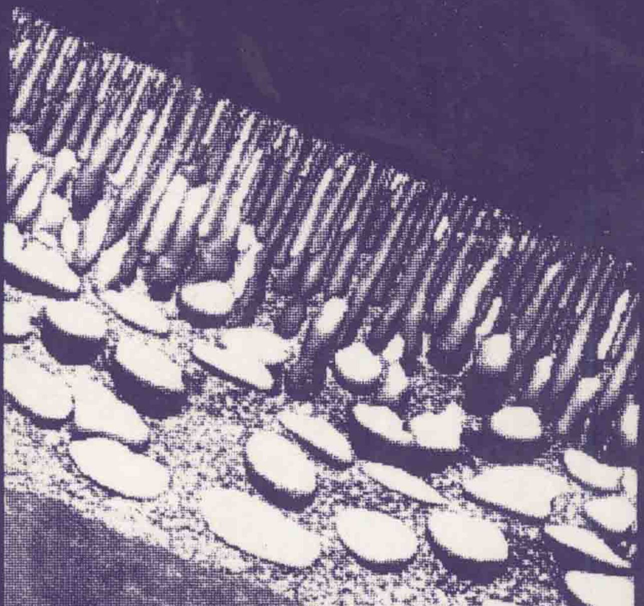
MEMBRANE PROCESSES
A TECHNOLOGY GUIDE



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Membrane Processes: A Technology Guide

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PROLOGUE

This book is not meant as a "do it yourself" guide to membrane technology, nor is it a comprehensive treatise. These aims could not be met in a single volume. Instead our objective is to provide a book for those engineers and scientists who are coming across membranes for the first time and are interested in looking under the "bonnet" to see whether or not the membrane engine meets their requirements. Even with this restriction, decisions have had to be made as to what to include, what to assume, what to leave out, what to approximate. Inevitably a balance is achieved which reflects our personal assessment of the key aspects of the technology.

The diversity of membranes is immediately apparent to those who visit different companies or talk to colleagues in different disciplines. A visit to a pharmaceutical company will engender a different response to that of a doctor, an engineer in the water industry, or a process engineer in the chemical industry. This diversity is reflected in the introductory chapters which range over a number of membrane technologies. However, the focus of the book is on the membrane process that has been most widely exploited - the filtration processes. For this reason the examples given in the final four chapters are all examples of filtration processes.

Membranes are undoubtedly a successful technology, but they have failures. Such failures occur because of over selling, over optimistic expectations, inadequate pilot testing, etc. Failures usually occur in new applications where the technical problems have not been fully resolved. This lack of robustness and simplicity of design has meant that certain groups have shied away from membranes. However, environmental pressures on the wastewater and water quality demands on potable water continue to change the separation landscape and drive membranes along the technological and learning curves. After 30 years the technological spotlight is once again on the application of membranes to potable water. The largest, and lowest cost process industries in the world, have traditionally seen membranes as applicable where water costs are high due to the lack of availability of low salinity water. This new wave of plants is being driven by increasing water quality demands, and the increasing scarcity of good quality supplies.

Membrane technology can be readily packaged as another chemical engineering unit operation. To this end the early part of the book focuses on the more basic aspects that impact on the design and operation of such processes. However, to divorce the technology from its applications is like "learning history without the politics". Many of the most successful examples of membrane technology come from a more holistic approach, where the needs of each process is considered in the context of the total process objective. For this reason the latter half of the book illustrates several significant examples of membranes with the full context in which they lie. In this way we hope to provide a greater understanding of the issues than a pure distillate of experience.

ACKNOWLEDGMENTS

The idea for this work was first initiated a number of years ago, just after ICI sold its membrane interests to North West Water. After several years of nurturing, North West Water transformed the business from a research organisation to a membrane company. Eventually, North West Water decided its interest lay elsewhere and sold this fledgling business to US Filter. We are indebted to the many colleagues and consultants, who have worked with us and through the shared experiences have contributed to this work.

Special thanks go to our families who have supported and encouraged us during the years of change.

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Chapter 1

OVERVIEW

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1.1 Membrane Technology - What is it?

Membrane technology is devoted to the separation of the minutiae of particles ranging from bacteria to atoms. To some people the concern is simply the removal of this detrious. To others the recovery of the inhabitants of this sub-microscopic kingdom is the essential goal. In size its constituents span some 4 orders of magnitude, and they are dominated by colloidal/molecular forces, rather than by the gravitational forces of their larger brethren. The various inlet and outlet streams can be all liquids, all gases or combinations. Not surprisingly membrane technology is not one technology but many technologies with one common aspect; the use of a membrane which separates two streams enabling materials to be selectively transported across it. As might be expected there is plenty of commonality between these various membrane processes, but, equally, the diversity and range of applications mean that there are significant differences. In recognition of these differences a classification of membrane processes has developed.

Of the various membrane technologies, the class of membrane filtration is the largest and most diverse. One of the commonest questions is where does conventional filtration end and membrane filtration begin. In a similar vein where does ultrafiltration take over from microfiltration. To answer this sort of question can be likened to defining where does the desert end and arable land begin; the two are clearly different but there is obviously some arbitrariness in defining the boundary. Nevertheless, a semantic definition provides a quick and expedient guide as to what to expect. However, to focus too heavily on the boundary is to miss the point. Customers are not interested in whether something lies on one side or other of a boundary but on what that something can do for them. The purpose of a classification is to convey the potential use.

Membrane technology is generally regarded as addressing the separation needs of sub-micron particles. Selectivity comes through the interaction between the membrane and the surrounding phases. Two factors contribute to selectivity, the partitioning of molecules and or particles between the membrane and the surrounding phase, and the relative diffusion rates of these materials once in the membrane. It is invariably the product of these two factors which contributes to the overall selectivity of the membrane.

One feature that is common to many membrane processes, though not to all, is cross-flow. Cross-flow involves moving fluid tangentially across the membrane surface (see figure 1.1) as well as normal to it. The benefit is that particles/solutes that would otherwise accumulate at the membrane surface are moved along, achieving a steady-state distribution of particles or solutes at the interface, rather than the continually developing one that is seen in conventional filtration. The consequence of cross-flow is that in continuous operation the flux through the membrane tends to a constant while in conventional filtration the flux continues to fall. If higher fluxes are desired then higher cross-flows are required.

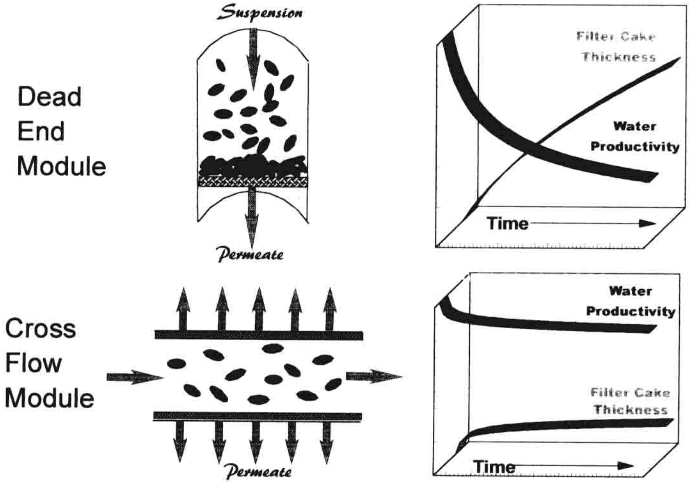

***Figure** 1.1 Schematic illustrating difference between cross-flow and dead-end filtration.*

The benefits of cross-flow do not come without a penalty, which is the energy required to move the fluid across the surface. Fortunately, the additional cost is small compared to that required in conventional filtration to push the fluid through a filter cake. A key factor in this effect is the ratio of the cross-flow to the permeate flow. Not surprisingly, this ratio is a key aspect underlying the design of membrane elements, and selecting optimal operating conditions.

Another consequence of cross-flow is that the system is basically designed to remove only a small proportion of the feed. Thus a feature of most membrane plants is how to design systems to overcome this limitation (see Chapter 8).

In the last few years the boundary between conventional filtration and membrane filtration has been further blurred with the development of hybrid processes. These processes allows some-build up of material at the membrane surface but then the material is dislodged by passing water or air back through the membrane. By repeating this process at frequent intervals (circa 15 min) a reasonable flux through the membrane can be maintained. In this way the deposits on the surface have limited effect and the membrane remains the controlling factor.

1.2 The Development of Membrane Technology

Membrane technology grew out of a 19th century endeavour to investigate a kingdom of particles too small to be seen. With no way of seeing these sub-microscopic constituents, membranes proved to be a useful tool to probe these invisible components. The resulting exploration that ensued provided key ingredients in the development of molecular theory of matter, which burst onto the scene at the start of the 20th century. In contrast it took nearly a 100 years to engineer membranes from a scientific tool to an industrial tool.

The Early Years - A Scientific Tool

A significant contributor in these early years was Thomas Graham, a Scottish chemical physicist and Master of the Mint. In 1861 he discovered that substances like salt and sugar rapidly passed through parchment, whereas material like gum arabic and gelatin would not pass. Materials that permeated he called crystalloids, since these materials could easily be crystallised. Those materials which did not pass, typified by glues, which at the time he believed did not crystallise, he called colloids after the Greek word for glue (Kolla). Graham showed how colloidal material could be purified from crystalloid contamination by putting the colloid in a porous container which was then placed in running water. The crystalloids pass through and the colloids remain. This process he called ***dialysis*** and the transport through - ***osmosis***.

Thomas Graham made another important contribution as a result of studying the diffusion of gases through flat rubber membranes. In explaining his results he regarded the rubber as a liquid in which the gas dissolves and then diffuses due to a concentration gradient. This is the so called solution-diffusion mechanism which is an important element in the molecular theory of transport in some of the membrane technologies.

Another early contributor was Thomas Fick, of Fick's law fame. In 1855 he made a membrane by dissolving collodion (cellulose nitrate) in ether/alcohol solution which he then coated onto a ceramic thimble. This enabled him to dialyse biological fluids.

Membranes Coming of Age - A subject of scientific investigation

The first half of the twentieth century saw membranes themselves become the topic of investigation. Bechold provided the first systematic study, and coined the term "ultrafiltration" [1]. He pointed out that in addition to particle size effects adsorption processes play a role in the degree of separation that is achieved. This was perhaps the first clear recognition that membrane filters frequently involve more than a mechanical basis of separation i.e. one depending purely on size. In 1911 Donnan published his work on the distribution of charged species across a semi-permeable membrane[2]. Teorell[3] and Meyers and Sievers [4] were able to build on this and provide a model for the behaviour of charged membranes which is the basis of much of our understanding of electrodialysis membranes.

By 1927 membranes were in sufficient demand for Sartorius to start selling ultrafiltration and microfiltration membranes. This commercial reality though was largely aimed at those who used membranes as a laboratory tool rather than an industrial tool.

***Table** 1.2.1 Some early contributions in the development of membranes*

Development	Contributors	Year
Laws of diffusion	Thomas Fick	1855
Dialysis	Thomas Graham	1861
Solution-diffusion transport mechanism	Thomas Graham	1866
Osmotic pressure	Van't Hoff	1887
Affinity effects in ultrafiltration	Bechold	1906
Distribution of ions	Donnan	1911
Pervaporation	Kober	1916
Membrane potential	Teorell, Meyer and Sievers	1935

Research into the nature of the microporous structure of membranes was severely hampered by a lack of tools to investigate these structural aspects. A significant development came in the 60's with the application of electron microscopy which allowed an understanding of the relationship between manufacturing variables and membrane morphology. At last the science that underpinned the empirical development of membrane manufacturing processes became understood, and meant that new manufacturing processes could be quickly developed the new generation of synthetic polymers such as the polysulphones could be exploited.

The Development of Membrane Technology - Commercialisation

Large scale commercial application of membrane technology started in the 50's, with the development of electrodialysis membranes for the desalination of brackish water[5]. The next major development was by Loeb and Sourirajan who successfully modified an ultrafiltration cellulosic membrane to create a viable reverse osmosis membrane for desalination of brackish water[6]. This opened the door, and by the mid 60's a number of companies had developed systems. Most notably to General Atomic (now Fluid Systems) who by 1965 had manufactured and built the first large scale reverse osmosis plant[7]. This industrialisation catalysed other membrane applications and developments. In particular it spurred on the development of ultrafiltration membranes for industrial usage, with applications like paint recovery in the electrocoat process. A process which is now used throughout the automotive industry. Another development of the 60's was Nafion. As part of a study into fuel cell technology by NASA, DuPont developed a hydrophilic type of PTFE by grafting onto the extremely hydrophobic polyfluoroethylene backbone, side chains with charged groups[8]. It was quickly recognised that this material could be exploited in the extremely challenging application of the production of chlorine and caustic from salt. The 70's and 80's saw a number of chemical companies trying to use their more advanced synthetic polymers and skills to enter the membrane market. One chemical company which had an initial success was Monsanto who developed the Prism membrane, based on polysulphone, for gas separation [9]. The interest of chemical companies waned in the late 80's and many who had entered in the 70's and 80's exited in the 90's as they sought to streamline their businesses.

A major development of the late 70's was the development of the composite membrane by Cadotte et al (see ref [10] for history of development). They had recognised that conventional reverse osmosis membranes were limited because different regions of the membrane had to carry-out the duties of mechanical support, and separation. They reasoned that if the separation layer and the mechanical support could be manufactured from different materials and tuned to the demands of each function, it should be possible to create a higher performing membrane. After many false starts they eventually succeeded in generating a good interfacial composite membrane that surpassed many others and laid the foundations for Film Tec which was later bought up by Dow in the late 80's.

As products have become established, suppliers have tried to open up new markets with varying degrees of success. The 90's brought a new factor into the equation, that of the environment. This has impacted on both the waste and supply side. Perhaps the largest single development has been the developing ultrafiltration and microfiltration technology for use in the municipal production of potable water to deal with cysts, bacteria, and viruses. What characterises many of these developments is not the universality of the technology but how the technology has to be developed for each application segment.

***Table** 1.2.2 Approximate dates for commercialisation of membrane technology for various applications*

Industrial Application	Commercialisation	Technology
Desalination of brackish water	1952	Electrodialysis
Desalination of brackish/sea water	1965	Reverse Osmosis
Paint recovery (Electrocoat)	1965	Ultrafiltration
Chlorine/caustic production	1972	Electrosynthesis
Hydrogen recovery	1979	Gas separation
Alcohol removal from water	1979	Pervaporation
Softening of hard water	1990	Nanofiltration
Filtration of potable water	1994	Microfiltration

As table 1.2.2 highlights different applications demand different membrane technologies (see table 1.2.3). Sometimes different membrane technologies can be used to solve the same problem. For example both reverse osmosis and electrodialysis can be used to produce potable water from sea water. In the former water is passed through the membrane , while in the latter the salts are removed. A comparison to determine which is best inevitably depends on the customers requirements, and circumstances. Despite the obvious differences in the various membrane technologies there are many common features at a fundamental level (see Chapter 2 and 3).

***Table** 1.2.3 List of various membrane technologies and abbreviations used*

Technology	Abb	Technology	Abb	Technology	Abb
Reverse osmosis	RO	Gas Separation	GS	Gas Contacting	GC
Nanofiltration	NF	Membrane Distillation	MD	Dialysis	D
Ultrafiltration	UF	Pervaporation	PV	Haemodialysis	HD
Microfiltration	MF	Electrodialysis	ED	Haemofiltration	HF
		Electrosynthesis	ES	Membrane Bioreactors	MBR

1.3 The Driving Forces of Separation

For processes like crystallisation, distillation, adsorption, the separation achieved is related to the thermodynamic stability, with kinetics serving to dictate the time and size of plant required. In contrast for membrane processes separation is determined by the relative kinetics of permeation, with thermodynamics providing the time-scale and size of plant required.

Irreversible thermodynamics provide the framework for understanding membrane separations. The driving force for separation comes from gradients in thermodynamic variables. Commercial separation processes are governed by the differences in 1 or more of four thermodynamic factors

- *Pressure*
- *Concentration*
- *Electric Potential*
- *Temperature*

that exist between two phases being separated by the membrane. In response to these forces there are flows of mass, heat, electricity. At a local level the relationship between the forces, X_i, and fluxes, J_j, is a linear one of the general form

$$J_i = \Sigma_j L_{ij} X_j \tag{1.3.1}$$

where the L_{ij} are phenomenological coefficients to be provided either by experimentation or molecular theories. These coefficients occur in a variety of problems and many have been given names (see table 1.3.1). In the application of these principles to membranes the problem frequently becomes more complex in that the coupled sets of equations have to be solved over regions. Nevertheless the linear nature of the equations means that the fluxes are in general related to the differences in the thermodynamic properties of the two phases on either side of the membrane.

***Table** 1.3.1 Relationship between thermodynamic driving forces and fluxes*

FLOWS	DRIVING FORCE			
	Pressure	**Concentration**	**Potential**	**Temperature**
Volume Flux	Filtration	Osmosis	Electro-osmosis	Thermo-osmosis
Solute Flux	Piezodialysis	Dialysis	Electrodialysis	Thermo-dialysis
Ionic Current	Streaming	Reverse Electrodialysis	Ionic conduction	Thermo-electricity
Heat Flow		Thermal osmosis	Thermo-potential	Thermal conduction