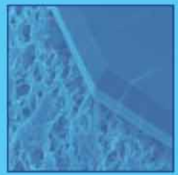

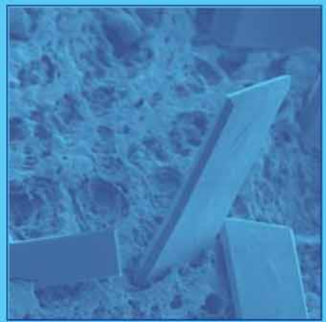

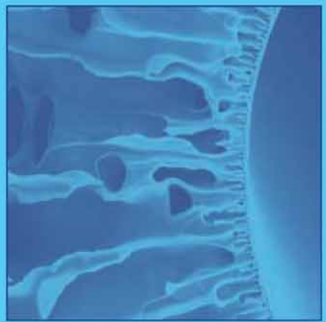

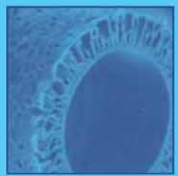

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An Introduction to Membrane Science and Technology

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CONTENTS

CHAPTER 3

PRINCIPLES OF MEMBRANE SEPARATION PROCESSES

CHAPTER 4

MEMBRANE SEPARATION PROCESSES DESIGN AND OPERATION

CHAPTER 5

CONCENTRATION POLARIZATION AND MEMBRANE MODULES

CHAPTER 6

MEMBRANE PREPARATION AND CHARACTERIZATION

CHAPTER 7
MEMBRANES AND MEMBRANE PROCESSES APPLICATIONS

PREFACE

Membranes and membrane processes are not a recent invention. They are part of our daily life and exist as long as life exists. The preparation of synthetic membranes and their utilization on a large industrial scale, however, are a more recent development which has rapidly gained a substantial importance due to the large number of practical applications. Today, membranes are used to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors. They are also key components in energy conversion systems, and in artificial organs and drug delivery devices. The membranes used in the various applications differ widely in their structure and function and the way they are operated in the various membrane processes. It is, therefore, difficult to obtain a reasonably comprehensive and complete overview of the entire field of membranes and membrane processes including their applications which is extremely fragmented and covered in the literature by a large number of publications in different scientific journals and in several excellent books focusing more on certain aspects of membrane science such as theoretical treatment of membrane functions, engineering consideration of membrane process design, or membrane preparation and large scale production.

The purpose of this book is to provide a short but reasonably comprehensive introduction to the membrane science for students and interested persons with an engineering or scientific background to gain a basic understanding of membranes and membrane processes in various applications and their present and future technical relevance and economic impact. The book is concentrated on the discussion of selected fundamental and application related aspects.

Following a short general introduction and definition of terms used in the description of membrane structures and properties some fundamental thermodynamic and mathematical relations necessary for an understanding of the membrane functions in the various processes and their applications are discussed.

In the next chapter of the book the basic principles of the more relevant practically utilized membrane processes are described in some detail and their technical and commercial advantages as well as their limitations are pointed out. New and emerging membrane processes are more briefly treated and their potential applications are indicated.

The design of membrane processes and the construction of hardware components for various applications are discussed in the following chapter which also contains membrane process cost assessments and general process optimization strategies.

This is followed by a chapter on the discussion of other engineering considerations such as mass transfer in membrane modules, the causes of concentration polarization and membrane fouling and their consequences for the module design and a proper operation of a membrane process in a certain application.

In the next chapter the preparation and characterization of porous symmetric, asymmetric and composite membranes made from polymers or inorganic materials to be used in the different membrane processes and applications are described. The preparation of ion-exchange membranes and supported and unsupported liquid membranes containing specific carrier components and other special property membranes is also discussed.

The final chapter is dedicated to the practical application of membranes and membrane processes. In selective examples the application of the mature membrane processes such as reverse osmosis, ultra- and microfiltration or dialysis and electrodialysis in water desalination and purification and in the chemical industry or food and drug production are described and energy requirements and process costs of a given plant capacity are estimated. The application of more membranes in new and emerging processes such as controlled release of drugs in medical therapy, in artificial organs and membrane reactors or membrane conversion systems is also discussed in selected examples. However, from the large number of applications only very few have been discussed or even mentioned. A more extensive treatise of all present and future possible applications of membranes and membrane processes is far beyond the scope of this book and further reading of the relevant publications on this subject is recommended.

A great deal of the literature on the practical application of membranes originated in the United States where units such as gallons, pounds, inches, mils, or pounds per square inch are widely in engineering practice. In Europe and most other countries, however, metric units, i.e. meter, second and kilogram are used. To facilitate the understanding of the membrane related literature an appendix is added which contains a number of tables with commonly used constants and the conversion of the different units.

AN OUTLOOK FOR FUTURE MEMBRANE DEVELOPMENTS

Membrane operations in the last years have shown their potentialities in the rationalization of production systems. Their intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability for the transport of specific components, low energy requirements, good stability under a wide spectrum of operating conditions, environment compatibility, easy control and scale-up have been confirmed in a large variety of applications and operations, as molecular separation, fractionation, concentrations, purifications, clarifications, emulsifications, crystallization, etc., in both liquid and gas phases and in a wide spectrum of operating parameters such as pH, temperature, pressure, etc.

Some of the largest plants in the world for sea water desalination are already based on membrane engineering. The Red-Sea/Dead-Sea desalination project, under discussion today, is based for example on RO with a productivity of $27 m^3/s$ of permeate. Membrane operations are practically the dominant technology in desalination and they will confirm this role in the next decades.

A similar situation in part exists in the treatment of gas streams, where for example the non-cryogenic nitrogen production and hydrogen purification are already present at industrial level. The development of new polymeric or inorganic membranes characterized by a high permeability and selectivity for CO_2 might offer a solution to the problem of CO_2 capture and purification, significantly impacting with the strategy for a sustainable industrial growth.

The possibility of having the membrane systems also as tools for a better design of chemical transformation is becoming attracting and realistic. For biological applications, synthetic membranes provide an ideal support to catalyst immobilization due to their available surface area per unit volume. In addition, membrane bioreactors are particularly attractive in terms of eco-compatibility because they do not require additives, are able to operate at moderate temperature and pressure, and to reduce the formation of by-products. Potential applications have been and will be at the origin of important developments in various technology sectors, mainly concerning induction of microrganisms to produce specific enzymes, techniques of enzymes purification, overall design of efficient productive cycles.

Development of catalytic membrane reactors for high temperature applications became realistic only in recent years with the development of high temperature resistant membranes. Most of these reactors use inorganic membranes that can be dense or porous, inert or catalytically active. No large scale industrial applications have been reported so far, because of a relatively high prize of membrane units. However, current and future advances in the material engineering might significantly reverse this trend.

Besides the huge progresses in the last years, membrane engineering is probably still at its infancy. Process intensification is the most interesting strategy offered today for realizing a sustainable industrial growth, compatible with a desirable high quality of our life. Membrane engineering in its various aspects, molecular separations, membrane reactors, membrane contactors, is quite consistent with practically all the requirements for making this strategy a reality.

Membrane based artificial organs such as the artificial kidney are a standard part of modern biochemical engineering and medicine. New hybrid artificial organs such as the artificial liver and artificial pancreas are expected to become more and more equally utilized in a relatively short period of time and new organs such as the artificial retina, or the artificial brain are attracting the interest of the new generation of membranologists.

Also traditional areas such as encapsulation and packaging will be substantially modified and innovated with the transfer of more basic understanding of transport phenomena and membrane phenomena in general in these sectors. The redesigning of overall industrial productions such as the petrochemical plants as integrated membrane systems might become real in few years from now.

Contributions of membrane technologies to the life in space and in other planets are already in progress in various laboratories around the world.

Membrane contactors in their various configurations and operations (emulsifiers, crystallizers, strippers, scrubbers, etc.) will make the opportunities of integrated membrane systems for an industrial sustainable growth more realistic.

The possibility of developing new nanostructured materials with specific configurations and morphology is offering powerful tools for the preparation of membranes with controlled selectivity and permeability higher than the membranes existing today.

Membranes characterized by highly selective transport mechanisms as the perovskite studied for oxygen separation from air, or the palladium for H_2 purification are suggesting the use of molecular dynamic studies for identifying new structures characterized by similar selectivity towards a larger spectrum of chemical species. Biological membranes reproduce themselves continuously, controlling important physiological processes, where fouling e.g. does not represent a problem as in artificial systems. The mechanisms which generate our memory or the function of our brain are other important membrane phenomena.

The role that membrane science and membrane engineering play in our life, justifies growing efforts in the education of young generations of researchers, engineers and technicians on their basic properties and on their possible applications. This book has been written with the scope of contributing to these efforts.

Chapter 1

Introduction

CHAPTER 1

INTRODUCTION

SUMMARY
In this chapter a general introduction on membrane science and technology is given. It begins with the definition of terms and provides a description of membrane structures and membrane processes that are used today in mass separation, in (bio)chemical reactors, in energy conversion and storage, and in the controlled release of drugs. The advantages as well as the limitations of membrane processes are indicated. Major applications of membranes are described and their technical and commercial relevance pointed out. A short overview over the historical development of membrane science and technology is given and possible future developments and research needs are indicated.

1.1. General considerations

The separation, concentration, and purification of molecular mixtures are major problems in the chemical industries. Efficient separation processes are also needed to obtain high-grade products in the food and pharmaceutical industries to supply communities and industry with high-quality water, and to remove or recover toxic or valuable components from industrial effluents. For this task a multitude of separation techniques such as distillation, precipitation, crystallization, extraction, adsorption, and ion-exchange are used today. More recently, these conventional separation methods have been supplemented by a family of processes that utilize semipermeable membranes as separation barriers.

Membranes and membrane processes were first introduced as an analytical tool in chemical and biomedical laboratories; they developed very rapidly into industrial products and methods with significant technical and commercial impact [Lonsdale, 1982; Ho et al., 1992; Osada et al., 1992; Zeman et al., 1996; Drioli et al., 2001; Bhattacharyya et al., 2003; Baker, 2004; Strathmann, 2004]. Today, membranes are used on a large scale to produce potable water from sea and brackish water, to clean industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors in petrochemical processes. They are also key components in energy conversion and storage systems, in chemical reactors, in artificial organs, and in drug delivery devices.

The membranes used in the various applications differ widely in their structure, in their function and the way they are operated. However, all membranes have several features in common that make them particularly attractive tools for the separation of molecular mixtures. Most important is that the separation is performed by physical means at ambient temperature without chemically altering the constituents of a mixture. This is mandatory for applications in artificial organs and in many drug delivery systems as well as in the food and drug industry or in downstream processing of bioproducts where temperature-sensitive substances must often be handled. Furthermore, membrane properties can be tailored and adjusted to specific separation tasks, and membrane processes are often technically simpler and more energy efficient than conventional separation techniques and are equally well suited for large-scale continuous operations as for batch-wise treatment of very small quantities.

Although synthetic membranes are widely used as valuable scientific and technical tools in a modern industrialized society, they are not very well defined in terms of their structure and function. The most prominent association that many people have when thinking of a membrane resembles that of a filter, i.e. a device capable of separating various components from a mixture according to their size.

However, a membrane can be much more complex in both structure and function. A membrane may be solid or liquid, homogeneous or heterogeneous, isotropic or anisotropic in its structure. A membrane can be a fraction of a micrometer or several millimeters thick. Its electrical resistance can vary from millions of Ohm to a fraction of an Ohm.

Another characteristic property of a membrane is its *permselectivity*, which is determined by differences in the transport rates of various components in the membrane matrix. The *permeability* of a membrane is a measure of the rate at which a given component is transported through the membrane under specific conditions of concentration, temperature, pressure, and/or electric field. The transport rate of a component through a membrane is determined by the structure of the membrane, by the size of the permeating component, by the chemical nature and the electrical charge of the membrane material and permeating components, and by the driving force, i.e. concentration, pressure or electrical potential gradient across the membrane. The transport of certain components through a membrane may be facilitated by certain chemical compounds, coupled to the transport of other components, or activated by a chemical reaction occurring in the membrane. These phenomena are referred to as *facilitated*, *coupled*, or *active transport*.

The versatility of membrane structures and functions makes a precise and complete definition of a membrane rather difficult. In the most general sense a membrane is a barrier that separates and/or contacts two different regions and controls the exchange of matter and energy between the regions. The membrane can be a selective or a contacting barrier. In the first case, it controls the exchange between the two regions adjacent to it in a very specific manner; in the second case, its function is mainly to contact the two regions between which the transport occurs.

We can distinguish between biological membranes, which are part of the living organism, and synthetic membranes that are man-made. Biological membranes carry out very complex and specific transport tasks in living organisms. They accomplish them quickly, efficiently, and with minimal energy expenditure, frequently using active transport.

Synthetic membranes are not nearly as complicated in their structure or function as biological membranes. They have only passive transport properties and are usually less selective and energy efficient. In general, however, they have significantly higher chemical and mechanical stability, especially at elevated temperature. The selectivity of synthetic membranes is determined by a porous structure according to their size or through a homogeneous structure according to the solute solubility and diffusivity. The permeability of the membrane for different components, however, is only one parameter determining the flux through the membrane. Just as important as the permeability is the driving force acting on the permeating components. Some driving forces such as concentration, pressure, or temperature gradients act equally on all components, in contrast to an electrical potential driving force, which is only effective with charged components. The use of different membrane structures and driving forces has resulted in a number of rather different membrane processes such as reverse osmosis, micro-, ultra- and nanofiltration, dialysis, electrodialysis, Donnan dialysis, pervaporation, gas separation, membrane contactors, membrane distillation, membrane-based solvent extraction, membrane reactors, etc.

Even more heterogeneous than membrane structures and membrane processes are their practical applications. The large-scale industrial utilization of membranes began about 1970 with water desalination and purification to produce potable and high quality industrial water. Since then membranes have become a widely used tool in process engineering with significant technical and commercial impact. Today membrane processes are used in three main areas. The first area includes applications such as seawater desalination or wastewater purification. Here, the use of membranes is technically feasible, but there are other processes such as distillation and biological treatment with which membranes must compete on the basis of overall economy. The second area includes applications such as the production of ultra pure water or the separation of molecular mixtures in the food and drug industry. Here, alternative techniques are available, but membranes offer a clear technical and commercial advantage. The third area includes membrane applications in artificial organs and therapeutic systems. There is no reasonable alternative to membrane operations.

With the development of new membranes having better separation efficiency, new membrane processes such as membrane contactors and membrane reactors are becoming common unit operations in process engineering [Ho et al., 1992; Drioli et al., 1999; Marcano et al., 2002; Klaassen et al., 2005]. The large-scale use of membranes is rapidly extending far beyond its present level.

1.2. Historical and key developments of membranes and membrane processes

Synthetic membranes are a rather recent development and the technical utilization of membrane processes on a large scale began just 40 years ago. The first recorded study of membrane phenomena and the discovery of osmosis dates back to the middle of the 18^{th} century when Nollet discovered that a pig's bladder passes preferentially ethanol when it was brought in contact on one side with a water-ethanol mixture and on the other side with pure water [Nollet, 1752]. Nollet was probably the first to recognize the relation between a semipermeable membrane and the osmotic pressure. More systematic studies on mass transport in semipermeable membranes were carried out by Graham who studied the diffusion of gases through different media and discovered that rubber exhibits different permeabilities to different gases [Graham, 1866].

Most of the early studies on membrane permeation were carried out with natural materials such as animal bladders or gum elastics. Traube was the first to introduce an artificially prepared semipermeable membrane by precipitating cupric ferrocyanide in a thin layer of porous porcelain [Traube, 1867]. This type of membrane was used by Pfeffer in his fundamental studies on osmosis [Pfeffer, 1877]. The theoretical treatment and much of the interpretation of osmotic phenomena and mass transport through membranes is based on the studies of

Fick who interpreted diffusion in liquids as a function of concentration gradients, and van t'Hoff who gave a thermodynamic explanation for the osmotic pressure of dilute solutions [Fick, 1855; van't Hoff, 1887]. Little later Nernst and Planck introduced the flux equation for electrolytes under the driving force of a concentration or electrical potential gradient [Nernst, 1888; Planck, 1890]. With the classical publications of Donnan describing the theory of membrane equilibria and membrane potentials in the presence of electrolytes, the early history of membrane science ends with most of the basic phenomena satisfactorily described and theoretically interpreted [Donnan, 1911].

With the beginning of the twentieth century membrane science and technology entered a new phase. Bechhold developed a method of making the first synthetic membranes by impregnating a filter paper with a solution of nitrocellulose in glacial acetic acid [Bechhold, 1908]. These membranes could be prepared and accurately reproduced with different permeabilities by varying the ratio of acetic acid to nitrocellulose. Nitrocellulose membranes were also used in the studies of Zsigmondy as ultrafilters to separate macromolecules and fine particles from an aqueous solution [Zsigmondy et al., 1918]. These studies were later continued by many others [Elford, 1931; McBain et al., 1931]. The relation between the streaming potential, electroosmosis, and electrodialysis were treated in a monograph [Prausnitz et al., 1931]. Based on a patent [Zsigmondy, 1922], Sartorius GmbH began in 1937 the production of a series of nitrocellulose membranes with various pore sizes. These membranes were used in microbiological laboratories in analytical applications. The development of the first successfully functioning hemodialyser [Kolff et al., 1944] was the key to the large scale application of membranes in the biomedical area.

In the early days of membrane science and technology membranes had been mainly a subject of scientific interest with only a very few practical applications. This changed drastically from 1950 on when the practical use of membranes in technically relevant applications became the main focus of interest and a significant membrane-based industry developed rapidly. Progress in polymer chemistry resulted in a large number of synthetic polymers which ultimately became available for the preparation of new membranes with specific transport properties plus excellent mechanical and thermal stability. Membrane transport properties were described by a comprehensive theory based on the thermodynamic of irreversible processes [Staverman, 1952; Kedem et al., 1961; Schlögl, 1964]. A second route for describing membrane processes was based on postulating certain membrane transport models such as the model of a solution-diffusion membrane [Merten, 1966]. The properties of ion-exchange membranes and their practical use were also subject of extensive studies [Spiegler, 1958].

A milestone in membrane science and technology was the development of a reverse osmosis membrane based on cellulose acetate which provided high salt rejection and high fluxes at moderate hydrostatic pressures [Reid et al., 1959; Loeb et al., 1964]. This was a major advance towards the application of reverse osmosis membranes as an effective tool for the production of potable water from the sea.

The membrane developed by Loeb and Sourirajan had an asymmetric structure with a dense skin at the surface which determined the membrane selectivity and flux and highly porous substructure which provided the mechanical strength. It was shown that the preparation of asymmetric cellulose acetate membranes was based on a phase inversion process in which a homogeneous polymer solution is converted into a two-phase system, i.e. a solid polymer rich phase providing the solid polymer structure and a polymer lean phase forming the liquid filled membrane pores [Kesting, 1971; Strathmann et al., 1975]. Soon, other synthetic polymers such as polyamides, polyacrylonitrile, polysulfone, polyethylene, etc. were used as basic material for the preparation of synthetic membranes. These polymers often showed better mechanical strength, chemical stability, and thermal stability than the cellulose esters. However, cellulose acetate remained the dominant material for the preparation of reverse osmosis membranes until the development of the interfacial-polymerized composite membrane [Cadotte et al., 1981; Riley et al., 1967]. These membranes showed significantly higher fluxes, higher rejection, and better chemical and mechanical stability than the cellulose acetate membranes. The first membranes developed for reverse osmosis desalination and other applications were manufactured as flat sheets and then installed in a so-called spiral wound module [Bray, 1968; Westmoreland, 1968]. A different approach to membrane geometry was the development of self-supporting hollow fiber membranes which had a wall thickness of only 6 to 7 microns [Mahon, 1966]. Asymmetric hollow fiber membranes with the main application in brackish and sea water desalination were produced by the Du Pont Corporation.

Soon after the development of efficient membranes, appropriate membrane housing assemblies, called modules, were devised. The criteria for the design of such modules included high membrane packing density, reliability, ease of membrane or module replacement, control of concentration polarization, and low cost. Membranes were produced in three different configurations, i.e. as flat sheets, as hollow fibers or capillaries, and as tubes. In today's reverse osmosis desalination plants mainly spiral wound modules are used while hollow fiber membrane modules are utilized in gas separation and pervaporation. In medical applications such as artificial kidney and blood oxygenator capillary membranes play a dominant role today. Tubular membranes are mainly used in micro- and ultrafiltration.

Even earlier than the large scale use of reverse osmosis for sea and brackish water desalination was the industrial scale application of electrodialysis. The history of electrodialysis goes back to the development of the first multi-cell stack [Meyer et al., 1940]. However, modern electrodialysis became a practical reality with the development of the first reliable ion-exchange membranes having both good electrolyte conductivity and ion-permselectivity [Juda et al., 1953]. Electrodialysis was first commercially exploited for the desalination of brackish water by Ionics Inc. The commercial success of Ionics was due to their membranes, their compact stacking, and the mode of operation referred to as electrodialysis reversal, which provided a periodic self-cleaning mechanism for the membrane stack and thus allowed long-term continuous operation at high concentrations of scaling materials without mechanical cleaning of the stack [Katz, 1979].

In the early 1980's a completely new area for the application of electrodialysis was opened up with the introduction of bipolar membranes for the recovery of acids and bases from the corresponding salt [Liu et al., 1977]. The large-scale separation of gases and vapors is also a relevant industrial area for membrane applications. Gas separation was pioneered by Monsanto Inc. [Henis et al., 1980]. Originally, the aim was to recover hydrogen from off-gases and to produce oxygen- or nitrogen-enriched air. Today, however, a large number of other applications such as the removal of CO_2 from natural gas or the recovery of organic vapors from off-gases are typical applications for gas and vapor separation. Pervaporation which is closely related to vapor separation was studied extensively, and a large number of interesting potential applications were pointed out [Aptel et al., 1968]. But so far very few large commercial plants have been built. Other applications of membranes which were developed in recent years that have reached large technical and commercial significance include the controlled release of drugs in therapeutic devices and the storage and conversion of energy in fuel cells and batteries. However, the commercially most important application of membranes today is in reverse osmosis water desalination and in hemodialysis and hemofiltration.

1.3. Advantages and limitations of membrane processes

In many applications, e.g. water desalination and purification the membrane processes compete directly with the more conventional water treatment techniques. However, compared to these conventional procedures membrane processes are often energy efficient, more simple to operate and yield a higher quality product. The same is true for the separation, concentration, and purification of drugs and food products or in medical and pharmaceutical applications. These membrane processes have in addition to high energy efficiency, simple operation, easy up and down scaling the advantage of operating at ambient temperature avoiding any change or degradation of products.

In water desalination reverse osmosis or electrodialysis can be used. Depending on local conditions, including water quality, energy cost and the required capacity of the desalination plant, either electrodialysis or reverse osmosis can be the more efficient process. For very large capacity units and in case a power plant can be coupled with the desalination unit, distillation is generally considered to be more economical. For surface water purification and waste-water treatment membrane processes, micro- and ultrafiltration are competing with flocculation, sand bed filtration, carbon adsorption, ion-exchange and biological treatment. In these applications the membrane processes are usually more costly but generally provide a better product water quality. Very often a combination of conventional water treatment procedures with membrane processes results in reliable and cost-effective treatment combined with high product water quality.

A disadvantage of membrane processes is that in many applications, especially in the chemical and petrochemical industry, their long-term reliability is not yet proven. Furthermore, membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization and membrane fouling due to chemical interaction with water constituents. Furthermore, membranes are mechanically not very robust and can be destroyed by a malfunction in the operating procedure. However, significant progress has been made in recent years, especially in reverse osmosis seawater desalination, in developing membranes which not only have significantly better overall performance but which also show better chemical and thermal stability and are less sensitive to operational errors.

1.4. Cost considerations and environmental impact

Membrane processes are considered as very energy efficient compared to many other separation processes. However, the energy requirement of a process is only one cost determining factor. Investment and maintenance related costs contribute often significantly to the overall process costs. Other factors that must be considered are pre- and post-treatment procedures, the required product quality and especially the composition of the feed mixture which has to be treated. For example, in water treatment, where membrane processes are widely used today, process costs depend strongly on the feed water composition which might require different membrane processes. For the purification of surface water and certain waste waters micro- and ultrafiltration can be used. In these processes the energy requirements are quite low. However, micro- and ultrafiltration are competing with biological treatment or sand bed filtration which need even less energy. In sea-water desalination the only economical membrane process is reverse osmosis which is competing with the various distillation techniques. As far as energy consumption is concerned, reverse osmosis is the more energy efficient process. However, it has to be taken into account that in reverse osmosis the pressure-generating pumps are driven either by electric or combustion engines. These engines usually have an efficiency of less than 40% in relation to the primary energy obtained from fossil fuels, whereas such energy may be used directly for heating purposes in the distillation processes. In electrodialysis electrical energy is used for the actual transfer of ions from the feed to the concentrated solution. Since the current required for the desalination process in electrodialysis is directly proportional to the number of ions that must be removed from the feed solution the energy consumption in electrodialysis increases with increasing feed solution concentration. There are, however, other factors determining the overall economics of a process such as the investment and operating costs or various pre- and post-treatment procedures of the feed solution and the product water. Plant capacity may also play a role in total cost. While in distillation processes usually a substantial cost reduction can be achieved with an increase in the plant capacity, the scale-up factor has a relatively smaller effect in reverse osmosis. In general, reverse osmosis seems to have a significant cost advantage over competing processes in seawater desalination. In desalination of brackish water, both electrodialysis and reverse osmosis have a clear technical and economic advantage over the distillation processes. The same is true for the desalting and purification of surface water for domestic and industrial use. Here, however, reverse osmosis and ultrafiltration give the higher quality product water. In these processes not only salts but also all other dissolved and dispersed feed water constituents are retained by the membrane, and the permeate, i.e. the product is more or less free of all pollutants. In electrodialysis, only ionic components are removed from a feed stream and the product water may still contain particles, bacteria, viruses, and other pollutants. However, the above assessment of water purification processes is very general and oversimplified. Depending on the feed water composition and the required product water quality, a combination of processes might be appropriate. For example, if ultra-pure water for certain industrial applications is required, a sequence of processes may be applied, such as reverse osmosis with microfiltration as a "point-of-use-filter" to remove traces of particles, and ion-exchange techniques to remove all ions. Often microfiltration is also used in combination with reverse osmosis as a pre-treatment procedure.

The environmental impact of all membrane processes is relatively low. There are no hazardous chemicals used in the processes that have to be discharged and there is no heat generation. The only effluent in desalination by reverse osmosis is a concentrated brine solution. In seawater desalination this brine causes little problems since it can be discharged directly into the sea. However, in brackish water desalination the discharge of the concentrated brine

can cause problems such that brine post-treatment procedures might be necessary. Also, in surface water treatment further processing of the concentrated effluent might be necessary.
Pressure-driven membrane processes do not cause any health hazard. The product obtained is generally of high quality. Thus, very little post-treatment procedures are required. Sometimes chlorination may be applied to guarantee the required sterility of potable water, especially when long-time storage is required in a hot climate.

1.5. The membrane based industry

Parallel to the development of membrane products and processes a membrane-based industry developed. Today, this industry has sales of several billion US $ per year and is growing steadily by more than 10% per year. The structure of this industry, however, is quite heterogeneous as far as the size of the companies and their basic approach towards the market is concerned. Several companies have concentrated on the production of membranes only. They offer a range of membrane products as flat sheets, hollow fibers or capillaries with different properties and for different applications ranging from sea water desalination and waste and surface water treatment to fuel cell separators and medical devices to an end-user or an equipment manufacturer.
Other companies manufacture membrane devices or complete systems. These companies buy the membranes or modules as key components from one or several membrane manufacturers, design and build the actual plant and very often also operate it, guaranteeing the customer a certain amount of product of a given quality. These companies generally provide a solution to customers separation needs which might be a combination of separation processes such as ion-exchange, carbon adsorption, flocculation and precipitation, or various chemical and biological treatment procedures in addition to membrane processes. Although the sales of membranes and membrane modules to anyone of these companies often is not very large they are of importance in the membrane industry because of their specific application know-how in different markets.
Finally, there are companies that provide the membranes, the system design, and the plant operation. The companies concentrate very often on a single, usually very large application such as potable water production from sea or brackish water or hemodialysis. They often not only provide the tools for producing potable water in the case of sea water desalination, they also operate the plant and distribute the water. Companies producing artificial kidneys also operate dialysis stations. Since the market for membranes and water supply systems is rapidly growing and continuously changing there is a substantial fluctuation in the industry characterized by mergers and acquisitions.
The membrane market is characterized by a few rather large market segments, such as sea and brackish water desalination, the production of ultra-pure water or hemodialysis and a large number of small market segments in the food, chemical, and pharmaceutical industry, analytical laboratories and especially in the treatment and recycling of industrial effluents. The larger markets for water desalination and hemodialysis are dominated by a relatively small number of large companies. A multitude of small companies are active in market niches such as treating certain waste water streams or providing service to the chemical or food and drug production industry.

Membrane and membrane module producers

Membrane producers are frequently divisions of major chemical companies. In general, these companies focus on a series of membrane products to be used in certain applications such as water desalination and purification, gas separation, bio-production or in hemodialysis. In most cases the company which produces the membranes also produces the appropriate modules. Flat sheet membranes are mainly installed in spiral wound modules and used mainly in water desalination and purification. Hollow fiber membrane modules are mainly used in gas separation. Both module types provide a rather large membrane area per unit volume but require in certain applications a substantial amount of pre-treatment. Plate-and-frame or tubular modules are used mainly in the chemical and food processing industry and in treating certain waste waters. Capillary type membrane modules dominate the hemodialysis market but are also applied in ultrafiltration and the production of ultra-pure water.

The basic materials and the actual manufacturing process that different companies use for their membranes and modules also vary. Some companies produce asymmetric membrane structures for reverse osmosis and ultra- and microfiltration from cellulose esters, polyamides, and polysulfone. Other companies are manufacturing composite membranes with a porous polysulfone support structure and a polyamide type barrier layer made by interfacial polymerization.

System manufacturers

The number of companies involved in the design and manufacturing of membrane water treatment systems is very large and heterogeneous. Most of these companies are specialized on certain applications such as the production of potable and industrial process water or the treatment and recycling of waste water streams from the food, the chemical, and the pharmaceutical or the metal processing industry. Some of these enterprises are quite small or are small divisions of bigger companies with membrane processes playing only a minor role in their overall business activity which may be focused for instance on water treatment in general and include a whole series of different techniques such as ion-exchange, carbon adsorption, flocculation and precipitation, or various chemical and biological treatment procedures. For these companies the membrane is just a commercially available item. Although the sales of membranes and membrane modules to any of these companies is often not very large they are of importance in the membrane industry because of their specific application know-how in different markets. Exceptions to this rule are major utility companies that provide membranes, modules, and systems as a complete package. In general, these companies have secured their membrane supply by acquiring small or medium size membrane manufacturers.

1.6. *The membrane market and its future development*

The membrane market is characterized by a few rather large market segments such as sea and brackish water desalination, the production of ultrapure water, or hemodialysis, and a large number of small market segments in the food, chemical, or pharmaceutical industry, analytical laboratories and especially in the treatment and recycling of industrial waste water. It is rather difficult to make a reasonably accurate forecast of the future membrane market. However, since the demand for potable and industrial water of adequate quality is increasing drastically and the sources of fresh water with the required quality are steadily decreasing worldwide, there will be a need for energy-efficient and affordable processes for the production of high quality water from sea and brackish water sources as well as from waste or polluted surface waters, and the market for membrane industry will most likely continue to grow for the foreseeable future in this area. The same is true for gas separation and many applications in the chemical process industry, and in medical life support systems. The growth will also depend on further developments of membranes with improved selectivity and higher fluxes as well as better chemical, thermal, and mechanical stability. Long-term experience in large plants will also contribute to increase the useful life of the membranes, thus making the processes more reliable and economical.

1.7. The future of membrane science and technology

In many applications today's membranes and processes are quite satisfactory while in other applications there is a definite demand for further improvements of both membranes and processes. For sea and brackish water desalination by reverse osmosis, e.g. there are membranes available today that are quite satisfactory as far as flux and salt rejection are concerned, and the processes are proven by many years of operating experience. The same is true for hemodialysers and hemofiltration. In these applications only marginal improvements can be expected in the near future. In micro- and ultrafiltration or electrodialysis the situation is similar. The properties of present membranes are satisfactory. However, there are other components such as the process design, process control, application know-how, and long-term operating experience that are of importance in the use of micro- and ultrafiltration in the chemical and food industry or in waste water treatment. Here, concentration polarization and membrane fouling play a dominant role and new membrane modules and process design concepts which provide a better control of membrane fouling resulting in a longer useful life of the membranes are highly desirable. In other membrane processes such as gas separation, pervaporation, fuel cell separators, membrane reactors, etc. the situation is quite different. Here, better membranes, improved process design, and extensive application know-how and long-term experience are mandatory to establish membrane processes as a proven and reliable technology.

In addition to the established membrane processes and applications, new membrane operations such as membrane contactors and membrane reactors are growing at industrial level and becoming common unit operations in process engineering, contributing also to the overall impact of membrane engineering on any industrial production [Ho et al., 1992; Drioli et al., 1999]. It is also particularly important that all membrane operations are well consistent with the requirements of the process intensification strategy and of a sustainable industrial development. Chemical process rationalization and miniaturization, the basic concepts of the process intensification are now a goal in all manufacturing processes. With their intrinsic properties of high energy efficiency and operational simplicity, high transport selectivity, large operational flexibility, and environment compatibility, membranes and processes are important tools for advanced molecular separations and chemical transformations overcoming existing limits of the traditional industrial processes.

1.8. *References*

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