow filter. The feed stream passes along the outside of microporous capillaries. It quickly builds a layer of retained material on the surface, acting as a filter-aid formed from retained material. When the layer has developed enough resistance to impede the filtration unacceptably, the filtration is stopped, and air is pushed through the inside of the capillaries and the pores to blow off the filter cake. This backwash frequency is every 10-30 minutes, with a duration of 30 seconds. For high solids loadings, Memtec is able to operate its system in crossflow, since it can run at conversions per pass as low as 50%.³

6.3.2.2 Crossflow devices

For the applications of greatest interest to this study, crossflow devices are dominant. Since they are discussed in more detail in the section on ultrafiltration, they are covered only briefly here.

When significant quantities of solids are present, crossflow operation gives the highest output per unit membrane area. The simplest crossflow device is a membrane formed inside a tube made from a strong, porous material. The feed runs down the inside of the tube, under pressure. Permeate passes through the membrane, then through the porous support.

Another commonly used device is the parallel-plate module, or cassette.

Capillaries, membranes spun so that their porous sublayer provides mechanical support against operating pressure, are operated with bore-side feed. By elevating the permeate pressure above the feed pressure periodically, forcing

Operating Mode

Backwash Mode

Figure 6-7. Operating and backwash mode for the Memtec air-pulsed capillary module.

permeate backwards through the membrane, capillary membranes may be cleaned effectively while still running on the process stream. By so doing, solids built up on the membrane are pushed back into the feed. This operation is fundamentally different than the air-purge dead-end filter, since it relies on crossflow to do almost all of the redispersion of retained solids. The permeate back-pressure cycle is used to remove small quantities of foulant material deposited on the membrane.

Reverse flow of capillaries is also useful to remove a partial blockage of the flow channels. Permeate being forced backwards into the capillary bore expands it slightly, and also pushes the blocked material back in the direction from which it entered. Reverse flow is also practiced in capillary membranes on some dirty streams. By reversing the feed direction, material that accumulates at or near the entrance to the capillary bundle is swept away from the face.

As mentioned under dead-end flow, the air-purged capillary membranes offered by Memtec may be set up to operate at the lower end of crossflow velocities. Because the feed is external to the capillaries, the effectiveness of the hydrodynamic sweeping is reduced. The use of periodic air-pulse cleaning seems to compensate for the reduced level of flow.

6.4 STATUS OF THE MICROFILTRATION INDUSTRY

6.4.1 Background

Membrane filters can be said to have begun with Zsigmondy during The Great War. Development was very gradual during the 1920s and 1930s, and it occurred principally at Sartorius GmbH. At the end of World War II, U.S. occupation forces in Germany were assigned to evaluate German technology and to transfer promising developments to the U.S. Membrane technology was one of the German developments determined to be critical, particularly for its usefulness in assessing the level of microbial contamination in water supplies. After a period of development in both academic and commercial laboratories, the company that is the predecessor of Millipore led in the commercialization of microfiltration membranes and supplies.

6.4.2 Suppliers

The microfiltration industry features some large companies with high growth rates, good profitability, and healthy balance sheets. That general situation has naturally attracted attention, and newer entrants are numerous. Table 6-1 estimates the sales attributable to microfiltration membranes from the total revenues of these suppliers. For the estimate, membranes and membrane-related hardware have been combined. The definition of a membrane is fairly broad, including polymeric, ceramic, inorganic or sintered metal dead-end or crossflow devices that make a separation in the 0.1-5 μm range. Wound, spun-bonded, and wire-based filters are excluded. The inclusion of sintered metal, while arbitrary, does not influence the total numbers significantly.

Table 6-1. The Microfiltration Industry

Company	Location	Approx. Membrane Sales (millions \$)	Products/Comments
Millipore	Bedford, MA	375	Dominant U.S. supplier of laboratory microfiltration membranes. Major producers of cellulose membranes for sterilizing filters, particulate removal.
Pall	Glen Cove, NY	150	Pall has expanded into the microfiltration market in recent years. Offers sterilization and particulate removal filters
Sartorius	Goettingen West Germany (Hayward, CA)	90	First commercial producer of microfiltration membranes. Principal supplier to the European laboratory market.
Gelman	Ann Arbor, MI	60	Sterilizing and particulate removal filters. Millipore's principal competitor in the laboratory market.
Fuji Filters	Japan	15	Principal Japanese micro-filtration company.
AMF Cuno	Meriden, CT	10	Produces surface-charged microfilters for use in pharmaceutical and food industries.
Amicon	Lexington, MA	10	Laboratory microfiltration membranes for sterilization and other applications.
Memtec	Windsor NSW, Australia	7	Laboratory microfiltration and innovative uses of MF.
Schleicher & Schuell	Dassel, West Germany	5	Originally German paper company. Serves laboratory filter market.
Nuclepore	Pleasanton, CA	5	Principal product is a nucleation track membrane used in laboratory and analytical applications.

Table 6-1. The Microfiltration Industry (continued)

Company	Location	Approx. Membrane	
		Sales (millions \$)	Products/Comments
Hoech-Celanese	Charlotte, NC	<5	Celgard® microporous membranes for various applications.
W. L. Gore	Elkton, MD	<5	GoreTex® microporous membranes.
Other specialized or small companies: Anotec, Norton, Alcoa, Osmonics, Mott, Brunswick, Whatman.		5-10 in total	Ceramic, metal, metal oxide membranes and other specialized products.

6.4.3 Membrane Trends

Early in the development of commercial microfiltration membranes, cellulose nitrate (collodion) became the material of choice. The abundance of polymeric materials favored today by membrane fabricators had not been invented. Collodion posed serious safety problems in manufacture, but it was a very good polymer for laboratory membranes, and is still used for a few specialty membranes, either by itself, or blended with cellulose acetate.

Since that time, the industry has moved toward tougher materials, both chemically and mechanically, that can be pleated, autoclaved, washed in solvents, acids, and bases, and still retain their original operating properties.

Polymer membranes are by far the market leaders in microfiltration. The major firms in the worldwide microfiltration business all sell polymer membranes in overwhelmingly greater quantities than the more trendy and more discussed inorganics. Nylon, polysulfone, and polyvinylidene fluoride are the major polymers used, in addition to the old workhorse cellulose. Polypropylene is widely used in process microfiltration.

Recently, a steady stream of innovative membranes have been introduced into the market. The traditional polymeric membranes are made by dissolving a polymer in a water-miscible solvent, then casting it on a surface from which the solvent is removed by exchange with water, either from humid air, from an aqueous solution, or from another of many variants. This process, when properly conducted, forms a membrane. Commercial microfiltration membranes are made from cellulose acetate, several nylons, polysulfone, polyethersulfone, polyvinyl chloride, the copolymer of vinyl chloride and acrylonitrile, and polyvinylidene fluoride by this traditional method.

Polymeric microfiltration membranes can also be produced by other methods, such as thermal inversion (Enka and Memtec polypropylene membranes), selective leaching (Millipore), membranes made by sintering (Mott Metallurgical) or stretching⁴ (Goretex®, W.L. Gore and Associates, and Celgard®, Hoechst-Celanese) and polymeric membranes made as porous sheets by photopolymerization (Gelman). Photomicrographs of the Goretex and Celgard polymeric membranes are shown in Figure 6-8.

Some of the newer microfiltration membranes are ceramic membranes based on alumina (Alcoa-Ceraver), membranes formed during the anodizing of aluminum (Anotec),⁵ and carbon membranes (GFT). As with organic membranes, there are several ways to prepare inorganic membranes. Ceramic membranes may be made by slipcasting onto a porous support, then firing. Preparation of the particles for the slip so that they are both fine enough and monodisperse is difficult, and the sol-gel technique is favored. Organic additives to promote adhesion and to modify viscosity are commonly used. The slip, as an aqueous dispersion, is cast onto a dry porous support, where capillary effects draw water out of the slip and into the support, leaving the gel particles from the slip concentrated at pore openings in the support.⁶ Subsequent firing fixes the particles to the substrate, fusing them into a permanent layer. The unconsolidated openings make up the active membrane layer. The Alcoa alumina membrane is shown in Figure 6-9.

In addition to polymeric and ceramic membranes, there are some other less widely used microfiltration membranes. Glass membranes are normally prepared by the thermal separation of a glass into two phases, one of which is soluble enough in a leachant to be extracted. Sintered metal membranes are fabricated from stainless steel, silver, gold, platinum, and nickel, in disks and tubes.

Dynamically formed membranes have long been of interest, and some are sold in the microfiltration field. The most prominent by far is zirconium oxide deposited on a porous carbon tube. The membrane is formed by passing the suspension of ZrO_2 across the porous support, laying down a semipermanent precoat. The membrane seems to be stable when required, and unstable (removable) when desired. Ultrafiltration and reverse osmosis membranes have also been made by this technique. Rhone Poulenc recently bought SFEC, the primary supplier of these types of membranes in ultrafiltration, who do some business in microfiltration.

Aluminum oxide membranes are formed by the anodic oxidation of metallic aluminum. If the oxidation bath is properly controlled, it is possible to make a membrane with a very high density of uniform, thin, pores.⁷ Anotec is the supplier of these membranes.

a) Goretex®

b) Celgard®

Figure 6-8. Photomicrographs of a) Goretex®, and b) Celgard® polymeric microfiltration membranes.

Figure 6-9. Photomicrograph of an Alcoa alumina membrane.

Carbon membranes are prepared by the controlled pyrolysis of microporous polymeric membranes. Carbon composite membranes are still under development, but these membranes have the potential for toughness, pore-size tailoring, and extremely thin active skins. These properties would make them important industrial membranes if applications develop in sufficient volume to make their manufacture economical.⁸ GFT is the leading supplier of carbon microfiltration membranes.

In some applications, membrane microfiltration competes with depth filtration. Unstructured depth filtration employs diatomaceous earth, pearlite, asbestos, or other finely divided filter aids. Structured depth filtration uses paper or other fiber structures, including glass and polypropylene.

6.4.4 Module Trends

Microfiltration modules began as flat-sheet filters for use in the laboratory, and were soon incorporated into plate-and-frame devices. A growing diversity of applications has led to the development of numerous devices such as the spiral-wound module, copied from other membrane applications, the pleated cartridge, referred to above, the stack-filter module, designed for certain pharmaceutical applications, and capillary modules. Continued development of module types is likely, but the low manufacturing cost of spirals and capillaries makes them the product to beat for volume applications in crossflow. Pleated cartridges enjoy a similar advantage in dead-end applications.

Some of the more innovative membranes developed recently are amenable to compact, economical fabrication. Carbon membranes may be pyrolyzed from fibers, and are described as being formed already sealed to an end plate.¹⁰ Most ceramics are available in tubular form, but one firm has pioneered a low-cost monolith,⁹ and another makes ceramic capillary tubules which can be wound up into a cartridge.

6.4.5 Process Trends

Microfiltration, a relatively mature industry, has had its most profitable growth in relatively small filters operating in high-value applications. The industry trend is to build on this base, but to expand into lower value, higher volume applications. Most of this growth will be with membrane devices operating in a manner that handles retained material efficiently, meaning either crossflow or backwash.

6.5 APPLICATIONS FOR MICROFILTRATION TECHNOLOGY

6.5.1 Current Applications

Most applications for microfiltration membranes are relatively small, specialized uses that add up to a large market. These applications, while very important to industry, health, and research, do not have a significant impact on energy use.

The existing market for microfiltration membranes and equipment is on the order of \$1 billion. This market is served by large companies, commanding generous R&D budgets and possessing excellent market research, marketing, and management. Within the areas they have chosen to pursue, sterile filtration,

medical and biotechnology applications, and fluid purification, it is hard to imagine a real research need that has not been identified or that could not be supported by internal funds.

In addition to those well-established applications, there is a major effort to introduce microfiltration into a wide variety of process applications. These applications, while presently small in number, use large quantities of membrane. Their potential for growth is great, and in terms of membrane area installed, they may grow fast enough to catch the other applications in the 20-year timespan of this report. It is unlikely that they will match the conventional microfiltration applications in dollar value, however. Table 6-2 lists a number of these applications, their primary markets and competing processes, and points out some of the problems of the technology for each.

Table 6-2. Current Process Microfiltration Applications

Application	Customers	Equip. Type	Competing Processes	Problems
Haze removal from gelatin	Food companies	Spiral-wound; plate-and-frame	Diatomaceous earth filtration	High viscosity; very high protein passage required
Dextrose clarification	Corn refiners	Spiral-wound; plate-and-frame	Diatomaceous	High viscosity permeate
Wine	Wineries	Spiral-wound; capillary plate-and-frame	Asbestos	Fouling; yield; flavor
Beer bottoms recovery	Breweries	Spiral-wound; capillary plate-and-frame	Centrifuge	Foam stability; flavor
Bright beer sterilization	Breweries		Pasteurization	Reliability; Huge market potential
Pharmaceutical/Biological	Biotech and Pharmaceutical companies	Dead-end filtration		Market huge, but usually done on a smaller scale than others

6.5.2 Future Applications

Although microfiltration is a mature technology, there are several new applications in which it could become the filtration method of choice. These are summarized in Table 6-3 and discussed below. Their importance for the future growth of microfiltration has been rated between 1 and 10, 1 being the lowest.

Table 6-3. Future Applications for Microfiltration

Application Area	Prospect for Realization	Importance	Comments/Problems
Drinking water	Good	8	Economics potentially superior to sand filters if market acceptance is good. Large scale use would complement displacement of chlorine disinfection. Modular construction could change economics of waterworks.
Municipal sewage treatment	Fair	5	Competes with other technologies. Superior to ultrafiltration in cost, inferior for containing fermentation reactions. Seems capable of virus retention. Impact of success would be large. Economic and technical impediments. Long-range potential for distributed processing of sewage.
Diatomaceous earth displacement	Excellent	9	Membrane does superior job; economics dictate pace.
Hydrocarbon separations	Poor	9	Removing waxes, asphaltenes. Economic hurdle high, working conditions extreme
Milk-fat separation	Fair	5	Membrane could replace centrifuge in recovery of butterfat. Huge volume.
Abattoirs	Fair	3	Membrane could remove cellular material and debris prior to use of ultrafiltration to recover proteins.
Food and beverage	Excellent	7	Many applications in broad food areas based on microfiltration ability to retain microorganisms without affecting desirable properties. Applications to be large, but to grow slowly.
Non-sewage waste treatment	Good	7	Microfiltration looks good for removing intractable particles in oily fluids, aqueous wastes containing particulate toxics, and stack gas.
Coal liquids	Fair	6	Particulates a tough problem. Membranes ought to succeed, if tough enough and cheap enough.
Paint	Good	5	Separation of solvents from pigments
Biotech	Excellent	8	Concentration of biomass; separation of soluble products.

6.5.2.1 Water treatment

The largest emerging opportunity for microfiltration is for the treatment of municipal water, permitting it to be sterilized without chlorine. This would take microfiltration back to its World War II roots. There is no doubt that microfiltration membranes have the ability to remove bacteria from water. A recent Australian study¹⁰ showed that microfiltration membranes can also remove viruses from contaminated surface water. Since viruses are much smaller than the pores in an microfiltration membrane, the finding has been attributed to the viruses being adsorbed on clay particles, which are large enough to be caught by a microfilter. There are, however, concerns about subsequent contamination in the water distribution system, since chlorine has a residual effect that protects water against contamination after treatment. Recent Federal regulations probably mean that chlorination will continue to be required for drinking water supplies.

For communities whose water is hard, it has also been proposed to incorporate lime softening into the microfiltration system. This ancient technology relies on the fact that most calcium hardness is in the form of the bicarbonate. By adding calcium hydroxide to the water, the reaction

reduces the calcium level in the water to the solubility limit of calcium carbonate. The newly precipitated calcium carbonate acts as a precoat on the very open microfiltration membrane.¹¹ Fresh calcium hydroxide may be generated by heating some of the calcium carbonate to the calcining temperature. Either approach to the microfiltration of water would require a major change in the economics of microfiltration. Public health regulations are an additional limiting factor, as those responsible will need to be shown that the new technology is safe.

6.5.2.2 Sewage treatment

The other potentially very large market for which microfiltration might be a candidate is the treatment of municipal sewage. A scheme proposed by Memtec (Australia) would shift the treatment of sewage to distributed processing, a plan that envisions many small sewage treatment facilities, centrally monitored. Should this plan ever become reality, the market for microfiltration membranes would be immense.

6.5.2.3 Clarification: diatomaceous earth replacement

The economics of diatomaceous earth purchase and disposal make it an attractive target for displacement by microfiltration. Microfiltration membranes are usually capable of doing the same job as diatomaceous earth filters, only better, with higher clarity products and higher yield. These advantages are currently marginal in the biggest applications, with not enough economic incentive to achieve the displacement of installed diatomaceous earth filters. As microfiltration starts to chip away at the more attractive applications, however, costs will drop. There is a likelihood that microfiltration will become preferred over diatomaceous earth filtration in new installations within five years, and that it will become attractive enough to displace existing applications at some time within 15 years.

6.5.2.4 Fuels

Fuel-oriented hydrocarbon separations by means of microfiltration represent a high-risk, high-reward opportunity. Presently, most fuel applications appear to be in high-temperature, physically aggressive environments. Economics will be a severe test. To become the process of choice, microfiltration will need to be cheap. Based on what we know today, ceramic or inorganic membranes are the likeliest candidates, but the economic viability of processes based on these membranes is a major uncertainty.

6.5.3 Industry Directions

For any of the major new process opportunities to come to fruition, low-cost process equipment will be required. There is every indication that low-capital designs are viable in process microfiltration. Historically, microfiltration has worked from a massive and diffuse base in which low capital was desirable but not really necessary. Economics were dominated by the cost of membrane replacement, daily in some cases, but rarely less frequently than monthly. As process engineers have started to attack applications such as glucose, beer bottoms, and gelatin, the picture has changed. In these applications, membrane life is dramatically longer. Classic microfiltration firms were competing with ultrafiltration firms, for whom long membrane life is normal. Since this trend means there will be less revenue from membrane replacement, there is a greater incentive to make money on the original capital equipment sale. However, this requires a reversal of the historical trend of declining equipment costs.

As the microfiltration industry targets water and sewage treatment, another major cost decrease must be achieved. In time, and with sufficient volume, this should be possible. However, this will require a well-coordinated effort, designed to deal with the public policy issues of health, sanitation, and regulation for new technologies for water and sewage treatment. Such an effort would cut years off the implementation time for new technologies such as microfiltration. Past efforts to improve equipment design and process economics in this market suggest that dealing with the shape of a publicly acceptable solution at the front end might produce a more cost-effective solution. Firms that are focused on this potential are Memtec (Australia) and Allied Signal.

In the area of food processing, beverages, milk fat removal, and general displacement of diatomaceous earth, the concerns are so dominantly in the private sector, that given the absence of any overriding public issue, neither need nor opportunity for a government program are apparent. Many ultrafiltration firms are active in this area, particularly DDS, Koch Membrane Systems, Dorr Oliver/Amicon (Grace), Romicon (Rohm & Haas), and Enka.

Large microfiltration firms continue their quest for products to fit their vital medical, biological, and pharmaceutical markets. This huge, ongoing effort is totally outside the scope of this report, even though it represents the major activity in the microfiltration field.

As biotechnology begins to increase in scale, the size of the microfiltration equipment will grow to process size. These markets should be intensely scrutinized and hotly contested, if recent history is any guide. Membrane makers

will need to address issues of fouling, non-selective protein adsorption, and lifetime, in addition to specificity and compatibility.

There is every indication that market forces will satisfy the demand, and that U.S. firms will continue to lead even though they will be continue to be challenged from Japan and Europe.

Some of the trends that will dominate the microfiltration industry are summarized in Table 6-4.

Table 6-4. Future Industry Trends for Microfiltration

Topic	Prospect For Realization	Importance	Comments/Problems
Cost	Excellent	10	Huge potential applications will require commodity pricing, far from today's reality. Bright prospects for success based on hemodialysis experience.
Continuous integrity testing	Good	8	Applications where biological integrity is required need evidence of continued compliance, especially if operation is remote and automatic.
Nonfouling, cleanable, durable membranes	Good	7	Critical for abattoirs, dairies, beer, wine. Must be tolerant of the industry approved sanitizer.
Cheap, trash-tolerant designs	Fair	5	Current prospects for cheap membranes do not lend themselves to incorporation into trash-tolerant modules. Problem could be solved less desirably by pretreatment.
Fouling	Good	9	Critical to improving rates. See also ultrafiltration.
High-temperature solvent resistant membranes	Good	9	Inorganics best bet, but refractory polymers good long-shot.

6.6. PROCESS ECONOMICS

The economics of small microfiltration plants are so sensitive to the application that it is difficult to generalize costs meaningfully. In this report, a moderate-sized water plant is used to illustrate the current economics of one of

the least costly applications. The capital and operating costs are given in Tables 6-5 and 6-6, respectively. In fact, all other known applications will have higher capital and operating costs.

A good approximation of the costs of operating a large-scale industrial microfilter in crossflow mode can be found in the ultrafiltration section (Chapter 7) of this report, since the equipment in large-scale applications is similar. Membrane life for a prototype microfiltration application would be 4 years on average, somewhat longer than for ultrafiltration.

Table 6-5. Capital Costs for a Surface Water Microfiltration Plant

Basis: A microfiltration surface water treatment plant processing 500 m³/day (130,000 gpd), using capillary modules with air backwash.

Item	Installed Cost (\$)	% of Total
Replaceable Membranes	60,000	37
Pumps	29,000	18
Pipes and Valves	26,000	16
Tanks and Frame	24,000	15
Instruments and Controls	<u>22,000</u>	<u>14</u>
TOTAL	161,000	100

The total installed cost of this base-case plant is \$320/m³ water treated per day, or \$1.30/gpd. Note that the fraction of the capital in the replaceable membranes is relatively high in this plant because the housing and membranes are integral. This is normal for capillary membranes. Costs for the replaceable elements for a spiral plant would be lower. The total operating costs are estimated to be \$0.23/m³ treated (\$0.06/kgal).

Table 6-6. Operating Costs of a Surface Water Microfiltration Plant

Item	\$/Yr	% of Total
Membrane replacement (2-yr guarantee)	30,000	57
Power (0.6 kWh/m ³ , \$0.07/kWh, 500x365 m ³ /yr)	7,700	15
Maintenance, P & I @ 6% of non-membrane capital	6,000	11
Labor, 10 hr/wk	<u>9,000</u>	<u>17</u>
TOTAL	52,700	100

6.7. ENERGY CONSIDERATIONS

Microfiltration uses mechanical energy to drive fluids through and past the membrane. The ideal energy required to move a fluid through a microporous membrane is negligible. At an operating pressure difference across the membrane of 5 psi in a dead-end filter, energy requirements are only 0.01 kWh/m³ of permeate passing through the membrane.

Crossflow devices consume energy to keep the membrane surface clean, as well as to push the permeate through the membrane. Practical crossflow devices consume about 5 kWh/m³ permeate, essentially all of which is used to minimize polarization, increase rate, and thus lower the membrane area requirement and capital cost. Membrane microfilters compete with centrifuges, clarifiers, coagulation, and with nonmembrane filtration devices such as precoat filters. Microfilters running in dead-end configuration are comparable in energy requirements to competitive processes. Crossflow microfiltration consumes somewhat more energy than processes that compete with it, but it is not an energy-intensive process.

There are numerous energy trade-offs to be considered in determining whether membrane microfiltration saves energy on balance compared to competing processes. For instance, there is a minor benefit from considering energy required to mine and dispose of diatomaceous earth. Balanced against the materials needed to construct a microfilter, it is not clear which requires more energy. It is far easier to make an argument for microfilters as a pollution reduction device than as an energy reduction device.

There are several potential uses of microfiltration, primarily related to fuel processing, that would provide energy savings, if successfully developed. These fuel-related applications are discussed briefly below. In spite of the massive alteration in the microfiltration market that these changes would create, the overall reduction in direct energy consumed would be small. Microfiltration plants do not differ greatly in energy consumption from conventional filters, no matter how large. There will be savings indirectly, from mining, transport, and disposal of diatomaceous earth, but these are small.

Microfiltration membranes have the potential for significant impact on the processing of fuels. Given the fact that most liquid fuels are viscous, and that viscosity declines with temperature, processes in fuel-related applications are likely to be at temperatures above the operating limits of all but the most exotic polymer materials. Potential gas-phase applications for microfiltration also require stable operation at high temperature. Therefore, these applications will require membranes different from those with which we are familiar, such as advanced ceramic, mineral, carbon, metallic, or exotic polymeric membranes.

Oil refining has several potential applications for microfiltration and ultrafiltration membranes. Separation of asphaltenes is the application most frequently mentioned, and if it can be achieved, it would reduce the energy necessary to accomplish solvent de-asphalting. Asphaltene removal can be an ultrafiltration or a microfiltration application, depending on the process. The microfiltration process uses a 0.03- μ m membrane to catch catalyst particles in a residual hydrotreater blowdown. Colloidal asphaltenes and some of the metal

content are captured as well, and recycled to the hydrotreater with the catalyst. The application uses a membrane at 450°C.¹² Heavy crudes, shale oils and tar sands all have particulate problems for which high-temperature microfiltration membranes might be a good solution.

Coal liquefaction produces liquids with submicron ash difficult to remove by conventional means. Microfiltration is a promising candidate for this separation. Microfiltration of gas streams in fuel related applications will be at high temperature. Two applications with a strong energy angle are the removal of soot from diesel exhaust, and the removal of particulates from boiler stack gases. In both these applications, there is existing or emerging technology which competes with a membrane solution. A membrane may be superior, due to compactness, selectivity, and high operating temperature, perhaps higher than is available with competing technology.

A third application with a strong relationship to energy is the removal of particulates from coal gasification plants. In addition to the ability to operate at very high temperature, these membranes would need to be very resistant to erosive and chemical attack.

Treatment of used lubricating oil, particularly automotive crankcase oil is another possible use for high-temperature microfiltration membranes. Many of the contaminants are particulates, and it is possible that microfiltration technology could help this spent oil find a higher use, with less environmental impact than the present technology for treating this waste.

6.8 OPPORTUNITIES IN THE INDUSTRY

6.8.1 Commercially-Funded Opportunities

Many current trends in the microfiltration industry will proceed regardless of outside support. Membrane producers will continue to work on continuous cleaning, pulse cleaning, backflushing, reduced fouling, and exotic membrane materials. Progress will be slow, because the markets for these materials are too small and the costs too high to assure high growth.

6.8.2 Opportunities for Governmental Research Participation

In reviewing the possibilities for the future of this robust and healthy technical field, where so much money has been spent by private companies with numerous dramatic successes, the question arises as to whether outside support is needed at all. Millipore was founded in 1954; Pall entered the microfiltration field just twenty years ago. Those two firms alone have membrane microfiltration sales exceeding \$0.5 billion, with sales doubling every 5 years.

Nonetheless, shifts in membrane materials and markets have been slow. Major capital and commitment is required to launch a new sub-technology. Some of the more innovative, but as yet unproven, technologies are the result of the acquisition of assets developed for other purposes at a price below the cost of development.

Ceramic membranes are an example of this type of technology acquisition. Alcoa bought Ceraver, a firm which had built ceramic barriers for the French uranium isotope separation enterprise. During its early history, Ceraver was heavily funded by an outside institution to develop a product similar to a microfiltration membrane. Therefore, Ceraver easily mastered the microfiltration technology. In their purchase of Ceraver, Alcoa acquired a small but successful marketing organization, large capacity, and a presumably competitive cost of manufacture, all of which permitted rapid advancement down the learning curve.

In contrast, in an attempt to enter the same business, Norton relied on internal funding and internal know-how. Attempts to capitalize on one-of-a-kind government procurements, and then to force the technology into markets where there was adequate, lower cost technology, produced too little cash flow to sustain the business, and it was offered for sale. Limited demand for the unique traits of Norton's technology forced them to attack markets served adequately by other membranes, in an attempt to build volume, improve the product, and thus lower costs.

When there are societal or strategic interests at issue, outside support is essential to get past the high early technical and economic hurdles. With enough lead-time, the existing manufacturers will expand into new markets. However, if those applications are to appear suddenly in the future, outside support may be necessary to achieve quick implementation.

Where public agencies are the major market, the public procurement process discourages expensive proprietary innovation. The innovator is often precluded from harvesting the fruits of his innovation by the nature of civil procurement. If innovation that primarily benefits the public sector is to come about, it will almost certainly require support from outside.

A second area ripe for governmental research participation is in adapting existing technology for high-visibility applications. An example is in petroleum refining. For microfiltration techniques to find industrial process acceptance, they must have some attributes absent in current offerings. They must be very reliable at very demanding environmental conditions, cheap, and easily tailored to fit dynamic needs. Oil refiners usually have ample assets, and a cost-saving new technology will get attention from capable engineers. The development time and cost, however, makes that future market less attractive than the less demanding applications which have a far lower importance insofar as energy saving is concerned.

Building on the huge technical advantage possessed by the U.S., and extending the technology in ways that make it attractive to energy intensive applications, is a prudent policy option. For the technology to be useful, it must have excellent reliability under the most demanding conditions of temperature and chemical stress. It must be very cheap to use, because most operations in the fuels industry are quite low cost. Projects that promote invention and early development of devices that fit potential needs in coal, shale, heavy crudes, and other future fuel sources would be prudent additions to our technological base.

In summary, there are two major areas in which microfiltration could make a significant change in between 1995 and 2010, and which are not likely to occur as the result of a private, ongoing initiative. The first is the general handling of water and waste water. As the report indicates, the energy consequences of changing this are not very large. The second general area is fuel and combustion related applications. Since the rewards are more speculative, only firms with significant long-term resources, or those supported by an agency with a visionary mission, will be able to discover whether microfiltration membranes will have a future role in this area. The fuel field is energy-related. The separations in this field tend to be energy intensive, and microfiltration is a low-energy alternative.

There are three companies that are positioned for some of these high-risk potential opportunities. The major player with potential in this area is Alcoa, through its Ceraver subsidiary. If any firm has the potential to innovate in this field without assistance, it is Alcoa. Minor players are Westinghouse, who has worked in the area of high-temperature gas cleanup for some time under contract from the Office of Fossil Energy, and CeraMem.

CeraMem is a small startup firm whose major accomplishment has been the adaptation of a cheap, high-temperature porous device into a cheap support for microfiltration membranes. The Department of Energy has supported CeraMem's development through several SBIR projects. The effort is directly focused on how to make a cheap module, a critical necessity if microfiltration is to have any role in the fuels field.

Memtec's basic interest is microfiltration, and its product is a capillary polypropylene membrane with 0.2 micrometer pores. It is operated with shellside feed, and operates in crossflow with relatively high (50%) typical conversion. Modules operate at low pressure, 1.5-2 bar being common. Memtec's unique feature is a periodic gas backwash, occurring 4-6 times per hour, typically. Membrane fouling is well controlled by this technique, and it lends itself to periodic leak checking, to insure that the pores have not grown. Memtec claims the ability to detect one large pore in 10^{12} normal pores. Their energy requirement is modest, in the range of 0.2-0.5 kWh/m³ depending on flux. The air backwash requires about 10 L (STP)/m², adding only about 10% to the energy requirement.

REFERENCES

1. R.H. Meltzer, Filtration in the Pharmaceutical Industry, Marcel Dekker, New York (1987).
2. A.L. Zydney, and C.K. Colton, "A Concentration Polarization Model for the Filtrate Flux in Cross-Flow Microfiltration of Particulate Suspensions," Chem. Eng. Commun. 47, 1-21 (1986).
3. Memtec/Memcor product bulletin, PB88/02, Memtec, Locked Mail Bag 1, Windsor NSW 2756, Australia.
4. R.W. Gore, "Porous Products and Process Therefor," U.S. Patent 4,187,390 (February 5, 1980).
5. R.C. Furneaux, et al., U.S. Patent 4,687,551 (August 18, 1987).
6. H.P. Hsieh, "Inorganic Membranes," in New Membrane Materials and Processes for Separation, K.K. Sirkar and D.R. Lloyd (Ed.), A.I.Ch.E. Symposium Series 84, No. 261, 1 (1988).
7. R.C. Furneaux, et al., "The Formation of Controlled-Porosity Membranes from Anodically Oxidized Aluminium," Nature 337, No. 6203, 147-9 (1989).
8. H.L. Fleming, "Carbon Composites: A New Family of Inorganic Membranes," 1988 Sixth Annual Membrane Planning Conference, Cambridge, MA (1988).
9. R.L. Goldsmith, U.S. Patent 4,781,831 (November 1, 1988).
10. M. Kolega, R.B. Kaye, R.F. Chiew and G.S. Grohmann, "Disinfection of Secondary Sewage Effluent by Advanced Membrane Treatment Technology," Memtec Ltd., Windsor NSW, Australia.
11. N. Li, private communication (1987).
12. R.L. Goldsmith, private communication (1989).

CHAPTER SEVEN

ULTRAFILTRATION

TABLE OF CONTENTS

7.1	PROCESS OVERVIEW	7-1
7.1.1	The Gel Model	7-3
7.1.2	Concentration Polarization	7-8
7.1.3	Plugging	7-8
7.1.4	Fouling	7-9
7.1.5	Flux Enhancement	7-10
7.1.6	Module Designs	7-11
7.1.7	Design Trends	7-11
7.2	APPLICATIONS	7-13
7.2.1	Recovery of Electrocoat Paint	7-13
7.2.2	Fractionation of Whey	7-13
7.2.3	Concentration of Textile Sizing	7-13
7.2.4	Recovery of Oily Wastewater	7-16
7.2.5	Concentration of Gelatin	7-16
7.2.6	Cheese Production	7-16
7.2.7	Juice	7-16
7.3	ENERGY BASICS	7-18
7.3.1	Direct Energy Use vs. Competing Processes	7-19
7.3.2	Indirect Energy Savings	7-19
7.4	ECONOMICS	7-20
7.4.1	Typical Equipment Costs	7-20
7.4.2	Downstream Costs	7-23
7.4.3	Product Recovery	7-23
7.4.4	Selectivity	7-25
7.5	SUPPLIER INDUSTRY	7-25
7.6	SOURCES OF INNOVATION	7-26
7.6.1	Suppliers	7-26
7.6.2	Users	7-27
7.6.3	Universities	7-28
7.6.4	Government	7-28
7.6.5	Foreign Activities	7-28
7.7	FUTURE DIRECTIONS	7-28
7.8	RESEARCH NEEDS	7-31
7.9	DOE RESEARCH OPPORTUNITIES	7-34
	REFERENCES	7-35

CHAPTER SEVEN

ULTRAFILTRATION

by W. Eykamp, University of California, Berkeley

7.1 PROCESS OVERVIEW

Ultrafiltration is a membrane process with the ability to separate molecules in solution on the basis of size. An ultrafiltration membrane acts as a selective barrier. It retains species with molecular weights higher than a few thousand Daltons (macrosolutes), while freely passing small molecules (microsolutes and solvents). The separation is achieved by concentrating the large molecules present in the feed on one side of the membrane, while the solvent and microsolutes are depleted as they pass through the membrane.

For example, an ultrafiltration membrane process will separate a protein (macrosolute) from an aqueous saline solution. As the water and salts pass through the membrane, the protein is held back. The protein concentration increases and the salts, whose concentration relative to the solvent is unchanged, are depleted relative to the protein. The protein is, therefore, both concentrated and purified by the ultrafiltration. Figure 7-1 illustrates the ultrafiltration process.

Ultrafiltration may be distinguished from two related processes, reverse osmosis and microfiltration. Given the same example of a solution of protein, water and salt, the reverse osmosis membrane will pass only the water, concentrating both salt and protein. The protein is concentrated, but not purified. The microfiltration membrane will pass water, salt and protein. In this case, the protein will be neither concentrated nor purified, unless there is another larger component present, such as a bacterium.

Ultrafiltration membranes are typically rated by molecular weight cutoff, a convenient but fictitious value giving the molecular weight of a hypothetical macrosolute that the membrane will just retain. Microfiltration membranes, however, are rated by pore size, specifically the pore diameter. In practice, the distinction between the two membrane processes is blurred. There is some overlap in size between the largest polymer molecules and the smallest colloids. Microfiltration membranes with the smallest pore sizes sometimes retain large macrosolutes. An ultrafiltration membrane is sometimes used for what appears to be a microfiltration application because in that use it has a greater throughput.

Most ultrafiltration processes operate in crossflow mode, although a few laboratory devices and industrial applications operate in dead-end flow. The use of check filters or guard filters at the point-of-use in ultrapure water applications is an example of dead-end ultrafiltration.

Most ultrafiltration membranes are made from polymers, by the phase inversion process. Ultrafiltration membranes may also be formed dynamically, for example by the deposition of hydrous zirconium oxide on a porous support under controlled conditions of flow and pressure. A few ultrafiltration membranes prepared from ceramic materials are available.

MTR-034-1S

Figure 7-1. A schematic diagram of the ultrafiltration process.

Ultrafiltration membranes may be characterized in terms of pore size and porosity, even though there is little direct evidence for the kinds of pores that the terminology suggests.¹⁻³ A frequently used model characterizes the membrane as a flat film with conical pores originating at its surface, as seen in Figure 7-2. The surface pores are large enough to permit passage of solvent and microsolite molecules, but are too small for effective penetration of the larger macrosolute. The conical shape is desirable, in that any entity that makes it through the opening at the membrane surface can continue unimpeded; there is no danger of pore-plugging.

Membranes may be made with differing pore sizes, pore densities, and pore-size distributions. These attributes are determined by measuring the flux of pure water through the membrane. The membrane is tested with dilute solutions of well characterized macromolecules, such as proteins, polysaccharides, and surfactants of known molecular weight and size, to determine the molecular weight cutoff. The above description implies the possibility of separating large macrosolutes from small macrosolutes by using an appropriate pore size. In practice, however, due to concentration polarization, only limited changes in the relative concentration of macrosolutes of different size are feasible.

7.1.1 The Gel Model

Ultrafiltration is a pressure-driven operation. The flow of solvent through the membrane increases linearly with pressure, according to Darcy's law. However, experimental data fit this law only in the case of very clean feeds, or at very low pressures as can be seen in Figure 7-3, a typical experimental result for an ultrafiltration membrane.

The flow through the membrane increases linearly with pressure at low pressure values. As pressure is increased to higher values, the membrane throughput levels off and becomes constant. This unexpected behavior has attracted considerable attention,⁴⁻⁶ starting with a seminal paper by Blatt, who pointed out that the concentration of macrosolute at the face of the membrane must increase to a higher level than its concentration in the bulk of the fluid, even in the presence of vigorous stirring. The macrosolute is carried to the membrane by the bulk flow of solvent, but it cannot pass through the membrane. It must then "swim upstream" back into the bulk of the solution whence it came. Because the effects of stirring are insignificant very near the surface of the membrane, diffusion becomes the only means by which the macrosolute may redistribute itself. Fick's law describes the flux of the macrosolute, J_{ms} , away from the membrane. D is the molecular diffusivity of the macrosolute, and ΔC is its concentration gradient

$$J_{ms} = D \nabla C \quad (1)$$

MTR-049-F

Figure 7-2. A model of the ultrafiltration of a solution containing macrosolutes (e.g., proteins) and microsolute (e.g., salts).

MTR-045-GRP

Figure 7-3. The effect of transmembrane pressure on the ultrafiltration flux.

Macrosolutes have low molecular diffusivities, so the rate of redispersion into the bulk fluid is low, especially in the first few moments when the concentration gradient is low. At first, macrosolute will arrive at the membrane faster than it diffuses away. This accumulation cannot continue for long, however, and a steady state soon develops in which the rate of redispersion balances the rate of arrival. It is more important to state the converse of this equivalence, that the rate of arrival balances the rate of redispersion, for that is the critical factor in controlling the rate of an ultrafiltration process.

The ultrafiltration flux declines as the concentration of macrosolutes in the feed increases. This is indicated in Figure 7-4, a typical plot of experimental data in which each of the data lines shown represents a constant stirring rate. The fact that the intercept is approximately 35% macrosolute by volume for many different materials and for differing rates of stirring, led Blatt to propose that the macrosolute in fact forms a new phase, that of a polymer gel layer. Increasing the transmembrane pressure difference will then result in an increased gel layer thickness, which negates the increase driving force; i.e., the flux remains constant. This model is a good predictor of experimental data, and has been used widely. In recent years, it has become clear that the concentrated boundary layer adjacent to the membrane surface does not have to be gelled in order to reduce or limit the ultrafiltration flux. The concentrations in the boundary layer can be so high that osmotic pressure plays a significant role, even with macromolecules. The osmotic pressure of macromolecular solutions increases very rapidly with concentration and can lead to flux limitation just as severe as a gel layer.

The existence of a polymer gel immediately raises problems about the ability of an ultrafiltration membrane to fractionate polymers. Gels are known to be highly entangled polymeric networks. How can a smaller polymer wiggle through a concentrated tangle of larger polymers and find the membrane pore through which it may theoretically fit? In fact, whether the gel hypothesis is literally true or not, if there is a "traffic jam" at the membrane surface, the cars may be just as stuck as the trucks. The common heuristic is that for the separation to take place in ultrafiltration with reasonable efficiency, there needs to be a factor of 100 in the ratio of the sizes of the materials separated.

Ultrafiltration membranes are used to separate colloidal materials from fluid mixtures, as well as macrosolutes from true solutions. In principle, microfiltration would be expected to be the process of choice for colloidal suspensions. However, for one major application, electrocoat paint, and some minor applications, ultrafiltration is the process of choice. Apparently, the ultrafiltration membranes resist being grossly plugged by the sticky paint solids, because their critical dimension is too small for the paint particles to penetrate.

The use of ultrafiltration membranes for separating colloids presents problems for the gel model, since colloids have much lower diffusivities than macromolecules in solution. This problem has been discussed in the literature and is analyzed further in Chapter Six on microfiltration.^{7,8}

MTR-044-GRP

Figure 7-4. Variation in membrane flux with feed concentration at different stirring rates.

Mass transfer in the boundary layer is the rate-controlling mechanism in ultrafiltration. The design of ultrafiltration equipment is governed by the need to reduce concentration polarization. Plugging and fouling are other important factors that affect membrane system design and operation.

7.1.2 Concentration Polarization

The dynamic equilibrium established as retained material is carried towards the membrane and is transferred backwards from the membrane is the process that limits the output of an ultrafilter once the "knee" of the flux vs. pressure curve, illustrated in Figure 7-3, has been reached. The retained material cannot continue to build up at the membrane without limit. At steady state, the flow of macrosolute carried by solvent towards the membrane must be equivalent to the flow of macrosolute back into the bulk solution, regardless of the mechanism. Therefore, the flow of solvent towards the membrane, and consequently the solvent flux through the membrane, is limited by macrosolute redistribution.

The retained materials are large molecules with very low diffusivities so unaided molecular diffusion would result in a very low redistribution rate. Designers of ultrafiltration equipment have found that controlling the ultrafiltration rate is primarily a matter of controlling mass transfer in the channel next to the membrane surface. The variables determining mass transfer rates in a channel bounded by a membrane are velocity, diffusivity, viscosity, density, and channel height. Increasing mass transfer in the membrane channel is possible by varying any of these, or by varying temperature, which affects most of the variables. In practice, however, viscosity, pH, density and permissible temperature are fixed by the properties of the feed stream. The only variables available to the designer are channel geometry, velocity, and sometimes, within limits, temperature.

Early in the evolution of ultrafiltration equipment, there was an emphasis on clever devices for disrupting the polarization layer near the membrane. Amicon worked on devices to utilize the enhanced mass transfer at the entrance region to laminar flow channels. Abcor (presently Koch Membrane Systems) developed various devices for disrupting the flow and increasing turbulence, in an attempt to transfer momentum into the boundary layer. None of these devices was successful, and the search for good design soon became a contest of geometry.

Today, commercial ultrafiltration modules use fluid mechanics to control polarization. Most designs are for turbulent flow, operating at Reynolds numbers of up to 10^5 . Some spiral-wound modules operate in laminar flow, although this is unusual.

7.1.3 Plugging

Plugging of the flow channels by solids present in the feed is another major design concern. Apple juice is a good example of a solid-containing feed solution. The juice coming from a press may contain pomace, which has a fairly high fibre content. As the juice is concentrated, the retained solids approach a level at which they do not flow. Since high juice yield is economically vital, the system is operated right up to the onset of plugging. Tubular membranes

captured important early markets because their design, properly executed, was resistant to fibers, dirt, and debris. Tubes are also very easy to clean, which made them a good choice for edible product applications. Even though tubes are inherently expensive to build and operate, they still dominate those applications in which plugging is a serious concern.

Capillary membranes are inherently inferior to tubes but may be operated safely with feed in the bore and periodic reversal of the permeate flow under back pressure.

7.1.4 Fouling

Fouling is the term used to describe the loss of throughput of a membrane device because it has become chemically or physically changed by the process fluid.⁹ Fouling is different from concentration polarization, but the effects on output are additive. Fouling results in a loss of flux that is irreversible under normal process conditions. Normally a decrease in flux will result from an increase in concentration or viscosity, or a decrease in fluid velocity. This decline is reversible by restoring concentration, velocity, etc. to prior values. In fouling, however, restoration to prior conditions will not restore the flux.

There are several fouling effects. Prompt fouling is an adsorption phenomenon caused by some component in the feed, most commonly protein, adsorbing onto the surface and partially obstructing the passages through the membrane. This effect occurs in the first seconds of an ultrafiltration operation and may sometimes even result from dipping a membrane into a process fluid without forcing material through it. Although this type of fouling raises the retention, it also lowers the flux through the membrane and is a negative effect. Prompt fouling is very common, although not always recognized as such, and most membranes are characterized after it has occurred.¹⁰ In fact, many membranes are not commercially useful until prompt fouling has taken place.

Cumulative fouling is the slow degradation of membrane flux during a prolonged period of operation. It can reduce the flux to half its original value in minutes or in months. It may be caused by minute concentrations of a poison, but is commonly the result of the slow deposition of some material in the feed stream onto the membrane. Usually, the deposition is followed by a rearrangement into a more stable layer that is harder to remove. This effect is related to prompt fouling, because the prompt fouling layer provides the foothold for a subsequent accumulation of foulant.

Fouled membranes are frequently restorable to their prior condition by cleaning. The vast preponderance of membranes used commercially foul, and are cleaned to restore their output. Membrane producers devote considerable effort to finding safe, effective, and economical means of returning the membranes to full productivity. It is usually true, however, that the cleaning agents themselves slowly damage membranes, making them more susceptible to future fouling. There are totally benign cleaning agents for some types of foulant, but the more common types, such as protein-based foulants, usually require aggressive cleaning agents to keep the cleaning cycle short. It is said that the cleaning requirements for membranes are the single major determinant of membrane life.¹¹

Some fouling is totally irreversible. An occasional culprit is a material present in the feed at low concentration, especially if it is a sparingly soluble material at or near its saturation concentration, which has affinity for the membrane. Such a material can slowly sorb in the membrane and, in the worst case, change the membrane's structure irreversibly. Antifoams are the usual culprit. With the chemically robust membranes in use today, this effect is very unusual, unless a membrane feed has been contaminated with a damaging solvent.

The rate of fouling is influenced by system design and operation. Figure 7-3 shows the pressure-flux output curve for a normal ultrafiltration process. Operating in the high-pressure region at the right will produce fouling more quickly than operation around the knee of the curve.¹² A high-pressure, low-flow ultrafiltration regime such as occurs in dead-end filtration represents a worst case operating condition. Experience indicates that thick, dense, boundary layers promote fouling.^{13,14} Unfortunately, equipment that operates membranes only in the low-fouling region, at or below the knee of the operating curve, is very hard to design.

7.1.5 Flux Enhancement

The flux in ultrafiltration systems is, with rare exceptions, determined by mass transfer at the membrane surface. As has been shown, the rate of passage through an ultrafiltration membrane is determined by the rate at which retentate can be removed from the membrane. The cleaning of fouled membranes relies on the same principle. Foulants are removed from the membrane by a combination of fluid flow past the membrane and chemical action to emulsify the foreign deposit or to attack it so as to reduce its size or change its chemical form and lower its adhesion to the membrane. Both these critical steps mandate a design which emphasizes mass transfer at the membrane surface.

Early designs attempted to achieve mass transfer without excessive pressure drop or energy loss. Attempts to design devices that run in laminar flow and take advantage of enhanced mass transfer due to hydrodynamic entrance effects were unsuccessful. Turbulence promoters were tried in a variety of membrane devices operating in turbulent flow. The idea was to transfer some of the momentum from the turbulent core into the boundary layer to enhance mass transfer, thus increasing flux. None of these designs was found to be practical. Operating at high fluid velocities in the feed channel is presently the only way of enhancing mass transfer.

Spiral-wound modules may prove to be the first real success in improving the flux in a steady-state device by a passive technique. Optimization of the spacer net separating the membrane surfaces in spirals has been a serious, ongoing effort and has led to considerable improvement in performance.

Another promising design is the capillary module developed by Mitsubishi Rayon Engineering under the Japanese Aqua Renaissance program. These modules consist of capillary bundles that are fixed at one end only and operate with a shell-side feed. If it is demonstrated that the flux enhancement is due to "flapping," of the capillary bundles, this would represent a second successful technique for passive mass transfer enhancement.

Flux enhancement by dynamic techniques was first commercialized by Westinghouse in the early 1970s. Their design was a multitubular "sand log," in which the membranes were cast inside 25-mm-diameter channels. They used a gravity head on the permeate side of the membrane, and shut the feed pumps off every minute or so for 5 seconds. As the permeate returned backwards through the membrane, it lifted the polarized layer of retentate from the membrane. Mass transfer was improved more than enough to justify the exercise. The technique fell into disuse when Westinghouse exited the market. Permeate backwashing is still used by Romicon (capillaries), Memtec (air backwash) and others, although it is mostly a way to control fouling by removing nascent foulants before they consolidate.

7.1.6 Module Designs

Early in the development of industrial ultrafiltration there was a proliferation of module designs. Almost all of these designs are still being marketed, although over half of the current sales are spiral-wound modules.

The most successful early design was the 25-mm tubular membrane (Abcor). The module was a 2.8-m long porous pipe, with a membrane cast inside. It had the great virtue of simplicity and reliability. The design was made practical by connecting successive membranes together with minimum pressure loss U-bends, carefully avoiding any changes in diameter in the flow channel. When this arrangement was properly executed, 90% of the total process pressure drop took place adjacent to active membrane. The absence of stagnation points proved highly desirable when processing fluids containing fibrous contaminants. The large tube design suffered from its large physical size, and from very low conversion per pass, leading inevitably to high energy costs. Early models were prone to rupture, but reliability now is almost absolute.

Other early designs which proved viable were plate-and-frame, parallel-plate devices, and capillaries. Capillaries have been prone to problems because of difficulties in incorporating them into modules. A series of potting-related problems have made them difficult to produce reliably. However, for some applications, such as ultrapure water, capillaries continue to hold a significant share of the market.

Parallel-plate and plate-and-frame modules encountered many design problems, principally improper flow distribution and sensitivity to fibrous debris that led to cracks and module failures. These designs were eventually refined and have achieved some commercial success.

The spiral-wound module dominates the ultrafiltration market. This design did not achieve much early success due to plugging, rapid fouling and difficulty in cleaning. New materials, better designs and manufacturing quality control overcame all of these problems, resulting in the present favored status of spiral-wound modules.

7.1.7 Design Trends

Two factors have pushed ultrafiltration equipment manufacturers towards compact, energy-efficient designs. In Europe and Japan, and, to a much lesser extent, in the U.S., buyer reaction to the oil crisis in the late 1970s made it clear that high energy-consuming ultrafiltration designs would be displaced as lower-energy alternatives became available. The second factor was the growing realization that ultrafilters, in growing larger, were becoming significant consumers of valuable floorspace. Higher conversion per pass was the best answer to both concerns.

One approach to high-conversion design is to use more membrane area at lower energy intensity. This necessitates compact module designs, such as capillaries and spiral-wound modules. Making more compact modules required significant improvements in membranes and in module fabrication techniques. In the early 1970s, most membranes were made from cellulose acetate. This material was not suitable for capillaries, and was only marginally suitable for spiral-wound modules, because the mild cleaning agents appropriate for cellulosic membranes could not clean the modules properly.

The search for new polymer materials led to membranes being prepared from every available commercial polymer that exhibited any hope for success. Commercial replacements for the early cellulose included an acrylonitrile-vinyl chloride copolymer, polyacrylonitrile, polyvinylidene fluoride, polyethersulfone, and polysulfone, which has become the most important ultrafiltration membrane polymer.

Polysulfone can be made into a variety of ultrafiltration membranes with very retentive or fairly open properties. It is chemically tough enough to resist aggressive cleaning, and it can be made into high-quality flat membrane with good dimensional stability, suitable for winding into spiral-wound membrane modules. It is one of the few polymers suitable for capillary devices, and is also used widely in plate-and-frame and parallel-plate modules.

The effort to make membranes out of better polymers also resulted in the production of a highly reliable capillary module by Asahi Kasei in Japan, using a proprietary acrylic polymer. Market share for this membrane module in the traditionally difficult electrocoat paint market rose dramatically in the early 1980s.

Since the beginning of the modern membrane era, significant effort has been applied towards making inorganic membranes. Union Carbide developed a dynamic membrane from hydrous zirconium oxide inside a porous carbon tube, but this technology had a weak market acceptance. At present a number of ceramic devices are available, but their primary use is in microfiltration. Some of the tighter membranes are useful in the upper end of the ultrafiltration range.

The big potential advantage of ceramic membrane materials is their high temperature capability. They are expensive, however, and there are no developed markets where the need for temperature resistance warrants the extra expense. Additionally, they are still too new to have demonstrated the long life needed to justify their higher initial cost. At present, ceramic membranes are made in

multi-tube monoliths, which are inherently compact. They have not yet been packaged into compact, high-conversion modules. There is a high operating energy cost associated with ceramic membranes, as the membrane purchase cost requires operation at high fluxes, to keep the conversion rate high and the membrane area requirement low. One start-up company claims to have developed a low-cost, high-temperature membrane, but its primary use is in microfiltration.¹⁵

7.2 APPLICATIONS

Ultrafiltration has several important applications, particularly in the food industries, which are discussed below.

7.2.1 Recovery of Electrocoat Paint

In the coating of industrial metal, an efficient and corrosion resistant way of applying the prime coat (for automobiles) or a one-coat finish (for appliances, coat hangers, etc.) is the electrophoretic deposition of a colloidal paint from an aqueous bath. This process is illustrated in Figure 7-5. After suitable pretreatment, the metal object is immersed in a paint tank, and the paint is plated on. During the process, the paint film undergoes electroendosmosis, and it emerges from the tank already robust, although still wet. The "dragout" paint, the droplets adhering to the fresh wet film, is washed off and recovered.

Ultrafilters are used throughout the world for this application. In the automobile industry, the savings in paint is around \$4 per vehicle. A large paint recovery installation typically contains 150 m² of membrane area, and produces 3 m³/hr of permeate.

7.2.2 Fractionation of Whey

In the production of cheese and casein, about 90% of the volume of the milk fed to the process ends up as whey. The quantity of whey produced in the United States, a tiny fraction of world production, is about 25 million cubic meters per annum. About half this amount is processed in one way or another. Ultrafiltration is used to produce high-value products, which can range from 35% protein powder (a skim-milk replacement) to 80%+ protein products, used as high-value high-functionality food ingredients. A large dairy ultrafilter operating on whey will contain 1,800 m² of membrane, and have a whey intake of 1,000 m³ per day. Figure 7-6 is a flowsheet of the whey treatment process.

7.2.3 Concentration of Textile Sizing

In the knitting and weaving of textiles, a sizing material is commonly applied to lubricate the threads and protect them from abrasion. The sizing material is removed before the fabric is dyed. Ultrafiltration provides an economical means to recover and reuse the sizing solution. Recovery of the sizing encourages the use of more expensive but more effective sizing agents, such as polyvinyl alcohol. Since desizing baths operate at high temperatures, it is necessary for the ultrafilter to withstand constant operation at 85°C. Some inorganic membranes have been used in this application, but polymeric membranes operating at low flux are more economical, especially in their much lower power consumption. A large recovery plant has a membrane area of 10,000 m², and a feed rate of 60 m³ per hour.

Figure 7-5. Ultrafiltration for the recovery of electrocoat paint in the automotive industry.

MTR-033-1S

Figure 7-6. A flowsheet for the ultrafiltration of whey. The prices are as of November 1989. The cost basis is 1 ton of cheese (2,000 lb).

7.2.4 Recovery of Oily Wastewater

In the metal working industry, lubricants and coolants are used in numerous operations, such as metal cutting, rolling and drawing. Lubricants and coolants usually take the form of oil-in-water emulsions. Parts that have been cooled or lubricated are generally washed, creating a dilute oily emulsion. The quantity of spent, dilute emulsion just from washing newly formed aluminum cans is over 8 m³ per hour per can line. Ultrafiltration is the principal technology employed to concentrate this waste into a stream of water suitable for a municipal sewer, and an oily concentrate rich enough to support combustion, or for oil recovery.

7.2.5 Concentration of Gelatin

Gelatin coming from the extractor is a dilute solution of hydrolyzed collagen. It can be dried economically once the total solids concentration in the stream reaches about 30%. Ultrafiltration or evaporation may be used to remove the bulk of the water before drying. Because the membrane passes some of the salts along with the water, ultrafiltration reduces the extent of treatment in the subsequent ion-exchange step. Ultrafiltration can achieve a 30% solids concentration, but is usually used only to remove 80-90% of the water in the feed, at a much reduced energy cost compared with evaporation.

7.2.6 Cheese Production

An emerging process for the production of cheese uses ultrafiltration before the cheese production process, rather than behind it as in the whey application. The process is proven for soft cheeses, and is in commercial operation for cheese base, an intermediate in the production of several mass-consumption cheese products. CSIRO, in Australia, has developed an ultrafiltration process applicable to cheddar cheese. As a conservative average, the use of ultrafiltration reduces the milk required to make cheese by 6%. This reduction is accomplished largely by capturing soluble proteins in the cheese curd that would normally pass into the whey.

7.2.7 Juice

A significant fraction of all clarified apple juice produced in North America is passed through an ultrafiltration membrane. The membrane process is rapidly displacing rotary vacuum filtration because of higher yield, better and more reliable quality and ease of operation.

No reliable estimates have been found for the energy savings resulting from a higher yield of juice by the ultrafiltration process. However, one 530-m³ plant, operating seasonally, is reported to save about 400 tons/year of diatomaceous earth.

Table 7-1 summarizes the principal applications of ultrafiltration.

Table 7-1. Principal Applications of Ultrafiltration

Application	Customer	Leading Membrane Configuration	Leading Membrane Suppliers
Ultrafiltration of electropaint wastewater for paint recovery	auto, appliance firms, etc.	tubular spiral plate-&-frame capillary	Koch Rhone-Poulenc Asahi Romicon Nitto
Recovery of protein from cheese whey	dairies	spiral plate & frame	Koch DDS
Ultrafiltration of milk to increase cheese yield	dairies	spiral plate-&-frame	Koch DDS
Concentration of oily emulsions for pollution abatement	metal cutting and forming, can makers, industrial laundries	tubular plate-&-frame capillary	Koch Rhone-Poulenc Romicon
High purity water	chip producers	capillary spiral	Asahi Nitto Osmonics Romicon
Pyrogen removal	pharmaceutical and glucose producers	capillary	Asahi Romicon
Size recovery	textile firms	spiral	Koch
Enzyme recovery	enzyme producers, biotech	plate-&-frame spiral capillary	DDS Koch Romicon
Gelatin concentration	food firms	spiral	Koch
Juice clarification	fruit processors	tubes capillary ceramics	Koch Romicon Alcoa
Pharmaceutical	drug firms	plate & frame spirals	DDS Koch Rhone-Poulenc
Latex	chemical firms (PVC, SBR)	tubes	Koch Kalle
Gray water (domestic waste)	hotels, offices, apartment blocks	plate-&-frame tubes,sheet,disk	Rhone-Poulenc Nitto
Laboratory	small purchases	capillary	Amicon Millipore

7.3 ENERGY BASICS

Ultrafiltration is a pressure-driven process. Under ideal conditions, the pressure need only exceed the osmotic pressure across the membrane, at most a few psi. For example, if the osmotic pressure is 5 psi, the process could operate at energy levels as low as 0.01 kWh/m³ of permeate. At this energy level, the process would be very slow, and most membranes would not operate at high retention.

The poor retention at low pressure is due to inevitable leaks in the membrane. The flow of solvent and microsolute is pressure-dependent, and small at low pressures. The diffusion of macrosolutes through the larger openings, however, is fairly independent of operating pressure. At low pressures the two flows are equivalent and retention is low. Under normal operating conditions, i.e., higher pressure, high flow, high flux, and thus high energy consumption, leaks due to membrane imperfection are diluted to insignificance. Ideal energy is thus an elusive concept. It is certainly low, but operation near the ideal energy is expensive, requiring large membrane area and near perfect membranes to achieve a good separation.

Early ultrafilters, of the tubular or plate-and-frame types, consumed over 25 kWh/m³ of permeate produced. Major improvements in all facets of equipment and membrane design have lowered this figure to 5 kWh/m³ or less. Recent trends indicate that further improvements are possible. The Japanese Aqua Renaissance '90 project has a design goal of 0.3 kWh/m³ for the ultrafiltration of a digester overflow stream, a target that is close to being met.¹⁶

Ultrafilters are operated at high fluxes to achieve adequate retention and the major use for energy is to reduce concentration polarization. The energy required to push the liquid through the membrane is trivial. The energy required to deliver the fluid to the membrane surface is significant. The centrifugal pumps universally employed run at 77% to 60% hydraulic efficiency. Sanitary pumps require a greater sacrifice in efficiency in order to maintain hygienic design. Piping and valves, manifolding in and out of the membrane array and cleaning operations contribute to further energy losses.

The overall efficiency from electricity to fluid energy in the membrane channel ranges from 45% for hygienic plants to 64% for the very best designed industrial plants requiring infrequent cleaning. The energy analysis for a typical electrocoat paint recovery plant is presented in Table 7-2. The plant operates at an overall energy efficiency of 57%. Dairy units operate with higher cleaning down time and lower efficiency sanitary pumps, resulting in a lower overall energy efficiency. The weighted average energy efficiency of ultrafiltration systems in operation today is closer to 45% energy efficiency than to 64%, due to the large number of food and dairy installations.

Table 7-2. Power Losses in a Typical Ultrafiltration Unit

Item	Power Loss (W/M ²)
Power delivered to the membrane	50 (58%)
Pump losses	25 (29%)
Switchgear and motor losses	5 (6%)
Piping, valve and header losses	5 (6%)
Losses during cleaning	1 (1%)
Total	<u>86</u>

7.3.1 Direct Energy Use vs. Competing Processes

There are no competing processes for many ultrafiltration applications, such as the recovery of electrocoat paint. For processes such as the separation of proteins from microsolute, competing processes include chromatography and precipitation. However, chromatographic separation produces a diluted intermediate stream that must be concentrated by evaporation. Precipitation also requires an evaporation step to recover the precipitant. In this case, ultrafiltration is the most energy-efficient process as both of the competing processes require an energy-intensive evaporation step.

Gelatin is concentrated in multiple effect evaporators at an energy consumption of 73 kWh/m³ of water removed. In contrast, recovery by membrane ultrafiltration requires only about 7 kWh/m³ of water removed. In the recovery of textile sizing, ultrafiltration typically requires only 10% of the energy used by evaporation.

Ultrafiltration can also deliver significant energy savings by reducing the level of downstream waste treatment required, as in the case of electrocoat paint, or by producing a waste with a fuel value, as in the case of oily wastewater treatment.

7.3.2 Indirect Energy Savings

The substitution of ultrafiltration for conventional unit operations can lead to ancillary energy savings, by increasing intermediate recovery and reducing the level of processing per volume of product. A recent DOE-sponsored study has illustrated this effect in use of ultrafiltration in cheese manufacture.¹⁷

The cumulative value of thermal energy required for animal feed, on farm milking and refrigeration, and farm-to-plant transportation is 53 MBtu/ton of cheese produced. The ultrafiltration of milk before cheese production increases the yield of cheese by 6%. Since a ton of cheese can now be made with 6% less milk, this translates to an energy savings of 3.2 MBtu/ton. The energy required to operate the ultrafilter is 0.6 MBtu/ton, resulting in a net energy savings of 2.6 MBtu/ton of cheese produced. The annual U.S. production of cheese is 3.4 million tons, so the savings from the increased efficiency in the use of milk could amount to 0.01 quads annually.

When cheese is made after milk has been ultrafiltered, there is a reduction in the amount of whey produced. As a first approximation, assume that the amount of whey produced is a function of the milk input, not the cheese output. Since the treatment of whey consumes energy, there is the energy saving resulting from the whey not produced. But if whey is available in excess, and the evidence available indicates that only about half the whey produced is manufactured into products, whey not made could be deducted from the whey not now treated. In that case, the energy savings would be minimal, since the energy cost of feeding or spreading whey is fairly low. If the whey not produced results in whey products not being manufactured, the analysis becomes too complicated for this study.

Whey is manufactured into many products of various values, but one that bears on the energy picture is "35% whey protein concentrate," a product sold as a skim-milk replacement. While the picture is very complicated, a ton of cheese produces, as an ultrafiltration byproduct, roughly a ton of a fluid with properties similar to skim milk. It is always dried, and sold in the market as a replacement for non-fat dry milk. Since the energy to dry milk and whey protein concentrate is similar, that part of the energy picture will be ignored as not very different. The energy saving produced by ultrafiltration is really the energy not needed to produce the ton of skim milk in the first place. The power required to produce the skim milk replacement by ultrafiltration is about 20 kWh/m³ of product.

7.4 ECONOMICS

7.4.1 Typical Equipment Costs

The dairy industry offers the largest potential energy savings of any ultrafiltration application. This section presents the economics for a large whey ultrafilter. The general cost structure for whey and milk applications is similar.

This example considers a plant, producing 35% whey protein concentrate, containing 1,200 m² of membrane area and operating on a feed of 1,000 m³/day. The feed stream contains 6 g/L true protein, 2 g/L non-nitrogen protein, 48 g/L lactose, 5.5 g/L ash and 0.5 g/L fat. The average flux is about 35 L/m²h (21 gfd). The plant typically operates for less than 20 h/day. The installed cost is approximately \$600,000, or \$500/m² of membrane area, exclusive of buildings.

The equipment costs for the plant are presented in Table 7-3. This analysis is based on an installed cost of \$600,000, and a skid-mounted ex-factory cost of \$500,000.

Table 7-3. Equipment Costs for a 1,000 m³/day Whey Ultrafiltration Plant

Item	Cost Fraction	Comments
Pumps	30%	Assumes a power density of 50 watts/m ² membrane at the surface of the membrane
Replaceable Membrane Elements	20%	
Housings for Membranes	10%	Assumes spiral-wound membranes with re-usable housings
Piping and Framework	20%	Assumes stainless steel pipe and painted steel framework
Controls	15%	Automatic cleaning cycle programmable controller
Other	5%	Heat exchanger, cleaning tanks, etc.

Capital costs: The residual capital cost of the ultrafilter is \$480,000, which is the actual cost, \$600,000, less the cost of the replaceable membranes, \$120,000. The capital charges are based on residual net capital cost, plus any allocation for building charges, which are not considered in this analysis. The residual capital cost is spread over the capacity of the plant in terms of dry product recovered. We assume that the plant operates 275 days/year at 20 h/day with an average productivity of 35 L/m²h. If the desired product is present at a level of 6 g/L in the feed stream, then the plant produces 5,000 tons/year of dry product. At a 33% capital charge rate, the capital expenses attributable to the product are \$160,000/year, or \$32/ton (\$0.032/kg, \$0.015/lb) of total product.

If the product of interest were present in the feed at 0.6 g/L, the flux would rise by about a factor of 3, so the plant would need to be about 3.3 times as large, which might increase the total capital cost and capital charges per unit of production by a factor of 2.5.

Energy costs: For a plant designed for 50 watts/m², and an overall efficiency of 45%, with an average flux of 35 L/m²hr, the energy consumption is 3.2 kWh/m³. At a cost of \$0.07/kWh, the energy cost to produce permeate is \$0.22/m³. For a 35% whey concentrate, the energy cost is \$0.012/kg (\$0.006/lb) of solids.

Membrane replacement Membrane life is largely a function of cleaning frequency. Daily cleaning is the custom in the food industry and necessitates annual membrane replacement at a price of \$100/m². For the assumed operating schedule of 300 days/year, the membrane then has a useful life of 6,000 hours. If its average flux is 35 L/m²h, it will produce 4,200 kg/m² of dry product over its lifetime. This works out to a membrane replacement cost \$0.024/kg (\$0.011/lb) of dry product.

Labor: Membrane plants operate with a high level of automation, and they often run unattended. A conservative estimate of the labor costs would be \$60,000/year, or \$0.012/kg (\$0.005/lb) on the same basis as above.

Other Costs: Cleaning chemicals, heat, and other costs are estimated to add \$0.025/kg (\$0.011/lb).

The operating costs for the plant are presented in Table 7-4, listed in order of importance.

Table 7-4. Operating Costs for an Ultrafiltration Unit Producing a 35% Whey Concentrate

Item	Cost/kg	% of Total
Capital Charges @ 33%	\$0.032	31
Cleaning & miscellaneous	0.025	24
Membrane Replacement	0.024	23
Energy	0.012	11
Labor	0.012	11
Total	\$0.105 (\$0.048/lb)	100

7.4.2 Downstream Costs

An ultrafilter is a separation device that produces at least two products. Usually, one is the product desired, and the other is the product one would prefer to forget about.

Costs of disposal can be so significant that, in some cases, they may dominate the economics of the ultrafiltration installation. An extreme, but illustrative example is the concentration by PVC latex by ultrafiltration. The latex is typically 40% solids by volume and contains 10^{22} PVC particles/m³. A membrane retaining 99.99% of this latex produces permeate containing 10^{18} particles/m³, which is still a turbid fluid. The cost of treating this permeate to remove the remaining particles is very high. Therefore ultrafiltration is not economically feasible if the membrane is unable to retain enough particles to produce a permeate well below the turbidity threshold.

7.4.3 Product Recovery

Many potential applications for ultrafiltration are heavily influenced by product recovery. Getting all of the valuable product out of the feed stream and into useful or salable form is often critical. In most applications, a more retentive membrane will displace a less retentive rival, even at a higher price.

However, membrane retention is a function of time and increases with fouling in most cases, especially for streams containing proteins. Most commercial membranes rely on fouling to get the very high retention advertised. During the first 30 minutes of batch ultrafiltration, the retention may be much lower than the steady-state value. This is also a period when the membrane produces its highest flux, because it is not yet fouled. Since all edible product operations run in batches that rarely exceed 20 hours between cleaning, a small but significant fraction of the operation occurs during the initial non-steady-state period. Most processes requiring a product to feed concentration ratio greater than 1.5 use multiple membrane stages in series. All of the stages begin the operation filled with unconcentrated feed and the initial unsteady period increases with the number of stages used.

During the initial unsteady state, losses are difficult to assess, but are thought to be higher than normal. Most membrane equipment suppliers base the membrane specifications and guarantees only on the steady-state operating characteristics. However, during the initial unsteady period, which may last as long as 120 minutes, several percent of the entire day's charge of desired product may be lost.

Product losses during cleaning are also important. An edible products unit is shut down for cleaning after a 20-hour batch operation. Any product in the membrane modules is flushed out with water. Although the process is relatively efficient, there is some product dilution and product losses are inevitable. Losses also occur due to product that has fouled the membrane, and in product otherwise retained in the apparatus. These losses, which may easily total several percent of the product in the batch, are very hard to measure and are known only in the most general terms even after decades of operating experience.

Industrial users sometimes operate their ultrafilters for very long periods between cleanings or down-times. In fact, to avoid startup losses and instability problems, some users even leave the ultrafilter operating on a recycled permeate stream when the device is not needed onstream. The recovery of polyvinyl alcohol in the textile industry is an example of an application where long runs and high product recovery with low losses is the rule. Virtually all of the

product losses are through the membrane through leaks, or in upstream pretreatment operations.

In some cases, the economics are determined by the quality of the permeate stream, as in the recovery of electrocoat paint. In normal operation, the permeate and retentate streams are recycled to the process and a small loss of paint into the permeate stream does not change the process economics. However, when the ultrafilter is used as a "kidney" (some of the permeate is removed to eliminate electrolytes or other impurities from the paint tank) minor leaks have a significant impact on the process economics due to the need for additional waste treatment.

Another application where the permeate dictates the process economics is in the clarification of juice. The recovery of juice is more important than the retention of macromolecules. The typical process operates by first concentrating the retentate as much as possible without plugging the modules. The concentrated retentate is then washed to recover as much of the sugar and essence as possible. All of this water of dilution must be subsequently removed by evaporation, resulting in a higher energy cost. The ultrafilter is rated by the quality and yield of the undiluted juice, and the amount of recovery of diluted juice that is required.

7.4.4 Selectivity

Ultrafiltration membranes discriminate between macrosolutes and microsolute. This selectivity is critical to their usefulness. When high-purity products are needed, it is often necessary to flush the microsolutes through the membrane, a process analogous to the rinsing of juice residues.

For example, whey is fed to an ultrafilter with a protein-to-microsolute ratio of about 1:10. If a product with a ratio of 1:1 is needed, it is a simple matter to concentrate the feed tenfold. The protein concentration will have increased tenfold, but in an ideal case, the microsolutes concentration will remain unchanged, so the result is achieved. Suppose however the desired result is a protein-to-microsolute ratio of 10:1. A 100-fold concentration of the feed could produce the result, in principle. Whey, however, has a protein content of roughly 0.5%. Increasing this 100-fold would produce a product with 50% protein, far in excess of the ability of any ultrafilter. In fact, 20% protein is the upper limit for practical operation.

The industry practice is to lower the concentration of microsolute by adding water to the feed. This operation is called diafiltration and is expensive and inconvenient. The cost of diafiltration can be minimized by using high selectivity membranes, although a highly polarized protein layer forms on the membrane surface due to fouling and some microsolutes retention is inevitable.

7.5 SUPPLIER INDUSTRY

The principal suppliers of ultrafiltration equipment are listed in Table 7-5.

Table 7-5. Major Suppliers of Ultrafiltration Membranes and Equipment
(1989 UF Sales over \$3,000,000)

Company and Scope	Principal Location	Major Products	Estimated UF Sales (\$M)
Koch Membrane Systems (Abcor) ^{1,2}	Wilmington, MA	25 mm & 13 mm tubes spirals	32
De Danske Sukker-fabriker (DDS) ^{1,2}	Nakskov, Denmark	plate-&-frame	15
Techsep (Rhone Poulenc) ^{1,2}	Paris, France	plate-&-frame, carbon tube	15
Romicon (Rohm & Haas) ^{1,2}	Woburn, MA	capillary	11
Asahi Kasei ¹	Tokyo, Japan	capillary	6
Nitto Denko ¹	Osaka, Japan	12 mm tubes, capillary, spiral	4
Osmonics ^{1,2}	Minnetonka, MN	spiral	9
Amicon, Dorr-Oliver (Grace) ^{1,2}	Lexington, MA	capillary, leaf	25
DSI ¹	Escondido, CA	spiral	--
Allied-Signal (Fluid Systems) ¹	San Diego, CA	spiral	--
Daicel	Osaka, Japan		3
Alcoa Separations Tech (Cera-ver) ¹	Warrendale, PA	ceramic tubes	--

¹ Membranes

² Equipment

7.6 SOURCES OF INNOVATION

The major source of innovation in ultrafiltration has been the supplier industry, with minor contributions from users and academic and governmental researchers.

7.6.1 Suppliers

The origins of the modern ultrafiltration industry grew out of the work on reverse osmosis membranes being done at MIT in the early 1960s for the Office of Saline Water. The formation of the Amicon Corporation, and the subsequent decline in government funding for membrane-related work, effectively transferred the locus of innovative activity to industry, where it has remained.

The early reduction to practice for ultrafiltration was done at Amicon Corporation, with financial sponsorship from Dorr-Oliver. Both these companies benefitted from their pioneering work. (The membrane portions of both of these firms are now owned by W. R. Grace.) Shortly thereafter, Abcor (now Koch Membrane Systems) entered the industry, quickly becoming the major competitor of Dorr-Oliver. Many other firms began ultrafiltration efforts in the late 1960s, but most merged or exited the business in the following five years. De Danske Sukkerfabriker (DDS), a major European firm, joined the field shortly after Abcor. Its membrane activity is now owned by Dow Chemical Co. Berghof and several other firms were also active in the early development of ultrafiltration.

Suppliers have huge incentives for innovation in the ultrafiltration field. Not only do they have the most to gain from successful innovation, but most of the more difficult problems in ultrafiltration are amenable to supplier or user innovation. Membrane stability can be tested in a laboratory, but field tests are the only reliable measure. Fouling can be modeled only with difficulty, and modeling results are not always transmutable into profitable designs. Mechanical innovations require customer feedback and information about manufacturing techniques, which are very difficult to see from outside the industry.

The major supplier innovators are listed in Table 7-6, with estimates of their research and development expenses.

Table 7-6. Major Supplier Innovators

Company	Budget (\$000)	Emphasis
Koch Membrane	3,000	Food and industrial processes, membranes
Techsep (Rhone Poulenc)	3,000	Dairy, paint, general industrial, support of outside research
DDS	2,000	Membranes, dairy processes
Osmonics	1,000	Industrial processes, membranes, low cost equipment
Romicon	1,000	Membranes, industrial processes
Asahi Kasei	800	Membranes
Nitto Denko		Ceramic membranes
Alcoa		Carbon membranes
GFT		Ceramic membranes

7.6.2 Users

Few users have provided any innovation in ultrafiltration membranes. Users have occasionally forced suppliers to alter their designs by maintaining vigorous test programs, and by insisting on certain features. Volkswagen (VW) is an example of a firm with a single-minded insistence on energy reduction. VW created a major test bed at Wolfsburg, and used the data from it to intelligently and firmly guide the direction of membrane equipment development by suppliers. Through sheer determination and an internal experimental program, VW succeeded in forcing improvements in line with their needs. They probably deserve credit for the emergence of spiral-wound membrane modules in the automotive paint field. VW may be unique in its use of technical innovation by a customer to change the offerings of the suppliers.

Other firms, such as Kraft, have had heavy influence on ultrafiltration applications through their competent internal engineering departments. Kraft engineers have seen new applications develop and encouraged designs that would allow them to be implemented economically. They and other engineers have influenced equipment design through their purchasing practices, sometimes rewarding higher quality, usually rewarding lower cost, trying always for both.

7.6.3 Universities

Historically, the academic community has been involved at the beginning of most membrane efforts. The invention of phase-inversion membranes at UCLA, development of early ultrafiltration membranes at MIT and the recent developments in the use of bacterial-cell-wall membranes at the University for Agriculture, Vienna, are all examples of watershed inventions occurring at a university. University researchers have a poor record of follow-up work and development efforts. The major reasons may be the difficulty of working with real separation streams in the context of academic research and the fact that the model streams chosen are seldom accurate representatives of actual commercial streams. At present the major universities involved in ultrafiltration research are Rensselaer Polytechnic Institute, Syracuse University, the University of Twente (Enschede, Holland) and the University of New South Wales (Kensington, NSW, Australia).

7.6.4 Government

The U.S. government has supported research on ultrafiltration, most notably the studies of ultrafiltration in the pulp and paper and petroleum processing industries that were funded by the DOE's Office of Industrial Programs. There is also considerable support for the development of inorganic and ceramic membranes. A more comprehensive analysis is presented in the section on government support of research.

7.6.5 Foreign Activities

Several foreign governments are actively sponsoring ultrafiltration research. Japan's major governmental effort in ultrafiltration is the Aqua Renaissance '90 Project, which is developing techniques for treating wastewater from a variety of sources. Membranes fit well into plans to build new types of waste-treatment facilities. The state of the membrane art has been advanced significantly for several Japanese ultrafiltration membrane firms through the Aqua Renaissance project.

In Europe, the Brite program supports a number of membrane activities, but there are no outstanding ultrafiltration projects among them. The UK, through its Harwell-sponsored programs, does support some ultrafiltration-related work.

In Australia, the major research center is the Centre for Membrane and Separation Technology, at the University of New South Wales, which conducts research into mechanisms and control of fouling.

7.7 FUTURE DIRECTIONS

Potential applications for ultrafiltration that may be important from the separations and the energy-savings viewpoints are listed in Table 7-7.

Table 7-7. Future Directions for Ultrafiltration

Application Area	Prospect for Realization	Importance	Comments/Problems
Ultrafiltration of milk for modified products	Good	8	Potential for economic gain great. Technical problems difficult. Regulatory/consumer acceptance major hurdle.
Municipal sewage treatment	Fair	5	Competes with non-membrane technologies, and may not win. Impact of success would be large but slow. Impediments are economic and technical.
Industrial waste treatment excluding pulp & paper	Good	7	Oily emulsions established: other oily wastes to follow. Economics chief barrier; membranes will cheapen. Membrane enhanced biotreatment looks a good bet to treat high BOD wastes.
Food	Excellent	8	Many applications in broad food areas based on the ability to change protein and starch/sugar, salt and water ratios. Longer term prospects include refining of oils. Applications will be large, and increase with technical progress and customer acceptance
Pulp and paper mills	Good	8	Good prospects for water recycle, as in white water loop. Prospects for black liquor, lignin separation, etc. are fair.
Bioprocessing	Fair	8	Separation and concentration of biologically active components from broths, etc. Ultrafiltration will compete with more exotic processes, but will certainly be a major factor as the generic biomaterials industry grows.
Abattoirs	Fair	3	Recovery of blood fractions should eventually be a significant market. Industry conservatism, general inertia, and regulatory concerns may delay for another decade. Technically possible.

Table 7-7. Future Directions for Ultrafiltration (continued)

Application Area	Prospect for Realization	Importance	Comments/Problems
Small scale water reuse	Good	6	Water recycle on small scale, to pass purified gray water through toilet flush, cutting local use 40%. Economics now favorable in high water cost markets, and where high infrastructure costs passed back to builders. Likely only in new construction of 500+ person buildings. Will require regulation changes.
Drinking water	Fair	4	Under-sink units now sold in Japan. Ultrafiltration is one alternative as concern grows over trihalo-methanes. Will face competition from nanofiltration and probable restrictions if water yield problem not solved.
Petroleum processing	Poor	7	Requires revolutionary performance and cost improvements to displace conventional petroleum processes. Could have big role in shale. Would likely result in significant energy savings.
Protein harvesting	Good	5	Now useful for grass proteins, may be useful for algal/plankton proteins. Soy meal price now high enough to support feed applications.

The major dairy applications have already been discussed. Although the benefits are indirect, the potential impact on energy consumption is large, even if the market size for the technology is small. A recent DOE-sponsored study gives a good summary of the economics and energy-saving potential of the on-farm ultrafiltration of milk, estimated at 0.01 quads annually.¹⁷ On-farm ultrafiltration is not included in Table 7-7 because the negative arguments enumerated in the study were convincing to the expert panel reviewing this area. The technology faces many regulatory, economic and technical obstacles, in that order of significance, and the panel concluded that this is an application of ultrafiltration that will never be developed.

Municipal waste treatment is viewed as a promising application, with competition from microfiltration systems. Industrial waste treatment, with the exception of pulp and paper wastes, has a high chance of successful implementation, especially if the Aqua-Renaissance/Dorr-Oliver technology generates enough interest to attract an aggressive development effort.

In the food area, there are many applications that will gain acceptance incrementally. Many of the good ideas have been around for years but the technology has been limited by lack of industrial acceptance.

Edible oil fractionation does have significant energy potential, perhaps 0.01 quads/year, but this application has already been under development for 15 years, and there are good alternative technologies.¹⁷

Pulp and paper is another industry in which the adoption of membrane technology is expected to be slow, but important, with the emphasis primarily on pollution control and secondary emphasis on energy savings.

Ultrafiltration is certain to be a significant participant in the bioprocessing industry, but the energy impact will not be major.

Finally, petroleum processing remains the most speculative application. Energy savings from deasphalting would be large, but the technology is far away from being economical even if the technical problems could be solved.

7.8 RESEARCH NEEDS

Ultrafiltration has been an industrial process for 20 years, but existing membranes suffer from a number of shortcomings, namely fouling, limited useful economic life, pore size distribution, chemical instability and temperature instability.

Fouling is influenced by many factors. The most important is the chemical nature of the exposed membrane surface, including charge, surface free energy, and response to the environment. Other factors are the membrane texture and rugosity, pore shape, and pore density. The solute concentration at the membrane surface, a function of hydrodynamics and pressure, is also important. Membranes have been made from many different materials, primarily by the phase-inversion process. The availability of novel techniques for preparing membranes, such as thermal inversion, oxidation, carbonization, thin-film composite formation, dynamic formation and methods used for ceramic membranes should be systematically studied to learn how the many variables affect fouling.

A membrane has come to the end of its useful life at the point where replacing it produces a positive discounted cash flow. Membranes are replaced most often because they are leaking valuable product, or because their productivity has declined. Both issues are often related to fouling, and the periodic cleaning necessary to reverse the pernicious effects of fouling on system productivity. Cleaning agents usually damage the membrane, at least slightly. The search for better cleaning agents is a promising research project but more emphasis should be placed on reducing the need for them.

Membranes are also required to withstand extremes of temperature and pH, and abuse from agents intrinsic or fortuitous to the application. The life of the membrane module is determined by the most fragile component, which is often not the actual retaining surface. Membrane sublayer failure and membrane substrate failure are often to blame for shortened life. An intact membrane separation surface is useless if the substrate fails or the module develops a leak. Research aimed at improving membrane life must look at the whole module.

Pore-size distribution is an important concept, even if the "pores" exist only hypothetically. The goal of all ultrafiltration membrane manufacture is to have a uniform retaining layer with a very high pore-volume fraction. Uniformity in the retaining layer is a necessary although not sufficient condition for a clean separation.

Chemical stability includes resistance to physical attack by solvents, pH resistance, and very importantly, the ability to withstand cleaning and sanitizing by aggressive chemicals. Chemical resistance to adventitious impurities is a general but important goal. In particular, resistance to substances with high activity, such as antifoams, is desirable even at low concentrations. Stability also implies resistance to any phenomenon that modifies membrane properties, such as an attack that increases rugosity.

Although thermal stability has been ranked least important of the factors needing improvement, it is nevertheless an important property. Organic membranes have proven their ability to perform well at 85°C for prolonged periods in benign aqueous media. Membrane chemists believe that polymer membranes could be fabricated that would briefly withstand 150°C. Ceramic membranes are operable at higher temperatures. In fact, there is no theoretical barrier to the operation of certain inorganic membranes at temperatures in excess of 200°C. The membranes ought to work, and modules to contain them ought to be achievable. However, this has not yet been done and there is insufficient evidence to verify that dependable operation of a membrane system can be maintained above 150°C indefinitely.

The important research needs required to endow ultrafiltration systems with the features discussed are listed in Table 7-8.

Fouling is at the top of the list of needs. It is a universal problem, or set of problems. Some of the experts consulted doubt that there is a universal solution. Others think that there is background knowledge that will help all interested investigators in solving what may be a series of related problems. Good fundamental work is needed to establish the direction most likely to produce meaningful, energy-saving answers.

A comparative study of how and why membranes foul should seek to connect effects with causes. It should reveal the mechanism of fouling, from the first sorption or attachment through the loss of permeability and change in selectivity of the membrane. Such a study needs to go well beyond the ability of any single industrial or academic group.

Table 7-8. Ultrafiltration research needs

Topic	Prospect for Realization	Importance	Comments/Problems
Fouling	Good	10	Fouling is ubiquitous in Ultrafiltration. Its elimination would boost total throughput >30%, and reduce capital costs 15% further by eliminating cleaning. Better fractionation would also result, expanding ultrafiltration use significantly. The goal is too ambitious for 2015, but very substantial progress will be made.
Membrane cost/unit permeate	Excellent	9	Real membrane costs should continue to drop as markets expand and economy of scale is realized. Longer life will have decreasing impact on economics, and will not be an issue by 2005.
Low-energy desings	Excellent	9	Improved, lower cost membranes would permit lower energy process designs operating away from the fully polarized regime. Results should be better selectivity, lower fouling, lower energy, cleaning and maintenance, and lower capital cost.
High-temperature/solvent-resistant, inexpensive membranes	Fair	7	Required for petroleum applications but must also have low use cost. Volumes would be large.
Membranes resistant to high pH and oxidants	Good	5	Needed for aggressive industrial and recycle applications such as paper. Cost a major consideration.

Reduction of membrane cost is an issue that may be solved in the marketplace. Market expansion is at last taking ultrafiltration out of purely niche markets and should soon start showing economies of scale. Part of the economic burden for ultrafiltration users has been membrane replacement. As the membrane life increases due to better membrane materials and module designs, such as the introduction of ceramics, the economics will continue to improve.

Low-energy design has been a refractory problem for the industry. In the early stages, dependability and a robustness were much more highly prized than low-energy designs. However, customer demand for lower energy consumption has been the necessary motivation for manufacturing innovation. We can propose no better mechanism for achieving low energy designs.

High temperature, solvent resistant, oxidation resistant membranes are possible. However, they are difficult to operate economically because of the high manufacturing cost. There is no incentive for supplier innovation as the market size is too small to recover development costs. If a petrochemical or fuel stream separation application should develop, then the sales volume would be huge and the development effort would be self-sustaining.

7.9 DOE RESEARCH OPPORTUNITIES

The primary research opportunity in ultrafiltration identified by the panel is the study of fouling and the development of fouling-resistant membranes. In our view, this research opportunity fits well with the DOE mission and goals. Fouling is an important problem because it significantly raises the energy consumption of every ultrafiltration. It has also retarded the growth of ultrafiltration into areas where it would reduce energy consumption, such as the dairy industry, for which the biggest potential energy savings were identified. Fouled membranes are less selective, which is another impediment to the use of ultrafiltration.

The study of fouling is an important, high impact problem not likely to be solved by industry and therefore is an ideal program for DOE sponsorship. The effort required is likely to be too big, too long-term, and unlikely to give any competitive benefit to the industrial sponsor. On the contrary, research in this area is likely to benefit the producers, users and the public. Without a government-sponsored joint effort, the industry will continue to work on the problem with a piecemeal approach unlikely to produce a general, systematic understanding.

The second research priority is for lower cost, longer life membranes, which is equivalent in importance to low-energy module designs. These two can be packaged together as the development of low-cost, low-energy membranes. Although regarded as an unreasonable target, Japan's Aqua-Renaissance project in Japan shows what can be achieved. While most ultrafiltration suppliers were contemplating the possibility and implementation of the 3 kWh/m³ membrane module, the Japanese found that they needed a 0.3 kWh/m³ membrane module to meet requirements of their sewage treatment project. It now appears that they will succeed. The project was well planned and implemented, and the cost was modest. It is very likely that this project will put the Japanese ultrafiltration industry on an even more competitive footing with the historically dominant U.S. ultrafiltration industry. Some DOE sponsored competition, or cooperative

competition among and between people with module design and inexpensive, long-life membrane expertise should propel U.S. firms back into a leadership role.

Finally, the real speculative work is in high-temperature, solvent-resistant membranes for use in hydrocarbon separations. This could be so important, yet it is such a difficult and long-term effort, that without a visionary sponsor, it is unlikely to take place. Membrane separation as we know it would not be in place today were it not for the visionary effort of the Office of Saline Water. Hydrocarbon separations by membranes will not happen by 2010 without a similar program in the 1990s.

REFERENCES

1. Sarbolouki, M. N., "A General Diagram for Estimating Pore Size of Ultrafiltration and Reverse Osmosis Membranes," Sep. Sci. & Tech. **17** (2) 381-6 (1982).
2. Fane, A. G., "Factors affecting Flux and Rejection in Ultrafiltration," J. Sep. Proc. Technol. **4** (1) pp15-23 (1983).
3. Capanelli, G., F. Gigo, and S. Munari, "Ultrafiltration Membranes - Characterization methods," J. Memb. Sci. **15**, pp 289-313 (1983).
4. Jonsson, G., "Boundary Layer Phenomena During Ultrafiltration of Dextran and Whey Protein Solutions," Desalination **51**, pp 61-77 (1984).
5. Vilker, Vincent L., et al., "The Osmotic Pressure of Concentrated Protein and Lipoprotein Solutions and its Significance to Ultrafiltration," J. Memb. Sci. **20**, p 63-77 (1984).
6. Wijmans, J. G., et al., "Flux Limitation in Ultrafiltration: Osmotic Pressure Model and Gel Layer Model," J. Memb. Sci. **20**, p 115-124 (1984).
7. Fane, A. G., "Ultrafiltration of Suspensions," J. Memb. Sci. **20**, pp 249-259 (1984).
8. Zydney, Andrew L., and Clark K. Colton, "A Concentration Polarization Model for the Filtrate Flux in Cross-Flow Microfiltration of Particulate Suspensions," Chem. Eng. Commun., **47**, pp 1-21 (1986).
9. Belfort, Georges, and Frank W. Altena, "Toward an Inductive Understanding of Membrane Fouling," Desalination **47**, p 105-127 (1983).
10. Zeman, Leos J., "Adsorption effects in Rejection of Macromolecules by Ultrafiltration Membranes," J. Memb. Sci. **15**, pp 213-230 (1983).
11. Eykamp, W., and J. Steen, "Ultrafiltration and Reverse Osmosis," in Handbook of Separation Process Technology, R. W. Rousseau (Ed.), John Wiley & Sons, 1987.
12. Fell, C. J. D., Dianne E. Wiley, and A. G. Fane, "Optimization of module Design for Membrane Ultrafiltration," World Congress III of Chemical Engineering, Tokyo, 1986.

13. Reihanian, H., C. R. Robertson, and A. S. Michaels, "Mechanisms of Polarization and Fouling of Ultrafiltration Membranes by Proteins," J. Memb. Sci. **16**, pp237-258 (1983).
14. Matthiasson, E., "The Role of Macromolecular Adsorption in Fouling of Ultrafiltration Membranes," J. Memb. Sci. **16**, p 23-36 (1983).
15. Goldsmith, R. L., personal communication, 1990.
16. Kimura, Shoji, "Japan's Aqua Renaissance Project - Ultrafiltraton Energy," AIChE, San Francisco, November 1989.
17. Mohr, Charles M., et al., Membrane Applications and Research in Food Processing, Noyes Data Corp., 1989.

CHAPTER EIGHT

ELECTRODIALYSIS

TABLE OF CONTENTS

8.1	INTRODUCTION	8-1
8.2	PROCESS OVERVIEW	8-1
8.2.1	The Principle of the Process and Definition of Terms	8-1
8.2.1.1	The process principle	8-2
8.2.1.2	Limiting current density and current utilization	8-2
8.2.2	Design Features and their Consequences	8-8
8.2.2.1	The electrodialysis stack	8-9
8.2.2.2	Concentration polarization and membrane fouling	8-9
8.2.2.3	Mechanical, hydrodynamic, and electrical stack design criteria	8-11
8.2.3	Ion-Exchange Membranes Used in Electrodialysis	8-13
8.2.4	Historical Developments	8-17
8.3	CURRENT APPLICATIONS OF ELECTRODIALYSIS	8-18
8.3.1	Desalination of Brackish Water by Electrodialysis	8-18
8.3.2	Production of Table Salt	8-20
8.3.3	Electrodialysis in Wastewater Treatment	8-20
8.3.3.1	Concentration of Reverse Osmosis Brines	8-20
8.3.4	Electrodialysis in the Food and Pharmaceutical Industries	8-21
8.3.5	Production of Ultrapure Water	8-21
8.3.6	Other Electrodialysis-Related Processes	8-23
8.3.6.1	Donnan-dialysis with ion-selective membranes	8-23
8.3.6.2	Electrodialytic water dissociation	8-23
8.4	ELECTRODIALYSIS ENERGY REQUIREMENT	8-26
8.4.1	Minimum Energy Required for the Separation of Water from a Solution	8-26
8.4.2	Practical Energy Requirement in Electrodialysis Desalination	8-26
8.4.2.1	Energy requirements for transfer of ions from the product solution to the brine	8-27
8.4.2.2	Pump energy requirements	8-28
8.4.2.3	Energy requirement for the electrochemical electrode reactions	8-28
8.4.3	Energy Consumption in Electrodialysis Compared with Reverse Osmosis	8-28
8.5	ELECTRODIALYSIS SYSTEM DESIGN AND ECONOMICS	8-30
8.5.1	Process Flow Description	8-30
8.5.2	Electrodialysis Plant Components	8-30
8.5.2.1	The electrodialysis stack	8-30
8.5.2.2	The electric power supply	8-32
8.5.2.3	The hydraulic flow system	8-32
8.5.2.4	Process control devices	8-32

8.5.3	Electrodialysis Process Costs	8-32
8.5.3.1	Capital	8-32
8.5.3.2	Operating costs	8-35
8.5.3.3	Total electrodialysis process costs	8-35
8.6	SUPPLIER INDUSTRY	8-38
8.7	SOURCES OF INNOVATION - CURRENT RESEARCH	8-40
8.7.1	Stack Design Research	8-40
8.7.2	Membrane Research	8-41
8.7.3	Basic Studies on Process Improvements	8-42
8.8	FUTURE DEVELOPMENTS	8-44
8.8.1	Areas of New Opportunity	8-44
8.8.2	Impact of Present R&D Activities on the Future Use of Electrodialysis	8-44
8.8.3	Future Research Directions	8-49
	REFERENCES	8-51

CHAPTER EIGHT

ELECTRODIALYSIS

by H. Strathmann, Fraunhofer IGB

8.1 INTRODUCTION

Electrodialysis is an electrochemical separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. Electrodialysis is widely used for desalination of brackish water. In some areas of the world it is the main process for the production of potable water. Although of major importance, water desalination is by no means the only significant application. Stimulated by the development of new ion-exchange membranes with better selectivities, lower electrical resistance and improved thermal, chemical, and mechanical properties, other uses of electrodialysis, especially in the food, drug, and chemical process industry, have recently gained a broader interest.

Electrodialysis in the classical sense can be utilized to perform several general types of separations, such as the separation and concentration of salts, acids, and bases from aqueous solutions, or the separation of monovalent ions from multiple charged components, or the separation of ionic compounds from uncharged molecules.

Slightly modified electrodialysis is also used today to separate mixtures of amino acids or even proteins. It is also used to produce acids and bases from the corresponding salts by forced water dissociation in bipolar membranes.

In many applications electrodialysis is in direct competition with other separation processes such as distillation, ion-exchange, reverse osmosis and various chromatographic procedures. In other applications there are few economic alternatives to electrodialysis. Total worldwide sales of electrodialytic equipment exceeded \$150 million in 1988. At least some of this equipment was intended for use in the chemical process industry, in biotechnology and in water-pollution control. Although the process has been known in principle for more the 50 years, large scale industrial utilization began about 15 years ago. Over the last 10 years the electrodialysis equipment-producing industry has enjoyed an annual increase in sales of about 15%. Because of the inherent features of the process, it seems likely that electrodialysis and related processes will continue to find new applications in the chemical process, food and pharmaceutical industries. Market growth may then exceed the present level.

8.2 PROCESS OVERVIEW

8.2.1 The Principle of the Process and Definition of Terms

Electrodialysis is a process by which electrically charged membranes are used to separate ions from an aqueous solution under the driving force of an electrical potential difference.

8.2.1.1 The process principle

The principle of the process is illustrated in Figure 8-1, which shows a schematic diagram of a typical electrodialysis cell arrangement. The arrangement consists of a series of anion- and cation-exchange membranes arranged in an alternating pattern between an anode and a cathode, to form individual cells. If an ionic solution, such as an aqueous salt solution, is pumped through these cells and an electrical potential established between anode and cathode, the positively charged cations in the solution migrate toward the cathode and the negatively charged anions migrate toward the anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion-exchange membrane. Likewise, the negatively charged anions pass through the anion-exchange membrane and are retained by the cation-exchange membrane. The overall result is an ion concentration increase in alternate compartments, while the other compartments simultaneously become depleted of ions. The depleted solution is generally referred to as the diluate and the concentrated solution as the brine, or concentrate.

The efficiency of electrodialysis as a separation process is mainly determined by the ion-exchange membranes used in the system. The operating costs are dominated by the energy consumption and investment costs for a plant of a desired capacity, which are a function of the membranes used in the process and various design parameters such as cell dimensions, feed flow velocity and pressure drop of the feed solution in the cell.¹

The energy required in an electrodialysis process is an additive of two terms: one, the electrical energy to transfer the ionic components from one solution through membranes into another solution²; and two, the energy required to pump the solutions through the electrodialysis unit. Depending on various process parameters, particularly the feed solution concentration and the current utilization, either one of the terms may dominate. At high feed solution ion concentration, the energy needed for the transfer of ions is generally the dominating factor. The capital cost of an electrodialysis plant is proportional to the membrane area required for a certain plant capacity, which is determined mainly by the feed solution concentration and the limiting current density discussed below.³

8.2.1.2 Limiting current density and current utilization

The limiting current density is the maximum current which may pass through a given membrane area without giving rise to higher electrical resistance or lower current utilization.⁴ The current that can pass through a membrane is limited because the solution immediately adjacent to the diluate side of the membrane becomes depleted of ions. If the limiting current density is exceeded, the process efficiency is drastically diminished. Not only does the electrical resistance of the solution increase, wasting energy, but the current splits water into H^+ and OH^- ions, causing pH changes and various operational problems.³ The limiting current density is determined by the initial ion concentration in the diluate stream and by the turbulence in this stream. Figure 8-2 shows the concentration gradient of cations in the boundary layer at the surface of a cation-exchange membrane during an electrodialysis desalting process.

C: Cation transfer membrane
A: Anion transfer membrane

Figure 8-1. Schematic diagram of the electrodialysis process.

Figure 8-2. Schematic diagram of the concentration profiles of the cations in the laminary boundary layer at both surfaces of a cation-exchange membrane during electro dialysis. C is the cation concentration, the subscripts b and m refer to the bulk solution and the superscripts c and d refer to concentrate and diluate.

Similar anion concentration profiles are obtained at the surface of an anion-exchange membrane. The transport of charged particles to the anode or cathode through a set of ion-exchange membranes leads to a decrease in concentration of counter-ions (i.e. the ions that will pass the membrane) in the laminar boundary layer at the membrane surface facing the diluate cell and an increase at the surface facing the brine cell. The concentration increase on the brine side does not have a severe impact on the cell performance, but the decrease in the concentration of counter-ions on the diluate side increases the electrical resistance of the solution in the boundary layer.⁵ The limiting current density is the current density at which the ion concentration at the surfaces of the cation- or/and anion-exchange membranes in the cells with the depleted solution will approach zero. The limiting current density can be described by:⁴

$$i_{\text{lim}} = \frac{C_b^d D z_+ F}{Y_b \left[T_+^M - T_+ \right]} \cdot \frac{C_b^d z_+ F \cdot k}{\left[T_+^M - T_+ \right]} \quad (1)$$

Here i_{lim} is the limiting current density, C_b^d is the bulk solution concentration in the cell with the depleted solution, D and z are the diffusion coefficient and the electrochemical valence of the ions in the solution, F is the Faraday constant, Y_b is the boundary layer thickness, and T_+^M and T are the ion transport numbers in the membrane and the solution, respectively, and the subscripts $+$ and $-$ refer to cations and anions. The constant k is the mass transfer coefficient, which depends on hydrodynamics, flow channel geometry, and spacer design.

According to Equation (1), the limiting current density is proportional to the ion concentration in the diluate and inversely proportional to the boundary layer thickness at the membrane surface. The boundary layer thickness is determined by the cell design and the feed solution flow velocity, which determine the mass transfer coefficient.² The mass transfer coefficient can be related by the well-known relations for the mass transfer by the Sherwood number, which again is a function of the Schmidt and Reynolds number. Introducing the proper relations in Equation (1) leads to an expression which describes the limiting current density as a function of the feed flow velocity in the electrodialysis stack:

$$i_{\text{lim}} = C_b^d a u^b \quad (2)$$

Here C_b^d is the concentration in the diluate cell, u is the linear flow velocity of the solution through the electrodialysis cells and a and b are constants, the value of which are determined by parameters such as cell and spacer geometry, solution viscosity, and ion-transfer numbers in the membrane and the solution.

The constants a and b, and hence the limiting current density, are different for different electrodialysis stack designs and must be determined experimentally. Exceeding the limiting current density generally leads to an increase of the total resistances and a decrease in the pH-value in the diluate cell. The limiting current density can, therefore, be determined by measuring the total resistance of a cell pair and the pH-value in the diluate cell as a function of the current density. When the pH-value is plotted vs. $1/i$, a sharp decrease in the pH-value is noted when the limiting current density is exceeded. Likewise, when the total resistance of a cell pair is plotted vs. $1/i$, a minimum is obtained at the limiting current density. This is shown schematically in Figures 8-3a and b.

The limiting current density affects the membrane area necessary to achieve a certain desalting effect and therefore also effects the investment costs for an electrodialysis plant.⁶

Another key parameter determining the overall performance of the electrodialysis process is the current utilization. The current utilization refers to the portion of the total current that passes through an electrodialysis stack that is actually used to transfer ions from a feed solution. The current utilization is always less than 100%, and is affected by three factors:

1. The membranes are not strictly semipermeable, i.e. the co-ions that carry the same charge as the membrane are not completely excluded, especially at high feed solution concentrations.
2. Some water is generally transferred through the membrane by osmosis and/or with the solvated ions.
3. A portion of the electrical current flows through the stack manifold by-passing the membranes.

The total current utilization can therefore be expressed by the following relation:⁴

$$\zeta = n \eta_w \eta_m \eta_s \quad (3)$$

Here ζ is the current utilization, n is the number of cells in the stack, and η_w , η_m and η_s are efficiency terms, all less than one. The subscripts m, w, s refer to efficiency losses due to current flow through the stack manifold, to water transfer and to incomplete membrane selectivities. The stack manifold factor, η_m , is determined by the cell design and in modern electrodialysis systems it can be kept close to one. The water transfer factor, η_w , is determined by the water transferred with the hydration shell of the ions. For feed solutions with low ion concentrations it is also close to one, but for feed solutions with very high salt concentrations it may be significantly smaller. The counter-ion leakage factor, η_s , is a membrane constant which depends strongly on the feed solution salt concentration. This is due to a phenomenon referred to as the Donnan equilibrium relationship,⁶ which can be expressed for a monovalent salt by the following equation:

Figure 8-3. Schematic diagram illustrating the determination of the linking current density by plotting: a) the pH-value of the diluate cell vs. $1/i$ and b) the total resistance of a cell pair vs. $1/i$.

$$\bar{C}_{\text{co-ion}} = \left(\frac{C_{\text{co-ion}}^2}{\bar{M}_R + \bar{C}_{\text{co}}} \right) \left(\frac{\gamma_{\pm}}{\gamma_{\pm}} \right)^2, \quad (4)$$

where the overbar refers to the membrane phase, $\bar{M}_R$ is the concentration of fixed charges per unit volume of water in the membrane and $\gamma_{\pm}$ is the mean activity coefficient of the salt in the designated phase.

Equation (4) indicates that the concentration of the co-ion in an ion-exchange membrane, i.e. the ion that carries the same charge as the membrane, is a function of the concentration of the fixed charges in the membrane and the concentration of the co-ions in the feed solution. The concentration in the membrane is proportional to the square of the concentration in the external solution and inversely proportional to the fixed ion concentration of the membrane. Since the transfer of ions through a membrane is proportional to their concentration in the membrane interphase, the selectivity of ion-exchange membranes is determined by their fixed ion concentration and the concentration in the feed and/or concentrated brine solution.⁸ Thus, when the ion concentration in the feed solution is much lower than the concentration of the fixed charges in the membrane, an ion-exchange membrane is essentially semipermeable, i.e. permeable to counter-ions only. When the ion concentration in the feed solution is of the same order as that of the fixed charges in the membrane, however, co-ions may enter the membrane, thereby reducing the selectivity. The current efficiency as expressed in Equation (3) then becomes smaller and the energy cost of electrodialysis higher. In most membrane selectivity calculations an activity coefficient ratio of 1 is assumed. Although activity coefficients generally approach unity in diluted solutions, this is not the case within the membrane. Here the ratio of the activity coefficients may be significantly higher than 1.⁷

8.2.2 Design Features and their Consequences

The performance of electrodialysis in a practical application is largely determined by the properties of the ion-exchange membranes. However, system design features such as stack construction, feed flow velocities, and type of electrode are also of prime importance for the overall performance of the process, as is the operating mode.^{8,9}

8.2.2.1 The electro dialysis stack

An electro dialysis stack is a device to hold an array of membranes between electrodes in such a way that the streams being processed are kept separated.¹⁰ A typical electro dialysis stack design is shown in Figure 8-4.

The membranes are separated by spacers which also contain manifolds to distribute the process fluids in the different compartments. The supply ducts for the diluate and the brine are formed by matching the holes in the spacers, the membranes, and the electrode cells. The distance between the membrane sheets should be as small as possible because water, even with salt in it, has a relatively high electrical resistance. In industrial-size electro dialysis stacks, membrane distances are typically between 0.5 and 2 mm.^{11,12} A spacer is placed between the individual membrane sheets to support the membrane, to control the feed solution flow distribution and, most importantly, to seal the cell. It is critically important in any electro dialysis system to prevent leakage of liquid from the compartment with the concentrated solution into the compartment with the diluate.¹³

In a practical electro dialysis system, 200 to 1,000 cation- and anion-exchange membranes are installed between two electrodes to form an electro dialysis stack with 100 to 500 cell pairs, each cell pair having an anionic and a cationic membrane.¹⁴ Because the multicell stack contains only two electrodes, the irreversible energy-consuming processes represented by the formation of hydrogen and oxygen or chlorine at the electrodes do not affect the efficiency of the operation.¹⁵

8.2.2.2 Concentration polarization and membrane fouling

Electro dialysis is affected by concentration polarization and membrane fouling, as are all membrane separation processes. The magnitude of concentration polarization is largely determined by the electrical current density, by the cell and particularly spacer design, and by the flow velocities of the diluate and brine solutions.² Ion transport through the membrane leads to a depletion of ions in the laminar boundary layer at the membrane surfaces in the cell containing the diluate flow stream and an increase of ions in the laminar boundary layer at the membrane surfaces in the cell containing the brine solution. This has an adverse effect on the separation efficiency of the process. One unique consequence of concentration polarization in electro dialysis is its effect on the limiting current density, which may lead to significantly larger membrane area required for a given plant capacity.^{16,17} The salt concentration increases in the boundary layer at the membrane surface facing the cell with the concentrated solution. This may lead to precipitation of salts with low solubility and it will also decrease the selectivity of the membrane due to the reduced Donnan exclusion of co-ions described in Equation (3). These concentration polarization effects can be controlled by providing proper spacer and cell construction and feed flow velocities.

More difficult to control and more potentially damaging is membrane fouling due to adsorption of polyelectrolytes, such as humic acids, surfactants or proteins. These large molecules penetrate partially into the membrane, resulting in severely

Figure 8-4. Exploded view of components in an electrodialysis stack.

reduced ion permeability. Multivalent cations and polyelectrolytes are often very strongly attached to the corresponding counter-ions within the membrane, so they are very difficult to remove. Hydrodynamic procedures generally have no effect at all. Cleaning procedures with solutions of either very high or low pH-values are generally more effective. A very efficient cleaning technique is short-term operation of the unit with reversed polarity, which will be described in more detail later.¹⁸

8.2.2.3 Mechanical, hydrodynamic, and electrical stack design criteria

In designing an electrodialysis stack, several general criteria concerning mechanical, hydrodynamic, and electrical properties have to be considered. Since some criteria conflict, the final stack construction is usually a compromise.^{8,9}

A proper electrodialysis stack design should first provide the maximum effective membrane area per unit stack volume. Consequently, the membrane area obscured by seals or spacers should be small. Second, the stack's solution distribution design should ensure equal and uniform flow distribution through each compartment and the solution distribution channel should not be easily blocked by particles in the feed stream. The correct flow distribution is provided by the spacer screen which should provide closely spaced support points for the membranes without obscuring a large membrane area. The spacer should provide a maximum of mixing of the solution in the cell, but at the same time should cause a minimum in pressure loss to minimize pumping costs. The flow distribution of the solution being processed should be equal over the entire width of each compartment and the solution velocity should be equal at all points within a compartment. This requires that the compartment thickness and the hydraulic resistance of the spacer screen be uniform over the entire width and length of the compartments. Low pressure drop across the stack is desirable to minimize the pumping energy requirements and to avoid pressure differences between different compartments within the stack, which could lead to bulging of the compartment, thus changing its flow cross section and putting additional stress on the membranes. Third, leakage between the diluate, concentrate, and the electrode cells has to be prevented. Leakage between the individual cells and to the outside can also be a severe problem.¹⁹ Finally, to ensure a maximum current utilization, electrical leakages through the solutions in the supply ducts should be small. Therefore the resistance of the solution in the supply ducts should be high and the cross-sectional area of the duct small. All gaskets and spacer materials should have high electrical resistance.

Consideration of the various criteria discussed above has led to a variety of electrodialysis stack designs. Most stack designs used in modern large-scale electrodialysis plants are one of two basic types: tortuous path or sheet flow. These designations refer to the type of solution flow path in the compartments of the stack. In the tortuous-path stack, the membrane spacer and gasket have a long serpentine cut-out which defines a long narrow channel for the fluid path. The objective is to provide an extended residence time for the solution in each cell, in spite of the high linear velocity that is required to limit polarization effects. A tortuous-path spacer gasket is shown schematically in Figure 8-5. The flow channel makes several 180° bends between the entrance and exit ports, which are positioned in the middle of the spacer. The channels contain cross-straps to promote turbulence of the feed solution.

Figure 8-5. Schematic diagram of a tortuous-path electro dialysis spacer gasket.

In stack designs employing the sheet-flow principle, a peripheral gasket provides the outer seal and a plastic net or screen is used to prevent the membranes touching each other. The solution flow in a sheet-flow type stack is a straight path from the entrance to the exit ports, which are located on opposite sides in the gasket. Figure 8-6 shows a schematic diagram of a sheet-flow spacer. Solution flow velocities in sheet-flow stacks are typically between 5 and 10 cm/sec, whereas, in tortuous-path stacks, solution flow velocities of 30 to 50 cm/sec are required. Because of the higher flow velocities and longer flow paths, pressure drops on the order of 5-6 bars occur in tortuous-path stacks. In contrast, the pressure drop in a sheet-flow system is usually 1-2 bars. The membranes used in tortuous-path stacks are thicker and more rigid than those used in sheet-flow systems, because they must resist deflection between the widely spaced support.

There are several other stack concepts described in the literature, especially in patents. Most are not used in any practical application. Stack constructions which provide three or four independent solution flow cycles are used in some specific applications, for example in combination with bipolar membranes.^{20,21,22}

8.2.3 Ion-Exchange Membranes Used in Electrodialysis

The most important components in an electrodialysis unit are the ion-exchange membranes. They should have a high selectivity for oppositely charged ions and a high ion permeability, i.e. a low electric resistance. Furthermore they should have high form stability, i.e. a low degree of swelling and good mechanical strength at ambient and elevated temperatures. Good chemical stability over a wide pH-range and in the presence of oxidizing agents is also required. The properties of ion-exchange membranes are closely related to those of ion exchange resins. There are two different types of membranes: cation-exchange membranes, which contain negatively charged groups fixed to a matrix; and anion-exchange membranes, containing positively charged groups. There are many possible types of ion-exchange membranes with different matrices and different functional groups to confer the ion-exchange properties. There are a number of inorganic ion-exchange materials, most of them based on silica, bentonites and oxyhydrates of aluminum and zirconium. These materials are unimportant in ion-exchange membranes, which are produced almost exclusively from synthetic polymers.

A typical ion-exchange membrane is shown schematically in Figure 8-7. The membrane is composed of a polymer matrix containing fixed negatively charged groups, which are counterbalanced by mobile positively charged cations, usually referred to as counter-ions. Mobile anions, usually called co-ions, are essentially excluded, since they are carrying the same charge as the fixed negatively charged groups. This type of exclusion is referred to as Donnan exclusion in honor of the pioneering work of F. S. Donnan.²³ Due to the exclusion of the co-ion in a cation-exchange membrane, the cations carry virtually all of the electric current through the membrane. Likewise, in anion-exchange membranes the current is mainly carried by anions.

Figure 8-6. Schematic diagram of a sheet-flow electro dialysis spacer gasket.

Figure 8-7. Schematic diagram of a cation-exchange membrane.

Many methods of making ion-exchange membranes are described in the literature. Some companies have more than 500 issued patents describing detailed recipes for making membranes with special properties. Most of these patents were issued between 1950 and 1970 and have no commercial significance today. Ion-exchange membranes may be homogeneous or heterogeneous. Heterogeneous membranes can be made by incorporating ion-exchange particles into film-forming resins by various methods, including dry molding, calendering, dispersing the ion-exchange material in a solution of the film-forming polymer, then solution casting, and dispersing the ion-exchange material in a partially polymerized film-forming polymer, casting films and completing the polymerization. Heterogeneous exchange membranes have several disadvantages, the most important of which are relatively high electrical resistance and poor mechanical strength. Homogeneous ion-exchange membranes have significantly better properties in this respect, because the fixed ion charges are distributed more homogeneously over the entire polymer matrix.⁷ Most commonly used ion-exchange membranes are of the homogeneous type.

The common methods of preparing homogeneous membranes are as follows:

- (1) Polymerization of mixtures of reactants (e.g. phenol, phenolsulfonic acid, and formaldehyde) that can undergo condensation polymerization. At least one of the reactants must contain a moiety that either is or can be made anionic or cationic.
- (2) Polymerization of mixtures of reactants (e.g. styrene, vinylpyridine, and divinylbenzene) that can polymerize. At least one of the reactants must contain an anionic or cationic moiety, or one that can be made to do so.
- (3) Introduction of anionic or cationic moieties into a polymer or preformed films by techniques such as imbibing styrene into polyethylene films, polymerizing the imbibed monomer, and then sulfonating the styrene. Other similar techniques, such as graft polymerization, have been used to attach ionized groups onto the molecular chains of preformed films.²⁷
- (4) Introduction of anionic or cationic moieties into a polymer chain such as polysulfone, followed by dissolving the polymer and casting the solution into a film.²⁸
- (5) Forming polymer alloys or interpolymers by mixing a finely dispersed ion-exchange resin in a polymer matrix.

Membranes made by any of the above methods may be cast or formed around screens or other reinforcing materials to improve their strength and dimensional stability. Anionic or cationic moieties most commonly found in commercial ion-exchange membranes are -SO_3^- or -NR_3^+ . However, other charged groups, such as -COO^- , PO_3^{2-} , and -HPO_4^{2-} , as well as various tertiary or quaternary amines, are used in ion-exchange membranes. The resistance of ion-exchange membranes used today is in the range of 1 - 2 $\Omega \text{ cm}^2$ and the fixed charge density is about 1 - 2 m equiv./g.

8.2.4 Historical Developments

Studies of electrodialysis began in Germany in the early part of this century.²⁹ Originally, the process was carried out in single cell arrangements with nonselective membranes and was of no practical use. Manegold and Kalauch³⁰ suggested the use of selective cation- and anion-exchange membranes and Meyer and Strauss³¹ introduced the multicell arrangement between a pair of electrodes as indicated in Figure 1. In such a multicompartiment electrodialyser, demineralization or concentration of solutions containing ionic components was possible with reasonable energy efficiency, since irreversible effects represented by the water decomposition at the electrode could be distributed over many demineralization compartments.

With the development of ion-exchange membranes with low electrical resistance directly after the second world war, multicompartiment electrodialysis became commercially available for demineralizing or concentrating various electrolyte solutions.^{32,33} During the 1960s the United States Office of Saline Water directly supported research and development of electrodialysis for the production of potable water from brackish water. Similar smaller programs in Europe, Israel and South Africa stimulated the development of new membranes and improved processes. At the same time, several Japanese companies developed electrodialysis as a means of concentrating seawater for use as a brine for the chlor-alkali industry and for producing table salt. These early electrodialysis systems were all operated unidirectionally, i.e. the polarity of the two electrodes, and hence the position of the dilute and concentrated cells, was permanently fixed in an electrodialysis stack. This mode of operation often led to scale formation and membrane fouling caused by the precipitation of low solubility salts on the membrane surface. Scaling affects the efficiency of electrodialysis significantly and the materials precipitated at the membrane surface have to be removed by flushing with cleaning solutions, the frequency depending on the concentration of such materials in the feed solution. The control of scaling and membrane fouling generally leads to an increase in the capital and operating costs. Extreme cases of membrane scaling and fouling can make the process economically unattractive. A significant advance in scaling control was the introduction of a special operating mode referred to as electrodialysis reversal (EDR). EDR was introduced by Ionics Inc. to continuously produce demineralized water without constant chemical addition.¹⁸

In EDR systems, the polarity of the electrodes is periodically reversed. This reverses the direction of ion movement within the membrane stack, thus controlling membrane fouling and scale formation. Typically, reversal occurs approximately every 15 minutes and is accomplished automatically. Upon reversal the streams that formerly occupied concentrate compartments become demineralized streams. Automatic valves switch the inlet and outlet streams, so that the incoming feed water flows into the new demineralizing compartments and any concentrate stream remaining in the stack must now be desalted. This creates a brief period of time in which the demineralized stream (product water) salinity is higher than the specified level.

Because of reversal, no flow compartment in the stack is exposed to high solution concentrations for more than 15 to 20 minutes at a time. Any build-up of precipitated salts is quickly dissolved and carried away when the cycle reverses. EDR effectively eliminates the major problems encountered in unidirectional systems.

In summary, the development of electrodialysis as an efficient demineralization and ion exchange process is characterized by three major innovations:

- (1) the use of highly selective cation and anion-exchange membranes,
- (2) the use of a multi-compartment stack design,
- (3) the polarity-reversal operating mode.

8.3 CURRENT APPLICATIONS OF ELECTRODIALYSIS

Electrodialysis was developed first for the desalination of saline solutions, particularly brackish water. The production of potable water is still the most important industrial application of electrodialysis. But other applications, such as the treatment of industrial effluents, the production of boiler feed water, demineralization of whey and deacidifying of fruit juices are gaining increasing importance and are found in large-scale industrial installations. Another application of electrodialysis, limited to Japan and Kuwait, that has gained considerable commercial importance is the production of table salt from seawater. Diffusion dialysis and the use of bipolar membranes have expanded the application of electrodialysis significantly in recent years.⁵²

The industrial applications of electrodialysis, their present status, market size, expected future growth and the market leaders are summarized in Table 8-1. In the following sections, each of these application areas is briefly reviewed.

8.3.1 Desalination of Brackish Water by Electrodialysis

Electrodialysis competes directly with reverse osmosis and multistage flash evaporation in desalination applications. For water with relatively low salt concentration (less than 5000 ppm) electrodialysis is generally the most economic process, as indicated earlier. One significant feature of electrodialysis is that the salts can be concentrated to comparatively high values (in excess of 18 to 20 wt%) without affecting the process economics significantly. Most modern electrodialysis units operate in EDR mode, preventing scaling due to concentration polarization effects. Ionics leads the brackish water treatment market, with more than 1,500 plants with a total capacity of more than 600,000 m³/day of product, requiring a membrane area in excess of 1,000,000 m². The largest installation produces 24,000 m³/day for a refinery in the Middle East. Installations in Russia and China for the production of potable water are estimated as being of the same order of magnitude. Exact data, however, are difficult to obtain. Other manufacturers of electrodialysis equipment in Europe and Japan seem to be of minor importance for the production of potable water.

Table 8-1. Industrial Applications of Electrodialysis, Status of the Art, Current Problems, and Future Developments

Application	Membranes & stack design	Status of the art	Key problems	Market size \$ millions	Market growth %	Market leaders
brackish water desalination	anion- & cation-exchange membranes	com- mercial	costs	50	10	Ionics
boiler feed-water, industrial process water	anion- & cation-exchange membranes, tortuous path stack	com- mercial	scaling costs	30	15	Ionics
production of table salt	anion- & cation-exchange membranes, sheet flow stack	com- mercial	costs	15	-	Tokuyama
industrial effluent treatment	anion- & cation-exchange membranes, sheet-flow & tortuous stack	com- mercial	costs nontoxic removal	15	15	Ionics
food and pharmaceutical industry	anion- & cation-exchange membranes, sheet flow stack	com- mercial	membrane fouling, product loss	25	15	Ionics
diffusion dialysis of acids	cation-exchange membranes, sheet flow stack	com- mercial	costs	5	-	Tokuyama
ultrapure water		lab scale	process reliability	2	large	Millipore
water splitting	bipolar membranes three cell stack design	com- mercial	membrane performance and life	2	very large	Allied Signal

8.3.2 Production of Table Salt

The production of table salt from seawater by using electrodialysis to concentrate sodium chloride up to 200 g/L prior to evaporation is a technique developed and used nearly exclusively in Japan. More than 350,000 tons of table salt are produced annually by this technique, requiring more than 500,000 m² of installed ion-exchange membranes. Market leaders in this application are Tokuyama Soda, Asahi Glass, and Asahi Chemical. The key to the success of this technology has been low-cost, highly conductive membranes, with a preferred permeability for monovalent ions. In Japan, however, table salt production by electrodialysis is heavily subsidized, so the method may not be cost-effective elsewhere.

8.3.3 Electrodialysis in Wastewater Treatment

The main application of electrodialysis in wastewater treatment systems is in processing rinse waters from the electroplating industry. Complete recycling of the water and the metal ions is achieved. Compared to reverse osmosis, electrodialysis has the advantage of being able to utilize thermally and chemically stable membranes, so the process can be run at elevated temperatures and in solutions of very low or high pH values. Furthermore, the concentrations which can be achieved in the brine can be significantly higher. The disadvantage of electrodialysis is that only ionic components can be removed and additives usually present in a galvanic bath cannot be recovered.

An application which has been studied in a pilot-plant stage is the regeneration of chemical copper plating baths. In the production of printed circuits, a chemical process is often used for copper plating. The components which are to be plated are immersed into a bath containing, besides the copper ions, a strong complexing agent, for example, ethylene diamine tetra acetic acid (EDTA), and a reducing agent such as formaldehyde. Since all constituents are used in relatively low concentrations, the copper content of the bath is soon exhausted and copper sulfate has to be added. During the plating process, formaldehyde is oxidized to formate. After prolonged use, the bath becomes enriched with sodium sulfate and formate and consequently loses useful properties. By applying electrodialysis in a continuous mode, the sodium sulfate and formate can be selectively removed from the solution, without affecting the concentrations of formaldehyde and the EDTA complex. Hereby, the useful life of the plating solution is significantly extended.⁵⁰ Several other successful applications of electrodialysis in wastewater treatment systems that have been studied on a laboratory scale are reported in the literature.⁵² Large, commercially operated plants are at present, however, rare. Ionics and Tokuyama Soda are the market leaders. However, because the plant capacities needed for this application are smaller than in desalination, there are good opportunities for smaller companies to compete.

8.3.3.1 Concentration of Reverse Osmosis Brines

A further application of electrodialysis is concentration of reverse osmosis brines. Because of limited membrane selectivity and the osmotic pressure of concentrated salt solutions, the concentration of brine in reverse osmosis desalination plants cannot exceed certain values. Often the disposal of large

volumes of brine is difficult and further concentration is desirable. This further concentration may be achieved at reasonable cost by electrodialysis.

8.3.4 Electrodialysis in the Food and Pharmaceutical Industries

The use of electrodialysis in the food and pharmaceutical industries has been studied extensively in recent years. Several applications have considerable economic significance and are already well established. One is the demineralization of cheese whey. Normal cheese whey contains between 5.5 and 6.5% of dissolved solids in water. The primary constituents in whey are lactose, protein, minerals, fat and lactic acid. Whey provides an excellent source of protein, lactose, vitamins, and minerals, but in its normal form it is not considered a proper food material because of its high salt content. With the ionized salts substantially removed, whey approaches the composition of human milk and, therefore, provides an excellent source for the production of baby food. The partial demineralization of whey can be carried out efficiently by electrodialysis. The process is used extensively and is described in detail in the literature.⁵³

The removal of tartaric acid from wine is another application. Especially in the production of bottled champagne, the formation of crystalline tartar in the wine must be avoided, so the tartaric acid content must be reduced to a value below the solubility limit. This can be done efficiently by electrodialysis. Desalting of dextrane solutions, another application for electrodialysis, has technical significance as a potential large-scale industrial process.

Other applications of electrodialysis in the pharmaceutical industry have been studied on a laboratory scale. Most applications are concerned with desalting or with treating solutions containing active agents that have to be separated, purified, or isolated from certain substrates. Here, electrodialysis is often in competition with other separation procedures, including dialysis and solvent extraction. In many cases, for example the separation of amino acids and other organic acids, electrodialysis is the superior process as far as economics and product quality are concerned.

To date, the largest food industry application of electrodialysis is in cheese whey processing. There is an installed capacity of more than 35,000 m² of membrane area to produce more than 150,000 tons of desalted lactose per year. The market leaders are Tokuyama Soda, Asahi Glass and Ionics.

8.3.5 Production of Ultrapure Water

Recently, electrodialysis has been used for the production of ultrapure water for the semiconductor industry, especially in combination with mixed bed ion exchange resins as shown in Figure 8-8. In this process, ion exchange resin beads are sandwiched between the electrodes of an electrodialysis stack. The applied current continuously removes the ions trapped by the ion exchange resin. In this way, the feed water can be almost completely deionized and no chemical regeneration of the resin bed is required. This process was suggested many years ago by O. Kedem and coworkers⁴⁹ and has recently been commercialized by Millipore.⁵⁵

Figure 8-8. Principle of electro-dialytic regeneration of mixed bed ion exchange resins for the production of deionized water. (IX: Ion exchange resin; A: Anion transfer membrane; C: Cation transfer membrane.)

8.3.6 Other Electrodialysis-Related Processes

In addition to conventional electrodialysis, several processes closely related to electrodialysis have been discussed in the literature. Most of these processes are still in the laboratory stage.

8.3.6.1 Donnan-dialysis with ion-selective membranes

In Donnan-dialysis, the ion concentration difference in two phases separated by an ion-exchange membrane is used as the driving force for the transport of ions with the same electrical charges in opposite directions. The principle of the process is shown schematically in Figure 8-9. This figure shows as an example solutions of CuSO_4 and H_2SO_4 , separated by a cation-exchange membrane. Since the H^+ ion concentration in solution 1 is significantly higher ($\text{pH} = 1$) than the H^+ ion concentration in solution 2 ($\text{pH} = 7$) there will be a constant driving force for the flow of H^+ ions from solution 1 into solution 2. Since the membrane is permeable for cations only, there will be a build-up of electrical potential that will balance the concentration difference driving force of the H^+ ions. As a result, ions of the same charge will be transported in the opposite direction as indicated by the flow of Cu^{++} ions from solution 2 into solution 1 in Figure 8-9. As long as the H^+ concentration difference between the two phases separated by the cation-exchange membrane is kept constant, there will be a constant transport of Cu^{++} ions from solution 2 into solution 1 until the Cu^{++} ion concentration difference reaches the same order of magnitude as the H^+ ion concentration difference, i.e. Cu^{++} ions can be transported against their concentration gradient driving force by Donnan-dialysis.

The same process can be carried out with anions through anion-exchange membranes. An example of anion Donnan-dialysis is the sweetening of citrus juices. In this process, hydroxyl ions furnished by a caustic solution replace the citrate ions in the juice.

8.3.6.2 Electrodialytic water dissociation

A process referred to as electrodialytic water dissociation or water splitting⁵⁴ to produce acids and bases from salts, has been known for a number of years. The process is conceptually simple, as shown in the schematic diagram in Figure 8-10.

A cell system consisting of an anion-, a bipolar-, and a cation-exchange membrane as a repeating unit is placed between two electrodes. Sodium sulfate or other salt solution is placed in the outside phase between the cation- and anion-exchange membranes. When a direct current is applied, water will dissociate in the bipolar membrane to form an equivalent amount of hydrogen and hydroxyl ions. The hydrogen ions will permeate the cation-exchange side of the bipolar membrane and form sulfuric acid with the sulfate ions provided by the sodium sulfate from the adjacent cell. The hydroxyl ions will permeate the anion-exchange side of the bipolar membrane and form sodium hydroxide with the sodium ions permeating into the cell from the sodium sulfate solution through the adjacent cation-exchange membrane. The net result is the production of sulfuric acid and sodium hydroxide at significantly lower cost than by conventional

techniques. The most important part of the cell arrangement is the bipolar membrane, which consists of an anion- and a cation-exchange membrane laminated together. The membrane should have good chemical stability in acid and base solutions and low electrical resistance. Laboratory tests have demonstrated that production costs for caustic soda by utilizing bipolar membranes are only one-third to one-half the costs of the conventional electrolysis process. The process has recently been commercialized by Allied Corporation's Aquatech Systems Division. The process is affected by limited alkaline and temperature stability of the anion-exchange part of the bipolar membrane. Further improvements can, however, be expected in the near future.^{46,47}

Figure 8-9. The principle of Donnan-dialysis.

Figure 8-10. Schematic diagram showing the electrodialytic regeneration of an acid and sodium hydroxide from the corresponding salt employing bipolar membranes.

8.4 ELECTRODIALYSIS ENERGY REQUIREMENT

8.4.1 Minimum Energy Required for the Separation of Water from a Solution

In electrodialysis, as in any other separation process, there is a minimum energy required for the separation of various components. For the removal of salt from a saline solution this energy is given by:

$$W^{\circ} = RT \ln \frac{a_w^{\circ}}{a_w^s} \quad (5)$$

Here W° is the minimum energy required to remove one mole of water from a solution, R the gas constant and T the temperature in $^{\circ}\text{K}$; a_w° and a_w^s are the water activities in the pure state and the solution. Expressing the water activity in the solution by the concentration of the dissolved ionic components, the minimum energy required to remove water from a monovalent salt is given by:

$$W^{\circ} = 2RT (c^{\circ} - c') \left[\frac{\ln \frac{c^{\circ}}{c''}}{\frac{c^{\circ}}{c''} - 1} - \frac{\ln \frac{c^{\circ}}{c'}}{\frac{c^{\circ}}{c'} - 1} \right] \quad (6)$$

where W° refers to the minimum required energy for the production of 1 L of diluate solution, and C° , C' and C'' refer to the salt concentration in the feed solution, the diluate and the concentrate.

8.4.2 Practical Energy Requirement in Electrodialysis Desalination

Because of irreversible effects, the energy required to remove water from a solution by electrodialysis is significantly higher than the theoretically minimum energy. The practical required energy may be 10 to 20 times the theoretical value. The energy required in practical electrodialysis is an additive of three terms. The first is the electrical energy, E_{it} , to transfer the ions from the feed solution through the membrane into the brine. The second term is the energy consumption, E_{elr} , due to the electrochemical reactions at the electrodes and the resistance of the electrode cells. The third term is the energy required to pump the feed solution, the diluate and the brine through the electrodialysis stack, E_{pump} . Thus, the total energy consumption is given by

$$E_{tot} = E_{it} + E_{elr} + E_{pump} \quad (7)$$

Depending on various process parameters, particularly the feed solution concentration, any of these terms may be dominant, thus determining the overall energy costs.

8.4.2.1 Energy requirements for transfer of ions from the product solution to the brine.

The energy necessary to remove salts from a solution is directly proportional to the total current flowing through the stack and the voltage drop between the two electrodes in a stack. The energy consumption in a practical electrodialysis separation procedure can be expressed as:

$$E = n I^2 R t \quad (8)$$

Here E is the energy consumption, I the electric current through the stack, R the resistance of the cell, n the number of cells in a stack, and t the time. The electric current needed to desalt a solution is directly proportional to the number of ions transferred through the ion-exchange membranes from the feed stream to the concentrated brine. This is expressed as:

$$I = \frac{z F Q \Delta C}{\xi} \quad (9)$$

where F is the Faraday constant, z the electrochemical valence, Q the product solution flow rate, ΔC is the concentration difference between the feed solution and the diluate and ξ the current utilization. The current utilization is directly proportional to the number of cells in a stack and is governed by the current efficiency. In practical electrodialysis, the efficiency with which ions can be separated from the mixture by the electrical current is usually less than 100%.

A combination of Equations (8) and (9) gives the energy consumption in electrodialysis as a function of the current applied in the process, the electrical resistance of the stack (i.e. the resistance of the membrane and the electrolyte solution in the cells), current utilization and the amount of salt removed from the feed solution. Thus:

$$E = \frac{n I R t z F Q \Delta C}{\xi} \quad (10)$$

Equation (10) indicates that the electrical energy required in electrodialysis is directly proportional to the amount of salt that has to be removed from a certain feed volume to achieve the desired product concentration. Energy consumption is also a function of the number of cells in a stack and the electrical resistance in a cell. Electrical resistance is a function of individual resistances of the membranes and of the solutions in the cells. Because the resistance of the solution is directly proportional to its ion concentration, the overall resistance of a cell will in most cases be determined by the resistance of the diluate solution. This is a factor that must be taken into account in the design of an electrodialysis stack. A typical value for the resistance of an electrodialysis cell pair, including the cation- and anion-exchange membrane plus the dilute and concentrated solution, is in the range of 10 to 100 $\Omega \text{ cm}^2$.

8.4.2.2 Pump energy requirements

Electrodialysis systems use three pumps, to circulate the diluate (the solution depleted of ions), the brine (the solution into which the ions are transferred), and the electrode rinse solutions. The energy required for pumping these solutions is determined by the volumes to be circulated and the pressure drop in the electrodialysis unit. It can be expressed by the following relation:

$$E_p = k_1 Q_D \Delta P_D + k_2 Q_B \Delta P_B + k_3 Q_E \Delta P_E \quad , \quad (11)$$

where E_p is the pump energy, k_1 , k_2 , and k_3 are constants referring to the efficiency of the pumps, Q_D , Q_B , and Q_E are volume flows of the diluate, brine, and electrode rinse solutions, and ΔP_D , ΔP_B , and ΔP_E are the pressure losses in the diluate, the brine and the electrode cells. The pressure losses in the various cells are determined by the solution flow velocities and the cell design. The energy requirements for circulating the solution through the system may become significant or even dominant when solutions with low salt concentrations, less than 500 ppm, are processed.

8.4.2.3 Energy requirement for the electrochemical electrode reactions

An electrodialysis cell usually generates hydrogen at the cathode and oxygen or chlorine at the anode. The energy consumed in electrochemical reactions at the electrodes is given by the total current passing through the stack multiplied by the voltage drop at the electrodes and in the electrode cells. In a multicell arrangement the energy consumed at the electrodes is small, generally less than 1% of the total energy used for the ion transfer from a feed to a brine solution.

8.4.3 Energy Consumption in Electrodialysis Compared with Reverse Osmosis

Electrodialysis competes with other separation processes in many applications. The minimum energy required to perform a theoretical separation is identical in all processes, but there are significant differences as far as the energy consumption in a practical separation problem is concerned. For desalination, for instance, reverse osmosis, ion exchange, distillation, or electrodialysis can all be used. All four processes require different amounts of energy depending on the composition of the feed solution. The differences between the energy demands of reverse osmosis and electrodialysis can be illustrated by comparing the basic principles of the processes as shown in Figure 8-11.

In reverse osmosis, water passes through the membrane under a driving force created by a hydrostatic pressure difference. Ignoring concentration polarization effects, the irreversible energy loss is caused primarily by friction between the individual water molecules and the polymer membrane matrix. This frictional energy loss is independent of the salt concentration in the feed solution. In electrodialysis, ions pass through the membrane under a driving force created by an electrical potential difference. In this case, therefore, the irreversible frictional energy losses are directly proportional to the salt concentration in the feed water. Thus, for feed solutions with low salt concentration, the energy

requirements are lower in electrodialysis than in reverse osmosis, and at high feed-solution salt concentration the energy consumption in electrodialysis is higher than in reverse osmosis. This is shown in Figure 8-12, where the irreversible energy consumption is plotted versus the feed solution concentration, assuming identical product water concentrations.

A comparison of the energy consumptions of different mass separation processes has to take into account the different forms in which the energy may be required. Electrodialysis uses electricity, a relatively expensive form, but distillation uses heat, which is comparatively inexpensive. In ion exchange, very little energy is required directly, but the chemicals used to regenerate the resin require a significant amount of energy for their production.

Figure 8-11. Schematic diagram comparing the operating principles of reverse osmosis and electrodialysis.

Figure 8-12. Schematic diagram showing the irreversible energy losses in electrodialysis and reverse osmosis as a function of the feed-solution salt concentration.

8.5 ELECTRODIALYSIS SYSTEM DESIGN AND ECONOMICS

8.5.1 Process Flow Description

A flow diagram of a typical electrodialysis plant as used for desalination of brackish water is shown in Figure 8-13. After proper pretreatment, which may consist of flocculation, removal of carbon dioxide, pH control or prefiltration, the feed solution is pumped through the electrodialysis unit. A deionized solution and a concentrated brine are obtained. The concentrated and depleted process streams leaving the last stack are collected in storage tanks, or are recycled if further concentration or depletion is desired. Acid is frequently added to the concentrated stream to prevent scaling of carbonates and hydroxides. To prevent the formation of free chlorine by anodic oxidation, the electrode cells are generally rinsed with a separate solution which does not contain any chloride ions. In many cases, the feed or brine solution is also used in the electrode cells.

An important variation to the basic operating mode of Figure 8-13 is electrodialysis reversal (EDR). In this operating mode the polarity of the current is changed at specific time intervals ranging from a few minutes to several hours. When the current changes, the diluate cell becomes the brine cell, and vice versa. The advantage of the reverse polarity operating mode is that precipitation in the brine cells is essentially prevented. Any precipitation that does occur will be redissolved when the brine cell becomes the diluate cell in the reverse operating mode. The flow scheme of a typical electrodialysis reversal plant, taken from Ionics Inc. brochures, is shown in Figure 8-14.

8.5.2 Electrodialysis Plant Components

An electrodialysis plant consists of four basic components: the membrane stack, the power supply, the hydraulic flow system, and process control devices.

8.5.2.1 The electrodialysis stack

A typical electrodialysis stack consists of 200 to 500 cation- and anion-exchange membranes arranged in an alternating pattern between two electrodes, which are generally assembled in separate cells. The membranes are separated by suitable gaskets, with two membranes forming a cell pair. Typical spacer-gasket configurations have been discussed earlier and are shown in Figures 8-5 and 8-6.

The final stack design is almost always a compromise between a number of conflicting criteria and considerations, e.g. short distances between membranes for low electrical resistance, high feed flow velocities and high turbulence for control of concentration polarization effects, low pressure losses in the solution pumped through the stack and low production costs.

Figure 8-13. Flow diagram of a typical electrodialysis desalination plant.

Figure 8-14. Typical electrodialysis reverse polarity (EDR) plant.⁵⁶

8.5.2.2 The electric power supply

Electrodialysis requires DC electrical power for the stack and AC power for the pumps. The DC power is usually supplied on-site by utilizing an AC-to-DC converter. Conversion efficiencies of about 90 percent are typical. Constant voltage regulators are utilized to maintain stable plant operation and used to prevent stack damage. Stack resistance changes occur as a result of scale formation, membrane deterioration and changes in the fluid concentrations within the stack. The voltage regulator is adjusted periodically to compensate for these changes. The voltage drop across each cell pair in an electrodialysis stack is about 0.5-2 V, so the total voltage drop across the stack is typically about 200-800 V. The current flowing through the stack is 400 A, which yields a current density up to 40 mA/cm² if the membrane area of the cell is 1 m².

8.5.2.3 The hydraulic flow system

The primary considerations in designing the hydraulic flow system are to obtain low hydraulic pressure drops, yet simultaneously achieve high volume flow rates. The pressure drop in an electrodialysis system is on the order of 2-6 bars. Simple plastic centrifugal pumps are generally used for circulating the different solutions through the stack.

8.5.2.4 Process control devices

The following variables are usually measured or controlled, or both:

- 1) DC voltage and current supplied to each electrodialysis unit,
- 2) Flow rates and pressures of the depleted and concentrated streams, and of the electrode rinse streams,
- 3) Electrolyte concentrations of the depleted and concentrated streams at the inlets and outlets to the electrodialysis stacks,
- 4) pH of the depleted stream and the electrode rinse streams,
- 5) Temperature of the feed stream.

All the above variables are interrelated. Automatic control of the flows of the depleted and concentrated streams can be achieved by the use of flow-type conductivity cells in the effluent streams, along with a controller that compares the conductivities of the streams with that of a preset resistance and actuates flow-control valves in the liquid supply lines.

To prevent damage to the membranes or other components in the event of stoppage of liquid flow to the stacks, an electrodialysis unit is normally provided with fail-safe devices that will turn off the power to the stacks and pumps.

8.5.3 Electrodialysis Process Costs

8.5.3.1 Capital

The capital cost of an electrodialysis plant is made up of depreciable and nondepreciable items. Nondepreciable items include land and working capital, and are outside the scope of this outline. Depreciable items include the electrodialysis stacks, pumps, electrical equipment, membranes, etc.

The capital costs of an electrodialysis plant will strongly depend on the number of ionic species to be removed from a feed solution. This can easily be demonstrated for an electrodialysis plant producing potable water from saline water sources. The total membrane area required by a plant is given by:

$$A = \frac{z F Q \Delta c n}{i \xi} , \quad (12)$$

where A is the membrane area, z the chemical valence, Q the volume of the produced potable water, Δc the difference in the salinity of feed and product water, n the number of cells in a stack, i the current density which should be about 80% of the limiting current density, ξ the current utilization and F the Faraday constant. The limiting current density is a function of the diluate concentration, which changes from the concentration of the original feed to the product solution concentration. The calculation of the minimum membrane area required for a given desalting capacity is based on an average diluate concentration and average limiting current density, given by:

$$\bar{i}_{\text{lim}} = a \cdot \bar{c}_d = a \cdot \frac{c_o - c_d}{\ln \left(\frac{c_o}{c_d} \right)} , \quad (13)$$

where $\bar{i}_{\text{lim}}$ is the average limiting current density, $\bar{c}_d$ is the average diluate concentration, a is a constant, which depends on the flow cell and spacer geometry and feed flow velocity, and c_o and c_d are the feed and diluate concentrations. Substituting Equation (13) into Equation (12) yields the minimum membrane area, A_{min} , required for a certain plant capacity and feed and product solution concentrations.

$$A_{\text{min}} = a \cdot z F Q \ln \left(\frac{c_o}{c_d} \right) , \quad (14)$$

For a given plant capacity and current density, the required membrane area is directly proportional to the feed water concentration. This is illustrated in Figure 8-15.

MTR-054-GRP

Figure 8-15. Membrane area required for electrodialysis desalination as a function of the feed water concentration at constant current density and plant capacity.

For typical brackish water containing 3,000 ppm TDS and an average current density of 12 mA/cm², the required membrane area for a plant capacity of 1 m³ product per day is about 0.4 m² of each cation- and anion-exchange membrane. The costs of pumps, electric power supply, etc. do not depend on feed water salinity, so the dependence of the total capital costs on the feed water salinity is nonlinear. For desalination of brackish water with a salinity of 3,000 ppm, the total capital costs for a plant with a capacity of 1,000 m³/day will be in the range \$200-300 per m³/d capacity. The cost of the membranes is less than 30% of the total capital costs. Assuming a useful life of the membranes of 5 years, of the rest of the equipment of 10 years and a plant availability of 95%, based on a 24-hour operating day, the amortization of the investment per m³ potable water, obtained from 3,000 ppm brackish water, is in the range \$0.10-0.15.

8.5.3.2 Operating costs

The largest single component of the operating cost is the required energy. All other components are minor in comparison for large-scale plants.

The energy costs in electrodialysis are determined by the electrical energy required for the actual desalting process and the energy necessary for pumping the solution through the stack. These factors were discussed in detail in Section 4.2. The energy requirements for the production of potable water with a TDS of < 500 ppm of saline feed water is shown schematically as a function of the feed water concentration in Figure 8-16.

The pumping energy is independent of the feed solution salinity. Assuming a pressure drop in the unit of about 400 KPa (4 bar), a pump efficiency of 70%, and 50% recovery, the total pumping energy will be about 0.4 kWh/m³ product water. This indicates that, at low feed-water salt concentration, the cost for pumping the solution through the unit might become significant.

Other components of the operating cost include costs associated with pretreatment, which obviously may vary from nothing to a significant portion of the total cost, and labor costs.

8.5.3.3 Total electrodialysis process costs

The total costs of electrodialysis are shown in Figure 8-17 as a function of the applied current density for a given feed solution calculated according to Equations (7) and (8).

The graph in Figure 8-17 shows that capital costs decrease with increasing current density and other costs are essentially independent of current density. For a given feed solution, there is a current density at which the total electrodialysis process costs will reach a minimum.

A comparison of the cost of desalination by various processes as a function of the feed water salinity, is shown in Figure 8-18.

Figure 8-16. Energy requirements for the production of potable water with a solid content of 500 ppm as a function of the feed solution concentration (ΔV per cell pair = 0.8 V)

Figure 8-17. Schematic diagram of the electrodialysis process costs as a function of the applied current density.

Figure 8-18. Costs of desalination of saline water as a function of the feed solution concentration for ion exchange (IE), electrodialysis (ED), reverse osmosis (RO), and multistage flash evaporation (MSF).

Figure 8-18 indicates that, at very low feed-solution salt concentration, ion exchange is the most economical process. The costs of ion-exchange processes increase sharply with the feed solution salinity, and at about 500 ppm TDS electrodialysis becomes the most economical process. Above 5,000 ppm TDS, reverse osmosis is the least costly. At very high feed-solution salt concentrations, in excess of 100,000 ppm TDS, multistage flash evaporation becomes the most economical process. The costs of potable water produced from brackish water sources are in the range \$0.2-0.5/m³.

8.6 SUPPLIER INDUSTRY

The electrodialysis supply industry is dominated by four large companies that produce membranes as well as equipment. These are Ionics, Tokuyama Soda, Asahi Chemical and Asahi Glass. The three Japanese companies sell membranes, stacks and complete installations; Ionics sells complete installations only. There are also several companies that produce and sell only ion-exchange membranes for the specialized equipment manufacturing industry. In addition to these market leaders, there are a number of small companies that specialize in certain applications that require specially designed membranes and equipment. These organizations often operate in regionally limited areas, unlike the larger suppliers, who all operate on a worldwide scale. The supplier industry, broken down by companies, with their main products and area of applications, is summarized in Table 8-2.

The three major Japanese manufacturers of electrodialysis equipment sell more than 80% of their products in Japan; Ionics, on the other hand, sells almost 50% of its products outside the United States. Table 8-3 lists the market distributions of the major suppliers.

It is interesting to note that companies have specialized in applications of importance to their home country. Table salt production is of interest only in Japan and, not unnaturally, Japanese companies dominate this application. The market for brackish water desalination lies predominantly in America, the Middle East, and Europe, and here a United States based company is the market leader. Food processing, especially deashing of whey, is of interest in almost any industrialized nation and this market is more evenly distributed among the four large equipment manufacturers.

Table 8-2. Manufacturers of Electrodialysis Equipment and Membranes⁵⁷

Company	Membrane manufacturer (trade names)	Equipment producer	Area of application	Annual electrodialysis estimated sales (\$ millions)
Asahi Chemical Co. Ltd.	Aciplex®		table salt production	20
Asahi Glass Co. Ltd.	Selemion®		table salt production	20
Ben Gurion University	Neginst®			-
Ionics Inc.		Aquamite	brackish, waste water, food	70
Soc. Recherches Techniques et Industrielles (SRTI)			whey	<5
Stantech GmbH			wastewater, food	<5
Ionac Chem. Co. Div. of Sybron Corp.				
Pall/RAI Research Corp.	Permion®			
Tokuyama Soda Co. Ltd.	Neosepta®		table salt production	20
Morinaga Milk Ind.			whey	10
Toyo Soda Manu- fact. Co. Ltd.	Scrion®			5
Others				<20

Table 8-3. Market Distribution in Various Electrodialysis Applications for the Major Electrodialysis Supplier Companies

Company	Salt production (%)	Water desalination (%)	Food processing (%)
Asahi Chemical	40	5	5
Asahi Glass	25	2	8
Tokuyama Soda	30	3	8
Toyo Soda Organo	5	1	4
Ionics	0	80	65
Others	0	9	10

8.7 SOURCES OF INNOVATION - CURRENT RESEARCH

Electrodialysis has a wide potential range of applications, requiring a multitude of different process and stack design concepts, and/or membranes with special properties. Applications such as brackish water desalination or table salt production can be considered as state-of-the-art techniques. In other applications, such as the recovery of bioproducts from a fermentation broth, treatment of a special industrial effluent or the recovery of bases and acids from the corresponding salts, electrodialysis is still a developing process being moved forward by academic research.

Compared to other membrane processes, there is considerably less research in electrodialysis being carried out in academic institutions and publicly funded research centers. Most research at all levels is carried out within private industry.

The principal problems encountered in state-of-the-art electrodialysis relate to membrane properties and stack design criteria. Consequently much industrial research focuses on these areas.

8.7.1 Stack Design Research

Electrodialysis efficiency, power consumption and costs are strongly affected by the stack design. The limiting current density, feed-flow pressure losses, and internal and external leakages impact the investment costs particularly. These features are all determined by the stack configuration. A considerable amount of research is being carried out in private industry to optimize spacers, gaskets and flow ducts. Fouling and scaling, both of which are related to stack design, are also active research topics. The best source of information concerning private research is the patent literature. Table 8-4 lists companies active in research related to stack design problems, with representative patent references.

Table 8-4. Companies Engaged in Electrodialysis Stack Design Research

Company	Topic	Representative U.S. Patents
PPG Industries	Improved electrodes	4,581,111
Ionics	Cell design	4,441,978
	Stack design	4,608,140
	Electrode design	4,707,240
Scheicher & Schuell	Cell design	4,608,147
Millipore Corp.	Stack design	4,632,745
Dorr Oliver	General process	4,639,380
	Electrode assembly	4,670,118
Ajinomoto Co. Inc.	Fouling reduction	4,711,722
Electrochem International, Inc.	Stack design	4,525,259

8.7.2 Membrane Research

Basic research is now concentrated on the mass-transport properties of membranes, particularly bipolar membranes. Applications research in this area is concerned with finding ion-exchange membranes with improved properties. The most important properties required from ion-exchange membranes are low electrical resistance, high fixed-ion concentrations, good chemical stability at high and low pH-values, good thermal and mechanical stability, low transfer rate of water or neutral components, low fouling tendency, and long life expectancy under operating conditions. The fixed-ion concentration in most commercially available membranes is on the order of 1-2 m equiv./gram dry polymer. This limits the concentration which may be obtained in the brine to a 2 N solution, because of Donnan exclusion. A particular research goal is to obtain membranes with higher fixed charge density, but low swelling and good mechanical stability. Furthermore, most commercial anion-exchange membranes show poor chemical stability in alkaline solutions at pH-values in excess of 12. Improved temperature stability of both cation- and anion-exchange membranes is also the objective of research activities carried out mainly in industry. The outcome of this research work is documented mainly in the patent literature. Table 8-5 summarizes the research as it can be established from the literature, with representative recent references.

Table 8-5. Companies Engaged in Electrodialysis Membrane Research

Company	Topic	Representative U.S. Patents
Allied Corporation	Bipolar membranes/water splitting	4,584,077 4,592,817 4,608,141 4,629,545 4,636,289
Azkona, Inc.	Higher conductivity membranes	4,652,396
BASF	Bipolar membrane assembly Improved ion-exchange membranes Chemical-resistant membranes	4,670,125 4,585,536 4,711,907
Du Pont	Improved fluorinated polymer membranes	4,437,951
Eltech Systems Corporation	Improved ion-exchange membranes	4,568,441
Celanese Corporation	Improved ion-exchange membranes	4,634,530

8.7.3 Basic Studies on Process Improvements

There are many theoretical and experimental studies to improve the electrodialysis process efficiency. The development of conductive spacers or sealed-cell electrodialysis are typical examples.^{48,49} Combination of electrodialysis with other mass separation processes, for example, reverse osmosis or ion exchange, has also been subject to various studies. The application of electrodialysis in a more or less modified form to a very specific separation problem in the chemical and pharmaceutical industries and in the treatment of industrial effluents has also been subject to a multitude of studies.^{50,51} Some representative applications research is summarized in Table 8-6.

Table 8-6. Companies Engaged in Electrodialysis Applications Research

Company	Topic	Representative U.S. Patents
Solco Basel AG	Bioprocessing	4,576,696 4,599,176
Mitsubishi Gas	Amino acid recovery	4,605,477
Shell Oil	Chemical processing	4,620,910 4,620,911 4,620,912 4,427,507
BASF	Chemical processing	4,645,579
Ionics	Treatment of radioactive waste Bioprocessing	4,645,625 4,678,553 4,426,323
Morton Thiokol	Electroless copper plating	4,671,861
L'Air Liquide	Amino alcohol production	4,678,549
Rhone-Poulenc	Methionine production	4,454,012
Babcock-Hitachi	Seawater desalination	4,539,088 4,539,091
Electrochem International	Electroless copper plating	4,549,946
Allied Corporation	Waste liquid treatment	4,552,635
Stamicarbon B.V.	Chemical processing	4,552,636
ICI, plc	Chemical processing	4,556,465 4,556,466 4,557,815
Laiterie Triballat	Whey processing	4,559,119

8.8 FUTURE DEVELOPMENTS

8.8.1 Areas of New Opportunity

The electrodialysis industry has experienced a steady growth of about 15% per year since it made its appearance as an industrial-scale separation process about 15 years ago. This growth has been based on two major applications, brackish water desalination and salt production. Today the markets for both applications have very limited growth potential. To ensure further growth, new areas of application have to be exploited. These areas will probably be in the chemical, food and pharmaceutical industries, in the treatment of industrial and municipal effluent, and in replacing other separation processes with high energy consumption. In some cases the expansion of electrodialysis into new areas of application will require only slight modifications of the conventional process. In other cases, extensive research and development work will be needed to adapt electrodialysis to a given separation problem. Table 8-7 lists new opportunities for electrodialysis as a separation process as well as the developments that will be required to realize those opportunities. The new applications of electrodialysis are insufficiently developed to make possible any statement about the future market. Electrodialysis processes using bipolar membranes may become increasingly important because of their low energy consumption compared with alternative technologies. Electrodialytic regeneration of ion-exchange membranes may become increasingly attractive as stricter environmental discharge regulations are enforced.

8.8.2 Impact of Present R&D Activities on the Future Use of Electrodialysis

The impact which present R&D activities will have on the future development of electrodialysis depends on when, or if, key items such as membranes with higher selectivities, better temperature stability or fouling resistance, are available. A prediction of the total installed membrane area in electrodialysis applications that are commercially available today is shown schematically in Figure 8-19. In the production of potable and industrial process water, and in the food industries, this prediction is expected to be fairly reliable; applications in wastewater treatment and especially the use of bipolar membrane technology are speculative. The current and possible future applications of electrodialysis have been ranked in terms of their technical and commercial impact and their prospects for realization in Table 8-8. The importance of the items is rated from 1 to 10, 1 being the lowest.

Table 8-7. New Areas of Application for Electrodialysis and Related Processes

Application	Limiting factors	Required R&D	Key developments	Expected benefits
<u>Electrodialysis for Potable Water Production</u>				
Nitrate removal	Membrane selectivity resistance	New membranes	Ion-selective membrane	Low cost high quality water
Seawater desalination	Membrane resistance	New membranes	High temperature ED	Low cost potable water
<u>Electrodialysis for Wastewater Treatment</u>				
Electroplating wastewater treatment	Alkaline stability of membrane	New anion-exchange membrane	Temperature & alkaline & acid stable membranes	Recycling of metal ions
Pickling wastewater treatment	Fixed charge density	New membranes	Membranes with high charge density	Acid recovery
Paper mill wastewater treatment	Fouling behavior	Stack designs, new membrane	New stack design nonfouling membranes	Low cost effluent treatment
Acid and base recovery from etching processes	Fixed charge density, selectivity	New membranes, stack design	Membranes with high charge density, chemically stable	Process cost reduction
<u>Bipolar Membrane Technology</u>				
Recovery of acids and bases from corresponding salts	Membrane efficiency, stack design	Bipolar membrane stack design	Low resistance, alkaline stable bipolar membrane, three-compartment stack design	Energy saving recycling of acids and bases
Electroplating effluent treatment	Membrane efficiency, stack design	Bipolar membrane development, stack design	Low resistance, alkaline stable, bipolar membrane, three-compartment stack design	Energy saving recovery of toxic materials
Recovery of organic acids from corresponding salts	Bipolar membranes, anion-exchange membranes, stack design	Bipolar membrane, stack design	Low resistance bipolar membrane, "open" anion-exchange membranes	Cost savings

Table 8-7. (continued)

Application	Limiting factors	Required R&D	Key developments	Expected benefits
<u>Donnan Dialysis Technology</u>				
Acid recovery	Membrane stability	Membrane stack design	Proton selective membranes	Cost savings
Water softening	Membrane selectivity	Membrane stack design	High permeability membranes	Cost savings
Recovery of organic acids	Membrane selectivity	Membrane process development	Selective membranes	Cost savings
<u>Electrodialysis in Food, Pharmaceutical and Chemical Industries</u>				
Desalination of process water	Membrane resistance	New membrane	Thin membrane, low resistance	Cost savings, low waste emission
Ultrapure water production	Membrane resistance	Conductive spacers	Thin membranes, conductive spacers	Cost savings
Removal of organic acids from wine and fruit juices	Low membrane permeability	New membranes, stack design	"Open" non-fouling anion-exchange membranes	Cost savings, higher quality products
Production of organic acid	Low membrane permeability	Membrane stack design	"Open" non-fouling anion-exchange membranes	Cost savings
Recovery of amino acids from fermentation	Low membrane permeability	Membrane stack design	"Open" membranes, no leakage, stack design	Cost savings
Separation of proteins	Low membrane permeability, pH adjustment	Process development, membrane stack design	Microporous ion exchange membranes, non-fouling membranes	Cost savings
Desalting of protein solutions	Membrane fouling	Membrane stack design	Nonfouling membranes	Cost savings

Figure 8-19. Estimated total membrane area installed in electrodesalination between 1989 and 1995 in various applications.

Table 8-8. Current and Future Applications for Electrodialysis, Their Relevance and Prospect of Realization

Application	Prospects for Realization	Importance	Comments
<u>Potable & Process Water Production</u>			
Brackish water desalination	Excellent	10	Temperature (>60°C) stable membranes
Seawater desalination	Good	8	Low resistance, temperature (>80°C) stable membranes
Nitrate removal	Good	10	Ion-selective membranes
De-ionized water	Very good	10	Development of conductive spacers
Brine concentration (salt production)	Good	5	Ion-selective, low resistance membranes
<u>Wastewater Treatment</u>			
Electroplating rinse water (heavy metals removal)	Good	8	Membranes with very high fixed charge density
Etch bath rinse water	Excellent	8	Proton-selective, acid resistant membranes
Pickling wastewater	Good	8	Membranes with very high fixed charge density
Desalination of special effluent (e.g. glycerine)	Good	6	Excellent chemical (alkaline) stability
Radioactive wastewater treatment	Good	6	Radiation-resistant membranes
Regeneration of ion-exchange resins	Fair	8	Improved process design
<u>Food & Drug Industry</u>			Thermal & chemical stability sterilizable membranes
Desalting of whey	Excellent	8	Low lactose permeability membranes
Desalting of molasses	Excellent	6	Low sugar permeability
Desalting of proteins	Very good	5	Low-fouling membranes
Deacidification of fruit juices	Good	5	Acid/sugar selective ion-exchange membranes

Table 8-8. (continued)

Application	Prospects for Realization	Importance	Comments
Salt removal from fermentation broths	Good	8	
Potassium removal from wine	Good	5	
Organic acids removal from fermentation broths	Good	6	Anion exchange membranes with high acid permeability
Separation of amino acids	Good	4	
<u>Donnan Dialysis & Dialysis</u>			
Water softening	Good	4	High permeability cation exchange membranes
Heavy metal recovery	Good	7	
Acid recovery from etching baths	Good	3	
Recovery of acids & bases from salts	Fair	10	Chemically stable membranes; better process design
Recovery of organic acids from salts	Very good	8	
pH control w/o adding acid or base	Very good	10	

8.8.3 Future Research Directions

To guarantee the future growth and expansion of electrodialysis in new areas of application, continued research and development in membrane preparation and process design will be necessary. In Table 8-9, desirable future research topics, their prospects for realization and their technical and commercial importance are listed. The prospects have been rated excellent, good and fair. Importance for the future growth of electrodialysis has been rated between 1 and 10, 1 being the lowest.

Table 8-9. Future Research Directions in Electrodialysis, Their Relevance and Prospect of Realization

Research Topic	Prospects for Realization	Importance	Comments
Membranes with lower resistance	Good	5	Membrane resistance affects energy cost
Membranes with higher charge density	Good	5	Higher selectivity
Membranes with better mechanical properties	Good	5	Must be thin, but withstand pressure
Membranes with better temperature stability	Excellent	8	Temperature reduces electrical resistance
Better ion-selective membranes	Fair	10	Special interest for nitrate removal
Membranes with better chemical (acid & alkali chlorine) stability	Excellent	8	Enable treatment of concentrated streams
Fouling-resistant membranes	Excellent	9	Longer useful life
Steam-sterilizable membranes	Good	3	Better acceptance in food and drug industry
Membranes with high permeability for large anions	Good	5	Important for organic acid separations
Membranes with low permeability for neutral components	Fair	6	Requirements for the drug industry
Better bipolar membranes	Good	9	
Thinner cells	Fair	8	Lower electrical resistance
Better flow distribution (spacer design)	Good	10	Less concentration polarization
Leak elimination	Good	8	Better current utilization
Lower-cost stacks	Good	10	Lower investment cost

REFERENCES

1. E. Korngold, "Electrodialysis Membranes and Mass Transport," in Synthetic Membrane Processes, G. Belfort, (Ed.), Academic Press, New York (1984).
2. P. H. Prausnitz and J. Reitstotter, Electrophorese, Electroosmose, Electrodialyse, Steinkopff, Dresden (1931).
3. R. E. Lacey, (Ed.), Membrane Processes for Industry, Southern Research Institute, Birmingham, AL (1966).
4. L. H. Schaffer and M. S. Mintz, "Electrodialysis," in Principles of Desalination, K. S. Spiegler, (Ed.), Academic Press, New York (1966).
5. H. Strathmann, Trennung von molekularen Mischungen mit Hilfe synthetischer Membranen, Steinkopff-Verlag, Darmstadt, (1979).
6. F. G. Donnan, Z. Elektrochem. 17, 572 (1911).
7. F. Helfferich, Ion Exchange, McGraw-Hill, London (1962).
8. R. E. Lacey, "Basis of Electro Membrane Processes," in Industrial Processing with Membranes, R. E. Lacey and S. Loeb, (Eds.), John Wiley & Sons, New York (1972).
9. J. R. Wilson, Demineralization by Electrodialysis, Butterworth, London (1960).
10. S. B. Tuwiner, Diffusion and Membrane Technology, Reinhold, New York (1962).
11. M. S. Mintz, Ind. Eng. Chem. 55, 19 (1963).
12. Product bulletin, Ionics Inc., Watertown, MA 02172, USA (1984).
13. H. Strathmann and H. Chmiel, "Die Elektrodialyse - ein Membranverfahren mit Vielen Anwendungsmöglichkeiten," Chem.-Ing.-Tech. 56, 214 (1984).
14. Product bulletin, Tokuyama Soda, Tokyo (1987).
15. E. W. Lang and E. L. Huffmann, U.S. Off. Saline Water Res. Dev. Rep. 439 (1969).
16. R. E. Lacey and E. W. Lang, U.S. Off. Saline Water Res. Dev. Rep. 106 (1964).
17. R. E. Lacey and E. W. Lang, U.S. Off. Saline Water Res. Dev. Rep. 398 (1969).
18. W. E. Katz, "The Electrodialysis Reversal ("EDR") Process," presented at the International Congress on Desalination and Water Re-Use, Tokyo, Japan (1977).

19. R. E. Lacey, U.S. Off. Saline Water Res. Dev. Rep. 80 (1963).
20. A. L. Goldstein et al., U.S. Patent 4,608,140, August 26 (1986).
21. H. Schmoldt, H. Strathmann, U.S. Patent 4,737,260, April 2 (1988).
22. A. Clad et al., U.S. Pat. 4,608,147, August 26 (1986).
23. N. Lakshminarayanaiah, Chem. Revs. **65**, 494 (1965).
24. D. S. Flett, Ion Exchange Membranes, E. Horwood Ltd, Chichester U.K. (1983)
25. T. Sata et al., U.S. Pat. 3,647,086, March 7 (1972).
26. T. Sata, K. Kuzumoto and Y. Mizutani, Polymer J. **8**, 225-226 (1976).
27. A. Eisenberg and H. L. Yeager, "Perfluorinated Inomer Membranes," ACS Symposium Series 180, (1982).
28. P. Zschocke, D. Quellmalz, "Novel Ion-Exchange Membranes Based on an Aromatic Polyethersulfone," J. Membrane Sci. **22**, 325-332 (1985).
29. W. Pauli, Biochem. Z. **152**, 355 (1924).
30. E. Manegold and C. Kalauch, Kolloid-Z. **86**, 93 (1939).
31. K. H. Meyer and W. Strauss, Helv. Chim. Acta. **23**, 795 (1940).
32. J. G. Kirkwood, J. Chem. Phys. **9**, 878 (1941).
33. E. A. Murphy, F.V. Paton, and J. Ansell, U.S. Patent 2,331,494, October 12 (1943).
34. Th. C. Bissot et al., U.S. Patent 4,437,951, March 20 (1984).
35. R. B. Hodgdon et al., U.S. Patent 4,504,797, March 19 (1985).
36. M. J. Covitch et al., U.S. Patent 4,568,441, February 4 (1986).
37. H. Puetter et al., U.S. Patent 4,585,536, April 29 (1986).
38. H.-J. Sterzel et al., U.S. Patent 4,711,907, December 8 (1987).
39. J. E. Kuder et al., U.S. Patent 4,634,530, January 6 (1987).
40. K. B. Wagener et al., U.S. Patent 4,652,396, March 24 (1987).
41. S. Toyoshi et al., U.S. Patent 4,711,722, December 8 (1987).
42. H.-J. Sterzel et al., U.S. Patent 4,711,907, December 8 (1987).

43. P. R. Klinkowski et al., U.S. Patent 4,668,361, May 26 (1987).
44. A. J. Giuffrida et al., U.S. Patent 4,632,745, December 30 (1986).
45. K. J. Liu, F. P. Chlanda and K. J. Nagasubramanian, "Use of Bipolar Membranes for Generation of Acid and Base - an Engineering and Economic Analysis," J. Membrane Sci., 2, 109 (1977).
46. B. Bauer, F.-J. Gerner, H. Strathmann, "Development of Bipolar Membranes," Desalination 68, 279-292 (1988).
47. F. P. Chlanda et al., U.S. Patent 4,116,889, September 26 (1978).
48. O. Kedem and Y. Maoz, "Ion conductive spacers for improved electrodialysis," Desalination 19, 465-470 (1976).
49. O. Kedem, J. Kohen, A. Warshawsky and N. Kahana, "EDS - Sealed Cell Electrodialysis," Desalination 46, 291 (1983).
50. E. Korngold, K. Kock and H. Strathmann, "Electrodialysis in Advanced Waste Water Treatment," Desalination 24, 129 (1978).
51. H. Strathmann and K. Kock, "Effluent Free Electrodialytic Regeneration of Ion-Exchange Resins," in Polymer Separation Media, A. R. Cooper, (Ed.), Plenum Press, New York (1982).
52. H. Strathmann, "Electrodialysis and its Application in the Chemical Process Industry," Separation & Purification 14, 41-66 (1985).
53. R. M. Ahlgren, "Electro Membrane Processes for Recovery of Constituents from Pulping Liquors," in Industrial Processing with Membranes, R. E. Lacey and S. Loeb, (Eds.), John Wiley & Sons, New York (1972).
54. H. P. Gregor and C. D. Gregor, "Synthetic-Membrane Technology," Scientific American, Vol 239, No. 1, Page 88, July (1978).
55. Millipore Product Bulletin, Lit. No. CI001 (1987).
56. F. H. Miller, Ionics, Inc. Lit. (1984).
57. Science Relations Service, Market study 5 SRS-Project 068: Electrodialysis (1985).

9.1 GLOSSARY OF SYMBOLS AND ABBREVIATIONS

α	selectivity
Å	Angstrom unit (10^{-10} meter)
AIST	Agency of Industrial Science and Technology
AN	acrylonitrile
atm	atmosphere
β	separation factor
bbl	barrel
Btu	British thermal unit
c	concentration
°C	degrees Celsius
cf	cubic foot
cm	centimeter
d	day
DARPA	Defence Advanced Research Projects Agency
DDS	De Danske Sukkerfabriker
DEA	diethylamine
DOD	Department of Defense
DOE	Department of Energy
DuPont	E.I. duPont de Nemours & Co. (Inc.)
ED	electrodialysis
EDC	ethylene dichloride
EDTA	ethylene diamine tetra acetic acid
EEC	European Economic Community
ELM	emulsion liquid membranes
EOR	enhanced oil recovery
EPA	Environmental Protection Agency
EPO ₂	equivalent pure oxygen
EtOH	ethanol
ETP	Emerging Technologies Program
°F	degrees Fahrenheit
g	gram
δG	Gibbs free energy change
gal	gallon
GE	General Electric Corp.
h	hour
dH	enthalpy change
H/C	hydrogen-to-carbon ratio
HDS	hydrodesulfurization
HF	hollow fiber membranes
HFPC	Hexafluorinated bisphenol-A polycarbonate
HFTMPC	Hexafluorinated tetramethyl bisphenol-A polycarbonate

ILM	immobilized liquid membrane
in	inch
IX	ion exchange
J	Joule
°K	degrees Kelvin
L	liter
lb	pound
LIX	liquid ion-exchange
m	meter
ME	multiple effect evaporation/distillation
METC	Morgantown Energy Technology Center
MF	microfiltration
MGD	million gallons per day
MIT	Massachusetts Institute of Technology
MITI	Ministry of International Trade and Industry
MSF	multi-stage flash distillation
MTBE	methyl tertiary-butyl ether
MTR	Membrane Technology and Research, Inc.
NAMS	North American Membrane Society
NASA	National Aeronautical and Space Administration
NEDO	New Energy Development Organization
NIST	National Institute of Standards and Technology
NSF	National Science Foundation
OEM	original equipment manufacturer
OER	Office of Energy Research
OFE	Office of Fossil Energy
OPA	Office of Program Analysis
OSW	Office of Saline Water
ρ	osmotic pressure
p	pressure
P	permeability
Pa	pascal
PC	bisphenol-A polycarbonate
PCI	Patterson Candy International
PETC	Pittsburgh Energy Technology Center
PF	plate and frame membrane modules
ppm	parts per million
PPO	polyphenylene oxide
PSA	pressure swing adsorption
psi	pounds per square inch
psig	pounds per square inch gauge
PTMSP	polytrimethyl-silylpropyne
PVA	polyvinyl alcohol

δQ	enthalpy change
quad	10^{15} Btu
R	salt rejection
R&D	research and development
RO	reverse osmosis
s	second
ΔS	entropy change
SARA	Superfund Amendments Reauthorization Act
SBIR	Small Business Innovative Research Program
scf	standard cubic foot
scfd	standard cubic feet per day
scfm	standard cubic feet per minute
SDI	silt density index
SITE	Superfund Innovative Technologies Evaluation program
STP	Standard temperature and pressure
SW	spiral wound membrane modules
T	temperature
TDS	total dissolved solids
TMPC	tetramethyl bisphenol-A polycarbonate
TOC	total organic carbon
TPA	tissue plasminogen activator
tpd	tons per day
UF	ultrafiltration
UOP	Union Oil Products
VC	vapor compression
VOC	volatile organic chemicals
VSA	vacuum swing adsorption
VW	Volkswagen, Inc.
	$\omega \alpha \tau \tau \sigma$
$\delta W, \Delta W$	net work
WRPC	Water Re-use Promotion Center
wt	weight
y	year

PREFIXES

k	kilo (10^3)
m	milli (10^{-3})
MM	Mega (10^6)
μ	micro (10^{-6})
n	nano (10^{-9})